Mechanistic Duality in Palladium-Catalyzed, Cross-Coupling Reactions of Aryldimethylsilanolates. The Intermediacy of an 8-Si-4 Arylpalladium(II) Silanolate

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven-dried, (140 °C) or flame-dried vials or NMR tubes that were prepared in a drybox unless otherwise noted. Reaction temperatures reported are those from the oil bath or NMR probe setting. The temperatures for the NMR probe were calibrated using ethylene glycol as a temperature standard. Tetrahydrofuran and ether (Fisher, HPLC grade) was dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Toluene, pentane and

hexane (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Benzene (Fisher, ACS grade) was distilled from sodium; benzotrifluoride (Aldrich, ACS grade) was distilled from CaH_2. Commercial reagents were purified by distillation or recrystallization prior to use. 4-Bromofluorobenzene was sparged with argon for 30 min prior to use. tri(*tert*-butyl)phosphine (Strem) and Pd_2dba_3 (Alfa Aesar) were used as received.

^{1}H NMR spectra, ^{13}C NMR, ^{19}F NMR and ^{31}P spectra were recorded on a Varian Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C) or a Varian VXR (500 MHz, 1H; 126 MHz, ^{13}C) spectrometer. Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C), residual benzene (δ 7.16 ppm, ^{1}H; δ 128.0 ppm, ^{13}C) or residual methylene chloride where applicable. Phosphoric acid (40% in H_2O) was used as an external reference for ^{31}P NMR (δ 0.00 ppm, ^{31}P) and neat trichlorofluoromethane (0.00 ppm, ^{19}F) or 1% trifluoroacetic acid in D_2O (δ -75.9 ppm, ^{31}F) as an external reference for ^{19}F NMR. Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Corroboration of assignments was performed by 2D experiments (COSY, HETCOR) where needed.

Literature preparations

(4-Methoxyphenyl)dimethylsilanol,[1] potassium (4-methoxyphenyl)dimethylsilanolate,[2] (*t*-Bu_3)$_2$Pd[3] and palladium complex **4**[4] were prepared by literature methods.

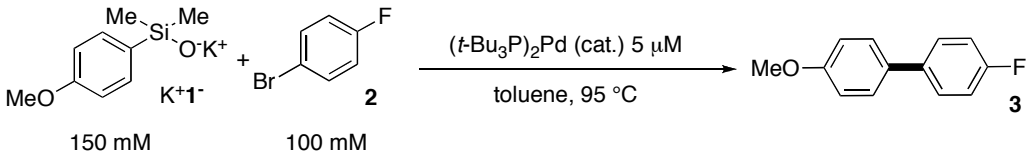
General Procedure I: Analysis and Kinetic Measurements for Catalytic Cross-Coupling of Arylsilanolates (Scheme 1).

Initial Parameters:

K^+**1**$^-$ 150 mM

2 100 mM

Pd cat. 5 mM

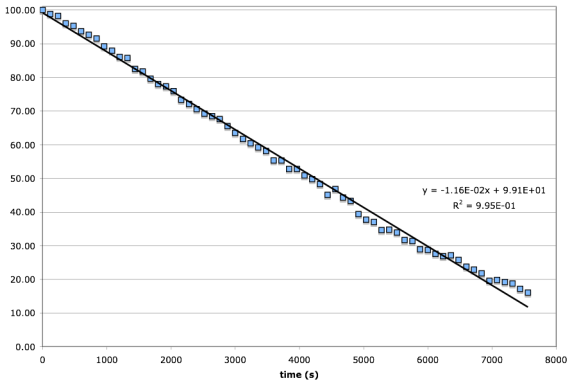


In a drybox, an oven-dried, 2.5-mL vial equipped with a magnetic stir bar was charged with (*t*-$Bu_3P)_2Pd$ (2.5 mg, 0.0049 mmol), toluene (0.8 mL), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) resulting in a colorless solution. K^+**1**$^-$ (33 mg, 0.15 mmol) was added as a solid and the sides of the vial were rinsed with toluene (0.2 mL). The mixture was stirred for 3 min to ensure complete dissolution. The resulting solution was transferred into an oven-dried, 5-mm NMR tube. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 95 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for 3 min prior to data collection.[5] The reaction progress was monitored by the disappearance of starting aryl halide (^{19}F NMR, -115.9 ppm) as compared to an internal reference ($PhCF_3$, ^{19}F NMR, -63.2 ppm)) via ^{19}F NMR spectroscopy using the following parameters: at = 0.328, d1 = 1, pw90 = 18.25, pw=pw90/2, nt=24, sampling every 120 s.[6] The rate of the reaction was determined by the slope of the linear plot[7]: $\mathbf{k_{obs} = 1.16 \times 10^{-2}\ mMs^{-1}}$.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalization (mM)
0	1.086	1.435	100.03
120	1.076	1.417	98.77
240	1.098	1.409	98.20
360	1.095	1.377	95.99
480	1.083	1.368	95.30

600	1.058	1.345	93.70
720	1.077	1.329	92.61
840	1.056	1.313	91.51
960	1.099	1.280	89.20
1080	1.079	1.261	87.91
1200	1.067	1.235	86.08
1320	1.089	1.231	85.77
1440	1.042	1.183	82.47
1560	1.039	1.173	81.74
1680	1.053	1.143	79.63
1800	1.055	1.119	77.97
1920	1.040	1.109	77.31
2040	1.045	1.089	75.91
2160	1.059	1.052	73.32
2280	1.069	1.034	72.07
2400	1.062	1.012	70.55
2520	1.037	0.993	69.19
2640	1.045	0.982	68.44
2760	1.055	0.970	67.59
2880	1.027	0.940	65.52
3000	1.017	0.911	63.50
3120	1.031	0.886	61.71
3240	1.031	0.867	60.38
3360	1.040	0.849	59.14
3480	1.042	0.834	58.12
3600	1.003	0.793	55.29
3720	1.048	0.794	55.32
3840	1.022	0.757	52.75
3960	1.012	0.758	52.80
4080	1.002	0.730	50.86
4200	1.006	0.714	49.75
4320	1.052	0.693	48.29
4440	1.009	0.647	45.09
4560	1.029	0.672	46.83
4680	1.005	0.636	44.31
4800	1.024	0.621	43.29
4920	0.982	0.565	39.36
5040	0.999	0.541	37.72
5160	1.012	0.532	37.04
5280	0.990	0.497	34.65
5400	1.015	0.499	34.74
5520	0.978	0.486	33.86
5640	0.980	0.454	31.66
5760	0.976	0.450	31.37
5880	0.966	0.414	28.88
6000	0.973	0.412	28.70
6120	0.978	0.396	27.57
6240	0.970	0.385	26.86
6360	1.001	0.390	27.15
6480	0.985	0.370	25.80
6600	0.974	0.341	23.77
6720	0.985	0.328	22.86
6840	1.000	0.313	21.79
6960	0.965	0.281	19.57
7080	0.974	0.284	19.81
7200	0.971	0.275	19.18

7320	0.964	0.269	18.76
7440	1.001	0.246	17.15
7560	0.966	0.230	16.05
7680	0.964	0.232	16.17
7800	0.979	0.210	14.61
7920	0.988	0.208	14.49
8040	0.980	0.203	14.14
8160	1.001	0.190	13.22
8280	0.982	0.168	11.68
8400	0.978	0.161	11.18
8520	0.979	0.160	11.13
8640	0.924	0.151	10.55
8760	0.936	0.141	9.84
8880	0.952	0.137	9.51
9000	0.973	0.108	7.55
9120	0.957	0.128	8.91
9240	0.962	0.114	7.97



Initial Parameters:

K^+**1**$^-$ 150 mM

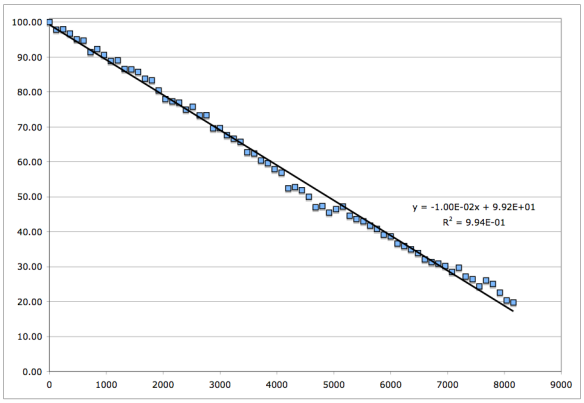
2 100 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (2.7 mg, 0.0053 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **1.00 x 10^{-2} s^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalization (mM)
0	0.968	1.255	99.98
120	0.935	1.228	97.81
240	0.970	1.229	97.91
360	0.964	1.214	96.71
480	0.959	1.193	95.06
600	0.942	1.188	94.66
720	0.932	1.147	91.36
840	0.951	1.158	92.30
960	0.967	1.136	90.55
1080	0.962	1.115	88.88
1200	0.951	1.117	89.01
1320	0.964	1.087	86.58
1440	0.934	1.085	86.46
1560	0.958	1.076	85.75
1680	0.939	1.052	83.80
1800	0.980	1.045	83.30
1920	0.977	1.009	80.42
2040	0.945	0.978	77.94
2160	0.958	0.970	77.29
2280	0.972	0.966	76.95
2400	0.945	0.941	74.96
2520	0.917	0.951	75.75
2640	0.965	0.920	73.27
2760	0.926	0.920	73.33
2880	0.960	0.874	69.60
3000	0.973	0.874	69.63
3120	0.925	0.848	67.61
3240	0.929	0.836	66.64
3360	0.927	0.825	65.72
3480	0.932	0.787	62.72
3600	0.932	0.783	62.37
3720	0.964	0.758	60.40
3840	0.941	0.748	59.63

3960	0.961	0.727	57.89
4080	0.923	0.714	56.89
4200	0.958	0.658	52.42
4320	0.952	0.662	52.75
4440	0.922	0.651	51.91
4560	0.904	0.627	49.98
4680	0.946	0.590	47.01
4800	0.943	0.594	47.36
4920	0.946	0.570	45.45
5040	0.944	0.583	46.47
5160	0.963	0.593	47.25
5280	0.957	0.560	44.58
5400	0.946	0.547	43.61
5520	0.958	0.539	42.96
5640	0.956	0.524	41.74
5760	0.929	0.512	40.77
5880	0.942	0.492	39.16
6000	0.941	0.485	38.66
6120	0.931	0.459	36.59
6240	0.969	0.450	35.88
6360	0.965	0.439	34.95
6480	0.943	0.426	33.91
6600	0.959	0.403	32.10
6720	0.973	0.393	31.28
6840	0.955	0.388	30.90
6960	0.937	0.379	30.18
7080	0.970	0.357	28.46
7200	0.956	0.373	29.69
7320	0.978	0.341	27.17
7440	0.963	0.331	26.41
7560	0.961	0.306	24.37
7680	0.939	0.327	26.08
7800	0.952	0.314	25.04
7920	0.955	0.284	22.60
8040	0.924	0.256	20.36
8160	0.926	0.248	19.74
8280	0.919	0.224	17.89
8400	0.905	0.216	17.24
8520	0.914	0.229	18.29
8640	0.921	0.214	17.06
8760	0.952	0.197	15.71
8880	0.947	0.186	14.82
9000	0.936	0.166	13.23
9120	0.948	0.169	13.44
9240	0.934	0.162	12.90



avg k_{obs} = 1.08 x 10^{-2} s^{-1} ± 1.1 x 10^{-3}

INDEX OF KINETIC EXPERIMENTS FOR CATALYTIC CROSS-COUPLING OF ARYLSILANOLATES

Order in $K^+\mathbf{1}^-$

$K^+\mathbf{1}^-$ 75 mM

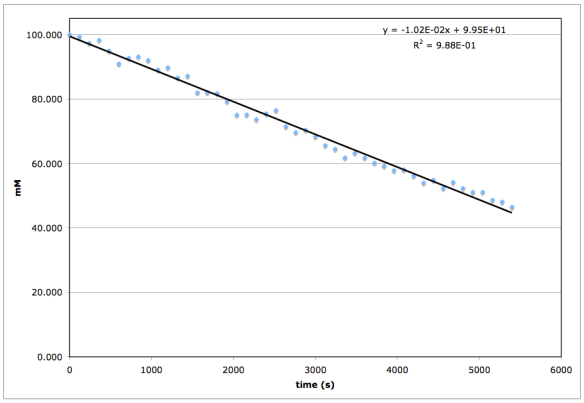
2 100 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of $(t\text{-}Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **1.02 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	1.335	1.744	99.99
120	1.320	1.712	98.18
240	1.342	1.707	97.88
360	1.305	1.676	96.11
480	1.314	1.630	93.47
600	1.336	1.587	91.01
720	1.292	1.566	89.77
840	1.275	1.553	89.04
960	1.264	1.520	87.14
1080	1.282	1.492	85.54
1200	1.244	1.459	83.66
1320	1.261	1.427	81.82
1440	1.240	1.413	81.00
1560	1.267	1.357	77.82
1680	1.243	1.332	76.40
1800	1.229	1.312	75.25
1920	1.235	1.279	73.34
2040	1.257	1.233	70.72
2160	1.240	1.218	69.82
2280	1.245	1.199	68.78
2400	1.201	1.184	67.92
2520	1.164	1.163	66.71
2640	1.204	1.124	64.46
2760	1.193	1.087	62.30
2880	1.172	1.079	61.85
3000	1.186	1.059	60.71
3120	1.209	1.036	59.42
3240	1.200	1.012	58.02
3360	1.210	0.977	56.03
3480	1.183	0.978	56.06
3600	1.154	0.932	53.44
3720	1.199	0.943	54.08
3840	1.168	0.904	51.85

3960	1.181	0.893	51.19
4080	1.164	0.883	50.66
4200	1.175	0.862	49.45
4320	1.165	0.823	47.16
4440	1.173	0.842	48.26
4560	1.169	0.800	45.85
4680	1.137	0.806	46.20
4800	1.154	0.789	45.25
4920	1.160	0.775	44.45
5040	1.135	0.758	43.48
5160	1.144	0.727	41.71
5280	1.154	0.726	41.61
5400	1.164	0.708	40.61
5520	1.150	0.706	40.47
5640	1.128	0.674	38.64
5760	1.169	0.693	39.74
5880	1.117	0.679	38.96
6000	1.150	0.668	38.31
6120	1.118	0.656	37.62
6240	1.139	0.637	36.52



Order in $K^+\mathbf{1}^-$

$K^+\mathbf{1}^-$ 75 mM

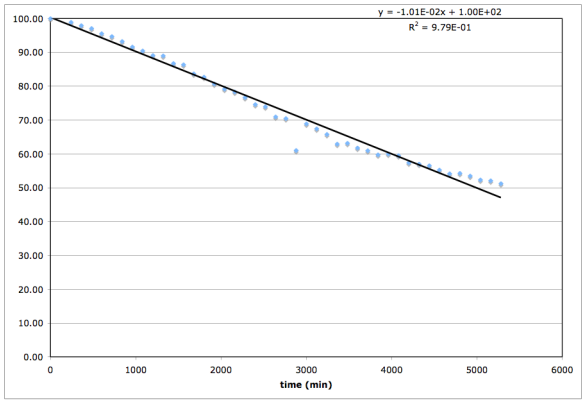
2 100 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of $(t\text{-}Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by 19F NMR spectroscopy. $\mathbf{k_{obs}}$ = **1.01×10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	1.335	1.744	100.00
120	1.320	1.712	100.74
240	1.342	1.707	98.93
360	1.305	1.676	97.93
480	1.314	1.630	97.06
600	1.336	1.587	95.57
720	1.292	1.566	94.67
840	1.275	1.553	93.23
960	1.264	1.520	91.58
1080	1.282	1.492	90.46
1200	1.244	1.459	89.07
1320	1.261	1.427	88.98
1440	1.240	1.413	86.75
1560	1.267	1.357	86.35
1680	1.243	1.332	83.68
1800	1.229	1.312	82.71
1920	1.235	1.279	80.72
2040	1.257	1.233	79.18
2160	1.240	1.218	78.30
2280	1.245	1.199	76.65
2400	1.201	1.184	74.62
2520	1.164	1.163	73.96
2640	1.204	1.124	70.94
2760	1.193	1.087	70.44
2880	1.172	1.079	61.01
3000	1.186	1.059	68.85
3120	1.209	1.036	67.44
3240	1.200	1.012	65.76
3360	1.210	0.977	62.92
3480	1.183	0.978	63.13
3600	1.154	0.932	61.73
3720	1.199	0.943	60.97
3840	1.168	0.904	59.72

3960	1.181	0.893	60.01
4080	1.164	0.883	59.48
4200	1.175	0.862	57.37
4320	1.165	0.823	57.02
4440	1.173	0.842	56.52
4560	1.169	0.800	55.26
4680	1.137	0.806	54.17
4800	1.154	0.789	54.28
4920	1.160	0.775	53.46
5040	1.135	0.758	52.34
5160	1.144	0.727	52.04
5280	1.154	0.726	51.24
5400	1.164	0.708	51.39
5520	1.150	0.706	48.93
5640	1.128	0.674	48.85
5760	1.169	0.693	47.38
5880	1.117	0.679	48.22
6000	1.150	0.668	100.00
6120	1.118	0.656	100.74
6240	1.139	0.637	98.93



avg k_{obs} = 1.02 x 10^{-2} mMs^{-1} ± 7.1 x 10^{-5}

Initial Parameters:

