Table S1.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10a	C_6D_6	20	0.247	0.052	10
10b	C_6D_6	20	0.242	0.051	7.0
10c	C_6D_6	20	0.242	0.049	5.5
10c	C_6H_6	20	0.242	0.050	10
10d	C_6D_6	20	0.249	0.05	2.1
10d	C_6H_6	20	0.245	0.05	4.6
10e	C_6D_6	20	0.247	0.049	0.94
10e	C_6H_6	20	0.242	0.048	2.1

Table S2.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10a	C_6D_6	20	1.31	0.70	6.1
10b	C_6D_6	20	1.31	0.70	4.55
10c	C_6D_6	20	1.31	0.70	2.2
10d	C_6D_6	20	1.31	0.70	0.74

Table S3.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
11a	C_6D_6	35	1.50	0.194	3.4
11a	C_6H_6	35	1.50	0.194	3.8
11b	C_6D_6	35	1.43	0.183	2.6
11b	C_6H_6	35	1.51	0.195	2.75
11c	C_6D_6	35	1.51	0.194	1.6
11c	C_6H_6	35	1.51	0.194	1.8

Table S4.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
12a	C_6D_6	20	0.484	0.0475	1.6
12a	C_6H_6	20	0.481	0.0475	8.0
12a	C_6H_6	20	0.255	0.051	4.1
12b	C_6D_6	20	0.484	0.0475	1.04
12b	C_6H_6	20	0.48	0.047	3.7
12b	C_6H_6	20	0.245	0.049	1.8
12c	C_6D_6	20			
12c	C_6H_6	20			

Table S5.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10a	C_6D_6	20	0.247	1.31	1.78
10a	C_6D_6	20	0.40	1.27	2.6
10a	C_6D_6	20	0.555	1.26	3.3
10a	C_6D_6	20	0.70	1.233	3.86
10a	C_6H_6	20	0.252	1.33	0.87
10a	C_6H_6	20	0.395	1.245	1.29
10a	C_6H_6	20	0.559	1.257	1.9
10a	C_6H_6	20	0.706	1.233	2.35

Table S6.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10a	C_6D_6	20	0.247	0.052	10
10a	C_6D_6	20	0.252	0.35	2.95
10a	C_6D_6	20	0.252	0.68	1.73
10a	C_6D_6	20	0.252	1.33	0.87
10a	C_6H_6	20	0.25	0.35	6.45
10a	C_6H_6	20	0.254	0.68	3.0
10a	C_6H_6	20	0.247	1.31	1.78
10a	C_6H_6	20	0.23	1.94	1.2
10a	C_6H_6	20	0.23	2.66	0.88

Table S7.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10b	C_6D_6	20	0.247	0.027	7.5
10b	C_6D_6	20	0.242	0.051	7.0
10b	C_6D_6	20	0.247	0.164	3.85
10b	C_6D_6	20	0.263	0.361	1.86
10b	C_6H_6	20	0.27	0.072	15.0
10b	C_6H_6	20	0.255	0.22	6.2
10b	C_6H_6	20	0.240	0.365	3.95
10b	C_6H_6	20	0.255	0.683	2.4

Table S8.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
12a	C_6H_6	20	0.255	0.051	4.1
12a	C_6H_6	20	0.255	0.094	1.56
12a	C_6H_6	20	0.261	0.134	2.37

Table S9.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10b	C_9D_{12}	20	0.31	0.05	3.2
10b	C_9D_{12}	20	0.305	0.13	1.7
10b	C_9D_{12}	20	0.31	0.21	1.1
10b	C_9H_{12}	20	0.31	0.05	4.3
10b	C_9H_{12}	20	0.31	0.13	2.04
10b	C_9H_{12}	20	0.315	0.21	1.4
10b	C_8H_{10}	20	0.304	0.214	4.6
10b	C_9H_{12}	20	0.29	0.207	6.9

* C_9D_{12} = (mesitylene-d_{12}), C_9H_{12} = (mesitylene-d_0),C_8D_{10} = (*p*-xylene-d_{10}), C_8H_{10} = (*p*-xylene-d_0)

Table S10.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10b	C_6H_6	0	0.735	0.372	1.1
10b	C_6H_6	0	0.735	0.212	1.8
10b	C_6H_6	10	0.706	0.358	2.95
10b	C_6H_6	20	0.247	0.315	4.5
10b	C_6H_6	30	0.240	0.642	7.5
10b	C_6H_6	40	0.238	2.014	7.6
10b	C_6H_6	50	0.160	4.0	7.4
10b	C_6H_6	55	0.156	3.93	11.0

Table S11.

Pt Complex	Substrate	T (°C)	[substrate](*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10b	C_6D_6	0	0.734	0.369	0.42
10b	C_6D_6	10	0.713	0.358	1.44
10b	C_6D_6	20	0.263	0.361	1.86
10b	C_6D_6	30	0.247	0.372	6.3

Table S12.

Pt Complex	RH	T (°C)	[RH] (*M*)	[OTf$^-$] (*M*)	[H_2O] (*M*)	k_{obs} ($\times 10^4$)
10b	C_6H_6	20	0.24	0	0.366	3.95
10b	C_6H_6	20	0.244	0.0672	0.372	3.83
10b	C_6H_6	20	0.238	0.113	0.362	3.66
10b	C_6H_6	20	0.240	0.190	0.365	5.2
10b	C_6H_6	20	0.240	0.190	0.365	3.9

Summary of acetonitrile exchange data

Table S13.

