

Supplementary Information

Synthesis and Structure of $[\{N(CH_2CH_2NSiMe_3)_3\}URe(\eta^5-C_5H_5)_2]$: A Heterobimetallic Complex with an Unsupported Uranium-Rhenium Bond

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S1. Synthesis

S1.1. General Methods

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glove box, under an atmosphere of dry and oxygen free nitrogen. THF, toluene, and hexane were dried by passage through activated alumina, degassed prior to use, and stored over molecular sieves (THF) or potassium mirrors (toluene, hexane). Deuterated benzene was distilled from a potassium mirror, degassed by three freeze-pump-thaw cycles and stored under nitrogen. UCl_4 ,¹ $Tren^{TMS}H_3$,² $[Tren^{TMS}Li_3]$,³ $[Tren^{TMS}U(Cl)(THF)]$ (**2**)⁴ and $[(\eta^5-C_5H_5)_2ReH]^5$ were prepared according to literature procedures. The preparation of **1** is similar to a reported procedure to prepare the THF-free analogue.⁵ 1H NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2 MHz, chemical shifts are quoted in parts per

million and are relative to TMS. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. CHN analyses were carried out by Medac Ltd, Surrey, UK.

S1.2. Preparation of [Tren^{TMS}U(I)(THF)] (3)

Me₃SiI (2.13 ml, 15.00 mmol) was added to a cold (0 °C) mixture of [Tren^{TMS}U(Cl)(THF)] (2) (10.58 g, 15.00 mmol). The mixture was allowed to warm to room temperature and was stirred for one hour. Volatiles were removed at reduced pressure and the resulting green solid was extracted into warm toluene (12 ml). THF (1ml) was added and the solution stored overnight to afford **3** as green blocks. Yield: 10.16 g, 85%. Anal. Calcd for C₁₉H₄₇IN₄OSi₃U: C, 28.63; H, 5.95; N, 7.03. Found: C, 29.48; H, 6.32; N, 7.45. ¹H NMR (C₆D₆, 295K) δ 27.35 (4H, s, THF), 15.02 (6H, s, br, CH₂), 7.46 (27H, s, SiMe₃), 2.48 (4H, s, THF), -43.76 (6H, s, br, CH₂). FTIR (Nujol): ν 676.9 (m), 720.4 (m), 774.4 (m), 833.8 (s), 907.9 (s), 927.7 (s), 1021.1 (m), 1060.7 (m), 1081.9 (m), 1247.6 (m). μ_{eff} (Evans method, C₆D₆, 295K): 2.79 μ_B.

S1.3. Preparation of [(Tren^{TMS})URe(η⁵-C₅H₅)₂] (4)

THF (30 ml) was added to a cold (-78 °C) mixture of [(tren^{TMS})U(I)(thf)] (0.797 g, 1.00 mmol) and [(η⁵-C₅H₅)₂ReK] (0.335 g, 1.00 mmol). The resulting dark brown suspension was allowed to slowly warm to ambient temperature while stirring. The reaction mixture was then stirred for a further 12 hours and after being allowed to settle over 1 hour, a dark red solution and white precipitate was afforded. The solution was filtered and volatiles were removed *in vacuo* to give a red solid. Recrystallisation at -30 °C over 12 hours from hot (70 °C) toluene (2 ml) afforded single crystals of **4** suitable for X-ray diffraction. Yield: 0.59 g, 65%. Anal. Calcd for C₂₅H₄₉N₄ReSi₃U: C, 32.85; H, 5.40; N, 6.13. Found: C, 32.84; H, 5.60; N, 6.15. ¹H

NMR (C_6D_6 , 295K) δ 7.65 (6H, s, br, CH_2), 0.20 (27H, s, br, $SiMe_3$), -0.02 (10H, s, C_5H_5), -11.50 (6H, s, br, CH_2). FTIR (Nujol): ν 799 (m), 836 (w), 1020 (m), 1047 (m), 1095 (m), 1260 (m), 1299 (w). (MS/EI) m/z : 318 $[(\eta^5-C_5H_5)_2ReH]^+$, 630 $[(\eta^5-C_5H_5)_2ReUH_2SiMe_3]^+$, 849 $[M^+]-C_5H_5$. μ_{eff} (Evans method, C_6D_6 , 295K): 2.88 μ_B .

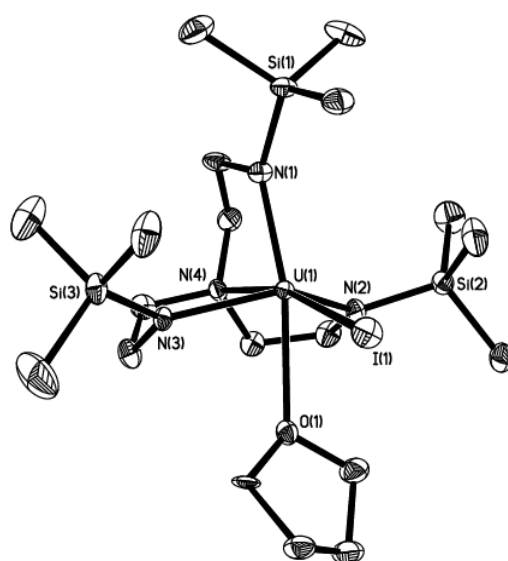
S1.4. NMR Tube Scale reaction of CCl_4 with 4

A solution of **3** (20 mg, 0.022 mmol) in C_6D_6 (0.55 ml) was treated with CCl_4 (2.1 μL , 0.022 mmol) and the solution shaken then a 1H NMR spectrum was recorded. No change was observed in the range δ 5-9 ppm. CCl_4 (15.0 μL , 0.110 mmol) was added, the tube shaken and another 1H NMR recorded with no change. Finally, $CHCl_3$ (14 μL , 0.22 mmol) was added and the resulting 1H NMR spectrum exhibited a new resonance at δ 6.39 ppm.

