Reduction of Allylpalladium(II)chloride Dimer by Formation of Allyloxysilanes

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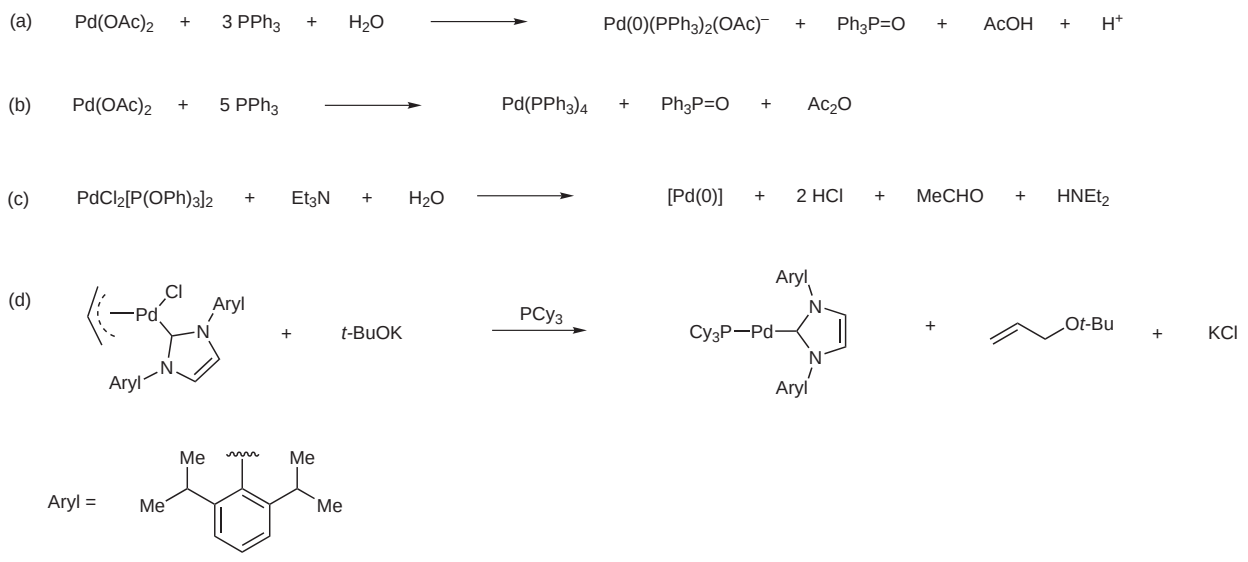
Abstract: The reduction of allylpalladium(II)chloride dimer (APC) to a Pd(0) species can be effected by reaction with alkali metal silanolates. The reduction is extremely rapid in the presence of chelating bisphosphine ligands and for a variety of silanolates.

Key words: palladium, silanolate, cross-coupling, reduction, mechanism

Since its initial discovery in 1959, allylpalladium(II)chloride dimer (APC, $[C_3H_5PdCl]_2$) has been widely employed in many catalytic reactions as a palladium(0) precursor.[1] APC was initially used stoichiometrically as an electrophile for transfer of an allyl group to carbon nucleophiles such as malonate anions and enamines to provide allylated products.[2] This fundamental process has since been extended to the use of APC as a catalyst in the presence of chiral ligands to promote asymmetric allylic alkylations.[3] Other synthetic transformations that have used APC as a precatalyst include: (1) enantioselective hydrosilylation of olefins,[4] (2) carbostannylation of alkynes,[5] and (3) a variety of cross-coupling reactions.[6] In all of these processes, the Pd(II) complex that is charged into the reaction must be reduced to a catalytically active Pd(0) species to initiate the Pd(0)/Pd(II) cycle. Each of these catalyst systems use different components including ligands, solvents, bases and other additives which can influence the reductive pathway of APC to a Pd(0) catalyst.

The reduction of Pd(II) complexes and salts to active Pd(0) catalysts has been studied in depth.[7] For example, PdX_2 salts (where X = Br, Cl and OAc) are readily reduced to Pd(0) in the presence of common phosphine ligands with concomitant formation of phosphine oxides (Scheme 1, a and b).[8] In addition, secondary or tertiary amines are capable of reducing Pd(II) sources to Pd(0) (Scheme 1, c).[9] Other heteroatom nucleophiles such as hydroxide, alkoxide, fluoride and even water have been shown to assist in this reduction as well.[10] Potassium *tert*-butoxide has been shown to act as a nucleophile in forming N-heterocyclic carbene Pd(0) species through formation of allyl ethers (Scheme 1, d).[11] Finally, even hydrosilanes have been employed for the reduction of APC in cross-coupling reactions reported from these



Scheme 1 Reduction pathways of Pd(II) sources: reduction by formation of (a) and (b) phosphine oxides, (c) aldehyde from imine, (d) *tert*-butyl allyl ether

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Scheme 2 Formation of (allyloxy)dimethylphenylsilane **2a**

laboratories.[12] Carbon nucleophiles, such as malonate anions, can also reduce APC to a Pd(0) species by nucleophilic 'deallylation'. The process is greatly facilitated by splitting APC into mononuclear complexes in the presence of phosphine ligands.[13]

