Communication

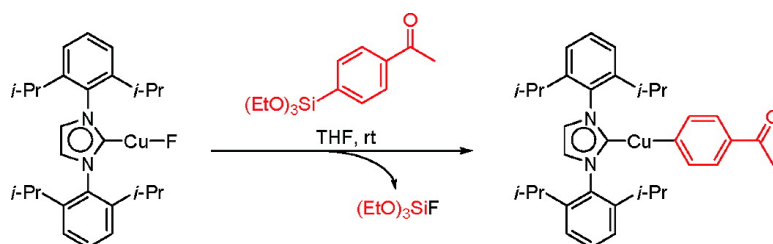# Synthesis and Reactivity of Functionalized Arylcopper Compounds by Transmetalation of Organosilanes
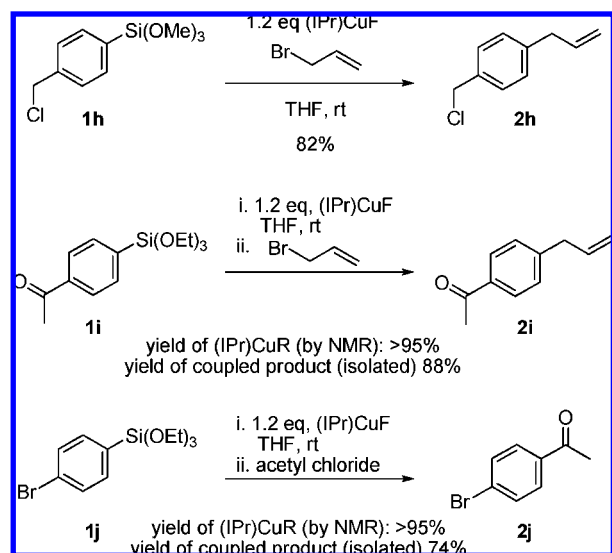
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Synthesis and Reactivity of Functionalized Arylcopper Compounds by Transmetalation of Organosilanes

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The generation of functionalized organometallic reagents is of great value for the synthesis of complex target structures. In one approach to this problem, we have initiated a program to develop and study functional-group tolerant methods for the generation of organocopper species. Copper reagents are generally produced from organomagnesium or other highly reactive organometallics, by selective metalation of organohalides,[1] or through direct metalation with strongly basic reagents.[2] Important efforts have been made to develop selective cupration strategies, including from stable organoboron[3] and organostannane[4] precursors. However, there are significant potential benefits to the use of organosilanes as potentially cheap, stable, and environmentally benign direct precursors to functionalized organocopper reagents.

The use of fluoride to activate organosilanes is well established, but this approach to the synthesis of reactive organometallics, and to organocopper reagents in particular, is limited by the poor availability of soluble, anhydrous fluoride sources,[5] the instability of copper(I) fluoride toward disproportionation,[6] and the relatively inert C−Si bond. The intermediacy of organocopper species has been inferred in reactions of highly strained silanes[7] and of those activated by intramolecular alkoxides.[8] A few reports demonstrating copper catalysts for organosilane dimerization,[9] for coupling of alkynylsilanes,[10] or for nucleophilic addition of organosilanes have appeared,[11] primarily with more easily transferable allylsilane nucleophiles.[12,13] The intermediacy of organocopper species can be inferred in these reactions on the basis of kinetics, NMR, and enantioselection observations,[11,14] but it can be difficult to distinguish reactivity of an organocopper intermediate from that from a fluoride-activated silicate.[15] To our knowledge, direct observation or characterization of silicon-to-copper transmetalation has not been observed with simple sp²- or sp³-organosilanes.[16]

To surmount the difficulties associated with copper(I) fluoride complexes, we employ a N-heterocyclic carbene ligand for copper[17,18] to stabilize the copper(I) fluoride and to afford solubility in anhydrous, aprotic solvents. Specifically, we employ the fluoride complex (IPr)CuF (IPr = 1,3-bis(2′,6′-diisopropylphenyl)imidazol-2-ylidene), available upon treatment of (IPr)Cu(Ot-Bu) with Et$_3$N·3HF in anhydrous benzene, followed by filtration of the product.[19] Uniquely, (IPr)CuF is a monomeric, anhydrous copper(I) fluoride complex soluble in ethereal solvents.

