

Supporting Information for

Intrinsic reactivity of $[\eta^5\text{-}1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3]_2\text{U}(\eta^4\text{-C}_4\text{Ph}_2)$
in small molecule activation

Shichun Wang,^a Yi Heng,^a Tongyu Li,^a Dongwei Wang,^a Guohua Hou,^a Guofu Zi,^{*a} and Marc D.

Walter^{*b}

^aDepartment of Chemistry, Beijing Normal University, Beijing 100875, China

^bInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30,
38106 Braunschweig, Germany

Table of contents

1. Figures	S2
2. Crystallographic details	S4

1. Figures

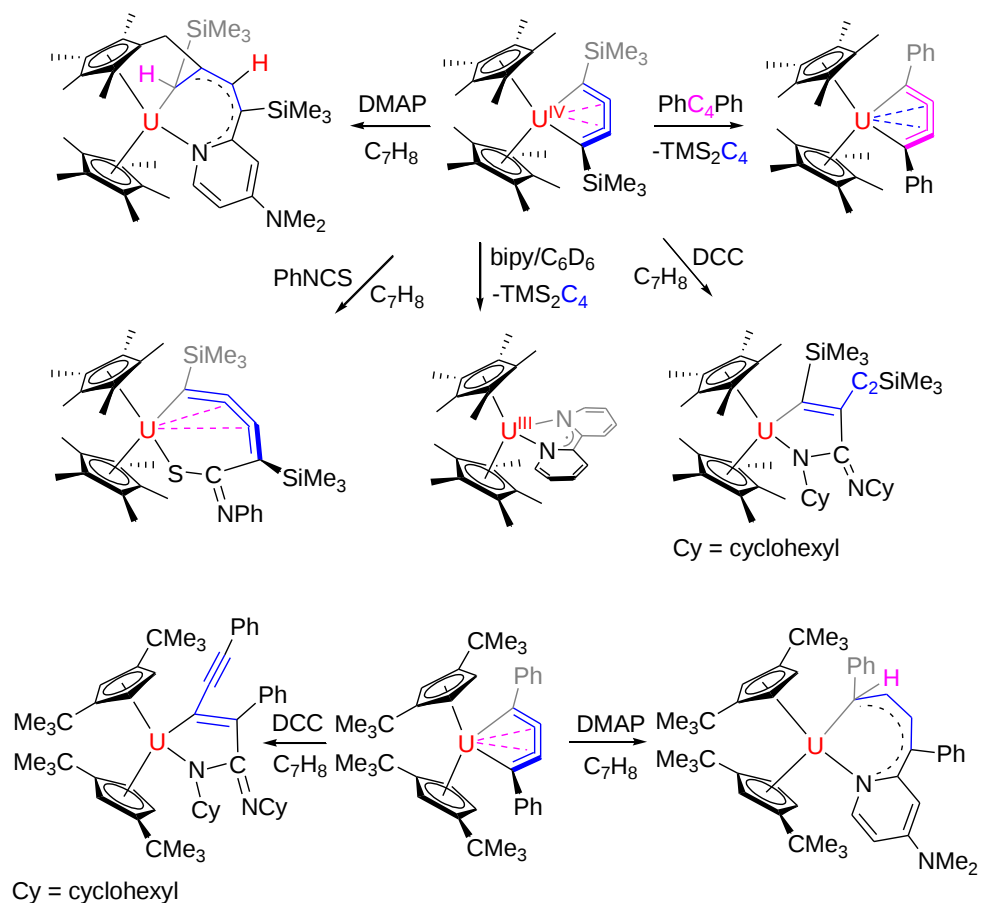


Figure S1. Selected examples concerning the reactivity of uranium metallacyclopentatrienes.