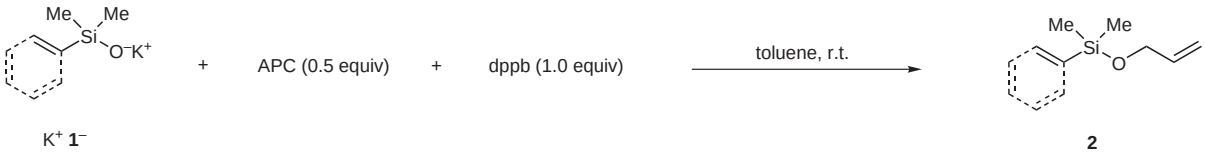
The development of silicon-based, cross-coupling reactions as practiced in these laboratories has made extensive use of APC as a Pd(0) precursor.[14] The cross-coupling of alkenylsilanols,[15a] α-alkoxyalkenylsilanols,[15b] arylsilanols,[15c,d] and cyclic silyl ethers[12,15e,f] all use APC as the Pd source under different reaction conditions. The cross-coupling of alkenylsilanols employs APC without the need for external ligands in the presence of *n*-$Bu_4NF{\cdot}3H_2O$.[15a–c] Under these reaction conditions, the presence of fluoride or water from the TBAF may serve to reduce the Pd(II) catalyst to Pd(0).[8a] However, in the coupling of arylsilanols, cesium carbonate is used in conjunction with a phosphine or arsine additive.[14] Furthermore, recent advances from these laboratories have introduced the use of preformed silanolates to promote cross-coupling reactions, also in the absence of ligands.[16] Therefore, the nature of the reduction pathway for APC using alkali silanolates as the coupling partners remains unanswered. Herein, we wish to report a study of the reduction of APC using preformed silanolates. This study probes the generality of the reduction for a range of electronically and sterically differentiated silanolates, the effect of ligands, and the role that metal counter ions play on the ease of reduction.

In the context of an investigation on the mechanism of the cross-coupling of arylsilanols with aryl halides we were faced with answering the question of APC reduction to understand the components in the active catalytic system. Our initial efforts focused on investigating the fate of the ligand under the established reaction conditions {$CsCO_3$ + 3 H_2O (3 equiv), APC (5 mol%), dppb [1,4-bis(diphenylphosphino)butane, 10 mol%], toluene, 90 °C}. Attempts to isolate the ligand following the cross-coupling reaction provided a mixture of products including recovered dppb as well as the oxidized forms (dppbO and $dppbO_2$) in varying ratios.[17] The ambiguity of these results forced us to consider other possibilities for the reduction. Therefore, our attention turned to using preformed potassium dimethylphenylsilanolate (K^+**1a**$^-$) under anhydrous conditions to eliminate the action of water as a possible reducing agent. Following stoichiometric complexation of $[C_3H_5PdCl]_2$ with dppb, the addition of preformed (K^+**1a**$^-$) afforded a new organic product in addition to copious amounts of palladium black. Careful inspection of the ^{1}H NMR spectrum showed peaks consistent with the formation of an allyl ether. Following isolation and purification, the corresponding allyloxysilane was identified (Scheme 2). This led to the conclusion that the silanolate was acting as a nucleophile, and was attacking the allyl group of APC to give Pd(0) species.[18]

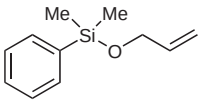
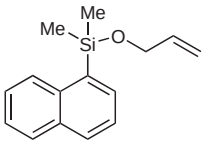
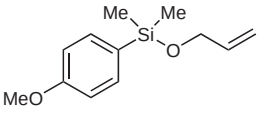
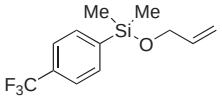
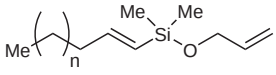
To establish the generality of this reduction pathway a series of potassium silanolates was surveyed and the results are summarized in Table 1. The reaction was conducted by preforming the Pd complex by stirring APC and dppb in toluene at room temperature, which produced a white precipitate. The white solid was later determined to be the neutral bidentate η^1-allyl complex as described by Jutand et al.[19] Following addition of the silanolate, the reaction mixture immediately darkened to a yellow color. The conversion to the allyloxysilane was monitored by GC analysis using an internal standard. The formation of the corresponding phenyl **2a** and 4-methoxyphenyl(allyloxysilane) (**2c**) (entries 1 and 3) was extremely rapid requiring only 5 minutes to reach 100% conversion at room temperature. The more bulky 1-naphthylsilanolate (K^+**1b**$^-$) reacted more slowly reaching only 61% conversion in 5 minutes and requiring 45 minutes to reach 88%. A similar result was observed with the (*E*)-1-heptenylsilanolate (K^+**1e**$^-$), which reacted more slowly than the phenyl silanolate. Though no quantitative kinetic studies were performed, the bulkier aromatic and long chain aliphatic silanolates were less reactive. Finally, the electron poor 4-trifluormethylphenylsilanolate (K^+**1d**$^-$) gave an inconclusive result. The consumption of the silanolate was rapid, however only 33% of the expected allyloxysilane was found. The remainder of the mass was identified as the corresponding disiloxane.[20] This discrepancy is discussed in the mechanistic analysis below.

With the generality of this reduction pathway for various electronically and sterically disparate silanolates now established, the focus shifted to the effect that ligands may play on the reduction. In recent years a number of investigations have addressed the effect of ligand bite angle on the rate and selectivity of allylic alkylations.[21] This behavior may correlate with the reduction of APC in the presence of silanolates. It has been shown that as the bite angle increases from dppe [1,2-bis(diphenylphosphino)ethane] to dppb, the turnover frequency increases dramatically in the allylic alkylation.[21c] However, as the bite angle increases further through the use of the dppf [1,2-bis(diphenylphosphino)ferrocene], the turnover frequency drops because of unfavorable steric interactions between the phenyl groups of the ligand with the allyl group. To examine if this bite angle effect is also relevant in the reduction of APC, we needed to identify conditions in which the reaction was suitable for these studies (i.e. the Pd complexes must be completely soluble).