K^+**1**$^-$ 300 mM

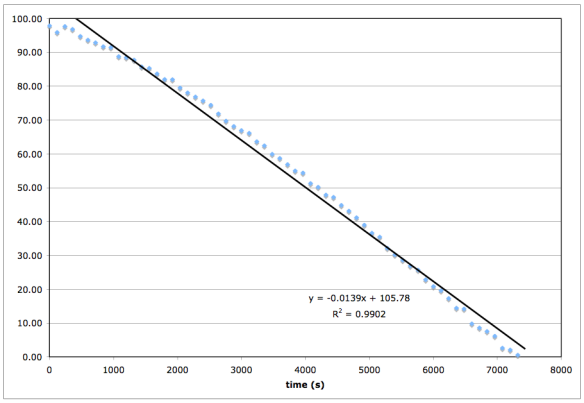
2 100 mM

Pd cat. 5 mM

Following General Procedure I, the following modifications were required for experiments involving >150 mM in K^+**1**$^-$:[8] In a drybox, an oven-dried, 2.5-mL vial equipped with a magnetic stir bar was charged with (*t*-$Bu_3P)_2Pd$ (2.5 mg, 0.0049 mmol), toluene (0.8 mL), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) resulting in a colorless solution. Silanolate K^+**1**$^-$ (33 mg, 0.15 mmol) was added as a solid and the sides of the vial were rinsed with toluene (0.2 mL). The mixture was stirred for 3 min to ensure complete dissolution. The remaining K^+**1**$^-$ (33 mg, 0.15 mmol) was added into an oven-dried, 5-mm NMR tube. The reaction solution was transferred into the NMR tube containing the excess silanolate and was shaken vigorously. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 95 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for 3 min at which point the NMR tube was ejected and shaken to ensure complete homogeneity. The tube was returned to the heated probe and the reaction progress was monitored by the disappearance of starting aryl halide (^{19}F NMR, -115.9 ppm) as compared to an internal reference ($PhCF_3$, ^{19}F NMR, -63.2 ppm)) via ^{19}F NMR spectroscopy using the following parameters: at = 0.328, d1 = 1, pw90 = 18.25, pw=pw90/2, nt=24, sampling every 120 s.[9] $\mathbf{k_{obs} = 1.3 \times 10^{-2}\ mMs^{-1}}$.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.465	1.992	97.86
120	2.486	1.982	95.89
240	2.478	1.982	97.70
360	2.501	1.967	96.85
480	2.489	1.954	94.75
600	2.486	1.960	93.69
720	2.494	1.978	92.89
840	2.528	1.931	91.72
960	2.516	1.927	91.44
1080	2.521	1.895	88.78
1200	2.550	1.915	88.50
1320	2.534	1.898	87.76
1440	2.501	1.872	85.77
1560	2.511	1.859	85.35
1680	2.534	1.822	83.67
1800	2.551	1.856	82.04
1920	2.528	1.840	81.97
2040	2.540	1.800	79.53
2160	2.538	1.780	78.11
2280	2.524	1.765	76.84
2400	2.531	1.743	75.70
2520	2.548	1.737	74.44
2640	2.536	1.687	71.88
2760	2.554	1.682	69.76
2880	2.529	1.667	68.16
3000	2.518	1.630	66.96
3120	2.559	1.622	66.16
3240	2.526	1.590	63.65
3360	2.548	1.559	62.45
3480	2.541	1.557	59.92
3600	2.554	1.511	58.68
3720	2.559	1.484	56.90
3840	2.579	1.460	54.99
3960	2.552	1.438	54.40
4080	2.548	1.414	51.29
4200	2.552	1.366	50.20
4320	2.551	1.325	47.89
4440	2.581	1.295	47.19
4560	2.554	1.272	44.82
4680	2.549	1.257	43.12
4800	2.549	1.209	41.19
4920	2.564	1.187	38.97
5040	2.579	1.138	36.60
5160	2.567	1.115	35.45
5280	2.548	1.081	32.16
5400	2.548	1.045	30.21
5520	2.555	1.034	28.60
5640	2.574	0.975	26.94
5760	2.553	0.954	25.73
5880	2.559	0.910	22.82
6000	2.557	0.897	20.83
6120	2.550	0.852	19.59
6240	2.569	0.819	17.27

6360	2.541	0.783	14.43
6480	2.577	0.740	14.17
6600	2.582	0.695	9.80
6720	2.575	0.674	8.61
6840	2.584	0.611	7.56
6960	2.589	0.574	6.14
7080	2.597	0.543	2.60
7200	2.558	0.512	2.07
7320	2.581	0.489	0.57



Order in $K^+\mathbf{1}^-$ with $(t\text{-}Bu_3P)_2Pd$

$K^+\mathbf{1}^-$ 300 mM

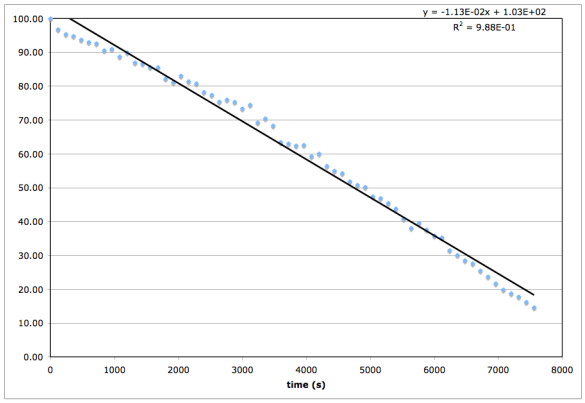
2 100 mM

Pd cat. 5 mM

Following General Procedure II, a mixture of $(t\text{-}Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (66 mg, 0.30 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 1.13 \times 10^{-2}\ mMs^{-1}}$.

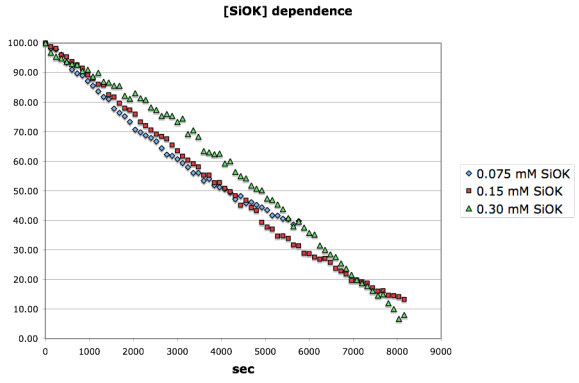
Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	0.997	1.135	100.00
120	0.959	1.254	96.78
240	0.961	1.214	95.40
360	0.966	1.196	94.81
480	0.966	1.189	93.75
600	0.948	1.176	92.99
720	0.943	1.166	92.66
840	0.987	1.162	90.59
960	0.997	1.136	91.00
1080	0.961	1.141	88.71
1200	0.974	1.112	89.92
1320	0.980	1.128	86.96
1440	0.954	1.091	86.66
1560	0.942	1.087	85.64
1680	0.951	1.074	85.56
1800	0.957	1.073	82.24
1920	0.959	1.031	81.19
2040	0.958	1.018	83.08
2160	0.973	1.042	81.40
2280	0.935	1.021	80.79
2400	0.939	1.013	78.26
2520	0.963	0.981	77.42
2640	0.960	0.971	75.37
2760	0.963	0.945	76.00
2880	0.943	0.953	75.35
3000	0.954	0.945	73.37
3120	0.954	0.920	74.50
3240	0.954	0.934	69.22
3360	0.928	0.868	70.49
3480	0.962	0.884	68.36
3600	0.955	0.857	63.45
3720	0.968	0.796	63.01
3840	0.985	0.790	62.40

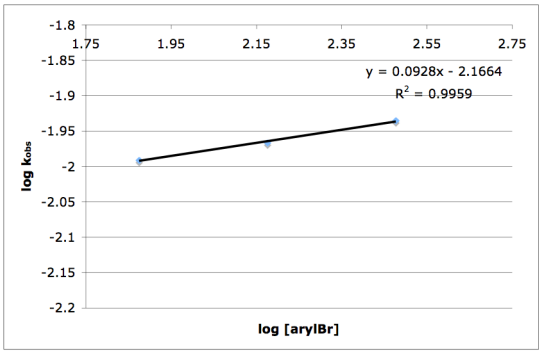
3960	0.939	0.782	62.59
4080	0.973	0.785	59.29
4200	0.926	0.743	60.03
4320	0.976	0.753	56.39
4440	0.947	0.707	54.99
4560	0.967	0.690	54.26
4680	0.949	0.680	51.83
4800	0.932	0.650	50.80
4920	0.971	0.637	50.19
5040	0.979	0.629	47.39
5160	0.946	0.594	46.92
5280	0.945	0.588	45.42
5400	0.921	0.570	43.77
5520	0.951	0.549	40.83
5640	0.958	0.512	38.04
5760	0.952	0.477	39.58
5880	0.963	0.496	37.59
6000	0.937	0.471	35.78
6120	0.936	0.449	35.25
6240	0.944	0.442	31.50
6360	0.936	0.395	30.06
6480	0.949	0.377	28.50
6600	0.970	0.357	27.58
6720	0.958	0.346	25.46
6840	0.970	0.319	23.72
6960	0.944	0.297	21.65
7080	0.935	0.272	19.84
7200	0.969	0.249	18.77
7320	0.935	0.235	17.78
7440	0.954	0.223	16.20
7560	0.942	0.203	14.60
7680	0.965	0.183	14.96
7800	0.917	0.188	12.02
7920	0.953	0.151	10.06
8040	0.982	0.126	6.70
8160	0.966	0.084	8.03
8280	0.934	0.101	7.37



<u>avg k_{obs} = 1.22 x 10^{-2} mMs^{-1} ± 1.2 x 10^{-3}</u>

Order in $K^{+}1^{-}$ (pp. S3, S9, S13):





Order in **2** with (t-$Bu_3P)_2Pd$

$K^+\mathbf{1}^-$ 150 mM

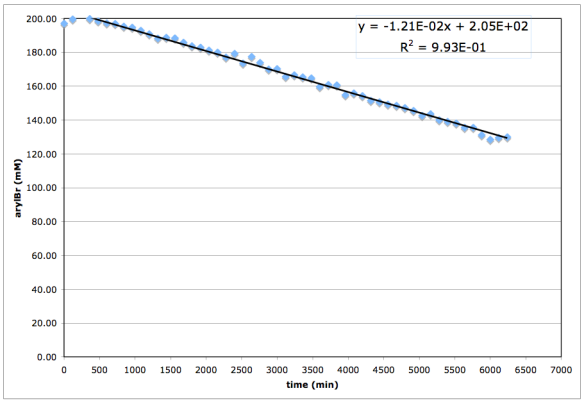
2 200 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (22 μL, 35 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **1.21 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	0.984	2.266	197.08
120	0.996	2.295	199.59
240	1.009	2.309	200.78
360	1.028	2.298	199.86
480	1.025	2.283	198.56
600	1.007	2.269	197.33
720	0.998	2.265	196.98
840	1.028	2.247	195.43
960	1.035	2.240	194.81
1080	1.029	2.219	192.97
1200	0.995	2.195	190.86
1320	0.982	2.166	188.33
1440	1.034	2.171	188.81
1560	1.017	2.167	188.39
1680	1.051	2.137	185.82
1800	1.030	2.113	183.78
1920	1.022	2.104	182.94
2040	1.008	2.084	181.19
2160	1.028	2.070	180.01
2280	1.035	2.037	177.09
2400	1.003	2.062	179.31
2520	1.023	1.996	173.59
2640	0.989	2.041	177.46
2760	1.034	2.000	173.92
2880	1.020	1.955	170.01
3000	1.001	1.959	170.32
3120	1.026	1.905	165.64
3240	1.009	1.917	166.66
3360	1.023	1.902	165.42
3480	1.004	1.896	164.83
3600	1.025	1.836	159.66
3720	0.991	1.850	160.87
3840	1.018	1.847	160.64

3960	1.040	1.780	154.82
4080	1.019	1.793	155.94
4200	0.999	1.775	154.36
4320	1.026	1.742	151.50
4440	1.017	1.732	150.63
4560	1.009	1.718	149.36
4680	0.998	1.709	148.64
4800	1.026	1.694	147.29
4920	1.019	1.674	145.54
5040	1.019	1.640	142.62
5160	0.994	1.651	143.57
5280	1.012	1.610	140.03
5400	1.039	1.599	139.08
5520	0.998	1.589	138.16
5640	0.995	1.559	135.53
5760	0.985	1.559	135.60
5880	1.004	1.508	131.13
6000	0.983	1.478	128.49
6120	1.007	1.490	129.54
6240	1.020	1.494	129.94
6360	1.033	1.463	127.23
6480	0.984	1.437	124.99
6600	0.991	1.379	119.89
6720	1.025	1.360	118.28
6840	1.050	1.345	116.99
6960	1.009	1.340	116.52
7080	1.032	1.320	114.79
7200	1.005	1.355	117.87
7320	1.003	1.329	115.59
7440	1.040	1.316	114.41
7560	0.993	1.314	114.26
7680	1.010	1.291	112.29
7800	1.012	1.264	109.91
7920	1.020	1.272	110.57
8040	1.019	1.269	110.34
8160	1.030	1.273	110.68
8280	1.008	1.235	107.43



Order in **2** with (t-$Bu_3P)_2Pd$

$K^+\mathbf{1}^-$ 150 mM

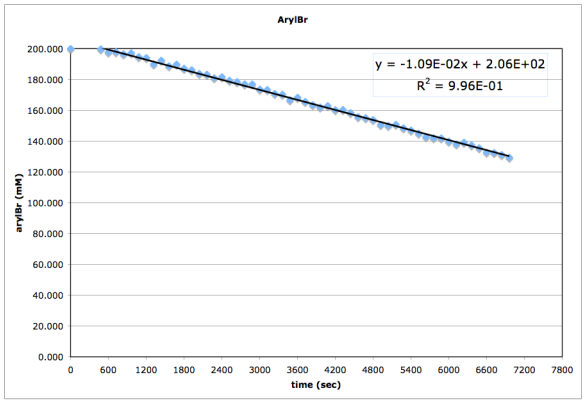
2 200 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (22 μL, 35 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 1.09 \times 10^{-2}\ mMs^{-1}}$.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	4.745	7.762	100.00
120	4.728	7.791	100.37
240	4.714	7.745	99.78
360	4.669	7.762	100.00
480	4.657	7.610	98.04
600	4.672	7.555	97.34
720	4.726	7.648	98.53
840	4.689	7.541	97.15
960	4.715	7.605	97.98
1080	4.697	7.477	96.33
1200	4.715	7.487	96.46
1320	4.727	7.345	94.63
1440	4.730	7.441	95.87
1560	4.719	7.287	93.88
1680	4.756	7.388	95.18
1800	4.868	7.451	96.00
1920	4.810	7.327	94.40
2040	4.810	7.233	93.19
2160	4.847	7.265	93.60
2280	4.818	7.132	91.88
2400	4.774	7.097	91.43
2520	4.784	7.020	90.44
2640	4.844	7.073	91.13
2760	4.811	6.966	89.74
2880	4.758	6.890	88.77
3000	4.856	6.896	88.84
3120	4.811	6.827	87.95
3240	4.842	6.767	87.18
3360	4.832	6.732	86.73
3480	4.872	6.645	85.61
3600	4.821	6.638	85.52
3720	4.840	6.558	84.49
3840	4.870	6.512	83.90

3960	4.868	6.453	83.14
4080	4.848	6.463	83.27
4200	4.946	6.487	83.57
4320	4.871	6.391	82.33
4440	4.904	6.357	81.90
4560	4.950	6.307	81.26
4680	4.907	6.224	80.19
4800	4.922	6.195	79.81
4920	4.930	6.078	78.31
5040	4.979	6.109	78.70
5160	4.926	6.075	78.27
5280	4.948	6.012	77.46
5400	4.933	5.934	76.45
5520	4.906	5.823	75.02
5640	4.949	5.782	74.49
5760	4.992	5.804	74.78
5880	4.903	5.695	73.37
6000	4.896	5.601	72.16
6120	4.907	5.546	71.45
6240	4.869	5.541	71.38
6360	4.871	5.478	70.58
6480	4.894	5.425	69.89
6600	4.940	5.367	69.15
6720	4.971	5.387	69.40
6840	4.980	5.343	68.83
6960	4.926	5.215	67.19
7080	4.929	5.154	66.40
7200	4.913	5.177	66.70
7320	4.923	5.092	65.60



avg k_{obs} = 1.15 x 10^{-2} s^{-1} ± 8.5 x 10^{-4}

Order in **2** with (t-$Bu_3P)_2Pd$

K^+**1**$^-$ 150 mM

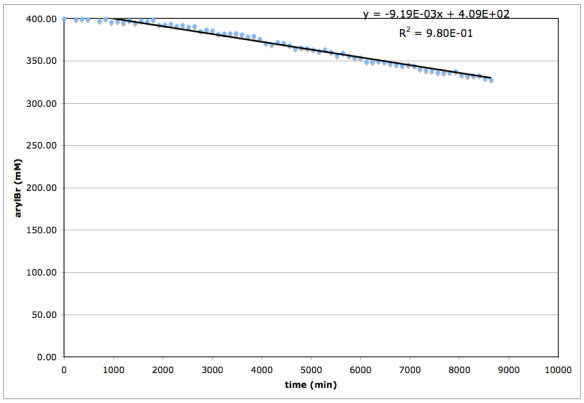
2 400 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (44 μL, 70 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **9.19 x 10^{-3} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.424	8.506	400.02
120	2.445	8.559	402.47
240	2.466	8.484	398.96
360	2.464	8.500	399.70
480	2.491	8.492	399.35
600	2.486	8.511	400.23
720	2.502	8.450	397.37
840	2.483	8.501	399.77
960	2.511	8.420	395.95
1080	2.498	8.436	396.73
1200	2.506	8.405	395.24
1320	2.576	8.460	397.82
1440	2.556	8.403	395.15
1560	2.543	8.446	397.20
1680	2.535	8.440	396.87
1800	2.554	8.478	398.70
1920	2.555	8.350	392.68
2040	2.574	8.355	392.88
2160	2.558	8.369	393.55
2280	2.574	8.322	391.33
2400	2.575	8.346	392.50
2520	2.546	8.297	390.17
2640	2.578	8.315	391.00
2760	2.576	8.194	385.34
2880	2.584	8.234	387.21
3000	2.603	8.207	385.93
3120	2.583	8.124	382.03
3240	2.618	8.129	382.28
3360	2.631	8.131	382.35
3480	2.566	8.137	382.65
3600	2.610	8.107	381.25
3720	2.622	8.057	378.90
3840	2.619	8.069	379.44

3960	2.602	7.992	375.82
4080	2.626	7.896	371.33
4200	2.574	7.860	369.61
4320	2.634	7.918	372.34
4440	2.643	7.893	371.18
4560	2.639	7.836	368.51
4680	2.923	7.762	365.02
4800	2.606	7.778	365.77
4920	2.624	7.761	364.95
5040	2.620	7.730	363.51
5160	2.605	7.688	361.51
5280	2.618	7.728	363.40
5400	2.639	7.668	360.61
5520	2.628	7.580	356.46
5640	2.634	7.646	359.57
5760	2.631	7.576	356.26
5880	2.638	7.529	354.05
6000	2.657	7.522	353.75
6120	2.620	7.422	349.04
6240	2.623	7.419	348.87
6360	2.625	7.444	350.05
6480	2.634	7.420	348.93
6600	2.646	7.379	346.99
6720	2.637	7.351	345.68
6840	2.636	7.325	344.47
6960	2.646	7.347	345.52
7080	2.645	7.319	344.17
7200	2.650	7.242	340.58
7320	2.638	7.204	338.79
7440	2.680	7.198	338.47
7560	2.626	7.152	336.34
7680	2.611	7.144	335.93
7800	2.663	7.156	336.51
7920	2.671	7.178	337.56
8040	2.631	7.092	333.50
8160	2.645	7.062	332.09
8280	2.633	7.071	332.51
8400	2.631	7.078	332.85
8520	2.634	7.009	329.60
8640	2.647	6.973	327.90



Order in **2** with (t-$Bu_3P)_2Pd$

$K^+\mathbf{1}^-$ 150 mM

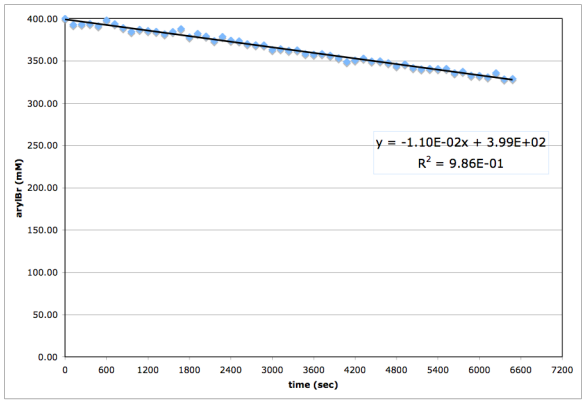
2 400 mM

Pd cat. 5 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (2.6 mg, 0.0050 mmol), benzotrifluoride (5 μL) and **2** (44 μL, 70 mg, 0.20 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 1.10 \times 10^{-2}\ mMs^{-1}}$.

