Supplementary Material (ESI) for Chemical Communications

Supplementary Information

for

Synthesis and Reactivity of Bis(imido) Uranium(VI) Cyclopentadienyl Complexes

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of helium or argon. Hexanes were dried by passage over activate alumina and CH_2Cl_2 was purchased anhydrous and stored over activated molecular sieves for 24 h before use. CD_2Cl_2 and C_5D_5N were dried over activated 4Å molecular sieves for 24 h before use. $U(N^tBu)_2I_2(THF)_2$, $Na(C_5H_5)$, and $Na(C_5Me_5)$ were synthesized by the published procedures. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on a Bruker AVA300. ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). The $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Elemental analyses were performed at the UC Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer.

Synthesis of $(C_5H_5)_2U(N^tBu)_2$ (2) and $(C_5Me_5)_2U(N^tBu)_2$ (3)

The following procedure is representative of the synthesis of complexes **2** and **3**. To a toluene solution (5 mL) of $U(N^tBu)_2I_2(THF)_2$ (500 mg, 0.64 mmol) was added a 2.0 M THF solution of NaC_5H_5 (640 μL, 1.28 mmol). The dark colored reaction was stirred overnight and then filtered thru Celite to remove a precipitate which had formed. The solvent was removed until dryness and the residue dissolved into hexane (1 mL) and cooled to -30°C. A dark crystalline solid had formed after several days which were recovered by carefully decanting the solvent (207 mg, 63 % yield).

2: ^{1}H NMR (300 MHz, CD_2Cl_2, 25° C): δ 1.14 (s, 18 H, $-NC(CH_3)_3$), 6.15 (s, 10H, $-C_5H_5$).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25° C): δ 25.1 (s, $-NC(CH_3)_3$), 64.7 (s, $-NC(CH_3)_3$), 127.2 (s, C_5H_5).

Anal. Calcd for $C_{18}H_{28}N_2U$: C, 42.35; H, 5.53; N, 5.49. **Found**: C, 42.58; H, 5.13; N, 5.76.

3: (Yield = 19%) **^{1}H NMR** (300 MHz, CD_2Cl_2, 25° C): δ 1.40 (s, 18 H, -NC(C*H*$_3$)$_3$), 3.95 (s, 30H -C_5*Me*$_5$).

^{13}C{^{1}H} NMR (MHz, CD_2Cl_2, 25° C): δ 9.7 (-C_5*Me*$_5$), 23.6 (s, -NC(*C*H$_3$)$_3$), 68.2 (s, -N*C*(CH$_3$)$_3$), 134.9 (-*C*$_5$Me$_5$).

Anal. Calcd for $C_{28}H_{48}N_2U$: C, 51.56; H, 7.43; N, 4.30. **Found**: C, 51.68; H, 7.22; N, 4.31.

Synthesis of $(C_5H_5)_2U(N^tBu)_2$(dmpe) (4)

A toluene (2 mL) solution of **2** (50 mg, 0.098 mmol) was treated with a 1 mL toluene solution of dmpe (22 mg, 0.15 mmol) and the solution left to stand at -30°C overnight. Dark long needles formed slowly upon standing which were collected by decanting the solvent (56 mg, yield = 87 %).

4: ^{1}H NMR (300 MHz, CD_2Cl_2, 25° C): δ 1.11 (s, 18 H, -NC(C*H*$_3$)$_3$), 1.28 (br s, 12H, -PC*H*$_3$), 1.83 (br s, 4H, -PC*H*$_2$), 5.95 (s, 10H, -C_5*H*$_5$).

^{13}C{^{1}H} NMR (MHz, CD_2Cl_2, 25° C): δ 17.8 (t, $J_{^{13}C\text{-}^{31}P}$ = 7 Hz, -P*C*H$_3$), 27.4 (s, -NC(*C*H$_3$)$_3$), 30.2 (t, $J_{^{13}C\text{-}^{31}P}$ = 14 Hz, -P*C*H$_2$), 75.2 (s, -N*C*(CH$_3$)$_3$), 128.3 (s, *C*$_5$H$_5$).

^{31}P{^{1}H} NMR (MHz, CD_2Cl_2, 25° C): δ 84.3 (s).

Anal. Calcd for: C, 43.63; H, 6.71; N, 4.24. **Found**: C, 43.68; H, 6.93; N, 3.92.

