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Supporting Information

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An Inverted-Sandwich Diuranium μ-η^5:η^5-Cyclo-P$_5$ Complex Supported by U-P$_5$ δ-Bonding**

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Experimental

General

All manipulations were carried out using Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina towers and degassed before use or were distilled from calcium hydride. All solvents were stored over potassium mirrors except ethers which were stored over activated 4 Å sieves. Deuterated solvent was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. [U(Tren^{TIPS})] [**1** = Tren^{TIPS} = {N(CH$_2$CH$_2$NSiPr$^i_3$)$_3$}] was prepared as described previously.[1] ^{1}H and ^{29}Si NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2 and 79.5 MHz respectively; chemical shifts are quoted in ppm and are relative to TMS (^{1}H, ^{29}Si). FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. UV/Vis/NIR spectra were recorded on a Perkin Elmer Lambda 750 spectrometer. Data were collected in 1mm path length cuvettes loaded in an MBraun UniLab glovebox and were run versus the appropriate reference solvent. Static variable-temperature magnetic moment data were recorded in an applied dc field of 0.1 T on a Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer using doubly recrystallised powdered samples. Samples were carefully checked for purity and data reproducibility between several independently prepared batches for each compound examined. Care was taken to ensure complete thermalisation of the sample before each data point was measured and samples were immobilised in an eicosane matrix to prevent sample reorientation during measurements. Diamagnetic corrections were applied for **2** using tabulated Pascal constants and measurements were corrected for the effect of the blank sample holders (flame sealed Wilmad NMR tube and straw) and eicosane matrix. X-band EPR data were acquired on a Bruker EMX spectrometer. CHN microanalyses were carried out by Tong Liu at the University of Nottingham. CCDC deposition number for **2** is 1049738.

Preparation of [{U(Tren^{TIPS})}$_2$(μ-η^5:η^5-P$_5$)] (2)

THF (20 ml) was added to a cold (−78 °C) mixture of [U(Tren^{TIPS})] (**1**) (0.51 g, 0.6 mmol) and P_4 (19 mg, 0.15 mmol). The dark blue-green suspension was allowed to warm to ambient temperature whilst stirring and the dark mixture produced was stirred at room temperature for a further 16 hours. The dark brown solution was reduced to dryness *in vacuo* to afford a sticky dark brown solid, which was extracted into toluene (10 ml), filtered and reduced in volume to *ca*. 2 ml. Storage at 5 °C for 72 hours yielded brown crystals of **2**, which were isolated by filtration, washed with hexanes (3 × 1 ml) and dried *in vacuo* for 30 minutes. Yield: 60 mg (25% based on P). ^{1}H NMR (C_6D_6, 298 K): −32.32 (s, 8H, CH_2), −22.21 (s, 8H, CH_2), −12.68 (s, 8H, CH_2), 5.21 (s, 54H, Me), 6.04 (s, 18H, CH), 8.86 (s, 54H, Me) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, 298 K): −96.87 ppm. ^{31}P signal not observed. μ_{eff} (Evans method, C_6D_6, 298 K): 4.09 μ_B. FTIR (Nujol): 1631.54 (m), 1598.74 (m), 1556.95 (m), 930.86 (s), 670.39 (s), 576.97 (m), 558.70 (m), 541.05 (w), 472.13 (w), 416.37 (w) cm^{-1}. Anal. calc'd for $C_{66}H_{150}N_8P_5Si_6U_2$: C 42.74%; H 8.15%; N 6.04%. Found: C 42.52%; H 8.29%; N 5.77%.