Table 1 Substrate Scope in the Reduction of APC to Form Allyloxysilanes



K^+ **1**$^-$ **2**

Entry	Product		Conversion (%), 5 min	Completion time (min)	Conversion (%)[a]
1		**2a**	100	5[b]	100 (79)[c]
2		**2b**	23	45[d]	88
3		**2c**	100	5[e]	100
4		**2d**	28	30[d]	33[f]
5	 n = 5	**2e**	69	30[e]	83

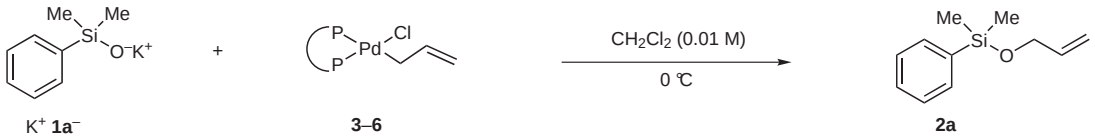
[a] Yields based on GC conversion using an internal standard.
[b] Reaction was performed at 0.5 M.
[c] Yield of isolated material.
[d] Reaction was performed at 0.4 M.
[e] Reaction was performed at 0.3 M.
[f] Remaining mass balance was identified as disiloxane.

After a broad survey of solvents, dichloromethane was chosen, as all reagents were soluble and stable in this solvent.[22] Initial studies were performed at room temperature using the preformed dppb complex **5**. The reduction of APC was instantaneous upon addition of a solution of K^+**1a**$^-$ (Table 2). To facilitate useful comparisons, both the temperature and the concentration of the reaction were decreased. Surprisingly, even at 0.01 M and 0 °C the reduction was complete within 1 minute! The results of reduction of complexes of other bidentate phosphines are shown in Table 2. It was found that, independent of the ligand used in the preformed complex, the reduction was rapid and quantitative. Further, we found that APC itself did not reduce in the absence of ligands at room temperature (Table 2, entry 1), which is consistent with literature reports.[13]

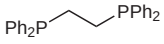
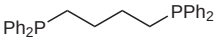
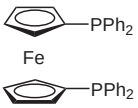
To establish if the metal counter ion would have an effect on the reduction of the APC complexes, we prepared various alkali metal silanolates and compared their competence in this reduction. Having already demonstrated the rapid reduction of the dppb complex using the potassium silanolate K^+**1a**$^-$, it was not surprising that both the rubidium Rb^+**1a**$^-$ and cesium silanolates Cs^+**1a**$^-$ also reduced the dppb complex **5** almost instantaneously. However, the sodium silanolate Na^+**1a**$^-$ was slower compared to the other metal silanolates (Table 3). This result is consistent with the expected trend in the nucleophilicity of the different metal silanolates.[23]

The complexes derived from the reaction of APC with a variety of ligands have provided useful insights into the reactivity of these compounds.[19,24] As early as 1964, it was observed that these complexes were η^1-allyl-Pd(II)ClL_2 and that the neutral complexes exist in rapid metallotropic equilibrium in solution.[24a] This behavior was contrary to earlier suppositions that the complexes were cationic Pd(II) species. The relative reactivity of the cationic complexes and the neutral Pd complexes were later evaluated and it was determined that the cationic complexes react more rapidly.[24b] The decreased reactivity of the neutral complexes was subsequently confirmed by Jutand and co-workers who showed that, in the presence of chloride ions, neutral complexes are formed from cationic Pd species.[19] The structure of the neutral bidentate L_2Pd(allyl)Cl complexes were determined to be η^1 by X-ray crystal structure analysis which clearly show the σ-bonding (Pd–C) of the allyl group.[25] From the current

Table 2 Effect of Ligands on the Reduction of APC Using Silanolates



K^+ **1a**$^-$ **3–6** **2a**

Entry	Ligand	Complex	Time (min)	Conversion (%)[a]
1	no ligand[b]		5	NR[c]
2		**3**	1	86
3		**4**	2	96
4		**5**	1	100
5		**6**	1	100

[a] Yields based on GC conversion using an internal standard.
[b] $[C_3H_5PdCl]_2$.
[c] NR = no reaction; reaction was performed at r.t.

knowledge of the reactivity as well as solution and solid state structures of $L_2Pd(allyl)Cl$ complexes, a mechanistic picture for the reduction can be formulated.

There are four limiting pathways by which the allyloxysilane may be formed by considering the permutations of peripheral or internal attack of the silanolate on the neutral or cationic complexes (Scheme 3). Attack by the silanolate at the palladium center on the neutral complexes (path Pd_N) or the cationic complex (path Pd_C) generates the palladium(II) silanolate complex **i**. This complex must undergo reductive elimination to form the observed allyl silyl ether **2** and Pd(0). Alternatively, attack of K^+**1**$^-$ on the σ-bound allyl group (path $allyl_N$) or the π-bound allyl group (path $allyl_C$) leads directly to the formation of **2** with concomitant generation of Pd(0). Although we cannot unambiguously rule out any of these pathways, we can bring some previous insights to bear on the question. First, studies on the reaction of palladium aryloxides have shown that the reductive elimination to form C–O bonds is slow and generally requires elevated temperatures therefore disfavoring the paths involving attack at palladium.[26] Second, although it has been established that the cationic complex is a more reactive electrophile than the neutral complex,[19,21] the use of fairly non-polar solvents would favor the neutral form. These findings would lead to suggest that path $allyl_N$ to be the course of reduction.

