Electronic Supporting Information for

Synthesis and Reactivity of the Uranium Phosphinidene Metallocene [η^5-1,3-$(Me_3Si)_2C_5H_3]_2U$(=P-2,4,6-$^i Pr_3C_6H_2$)($OPMe_3$): Influence of the Coordinated Lewis Base

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Table of contents

1. Figures

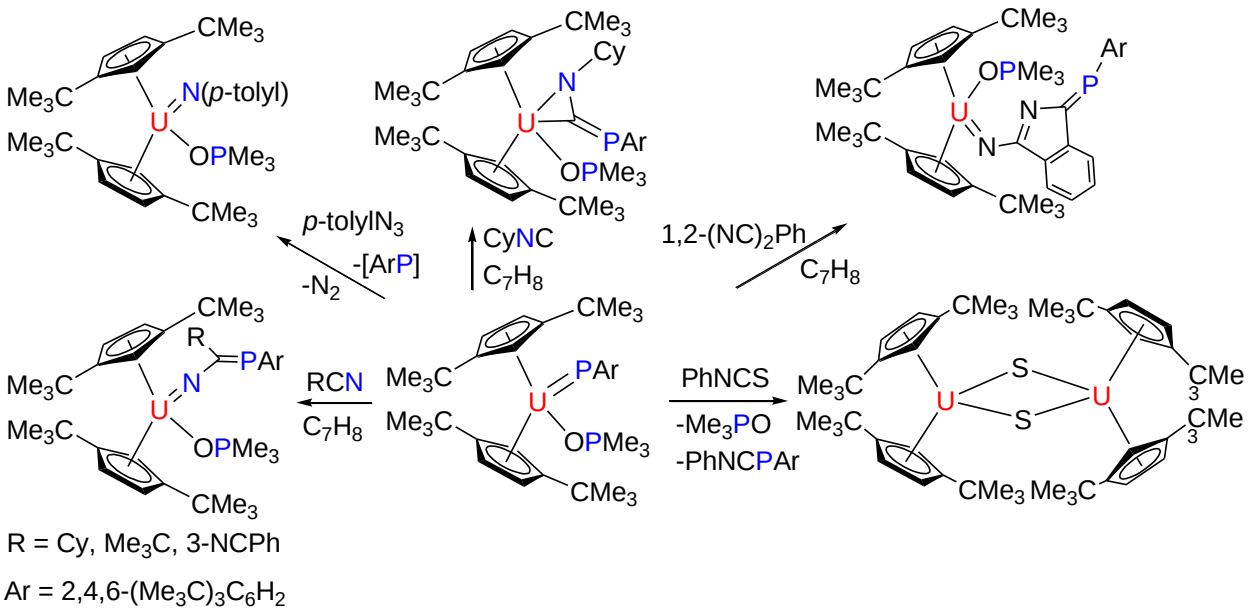

Figure S1. Selected reactivity of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$U(=P-2,4,6-^{t}Bu$_3$C$_6$H$_2$)(OPMe$_3$).