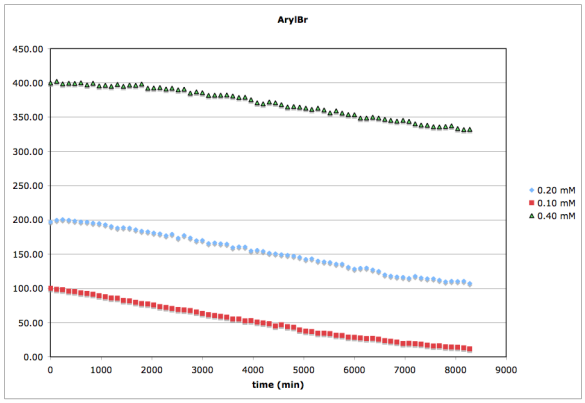
Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	5.088	16.116	400.01
120	5.087	15.823	392.72
240	5.061	15.839	393.12
360	5.124	15.868	393.85
480	5.136	15.762	391.22
600	5.129	16.033	397.93
720	5.114	15.862	393.69
840	5.119	15.671	388.97
960	5.122	15.492	384.52
1080	5.063	15.600	387.18
1200	5.072	15.535	385.59
1320	5.067	15.494	384.55
1440	5.102	15.384	381.82
1560	5.103	15.489	384.43
1680	5.092	15.630	387.93
1800	5.102	15.229	377.98
1920	5.108	15.395	382.12
2040	5.125	15.268	378.96
2160	5.129	15.058	373.73
2280	5.105	15.255	378.63
2400	5.125	15.073	374.11
2520	5.076	15.043	373.36
2640	5.117	14.913	370.15
2760	5.091	14.861	368.85
2880	5.144	14.846	368.48
3000	5.085	14.637	363.29
3120	5.105	14.670	364.12
3240	5.142	14.592	362.16
3360	5.106	14.611	362.66
3480	5.142	14.441	358.43
3600	5.098	14.412	357.71
3720	5.131	14.434	358.25
3840	5.113	14.359	356.39

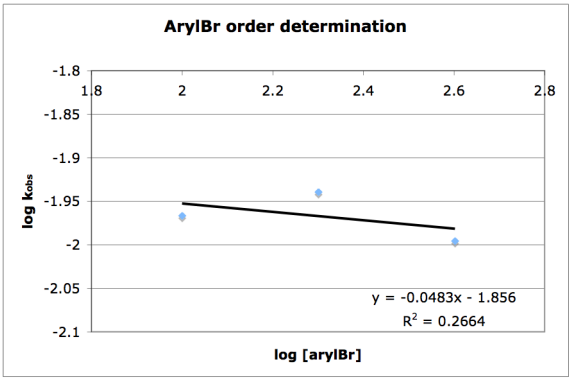
3960	5.091	14.243	353.52
4080	5.087	14.059	348.94
4200	5.177	14.129	350.69
4320	5.171	14.225	353.07
4440	5.219	14.085	349.60
4560	5.177	14.099	349.93
4680	5.250	14.010	347.74
4800	5.132	13.857	343.93
4920	5.230	13.947	346.16
5040	5.190	13.766	341.67
5160	5.196	13.709	340.26
5280	5.208	13.726	340.69
5400	5.207	13.719	340.50
5520	5.235	13.729	340.76
5640	5.190	13.528	335.77
5760	5.186	13.597	337.47
5880	5.187	13.411	332.86
6000	5.161	13.400	332.59
6120	5.198	13.326	330.76
6240	5.255	13.530	335.81
6360	5.116	13.226	328.27
6480	5.179	13.245	328.75
6600	5.190	13.283	329.67



avg k_{obs} = 1.01 x 10^{-2} mMs^{-1} ± 1.3 x 10^{-3}

Order in 2 with (*t*-$Bu_3P)_2Pd$ (pp. S3, S18, S22):





Order in **Pd** with (t-$Bu_3P)_2Pd$

$K^+\mathbf{1}^-$ 150 mM

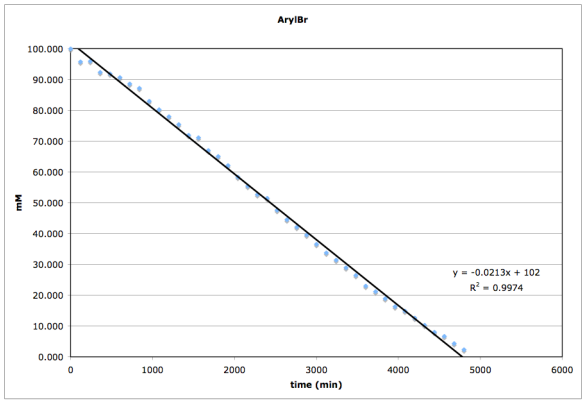
2 100 mM

Pd cat. 10 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (5.1 mg, 0.010 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by $K^+\mathbf{1}^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 2.13 \times 10^{-2}\ mMs^{-1}}$.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.881	2.434	99.959
120	2.925	2.366	95.725
240	2.930	2.375	95.921
360	2.925	2.282	92.340
480	2.941	2.282	91.820
600	2.927	2.241	90.621
720	2.946	2.205	88.589
840	2.927	2.157	87.199
960	2.948	2.066	82.945
1080	2.976	2.017	80.188
1200	2.970	1.956	77.924
1320	2.999	1.911	75.425
1440	3.014	1.832	71.905
1560	2.974	1.787	71.121
1680	3.016	1.707	66.966
1800	3.028	1.665	65.063
1920	3.015	1.582	62.103
2040	3.045	1.501	58.331
2160	3.062	1.434	55.410
2280	3.033	1.350	52.661
2400	3.040	1.321	51.444
2520	3.055	1.228	47.562
2640	3.056	1.149	44.488
2760	3.069	1.092	42.122
2880	3.054	1.021	39.575
3000	3.042	0.940	36.580
3120	3.045	0.869	33.776
3240	3.034	0.805	31.398
3360	3.053	0.747	28.939
3480	3.055	0.684	26.504
3600	3.069	0.596	22.992
3720	3.029	0.542	21.182
3840	3.079	0.492	18.913

3960	3.080	0.425	16.335
4080	3.074	0.388	14.931
4200	3.093	0.331	12.666
4320	3.036	0.264	10.283
4440	3.103	0.211	8.037
4560	3.085	0.174	6.677
4680	3.092	0.113	4.324
4800	3.084	0.061	2.327



Order in **Pd** with (t-$Bu_3P)_2Pd$

K^+**1**$^-$ 150 mM

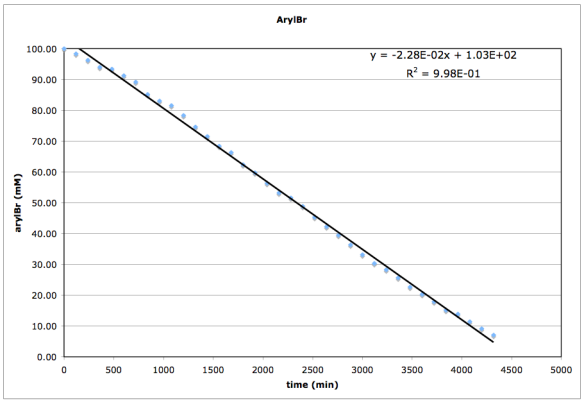
2 100 mM

Pd cat. 10 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (5.1 mg, 0.010 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **2.28 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	3.160	2.534	100.01
120	3.175	2.491	98.31
240	3.149	2.439	96.26
360	3.161	2.382	94.01
480	3.139	2.366	93.37
600	3.150	2.312	91.22
720	3.158	2.260	89.19
840	3.145	2.157	85.13
960	3.171	2.103	83.00
1080	3.176	2.067	81.56
1200	3.154	1.985	78.32
1320	3.143	1.891	74.62
1440	3.155	1.813	71.55
1560	3.157	1.733	68.39
1680	3.132	1.680	66.28
1800	3.196	1.580	62.37
1920	3.165	1.514	59.76
2040	3.195	1.428	56.34
2160	3.169	1.348	53.21
2280	3.182	1.307	51.57
2400	3.176	1.239	48.88
2520	3.154	1.148	45.32
2640	3.172	1.071	42.28
2760	3.166	1.001	39.52
2880	3.124	0.922	36.39
3000	3.207	0.840	33.16
3120	3.150	0.770	30.37
3240	3.196	0.717	28.29
3360	3.195	0.650	25.65
3480	3.171	0.575	22.68
3600	3.191	0.515	20.32
3720	3.194	0.454	17.90
3840	3.178	0.385	15.18

3960	3.190	0.352	13.88
4080	3.192	0.290	11.44
4200	3.164	0.232	9.15
4320	3.138	0.179	7.06



Order in **Pd** with (t-$Bu_3P)_2Pd$

K^+**1**$^-$ 150 mM

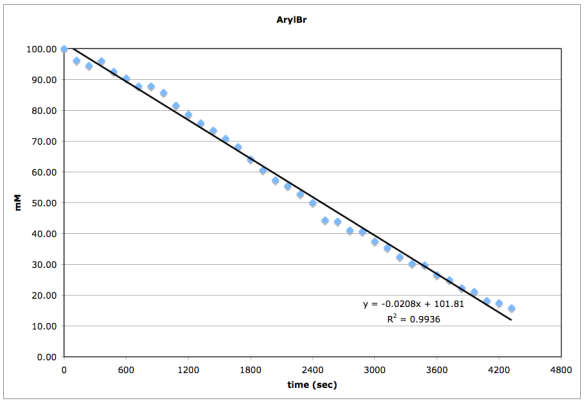
2 100 mM

Pd cat. 10 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (5.1 mg, 0.010 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 2.08 \times 10^{-2}\ mMs^{-1}}$.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	3.160	2.534	99.99
120	3.175	2.491	96.21
240	3.149	2.439	94.49
360	3.161	2.382	96.07
480	3.139	2.366	92.59
600	3.150	2.312	90.44
720	3.158	2.260	87.80
840	3.145	2.157	87.83
960	3.171	2.103	85.77
1080	3.176	2.067	81.60
1200	3.154	1.985	78.69
1320	3.143	1.891	75.84
1440	3.155	1.813	73.53
1560	3.157	1.733	70.86
1680	3.132	1.680	68.19
1800	3.196	1.580	64.16
1920	3.165	1.514	60.65
2040	3.195	1.428	57.37
2160	3.169	1.348	55.50
2280	3.182	1.307	52.85
2400	3.176	1.239	50.09
2520	3.154	1.148	44.38
2640	3.172	1.071	43.98
2760	3.166	1.001	41.12
2880	3.124	0.922	40.69
3000	3.207	0.840	37.52
3120	3.150	0.770	35.41
3240	3.196	0.717	32.49
3360	3.195	0.650	30.31
3480	3.171	0.575	29.83
3600	3.191	0.515	26.60
3720	3.194	0.454	25.01
3840	3.178	0.385	22.41

3960	3.190	0.352	21.17
4080	3.192	0.290	18.22
4200	3.164	0.232	17.55
4320	3.138	0.179	15.89



avg k_{obs} = 2.16 x 10^{-2} mMs^{-1} ± 1.0 x 10^{-3}

Order in **Pd** with (t-$Bu_3P)_2Pd$

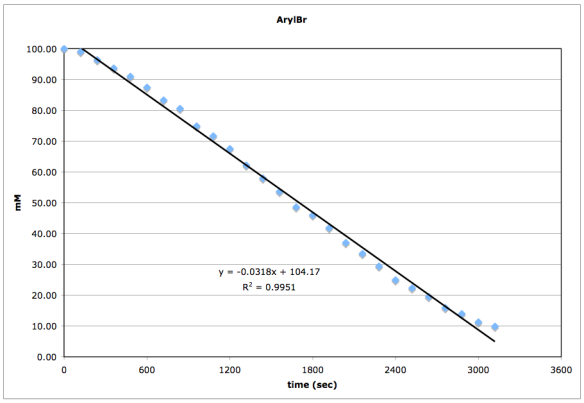
K^+**1**$^-$ 150 mM

2 100 mM

Pd cat. 15 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (7.6 mg, 0.015 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **3.18 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.415	3.030	99.99
120	2.364	3.000	99.00
240	2.377	2.919	96.33
360	2.392	2.837	93.63
480	2.364	2.757	90.98
600	2.399	2.648	87.40
720	2.359	2.524	83.30
840	2.324	2.441	80.56
960	2.391	2.269	74.88
1080	2.323	2.171	71.65
1200	2.359	2.045	67.50
1320	2.384	1.883	62.14
1440	2.398	1.757	57.98
1560	2.372	1.625	53.63
1680	2.359	1.472	48.57
1800	2.381	1.392	45.96
1920	2.344	1.267	41.82
2040	2.347	1.122	37.04
2160	2.372	1.015	33.50
2280	2.346	0.891	29.39
2400	2.374	0.755	24.92
2520	2.305	0.676	22.31
2640	2.313	0.592	19.53
2760	2.314	0.482	15.90
2880	2.301	0.423	13.95
3000	2.304	0.343	11.31
3120	2.340	0.300	9.90
3240	2.347	0.257	8.47
3360	2.329	0.226	7.44



Order in **Pd** with (t-$Bu_3P)_2Pd$

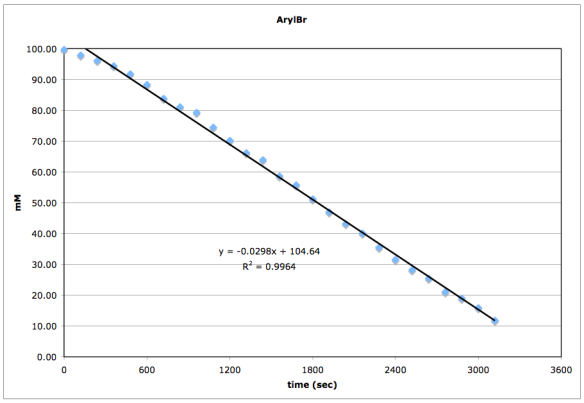
K^+**1**$^-$ 150 mM

2 100 mM

Pd cat. 15 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (7.6 mg, 0.015 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **2.98 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	5.023	4.397	99.64
120	5.012	4.319	97.88
240	5.042	4.242	96.12
360	5.109	4.166	94.40
480	5.117	4.050	91.77
600	5.148	3.896	88.29
720	5.049	3.698	83.80
840	5.028	3.578	81.08
960	5.023	3.498	79.26
1080	5.006	3.286	74.47
1200	5.050	3.098	70.19
1320	5.041	2.920	66.17
1440	5.522	2.618	63.92
1560	5.045	2.587	58.63
1680	5.038	2.462	55.78
1800	5.081	2.259	51.19
1920	5.073	2.073	46.99
2040	5.080	1.906	43.20
2160	5.096	1.769	40.08
2280	5.090	1.566	35.47
2400	5.069	1.392	31.55
2520	5.053	1.244	28.19
2640	5.091	1.123	25.44
2760	5.097	0.931	21.09
2880	5.113	0.839	19.01
3000	5.101	0.703	15.93
3120	5.090	0.523	11.85
3240	5.060	0.471	10.67