Synthesis of $U(N^tBu)_2(I)_2$(dmpe) (5)

To a CH_2Cl_2 (5 mL) solution of $U(N^tBu)_2I_2(THF)_2$ (250 mg, 0.32 mmol) was added a CH_2Cl_2 solution (1 mL) solution of dmpe (72 mg, 0.48 mmol). The orange-red solution was stirred for 2 hours and filtered through Celite. The solvent in the filtrate was removed to near dryness and hexanes (5 mL) added to precipitate a bright orange powder. This solid was recrystallized twice from CH_2Cl_2/hexanes to yield an orange powder (229 mg, 91 % yield).

5: ^{1}H NMR (300 MHz, CD_2Cl_2, 25° C): δ 0.58 (s, 18 H, -NC(C*H*$_3$)$_3$), 2.09 (br s, 12H, -PC*H*$_3$), 2.54 (br m, 4H, -PC*H*$_2$).

^{13}C{^{1}H} NMR (MHz, CD_2Cl_2, 25° C): δ 18.6 (t, $J_{^{13}C\text{-}^{31}P}$ = 7 Hz, -P*C*H$_3$), 28.9 (s, -NC(*C*H$_3$)$_3$), 29.7 (t, $J_{^{13}C\text{-}^{31}P}$ = 14 Hz, -P*C*H$_2$), 77.3 (s, -N*C*(CH$_3$)$_3$).

^{31}P{^{1}H} NMR (MHz, CD_2Cl_2, 25° C): δ 64.6 (s).

Anal. Calcd for: C, 21.44; H, 4.37; N, 3.57. **Found**: C, 21.35; H, 4.02; N, 3.92.

Synthesis of $(C_5H_5)U(N^tBu)_2(I)(dmpe)$ (6) and $(C_5H_5)_2U(N^tBu)_2(dmpe)$ (4)

The following procedure is representative of the synthesis of complexes **4** and **6**. To a toluene solution (5 mL) of $U(N^tBu)_2I_2(dmpe)$ (100 mg, 0.13 mmol) was added a THF (1 mL) solution of NaC_5H_5 (11 mg, 0.13 mmol). The dark colored reaction was stirred overnight and then filtered thru Celite to remove a precipitate which had formed. An equal volume of hexanes was added to the dark solution which was then stored at -30°C overnight. Dark long needles formed slowly upon standing which were collected by decanting the solvent (49 mg, 53 % yield).

6: ^{1}H NMR (300 MHz, CD_2Cl_2, 25° C): δ 0.72 (s, 18 H, $-NC(CH_3)_3$), 1.64 (d, $^{2}J_{^1H\text{-}^{31}P}$ = 5 Hz, 6H, $-PCH_3$), 2.26 (d, $^{2}J_{^1H\text{-}^{31}P}$ = 5 Hz, 6H, $-PCH_3$), 2.59 (m, 4H, $-PCH_2$), 6.68 (s, 10H, $-C_5H_5$).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25° C): δ 17.2 (t, $J_{^{13}C\text{-}^{31}P}$ = 7 Hz, $-PCH_3$), 17.8 (t, $J_{^{13}C\text{-}^{31}P}$ = 7 Hz, $-PCH_3$), 29.2 (s, $-NC(CH_3)_3$), 31.0 (t, $J_{^{13}C\text{-}^{31}P}$ = 14 Hz, $-PCH_2$), 34.3 (t, $J_{^{13}C\text{-}^{31}P}$ = 14 Hz, $-PCH_2$), 76.1 (s, $-NC(CH_3)_3$), 129.8 (s, C_5H_5).

^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 25° C): δ 71.3 (d, $^{2}J_{^{31}P\text{-}^{31}P}$ = 24 Hz, 1P), 88.3 (d, $^{2}J_{^{31}P\text{-}^{31}P}$ = 24 Hz, 1P).

Anal. Calcd for: C, 31.59; H, 5.44; N, 3.88. **Found**: C, 31.32; H, 5.41; N, 3.67.

4: The NMR spectra were identical to those described above (Yield = 82 %).

Disproportionation Reaction of 6 in THF at 60°C

A d_8-THF solution (1 mL) of **6** (25 mg, 0.035 mmol) was heated at 60°C overnight in a 20mL vial and monitored by ^{1}H and ^{31}P NMR spectroscopy. No reaction was observed.