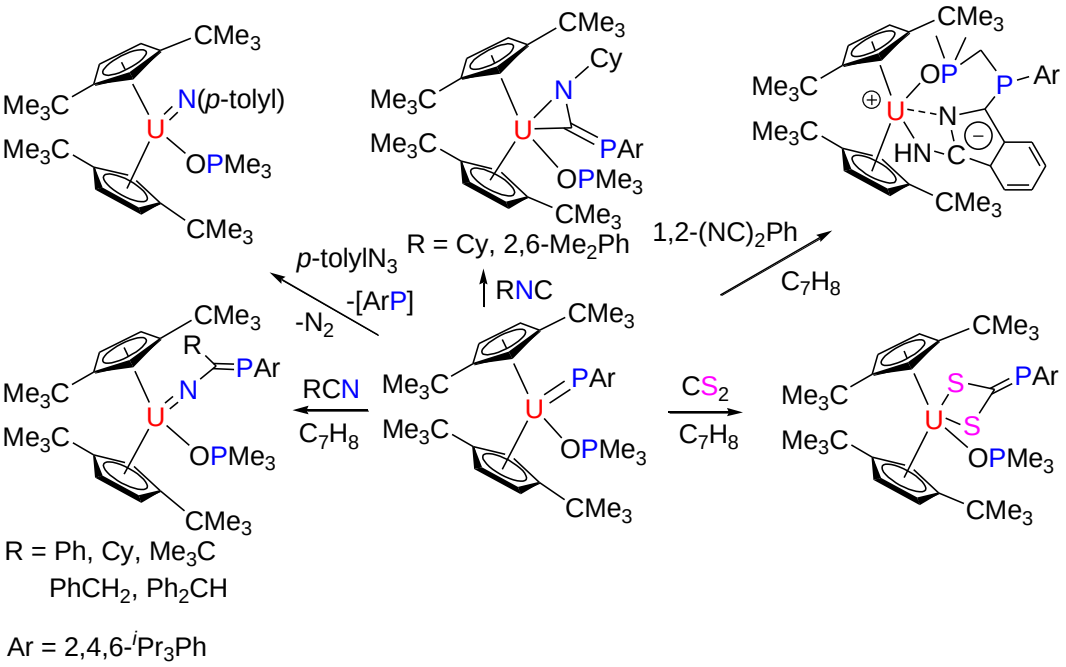

Figure S2. Selected reactivity of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$U(=P-2,4,6-^{i}Pr$_3$C$_6$H$_2$)(OPMe$_3$).

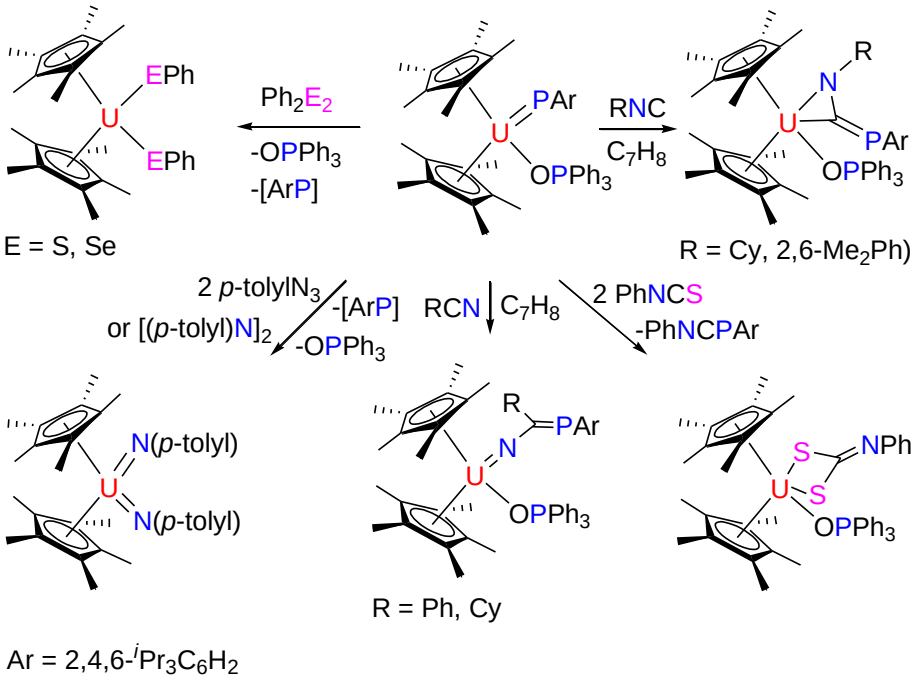

Figure S3. Selected reactivity of (η^5-$C_5Me_5)_2$U(=P-2,4,6-^{t}Pr$_3$C$_6$H$_2$)(OPPh$_3$).

