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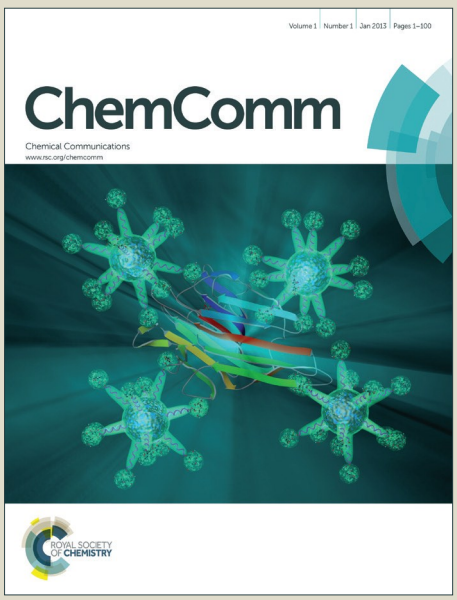

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Reductive Arene *ortho*-Silanolization of Aromatic Esters with Hydridosilyl Acetals

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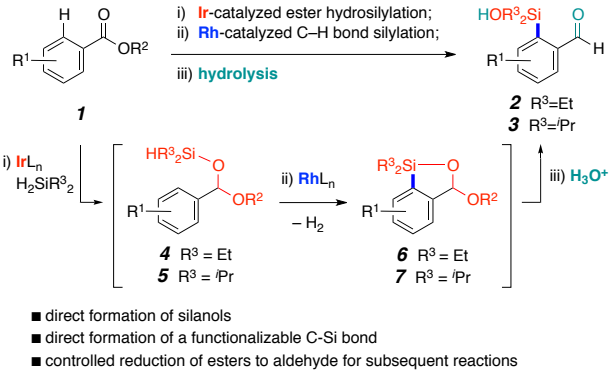
This work describes the design and application of a single-pot, reductive arene C–H silanolization of aromatic esters for synthesis of *ortho*-formyl arylsilanols. This strategy involves a sequence of two transition metal (Ir and Rh)-catalyzed reactions for reductive arene *ortho*-silylation directed by hydridosilyl acetals and hydrolysis.

Organosilanols[1] are, in general, environmentally benign, and their use has been significantly increased with wide application for silicon-based materials[2] and biomedically relevant agents.[3,4] They are also useful synthetic agents for a variety of chemical transformations, including silicon-based cross-coupling reactions,[5] oxidations,[6] silanol hydrogen bond donor catalysts,[7] directing groups for C–H bond functionalization.[8] In particular, arylsilanol synthesis often involves a two-step sequence of silylation and hydrolysis. Several silanolization methods have been developed, such as: 1) metal-halogen exchange/silylation,[9] 2) hydrolytic oxidation of hydrosilanes,[10] 3) metal-catalyzed silylation of haloarenes followed by hydrolysis,[11] and 4) a sequence of directed arene *ortho*-metalation, silylation, and hydrolysis.[12] These methods offer excellent site-selectivity, yet often require strongly basic and cryogenic conditions or a stoichiometric amount of reagents, thereby displaying poor functional group compatibility. Alternatively to direct silylation, prefunctionalized moieties [e.g., aryl (pseudo)halides] are demanded within substrates.

Metal-catalyzed arene dehydrogenative silylation have emerged as a powerful method for preparation of useful organosilanes.[13-19] To access diverse, functionalized organosilanols, which were previously difficult to access in an atom- and step-economical fashion, we envisioned dehydrogenative silanolization via catalytic C–H activation. This strategy consolidates two remarkable methods, developed by the Brookhart and Hartwig laboratories. Brookhart reported a method for highly controlled Ir-catalyzed ester reduction via hydrosilylation to afford corresponding aldehydes.[20a] Hartwig



Scheme 1 Reductive arene *ortho*-silanolization of esters via a sequence of Ir and Rh-catalyzed reactions and hydrolysis

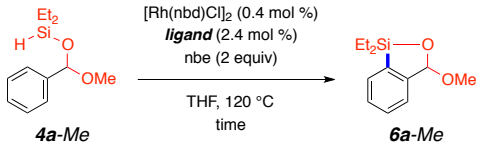
demonstrated that hydridosilyl ether-directed, Ir-catalyzed C_{sp2}–H and C_{sp3}–H silylation of alcohols, aldehydes, ketones, and amines could provide a variety of cyclic silyl ethers.[13f,21]