S1.5. References

1. J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Organometallics*, **2002**, *21*, 5978.
2. D. Gudat, J. G. Verkade, *Organometallics*, **1989**, *8*, 2772.
3. C. C. Cummins, R. R. Schrock, W. M. Davis, *Organometallics*, **1992**, *11*, 1452.
4. S. T. Liddle, J. McMaster, D. P. Mills, A. J. Blake, C. Jones, W. D. Woodul, *Angew.Chem. Int. Ed.*, **2009**, DOI: 10.1002/anie.200805481.
5. D. M. Heinekey, G. L. Gould, *Organometallics* **1991**, *10*, 2977.

S2. X-ray Crystallography



S2.1. Crystal structure of 3, thermal ellipsoids set at 30%, hydrogen atoms omitted for clarity.

S2.2. Crystal Data for 3.

Table 1. Crystal data and structure refinement for **3**.

Identification code	3	
Chemical formula	C ₁₉ H ₄₇ IN ₄ OSi ₃ U	
Formula weight	796.81	
Temperature	150(2) K	
Radiation, wavelength	MoK α , 0.71073 Å	
Crystal system, space group	Tetragonal, P4 ₃ 2 ₁ 2	
Unit cell parameters	a = 12.8637(3) Å	$\alpha = 90^\circ$
	b = 12.8637(3) Å	$\beta = 90^\circ$
	c = 36.1910(13) Å	$\gamma = 90^\circ$
Cell volume	5988.7(3) Å ³	
Z	8	
Calculated density	1.768 g/cm ³	
Absorption coefficient μ	6.588 mm ⁻¹	
F(000)	3072	
Crystal colour and size	Pale green, 0.37 × 0.12 × 0.11 mm ³	
Reflections for cell refinement	11530 (θ range 2.24 to 25.84°)	
Data collection method	Bruker SMART1000 CCD diffractometer	
	ω rotation with narrow frames	
θ range for data collection	1.94 to 27.51°	
Index ranges	h -16 to 15, k -16 to 16, l -47 to 46	
Completeness to $\theta = 26.00^\circ$	99.9 %	
Intensity decay	0%	
Reflections collected	53401	
Independent reflections	6891 ($R_{\text{int}} = 0.074$)	
Reflections with $F^2 > 2\sigma$	5977	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.17 and 0.51	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0000, 0.0000	
Data / restraints / parameters	6891 / 0 / 271	
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0279, wR2 = 0.0490	
R indices (all data)	R1 = 0.0424, wR2 = 0.0530	
Goodness-of-fit on F^2	1.063	
Absolute structure parameter	0.003(4)	
Largest and mean shift/su	0.002 and 0.000	
Largest diff. peak and hole	1.057 and -0.728 e Å ⁻³	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for **3**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
U(1)	0.469790(16)	0.883580(15)	0.435014(5)	0.01147(5)
I(1)	0.48120(3)	0.79595(3)	0.515979(9)	0.02423(10)
N(1)	0.4779(4)	1.0555(3)	0.42537(10)	0.0162(10)
N(2)	0.6101(3)	0.8421(3)	0.40179(10)	0.0162(10)
N(3)	0.2987(3)	0.8752(3)	0.42161(10)	0.0145(9)
N(4)	0.4400(3)	0.9140(3)	0.36552(10)	0.0161(10)
Si(1)	0.50263(12)	1.15478(12)	0.45650(4)	0.0191(3)
C(1)	0.3915(5)	1.2478(5)	0.45727(15)	0.0341(15)
C(2)	0.6247(5)	1.2267(5)	0.44478(16)	0.0382(17)
C(3)	0.5186(4)	1.1013(4)	0.50441(13)	0.0253(13)
C(4)	0.4549(5)	1.0950(4)	0.38759(13)	0.0225(13)
C(5)	0.4869(4)	1.0182(4)	0.35833(13)	0.0223(12)
Si(2)	0.73628(12)	0.85836(12)	0.41780(4)	0.0187(3)
C(6)	0.8102(4)	0.7344(5)	0.41545(16)	0.0284(14)
C(7)	0.8069(5)	0.9593(5)	0.39076(15)	0.0358(16)
C(8)	0.7320(5)	0.9051(5)	0.46660(15)	0.0371(17)
C(9)	0.6060(5)	0.8210(5)	0.36161(13)	0.0245(13)
C(10)	0.4968(4)	0.8286(4)	0.34687(13)	0.0204(13)
Si(3)	0.19473(12)	0.92483(13)	0.44596(4)	0.0212(4)
C(11)	0.1377(5)	1.0406(5)	0.42155(16)	0.046(2)
C(12)	0.2362(5)	0.9709(5)	0.49272(14)	0.0363(16)
C(13)	0.0912(5)	0.8249(6)	0.45188(19)	0.056(2)
C(14)	0.2733(4)	0.8414(5)	0.38341(13)	0.0224(13)
C(15)	0.3288(4)	0.9101(4)	0.35617(13)	0.0227(13)
O(1)	0.4432(3)	0.6890(3)	0.42505(9)	0.0183(9)
C(16)	0.3553(4)	0.6347(4)	0.44030(14)	0.0196(12)
C(17)	0.3954(5)	0.5374(4)	0.45785(15)	0.0259(13)
C(18)	0.4889(5)	0.5108(4)	0.43381(16)	0.0286(14)
C(19)	0.5316(5)	0.6180(4)	0.42536(15)	0.0282(14)

Table 3. Bond lengths [Å] and angles [°] for **3**.

