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Communication

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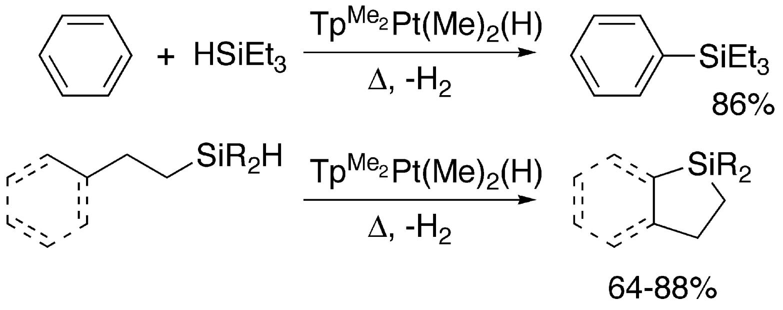

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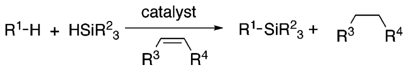
Intermolecular and Intramolecular, Platinum-Catalyzed, Acceptorless Dehydrogenative Coupling of Hydrosilanes with Aryl and Aliphatic Methyl C−H Bonds

Naofumi Tsukada and John F. Hartwig*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received January 30, 2005; E-mail: John.Hartwig@yale.edu

New selective methods to replace aromatic and aliphatic C−H bonds with functional groups are needed to realize the synthetic potential of C−H activation. We and others have contributed to C−H bond functionalization by developing reactions of boron reagents with arenes and alkanes that form aryl and alkylboronate esters.[1,2] These reactions occur with high selectivity for the least hindered aromatic C−H bond and for primary aliphatic C−H bonds, in some cases at room temperature.



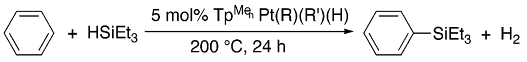
The scope of the silylation of aromatic[3] and aliphatic C−H bonds is more limited. Most reactions of C−H bonds with hydrosilanes have required a hydrogen acceptor,[4] photochemical conditions,[5] C−H bonds at aromatic or benzylic positions with accompanying ligating groups,[6] or a special *o*-disilylarene reagent.[7] An impressive reaction of a silane with methane has been reported, but this reaction occurs slowly with low turnover numbers and did not extend to arenes or higher alkanes.[8] The silylation of arenes with strained[9] or unstrained[10] disilane reagents also occurs, but these reagents require several steps to prepare.

If the dehydrogenative coupling of simple silanes with aromatic and aliphatic C−H bonds could be developed, then valuable reactions could result. Because silanes are more stable toward disproportionation than are boranes, silanes could undergo tandem or sequential reactions that would be impossible with borane, or even disilane, reagents. We report a series of new reactions of silanes with C−H bonds catalyzed by a platinum complex in the absence of ligating functionality or hydrogen acceptor. These reactions occur at both aromatic and aliphatic C−H bonds and show that hydrocarbon silylations can be irreversible, even in the absence of a hydrogen acceptor.

In parallel with reactions between arenes and boranes catalyzed by platinum(IV) complexes that would relate to the Rh(V) complexes involved in the borylation of alkanes,[2] we investigated reactions of silanes with arenes. $CpPtR_3$ compounds in which R is a hydride or organic ligand are limited in number and stability,[11] but the analogous $TpPtR_3$ are known and are more stable.[12,13] Thus, we tested the reactivity of $TpPtR_3$ derivatives for the dehydrogenative couplings of silanes with hydrocarbons.

The results of the reactions of benzene with triethylsilane in sealed reaction vessels to form phenyltriethylsilane catalyzed by a series of TpPt complexes are summarized in Table 1. Although the reactions catalyzed by Tp (**1a**) and Tp^{Me_2} (Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate, **1b**−**d**) derivatives occurred with similar rates and yields, the reactions catalyzed by $Tp^{Me_2}Pt$ complexes were strongly dependent on the covalent ligand R in the precatalyst. For example, $Tp^{Me_2}Pt(Me)_2H$ (**1b**) was much more reactive than the analogous methyl dihydride $Tp^{Me_2}Pt(Me)(H)_2$ (**1c**).