However, any mechanism for the reduction of APC must also account for the formation of disiloxane from K^+**1d**$^-$. The simplest explanation, that the disiloxane is generated by attack of K^+**1d**$^-$ on the allyl silyl ether **2d**, could be discounted by a control experiment, which clearly demonstrated that this pathway is not operative (in the absence of Pd; Scheme 4). Alternatively, attack of silanolate K^+**1d**$^-$ on the palladium silanolate **i** could also generate **2d** with formation of a palladium alkoxide. This pathway would not constitute reduction to Pd(0) and therefore could not contribute to the catalytic cycle.

In summary, we have unambiguously established that the reduction of APC in the presence of alkali metal silanolates proceeds via the formation of allyloxysilanes. This conclusion has preparative significance because an active Pd(0) species can be generated independent of substrate, ligand, and counter ion of the silanolate. Further studies to elaborate the full mechanistic picture of the fluoride-free cross-coupling of organosilanols are currently underway in these laboratories and the results will be reported in due course.

General Procedure for the Preparation of Allyloxysilanes

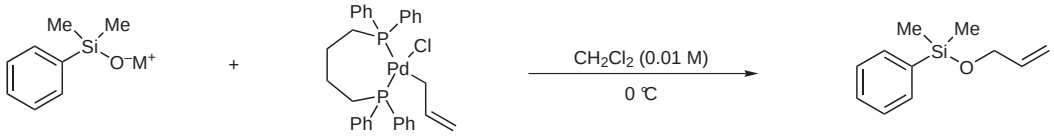
(Allyloxy)dimethylphenylsilane (2a)[27,28]

Et_3N (1.02 mL, 7.33 mmol, 2.0 equiv) was added to a solution of allyl alcohol (0.25 mL, 3.67 mmol, 1.0 equiv) in dry THF (7.3 mL) in a flame-dried, 3-neck, 25-mL round-bottomed flask equipped with an Ar inlet, septum, and glass stopper. The solution was cooled to 0 °C over 10 min. Then, phenyldimethylchlorosilane (0.61 mL, 3.67 mmol) was added dropwise over 1 min. Upon addition of the chlorosilane, a white precipitate formed. The resulting mixture was stirred at 0 °C for 1 h whereupon Et_2O (15 mL) was added. The mixture was then filtered through a medium-porosity fritted funnel and the collected solids were washed with Et_2O (10 mL). The filtrate was concentrated in vacuo and the residue was purified by column chromatography (silica gel, hexanes–EtOAc, 30:1) to afford 645 mg (91%) of **2a** as a colorless oil. The data for **2a** matched those reported in the literature.[27]

(Allyloxy)dimethyl(1-naphthyl)silane (2b)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, 1 H, J = 8.1 Hz), 7.86–7.91 (m, 2 H), 7.74 (dd, 1 H, J_1 = 1.0 Hz, J_2 = 6.6 Hz), 7.45–7.54 (m, 3 H), 5.92 (dddd, 1 H, $J_1 = J_2$ = 4.9 Hz, J_3 = 10.3 Hz, J_4 = 17.1 Hz), 5.26 (dddd, 1 H, $J_1 = J_2 = J_3$ = 1.7 Hz, J_4 = 17.1 Hz), 5.08 (dddd, 1 H, $J_1 = J_2 = J_3$ = 1.5 Hz, J_4 = 10.5 Hz), 4.15 (ddd, 2 H, $J_1 = J_2$ = 1.2 Hz, J_3 = 4.9 Hz), 0.56 (s, 6 H). ^{13}C NMR (125 MHz,

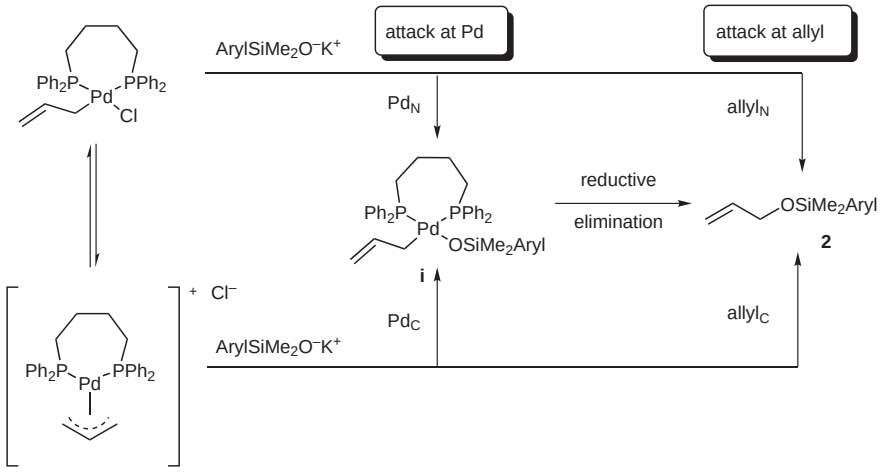
Table 3 Counter-Ion Effect on the Reduction of the Neutral dppb–η[1]-Allyl Complex **5**



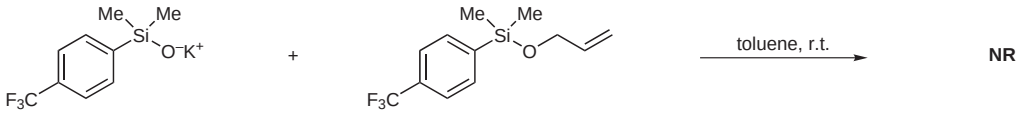
M⁺ **1a**⁻ **5** **2a**

Entry	Counter ion (M^+)	Time (min)	Conversion (%)[a]
1	Na	1	61
		10	94
2	K	1	100
3	Rb	1	99
4	Cs	1	99

[a] Yields based on GC conversion using an internal standard.