U(1)–N(2)	2.233(4)	U(1)–N(1)	2.241(4)
U(1)–N(3)	2.256(4)	U(1)–O(1)	2.552(4)
U(1)–N(4)	2.574(4)	U(1)–I(1)	3.1430(4)
N(1)–C(4)	1.488(6)	N(1)–Si(1)	1.733(4)
N(2)–C(9)	1.480(6)	N(2)–Si(2)	1.737(5)
N(3)–C(14)	1.486(6)	N(3)–Si(3)	1.724(4)
N(4)–C(15)	1.471(7)	N(4)–C(10)	1.483(6)
N(4)–C(5)	1.492(7)	Si(1)–C(1)	1.865(6)
Si(1)–C(2)	1.872(6)	Si(1)–C(3)	1.876(5)
C(4)–C(5)	1.506(7)	Si(2)–C(6)	1.858(6)
Si(2)–C(7)	1.863(6)	Si(2)–C(8)	1.866(6)
C(9)–C(10)	1.505(7)	Si(3)–C(13)	1.863(7)
Si(3)–C(12)	1.870(5)	Si(3)–C(11)	1.880(6)
C(14)–C(15)	1.505(7)	O(1)–C(16)	1.439(6)
O(1)–C(19)	1.458(6)	C(16)–C(17)	1.495(7)
C(17)–C(18)	1.523(8)	C(18)–C(19)	1.516(7)
N(2)–U(1)–N(1)	96.56(16)	N(2)–U(1)–N(3)	131.38(14)
N(1)–U(1)–N(3)	93.38(16)	N(2)–U(1)–O(1)	78.33(13)
N(1)–U(1)–O(1)	162.19(12)	N(3)–U(1)–O(1)	78.01(14)
N(2)–U(1)–N(4)	68.30(14)	N(1)–U(1)–N(4)	72.83(13)
N(3)–U(1)–N(4)	69.64(13)	O(1)–U(1)–N(4)	89.49(12)
N(2)–U(1)–I(1)	112.25(10)	N(1)–U(1)–I(1)	119.80(9)
N(3)–U(1)–I(1)	103.23(10)	O(1)–U(1)–I(1)	77.65(7)
N(4)–U(1)–I(1)	166.52(10)	C(4)–N(1)–Si(1)	112.5(3)
C(4)–N(1)–U(1)	118.1(3)	Si(1)–N(1)–U(1)	129.4(2)
C(9)–N(2)–Si(2)	112.5(3)	C(9)–N(2)–U(1)	123.0(3)
Si(2)–N(2)–U(1)	123.2(2)	C(14)–N(3)–Si(3)	114.4(3)
C(14)–N(3)–U(1)	115.4(3)	Si(3)–N(3)–U(1)	129.0(2)
C(15)–N(4)–C(10)	110.5(4)	C(15)–N(4)–C(5)	112.5(4)
C(10)–N(4)–C(5)	112.8(4)	C(15)–N(4)–U(1)	111.4(3)
C(10)–N(4)–U(1)	105.0(3)	C(5)–N(4)–U(1)	104.3(3)
N(1)–Si(1)–C(1)	110.0(3)	N(1)–Si(1)–C(2)	111.8(2)
C(1)–Si(1)–C(2)	109.2(3)	N(1)–Si(1)–C(3)	110.5(2)
C(1)–Si(1)–C(3)	107.8(3)	C(2)–Si(1)–C(3)	107.4(3)
N(1)–C(4)–C(5)	111.6(4)	N(4)–C(5)–C(4)	110.9(4)
N(2)–Si(2)–C(6)	111.1(2)	N(2)–Si(2)–C(7)	111.4(2)
C(6)–Si(2)–C(7)	108.9(3)	N(2)–Si(2)–C(8)	109.1(2)
C(6)–Si(2)–C(8)	109.5(3)	C(7)–Si(2)–C(8)	106.7(3)
N(2)–C(9)–C(10)	111.7(4)	N(4)–C(10)–C(9)	110.3(4)
N(3)–Si(3)–C(13)	111.0(3)	N(3)–Si(3)–C(12)	111.0(2)
C(13)–Si(3)–C(12)	108.5(3)	N(3)–Si(3)–C(11)	110.8(3)
C(13)–Si(3)–C(11)	108.8(3)	C(12)–Si(3)–C(11)	106.6(3)
N(3)–C(14)–C(15)	109.4(4)	N(4)–C(15)–C(14)	109.3(4)
C(16)–O(1)–C(19)	107.8(4)	C(16)–O(1)–U(1)	121.8(3)
C(19)–O(1)–U(1)	120.6(3)	O(1)–C(16)–C(17)	107.3(4)
C(16)–C(17)–C(18)	102.6(4)	C(19)–C(18)–C(17)	101.3(4)
O(1)–C(19)–C(18)	106.8(5)		