UV/Vis/NIR Spectra

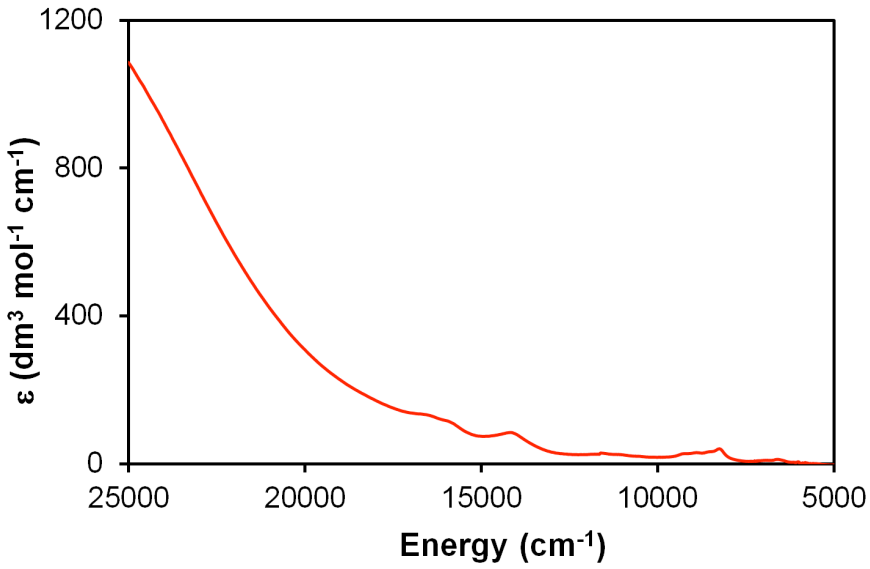

Figure S1. UV/Vis/NIR spectrum of **2** as a 20 mM solution in toluene.

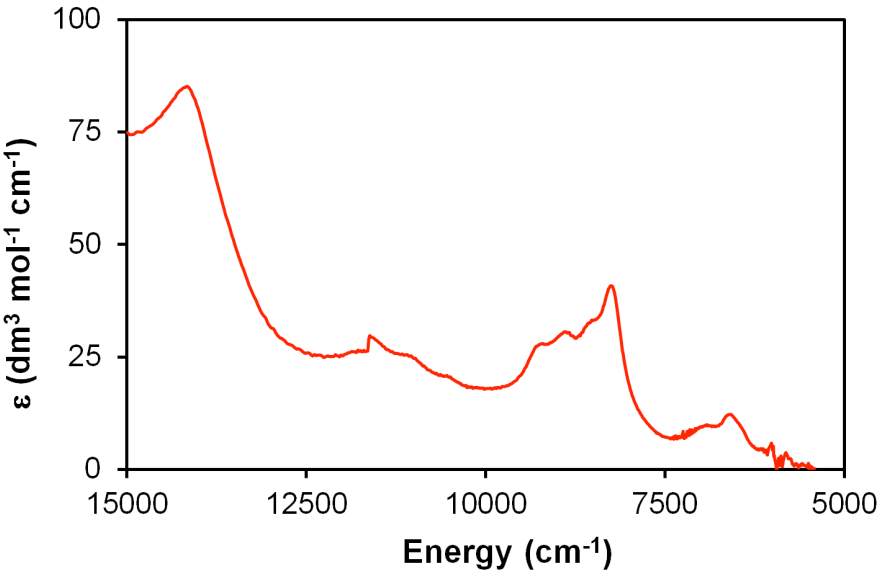

Figure S2. Zoom-in of the 5000-15000 cm^{-1} region of the UV/Vis/NIR spectrum of **2**.