Scheme 3 Possible reductive pathways to form allyloxysilanes



K⁺ **1d**⁻ **2d**

Scheme 4 Control experiment to probe formation of disiloxane from **2d**

$CDCl_3$): δ = 137.0, 136.9, 135.6, 133.9, 133.3, 130.5, 128.9, 128.2, 126.1, 125.6, 125.0, 114.8, 64.1, –0.5. HRMS: *m/z* calcd for $C_{15}H_{18}OSi$ [M^+]: 242.1127; found: 242.1123. R_f = 1.293; t_R = 6.15 min (HP-1, 150 °C, 3.5 min, 25 °C/min, 220 °C, 1 min, 16 psi).[29]

(Allyloxy)dimethyl(4-methoxy)phenylsilane (2c)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, J = 8.6 Hz), 6.95 (d, 2 H, J = 8.6 Hz), 5.92 (dddd, 1 H, $J_1 = J_2$ = 4.9 Hz, J_3 = 10.0 Hz, J_4 = 17.2 Hz), 5.27 (dddd, 1 H,, $J_1 = J_2 = J_3$ = 1.7 Hz, J_4 = 17.2 Hz), 5.10 (dddd, 1 H, $J_1 = J_2 = J_3$ = 1.5 Hz, J_4 = 10.3 Hz), 4.14 (ddd, 2 H, $J_1 = J_2$ = 1.5 Hz, J_3 = 4.9 Hz), 3.83 (s, 3 H), 0.40 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.9, 137.1, 135.1, 128.6, 114.6, 113.5, 63.9, 55.0, –1.6; HRMS: *m/z* calcd for $C_{12}H_{18}O_2Si$ [M^+]: 222.1076; found: 222.1077; R_f = 0.8775; t_R = 3.35 min (HP-1, 150 °C, 3.5 min, 25 °C/min, 175 °C, 0.5 min, 16 psi).

(Allyloxy)dimethyl(4-trifluoromethyl)phenylsilane (2d)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (d, 2 H, J = 7.6 Hz), 7.62 (d, 2 H, J = 7.8 Hz), 5.91 (dddd, 1 H, $J_1 = J_2$ = 4.9 Hz, J_3 = 10.0 Hz, J_4 = 17.1 Hz), 5.26 (dddd, 1 H, $J_1 = J_2 = J_3$ = 1.5 Hz, J_4 = 10.3 Hz), 5.11 (dddd, 1 H, $J_1 = J_2 = J_3$ = 1.7 Hz, J_4 = 17.1 Hz), 4.16 (ddd, 2 H, $J_1 = J_2$ = 1.7 Hz, J_3 = 4.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.6, 136.7, 133.8, 131.5 (q, J_{CF} = 32.2 Hz), 124.4 (q, J_{CF} = 3.7 Hz), 124.2 (q, J_{CF} = 272.5 Hz), 114.9, 64.2, –1.8. ^{19}F NMR (470 MHz, $CDCl_3$, ref. $CFCl_3$): δ = –63.4. HRMS: *m/z* calcd for $C_{15}H_{15}OSiF_3$ [M^+]: 260.0844; found: 260.0843. R_f = 0.8422; t_R = 3.35 min (HP-1, 115 °C, 2.0 min, 25 °C/min, 150 °C, 2.0 min, 16 psi).

(*E*)-(Allyloxy)dimethyl(1-heptenyl)silane (2e)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.18 (dt, 1 H, J_1 = 6.3 Hz, J_2 = 18.8 Hz), 5.92 (dddd, 1 H, J_1 = J_2 = 4.9 Hz, J_3 = 10.0 Hz, J_4 = 17.1 Hz), 5.62 (dt, 1 H, J_1 = 1.7 Hz, J_2 = 18.8 Hz), 5.24 (dddd, 1 H, J_1 = J_2 = J_3 = 1.7 Hz, J_4 = 17.1 Hz), 5.08 (dddd, 1 H, J_1 = J_2 = J_3 = 1.5 Hz, J_4 = 10.3 Hz), 4.13 (ddd, 2 H, J_1 = J_2 = 1.5 Hz, J_3 = 4.9 Hz), 2.12 (qd, 2 H, J_1 = 1.5 Hz, J_2 = 7.3 Hz), 1.40 (qn, 2 H, J = 7.6 Hz), 1.25–1.33 (m, 4 H), 0.89 (t, 3 H, J = 6.8 Hz), 0.17 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.4, 137.5, 127.0, 114.8, 64.0, 36.8, 31.6, 28.4, 22.7, 14.2, –1.6; HRMS: *m/z* calcd for $C_{12}H_{24}OSi$ [M$^+$]: 212.1597; found: 212.1596. R_f = 0.9121; t_R = 1.85 min (HP-1, 150 °C, 3.5 min, 16 psi).