Our approach to the development of a reductive arene *ortho*-silanolization reaction, which could directly prepare arylsilanols, features the sequence of two transition metal-catalyzed reactions and facile hydrolysis in a single vessel (Scheme 1). Specifically, *in situ* generation of hydridosilyl acetals **4**/**5** via Ir-catalyzed hydrosilylation of esters **1**[20] could direct C–H silylation under suitable catalytic conditions to afford cyclic silyl acetals **6**/**7**. Upon simple aqueous work-up, *ortho*-formyl arylsilanols **2**/**3** could be produced. Notably, the versatile, yet labile silyl acetals are shown to act as directing groups for catalytic C–H silylation, which has not been reported to date. Nonetheless, our strategy for the single-pot reductive *ortho*-silanolization of arenes required the resolution of two challenges: First, the compatibility of the two catalysts toward a combined single-pot reaction sequence had to be established. Secondly, the discovery of a catalytic system suitable for C–H functionalization directed by labile hydridosilyl acetals was

required. Herein, we report a regio- and chemoselective, single-pot reductive arene *ortho*-silanolization of aromatic esters via a sequential Ir-catalyzed ester hydrosilylation and Rh-catalyzed C–H silylation, directed by versatile hydridosilyl acetals, followed by hydrolysis of acetals.

From the outset, diethylhydridosilyl acetals were prepared via a controlled hydrosilylation of aromatic esters utilizing $[Ir(coe)_2Cl]_2$ (0.1 mol %) and diethylsilane (2 equiv).[20a] The resultant diethylhydridosilyl acetals did not require additional purification for the next steps. We then investigated arene *ortho*-silylation of hydridosilyl acetal **4a**-Me. Although we aimed to utilize a single Ir catalyst for both processes, neither the Ir/phen catalytic system (or phen derivatives as ligands), nor other screened Ir/ligand complexes efficiently afforded the cyclic silyl acetal **6a**-Me (ca. 30% yield upon complete conversion). Steric and electronic differences of hydridosilyl ether and hydridosilyl acetal directing groups had considerable impact on reactivity. This obstacle was overcome by utilizing Rh-catalyzed C–H bond silylation (Table 1).[14] Takai had shown that Rh-catalyzed C–H silylation could be used to prepare silafluorenes, by employing monodentate triphenylphosphine ligands.[14d] Gratifyingly, monodentate phosphine ligands effectively promoted the hydridosilyl acetal-directed dehydrogenative cyclization in the presence of norbornene as a hydrogen acceptor. For instance, triphenylphosphine afforded **6a**-Me in excellent yield (entry 1). However, sterically hindered and alkyl substituted phosphines, PPh_2(*o*-tol) and PPh_2Me, were not effective ligands (entries 2-3). To systematically study the influence of electronic perturbation of phosphine ligands in the C–H silylation, we examined a series of electronically tuned phosphine ligands (entries 4-7). Electron-donating ligand P(4-MeOPh)$_3$ efficiently promotes the cyclization to afford **6a**-Me in excellent yield (98%) within only 10 min. In comparison, well-established hydridosilyl ether-directed arene C–H silylation took 11-48 h at 80-120 °C employing 1 mol % of $[Ir(cod)OMe]_2$/phen.[13f] However, other phosphines such as P(4-$Me_2NPh)_3$ and $P(C_6F_5)_3$ drastically reduced the overall reaction efficiency (entry 5-6). Upon addition of P(2-furyl)$_3$ to the reaction, the yield was improved, but not comparable to P(4-MeOPh)$_3$. Moreover, the Rh/(4-MeOPh)$_3$ catalytic system achieved the reaction with sterically hindered 2- and 3-methyl benzoates to afford the corresponding cyclic silyl acetals (98% and 92% yields vis-à-vis 63% and 54% with PPh_3, respectively)

Table 1 Evaluation of ligands for Rh-catalyzed hydridosilyl acetal-directed arene *ortho*-silylation.[a]



4a-Me *6a-Me*

Entry	Ligand	Time (min)	Yield (%)[b]
1	PPh_3	10	98
2	PPh_2(*o*-tol)	60	10
3	PPh_2Me	60	20
4	P(4-MeOPh)$_3$	10	98
5	P(4-$Me_2NPh)_3$	60	20
6	$P(C_6F_5)_3$	60	20
7	P(2-furyl)$_3$	60	95