Conproportionation Reaction of 4 and 5 in THF at 60°C

A d_8-THF solution (1 mL) of **4** (25 mg, 0.032 mmol) and **5** (21 mg, 0.032 mmol) was heated at 60°C overnight in a 20mL vial and monitored by ^{1}H and ^{31}P NMR spectroscopy. No reaction was observed.

X-ray Crystallography. The crystal structures of compounds **2**, **4**, and **6** were determined as follows: The crystal was mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. The data were collected on a Bruker SMART APEX II chargecoupled-device (CCD) diffractometer, with KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with graphite monochromatized MoK_ X-ray source (λ = 0.71073 Å), with MonoCap X-ray source optics. A hemisphere of data was collected using ω scans, with 5-second frame exposures and 0.3º frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[3] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[4] The data were S5 corrected for absorption using the SADABS program.[5] Decay of reflection intensity was monitored *via* analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[6] ORTEP diagrams of **2**, **4**, and **6** are shown in Figures S1, S2 and S3 respectively, while X-ray crystallographic data for complexes **2**, **4**, and **6**can be found in Table S1.

References

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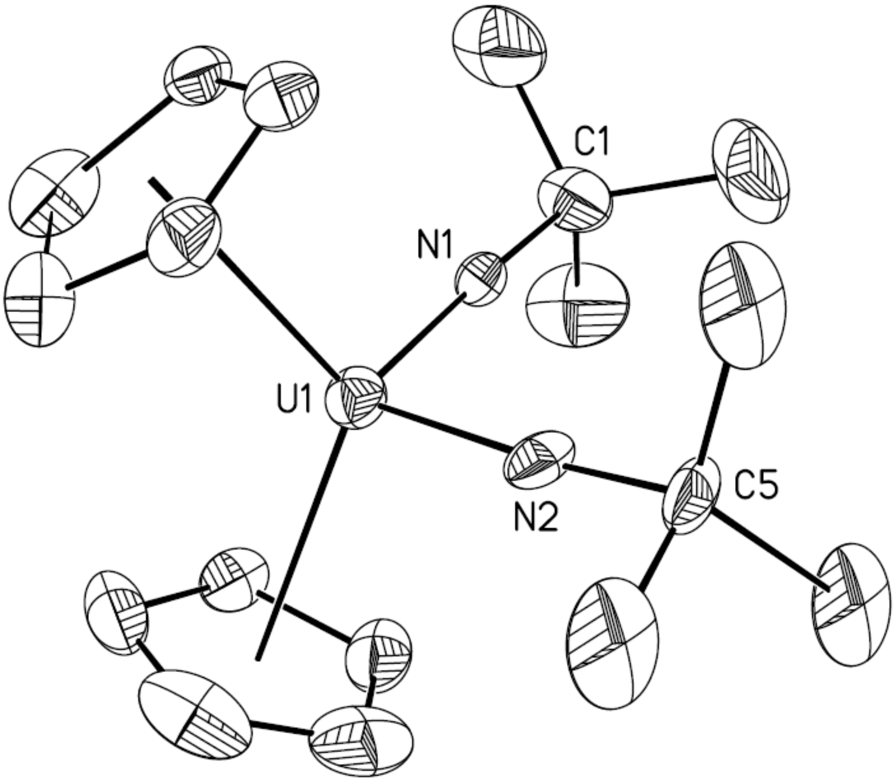

Figure S1. ORTEP view of one of the independent molecules in the unit cell of $(C_5H_5)_2U(N^tBu)_2$ **(2)**, depicted with 50% thermal ellipsoids.