Pt Complex	Solvent	T (°C)	[CD_3CN] (*M*)	k_{ex} ($\times 10^4$)
13b	TFE-d_3	40	0.43	0.79
13b	TFE-d_3	40	0.84	1.94
13b	TFE-d_3	40	1.36	3.42
13b	TFE-d_3	40	1.96	4.99
13d	TFE-d_3	30	0.41	3.4

Table S14.

Pt Complex	Solvent	T (°C)	[CD_3CN] (*M*)	k_{ex} ($\times 10^4$)
13b	CD_3OD	40	0.15	8.2
13b	CD_3OD	40	0.29	9.5
13b	CD_3OD	40	0.55	10.4
13b	CD_3OD	40	1.35	13.3

Table S15.

Pt Complex	Solvent	T (°C)	[CD_3CN] (M)	k_{ex} ($\times 10^4$)
13b	CD_3OD	30	0.15	2.7
13b	CD_3OD	30	0.26	3.4
13b	CD_3OD	30	0.84	4.5
13b	CD_3OD	30	1.43	5.5
13b	CD_3OD	30	1.96	6.5
13d	CD_3OD	30	0.26	1.2
13d	CD_3OD	30	0.58	1.4
13d	CD_3OD	30	0.82	1.64

Table S16.

Pt Complex	Solvent	T (°C)	[CD_3CN] (M)	k_{ex} ($\times 10^4$)
13b	CD_3OD	20	0.15	0.95
13b	CD_3OD	20	0.27	1.22
13b	CD_3OD	20	0.42	1.35
13b	CD_3OD	20	0.85	1.51
13b	CD_3OD	20	1.37	1.71

Table S17.

Pt Complex	Solvent	T (°C)	[CD_3CN] (M)	k_{ex} ($\times 10^4$)
13b	$(CD_3)_2CDOD$	40	0.067	3.3
13b	$(CD_3)_2CDOD$	40	0.127	4.8
13b	$(CD_3)_2CDOD$	40	0.26	6.04
13b	$(CD_3)_2CDOD$	40	0.56	9.1
13b	$(CD_3)_2CDOD$	40	0.89	11.5
13b	$(CD_3)_2CDOD$	40	1.29	15.0

Table S18.

Pt Complex	Solvent	T (°C)	[CD_3CN] (*M*)	k_{ex} ($\times 10^4$)
13b	CD_3CD_2OD	40	0.137	7.05
13b	CD_3CD_2OD	40	0.254	8.2
13b	CD_3CD_2OD	40	0.494	9.04
13b	CD_3CD_2OD	40	0.905	11.7
13b	CD_3CD_2OD	40	1.40	14.0

Table S19.

Pt Complex	Solvent	T (°C)	[CD_3CN] (*M*)	k_{ex} ($\times 10^4$)
13b	CD_3CD_2OD	30	0.15	2.8
13b	CD_3CD_2OD	30	0.29	3.1
13b	CD_3CD_2OD	30	0.81	4.4
13b	CD_3CD_2OD	30	1.34	5.5
13b	CD_3CD_2OD	30	1.90	6.6

Table S20.

Pt Complex	Solvent	T (°C)	[CD_3CN] (M)	k_{ex} ($\times 10^4$)
14b	TFE-d_3	40	0.41	0.88
14b	TFE-d_3	40	0.834	2.1
14b	TFE-d_3	40	1.36	3.5
14c	TFE-d_3	40	0.40	2.74
14c	TFE-d_3	40	0.76	6.2
14c	TFE-d_3	40	1.27	11.6

Table S21.

Pt Complex	Solvent	T (°C)	[CD_3CN] (M)	k_{ex} ($\times 10^4$)
14b	CD_3OD	30	0.263	3.1
14b	CD_3OD	30	0.775	4.1
14b	CD_3OD	30	1.29	4.9
14c	CD_3OD	30	0.27	7.44
14c	CD_3OD	30	0.775	9.85
14c	CD_3OD	30	1.27	12.0

Derivation of Rate Law in Scheme 11.

Define $[Pt]_T = [\mathbf{A}i] + [\mathbf{A}ii]$

$$K_{eq} = \frac{[\mathbf{A}i][TFE]}{[\mathbf{A}ii][H_2O]}$$

Then $[Pt]_T = [\mathbf{A}i]\left[1 + \frac{K_{eq}[H_2O]}{[TFE]}\right]$; $[\mathbf{A}i] = \frac{[Pt]_T}{1 + \frac{K_{eq}[H_2O]}{[TFE]}}$

$$-\frac{d[Pt]_T}{dt} = k_2[\mathbf{B}]$$

Applying the steady-state approximation on [**B**]:

$$\frac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}i][C_6H_6] - k_{-1}[\mathbf{B}][TFE] - k_2[\mathbf{B}] \equiv 0$$

$$[\mathbf{B}] = \frac{k_1[\mathbf{A}i][C_6H_6]}{-k_{-1}[TFE] + k_2}$$

$$-\frac{d[Pt]_T}{dt} = k_2 \cdot \frac{k_1[C_6H_6]}{k_{-1}[TFE] + k_2} \cdot \frac{[Pt]_T}{1 + \frac{K_{eq}[H_2O]}{[TFE]}}$$

$$= \frac{k_2}{k_{-1}[TFE] + k_2} \cdot \frac{k_1[TFE][C_6H_6][Pt]_T}{[TFE] + K_{eq}[H_2O]}$$