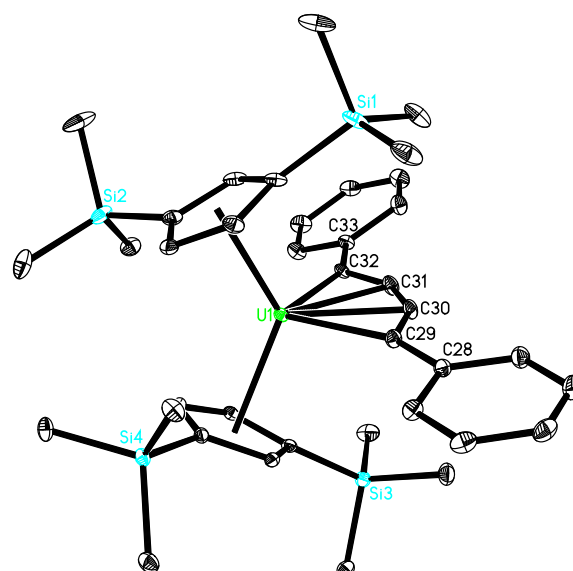


Figure S2. Molecular structure of $[\eta^5\text{-}1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3]_2\text{U}[\eta^4\text{-C}_4\text{Ph}_2]$ (**3**) (thermal ellipsoids drawn at the 35% probability level). Selected Distances (Å) and Angles (°): C(Cp)-U(average) 2.739(5), C(Cp)-U(range) 2.707(4) to 2.761(5), Cp(cent)-U(average) 2.458(5), U-C(29) 2.443(5), U-C(30) 2.447(5), U-C(31) 2.458(5), U-C(32) 2.469(5), C(29)-C(30) 1.316(7), C(30)-C(31) 1.303(7), C(31)-C(32) 1.313(7) Å, C(28)-C(29)-C(30) 129.6(5), C(33)-C(32)-C(31) 130.3(4)°, C(29)-C(30)-C(31) 149.2(5), C(32)-C(31)-C(30) 149.1(5)°, Cp(cent)-U-Cp(cent) 128.0(2), C(29)-U(1)-C(32) 92.9(2).

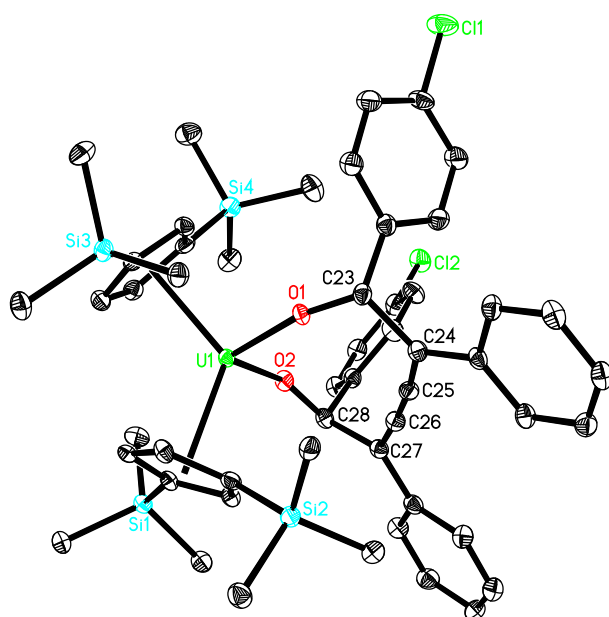


Figure S3. Molecular structure of **12** (thermal ellipsoids drawn at the 35% probability level).

