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Catalytic C−H Bond Functionalization: Synthesis of Arylsilanes by Dehydrogenative Transfer Coupling of Arenes and Triethylsilane

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Summary: A new catalytic route for the formation of arene−silicon bonds based on the transfer dehydrogenative coupling of triethylsilane with an arene (Ar−X: X = −CF_3, −F, −H, −CH_3, −Cl, −Br) in the presence of 3,3-dimethylbut-1-ene (^{t}Bu-ethylene) is reported. Rhodium and ruthenium catalysts (η^5-C_5Me_5)Rh(H)$_2$($SiEt_3$)$_2$ and (η^6-arene)Ru(H)$_2$($SiEt_3$)$_2$ and their corresponding dimeric chloride precursors not only catalyze the coupling of Et_3SiH with an arene but additionally promote the dimerization of Et_3SiH producing a carbosilane, Et_3Si−CHMe−$SiEt_2H$.

The ability of transition-metal complexes to react with the C−H bonds of simple hydrocarbons has become very well established over the past two decades. However, this knowledge has led to relatively few systems with the ability to catalytically functionalize C−H bonds.[1] This is unfortunate as the potential use of C−H bonds in place of more reactive carbon−halide bonds would be particularly attractive in several industrial processes. The synthesis of arylsilanes—important intermediates in the silicone industry—is an excellent case in point. The common methods such as the Direct (Rochow) Process[2] and the Barry Process[3] cannot be adapted for most specialty arylsilanes and mixed aryl−alkyl silanes, which must be produced using Grignard or lithium reagents. As a result, one focus of our research efforts has been the discovery of new catalytic methods for the formation of silicon−carbon bonds, especially arylsilanes.

In 1982, Curtis and co-workers reported that Vaska's complex promotes the formation of phenylsiloxanes from hydridosiloxanes and benzene in a catalytic, albeit low-yield, process.[4] More recently, Tanaka demonstrated the selective arylation of *o*-bis(dimethylsilyl)benzene using platinum catalysts.[5] This intriguing process gives high yields for a variety of arenes but appears limited to this particular silane. Tanaka has also reported that a rhodium phosphine complex catalyzes the dehydrocoupling of benzene and triethylsilane under photolytic conditions.[6] We have previously described the catalytic activation and functionalization of alkylsilanes to produce oligomeric carbosilanes using homogeneous ruthenium and rhodium complexes, a process which involves the dehydrogenative coupling of C−H and Si−H bonds.[7,8] Furthermore, the process is greatly accelerated when combined with the concurrent reduction of a suitable hydrogen acceptor. For example, the catalytic transfer dehydrogenative coupling of Et_3SiH in the presence of 3,3-dimethylbut-1-ene (^{t}Bu-ethylene) produces a carbosilane dimer Et_3Si−CHMe−$SiEt_2H$ and 2,2-dimethylbutane.[8] In the present paper, we now describe an analogous catalytic transfer dehydrocoupling of arene C−H and silane Si−H bonds which produces arylsilanes.[9]

The basic transfer dehydrocoupling reaction is illustrated in eq 1. Heating a solution containing ca. 5% each of Et_3SiH and ^{t}Bu-ethylene and the metal catalyst (1−8% metal with respect to Et_3SiH) in an arene Ar−X (X = H, CH_3, CF_3, F) leads to hydrogenation of ^{t}Bu-ethylene to 2,2-dimethylbutane and formation of two primary silicon-containing products: aryltriethylsilane and the carbosilane dimer. Small amounts of the hydrosilylation products ^{t}BuCH$_2$CH$_2$SiEt$_3$ and *E*-^{t}BuCH=CHSiEt$_3$ (5−10% total) are also observed. Two related

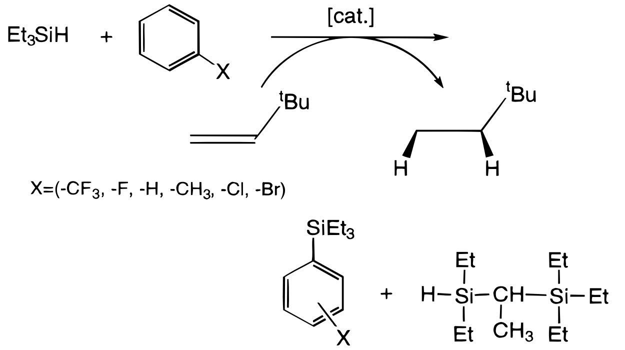

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Table 1. Transfer Dehydrocoupling of Et_3SiH and $C_6H_5CF_3$ at 50% Silane Conversion[a,b]

catalyst	T (°C)	time (min)	product selectivity (%)[c] arylsilane	carbosilane	hydrosilylation
1a	150	5	45	50	5
1a	100	90	18	74	8
1b	150	<5	40	56	4
1b	100	25	20	74	6
2a	150	90	90	5	5
2b	150	95	88	3	9