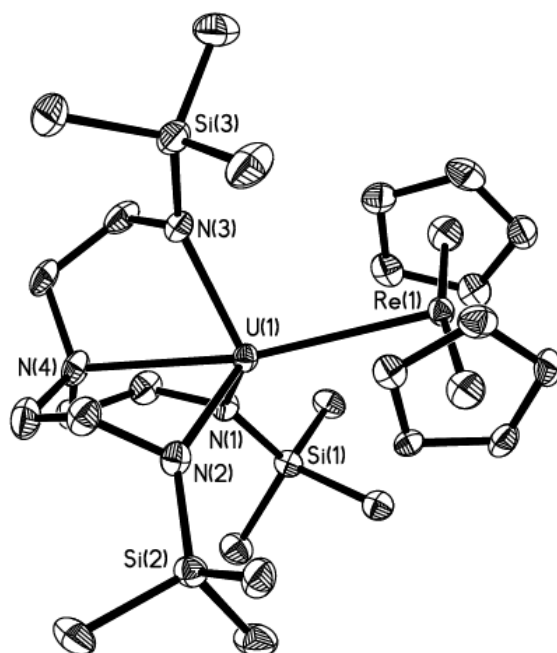
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
U(1)	0.01279(10)	0.01149(10)	0.01013(7)	0.00037(8)	-0.00033(8)	-0.00067(9)
I(1)	0.0316(2)	0.0267(2)	0.01432(16)	0.00458(14)	-0.00225(16)	-0.00342(19)
N(1)	0.021(3)	0.015(2)	0.0124(19)	0.0010(16)	0.0008(18)	-0.001(2)
N(2)	0.016(2)	0.022(2)	0.011(2)	0.0009(17)	-0.0013(18)	-0.001(2)
N(3)	0.013(2)	0.018(2)	0.0125(19)	-0.0005(19)	-0.0018(17)	0.002(2)
N(4)	0.013(2)	0.018(3)	0.017(2)	0.0010(18)	-0.0030(18)	-0.0016(18)
Si(1)	0.0255(10)	0.0127(8)	0.0192(7)	-0.0006(6)	-0.0009(6)	-0.0026(6)
C(1)	0.047(4)	0.025(4)	0.030(3)	-0.006(3)	-0.001(3)	0.013(3)
C(2)	0.048(5)	0.029(4)	0.037(4)	-0.008(3)	0.004(3)	-0.020(3)
C(3)	0.033(4)	0.021(3)	0.021(3)	-0.005(2)	0.000(3)	0.000(3)
C(4)	0.034(4)	0.013(3)	0.021(3)	0.004(2)	-0.006(3)	-0.007(2)
C(5)	0.025(3)	0.020(3)	0.022(3)	0.005(2)	-0.001(2)	0.000(3)
Si(2)	0.0144(8)	0.0205(9)	0.0213(7)	0.0021(7)	0.0025(6)	-0.0013(6)
C(6)	0.019(3)	0.032(4)	0.034(3)	-0.001(3)	-0.001(3)	0.003(3)
C(7)	0.034(4)	0.041(4)	0.032(3)	0.008(3)	0.005(3)	-0.007(4)
C(8)	0.025(4)	0.053(5)	0.033(3)	-0.007(3)	-0.006(3)	0.004(3)
C(9)	0.026(3)	0.027(3)	0.020(3)	-0.003(2)	0.002(3)	0.005(3)
C(10)	0.024(3)	0.024(3)	0.013(2)	-0.003(2)	0.001(2)	0.003(3)
Si(3)	0.0137(8)	0.0298(9)	0.0201(8)	-0.0010(7)	0.0006(6)	0.0019(7)
C(11)	0.048(5)	0.055(5)	0.036(4)	-0.001(3)	-0.003(3)	0.026(4)
C(12)	0.030(4)	0.058(5)	0.021(3)	-0.008(3)	0.002(3)	0.019(4)
C(13)	0.034(5)	0.072(6)	0.063(5)	-0.010(4)	0.017(4)	-0.023(4)
C(14)	0.020(3)	0.031(4)	0.016(3)	0.000(2)	-0.003(2)	-0.003(3)
C(15)	0.032(4)	0.023(4)	0.013(3)	0.000(2)	-0.008(2)	-0.002(3)
O(1)	0.014(2)	0.021(2)	0.0196(19)	-0.0014(15)	0.0007(15)	-0.0004(17)
C(16)	0.026(3)	0.007(3)	0.026(3)	0.001(2)	-0.002(2)	-0.007(2)
C(17)	0.029(3)	0.018(3)	0.031(3)	0.004(3)	0.004(3)	-0.004(3)
C(18)	0.035(4)	0.017(3)	0.034(3)	0.002(3)	-0.001(3)	-0.002(3)
C(19)	0.026(3)	0.020(3)	0.039(3)	-0.004(3)	0.005(3)	0.003(3)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($\text{\AA}^2$) for **3**.

	x	y	z	U(eq)
H(1A)	0.3849	1.2811	0.4330	0.051
H(1B)	0.4039	1.3010	0.4761	0.051
H(1C)	0.3272	1.2102	0.4630	0.051
H(2A)	0.6836	1.1784	0.4450	0.057
H(2B)	0.6364	1.2818	0.4630	0.057
H(2C)	0.6180	1.2577	0.4202	0.057
H(3A)	0.4523	1.0722	0.5128	0.038
H(3B)	0.5400	1.1572	0.5211	0.038
H(3C)	0.5716	1.0467	0.5042	0.038
H(4A)	0.4923	1.1613	0.3836	0.027
H(4B)	0.3795	1.1090	0.3854	0.027
H(5A)	0.4641	1.0436	0.3338	0.027
H(5B)	0.5636	1.0121	0.3580	0.027
H(6A)	0.7843	0.6865	0.4344	0.043
H(6B)	0.8841	0.7483	0.4198	0.043
H(6C)	0.8012	0.7032	0.3910	0.043
H(7A)	0.8120	0.9373	0.3649	0.054
H(7B)	0.8769	0.9684	0.4010	0.054
H(7C)	0.7690	1.0253	0.3922	0.054
H(8A)	0.6916	0.9695	0.4679	0.056
H(8B)	0.8029	0.9181	0.4753	0.056
H(8C)	0.6993	0.8521	0.4822	0.056
H(9A)	0.6336	0.7505	0.3567	0.029
H(9B)	0.6508	0.8716	0.3485	0.029
H(10A)	0.4989	0.8416	0.3199	0.024
H(10B)	0.4601	0.7620	0.3511	0.024
H(11A)	0.1913	1.0941	0.4186	0.069
H(11B)	0.0800	1.0686	0.4361	0.069
H(11C)	0.1122	1.0194	0.3972	0.069
H(12A)	0.2619	0.9118	0.5072	0.054
H(12B)	0.1767	1.0023	0.5054	0.054
H(12C)	0.2916	1.0226	0.4901	0.054
H(13A)	0.0694	0.7993	0.4276	0.084
H(13B)	0.0315	0.8560	0.4646	0.084
H(13C)	0.1182	0.7670	0.4666	0.084
H(14A)	0.1973	0.8457	0.3793	0.027
H(14B)	0.2950	0.7682	0.3798	0.027
H(15A)	0.3198	0.8823	0.3309	0.027
H(15B)	0.2990	0.9810	0.3570	0.027
H(16A)	0.3049	0.6175	0.4206	0.023
H(16B)	0.3199	0.6785	0.4589	0.023
H(17A)	0.3427	0.4814	0.4572	0.031
H(17B)	0.4164	0.5498	0.4838	0.031
H(18A)	0.5401	0.4679	0.4474	0.034
H(18B)	0.4677	0.4740	0.4110	0.034
H(19A)	0.5824	0.6392	0.4445	0.034
H(19B)	0.5668	0.6183	0.4010	0.034