General Procedure for the Reduction of APC with Silanolates (Table 1)

(Allyloxy)dimethylphenylsilane (2a, Table 1, entry 1)

Bis(1,4-diphenylphosphino)butane (43 mg, 0.10 mmol, 1.0 equiv) was added to a solution of $(C_3H_5PdCl)_2$ (18 mg, 0.049 mmol, 0.5 equiv) and biphenyl (6.7 mg, 0.043 mmol) in dry toluene (0.2 mL) in a flame-dried, 2-neck round-bottomed flask equipped with an Ar inlet and septum. Upon addition of the dppb, a white precipitate formed. The mixture was stirred for 5 min at r.t. Thereafter, potassium dimethylphenylsilanolate was added as a solid (19 mg, 0.010 mmol) or as a solution in toluene (396 μL, 0.252 M, 0.10 mmol). The reaction mixture was maintained at r.t. and the reaction progress was monitored by GC at certain time intervals. Sampling of the reaction was performed by removing a 30 μL aliquot of the mixture by syringe. The aliquot was quenched onto a 10% aq 2-(dimethylamino)ethanethiol hydrochloride solution (0.2 mL) and was diluted with Et_2O (0.5 mL). The organic portion was filtered through a small plug of silica gel and then was eluted with 1.0 mL of Et_2O. The aliquot was analyzed by GC (HP-1, 150 °C, 3.5 min, 25 °C/min, 225 °C, 0.5 min, 16 psi).

General Procedure for the Complex Study (Table 2)

Neutral dppb η^1-Allyl Complex [$(Ph_2P(CH_2)_4PPh_2)Pd(\eta^1$-$C_3H_5)Cl$] (5, Table 2, entry 4)

A solution of [$(Ph_2P(CH_2)_4PPh_2)Pd(\eta^1$-$C_3H_5)Cl$] (12.4 mg, 0.020 mmol, 1.0 equiv) and biphenyl (5.0 mg, 0.324 mmol) in dry CH_2Cl_2 (1.9 mL, 0.01 M) was charged into a flame-dried, 2-neck, round-bottomed flask equipped with an Ar inlet and septum. The reaction mixture was cooled to 0 °C. Thereafter, potassium dimethylphenylsilanolate was added as a solution in CH_2Cl_2 (70 μL, 0.284 M, 0.020 mmol). The reaction was maintained at 0 °C and the reaction progress was monitored by GC at certain time intervals. Sampling of the reaction was performed by removing a 80 μL aliquot of the mixture by syringe. The aliquot was quenched onto a 10% aq 2-(dimethylamino)ethanethiol hydrochloride solution (0.2 mL) and was diluted with Et_2O (0.5 mL). The organic portion was filtered through a small plug of silica gel and then was eluted with 1.0 mL of Et_2O. The aliquot was analyzed by GC (HP-1, 150 °C, 3.5 min, 25 °C/min, 225 °C, 0.5 min, 16 psi).

General Procedure for the Preparation of the Neutral η^1-allyl Complexes[19]

Neutral dppb η^1-Allyl Complex [$(Ph_2P(CH_2)_4PPh_2)Pd(\eta^1$-$C_3H_5)Cl$] (5)

Bis(1,4-diphenylphosphino)butane (291.2 mg, 0.6828 mmol, 2.0 equiv) was added to a solution of $(C_3H_5PdCl)_2$ (124.9 mg, 0.341 mmol, 1.0 equiv) in dry toluene (15.0 mL) in a flame-dried, 2-neck, 25-mL, round-bottomed flask equipped with an Ar inlet and septum. The resulting mixture was stirred for 30 min at r.t. at which point the mixture was filtered through a medium-porosity fritted funnel. The solids were further dried using high vacuum (0.05 mmHg) overnight to afford 401 mg (96%) of **5** as a white solid. Data for **5** matched those reported in the literature.[19]

Neutral dppe η^1-Allyl Complex [$(Ph_2P(CH_2)_2PPh_2)Pd(\eta^1$-$C_3H_5)Cl$] (2)

^{1}H NMR (500 MHz, $CDCl_3$): δ& nbsp;= 7.57–7.63 (m, 8 H), 7.47–7.50 (m, 12 H), 5.80 (qn, 1 H, J = 10.7 Hz), 4.15 (br s, 4 H), 2.86 (d, 4 H, J = 18.6 Hz). ^{13}C (125 MHz, $CDCl_3$): δ = 132.6 (t, J_{CP} = 6.4 Hz), 131.8, 129.6 (t, J_{CP} = 5.5 Hz), 122.9 (t, J_{CP} = 5.5 Hz), 70.9 (t, J_{CP} = 17.5 Hz), 27.5 (t, J_{CP} = 23.0 Hz). ^{31}P (202 MHz, $CDCl_3$, H_3PO_4): δ = 51.8.

Neutral dppp η^1-Allyl Complex [$(Ph_2P(CH_2)_3PPh_2)Pd(\eta^1$-$C_3H_5)Cl\cdot CH_2Cl_2$] (3)

The complex was recrystallized from CH_2Cl_2–hexane. Data for **3**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (br s, 8 H), 7.28–7.35 (m, 12 H), 5.58 (qn, 1 H, J = 10.8 Hz), 5.26 (s, 2H), 3.73 (br s, 4 H), 3.11 (br s, 4 H), 2.03 (br s, 2 H). ^{13}C (125 MHz, $CDCl_3$): δ = 132.8 (br), 130.2, 128.5 (t, J_{CP} = 4.6 Hz), 119.3 (t, J_{CP} = 6.4 Hz), 71.3 (t, J_{CP} = 16.6 Hz), 53.4, 24.9 (t, J_{CP} = 13.8 Hz), 19.4. ^{31}P (202 MHz, $CDCl_3$, H_3PO_4): δ = 6.4.