Magnetism Data

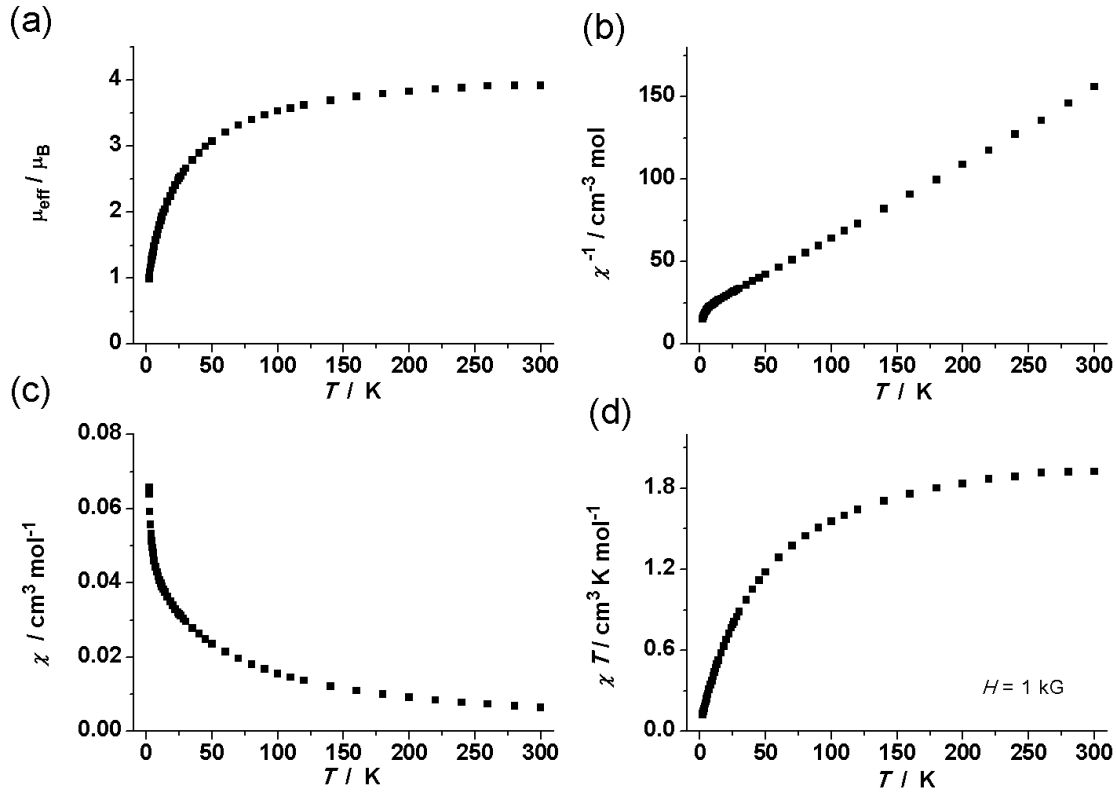

Figure S3. Variable-temperature SQUID data for: (a) μ_{eff} vs T, (b) $1/\chi$ vs T, (c) χ vs T, and (d) χT vs T for **2**.

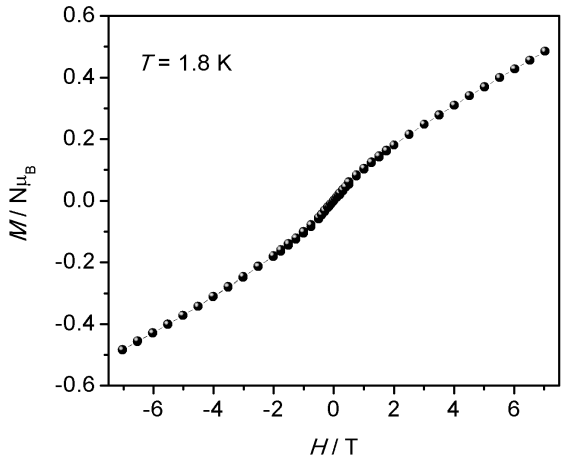

Figure S4. M vs H data for **2**.