[a] Standard conditions: $C_6H_5CF_3$:Et_3SiH:^tBu-ethylene:metal = 20:1:1:0.08. [b] Times and selectivities determined by GC and reported at 50% conversion of Et_3SiH. [c] Each mole of carbosilane is weighted 2 times in the selectivity calculation.

Table 2. Transfer Dehydrocoupling of Et_3SiH and $C_6H_5CF_3$ at >90% Silane Conversion[a,b]

			yield (%)[c]			
catalyst	T (°C)	time (min)	Et_3SiH	arylsilane	carbosilane	hydrosilylation
1a	150	250	0.0	67.0	20.3	4.6
1a	100	435	3.0	51.9	34.0	4.5
1b	150	50	0.3	51.0	22.5	3.6
1b	100	180	4.4	30.0	33.2	2.6
2a	150	1680	3.5	33.1	2.5	1.8
2b	150	660	8.5	38.4	1.5	3.0
1a[d]	150	1140	0.0	42.3	59.0	7.5

[a] Standard conditions: $C_6H_5CF_3$:Et_3SiH:^tBu-ethylene:metal = 20:1:1:0.08. [b] Yields determined by GC. [c] Each mole of carbosilane is weighted 2 times in each calculation. [d] $C_6H_5CF_3$:Et_3SiH:TBE: catalyst = 20:1:1:0.02.

organometallic systems have been found to be active as catalysts: $Cp^*Rh(H)_2(SiEt_3)_2$[10] (**1a**) and $(\eta^6\text{-}C_6Me_6)Ru(H)_2(SiEt_3)_2$[11] (**2a**) ($Cp^*$= η^5-C_5Me_5). In addition, the corresponding metal chloride dimers $[Cp^*RhCl_2]_2$[12] **(1b)** and $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$[13] (**2b**) can be used directly as catalyst precursors, without the need to isolate the silyl complexes. The Et_3SiCl produced (2 equiv/metal) does not appear to interfere with the catalysis. Control reactions attempted in the absence of ^tBu-ethylene yield only trace amounts of the dehydrocoupling products (<1 equiv/metal).

The results of several coupling reactions between triethylsilane and α,α,α-trifluorotoluene are listed in Tables 1 and 2. Table 1 lists reaction selectivities at 50% Et_3SiH conversion, and Table 2 lists product yields at longer reaction times. For example, reactions using **1b** require ca. 25 min to reach 50% conversion of Et_3SiH at 100 °C and ca. 5 min at 150 °C.[14] Interestingly, the selectivity for arylsilane formation is significantly greater at the higher temperature. Thus, at 50% Et_3SiH conversion, the selectivity for $Et_3Si(C_6H_4CF_3)$ (meta and para isomers) is 20% at 100 °C and 40% at 150 °C.[15]

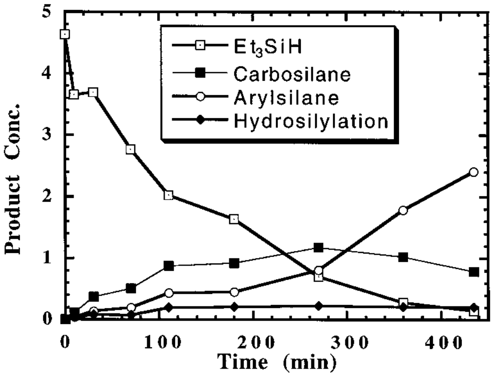

Figure 1. Evolution of products for the dehydrogenative coupling of triethylsilane and α,α,α-trifluorotoluene were followed by GC, clearly showing initial preference for the carbosilane dimer and ultimate dominance of arylsilane. Conditions: 100 °C, 8 mol % of **1a,** $C_6H_5CF_3$:Et_3SiH:^tBu-ethylene= 20:1:1.