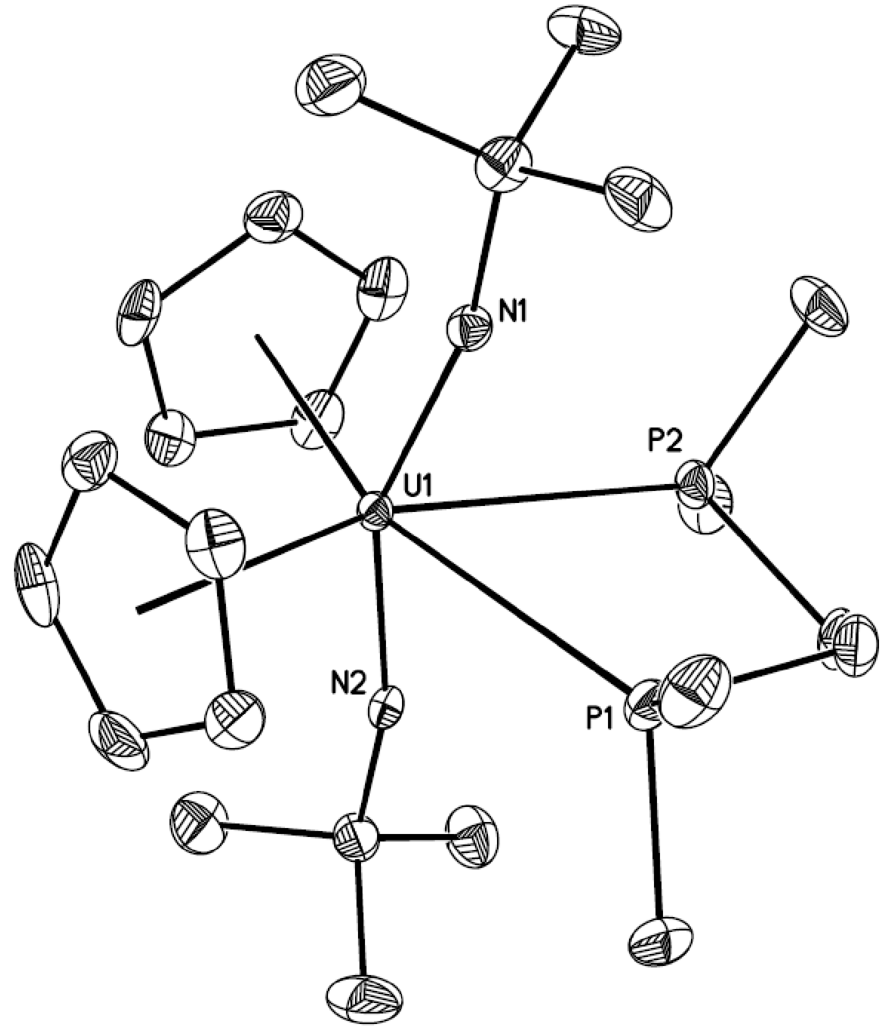

Figure S2. ORTEP view of $(C_5H_5)_2U(N^tBu)_2$(dmpe) (**4**), depicted with 50% thermal ellipsoids..