Order in **Pd** with (t-$Bu_3P)_2Pd$

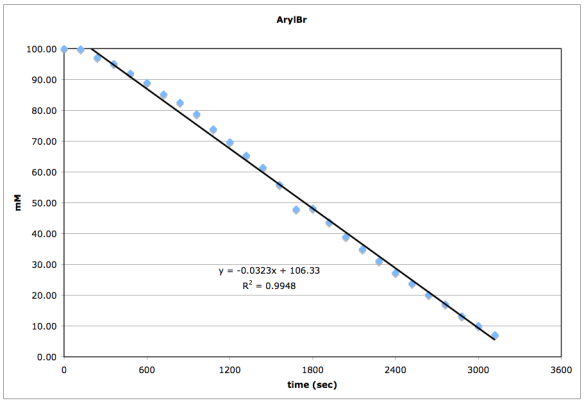
K^+**1**$^-$ 150 mM

2 100 mM

Pd cat. 15 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (7.6 mg, 0.015 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. **k_{obs} = 3.23 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	5.038	4.680	100.00
120	5.020	4.674	99.86
240	5.021	4.545	97.12
360	5.027	4.451	95.10
480	5.022	4.304	91.96
600	4.993	4.163	88.96
720	5.005	3.987	85.20
840	5.019	3.863	82.55
960	5.000	3.688	78.81
1080	5.085	3.461	73.95
1200	5.061	3.262	69.69
1320	5.040	3.061	65.40
1440	4.993	2.874	61.41
1560	4.999	2.614	55.85
1680	5.612	2.245	47.96
1800	4.983	2.254	48.17
1920	4.993	2.046	43.73
2040	5.017	1.823	38.96
2160	5.031	1.638	34.99
2280	5.062	1.458	31.15
2400	5.024	1.278	27.31
2520	5.016	1.116	23.86
2640	5.027	0.946	20.21
2760	5.009	0.801	17.11
2880	5.010	0.620	13.24
3000	5.055	0.472	10.09
3120	5.059	0.336	7.18
3240	5.020	0.274	5.85



avg k_{obs} = 3.13 x 10^{-2} mMs^{-1} ± 1.3 x 10^{-3}

Order in **Pd** with (t-$Bu_3P)_2Pd$

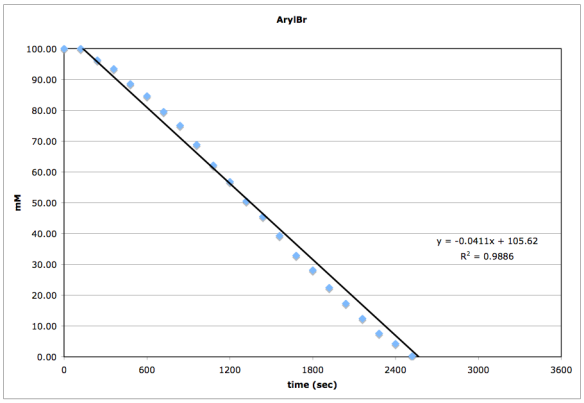
K^+**1**$^-$ 150 mM

2 100 mM

Pd cat. 20 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (10.2 mg, 0.020 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **4.11 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.813	2.571	100.00
120	2.757	2.570	99.98
240	2.806	2.474	96.23
360	2.818	2.403	93.45
480	2.800	2.277	88.55
600	2.790	2.176	84.62
720	2.788	2.044	79.51
840	2.780	1.929	75.04
960	2.799	1.770	68.86
1080	2.809	1.599	62.19
1200	2.777	1.460	56.81
1320	2.814	1.299	50.53
1440	2.771	1.171	45.54
1560	2.789	1.011	39.33
1680	2.811	0.845	32.87
1800	2.797	0.724	28.17
1920	2.759	0.577	22.43
2040	2.777	0.445	17.31
2160	2.765	0.319	12.40
2280	2.797	0.196	7.63
2400	2.821	0.109	4.25
2520	2.766	0.008	0.30



Order in **Pd** with (t-$Bu_3P)_2Pd$

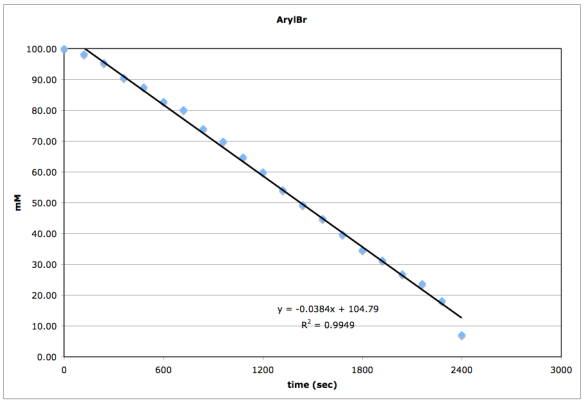
K^+**1**$^-$ 150 mM

2 100 mM

Pd cat. 20 mM

Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (10.2 mg, 0.020 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **3.84 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.661	3.132	100.00
120	2.633	3.076	98.21
240	2.610	2.988	95.40
360	2.569	2.837	90.59
480	2.591	2.741	87.52
600	2.537	2.594	82.82
720	2.509	2.509	80.12
840	2.508	2.317	73.97
960	2.492	2.189	69.90
1080	2.548	2.028	64.74
1200	2.462	1.878	59.96
1320	2.491	1.695	54.13
1440	2.517	1.544	49.31
1560	2.451	1.405	44.87
1680	2.446	1.246	39.77
1800	2.413	1.087	34.70
1920	2.435	0.981	31.34
2040	2.446	0.842	26.90
2160	2.390	0.742	23.70
2280	2.406	0.569	18.18
2400	2.397	0.223	7.12



Order in **Pd** with (t-$Bu_3P)_2Pd$

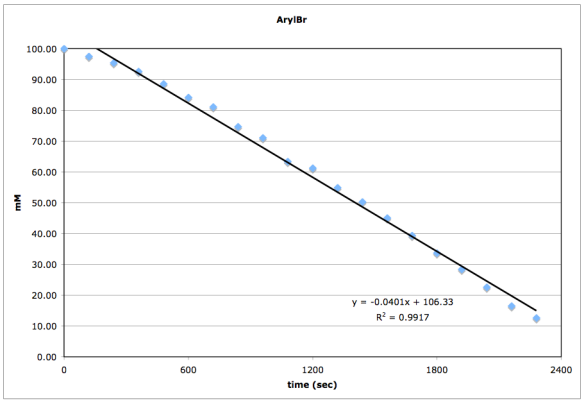
K^+**1**$^-$ 300 mM

2 100 mM

Pd cat. 20 mM

Following modified General Procedure I (p S13), a mixture of (t-$Bu_3P)_2Pd$ (10.2 mg, 0.020 mmol), benzotrifluoride (5 μL) and **2** (11 μL, 17.5 mg, 0.10 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (66 mg, 0.30 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 4.01 \times 10^{-2}\ mMs^{-1}}$.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	1.620	2.875	100.01
120	1.667	2.802	97.45
240	1.597	2.743	95.41
360	1.626	2.663	92.61
480	1.582	2.547	88.57
600	1.668	2.420	84.18
720	1.597	2.331	81.06
840	1.596	2.146	74.64
960	1.532	2.044	71.08
1080	3.006	1.594	63.35
1200	1.646	1.760	61.22
1320	1.608	1.578	54.89
1440	1.573	1.446	50.28
1560	1.619	1.295	45.04
1680	1.665	1.132	39.36
1800	1.640	0.969	33.71
1920	1.611	0.816	28.40
2040	1.611	0.650	22.61
2160	1.694	0.474	16.50
2280	1.614	0.363	12.62
2400	1.618	0.311	10.83



Order in **Pd** with (t-$Bu_3P)_2Pd$

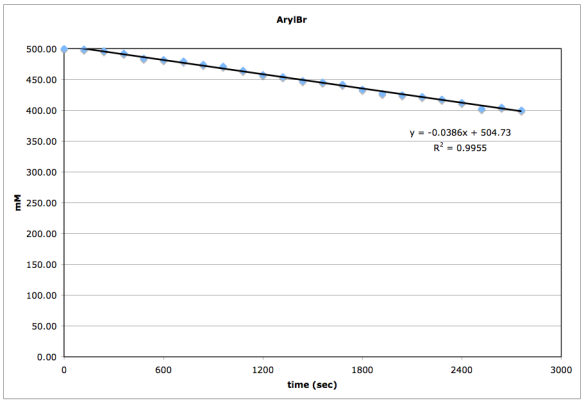
K^+**1**$^-$ 150 mM

2 500 mM

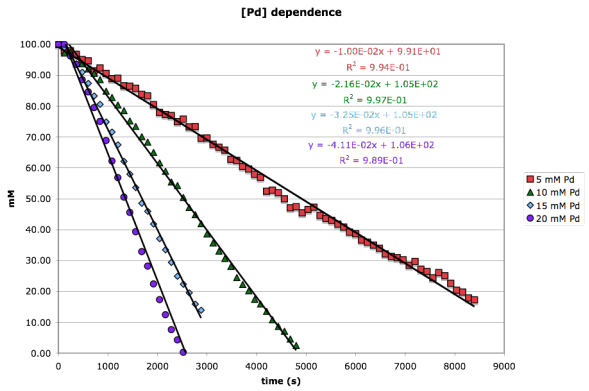
Pd cat. 20 mM

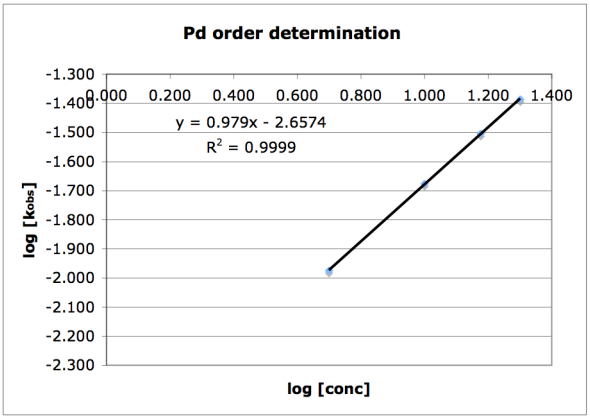
Following General Procedure I, a mixture of (t-$Bu_3P)_2Pd$ (10.2 mg, 0.020 mmol), benzotrifluoride (5 μL) and **2** (55 μL, 87.5 mg, 0.50 mmol) were dissolved in toluene (0.8 mL), followed by K^+**1**$^-$ (33 mg, 0.15 mmol) and toluene (0.2 mL) to afford a clear, colorless solution. The tube was placed into a preheated 95 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs}}$ = **3.86 x 10^{-2} mMs^{-1}**.

Time (s)	Integral IS (-63.2 ppm)	Integral **2** (-115.9 ppm)	Normalized (mM)
0	2.001	13.037	500.01
120	2.005	13.013	499.06
240	2.024	12.942	496.35
360	2.012	12.834	492.21
480	1.985	12.628	484.31
600	1.976	12.571	482.12
720	2.019	12.502	479.47
840	2.003	12.369	474.38
960	2.037	12.290	471.34
1080	2.798	11.648	464.72
1200	2.024	11.930	457.54
1320	2.050	11.844	454.25
1440	1.992	11.675	447.75
1560	2.010	11.613	445.39
1680	2.013	11.517	441.69
1800	2.038	11.313	433.88
1920	2.021	11.138	427.15
2040	2.020	11.080	424.96
2160	2.022	11.006	422.12
2280	2.000	10.893	417.79
2400	2.011	10.752	412.36
2520	2.022	10.494	402.48
2640	2.019	10.553	404.73
2760	1.982	10.430	400.02

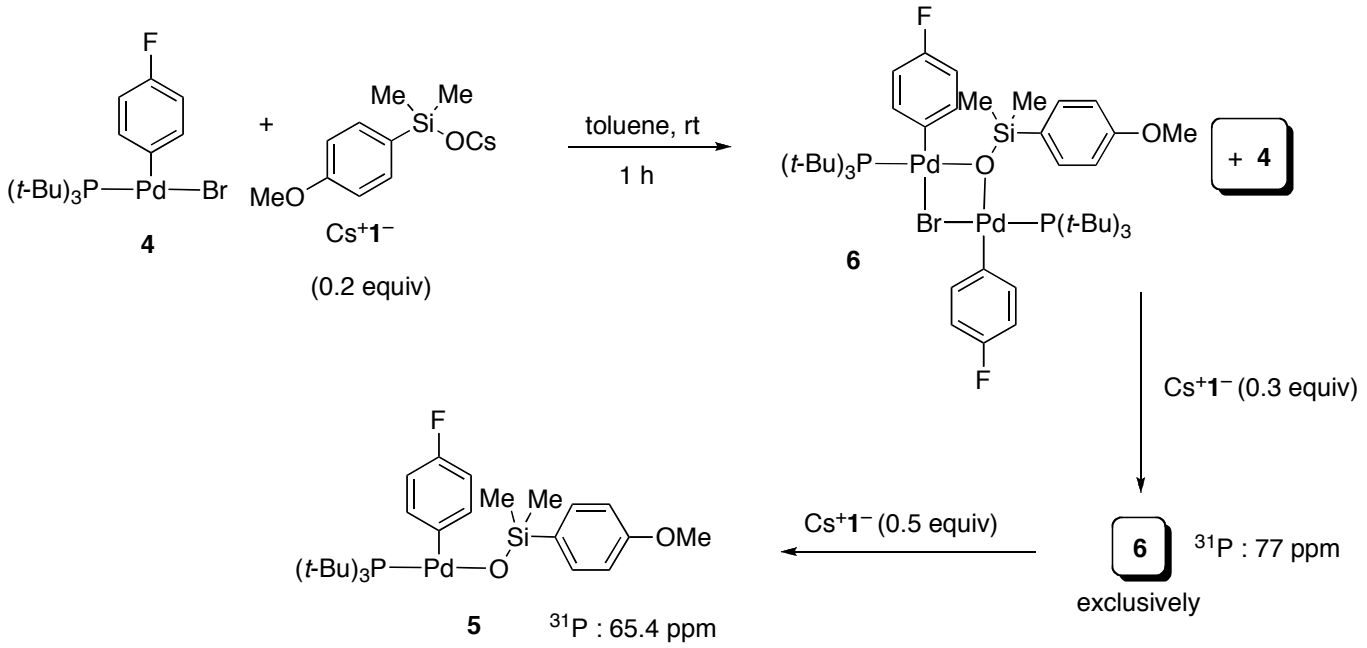


Order in Pd with (*t*-$Bu_3P)_2Pd$ (pp. S3, S26, S32, S35):





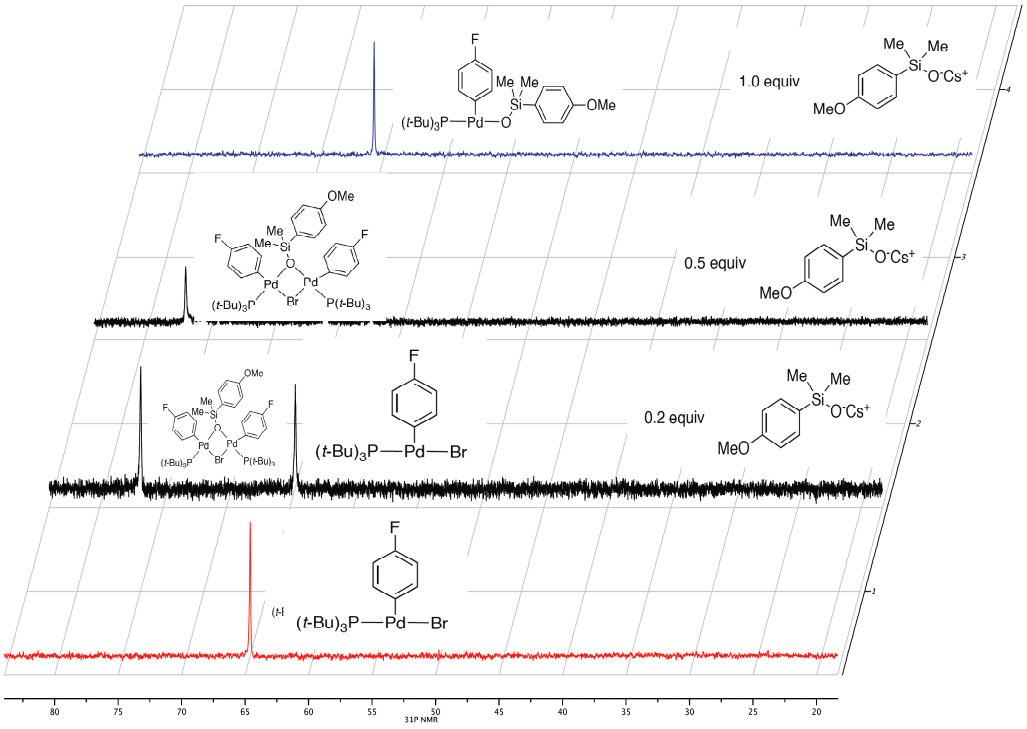
Study of Displacement Step of Palladium(II) Bromide with $Cs^+\mathbf{1}^-$



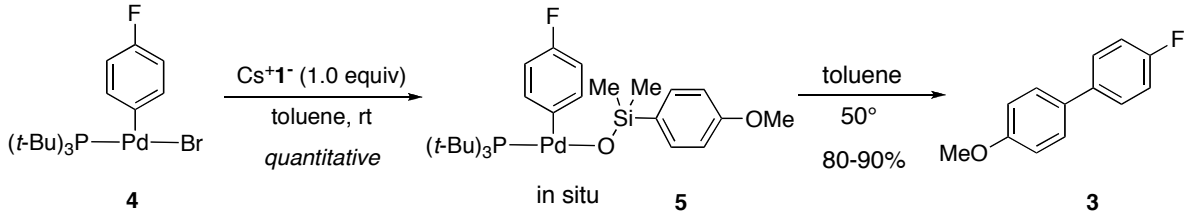
In a drybox, an oven-dried, 3-mL vial equipped with a magnetic stir bar was charged with **4** (5.2 mg, 0.011 mmol) and toluene (0.6 mL) resulting in an orange solution. Then, $Cs^+\mathbf{1}^-$ (0.8 mg, 0.002 mmol, 0.2 equiv) was added as a solid and the mixture was stirred until the mixture was completely homogeneous. The resulting solution was transferred into an oven-dried, 5-mm NMR tube using a syringe and the tube was sealed with a septum and Parafilm. The sample was analyzed by ^{31}P NMR spectroscopy (see figure below). The ^{31}P NMR spectrum contained a resonance at 77.0 ppm in addition to that for **4** (64.5 ppm). The NMR tube was returned to the drybox and an additional 0.3 equiv of $Cs^+\mathbf{1}^-$ (0.9 mg, 0.003 mmol) was added. The mixture was shaken to ensure homogeneity and the sample again analyzed by ^{31}P NMR spectroscopy. The signal for **4** completely vanished leaving a single species (77.0 ppm) visible in the ^{31}P NMR. The stoichiometry of this experiment suggested that displacement occurs rapidly and the mutual coexistence of the bromide complex **4** and silanolate product resulted in a dimerization.[10] Subsequent addition of 0.5 equiv of $Cs^+\mathbf{1}^-$ (1.5 mg, 0.006 mmol, 0.5 equiv) caused disappearance of the signal at 77.0 ppm with concomitant formation of a new signal at 65.4 ppm. This

new species has been established as the expected palladium(II) silanolate complex **5.**

Interestingly, the chemical environments of the ^{31}P nuclei in palladium(II) bromide **4** and palladium(II) silanolate **5** were sufficiently similar to cause the coincidence of the ^{31}P resonances. This result was initially confusing because it appeared that no displacement took place even after 30 min. However, the titration study described above eliminated this possibility and allowed for the subsequent studies to be undertaken.