Most significantly, the selectively for the desired arylsilane product increases as the reaction proceeds. This is illustrated in Figure 1 for a run using **1a** at 100 °C. Initially, >3 mol of carbosilane dimer is produced for each mole of arylsilane (<20% selective for arylsilane.) However, as the Et_3SiH is consumed, formation of carbosilane dimer slows relative to arylsilane formation. Indeed, the concentration of arylsilane appears to increase at the expense of carbosilane even after the Et_3SiH is exhausted, suggesting the carbosilane dimer is the kinetic product of the dehydrocoupling and that arylsilane is the thermodynamic product. This is confirmed by an independent reaction of trifluorotoluene with the carbosilane dimer catalyzed by **1b** in the *absence* of ^tBu-ethylene, which results in the formation of arylsilane and Et_3SiH.

There are two major differences in the transfer dehydrocoupling reaction catalyzed by the ruthenium complexes **2a** and **2b** compared with the rhodium complexes: the reaction is ca. 20 times slower, but selectivity for arylsilane at 150 °C is much greater. Thus, a reaction time of 95 min is required to reach 50% conversion of Et_3SiH using **2b**, but the reaction is 88% selective for arylsilane.[15]

The reactivity of various monosubstituted arenes, Ar−X (X = $-CH_3$, $-CF_3$, −F), in the dehydrocoupling reaction with Et_3SiH was examined using **1b** as the catalyst. Silylation of toluene and trifluorotoluene yielded both the *meta*- and *para*-silyl isomers in a 2:1 ratio; the ortho isomer was not detected in either case. The inability of this system to functionalize C−H bonds adjacent to methyl groups is also clearly seen in the regiochemistry exhibited by various xylenes. Thus, silylation of *m*-xylene yields only $Et_3Si(3,5\text{-}C_6H_3Me_2)$, and *o*-xylene yields only $Et_3Si(3,4\text{-}C_6H_3Me_2)$. *p*-Xylene and mesitylene, in which all aryl C−H bonds are ortho to at least one methyl group, do not yield arylsilane

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(14) Representative reaction using catalyst **1b:** 0.0281 g (4.55 × 10^{-5} mol) of **1b** was weighed out in a vial and dissolved in 4.0 mL of chloroform. The mixture was stirred and filtered. A 0.300 mL amount of the catalyst solution was placed into each of the 10 ampules. The chloroform was then evaporated, 0.3 mL of stock solution containing a 20:1:1:0.22 molar ratio of $C_6H_5CF_3$:Et_3SiH:*tert*-butylethylene:hexadecane was added under a dry nitrogen atmosphere, and then the ampules were sealed. The ampules were submerged in a constant temperature oil bath. Individual ampules were removed at various reaction times, cracked open, and analyzed by GC. GC peak areas were corrected with previously measured response factors. Hexadecane was used as an internal standard.

(15) Because 2 equiv of Et_3SiH is required to produce carbosilane dimer, the concentration of the dimer is weighted 2 times in calculating the product selectivity, e.g., a 1:1 ratio of arylsilane to carbosilane dimer would correspond to 33% selectivity for arylsilane based on the amount of Et_3SiH consumed.

products. In contrast, fluorobenzene is silylated to produce ortho, meta, and para isomers in a 3.0:3.8:1.0 ratio.[16,17]

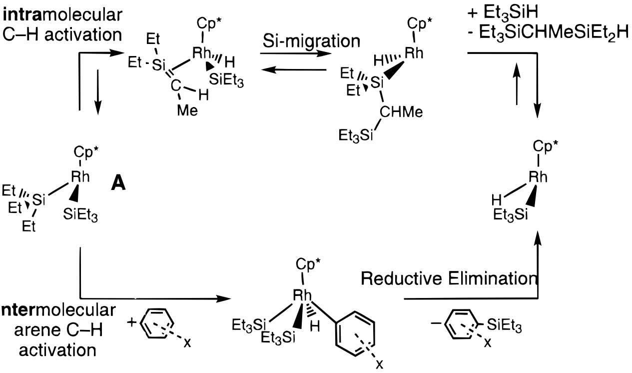
The relative reactivity of monosubstituted arenes was determined by reacting each with Et_3SiH and ^tBu-ethylene in an internal competition with benzene. The relative ratios of the substituted arylsilanes to phenylsilane product were found to be CF_3 (2.8) > F (1.4) > H (1.0) > CH_3 (0.32). Clearly, arene C−H functionalization is enhanced by electron-withdrawing substituents.