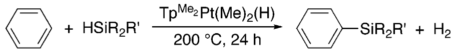
Table 1. Effect of Catalyst Structure on the Silylation of Benzene



	Tp^{Me_n}	R	R′	yield (%)
1a	Tp	Me	Me	72
1b	Tp^{Me_2}	Me	Me	86
1c	Tp^{Me_2}	Me	H	6
1d	Tp^{Me_2}	Ph	Ph	78

Because dimethyl **1b** reacts with arenes to form $Tp^{Me_2}Pt(Ph)_2H$ (**1d**),[13] we also conducted reactions catalyzed by isolated **1d**. The reactions catalyzed by **1d** occurred in an analogous fashion to those initiated with dimethyl hydride **1b**.

We also surveyed reactions of several mixed alkylsilanes, aryl alkylsilanes, and aryl halosilanes catalyzed by $Tp^{Me_2}PtMe_2H$ (eq 1). As expected, the reaction of tripropylsilane occurred in a fashion similar to the reaction of triethylsilane, but the reaction of *tert*-butyldimethylsilane did not occur with the catalyst containing Tp^{Me_2} as ligand. Aryl alkylsilanes also underwent the dehydrogenative coupling process: the reaction of benzene with phenyldimethylsilane and diphenylmethylsilane generated the corresponding diphenyldimethyl and triphenylmethylsilanes in good yield. No reaction of benzene with dichlorophenylsilane occurred, however.



(1)

R=R′=Et	86%	R=Me, R′=Ph	71%
R=R′=Pr^n	86%	R=Ph, R′=Me	64%
R=Me, R′=Bu^t	NR	R=Cl, R′=Ph	NR

In contrast to the low stability of monoalkylboranes to disproportionation,[14] even without a catalyst, the alkyl arylsilanes were relatively stable to disproportionation in the presence of the platinum catalyst. The reaction of diphenylmethylsilane (eq 2) at 200 °C in benzene generated only 8% of diphenyldimethylsilane from reaction of phenyldimethylsilane, and heating in cyclohexane with no arene generated less than 10% phenyldimethylsilane or other possible redistribution products.

For simplicity of characterization of the reaction products, we explored the scope of the silylation of arenes with triethylsilane. Reaction of toluene generated a 1.9:1 mixture of meta and para regioisomers. Little orthosilylated material was formed. Consistent with this result, the reaction with *o*-xylene generated a 96:4 mixture of 4-silylated and 3-silylated products. The reaction of trifluorotoluene generated a 2.1:1 mixture of meta and para regioisomers. The tolerance of functional groups at this time is not high; reactions with haloarenes occurred with low turnover.

To reveal the electronic effects on intermolecular selectivity, we measured the selectivity of the reactions of arenes possessing distinct electronic properties. The reaction occurs with a small preference

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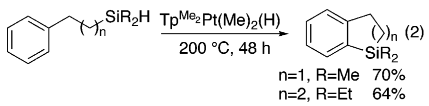
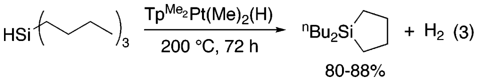
for reaction with more electron-poor arenes. The reaction of triethylsilane with a 1:1 molar mixture of trifluorotoluene and toluene generated a 1.5:1 ratio of products resulting from silylation of the trifluorotoluene and silylation of toluene (63% yield overall), and the reaction of tripropylsilane with the more electronically distinct *m*-xylene and 1,3-bistrifluoromethylbenzene generated a 3.3:1 mixture of the two products from silylation of the 5-positions favoring reaction with the electron-poor arene (51% yield overall). Although one might expect the relatively low selectivity to result from the high reaction temperature, most organometallic C−H activations of arenes occur without strong electronic effects.[15]