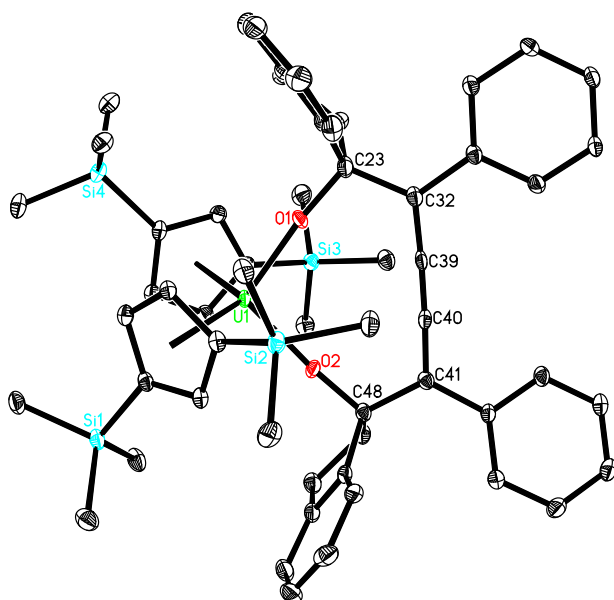


Figure S4. Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

2. Crystallographic details

Table S1. Crystal Data and Experimental Parameters for Compounds 4 and 7-10

Compound	4	7	8	9	10 C ₆ H ₆
Formula	C ₄₄ H ₆₈ Si ₆ U	C ₂₂ H ₄₂ N ₆ Si ₄ U	C ₄₅ H ₅₇ NSSi ₄ U	C ₅₁ H ₇₄ N ₂ Si ₄ U	C ₅₁ H ₆₈ N ₂ Si ₄ U
Fw	1003.55	741.00	994.36	1065.51	1059.46
crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.144(1)	12.795(2)	11.843(1)	21.505(1)	11.130(1)
<i>b</i> (Å)	12.586(1)	13.863(1)	13.547(1)	11.612(1)	11.563(1)
<i>c</i> (Å)	18.745(1)	17.783(1)	14.926(1)	20.710(1)	20.554(1)
α (deg)	99.81(1)	90	85.26(1)	90	93.07(1)
β (deg)	99.48(1)	93.54(1)	87.95(1)	91.07(1)	92.35(1)
γ (deg)	117.24(1)	90	74.72(1)	90	108.28(1)
<i>V</i> (Å ³)	2411.82(10)	3148.35(10)	2301.82(6)	5170.82(14)	2503.37(10)
<i>Z</i>	2	4	2	4	2
<i>D</i> _{calc} (g/cm ³)	1.382	1.563	1.435	1.369	1.406
μ (Mo/K α) _{calc} (cm ⁻¹)	11.097	16.126	11.565	9.968	10.295
size (mm)	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.08	0.10 × 0.10 × 0.10
<i>F</i> (000)	1016	1456	996	2168	1072
2 θ range (deg)	8.23 to 144.21	8.09 to 151.06	5.94 to 151.30	8.22 to 151.84	8.07 to 153.17
no. of reflns, collected	17242	19935	26302	33150	34664
no of obsd reflns	9229	6271	9180	10343	10052
no of variables	478	310	481	535	537
abscorr (<i>T</i> _{max} , <i>T</i> _{min})	1.00, 0.48	1.00, 0.52	1.00, 0.74	1.00, 0.64	1.00, 0.73
<i>R</i>	0.023	0.022	0.029	0.027	0.040
<i>R</i> _w	0.057	0.057	0.076	0.073	0.100
<i>R</i> _{all}	0.024	0.026	0.033	0.031	0.044
Gof	1.05	1.06	1.12	1.11	1.08
CCDC	2172353	2172344	2172352	2172346	2172354