S2.3. Crystal structure of 4, thermal ellipsoids set at 30%, hydrogen atoms omitted for clarity.

S2.4. Crystal Data for 4.

Table 1. Crystal data and structure refinement for 4.

Identification code	4	
Chemical formula	C ₂₅ H ₄₉ N ₄ ReSi ₃ U	
Formula weight	914.18	
Temperature	150(2) K	
Radiation, wavelength	MoK α , 0.71073 Å	
Crystal system, space group	Monoclinic, P2 ₁ /c	
Unit cell parameters	a = 15.805(2) Å	$\alpha = 90^\circ$
	b = 10.2483(12) Å	$\beta = 100.734(2)^\circ$
	c = 19.910(3) Å	$\gamma = 90^\circ$
Cell volume	3168.5(7) Å ³	
Z	4	
Calculated density	1.916 g/cm ³	
Absorption coefficient μ	9.055 mm ⁻¹	
F(000)	1744	
Crystal colour and size	Red, 0.27 × 0.26 × 0.05 mm ³	
Reflections for cell refinement	5311 (θ range 2.38 to 27.28°)	
Data collection method	Bruker SMART 1000 CCD diffractometer	
	ω rotation with narrow frames	
θ range for data collection	2.08 to 27.53°	
Index ranges	h -18 to 20, k -13 to 12, l -23 to 25	
Completeness to $\theta = 26.00^\circ$	99.6 %	
Intensity decay	0%	
Reflections collected	19270	
Independent reflections	7190 ($R_{\text{int}} = 0.0584$)	
Reflections with $F^2 > 2\sigma$	5416	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.12 and 0.64	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0361, 0.8064	
Data / restraints / parameters	7190 / 0 / 316	
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0396, wR2 = 0.0857	
R indices (all data)	R1 = 0.0632, wR2 = 0.0948	
Goodness-of-fit on F^2	1.019	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	2.675 and -1.293 e Å ⁻³	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for **4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
U(1)	0.229417(17)	0.76525(2)	0.389812(14)	0.02082(8)
N(1)	0.1122(4)	0.8738(6)	0.3316(3)	0.0266(14)
Si(1)	0.01390(14)	0.9024(2)	0.35544(11)	0.0256(4)
C(1)	0.0199(5)	0.8548(7)	0.4467(4)	0.0294(17)
C(2)	-0.0197(6)	1.0771(8)	0.3462(4)	0.037(2)
C(3)	-0.0755(5)	0.8059(8)	0.3028(4)	0.0331(18)
C(4)	0.1196(5)	0.9359(8)	0.2656(4)	0.0349(19)
C(5)	0.2009(5)	1.0215(7)	0.2750(4)	0.0339(19)
N(2)	0.3199(4)	0.9175(6)	0.4470(3)	0.0271(14)
Si(2)	0.32995(14)	1.0161(2)	0.51837(11)	0.0280(5)
C(6)	0.2212(6)	1.0668(9)	0.5358(5)	0.046(2)
C(7)	0.3911(5)	0.9339(8)	0.5966(4)	0.036(2)
C(8)	0.3883(6)	1.1721(8)	0.5078(5)	0.043(2)
C(9)	0.3875(5)	0.9395(8)	0.4051(4)	0.0345(19)
C(10)	0.3502(6)	1.0154(9)	0.3411(4)	0.044(2)
N(3)	0.3052(4)	0.6654(6)	0.3202(3)	0.0288(15)
Si(3)	0.39060(16)	0.5563(2)	0.32723(12)	0.0346(5)
C(11)	0.3570(7)	0.4018(9)	0.2781(6)	0.057(3)
C(12)	0.4285(6)	0.5147(10)	0.4187(5)	0.053(3)
C(13)	0.4838(6)	0.6274(9)	0.2938(5)	0.047(2)
C(14)	0.2731(6)	0.7177(8)	0.2512(4)	0.036(2)
C(15)	0.3039(6)	0.8576(8)	0.2470(4)	0.035(2)
N(4)	0.2767(4)	0.9365(7)	0.3020(3)	0.0303(15)
Re(1)	0.17393(2)	0.53576(3)	0.468796(15)	0.02294(9)
C(16)	0.1632(5)	0.6247(8)	0.5680(4)	0.0300(18)
C(17)	0.2187(5)	0.7047(7)	0.5366(4)	0.0253(16)
C(18)	0.2922(5)	0.6311(7)	0.5288(4)	0.0279(17)
C(19)	0.2813(6)	0.5024(8)	0.5541(4)	0.0342(19)
C(20)	0.2039(6)	0.4995(8)	0.5803(4)	0.036(2)
C(21)	0.1566(6)	0.3561(8)	0.4055(4)	0.040(2)
C(22)	0.0827(6)	0.3756(8)	0.4347(4)	0.035(2)
C(23)	0.0440(5)	0.4941(8)	0.4118(4)	0.0332(18)
C(24)	0.0917(5)	0.5482(8)	0.3643(4)	0.0314(18)
C(25)	0.1620(6)	0.4632(8)	0.3602(4)	0.0338(19)

Table 3. Bond lengths [Å] and angles [°] for **4**.