Intramolecular dehydrogenative coupling of silanes was also conducted for the first time in high yield to form both five- and six-membered organosilicon products (eq 2). Heating of dimethyl-2-phenylethylsilane ($n = 1$ in eq 3) in the presence of 5% $\mathrm{Tp^{Me_2}PtMe_2H}$ led to the extrusion of H_2 and formation of the cyclic organosilane in 70% yield. The hydrosilylation of allylbenzene with diethylsilane in the presence of Wilkinson's catalyst formed diethyl-3-phenylpropylsilane ($n = 2$ in eq 2), which underwent cyclization in the presence of 5% $\mathrm{Tp^{Me_2}PtMe_2H}$ in 64% yield. These intramolecular processes can be envisioned as a route to bifunctional products after Tamao−Fleming oxidation of appropriately substituted cyclization products.[16]

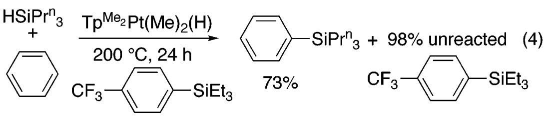


Intramolecular dehydrogenative coupling of silanes also occurred at aliphatic C−H bonds, as shown in eq 3. Heating of tributylsilane with 5% $\mathrm{Tp^{Me_2}PtMe_2H}$ generated the cyclic organosilane in 80−88% yield by GC and NMR spectroscopic methods. This reaction constitutes the first coupling of a silane Si−H bond with a purely aliphatic C−H bond in high yield.

Because oxidation of the organosilanes requires one aryl, halo, or alkoxo group on silicon,[16] we also investigated the cyclization of dibutylphenylsilane. Reaction of this material led to selective reaction at the butyl group over the arene. The yield of cyclized product was lower than that from tributylsilane, but 31% of the silacycle was formed. To date, reactions of tripentylsilane or trihexylsilane to generate the larger six-membered and seven-membered cyclic products have not been observed.

The thermodynamics for coupling of silanes with arenes and alkanes are not clear from previous work. Most reactions have been conducted with a hydrogen acceptor, but one with a special silane reagent was not.[7] Moreover, individual aryl−silicon bond energies have not been measured. However, the energies[17] of the Si−H bond in trimethylsilane, the C−H bond in methane, the Si−C bond in tetramethylsilane, and the H_2 bond imply that the dehydrogenative coupling reaction is nearly thermoneutral.

Thus, we probed the thermodynamics of arene silylation. To do so, we conducted the reaction of tripropylsilane with benzene in the presence of 1.5 equiv (relative to $\mathrm{HSiPr_3}$) of pure *p*-trifluoromethylphenyl triethylsilane (eq 4). If the silylation of arenes was reversible in the sealed reaction vessel, then *m*- and *p*-tripropylsilyl trifluoromethylbenzene would be formed along with triethylsilylbenzene, and the *p*-trifluoromethylphenyl triethylsilane would be expected to isomerize to a mixture of meta and para regioisomers. Instead, this process generated only phenyl tripropylsilane; 98% of the *p*-trifluoromethylphenyl triethylsilane remained unreacted. Moreover, heating of triethylsilyl *m*-xylene and 10 atm of hydrogen in a Parr reactor at 200 °C in the presence of either $\mathrm{Tp^{Me_2}PtMe_2H}$ or a combination of $\mathrm{Tp^{Me_2}PtMe_2H}$, benzene, and triethylsilane did not generate detectable amounts of *m*-xylene. Thus, the dehydrogenative silylation of the arenes appears to be irreversible, even in a sealed reaction vessel.



In summary, we have reported an acceptorless dehydrogenative coupling of silane Si−H bonds with aromatic and aliphatic C−H bonds to form products with new Si−C bonds in high yields. The rates and scope of this catalytic process must be improved, and current efforts focus on such reaction development.

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Supporting Information Available: Reaction procedures and characterization of reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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