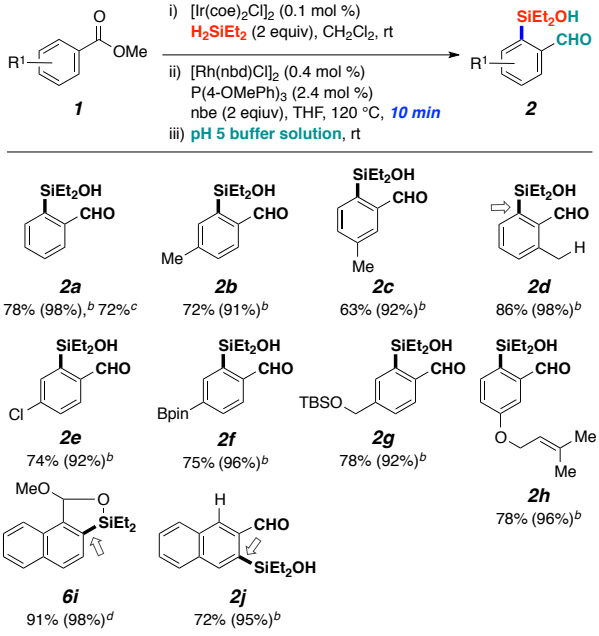
[a] Conditions: Silyl acetal **4a-Me** (0.2 mmol), THF (1 M). [b] Determined by ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2).

within 10 min. These results showed that the two catalytic systems (Ir and Rh) are compatible, and that a single-pot reductive arene *ortho*-silylation directed by hydridosilyl acetals is feasible.

Upon determination of optimal reaction conditions for the hydrosilylation of esters and concomitant C–H silylation via Ir and Rh sequential catalyses,[22] we investigated the substrate scope of the reductive arene *ortho*-silanolization of esters **1**. The sequential processes utilizing diethylsilane produce cyclic silyl acetals **6** in generally good yields, regardless of electronic and sterics of arenes. However, the propensity for silanol condensation to afford disiloxanes during hydrolysis resulted in inconsistent yields of *ortho*-formyl arylsilanols **2**. Denmark's method resolved this issue by utilizing a buffer solution (pH 5) to reliably produce **2** (Table 2).[11a] Under the conditions, the tandem reactions with electron-rich and deficient esters yielded the corresponding arylsilanols (**2a-2e**) in good yields. A boronic ester, silyl blocking group, and trisubstituted alkene[23] were tolerated in the reaction system to afford **2f-2h**. We observed chemoselective silanolization of aryl C_{sp2}–H over benzylic C_{sp3}–H within **2d**. Highly regioselective C–H silanolization of 1-naphthoate was achieved, where the corresponding hydridosilyl acetal exclusively triggers C–H activation of hydrogen at C2 over the hydrogen at C8 to afford **6i**. Hydrolysis of **6i** in a wide range of pH buffer solutions, however, provided either the recovered starting material or significant desilylation product. In 2-naphthoate, silanolization occurred at the C3 position regioselectively to provide **2j**. Lastly, the reaction of **1a** on 12 mmol scale provided **2a** in 72% isolation yield.

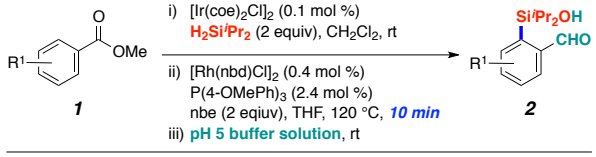
Silicon groups bearing larger substituents, such as isopropyl groups, greatly suppressed the silanol condensation, thereby consistently improving yields (Table 3). The reaction with electron-rich and deficient esters provided the corresponding silanols (**3b-l**) in good yields. The reactions

Table 2 Substrate scope of aromatic esters using diethyllsilane[a]

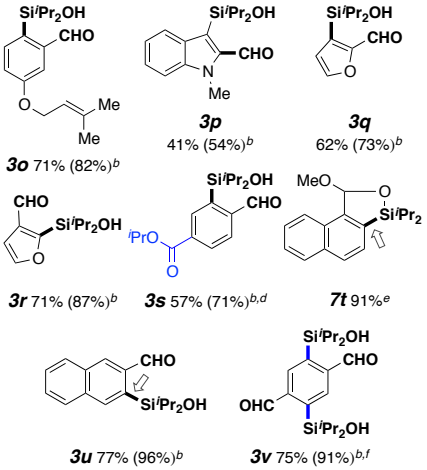


[a] Conditions: **1** (1.0 mmol), CH_2Cl_2 (3.3 M); THF (1 M). [b] Yield of isolated product **2**. Yield of cyclic silyl acetals **6** determined by ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2) is shown in parentheses. [c] Reaction of **1a** on 12 mmol (1.63 g) scale yielded **2a** in 72% isolation yield. [d] Isolated yield of **6i**.