Table S2. Crystal Data and Experimental Parameters for Compounds 11-14

Compound	11	12 0.5C ₆ H ₆	13 1.5C ₆ H ₆	14 2C ₆ H ₆
Formula	C ₅₄ H ₆₈ O ₂ Si ₄ U	C ₅₅ H ₆₅ Cl ₂ O ₂ Si ₄ U	C ₆₅ H ₇₇ O ₂ Si ₄ U	C ₇₆ H ₈₄ S ₂ Si ₄ U
Fw	1099.47	1179.36	1240.65	1411.94
crystal system	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.851(1)	11.982(1)	12.057(1)	12.501(1)
<i>b</i> (Å)	12.108(1)	12.006(1)	13.042(1)	14.176(1)
<i>c</i> (Å)	19.790(1)	21.403(1)	19.963(1)	19.806(1)
α (deg)	76.93(1)	105.43(1)	79.56(1)	86.34(1)
β (deg)	89.40(1)	93.62(1)	75.38(1)	88.71(1)
γ (deg)	68.02(1)	111.74(1)	81.03(1)	78.20(1)
<i>V</i> (Å ³)	2556.37(8)	2711.53(12)	2967.00(6)	3428.45(13)
<i>Z</i>	2	2	2	2
<i>D</i> _{calc} (g/cm ³)	1.428	1.444	1.389	1.368
μ (Mo/K α) _{calc} (cm ⁻¹)	10.123	10.470	8.789	8.208
size (mm)	0.20 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.05 × 0.05
<i>F</i> (000)	1112	1186	1262	1440
2 θ range (deg)	4.60 to 151.33	4.35 to 151.96	4.63 to 151.97	7.22 to 153.09
no. of reflns, collected	30586	32805	34843	49912
no of obsd reflns	10212	10799	11867	13809
no of variables	564	589	661	761
abscorr (<i>T</i> _{max} , <i>T</i> _{min})	1.00, 0.65	1.00, 0.35	1.00, 0.55	1.00, 0.61
<i>R</i>	0.061	0.037	0.039	0.042
<i>R</i> _w	0.160	0.100	0.092	0.107
<i>R</i> _{all}	0.064	0.042	0.046	0.046
Gof	1.09	1.13	1.02	1.11
CCDC	2172348	2172345	2172356	2172351

Table S3. Crystal Data and Experimental Parameters for Compounds 15-18

Compound	15 0.5C ₆ H ₆	16 C ₆ H ₆	17	18
Formula	C ₅₄ H ₇₆ NSSi ₆ U	C ₆₆ H ₉₀ O ₂ Si ₆ U	C ₅₇ H ₇₈ Osi ₆ U	C ₅₈ H ₇₈ N ₂ Si ₆ U
Fw	1177.78	1321.94	1185.76	1209.79
crystal system	triclinic	triclinic	orthorhombic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.689(1)	11.570(1)	13.372(1)	11.677(1)
<i>b</i> (Å)	12.062(1)	12.206(1)	15.318(1)	12.141(1)
<i>c</i> (Å)	23.104(1)	23.538(1)	28.483(1)	22.311(1)
α (deg)	87.66(1)	90.26(1)	90	97.36(1)
β (deg)	80.07(1)	102.48(1)	90	98.38(1)
γ (deg)	64.87(1)	90.68(1)	90	106.98(1)
<i>V</i> (Å ³)	2903.27(14)	3245.2(2)	5834.11(18)	2943.93(8)
<i>Z</i>	2	2	4	2
<i>D</i> _{calc} (g/cm ³)	1.347	1.353	1.350	1.365
μ (Mo/K α) _{calc} (cm ⁻¹)	9.635	8.408	9.276	9.201
size (mm)	0.10 × 0.10 × 0.10	0.15 × 0.15 × 0.15	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.20
<i>F</i> (000)	1198	1356	2416	1232
2 θ range (deg)	7.77 to 153.49	7.24 to 153.45	6.21 to 152.99	7.74 to 151.72
no. of reflns, collected	38484	42946	23646	34975
no of obsd reflns	11710	13023	10877	11780
no of variables	586	696	604	610
abscorr (<i>T</i> _{max} , <i>T</i> _{min})	1.00, 0.83	1.00, 0.51	1.00, 0.88	1.00, 0.45
<i>R</i>	0.050	0.066	0.039	0.064
<i>R</i> _w	0.130	0.169	0.100	0.183
<i>R</i> _{all}	0.054	0.073	0.044	0.073
Gof	1.09	1.07	1.09	1.04
CCDC	2172347	2172349	2172355	2172350