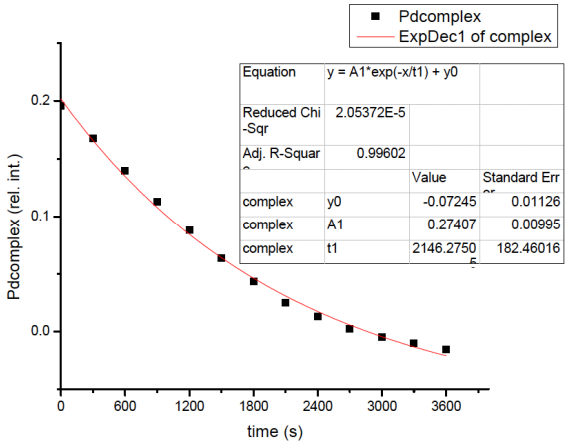
General Procedure II: Kinetic Measurements for Thermal Transmetalation at 50 °C (Scheme 2).



In a drybox, an oven-dried, 5-mm NMR tube was charged with **4** (9.4 mg, 0.0194 mmol), 1,4-difluorobenzene (1 μL) and toluene (0.4 mL) resulting in an orange solution upon vigorous mixing. Then, $Cs^{+}\mathbf{1}^{-}$ (6.0 mg, 0.0192 mmol, 0.98 equiv) was added as a solid and the sides of the tube were rinsed with toluene (0.4 mL).[11] The mixture was vigorously mixed using a vortex mixer for ca. 2 min to ensure complete dissolution. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and inserted into a preheated 50 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for ca. 90 s prior to data collection. The reaction progress was monitored by the disappearance of starting complex **5** (^{19}F NMR, -121.7 ppm) as compared to an internal reference (1,4-difluorobenzene, ^{19}F NMR, -119.8 ppm) via ^{19}F NMR spectroscopy using the following parameters: at = 0.328, d1 = 0, pw90 = 8.85, pw=pw90/2, nt=128, sampling every 300 s.[6] The rate of the reaction was determined by the slope of the 1st order decay: $\mathbf{k_{obs} = 5.37 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (25 mM)
0	0.121	0.228	25.00
300	0.149	0.203	22.25
600	0.118	0.186	20.41
900	0.103	0.158	17.29
1200	0.094	0.129	14.13
1500	0.089	0.104	11.44
1800	0.087	0.083	9.13
2100	0.081	0.063	6.94
2400	0.080	0.044	4.84
2700	0.077	0.029	3.13
3000	0.072	0.011	1.21
3300	0.072	0.001	0.13
3600	0.071	-0.011	-1.24
3900	0.071	-0.023	-2.47
4200	0.068	-0.029	-3.18

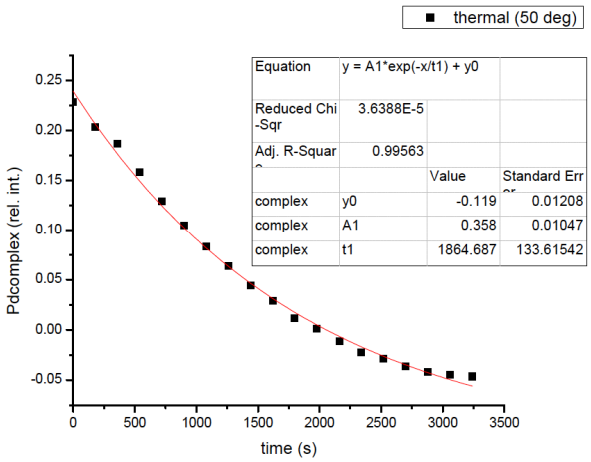
4500	0.06673	-0.03678	-0.55
4800	0.06807	-0.04211	-0.62
5100	0.06777	-0.04479	-0.66
5400	0.06577	-0.04647	-0.71



Thermal Transmetalation at 50 °C

Following General Procedure II, a mixture of **4** (9.8 mg, 0.0203 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of Cs^{+}**1**$^{-}$ (6.2 mg, 0.0199 mmol) and toluene (0.4 mL) to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy, sampling every 180 s. $\mathbf{k_{obs} = 5.37 \times 10^{-4}\ s^{-1}}$.

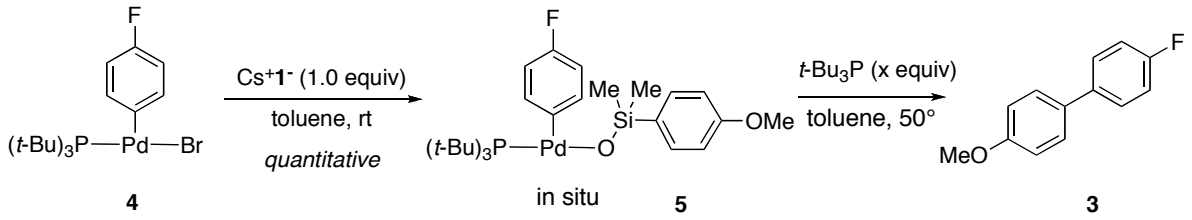
Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.133	0.196	25.40
180	0.129	0.168	21.76
360	0.110	0.139	18.09
540	0.101	0.113	14.60
720	0.098	0.088	11.39
900	0.093	0.063	8.19
1080	0.090	0.043	5.59
1260	0.089	0.025	3.22
1440	0.088	0.013	1.68
1620	0.086	0.002	0.24
1800	0.084	-0.005	-0.66
1980	0.085	-0.010	-1.35
2160	0.080	-0.016	-2.07



avg k_{obs} = 5.02 x 10^{-4} s^{-1} ± 5.0 x 10^{-5}

General Procedure III: Kinetic Measurements for Thermal Transmetalation in the Presence of Phosphine (Scheme 2).

Thermal Transmetalation in the Presence of Excess Phosphine (1.0 equiv) at 50 °C

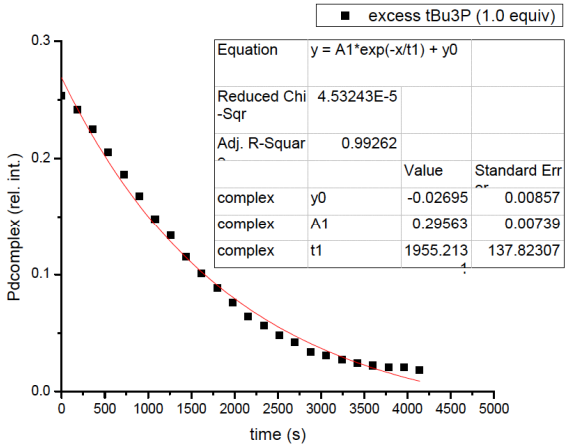


4 in situ **5** **3**

In a drybox, an oven-dried, 5-mm NMR tube was charged with **4** (9.6 mg, 0.0198 mmol), 1,4-difluorobenzene (1 μL) and toluene (0.4 mL) resulting in an orange solution upon vigorous mixing. Then, $Cs^{+}\mathbf{1}^{-}$ (6.0 mg, 0.0194 mmol, 0.98 equiv)[11] was added as a solid followed by a solution of *t*-Bu_3P (4.0 mg, 0.0198 mmol, 1.0 equiv) in toluene (0.4 mL). The mixture was vigorously mixed using a vortex mixer for ca. 2 min to ensure complete dissolution. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen and moisture. The NMR tube was removed from the drybox and inserted into a preheated 50 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for ca. 90 s prior to data collection. The reaction progress was monitored by the disappearance of starting complex **5** (^{19}F NMR, -121.7 ppm) as compared to an internal reference (1,4-difluorobenzene, ^{19}F NMR, -119.8 ppm) via ^{19}F NMR spectroscopy using the following parameters: at = 0.328, d1 = 0, pw90 = 8.85, pw=pw90/2, nt=128, sampling every 180 s.[6] The rate of the reaction was determined by the slope of the 1st order decay: $\mathbf{k_{obs} = 5.12 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.109	0.253	24.80
180	0.127	0.241	23.63
360	0.138	0.224	21.96
540	0.141	0.205	20.05
720	0.147	0.186	18.19
900	0.142	0.167	16.38
1080	0.145	0.148	14.47
1260	0.146	0.134	13.10
1440	0.146	0.115	11.29
1620	0.139	0.101	9.89

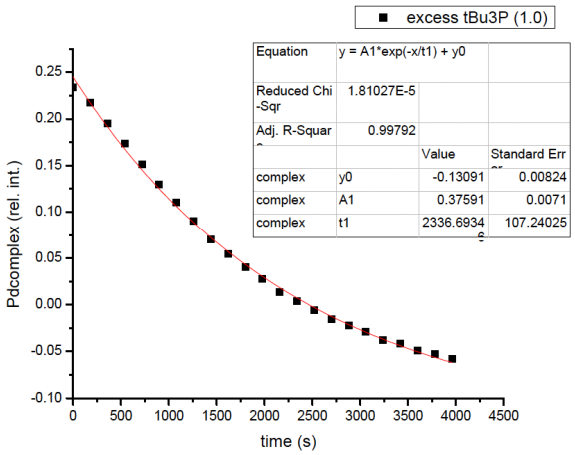
1800	0.143	0.088	8.64
1980	0.144	0.076	7.42
2160	0.139	0.064	6.24
2340	0.141	0.056	5.49
2520	0.136	0.048	4.71
2700	0.138	0.042	4.12
2880	0.136	0.034	3.30
3060	0.139	0.031	3.00
3240	0.140	0.027	2.61
3420	0.141	0.024	2.36
3600	0.135	0.022	2.15
3780	0.143	0.020	1.98
3960	0.143	0.020	2.00
4140	0.143	0.018	1.78



Thermal Transmetalation in the Presence of Phosphine (1.0 equiv) at 50 °C

Following General Procedure III, a mixture of **4** (9.8 mg, 0.0203 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of $Cs^{+}\mathbf{1}^{-}$ (6.2 mg, 0.0199 mmol, 0.98 equiv) and a solution of *t*-Bu_3P (4.1 mg, 0.0203 mmol , 1.0 equiv) in toluene (0.4 mL) to afford a yellow solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 4.28 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.109	0.234	25.40
180	0.126	0.217	23.54
360	0.136	0.195	21.15
540	0.132	0.173	18.82
720	0.129	0.151	16.43
900	0.129	0.130	14.07
1080	0.129	0.110	11.93
1260	0.124	0.090	9.74
1440	0.125	0.070	7.60
1620	0.122	0.055	5.94
1800	0.121	0.040	4.38
1980	0.120	0.027	2.98
2160	0.118	0.013	1.42
2340	0.118	0.004	0.38
2520	0.117	-0.006	-0.65
2700	0.116	-0.016	-1.69
2880	0.115	-0.022	-2.41
3060	0.115	-0.029	-3.17
3240	0.114	-0.038	-4.10
3420	0.115	-0.042	-4.52
3600	0.114	-0.049	-5.31
3780	0.111	-0.053	-5.75
3960	0.112	-0.058	-6.31
4140	0.112	-0.058	-6.30
4320	0.113	-0.060	-6.49

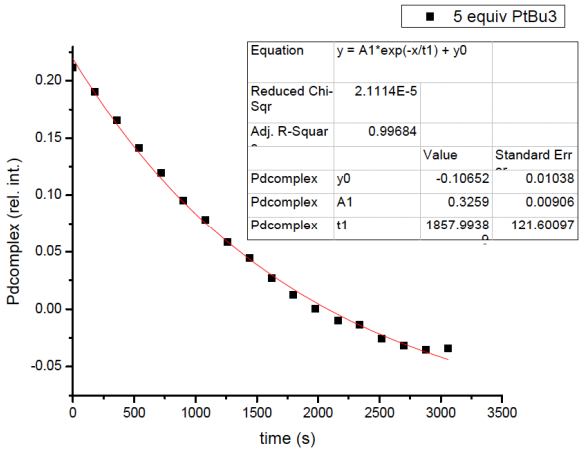


avg k_{obs} = 4.70 x 10^{-4} s^{-1} ± 5.9 x 10^{-5}

Thermal Transmetalation in the Presence of Excess Phosphine (5.0 equiv) at 50 °C

Following General Procedure III, a mixture of **4** (9.8 mg, 0.0203 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of $Cs^{+}\mathbf{1}^{-}$ (6.2 mg, 0.0199 mmol, 0.98 equiv) and a solution of *t*-Bu_3P (20.5 mg, 0.102 mmol, 5.0 equiv) in toluene (0.4 mL) to afford a yellow solution. The tube was placed into a preheated 50 °C NMR probe. The reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 5.38 \times 10^{-4}\ s^{-1}}$.

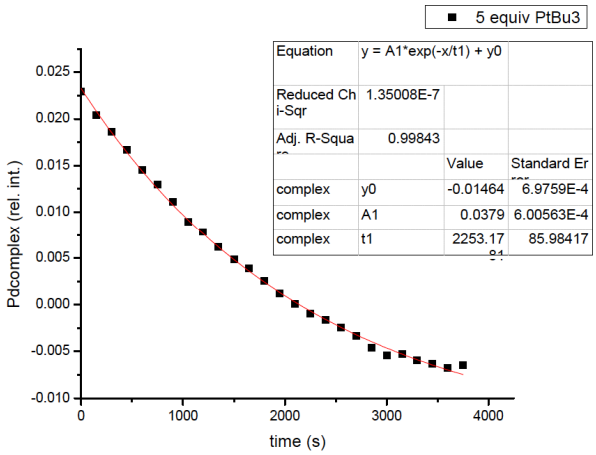
Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.108	0.212	25.40
180	0.115	0.191	22.88
360	0.105	0.166	19.89
540	0.109	0.142	17.01
720	0.109	0.119	14.26
900	0.109	0.095	11.38
1080	0.111	0.078	9.35
1260	0.106	0.058	6.95
1440	0.109	0.044	5.27
1620	0.107	0.027	3.23
1800	0.101	0.013	1.56
1980	0.102	0.001	0.12
2160	0.101	-0.01	-1.20
2340	0.104	-0.014	-1.68
2520	0.117	-0.026	-3.12
2700	0.115	-0.032	-3.83
2880	0.114	-0.035	-4.19
3060	0.105	-0.034	-4.07



Thermal Transmetalation in the Presence of Excess Phosphine (5.0 equiv) at 50 °C

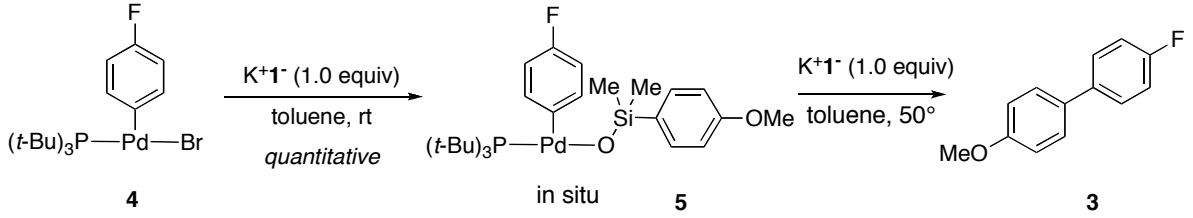
Following General Procedure III, a mixture of **4** (10.2 mg, 0.0211 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of $Cs^{+}\mathbf{1}^{-}$ (6.4 mg, 0.0206 mmol, 0.98 equiv) and a solution of *t*-Bu_3P (21.3 mg, 0.106 mmol, 5.0 equiv) in toluene (0.4 mL) to afford a yellow solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy and sampled every 150 s. $\mathbf{k_{obs} = 4.44 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.023	0.023	25.40
150	0.022	0.020	22.60
300	0.023	0.019	20.58
450	0.022	0.017	18.42
600	0.022	0.015	16.06
750	0.020	0.013	14.38
900	0.020	0.011	12.25
1050	0.020	0.009	9.92
1200	0.019	0.008	8.63
1350	0.015	0.006	6.83
1500	0.015	0.005	5.33
1650	0.015	0.004	4.26
1800	0.015	0.003	2.79
1950	0.015	0.001	1.36
2100	0.014	0.000	0.10
2250	0.014	-0.001	-1.07
2400	0.014	-0.002	-1.79
2550	0.013	-0.002	-2.67
2700	0.012	-0.003	-3.72
2850	0.019	-0.005	-5.08
3000	0.018	-0.005	-6.03
3150	0.012	-0.005	-5.83
3300	0.012	-0.006	-6.59
3450	0.012	-0.006	-7.01
3600	0.012	-0.007	-7.46
3750	0.015	-0.006	-7.15



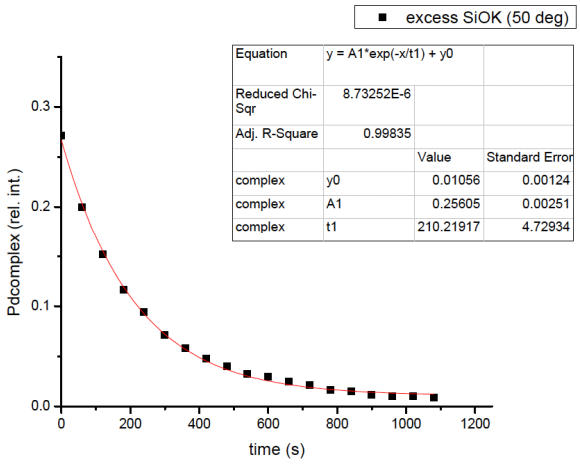
<u>avg k_{obs} = 4.91 x 10^{-4} s^{-1} ± 6.7 x 10^{-5}</u>

General Procedure IV: Kinetic Measurements for Activated Transmetalation in the Presence of $K^+\mathbf{1}^-$ at 50 °C (Scheme 2).