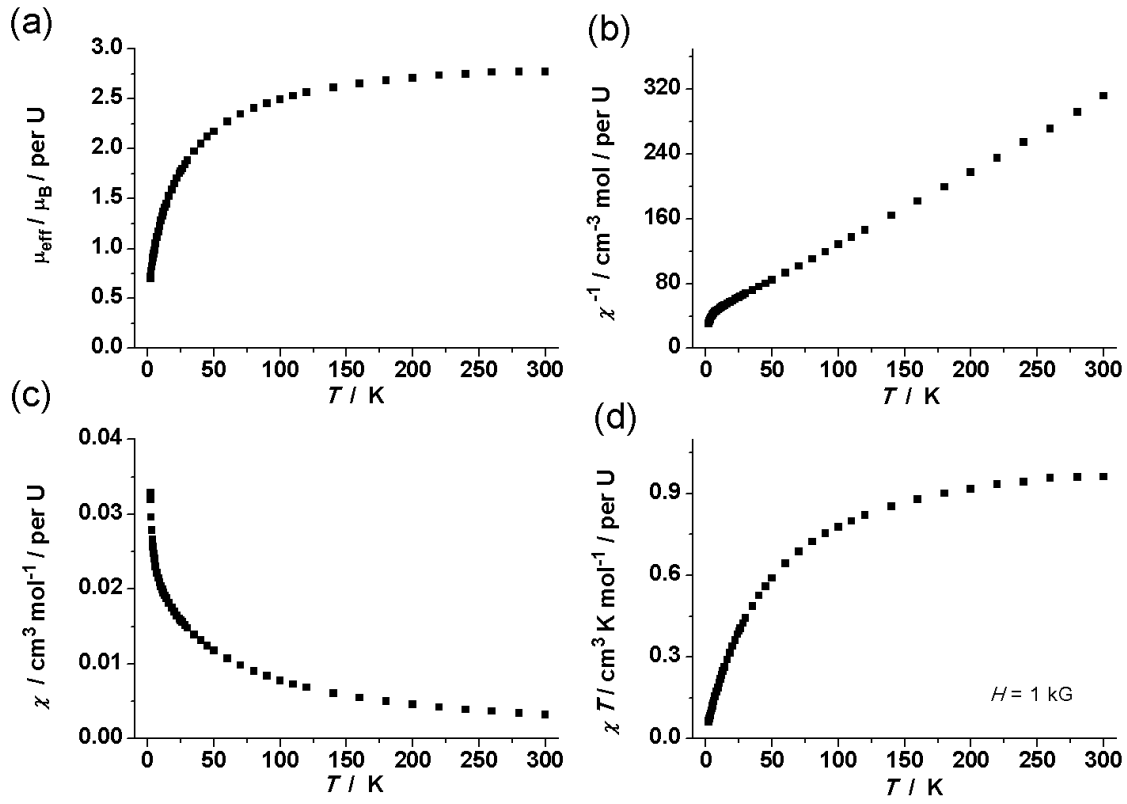

Figure S5. Variable-temperature SQUID data for: (a) μ_{eff} vs T, (b) $1/\chi$ vs T, (c) χ vs T, and (d) χT vs T peruranium ion in **2**.

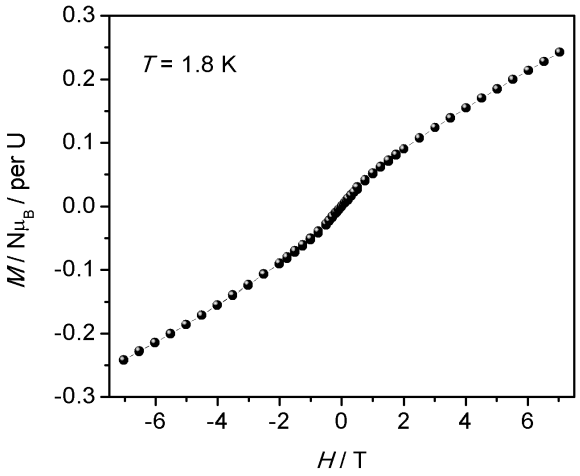

Figure S6. M vs H data per uranium ion in **2**.

Density Functional Theory Calculations

General

Unrestricted geometry optimisations were performed for the full model of **2** using coordinates derived from the X-ray crystal structure. No constraints were imposed on the structure during the geometry optimisation. The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2012.01.[2,3] The DFT geometry optimisations employed Slater type orbital (STO) triple-ζ-plus polarisation all-electron basis sets (from the ZORA/TZP database of the ADF suite). Scalar relativistic approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects and the local density approximation (LDA) with the correlation potential due to Vosko et al[4] was used in all of the calculations. Gradient corrections were performed using the functionals of Becke[5] and Perdew.[6] MOLEKEL[7] was used to prepare the three-dimensional plot of the electron density.

Final Coordinates and Single Point Energy of 2 After Geometry Optimisation

1.C	-4.873949	-0.872082	-6.393979
2.C	-1.715692	0.929753	-6.319785

3.C	-1.731897	-0.384809	-5.512403
4.C	-4.785184	-0.252130	-4.980837
5.C	-0.306261	-0.720190	-5.042595
6.C	3.646240	0.566301	-4.902049
7.C	3.876468	-1.880316	-4.314423
8.C	-5.996242	-0.720791	-4.148071
9.C	-3.196339	-3.367817	-4.334187
10.C	3.571334	-0.470942	-3.764027
11.C	7.036930	-0.024608	-3.603203
12.C	-3.190274	2.127722	-3.444828
13.C	-2.084478	6.428338	-2.887117
14.C	-2.908923	-2.241538	-3.318615
15.C	0.138707	3.737366	-3.400909
16.C	-4.567543	2.530346	-2.934722
17.C	4.998898	2.776996	-2.587717
18.C	1.556956	5.563814	-2.458327
19.C	6.408040	-0.428272	-2.250361
20.C	1.375890	-4.179421	-2.315729
21.C	-0.317568	-5.986188	-1.944644
22.C	0.631403	4.380674	-2.090212
23.C	-3.704699	-2.472738	-2.022869
24.C	-1.679467	6.448255	-1.397096
25.C	-0.947573	7.775012	-1.092419
26.C	4.233046	1.809835	-1.655395
27.C	0.289090	-4.692239	-1.353682
28.C	-4.277507	4.051367	-1.000489
29.C	7.260897	0.158601	-1.104260
30.C	4.361792	-2.535284	-0.970501
31.C	2.974074	-6.702158	-0.338382
32.C	-5.580699	1.956447	-0.751143
33.C	-5.072685	0.573054	-0.364440
34.C	4.537300	2.211174	-0.199389
35.C	-3.190268	4.031797	0.063914
36.C	1.048172	-7.789485	0.862820
37.C	5.299518	-2.750329	0.208783
38.C	1.880970	-6.494415	0.732706
39.C	-1.977467	-5.731302	1.105564
40.C	1.418870	5.890713	0.998777
41.C	0.080724	5.127107	0.947763
42.C	-0.777129	-4.904185	1.608289
43.C	-5.433423	-2.328023	1.474211
44.C	4.011653	-3.950121	1.955826
45.C	-0.889790	5.692200	2.006422
46.C	2.538822	-3.791582	2.313557
47.C	-4.365001	-1.636775	2.348024
48.C	4.543569	-0.412720	2.406235
49.C	5.135257	-1.813460	2.497527
50.C	-6.203384	0.993134	2.601690
51.C	-6.263175	2.511539	2.877731
52.C	-0.503486	-5.219291	3.094410