Neutral dppf η^1-Allyl Complex [$(Fe(C_5H_5PPh_2)_2)Pd(\eta^1$-$C_3H_5)Cl$] (6)

Data for **6** matched those reported in the literature.[19]

General Procedure for the Metal Counter Ion Study (Table 3)

Potassium Dimethylphenylsilanolate (Table 3, entry 2)

A solution of [$(Ph_2P(CH_2)_4PPh_2)Pd(\eta^1$-$C_3H_5)Cl$] (12.4 mg, 0.020 mmol, 1.0 equiv) and biphenyl (5.0 mg, 0.324 mmol) in dry CH_2Cl_2 (1.9 mL, 0.01 M) was charged into a flame-dried, 2-neck, round-bottomed flask equipped with an Ar inlet and septum. The solution was cooled to 0 °C. Thereafter, potassium dimethylphenylsilanolate was added as a solution in CH_2Cl_2 (70 μL, 0.284 M, 0.020 mmol). The mixture was maintained at 0 °C and the reaction progress was monitored by GC at certain time intervals. Sampling of the reaction was performed by removing a 80 μL aliquot of the mixture by syringe. The aliquot was quenched onto a 10% aq 2-(dimethylamino)ethanethiol hydrochloride solution (0.2 mL) and was diluted with Et_2O (0.5 mL). The organic portion was filtered through a small plug of silica gel and then was eluted with 1.0 mL of Et_2O. The aliquot was analyzed by GC (HP-1, 150 °C, 3.5 min, 25 °C/min, 225 °C, 0.5 min, 16 psi).

Preparation of Sodium Dimethylphenylsilanolate (Na$^+$1a$^-$)

To a suspension of NaH (81 mg, 3.31 mmol) in THF (4.5 mL) in a flame-dried, 50-mL scintillation flask equipped with a 3-way Ar adapter was added dimethylphenylsilanol (503.4 mg, 3.31 mmol) as a solution in THF (2.0 mL) dropwise over 5 min. The resultant solution was stirred for 30 min further. The volatiles were removed in vacuo to give a semi-solid. The material was washed with dry hexane (2.0 mL) and the volatiles were subsequently removed in vacuo to afford 500 mg (87%) of Na$^+$**1a**$^-$ as a white, powder solid. Data for Na$^+$**1a**$^-$: ^{1}H NMR (500 MHz, THF-d_8): δ = 7.58 (d, 2 H, J = 6.3 Hz), 7.15–7.24 (m, 3 H), 0.16 (s, 6 H).

Preparation of Potassium Dimethylphenylsilanolate (K$^+$1a$^-$)[14]

To a suspension of KH (356 mg, 8.87 mmol, 1.3 equiv) in THF (9.1 mL) in a flame-dried, 50-mL scintillation flask equipped with a 3-way Ar adapter was added dimethylphenylsilanol (1.039 g, 6.821 mmol) as a solution in THF (2.0 mL) dropwise over 5 min. The resultant mixture was stirred for 30 min further, and then was added by syringe into two oven-dried vials previously purged with argon. The vials were then centrifuged (1100 rpm) for 10 min, and the supernatant was removed by syringe, with care taken not to disturb the excess KH and KOH precipitate at the bottom of the vials. The supernatant was then placed in a preweighed, flame dried, argon-purged one-neck round-bottomed flask. The volatiles were removed in vacuo to give a semi-solid. The material was washed with dry hexane (2.0 mL) and the volatiles were subsequently removed in

vacuo two times to give 1.150 g (89%) of K^+**1a**$^-$ as an off-white solid. Data for K^+**1a**$^-$: ^{1}H NMR (500 MHz, THF-d_8): δ = 7.55 (d, 2 H, *J* = 7.8 Hz), 7.21 (t, 2 H, *J* = 7.6 Hz), 7.13–7.16 (m, 1 H), 0.07 (s, 6 H).

Potassium Dimethyl(1-naphthyl)silanolate (K^+1b$^-$)
^{1}H NMR (500 MHz, THF-d_8): δ = 8.67–8.69 (m, 1 H), 7.69–7.78 (m, 3 H), 7.31–7.38 (m, 3 H), 0.22 (s, 6 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 147.7, 138.7, 134.8, 132.7, 129.9, 129.5, 128.5, 126.0, 125.7, 125.4, 5.1.

Potassium Dimethyl(4-methoxy)phenylsilanolate (K^+1c$^-$)
^{1}H NMR (500 MHz, THF-d_8): δ = 7.45 (d, 2 H, *J* = 8.5 Hz), 6.79 (d, 2 H, *J* = 8.3 Hz), 3.72 (s, 3 H), 0.05 (s, 6 H).

Potassium Dimethyl(4-trifluoromethyl)phenylsilanolate (K^+1d$^-$)
^{1}H NMR (500 MHz, THF-d_8): δ = 7.73 (d, 2 H, *J* = 7.3 Hz), 7.51 (d, 2 H, *J* = 7.6 Hz), 0.12 (s, 6 H).

Preparation of Rubidium Dimethylphenylsilanolate (Rb^+1a$^-$)
In a dry box, a one-neck flask was charged with dry, degassed benzene (17 mL) followed by rubidium metal (296 mg, 3.46 mmol). To this suspension was added dimethylphenylsilanol (554 mg, 3.64 mmol, 1.05 equiv) dropwise over 5 min. The resulting mixture was stirred for 30 min further, and then was filtered through a medium-porosity fritted funnel into a preweighed one-neck flask fitted with a vacuum stopcock adaptor. The flask was removed from the dry box and the solvent evaporated in vacuo to give a semi-solid. The residue was transferred back into the dry box and was washed with dry hexane (5 mL) and filtered through a medium-porosity fritted funnel. The collected solids were further washed with dry hexane (3 × 5 mL). The solids were placed in a flame-dried, 15-mL recovery flask equipped with a vacuum stopcock adaptor and any excess volatiles were removed in vacuo to give 302 mg (37%) of Rb^+**1a**$^-$ as a white, powdered solid. Data for Rb^+**1a**$^-$: ^{1}H NMR (500 MHz, THF-d_8): δ = 7.55 (dd, 2 H, J_1 = 1.2 Hz, J_2 = 7.8 Hz), 7.12–7.21 (m, 3 H), 0.07 (s, 6 H).