In a drybox, an oven-dried, 5-mm NMR tube was charged with **4** (10.0 mg, 0.0207 mmol), 1,4-difluorobenzene (1 μL) and toluene (0.3 mL) resulting in an orange solution upon vigorous mixing. Then, $K^+\mathbf{1}^-$ (4.5 mg, 0.0203 mmol, 0.98 equiv) was added as a solid followed by toluene (0.3 mL). The mixture was vigorously mixed using a vortex mixer for ca. 2 min to ensure complete dissolution. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen and moisture. A separate oven-dried, 3-mL vial was charged with an additional amount of $K^+\mathbf{1}^-$ (4.7 mg, 0.0211 mmol, 1.02 equiv) and toluene (0.2 mL) resulting in a colorless solution. The vial was sealed with a septum and wrapped with Parafilm. The NMR tube and vial were removed from the drybox. Once near the NMR probe, the silanolate solution was injected into the NMR tube using a 1-mL syringe in one portion and was vigorously mixed by shaking the NMR tube (ca. 30 s). The tube was quickly inserted into a preheated 50 °C NMR probe. The temperature of the reaction solution was allowed to equilibrate for ca. 90 s prior to data collection. The reaction progress was monitored by the disappearance of the starting complex **5** (^{19}F NMR, -121.7 ppm) as compared to an internal reference (1,4-difluorobenzene, ^{19}F NMR, -119.8 ppm) via ^{19}F NMR spectroscopy using the following parameters: at = 0.328, d1 = 0, pw90 = 8.85, pw=pw90/2, nt=128, sampling every 60 s.[6] The rate of the reaction was determined by the slope of the 1st order decay: $\mathbf{k_{obs} = 4.76 \times 10^{-3}\ s^{-1}}$.

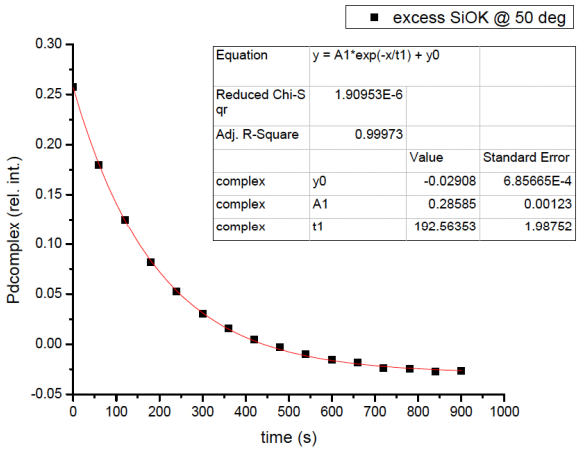
Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.109	0.271	25.80
60	0.088	0.200	19.00
120	0.084	0.152	14.46
180	0.085	0.116	11.06
240	0.089	0.094	8.93
300	0.091	0.071	6.76
360	0.091	0.058	5.51
420	0.097	0.048	4.52
480	0.102	0.040	3.80
540	0.105	0.032	3.05
600	0.105	0.029	2.79
660	0.112	0.024	2.33
720	0.112	0.021	2.02
780	0.110	0.016	1.56
840	0.116	0.015	1.42
900	0.106	0.012	1.12
960	0.106	0.010	0.97
1020	0.112	0.010	0.95



Activated Transmetalation in the Presence of $K^+\mathbf{1}^-$ (1.0 equiv) at 50 °C

Following General Procedure IV, a mixture of **4** (9.5 mg, 0.0196 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by $K^+\mathbf{1}^-$ (4.2 mg, 0.0192 mmol, 0.98 equiv). A solution of $K^+\mathbf{1}^-$ (4.4 mg, 0.0200 mmol, 0.99 equiv) in toluene (0.4 mL) was added to afford an orange solution. The tube was placed into a preheated 50 °C NMR probe and the reaction progress was monitored by ^{19}F NMR spectroscopy. **k_{obs} = 5.19 x 10^{-3} s^{-1}**.

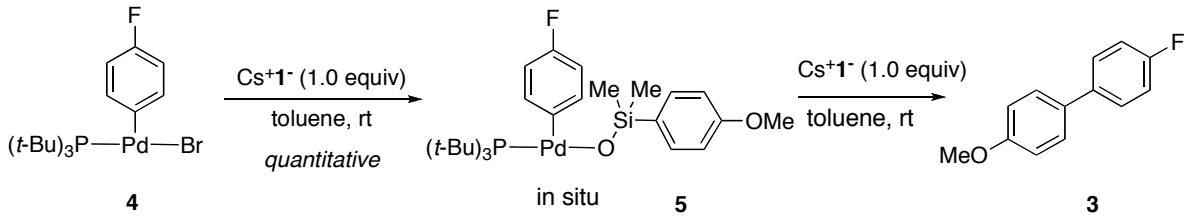
Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.104	0.258	24.50
60	0.076	0.179	17.00
120	0.078	0.125	11.87
180	0.076	0.082	7.79
240	0.078	0.052	4.94
300	0.084	0.03	2.85
360	0.084	0.015	1.42
420	0.091	0.004	0.38
480	0.095	-0.003	-0.28
540	0.099	-0.01	-0.95
600	0.097	-0.016	-1.52
660	0.101	-0.018	-1.71
720	0.102	-0.024	-2.28
780	0.102	-0.025	-2.37
840	0.101	-0.028	-2.66
900	0.102	-0.027	-2.56
960	0.096	-0.027	-2.56



<u>avg k_{obs} = 4.98 x 10^{-3} s^{-1} ± 3.0 x 10^{-4}</u>

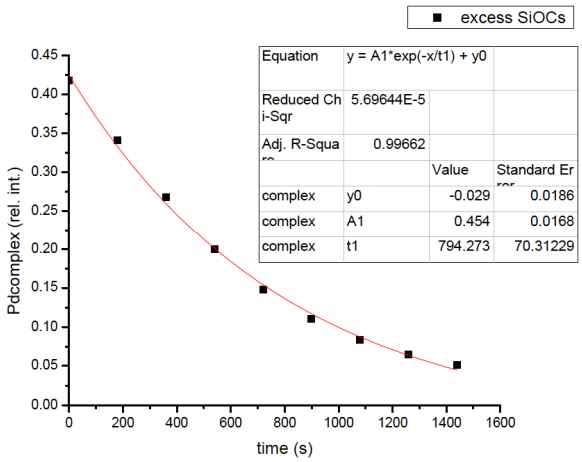
General Procedure V: Kinetic Measurements for Activated Transmetalation in Presence of M^+1^- at Room Temperature (Scheme 3).

Activated Transmetalation in the Presence of Cs^+1^- (1.0 equiv) at Room Temperature



In a drybox, an oven-dried, 5-mm NMR tube was charged with **4** (9.6 mg, 0.0198 mmol), 1,4-difluorobenzene (1 μL) and toluene (0.3 mL) resulting in an orange solution upon vigorous mixing. Then, $Cs^+\mathbf{1}^-$ (6.1 mg, 0.0194 mmol, 0.98 equiv) was added as a solid followed by toluene (0.3 mL). The mixture was vigorously mixed using a vortex mixer for ca. 2 min to ensure complete dissolution. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. A separate oven-dried, 3-mL vial was charged with an additional amount of $Cs^+\mathbf{1}^-$ (6.3 mg, 0.0202 mmol, 1.02 equiv) and toluene (0.2 mL) resulting in a colorless solution. The vial was sealed with a septum and wrapped with Parafilm. The NMR tube and vial were removed from the drybox. Once near the NMR probe, the silanolate solution was injected into the NMR tube using a 1-mL syringe in one portion and was vigorously mixed by shaking the NMR tube (ca. 30 s). The tube was quickly inserted into a NMR probe at room temperature (21.8 °C). The reaction progress was monitored by the disappearance of starting complex **5** (^{19}F NMR, -121.7 ppm) as compared to an internal reference (1,4-difluorobenzene, ^{19}F NMR, -119.8 ppm) via ^{19}F NMR spectroscopy using the following parameters: at = 0.328, d1 = 0, pw90 = 8.85, pw=pw90/2, nt=128, sampling every 180 s.[6] The rate of the reaction was determined by the slope of the 1st order decay: $\mathbf{k_{obs} = 1.26 \times 10^{-3}\ s^{-1}}$.

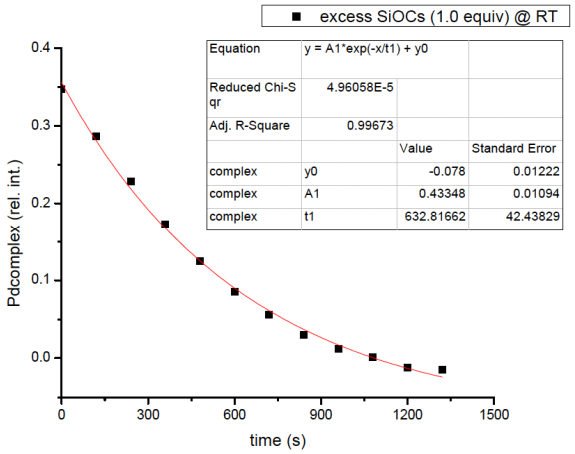
Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.24	0.417	24.80
180	0.24	0.341	20.28
360	0.237	0.268	15.94
540	0.242	0.199	11.84
720	0.24	0.148	8.80
900	0.237	0.11	6.54
1080	0.242	0.084	5.00
1260	0.239	0.065	3.87
1440	0.244	0.051	3.03



Activated Transmetalation in the Presence of $Cs^+\mathbf{1}^-$ (1.0 equiv) at Room Temperature.

Following General Procedure V, a mixture of **4** (9.8 mg, 0.0203 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of $Cs^+\mathbf{1}^-$ (6.2 mg, 0.0198 mmol, 0.98 equiv). A solution of $Cs^+\mathbf{1}^-$ (6.5 mg, 0.0207 mmol, 1.02 equiv) in toluene (0.4 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{19}F NMR spectroscopy every 120 s. $\mathbf{k_{obs} = 1.58 \times 10^{-3}\ s^{-1}}$.

Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.124	0.347	24.80
120	0.133	0.286	20.44
240	0.129	0.228	16.30
360	0.13	0.173	12.36
480	0.128	0.125	8.93
600	0.129	0.085	6.07
720	0.131	0.056	4.00
840	0.13	0.03	2.14
960	0.129	0.012	0.86
1080	0.131	0.002	0.14
1200	0.13	-0.012	-0.86
1320	0.132	-0.015	-1.07

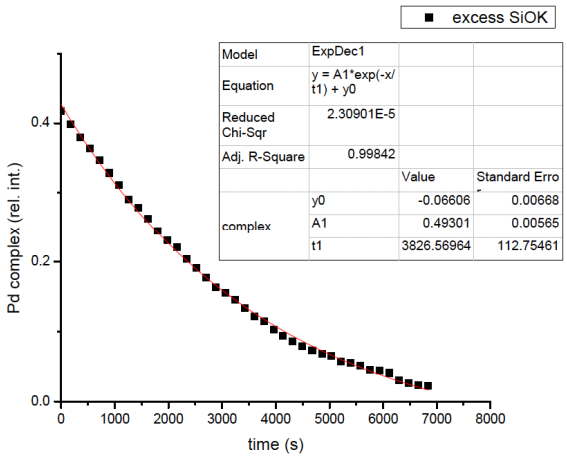


<u>avg $k_{obs} = 1.42 \times 10^{-3}\ s^{-1} \pm 2.3 \times 10^{-4}$</u>

Activated Transmetalation in the Presence of $K^+\mathbf{1}^-$ (1.0 equiv) at Room Temperature.

Following General Procedure V, a mixture of **4** (9.8 mg, 0.0203 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of $K^+\mathbf{1}^-$ (4.4 mg, 0.0199 mmol, 0.98 equiv). A solution of $K^+\mathbf{1}^-$ (4.7 mg, 0.0213 mmol, 1.02 equiv) in toluene (0.4 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{19}F NMR spectroscopy. $\mathbf{k_{obs} = 2.61 \times 10^{-4}\ s^{-1}}$.

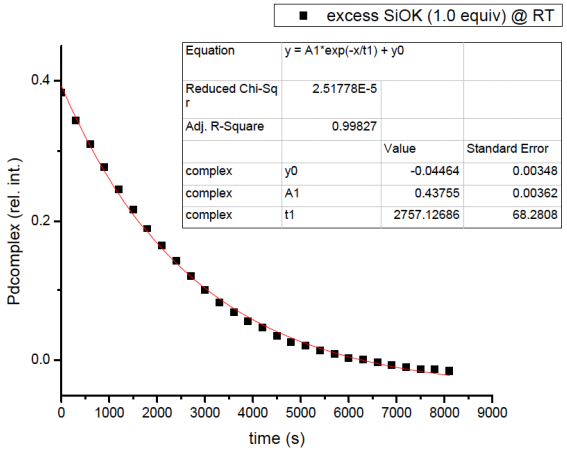
Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.178	0.417	25.40
180	0.186	0.399	24.30
360	0.189	0.38	23.15
540	0.193	0.364	22.17
720	0.192	0.347	21.14
900	0.197	0.328	19.98
1080	0.197	0.311	18.94
1260	0.2	0.291	17.73
1440	0.204	0.279	16.99
1620	0.206	0.262	15.96
1800	0.206	0.244	14.86
1980	0.209	0.231	14.07
2160	0.212	0.221	13.46
2340	0.212	0.204	12.43
2520	0.218	0.191	11.63
2700	0.224	0.177	10.78
2880	0.221	0.164	9.99
3060	0.221	0.155	9.44
3240	0.223	0.145	8.83
3420	0.224	0.134	8.16
3600	0.225	0.122	7.43
3780	0.222	0.115	7.00
3960	0.227	0.103	6.27
4140	0.233	0.094	5.73
4320	0.233	0.086	5.24
4500	0.23	0.078	4.75
4680	0.232	0.073	4.45
4860	0.232	0.068	4.14
5040	0.231	0.065	3.96
5220	0.233	0.057	3.47
5400	0.236	0.055	3.35
5580	0.237	0.051	3.11
5760	0.233	0.045	2.74
5940	0.232	0.044	2.68
6120	0.229	0.041	2.50
6300	0.242	0.03	1.83
6480	0.229	0.026	1.58
6660	0.242	0.023	1.40
6840	0.246	0.022	1.34



Activated Transmetalation in the Presence of $K^+\mathbf{1}^-$ (1.0 equiv) at Room Temperature.

Following General Procedure V, a mixture of **4** (9.8 mg, 0.0203 mmol) and 1,4-difluorobenzene (1 μL) were dissolved in toluene (0.4 mL), followed by addition of $K^+\mathbf{1}^-$ (4.3 mg, 0.0198 mmol, 0.98 equiv). A solution of $K^+\mathbf{1}^-$ (4.6 mg, 0.0207 mmol, 1.02 equiv) in toluene (0.4 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{19}F NMR spectroscopy. **k_{obs} = 3.63 x 10^{-4} s^{-1}**.

Time (s)	Integral IS (-119.8 ppm)	Integral **5** (-121.7 ppm)	Normalized (mM)
0	0.15	0.384	25.40
300	0.145	0.343	22.69
600	0.146	0.31	20.51
900	0.145	0.277	18.32
1200	0.146	0.246	16.27
1500	0.146	0.216	14.29
1800	0.148	0.189	12.50
2100	0.152	0.164	10.85
2400	0.156	0.142	9.39
2700	0.157	0.121	8.00
3000	0.158	0.1	6.61
3300	0.164	0.083	5.49
3600	0.167	0.069	4.56
3900	0.17	0.055	3.64
4200	0.174	0.047	3.11
4500	0.177	0.034	2.25
4800	0.184	0.026	1.72
5100	0.188	0.021	1.39
5400	0.194	0.014	0.93
5700	0.195	0.009	0.60
6000	0.199	0.003	0.20
6300	0.205	0.001	0.07
6600	0.207	-0.002	-0.13
6900	0.212	-0.007	-0.46
7200	0.217	-0.01	-0.66
7500	0.219	-0.013	-0.86
7800	0.223	-0.013	-0.86
8100	0.224	-0.015	-0.99



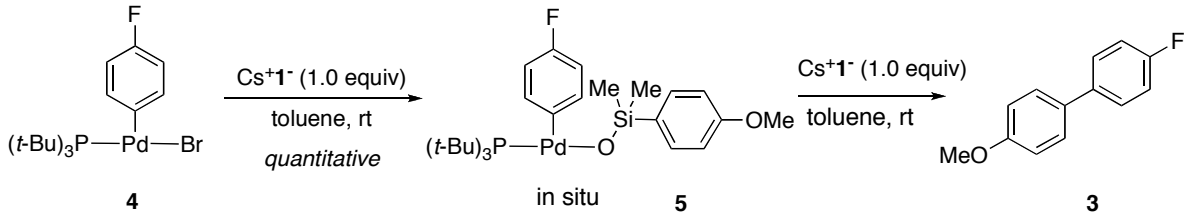
avg k_{obs} = 3.12 x 10^{-4} s^{-1} ± 7.1 x 10^{-5}

General Procedure VI: Kinetic Measurements for Activated Transmetalation in Presence of Cs^+1^- at Room Temperature: Order Determination for [Cs^+1^-] (Scheme 3).

Order in $Cs^+\mathbf{1}^-$ with **5**

5 25 mM

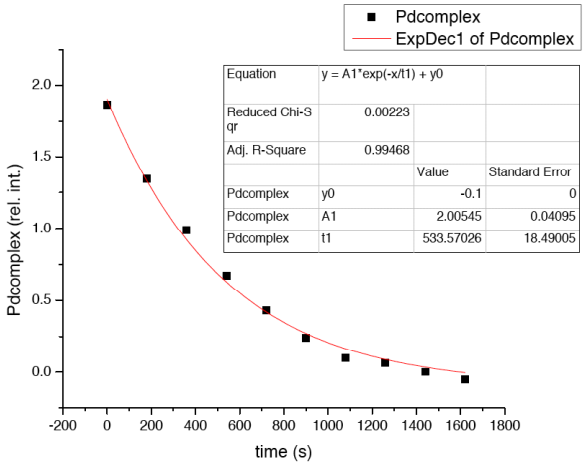
$Cs^+\mathbf{1}^-$ 25 mM



4 in situ **5** **3**

In a drybox, an oven-dried, 5-mm NMR tube was charged with **4** (9.7 mg, 0.0201 mmol), and toluene (0.3 mL) resulting in an orange solution upon vigorous mixing. Then, $Cs^+\mathbf{1}^-$ (6.0 mg, 0.0190 mmol, 0.98 equiv) was added as a solid followed by toluene (0.2 mL). The mixture was vigorously mixed using a vortex mixer for ca. 2 min to ensure complete dissolution. A capillary of $Ph_3P(O)$ in toluene (117 mM) was added and the tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. In a separate oven-dried, 3-mL vial was charged an additional amount of $Cs^+\mathbf{1}^-$ (6.6 mg, 0.0211 mmol, 1.02 equiv) and toluene (0.3 mL) resulting in a colorless solution. The vial was sealed with a septum and wrapped with Parafilm. The NMR tube and vial were removed from the drybox. Once near the NMR probe, the silanolate solution was injected into the NMR tube using a 1-mL syringe in one portion and was vigorously mixed by shaking the NMR tube (ca. 15 s). The tube was quickly inserted into a NMR probe at room temperature (21.8 °C). The reaction progress was monitored by the disappearance of starting complex **5** (^{31}P NMR, -62.4 ppm) as compared to the reference capillary ($Ph_3P(O)$, ^{31}P NMR, 21.8 ppm) via ^{31}P NMR spectroscopy using the following parameters[12]: at = 1.441, d1 = 4.0, pw90 = pw = 12.8, nt=30, sampling every 17 s.[6] The rate of the reaction was determined by the slope of the 1st order decay: $\mathbf{k_{obs} = 1.9 \times 10^{-3}\ s^{-1}}$.