53.C	-2.711247	2.463843	3.346057
54.C	-3.171882	1.012606	3.574202
55.C	1.967600	2.828467	3.764350
56.C	-4.324166	-2.288800	3.745039
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58.C	4.419359	2.499646	4.235849
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60.C	2.996130	1.987311	4.539318
61.C	0.914360	-0.296641	4.855418
62.C	-3.679698	0.883514	5.029313
63.C	3.994875	-0.754063	5.592144
64.C	3.678720	-2.224295	5.936212
65.C	0.615578	0.088199	6.319848
66.C	4.214421	0.035364	6.902648
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69.H	-1.060258	0.832873	-7.202303
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71.H	-4.760876	-1.966503	-6.371177
72.H	-2.048539	-1.186138	-6.208857
73.H	-1.316740	1.761335	-5.719579
74.H	0.395107	-0.727898	-5.894629
75.H	3.040438	0.225210	-5.758852
76.H	-4.891004	0.839559	-5.123597
77.H	3.289371	-2.066066	-5.229444
78.H	4.671827	0.718379	-5.272151
79.H	-6.943231	-0.415198	-4.626058
80.H	-2.603826	-3.266473	-5.254795
81.H	4.936407	-2.006466	-4.584439
82.H	-3.172712	2.139826	-4.544291
83.H	-4.257816	-3.397730	-4.623215
84.H	6.546496	-0.511437	-4.457531
85.H	-0.243906	-1.702624	-4.554514
86.H	3.247348	1.543320	-4.595777
87.H	-6.019345	-1.817819	-4.064254
88.H	0.061310	0.028869	-4.324216
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93.H	-0.487457	4.426528	-3.984705
94.H	-2.954634	-4.350387	-3.895408
95.H	-2.776037	7.258351	-3.113768
96.H	0.998831	3.463095	-4.033777
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98.H	-4.920443	3.468646	-3.402061
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125.H	-6.494696	1.901762	-1.372153
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206.H	4.968232	-0.744454	5.067620
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208.H	-2.873692	1.149498	5.732658
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213.H	4.572788	1.058197	6.724200
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216.H	3.293465	0.106850	7.500171
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218.N	-4.495161	2.663871	-1.463615
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220.N	-1.917228	3.508508	-0.514135
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222.N	1.752881	-3.443459	1.095970
223.N	4.505940	-2.650581	1.453196
224.N	3.073305	-0.453533	2.669113
225.Si	-3.053965	-0.493346	-4.105460
226.Si	4.494397	-0.051824	-2.110014
227.Si	-0.726032	4.850050	-0.795103
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230.Si	2.731848	0.080813	4.355360
231.P	0.552513	0.794034	-1.676350
232.P	-0.135084	-1.238995	-1.267988
233.P	1.218310	1.472055	0.298438
234.P	-0.950156	-1.206513	0.732318
235.P	-0.310609	0.650619	1.624789
236.U	-2.133132	1.256958	-0.745713
237.U	2.157999	-1.223911	0.727562

Energy: -1274.50108063 eV

References

1. D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012**, *337*, 717.
2. C. Fonseca Guerra, J. G. Snijders, G. te Velde E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391.
3. G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

4. S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.

5. A. D. Becke, *Phys. Rev. A.* **1988**, *38*, 3098.

6. J. P. Perdew, *Phys. Rev. B.* **1986**, *33*, 8822.

7. S. Portmann, H. P. Luthi, *Chimia* **2000**, *54*, 766.