The transfer dehydrocoupling of Et_3SiH with chlorobenzene does yield $Et_3Si(C_6H_4Cl)$ (meta and para isomers) but with low (ca. < 3.6%) selectivity. The primary products are benzene and Et_3SiCl, from the concurrent reduction of chlorobenzene. The unsubstituted arylsilane $Et_3Si{-}C_6H_5$ is also observed in the reaction mixture and appears to form directly by silylation of a C−Cl bond, as opposed to subsequent reduction of $Et_3Si(C_6H_4Cl)$. The reduction of chlorobenzene with Et_3SiH to benzene is catalyzed by **1b** in the absence of ^tBu-ethylene, even at room temperature. Similarly, attempts to silylate bromobenzene generated benzene and Et_3SiBr as the principal products.

Evidence for possible mechanisms for the formation of the carbosilanes has been presented and discussed previously,[7,8] but the most likely process involves β-hydrogen elimination from a silyl ligand in a $16e^-$ bis(silyl) intermediate, **A**, to yield an η^2-silene hydride complex (i.e., intramolecular C−H activation).[18] Furthermore, the fact that the carbosilane dimer is a kinetic product which is ultimately converted to arylsilane requires the reversibility of its formation. On the other hand, it is likely that arene functionalization is initiated by an independent intermolecular C−H activation by the same $16e^-$ intermediate **A** and that the arylsilane is formed by Si−C reductive elimination.[19] These paths are illustrated in Scheme 1. The formation of **A** (e.g., from **1a**) is not shown but could occur by sequential silane reductive elimination, coordination, and insertion of ^{t}-Bu-ethylene into a hydride, readdition of silane, and reductive elimination of 2,2-dimethylbutane.

Although it is suggested that productive C−H bond functionalization occurs from bis(silyl) intermediate **A**, one should not infer that the silyl hydride intermediate (e.g., $Cp^*Rh(H)(SiEt_3)$) does not oxidatively add the C−H bonds of arenes. On the contrary, this is clearly demonstrated by the very facile H/D scrambling catalyzed by **1a**[20]and **2a**,[11] which is rapid at 90 °C. It is likely that C−H addition to the silyl hydride yields a silyl phenyl dihydride species (i.e., $Cp^*Rh(H)_2(SiEt_3)(Ph)$) in which the silyl and phenyl groups cannot reductively eliminate arylsilane due to their transoid disposition. However, addition of an arene to bis(silyl) **A** must leave one silyl adjacent to the aryl ligand.

Scheme 1



The origin of the greater selectivity for arylsilane formation exhibited by the ruthenium complexes is not certain, although it is significant that **2a** catalyzes the reaction of the carbosilane with $PhCF_3$ much more slowly than does **1a**. This establishes that the selectivity of **2a** is determined prior to reductive elimination of the carbosilane from the ruthenium. Whether this reflects stronger precoordination of the arene to ruthenium than rhodium or some other effect is unknown.

Overall, aspects of the arene silylation such as the steric inhibition of activation of sites ortho to methyl groups, statistical meta:para isomer distributions, and acceleration by electron-withdrawing groups all mirror observations for “nucleophilic” C−H activation by low-valent late transition metals.[21] The trends are also quite similar to those observed by Tanaka in the platinum-catalyzed arylation of *o*-bis(dimethylsilyl)-benzene,[5] although there are some differences. In particular, the platinum/dibenzylideneacetone system seems to yield a significant amount of *o*-tolyl isomers, which may reflect the greater steric encumbrance of the Cp*Rh and $(\eta^6\text{-}C_6Me_6)$Ru complexes. Also, the platinum system is not reported to catalyze the reduction of Ph−Cl and Ph−Br by the hydridosilane.

In summary, transfer dehydrocoupling of an arene and $HSiEt_3$ is a selective process for preparing arylsilanes. Investigations to extend the reaction to include silanes other than triethylsilane are currently in progress.

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[16] The peaks for $Et_3Si(p\text{-}C_6H_4F)$ and $Et_3Si(o\text{-}C_6H_4F)$ could not be resolved by capillary GC; analysis of the *o*:*m*:*p* ratio in this instance was performed by ^{19}F NMR.

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