Treatment of (IPr)CuF in THF-d_8 with phenyltriethoxysilane induced clean transmetalation within 1 h at rt, affording the product (IPr)CuPh (Table 1, entry 1). Gratifyingly, the product organometallic could be isolated in analytically pure form by precipitation upon dilution with pentane and cooling. We set out to explore the generality and functional group tolerance of our approach to organocopper reagents. Although we have focused on triethoxysilanes, (dialkyl)monoalkoxysilyl groups are much more stable to silica chromatography and to hydrolysis generally, and so we were pleased to find that phenyldimethylethoxysilane (**1b**) undergoes efficient transmetalation as well (entry 2), with a rate only slightly

Table 1. Synthesis of Functionalized Organocopper Compounds

entry	silane	product	t (h)	yield[a]
1	Si(OMe)$_3$ **1a**	**2a**	1	82 (>95%)[c]
2	Si(OEt)Me$_2$ **1b**	**2b**	4	(>95%)[c]
3	Si(OEt)$_3$, Me **1c**	**2c**	4	71[h] (>95%)[c]
4	Si(OEt)$_3$, OMe **1d**	**2d**	1	88 (>95%)[c]
5	MeO$_2$C—Si(OEt)$_3$ **1e**	**2e**	4	73 (>95%)[c]
6	Br—Si(OEt)$_3$ **1f**	**2f**	4	65 (>95%)[c]
7	Si(OMe)$_3$ **1g**	**2g**	0.2	71 (>95%)[c]

[a] All reactions were performed at room temperature in THF unless otherwise indicated. Yields indicate isolated yields of analytically pure material. [b] Reaction performed in ether. [c] Yields in parenthesis are NMR yields.

slower than the trialkoxysilane **1a**. Despite the bulk of the IPr ligand, ortho-substituted arylcopper reagents are readily formed (entries 3−4), and both electron-rich and electron-poor arylsilanes are tolerated (entries 5−6).

The reaction of allyltriethoxysilane with (IPr)CuF is quite fast, proceeding to completion in less than 12 min by ¹H NMR analysis of the mixture in THF-d_8 (entry 7). The product (IPr)Cu(allyl) (**2g**) can be isolated in a manner similar to the arylcopper compounds above. Only two resonances corresponding to the allyl unit are seen in the ¹H NMR (δ 6.42, quintet, $J = 11.1$ Hz, 1H); 3.08, d, $J = 11.1$ Hz, 4H), indicating fast exchange between η^1 and η^3 coordination modes.[20] Cooling a THF-d_8 solution of the product allylcopper **2g** resulted in significant broadening of the resonances corresponding to the allyl moiety, but no static structure was observed upon cooling to −90 °C.

Having established a general preparative method for polyfunctionalized aromatic copper compounds, we next examined the reactivity of arylcopper compounds **2**. Pure phenylcopper **2a** reacts cleanly with allyl bromide, affording allylbenzene (quant yield by NMR). Other organocopper reagents, including bromide **1j** have been generated in quantitative yield (NMR) by treating **1j** with 1.2

Scheme 1. Reactivity of Organocopper Species

metallic precursors.[18,23] species. (NHC)copper species serve as increasingly valuable catalysts for reactions assumed to involve organocopper intermediates, and we believe that the method described here will allow a more thorough investigation of the mechanism and selectivity questions in these processes. Finally, copper(I) fluoride complexes have seen limited use in synthesis owing to the lack of soluble, anhydrous complexes available without the presence of protic solvent molecules, and the work here demonstrates that new, well defined, anhydrous copper(I) fluoride complexes enable new reactivity and catalysis.

Supporting Information Available: Complete experimental details and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

equiv of (IPr)CuF. Treatment of this crude mixture with acetyl chloride allowed isolation of the product ketone **2j**. Similarly, the acetophenone derivative **1i** affords a stable organocopper species observed by ^{1}H NMR, and the ketone **2i** was readily isolated following treatment with allyl bromide. The ability to form stable organocopper reagents from substrates bearing a methyl ketone group with acidic α-hydrogen atoms in this example is noteworthy. Finally, the reaction of benzylic chloride **1h** with (IPr)CuF affords an organocopper species, observable by ^{1}H NMR, which is significantly less stable than others in this study, and which decomposes at a rate competitive with its formation. In this case, performing the transmetalation in the presence of allyl bromide allowed clean coupling to afford the chloride **2h**.

An important future goal of the transmetalation procedure outlined here is the development of a bond-forming process of organosilanes using catalytic quantities of (NHC)CuF complexes. Toward this end, we find that (IPr)CuF catalyzes the allylation of octanal in good yield (Scheme 2).[12] This result indicates that

Scheme 2. Catalytic Aldehyde Allylation with (IPr)CuF
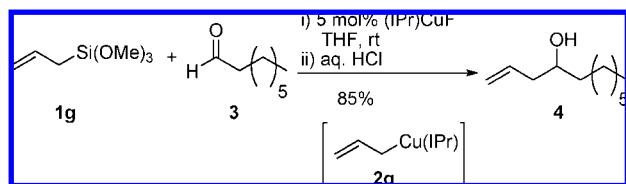
(IPr)Cu-alkoxides, such as that formed after 1,2-addition of an allylcopper intermediate, are catalytically competent to continue on the catalytic cycle and opens opportunities for the development of other catalytic and potentially stereocontrolled processes. The (IPr)CuF-catalyzed allylation is a part of the small class of a catalytic allylation reactions proceeding by a transmetalation mechanism.[21]

Organometallic (NHC)-copper complexes are important as presumed intermediates in a number of synthetically useful catalytic reactions. However, there are few general methods available for the synthesis of organocopper−NHC complexes,[22] and many of these require inconvenient or functional-group intolerant organo-

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JA8070804