U(1)–N(3)	2.241(6)	U(1)–N(2)	2.274(6)
U(1)–N(1)	2.282(6)	U(1)–N(4)	2.680(6)
U(1)–C(14)	3.007(7)	U(1)–C(17)	3.023(7)
U(1)–C(9)	3.040(8)	U(1)–Re(1)	3.0475(4)
N(1)–C(4)	1.485(9)	N(1)–Si(1)	1.732(6)
Si(1)–C(1)	1.866(8)	Si(1)–C(2)	1.867(8)
Si(1)–C(3)	1.876(8)	C(4)–C(5)	1.539(11)
C(5)–N(4)	1.498(10)	N(2)–C(9)	1.491(9)
N(2)–Si(2)	1.726(7)	Si(2)–C(7)	1.873(9)
Si(2)–C(8)	1.877(8)	Si(2)–C(6)	1.889(8)
C(9)–C(10)	1.515(12)	C(10)–N(4)	1.508(11)
N(3)–C(14)	1.473(10)	N(3)–Si(3)	1.739(7)
Si(3)–C(12)	1.858(9)	Si(3)–C(13)	1.874(8)
Si(3)–C(11)	1.884(10)	C(14)–C(15)	1.521(12)
C(15)–N(4)	1.487(9)	Re(1)–C(19)	2.192(9)
Re(1)–C(23)	2.195(8)	Re(1)–C(22)	2.207(8)
Re(1)–C(16)	2.210(7)	Re(1)–C(20)	2.214(8)
Re(1)–C(21)	2.219(8)	Re(1)–C(17)	2.228(7)
Re(1)–C(24)	2.242(8)	Re(1)–C(18)	2.246(8)
Re(1)–C(25)	2.260(8)	C(16)–C(17)	1.427(10)
C(16)–C(20)	1.436(11)	C(17)–C(18)	1.419(10)
C(18)–C(19)	1.434(11)	C(19)–C(20)	1.417(11)
C(21)–C(22)	1.413(12)	C(21)–C(25)	1.432(11)
C(22)–C(23)	1.397(11)	C(23)–C(24)	1.426(11)
C(24)–C(25)	1.426(11)		
N(3)–U(1)–N(2)	105.4(2)	N(3)–U(1)–N(1)	112.6(2)
N(2)–U(1)–N(1)	107.1(2)	N(3)–U(1)–N(4)	69.5(2)
N(2)–U(1)–N(4)	69.6(2)	N(1)–U(1)–N(4)	69.4(2)
N(3)–U(1)–C(14)	28.1(2)	N(2)–U(1)–C(14)	109.9(2)
N(1)–U(1)–C(14)	85.2(2)	N(4)–U(1)–C(14)	50.8(2)
N(3)–U(1)–C(17)	129.6(2)	N(2)–U(1)–C(17)	78.5(2)
N(1)–U(1)–C(17)	113.8(2)	N(4)–U(1)–C(17)	146.9(2)
C(14)–U(1)–C(17)	156.6(2)	N(3)–U(1)–C(9)	78.8(2)
N(2)–U(1)–C(9)	28.2(2)	N(1)–U(1)–C(9)	109.8(2)
N(4)–U(1)–C(9)	50.0(2)	C(14)–U(1)–C(9)	82.1(2)
C(17)–U(1)–C(9)	102.5(2)	N(3)–U(1)–Re(1)	101.83(16)
N(2)–U(1)–Re(1)	119.06(15)	N(1)–U(1)–Re(1)	110.72(15)
N(4)–U(1)–Re(1)	169.74(14)	C(14)–U(1)–Re(1)	119.08(17)
C(17)–U(1)–Re(1)	43.07(14)	C(9)–U(1)–Re(1)	135.38(16)
C(4)–N(1)–Si(1)	113.1(5)	C(4)–N(1)–U(1)	117.9(5)
Si(1)–N(1)–U(1)	128.9(3)	N(1)–Si(1)–C(1)	109.6(3)
N(1)–Si(1)–C(2)	112.9(3)	C(1)–Si(1)–C(2)	108.0(4)
N(1)–Si(1)–C(3)	112.3(3)	C(1)–Si(1)–C(3)	107.6(4)
C(2)–Si(1)–C(3)	106.2(4)	N(1)–C(4)–C(5)	109.8(7)
N(4)–C(5)–C(4)	107.8(6)	C(9)–N(2)–Si(2)	114.0(5)
C(9)–N(2)–U(1)	105.8(5)	Si(2)–N(2)–U(1)	140.1(3)
N(2)–Si(2)–C(7)	112.1(4)	N(2)–Si(2)–C(8)	112.2(4)
C(7)–Si(2)–C(8)	106.8(4)	N(2)–Si(2)–C(6)	111.4(4)
C(7)–Si(2)–C(6)	108.5(4)	C(8)–Si(2)–C(6)	105.6(4)
N(2)–C(9)–C(10)	109.9(7)	N(2)–C(9)–U(1)	46.0(3)
C(10)–C(9)–U(1)	91.9(5)	N(4)–C(10)–C(9)	107.5(6)
C(14)–N(3)–Si(3)	115.9(5)	C(14)–N(3)–U(1)	106.3(5)