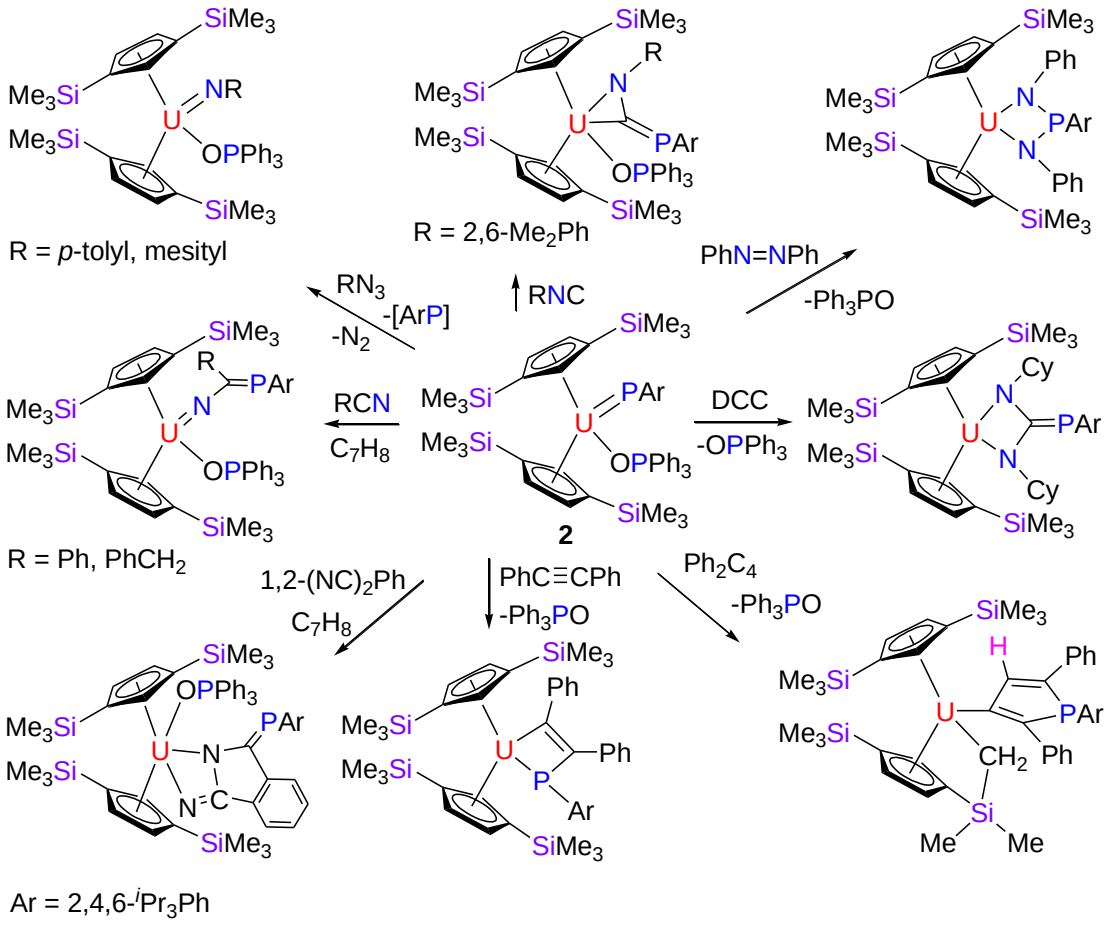

Figure S4. Selected reactivity of [η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$]$_2$U(=P-2,4,6-^{i}Pr$_3$C$_6$H$_2$)(OPPh$_3$).