Time (s)	Integral **IS** (21.8 ppm)	Integral **5** (62.4 ppm)	Normalized (mM)
0	2.95235	5.50491	25.10
180	3.07643	4.13401	18.85
360	3.19108	3.15955	14.41
540	3.05213	2.05131	9.35
720	2.99821	1.29048	5.88
900	3.26528	0.78234	3.57
1080	3.051	0.30455	1.39
1260	3.32973	0.21142	0.96
1440	3.28799	0.00641	0.03
1620	3.32771	-0.17447	-0.80



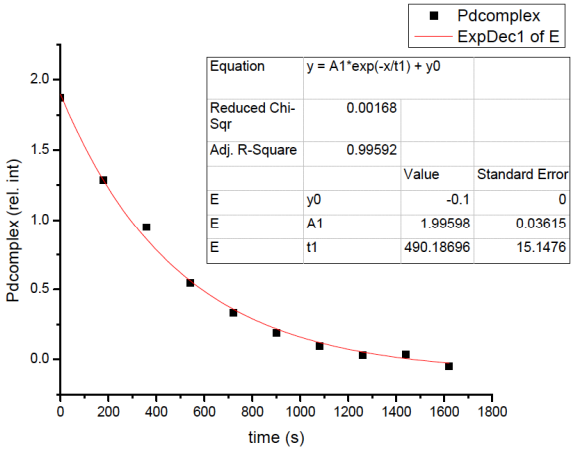
Order in $Cs^+\mathbf{1}^-$ with **5**

5 25 mM

$Cs^+\mathbf{1}^-$ 25 mM

Following General Procedure VI, a mixture of **5** (9.7 mg, 0.0201 mmol) was dissolved in toluene (0.3 mL), followed by addition $Cs^+\mathbf{1}^-$ (6.0 mg, 0.0190 mmol, 0.98 equiv) and toluene (0.2 mL) to afford an orange solution. A solution of $Cs^+\mathbf{1}^-$ (4.6 mg, 0.0207 mmol, 1.02 equiv) in toluene (0.3 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{31}P NMR spectroscopy. $\mathbf{k_{obs} = 2.0 \times 10^{-3}\ s^{-1}}$.

Time (s)	Integral IS (21.8 ppm)	Integral **5** (62.4 ppm)	Normalized (mM)
0	2.89263	5.4093	25.10
180	3.07286	3.9561	18.36
360	3.00904	2.85432	13.24
540	3.23458	1.75756	8.16
720	3.25465	1.08781	5.05
900	3.30085	0.61781	2.87
1080	3.30967	0.31303	1.45
1260	3.36175	0.10598	0.49
1440	3.2311	0.11661	0.54
1620	3.38445	-0.1632	-0.76



avg k_{obs} = 1.95 x 10^{-3} s^{-1} ± 7.1 x 10^{-5}

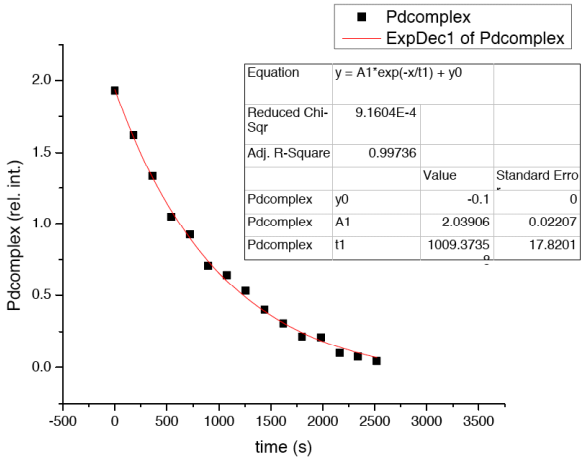
Order in $Cs^+\mathbf{1}^-$ with **5**

5 25 mM

$Cs^+\mathbf{1}^-$ 12.5 mM

Following General Procedure VI, a mixture of **5** (9.6 mg, 0.0198 mmol) was dissolved in toluene (0.3 mL), followed by addition $Cs^+\mathbf{1}^-$ (5.9 mg, 0.0189 mmol, 0.95 equiv) and toluene (0.2 mL) to afford an orange solution. A solution of $Cs^+\mathbf{1}^-$ (3.4 mg, 0.0109 mmol, 0.55 equiv) in toluene (0.3 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{31}P NMR spectroscopy. $\mathbf{k_{obs} = 9.9 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (21.8 ppm)	Integral **5** (62.4 ppm)	Normalized (mM)
0	2.409	4.650	24.80
180	2.466	3.992	21.29
360	2.506	3.341	17.82
540	2.572	2.701	14.41
720	2.585	2.387	12.73
900	2.699	1.906	10.17
1080	2.673	1.719	9.17
1260	2.734	1.450	7.73
1440	2.847	1.144	6.10
1620	2.890	0.885	4.72
1800	2.878	0.623	3.32
1980	2.743	0.578	3.08
2160	2.811	0.281	1.50
2340	2.757	0.208	1.11
2520	2.824	0.122	0.65
2700	2.884	0.119	0.64
2880	2.800	-0.013	-0.07
3060	2.836	-0.034	-0.18
3240	2.853	-0.088	-0.47
3420	2.899	-0.130	-0.69



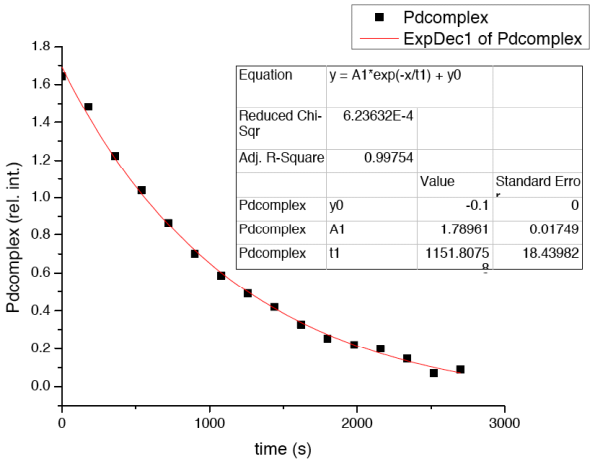
Order in $Cs^+\mathbf{1}^-$ with **5**

5 25 mM

$Cs^+\mathbf{1}^-$ 12.5 mM

Following General Procedure VI, a mixture of **5** (9.8 mg, 0.0203 mmol) was dissolved in toluene (0.3 mL), followed by addition $Cs^+\mathbf{1}^-$ (6.0mg, 0.0192 mmol, 0.95 equiv) and toluene (0.2 mL) to afford an orange solution. A solution of $Cs^+\mathbf{1}^-$ (3.5 mg, 0.0112 mmol, 0.55 equiv) in toluene (0.3 mL) was added to afford an orange solution. The tube was placed into an NMR probe at room temperature and the reaction progress was monitored by ^{31}P NMR spectroscopy. $\mathbf{k_{obs} = 8.7 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (21.8 ppm)	Integral **5** (62.4 ppm)	Normalized (mM)
0	3.06725	5.03523	25.40
180	2.90752	4.30533	21.72
360	3.01044	3.67887	18.56
540	2.95494	3.06727	15.47
720	2.9805	2.57784	13.00
900	3.03994	2.12368	10.71
1080	3.11647	1.82742	9.22
1260	3.0896	1.51888	7.66
1440	3.16933	1.32964	6.71
1620	3.26883	1.07022	5.40
1800	3.20157	0.81239	4.10
1980	3.25951	0.71964	3.63
2160	3.21656	0.63943	3.23
2340	3.24304	0.47345	2.39
2520	3.26158	0.22555	1.14
2700	3.2699	0.29468	1.49
2880	3.08359	0.11754	0.59
3060	3.18842	-0.01665	0.39
3240	3.08333	0.07665	-0.08
3420	3.22516	-0.02285	-0.12



avg k_{obs} = 9.31 x 10^{-4} s^{-1} ± 8.7 x 10^{-5}

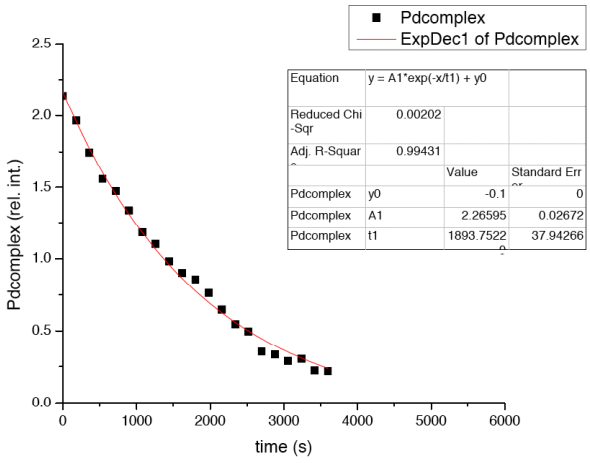
Order in $Cs^+\mathbf{1}^-$ with **5**

5 25 mM

$Cs^+\mathbf{1}^-$ 6.6 mM

Following General Procedure VI, a mixture of **5** (9.6 mg, 0.0198 mmol) was dissolved in toluene (0.3 mL), followed by addition $Cs^+\mathbf{1}^-$ (5.9 mg, 0.0189 mmol, 0.95 equiv) and toluene (0.2 mL) to afford an orange solution. A solution of $Cs^+\mathbf{1}^-$ (3.4 mg, 0.0109 mmol, 0.30) in toluene (0.3 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{31}P NMR spectroscopy. $\mathbf{k_{obs} = 5.28 \times 10^{-4}\ s^{-1}}$.

Time (s)	Integral IS (21.8 ppm)	Integral **5** (62.4 ppm)	Normalized (mM)
0	2.841	6.077	26.40
180	2.868	5.643	24.52
360	2.939	5.122	22.25
540	2.956	4.611	20.03
720	2.981	4.397	19.10
900	3.079	4.117	17.89
1080	3.251	3.843	16.69
1260	3.135	3.450	14.99
1440	3.214	3.157	13.71
1620	3.174	2.856	12.41
1800	3.141	2.696	11.71
1980	3.110	2.371	10.30
2160	3.107	2.011	8.74
2340	3.144	1.715	7.45
2520	3.059	1.513	6.57
2700	3.208	1.140	4.95
2880	3.078	1.031	4.48
3060	3.097	0.893	3.88
3240	3.036	0.924	4.01
3420	3.050	0.684	2.97
3600	3.221	0.704	3.06
3780	3.255	0.576	2.50



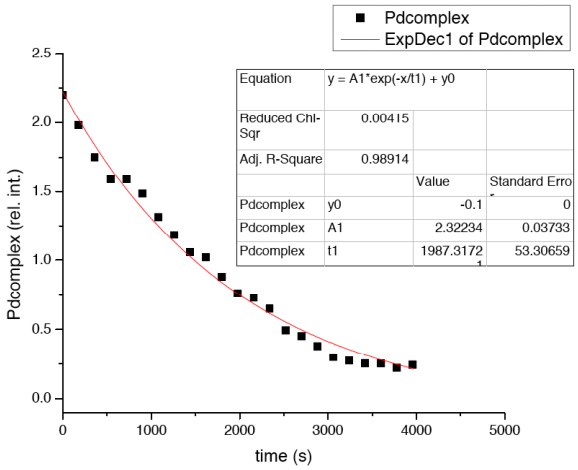
Order in $Cs^+\mathbf{1}^-$ with **5**

5 25 mM

$Cs^+\mathbf{1}^-$ 6.6 mM

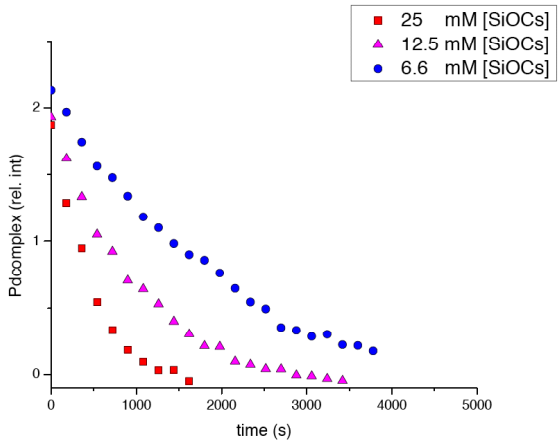
Following General Procedure VI, a mixture of **5** (9.6 mg, 0.0198 mmol) was dissolved in toluene (0.3 mL), followed by addition $Cs^+\mathbf{1}^-$ (5.9 mg, 0.0189 mmol, 0.95 equiv) and toluene (0.2 mL) to afford an orange solution. A solution of $Cs^+\mathbf{1}^-$ (3.4 mg, 0.0109 mmol, 0.30 equiv) in toluene (0.3 mL) was added to afford an orange solution. The tube was placed into a NMR probe at room temperature and the reaction progress was monitored by ^{31}P NMR spectroscopy. $\mathbf{k_{obs} = 5.0 \times 10^{-4}\ s^{-1}}$.

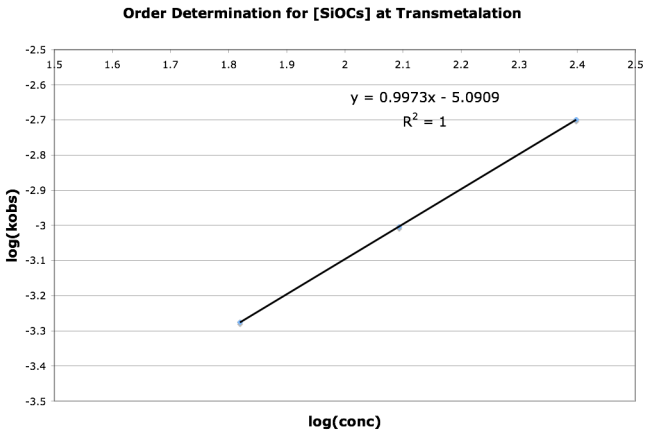
Time (s)	Integral IS (21.8 ppm)	Integral **5** (62.4 ppm)	Normalized (mm)
0	2.78717	6.13421	27.40
180	2.81319	5.57578	24.91
360	2.92143	5.11249	22.84
540	3.05343	4.86053	21.71
720	2.91124	4.62712	20.67
900	2.89273	4.30184	19.22
1080	2.99617	3.94143	17.61
1260	3.13424	3.70149	16.53
1440	3.10778	3.29032	14.70
1620	3.04095	3.10564	13.87
1800	3.11754	2.74419	12.26
1980	3.1671	2.40976	10.76
2160	2.96969	2.1593	9.65
2340	2.83896	1.83828	8.21
2520	3.13761	1.55021	6.92
2700	2.98934	1.35395	6.05
2880	3.02915	1.15125	5.14
3060	3.09039	0.91903	4.11
3240	2.95417	0.80743	3.61
3420	3.24022	0.82413	3.68
3600	3.24914	0.81552	3.64
3780	3.22024	0.71395	3.19
3960	3.29745	0.80479	3.59



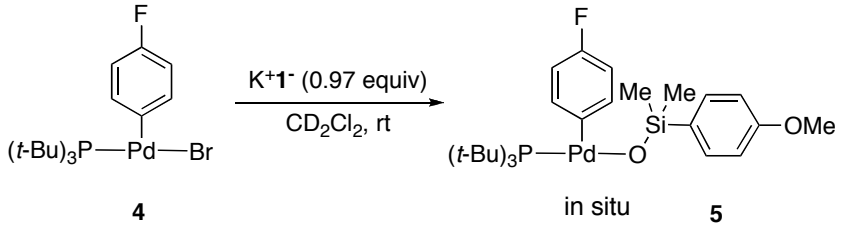
avg k_{obs} = 5.16 x 10^{-4} s^{-1} ± 1.8 x 10^{-5}

Order in [$Cs^{+}1^{-}$] for Activated Transmetalation





Spectroscopic Identification and Crystallization of Palladium(II)silanolate 5



In a drybox, an oven-dried, 3-mL vial was charged with **4** (12.2 mg, 0.0252 mmol) and toluene (0.4 mL) resulting in an orange solution upon vigorous mixing using a magnetic stir bar. Then, $K^{+}\mathbf{1}^{-}$ (5.4 mg, 0.0244 mmol, 0.97 equiv) was added as a solid and the sides of the tube were rinsed with toluene (0.4 mL).[11] The mixture was vigorously mixed (Vortex) ca. 5 min to ensure complete dissolution was observed. As the mixture stirred, a precipitate formed on the sides of the vial. The supernatant solution was transferred into an oven-dried, 5 mM NMR tube using a 25 G needle to ensure none of the precipitate was transferred. The tube was sealed with a septum and wrapped with Parafilm to exclude any oxygen or moisture. The NMR tube was removed from the drybox and placed into a CO_2/*i*-PrOH bath. The tube was then inserted into a cooled -70 °C NMR probe and the product was analyzed by NMR spectroscopy.