Si(3)–N(3)–U(1)	137.7(4)	N(3)–Si(3)–C(12)	109.3(4)
N(3)–Si(3)–C(13)	111.8(4)	C(12)–Si(3)–C(13)	107.8(5)
N(3)–Si(3)–C(11)	111.0(4)	C(12)–Si(3)–C(11)	109.0(5)
C(13)–Si(3)–C(11)	107.8(4)	N(3)–C(14)–C(15)	109.7(7)
N(3)–C(14)–U(1)	45.7(3)	C(15)–C(14)–U(1)	91.6(4)
N(4)–C(15)–C(14)	109.4(6)	C(15)–N(4)–C(5)	111.9(6)
C(15)–N(4)–C(10)	111.8(6)	C(5)–N(4)–C(10)	111.1(7)
C(15)–N(4)–U(1)	106.2(4)	C(5)–N(4)–U(1)	108.3(4)
C(10)–N(4)–U(1)	107.2(4)	C(19)–Re(1)–C(23)	152.2(3)
C(19)–Re(1)–C(22)	119.3(3)	C(23)–Re(1)–C(22)	37.0(3)
C(19)–Re(1)–C(16)	63.2(3)	C(23)–Re(1)–C(16)	108.8(3)
C(22)–Re(1)–C(16)	115.3(3)	C(19)–Re(1)–C(20)	37.5(3)
C(23)–Re(1)–C(20)	119.4(3)	C(22)–Re(1)–C(20)	100.9(3)
C(16)–Re(1)–C(20)	37.9(3)	C(19)–Re(1)–C(21)	107.8(3)
C(23)–Re(1)–C(21)	62.6(3)	C(22)–Re(1)–C(21)	37.2(3)
C(16)–Re(1)–C(21)	145.9(3)	C(20)–Re(1)–C(21)	114.3(3)
C(19)–Re(1)–C(17)	62.6(3)	C(23)–Re(1)–C(17)	128.7(3)
C(22)–Re(1)–C(17)	151.6(3)	C(16)–Re(1)–C(17)	37.5(3)
C(20)–Re(1)–C(17)	62.5(3)	C(21)–Re(1)–C(17)	168.7(3)
C(19)–Re(1)–C(24)	163.5(3)	C(23)–Re(1)–C(24)	37.5(3)
C(22)–Re(1)–C(24)	61.6(3)	C(16)–Re(1)–C(24)	132.7(3)
C(20)–Re(1)–C(24)	156.8(3)	C(21)–Re(1)–C(24)	62.0(3)
C(17)–Re(1)–C(24)	125.6(3)	C(19)–Re(1)–C(18)	37.7(3)
C(23)–Re(1)–C(18)	164.9(3)	C(22)–Re(1)–C(18)	156.7(3)
C(16)–Re(1)–C(18)	62.6(3)	C(20)–Re(1)–C(18)	62.5(3)
C(21)–Re(1)–C(18)	131.7(3)	C(17)–Re(1)–C(18)	37.0(3)
C(24)–Re(1)–C(18)	138.6(3)	C(19)–Re(1)–C(25)	127.2(3)
C(23)–Re(1)–C(25)	62.5(3)	C(22)–Re(1)–C(25)	61.8(3)
C(16)–Re(1)–C(25)	169.6(3)	C(20)–Re(1)–C(25)	150.2(3)
C(21)–Re(1)–C(25)	37.3(3)	C(17)–Re(1)–C(25)	142.7(3)
C(24)–Re(1)–C(25)	36.9(3)	C(18)–Re(1)–C(25)	124.4(3)
C(19)–Re(1)–U(1)	105.3(2)	C(23)–Re(1)–U(1)	102.4(2)
C(22)–Re(1)–U(1)	130.5(2)	C(16)–Re(1)–U(1)	102.7(2)
C(20)–Re(1)–U(1)	128.2(2)	C(21)–Re(1)–U(1)	111.3(2)
C(17)–Re(1)–U(1)	67.88(18)	C(24)–Re(1)–U(1)	69.5(2)
C(18)–Re(1)–U(1)	69.37(19)	C(25)–Re(1)–U(1)	75.0(2)
C(17)–C(16)–C(20)	107.2(7)	C(17)–C(16)–Re(1)	71.9(4)
C(20)–C(16)–Re(1)	71.2(4)	C(18)–C(17)–C(16)	109.0(7)
C(18)–C(17)–Re(1)	72.2(4)	C(16)–C(17)–Re(1)	70.5(4)
C(18)–C(17)–U(1)	79.0(4)	C(16)–C(17)–U(1)	133.7(5)
Re(1)–C(17)–U(1)	69.06(18)	C(17)–C(18)–C(19)	107.2(7)
C(17)–C(18)–Re(1)	70.8(4)	C(19)–C(18)–Re(1)	69.1(5)
C(20)–C(19)–C(18)	108.5(7)	C(20)–C(19)–Re(1)	72.1(5)
C(18)–C(19)–Re(1)	73.2(5)	C(19)–C(20)–C(16)	108.0(7)
C(19)–C(20)–Re(1)	70.4(4)	C(16)–C(20)–Re(1)	70.9(4)
C(22)–C(21)–C(25)	107.5(8)	C(22)–C(21)–Re(1)	70.9(5)
C(25)–C(21)–Re(1)	72.9(4)	C(23)–C(22)–C(21)	109.5(7)
C(23)–C(22)–Re(1)	71.0(5)	C(21)–C(22)–Re(1)	71.8(5)
C(22)–C(23)–C(24)	107.5(7)	C(22)–C(23)–Re(1)	72.0(5)
C(24)–C(23)–Re(1)	73.1(5)	C(25)–C(24)–C(23)	108.3(7)
C(25)–C(24)–Re(1)	72.2(5)	C(23)–C(24)–Re(1)	69.5(5)
C(24)–C(25)–C(21)	107.1(7)	C(24)–C(25)–Re(1)	70.8(4)
C(21)–C(25)–Re(1)	69.8(4)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