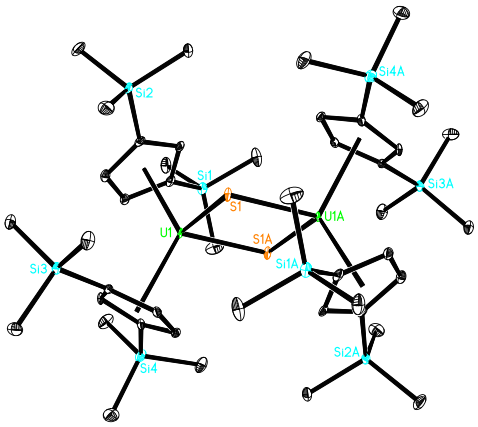

Figure S5. Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.780(12), U-C(Cp) (range) 2.730(11) to 2.818(12), U-Cp (cent) (av.) 2.502(12), U-S(1) 2.591(14), U-O(1A) 2.540(12), Cp(cent)-U-Cp(cent) 124.4(5), O(1)-U-O(1A) 92.0(5).

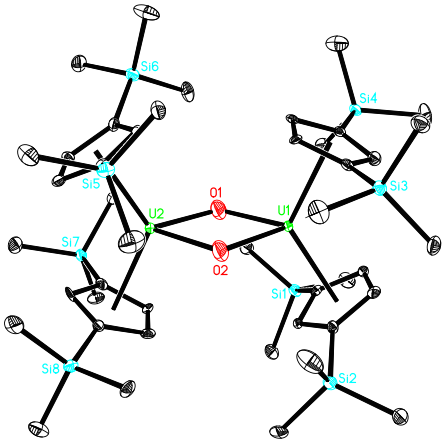

Figure S6. Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.778(12), U-C(Cp) (range) 2.735(10) to 2.823(12), U-Cp (cent) (av.) 2.499(10), U-O(1) 2.076(8), U-O(2) 2.240(8), Cp(cent)-U-Cp(cent) 125.0(3), O(1)-U-O(1A) 70.4(3).

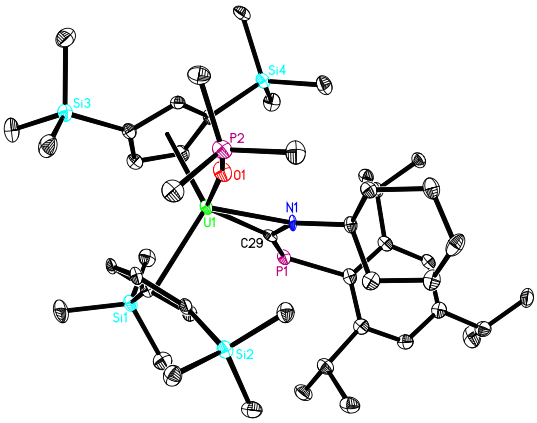

Figure S7. Molecular structure of **15** (thermal ellipsoids drawn at the 35% probability level).