Table 3 Substrate scope of aromatic esters using diisopropylsilane[a]



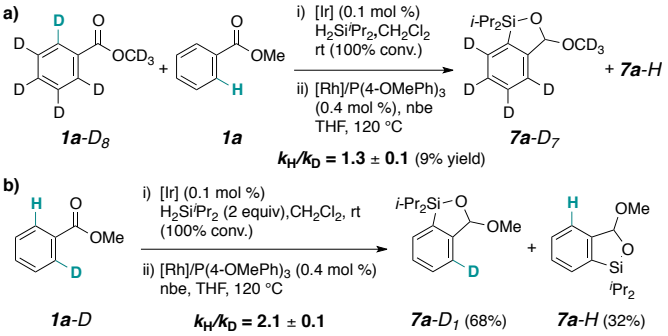
	R	yield of 3 (%)[b]
3a	H	91 (98)
3b	4-Me	90 (98)
3c	5-Me	67 (86)
7d	6-Me	90[c]
3e	4-F	85 (96)
3f	4-Cl	75 (86)
3g	5-Cl	78 (93)
3h	4-CF_3	72 (98)
3i	4-OMe	56 (92)
3j	5-OMe	77 (91)
3k	6-OMe	36 (48)
3l	5-NMe_2	91 (98)
3m	4-Bpin	77 (91)
3n	5-Bpin	72 (97)



[a] Conditions: **1** (1.0 mmol), CH_2Cl_2 (3.3 M); THF (1 M). [b] Yield of isolated product **3**. Yield of cyclic silyl acetals **7** determined by ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2) is shown in parentheses. [c] Isolated yield of cyclic silyl acetal **7d**. [d] $H_2Si^iPr_2$ (1.1 equiv), rt, 48 h. [e] Isolated yield of **7t**. [f] $H_2Si^iPr_2$ (4 equiv); $[Rh(nbd)Cl]_2$ (0.8 mol %), P(4-OMePh)$_3$ (4.8 mol %).

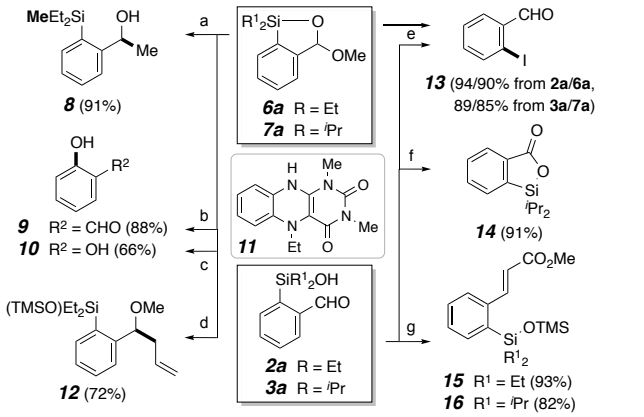
demonstrated reasonably good functional group tolerance in the presence of an amine, boronic ester, or trisubstituted alkene[23] (**3l-o**). Heterocyclic indolyl and furanyl esters were tolerated by the reaction conditions to provide 3-silanol indole 2-carbaldehyde **3p** and silanol furanals **3q-r**. In particular, **3r** was the sole product with excellent regioselectivity. *Remarkably, chemoselective arene C–H ortho-silanolization (methyl vs. isopropyl esters) within diester* ***1s*** *was viable, exclusively affording* ***3s***. As seen in Table 2, reactions using naphthoates and diisopropylsilane exhibited complete regioselectivity to afford **7t**, which did productively undergo, and **3u**. *Dual reductive C–H silanolization* was also achieved with additional reagents to yield doubly functionalized disilanol **3v**. It is worth noting that silyl hemi-acetal formation was only observed when diisopropylsilane was used. Presumably, this is due to substantial structure and reactivity difference of silanols and alcohols as well as conformational preference by diisopropyl silane substituents (cf., diethylsilane).[24,25]