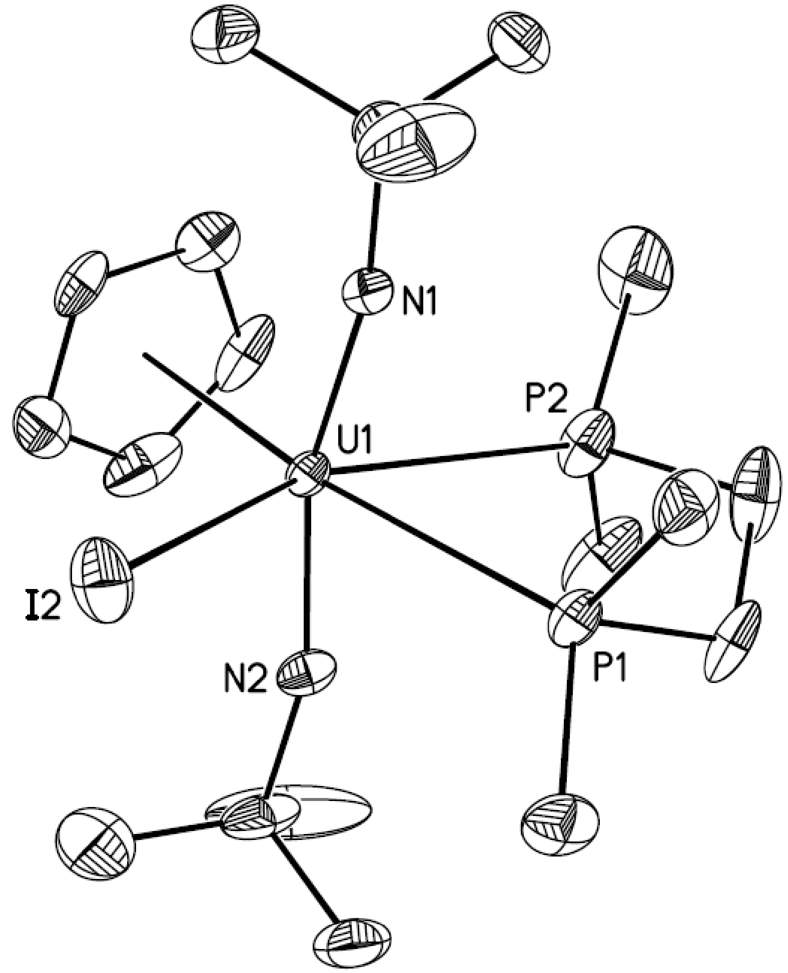

Figure S3. ORTEP view of $(C_5H_5)U(N^tBu)_2(I)(dmpe)$ (**6**), depicted with 50% thermal ellipsoids.

Table S1. X-ray Crystallographic Data for Complexes **2**, **4**, and **6**

Crystal Data	**2**	**4**	**6**
Empirical formula	$C_{18}H_{28}N_2U$	$C_{24}H_{44}N_2P_2U$	$C_{19}H_{39}IN_2P_2U$
Crystal habit, color	Needle, black	Block, dark red	Block, black
Crystal size (mm)	0.28 x 0.04 x 0.03	0.20 x 0.16 x 0.08	0.22 x 0.10 x 0.08
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/n$	$P\ 2_1/n$
Volume (Å^3)	3764.0(10)	2539.3(6)	2502.3(7)
a (Å)	9.0621(14)	10.2746(15)	10.2143(16)
b(Å)	14.759(2)	20.362(3)	16.498(3)
c(Å)	28.152(4)	12.1417(18)	14.854(2)
α(°)	90	90	90
β(°)	91.384(3)	91.546(2)	91.445(2)
γ(°)	90	90	90
Z	8	4	4
Formula weight (g/mol)	510.45	660.58	722.39
Density (calculated)(Mg/m^3)	1.802	1.728	1.918
Absorption coefficient (cm-^{1})	8.621	6.531	7.854
F_{000}	1936	1296	1368
Radiation	MoKα, 0.71073 Å	MoKα, 0.71073 Å	MoKα, 0.71073 Å
Data Refinement			
Final R indices^a	$R_1 = 0.0997$, $wR_2 = 0.1068$	$R_1 = 0.0458$, $wR_2 = 0.0775$	$R_1 = 0.0554$, $wR_2 = 0.0802$
Largest diff. peak and hole (eÅ^{-3})	1.659 and -1.568	1.587 and -1.565	1.407 and -1.095

^{a}Number of observed reflections: **2**, 7898 ($I_o > 2\sigma I_o$), $R_1 = \Sigma\,|\,(|F_o| - |F_c|)\,|\,/\,\Sigma\,|F_o|$, $wR_2 = [\,\Sigma\, w(\,|F_o|^2 - |F_c|^2\,)^2\,/\,\Sigma\, wF_o^4\,]^{1/2}$, $w = [\,\sigma^2 F_o^2 + (0.0534\cdot p)^2\,]^{-1}$, $p = [F_o^2 + 2\cdot F_c^2]/3$. **4**, 6013 ($I_o > 2\sigma I_o$), $R_1 = \Sigma\,|\,(|F_o| - |F_c|)\,|\,/\,\Sigma\,|F_o|$, $wR_2 = [\,\Sigma\, w(\,|F_o|^2 - |F_c|^2\,)^2\,/\,\Sigma\, wF_o^4\,]^{1/2}$, $w = [\,\sigma^2 F_o^2 + (0.0324\cdot p)^2\,]^{-1}$, $p = [F_o^2 + 2\cdot F_c^2]/3$. **6**, 5443 ($I_o > 2\sigma I_o$), $R_1 = \Sigma\,|\,(|F_o| - |F_c|)\,|\,/\,\Sigma\,|F_o|$, $wR_2 = [\,\Sigma\, w(\,|F_o|^2 - |F_c|^2\,)^2\,/\,\Sigma\, wF_o^4\,]^{1/2}$, $w = [\,\sigma^2 F_o^2 + (0.0354\cdot p)^2\,]^{-1}$, $p = [F_o^2 + 2\cdot F_c^2]/3$.