2. Crystallographic details

Table S1. Crystal Data and Experimental Parameters for Compounds 3-4, 7 and 9-10

Compound	**3**	**4** $3C_6H_6$	2(**7**) $\cdot 1.5C_6H_6$	**9**	**10** $0.5C_6H_6$
Formula	$C_{25}H_{51}ClOPSi_4U$	$C_{57}H_{99}O_2P_2Si_6U$	$C_{71}H_{121}O_2P_2S_2Si_8U_2$	$C_{44}H_{84}S_2Si_8U_2$	$C_{47}H_{87}O_2Si_8U_2$
Fw	784.46	1284.87	1833.51	1378.01	1384.94
crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P(-1)$	$P(-1)$	$P(-1)$
a (Å)	10.533(1)	12.133(1)	12.219(1)	11.499(1)	11.703(1)
b (Å)	12.608(1)	25.212(1)	17.122(1)	12.125(1)	12.818(1)
c (Å)	30.195(1)	22.367(1)	22.568(1)	12.664(1)	21.692(1)
α (deg)	90	90	81.94(1)	118.58(1)	77.43(1)
β (deg)	92.18(1)	101.98(1)	76.42(1)	104.52(1)	83.21(1)
γ (deg)	90	90	71.80(1)	92.91(1)	71.34(1)
V (Å^3)	4006.94(18)	6692.69(10)	4348.28(8)	1470.45(12)	3005.03(12)
Z	4	4	2	1	2
D_{calc} (g/cm^3)	1.300	1.275	1.400	1.556	1.531
μ(Mo/Kα)$_{calc}$ (cm^{-1})	13.635	8.569	12.535	17.798	16.815
size (mm)	0.15 × 0.10 × 0.10	0.10 × 0.06 × 0.05	0.20 × 0.15 × 0.15	0.20 × 0.15 × 0.15	0.25 × 0.20 × 0.20
F(000)	1556	2652	1842	676	1362
2θ range (deg)	7.60 to 151.41	7.01 to 153.10	6.54 to 152.80	8.11 to 152.38	7.42 to 152.21
no. of reflns, collected	28157	47682	60961	18222	39461
no of obsd reflns	8002	13506	17572	5854	12097
no of variables	361	638	815	265	550
abscorr (T_{max}, T_{min})	1.00, 0.25	1.00, 0.63	1.00, 0.19	1.00, 0.30	1.00, 0.01
R	0.036	0.034	0.040	0.077	0.085
R_w	0.091	0.097	0.098	0.198	0.224
R_{all}	0.041	0.038	0.045	0.086	0.094
Gof	1.10	1.12	1.03	1.07	1.09
CCDC	2089548	2089549	2089551	2089546	2089547

Table S2. Crystal Data and Experimental Parameters for Compounds 11 and 13-16

Compound	**11**	**13** C_6H_6	**14**	**15**	**16**
Formula	$C_{47}H_{79}NOP_2Si_4U$	$C_{54}H_{84}N_2OP_2Si_4U$	$C_{47}H_{79}NOP_2Si_4U$	$C_{47}H_{85}NOP_2Si_4U$	$C_{34}H_{62}NOPSi_4U$
Fw	1086.44	1189.56	1086.44	1092.48	882.20
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*(-1)	*P*(-1)	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	11.516(1)	15.211(1)	11.669(1)	22.098(1)	13.832(1)
b (Å)	14.265(1)	18.737(1)	11.499(1)	11.593(1)	20.334(1)
c (Å)	17.150(1)	22.070(1)	39.049(1)	21.529(1)	15.087(1)
α (deg)	101.50(1)	90.12(1)	90	90	90
β (deg)	101.45(1)	106.88(1)	92.69(1)	100.49(1)	93.18(1)
γ (deg)	98.36(1)	103.33(1)	90	90	90
V (Å^3)	2655.32(6)	5840.7(2)	5234.02(11)	5423.24(18)	4236.57(15)
Z	2	4	4	4	4
D_{calc} (g/cm^3)	1.359	1.353	1.379	1.338	1.383
μ(Mo/Kα)$_{calc}$ (cm^{-1})	10.273	9.396	10.424	10.060	12.400
size (mm)	0.20 ×0.15 ×0.15	0.10 ×0.06 ×0.02	0.15 ×0.10 ×0.10	0.20 ×0.15 ×0.15	0.10 ×0.10 ×0.10
F(000)	1108	2432	2216	2240	1776
2θ range (deg)	6.44 to 152.77	6.65 to 153.09	7.81 to 153.16	8.14 to 153.46	7.30 to 143.71
no. of reflns, collected	35134	23549	36497	10819	16471
no of obsd reflns	10732	23549	10471	10819	8116
no of variables	556	1194	526	527	397
abscorr (T_{max}, T_{min})	1.00, 0.35	1.00, 0.43	1.00, 0.64	1.00, 0.27	1.00, 0.87
R	0.027	0.062	0.039	0.056	0.036
R_w	0.069	0.165	0.091	0.133	0.075
R_{all}	0.028	0.070	0.045	0.060	0.053
Gof	1.10	1.04	1.06	1.08	1.02
CCDC	2089550	2089553	2089555	2089552	2089554