To gain insight into the reaction mechanism, we performed two KIE experiments (Scheme 2). The observed minimal isotopic selectivity (k_H/k_D=1.3) in the intermolecular KIE experiment suggests that C–H bond cleavage is not turnover-limiting and the small KIE suggests that a preceding, irreversible step (likely substrate binding) is the product-determining step (Scheme 2a). Assuming that C–H bond cleavage is irreversible, the significant KIE observed in the intramolecular experiment (k_H/k_D=2.1) arises only from the C–H bond cleavage step being product-determining in this case, as the proceeding irreversible and turnover-limiting step cannot select the product (Scheme 2b).[26] Together, these studies indicate that the turnover-determining step is an irreversible step involving substrate metal coordination that proceeds C–H bond cleavage.



Scheme 2 Studies on a) intermolecular and b) intramolecular kinetic isotope effects.

Cyclic silyl acetals **6**/**7** and *ortho*-formyl arylsilanols **2**/**3** are versatile intermediates for a number of transformations (Scheme 3): a) Nucleophilic addition to **6a** was achieved using MeMgBr to furnish silane **8**; b) Oxidation of **6a** salicylic aldehyde **9**;[13f] c) Fleming-Tamao/Dakin oxidation cascade of **6a** employing the flavin-type catalyst **11** afforded catechol **10**;[27] d) Lewis acid-catalyzed allylation of **6a** yielded homoallylic methyl ether **12**;[28] e) Iodo *ipso*-desilylation of **2a**/**6a** or **3a**/**7a** installed halogen to afford **13**. f) IBX-mediated oxidation of **3a** furnished benzosilalactone **14**; and g) Horner-Wadsworth-Emmons reaction of **2a**/**3a** gave enoates **15**/**16**.



Reagents and conditions: (a) MeMgBr, THF, 60 °C. (b) *t*-BuO_2H, TBAF, CsOH, DMF, rt. (c) *t*-BuO_2H, TBAF, CsOH, DMF, **11**, rt. (d) TMSOTf, $CH_2CHCH_2Si(CH_3)_3$, THF, rt. (e) ICl, CH_2Cl_2, rt. (f) IBX, DMSO, 40 °C. (g) *i)* $(MeO)_2P(O)CH_2CO_2Me$, KOTMS, THF, rt; *ii)* TMSOTf, CH_2Cl_2, rt.

Scheme 3 Synthetic applications of cyclic silyl acetals and *ortho*-formyl arylsilanols.

Conclusions

To summarize, we have developed a single-pot reductive arene *ortho*-silanolization of esters **1**. Two sequential transition metal catalytic reactions, followed by a mild hydrolysis step, allow direct access to *ortho*-formyl arylsilanols **2** and **3**. Our strategy interconnects Ir-catalyzed ester hydrosilylation with Rh-catalyzed C–H silylation to facilitate the reductive arene *ortho*-silylation in a single vessel. Hydrolysis reveals *ortho*-silanol and aldehyde functionalities. Notably, ester hydrosilylation was achieved with 0.1 mol % of $[Ir(coe)_2Cl]_2$ and the labile hydridosilyl acetal-directed C–H silylation was accomplished within 10 min, employing 0.4 mol % of $[Rh(nbd)Cl]_2$/P(4-MeOPh)$_3$. Further efforts toward application of this tactic to

more complex substrates and studies on the mechanistic details of reductive C–H bond silylation are currently underway.

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† Electronic Supplementary Information (ESI) available: Experimental procedures, spectroscopic characterization data, and copies of ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/b000000x/

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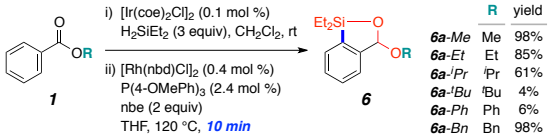
22 Methyl and benzyl esters **6a**-Me and **6a**-Bn were most efficient while sterically hindered *tert*-butyl ester **6a**-^{t}Bu did not efficiently undergo the hydrosilylation.[20a]



23 1,1-disubstituted alkenes via alkene migration were isolated along with the desired product as an inseparable mixture (8% in **2h** and 14% in **3o**).

24 For the ratio of *ortho*-formyl arylsilanols and silyl hemiacetals, see Supplementary Information.

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