Data for **5**:

^{1}H NMR: (500 MHz, CD_2Cl_2)

7.51 (d, 2 H, J = 7.3 Hz), 7.07 (br m, 2 H), 6.83 (d, 2 H, J = 7.6 Hz), 6.65 (t, 2 H, J = 8.5 Hz), 3.75 (s, 3 H), 1.24 (d, 9 H, J_{PH} = 12.5 Hz), -0.16 (s, 6 H)

^{13}C NMR: (126 MHz, CD_2Cl_2)

160.2 (d, J_{CF} = 235 Hz), 159.0, 136.2, 134.4, 134.2, 126.7, 113.0 (d, J_{CF} = 19.8 Hz), 112.7, 112.3, 54.7, 39.1 (d, J_{CP} = 13 Hz), 31.0, 1.6

^{19}F NMR: (470 MHz, CD_2Cl_2)

-123.5

^{31}P NMR: (202 MHz, CD_2Cl_2)

61.4

X-ray quality crystals were obtained following an identical procedure as described above with the following modifications. After the reaction mixture was stirred for ca. 5 min, the supernatant solution was transferred to a separate oven-dried, vial using a 25 G needle to ensure none of the inorganic salts were transferred. The volatiles were removed in vacuo (2 mm Hg) to afford a brown semi-solid. The residue was dissolved in a minimal amount of pentanes (1 mL) and the vial was sealed with a cap. The vial was thoroughly wrapped in Parafilm to exclude any oxygen or moisture and the vial removed from the drybox. The vial was then placed into a fitted Styrofoam container and inserted into a –80 °C freezer.[13] Small yellow needles formed and were analyzed by X-ray diffraction.

X-Ray Crystal Structure of 5 (ba80gas)

Crystal Data and Structure Refinement for ba80gas:

Identification code	ba80gas	
Empirical formula	C_{27} H_{44} F O_2 P Pd Si	
Formula weight	585.08	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.0154(13) Å	a= 90°.
	b = 11.3144(6) Å	b= 109.649(2)°.
	c = 22.0186(11) Å	g = 90°.
Volume	5869.1(5) $Å^3$	
Z	8	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.754 mM^{-1}	
F(000)	2448	
Crystal size	0.266 x 0.14 x 0.123 mm^3	
Theta range for data collection	1.96 to 25.39°.	
Index ranges	-30<=h<=30, -13<=k<=13, -26<=l<=26	
Reflections collected	48461	
Independent reflections	5412 [R(int) = 0.0613]	
Completeness to theta = 25.39°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.9473 and 0.8649	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5412 / 0 / 310	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0281, wR2 = 0.0611	

R indices (all data)	R1 = 0.0429, wR2 = 0.0668
Largest diff. peak and hole	0.369 and -0.280 e.Å^{-3}

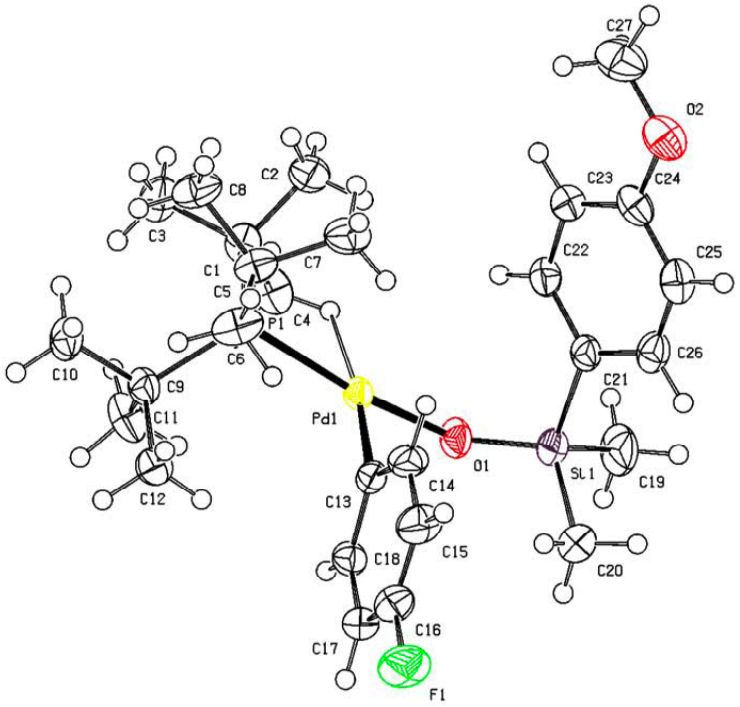


Figure 1. X-ray crystal structure of complex **5.**

The crystals were obtained directly from recrystallization (pentanes) as yellow needles 0.27 x 0.14 x 0.12 mM in size and mounted using oil (Paratone-N, Exxon) to a thin glass fiver with the (0 -1 1) scattering planes roughly normal to the spindle axis. Systematic absences for **5** were consistent with the space group C2/c. Unit cell dimensions were a = 25.0154(13) Å, b = 11.3144(6) Å, c = 22.0186(11) Å, α= 90.00°, β= 109.649(2)°, γ = 90.00°. Integration absorption correction was applied (absorption coefficient μ□= 0.754 mM^{-1}), and maximum and minimum transmission factors were 0.9473 and 0.8649. The 5412 data points were used in the full-matrix least-squares refinement. The structure was solved using direct methods by using SHELXTL software package.[14] A structural model consisting of the host molecule was developed. Methyl H atom positions, R-CH~3~, were optimized by rotation about R-C

bonds with idealized C-H, R--H and H--H distances. Remaining H atoms were included as riding idealized contributors. Methyl H atom U's were assigned as 1.5 times U~eq~ of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier U~eq~.

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ba80gas. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1128(1)	1928(1)	635(1)	27(1)
P(1)	1226(1)	3287(1)	1417(1)	26(1)
Si(1)	1429(1)	-77(1)	-269(1)	37(1)
F(1)	525(1)	-2489(2)	1831(1)	62(1)
O(1)	1069(1)	1046(2)	-181(1)	36(1)
O(2)	3919(1)	513(2)	1343(1)	47(1)
C(1)	1418(1)	4552(2)	957(1)	34(1)
C(2)	2043(1)	4482(3)	1001(1)	41(1)
C(3)	1310(1)	5809(2)	1151(2)	48(1)
C(4)	1074(1)	4339(3)	238(1)	44(1)
C(5)	1824(1)	3090(2)	2214(1)	36(1)
C(6)	1627(1)	2282(3)	2662(1)	45(1)
C(7)	2323(1)	2466(3)	2086(2)	44(1)
C(8)	2037(1)	4247(3)	2579(1)	47(1)
C(9)	539(1)	3654(2)	1567(1)	34(1)
C(10)	598(1)	4596(3)	2088(2)	48(1)
C(11)	95(1)	4065(3)	931(2)	50(1)
C(12)	292(1)	2529(3)	1764(2)	44(1)
C(13)	965(1)	528(2)	1071(1)	29(1)
C(14)	1371(1)	-118(2)	1536(2)	41(1)
C(15)	1222(1)	-1134(2)	1792(2)	48(1)
C(16)	669(1)	-1495(2)	1571(2)	42(1)
C(17)	258(1)	-910(2)	1095(1)	38(1)
C(18)	412(1)	110(2)	845(1)	32(1)
C(19)	1404(1)	-134(3)	-1129(2)	59(1)
C(20)	1164(1)	-1533(3)	-86(2)	54(1)

C(21)	2195(1)	75(2)	258(1)	32(1)
C(22)	2427(1)	1190(2)	435(1)	37(1)
C(23)	2992(1)	1391(3)	797(1)	37(1)
C(24)	3352(1)	429(3)	994(1)	35(1)
C(25)	3139(1)	-698(3)	828(1)	39(1)
C(26)	2576(1)	-868(2)	471(1)	37(1)
C(27)	4144(1)	1670(3)	1525(2)	58(1)

Table 2. Bond lengths [Å] and angles [°] for ba80gas.

Pd(1)-C(13)	1.965(3)
Pd(1)-O(1)	2.0163(17)
Pd(1)-P(1)	2.2591(7)
P(1)-C(5)	1.898(3)
P(1)-C(9)	1.902(3)
P(1)-C(1)	1.906(3)
Si(1)-O(1)	1.6063(19)
Si(1)-C(20)	1.870(3)
Si(1)-C(19)	1.875(3)
Si(1)-C(21)	1.884(3)
F(1)-C(16)	1.365(3)
O(2)-C(24)	1.370(3)
O(2)-C(27)	1.429(4)
C(1)-C(3)	1.534(4)
C(1)-C(2)	1.536(4)
C(1)-C(4)	1.547(4)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800

C(5)-C(8)	1.535(4)
C(5)-C(7)	1.540(4)
C(5)-C(6)	1.542(4)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.536(4)
C(9)-C(11)	1.537(4)
C(9)-C(12)	1.539(4)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.383(4)
C(13)-C(18)	1.387(3)
C(14)-C(15)	1.385(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.365(4)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.367(4)
C(17)-C(18)	1.387(4)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800

C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.388(4)
C(21)-C(26)	1.402(4)
C(22)-C(23)	1.389(4)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.385(4)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.382(4)
C(25)-C(26)	1.377(4)
C(25)-H(25A)	0.9500
C(26)-H(26A)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800

C(13)-Pd(1)-O(1)	94.08(9)
C(13)-Pd(1)-P(1)	99.39(7)
O(1)-Pd(1)-P(1)	166.51(6)
C(5)-P(1)-C(9)	110.02(12)
C(5)-P(1)-C(1)	108.50(12)
C(9)-P(1)-C(1)	109.44(12)
C(5)-P(1)-Pd(1)	118.29(9)
C(9)-P(1)-Pd(1)	114.15(9)
C(1)-P(1)-Pd(1)	95.08(8)
O(1)-Si(1)-C(20)	114.71(12)
O(1)-Si(1)-C(19)	108.58(13)
C(20)-Si(1)-C(19)	107.09(16)
O(1)-Si(1)-C(21)	110.38(11)
C(20)-Si(1)-C(21)	108.01(14)
C(19)-Si(1)-C(21)	107.82(13)
Si(1)-O(1)-Pd(1)	128.52(11)
C(24)-O(2)-C(27)	117.2(2)
C(3)-C(1)-C(2)	107.6(2)

C(3)-C(1)-C(4)	109.9(2)
C(2)-C(1)-C(4)	105.1(2)
C(3)-C(1)-P(1)	116.67(18)
C(2)-C(1)-P(1)	111.21(18)
C(4)-C(1)-P(1)	105.89(19)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(1)-C(4)-H(4A)	109.5
C(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(8)-C(5)-C(7)	109.0(2)
C(8)-C(5)-C(6)	107.5(2)
C(7)-C(5)-C(6)	107.4(2)
C(8)-C(5)-P(1)	114.23(19)
C(7)-C(5)-P(1)	108.71(19)
C(6)-C(5)-P(1)	109.79(19)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5

C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(11)	109.2(2)
C(10)-C(9)-C(12)	108.1(2)
C(11)-C(9)-C(12)	105.7(2)
C(10)-C(9)-P(1)	114.6(2)
C(11)-C(9)-P(1)	108.98(18)
C(12)-C(9)-P(1)	109.86(19)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(18)	118.7(2)

C(14)-C(13)-Pd(1)	124.5(2)
C(18)-C(13)-Pd(1)	116.47(19)
C(13)-C(14)-C(15)	120.6(3)
C(13)-C(14)-H(14A)	119.7
C(15)-C(14)-H(14A)	119.7
C(16)-C(15)-C(14)	118.8(3)
C(16)-C(15)-H(15A)	120.6
C(14)-C(15)-H(15A)	120.6
C(15)-C(16)-F(1)	118.5(3)
C(15)-C(16)-C(17)	122.6(3)
F(1)-C(16)-C(17)	118.9(3)
C(16)-C(17)-C(18)	118.0(3)
C(16)-C(17)-H(17A)	121.0
C(18)-C(17)-H(17A)	121.0
C(13)-C(18)-C(17)	121.2(3)
C(13)-C(18)-H(18A)	119.4
C(17)-C(18)-H(18A)	119.4
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(26)	115.1(3)
C(22)-C(21)-Si(1)	119.9(2)
C(26)-C(21)-Si(1)	124.9(2)
C(21)-C(22)-C(23)	124.0(3)
C(21)-C(22)-H(22A)	118.0
C(23)-C(22)-H(22A)	118.0
C(24)-C(23)-C(22)	118.7(3)

C(24)-C(23)-H(23A)	120.7
C(22)-C(23)-H(23A)	120.7
O(2)-C(24)-C(25)	116.5(2)
O(2)-C(24)-C(23)	124.2(3)
C(25)-C(24)-C(23)	119.4(3)
C(26)-C(25)-C(24)	120.6(3)
C(26)-C(25)-H(25A)	119.7
C(24)-C(25)-H(25A)	119.7
C(25)-C(26)-C(21)	122.3(3)
C(25)-C(26)-H(26A)	118.9
C(21)-C(26)-H(26A)	118.9
O(2)-C(27)-H(27A)	109.5
O(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ba80gas. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	26(1)	30(1)	26(1)	-4(1)	9(1)	1(1)
P(1)	30(1)	26(1)	22(1)	0(1)	11(1)	0(1)
Si(1)	37(1)	38(1)	38(1)	-13(1)	16(1)	-1(1)
F(1)	66(1)	37(1)	83(2)	15(1)	27(1)	-7(1)
O(1)	35(1)	44(1)	29(1)	-9(1)	12(1)	4(1)
O(2)	35(1)	61(1)	40(1)	8(1)	8(1)	7(1)
C(1)	45(2)	31(1)	30(2)	6(1)	19(1)	1(1)
C(2)	47(2)	39(2)	45(2)	3(1)	24(2)	-7(1)
C(3)	70(2)	31(2)	56(2)	7(1)	36(2)	2(2)
C(4)	50(2)	56(2)	31(2)	14(1)	20(1)	10(2)
C(5)	42(2)	35(2)	26(1)	2(1)	5(1)	-8(1)

C(6)	56(2)	41(2)	31(2)	7(1)	5(1)	-13(1)
C(7)	33(2)	43(2)	47(2)	6(2)	1(1)	-3(1)
C(8)	58(2)	46(2)	33(2)	-5(1)	10(2)	-19(2)
C(9)	37(2)	37(2)	35(2)	-2(1)	20(1)	1(1)
C(10)	63(2)	41(2)	56(2)	-9(2)	41(2)	-2(2)
C(11)	37(2)	66(2)	51(2)	6(2)	19(2)	15(2)
C(12)	45(2)	47(2)	48(2)	-11(2)	28(2)	-9(2)
C(13)	29(1)	27(1)	30(1)	-5(1)	9(1)	1(1)
C(14)	25(2)	33(2)	56(2)	-3(1)	2(1)	-1(1)
C(15)	43(2)	32(2)	57(2)	8(2)	3(2)	4(1)
C(16)	45(2)	29(1)	53(2)	1(1)	18(2)	-4(1)
C(17)	32(2)	36(2)	47(2)	-8(1)	14(1)	-6(1)
C(18)	27(1)	36(2)	31(2)	-3(1)	7(1)	1(1)
C(19)	58(2)	78(2)	44(2)	-25(2)	21(2)	4(2)
C(20)	48(2)	41(2)	76(2)	-18(2)	27(2)	-7(2)
C(21)	38(2)	32(1)	33(2)	-2(1)	21(1)	1(1)
C(22)	35(2)	34(2)	45(2)	-2(1)	18(1)	6(1)
C(23)	36(2)	35(2)	43(2)	-4(1)	18(1)	-2(1)
C(24)	31(2)	51(2)	25(1)	7(1)	13(1)	5(1)
C(25)	46(2)	38(2)	36(2)	9(1)	19(1)	12(1)
C(26)	51(2)	34(2)	34(2)	-1(1)	23(1)	3(1)
C(27)	39(2)	75(3)	51(2)	-1(2)	5(2)	-7(2)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for ba80gas.

	x	y	z	U(eq)
H(2A)	2108	5019	683	62
H(2B)	2133	3671	912	62
H(2C)	2287	4712	1435	62
H(3A)	1450	6384	907	72
H(3B)	1510	5921	1614	72
H(3C)	902	5925	1057	72

H(4A)	1148	4982	-22	66
H(4B)	668	4316	179	66
H(4C)	1188	3585	100	66
H(6A)	1951	2096	3048	68
H(6B)	1470	1549	2434	68
H(6C)	1334	2688	2787	68
H(7A)	2578	2128	2490	66
H(7B)	2532	3039	1918	66
H(7C)	2177	1834	1769	66
H(8A)	2329	4071	2994	70
H(8B)	1719	4658	2653	70
H(8C)	2198	4752	2322	70
H(10A)	221	4805	2099	72
H(10B)	780	5302	1988	72
H(10C)	830	4284	2509	72
H(11A)	-276	4137	988	75
H(11B)	70	3485	592	75
H(11C)	207	4833	808	75
H(12A)	-71	2716	1820	66
H(12B)	558	2226	2170	66
H(12C)	232	1929	1427	66
H(14A)	1755	137	1681	49
H(15A)	1500	-1571	2116	57
H(17A)	-121	-1192	941	46
H(18A)	133	530	514	38
H(19A)	1562	598	-1235	89
H(19B)	1009	-220	-1413	89
H(19C)	1627	-809	-1188	89
H(20A)	1176	-1542	364	80
H(20B)	1405	-2169	-153	80
H(20C)	772	-1653	-372	80
H(22A)	2184	1855	302	44
H(23A)	3130	2172	906	44
H(25A)	3384	-1361	962	46
H(26A)	2440	-1652	364	45
H(27A)	4554	1616	1754	86

H(27B)	3959	2031	1807	86
H(27C)	4074	2157	1137	86

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(5) The time for temperature equilibration was independently confirmed by determining the time for 1 mL of ethylene glycol to reach a temperature that fluctuated by less than 0.2 °C.

(6) The reaction progress was monitored through > 3 half lives to ensure consistency throughout the course of the reaction.

(7) The initial data points were normalized to the starting concentration of aryl halide. No product formation was observed at T = 0 min.

(8) The arylsilanolate $K^+\mathbf{1}^-$ proved to be insoluble at concentrations > 150 mM at room temperature. However independent studies showed that the silanolate was completely soluble up to a concentration of 600 mM at 90 °C.

(9) The reaction progress was monitored through > 3 half lives to ensure consistency throughout the course of the reaction.

(10) The presence of this species must be negligible under all conditions reported because an excess of silanolate is always present. Thus, this species is of no consequence.

(11) The cesium salt $Cs^{+}\mathbf{1}^{-}$ was used in place of the potassium salt in a few examples because of its greater solubility in toluene for the in situ generation of **4**. Control studies showed no difference in rate when using the different salts for the thermal transmetalation examples.

(12) For technical reasons, these experiments were conducted using ^{31}P NMR spectroscopy. However, the rate constants obtained from experiments using both the ^{19}F and ^{31}P nuclei were in good agreement.

(13) We acknowledge Prof. P. Hergenrother (University of Illinois Urbana-Champaign) for the use of his -80 °C freezer.

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