Preparation of Cesium Dimethylphenylsilanolate (Cs^+1a$^-$)
Following the same procedure for the preparation of the rubidium silanolate gave 272 mg (90%) of Cs^+**1a**$^-$ as a white, powdered solid. Data for Cs^+**1a**$^-$: ^{1}H NMR (500 MHz, THF-d_8): δ = 7.56 (dd, 2 H, J_1 = 1.2 Hz, J_2 = 7.8 Hz), 7.18–7.22 (m, 2 H), 7.12–7.15 (m, 1 H), 0.09 (s, 6 H).

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References and Notes

(1) (a) Smidt, J.; Hafner, W. *Angew. Chem.* **1959**, *71*, 284. (b) Hüttel, R.; Kratzer, J. *Angew. Chem.* **1959**, *71*, 456.
(2) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *49*, 4387.
(3) Trost, B. M. *Chem. Rev.* **1996**, *96*, 395; and references therein.
(4) Hayashi, T.; Uozumi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9887.
(5) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975.
(6) For representative examples, see: (a) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471. (b) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034. (c) Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2004**, *45*, 8443.
(7) Trzeciak, A. M.; Ziólkowski, J. J. *Coord. Chem. Rev.* **2005**, *249*, 2308.
(8) (a) Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 2212. (b) Amatore, C.; Jutand, A.; Barki', M. A. M. *Organometallics* **1992**, *11*, 3009. (c) Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177. (d) Amatore, C.; Carre, E.; Jutand, A.; Barki', M. A. M. *Organometallics* **1995**, *14*, 1818. (e) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254.
(9) Treciak, A. M.; Ciunik, Z.; Ziólkowski, J. J. *Organometallics* **2002**, *21*, 132.
(10) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009; and references therein.
(11) (a) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470. (b) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A.; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629.
(12) Denmark, S. E.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 5153.
(13) Trost, B. M.; Fullerton, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 292.
(14) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, Vol. 1; de Meijere, A.; Diederich, F., Eds.; Wiley-VCH: Weinheim, **2004**, Chap. 4.
(15) (a) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565. (b) Denmark, S. E.; Neuville, L. *Org. Lett.* **2000**, *2*, 3221. (c) Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, *5*, 1357. (d) Denmark, S. E.; Ober, M. H. *Adv. Synth. Catal.* **2004**, *346*, 1703. (e) Denmark, S. E.; Yang, S.-M. *Tetrahedron* **2004**, *60*, 9695. (f) Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2004**, *126*, 12432.
(16) Denmark, S. E.; Baird, J. D. *Chem. Eur. J.* **2006**, *12*, 4954.
(17) Denmark, S. E.; Ober, M. H., unpublished results.
(18) The formation of Pd(0) from this process was confirmed by the identification of dppbPd(dba) in the reduction mixture from K^+**1a**$^-$, dpppPd(allyl)Cl, and dba. In this experiment, no palladium black was observed. The ^{31}P NMR spectrum ($CDCl_3$) of this reaction mixture showed two broad peaks at δ = 23.3 and 17.2 ppm which are in good agreement with those reported by Jutand for this compound (in THF) at δ = 21.3 and 17.5 ppm. No free dppb was observed. See: Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.
(19) Cantat, T.; Génin, E.; Giroud, C.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *687*, 365.
(20) The presence of the disiloxane was confirmed by GC-MS analysis. This peak was the major constituent in the GC chromatogram as determined by relative area percents.
(21) (a) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133. (b) Oslob, J. D.; Åkermark, B.; Helquist, P.; Norrby, P. *Organometallics* **1997**, *16*, 3015. (c) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 25. (d) van Haaren, R. J.; Goubitz, K.; Fraanje, J.; van Strijdonck, G. P. F.; Oevering, H.; Coussens, B.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Inorg. Chem.* **2001**, *40*, 3363.
(22) The stability of the silanolate was tested using ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of a 0.075 M solution of K^+**1a**$^-$ in CH_2Cl_2 was unchanged after standing at r.t. for 5 h.

(23) Kurts, A. K.; Sakembaeva, S. M.; Beletskaya, I. P.; Reutov, O. A. *Zh. Org. Chim.* **1974**, *10*, 1572.
(24) (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839. (b) Åkermark, B.; Åkermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037.
(25) (a) Braunstein, P.; Naud, F.; Dedieu, A.; Rohmer, M.-M.; DeCain, A.; Rettig, S. J. *Organometallics* **2001**, *20*, 2966. (b) Kollmar, M.; Helmchen, G. *Organometallics* **2002**, *21*, 4711.
(26) However, this claim has not been established for allylpalladium complexes. See: Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109.
(27) Gregg, B. T.; Cutler, A. R. *Organometallics* **1994**, *13*, 1039.
(28) The procedure was modified from: Alonso, E.; Guijarro, D.; Yus, M. *Tetrahedron* **1995**, *51*, 11457.
(29) Response Factor (R_f) calculated using: R_f = (mmol of internal standard*area of x)/(mmol of x*area of internal standard).