U(1)	0.02119(15)	0.02348(14)	0.01732(14)	0.00176(11)	0.00241(10)	-0.00137(11)
N(1)	0.023(4)	0.028(3)	0.029(4)	0.005(3)	0.005(3)	0.004(3)
Si(1)	0.0233(11)	0.0248(11)	0.0274(11)	-0.0009(9)	0.0017(9)	0.0010(8)
C(1)	0.024(4)	0.030(4)	0.034(5)	0.000(4)	0.004(3)	0.003(3)
C(2)	0.037(5)	0.032(4)	0.043(5)	0.003(4)	0.005(4)	0.007(4)
C(3)	0.029(5)	0.030(4)	0.037(5)	-0.003(4)	-0.002(4)	-0.002(3)
C(4)	0.035(5)	0.041(5)	0.027(4)	0.008(4)	0.003(4)	0.010(4)
C(5)	0.045(5)	0.025(4)	0.034(5)	0.006(3)	0.012(4)	0.004(4)
N(2)	0.025(4)	0.033(3)	0.022(3)	0.003(3)	0.002(3)	-0.001(3)
Si(2)	0.0244(12)	0.0285(11)	0.0302(12)	-0.0046(9)	0.0028(9)	-0.0034(9)
C(6)	0.036(5)	0.038(5)	0.067(7)	-0.017(5)	0.017(5)	0.000(4)
C(7)	0.034(5)	0.046(5)	0.030(4)	-0.006(4)	0.008(4)	-0.016(4)
C(8)	0.044(6)	0.025(4)	0.059(6)	-0.003(4)	0.007(5)	-0.002(4)
C(9)	0.026(4)	0.045(5)	0.032(5)	-0.003(4)	0.004(3)	-0.007(4)
C(10)	0.052(6)	0.048(5)	0.037(5)	0.006(4)	0.019(4)	-0.009(5)
N(3)	0.032(4)	0.032(4)	0.025(3)	0.001(3)	0.011(3)	0.000(3)
Si(3)	0.0364(14)	0.0375(13)	0.0329(13)	0.0030(11)	0.0146(10)	0.0053(10)
C(11)	0.060(7)	0.039(5)	0.079(8)	-0.011(5)	0.027(6)	0.009(5)
C(12)	0.051(6)	0.069(7)	0.042(6)	0.016(5)	0.016(5)	0.031(5)
C(13)	0.036(5)	0.051(6)	0.059(6)	0.001(5)	0.021(5)	-0.002(4)
C(14)	0.040(5)	0.049(5)	0.021(4)	0.002(4)	0.011(4)	0.011(4)
C(15)	0.041(5)	0.048(5)	0.019(4)	0.009(4)	0.014(4)	0.004(4)
N(4)	0.033(4)	0.041(4)	0.018(3)	0.010(3)	0.007(3)	0.003(3)
Re(1)	0.02665(17)	0.02222(16)	0.01956(15)	0.00055(11)	0.00332(11)	-0.00354(12)
C(16)	0.032(5)	0.040(5)	0.019(4)	-0.002(3)	0.008(3)	-0.004(4)
C(17)	0.034(5)	0.025(4)	0.017(4)	-0.004(3)	0.006(3)	-0.003(3)
C(18)	0.027(4)	0.029(4)	0.026(4)	0.000(3)	-0.001(3)	-0.002(3)
C(19)	0.041(5)	0.033(4)	0.027(4)	-0.005(4)	0.001(4)	0.002(4)
C(20)	0.059(6)	0.033(4)	0.017(4)	0.008(3)	0.007(4)	-0.004(4)
C(21)	0.046(6)	0.028(4)	0.042(5)	-0.009(4)	-0.001(4)	-0.005(4)
C(22)	0.051(6)	0.031(4)	0.023(4)	-0.002(3)	0.004(4)	-0.009(4)
C(23)	0.027(4)	0.036(5)	0.035(5)	0.000(4)	-0.001(3)	-0.003(4)
C(24)	0.032(5)	0.032(4)	0.026(4)	-0.004(3)	-0.007(3)	-0.011(3)
C(25)	0.041(5)	0.037(5)	0.023(4)	-0.010(4)	0.003(4)	-0.007(4)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($\text{\AA}^2$) for **4**.

	x	y	z	U(eq)
H(1A)	0.0630	0.9088	0.4759	0.044
H(1B)	0.0364	0.7627	0.4526	0.044
H(1C)	-0.0364	0.8677	0.4595	0.044
H(2A)	0.0300	1.1331	0.3629	0.056
H(2B)	-0.0648	1.0935	0.3729	0.056
H(2C)	-0.0419	1.0964	0.2979	0.056
H(3A)	-0.0764	0.8221	0.2542	0.050
H(3B)	-0.1306	0.8326	0.3143	0.050
H(3C)	-0.0662	0.7128	0.3126	0.050
H(4A)	0.0681	0.9901	0.2492	0.042
H(4B)	0.1229	0.8676	0.2309	0.042
H(5A)	0.2075	1.0603	0.2307	0.041
H(5B)	0.1966	1.0931	0.3075	0.041
H(6A)	0.1990	0.9987	0.5625	0.069
H(6B)	0.1812	1.0792	0.4924	0.069
H(6C)	0.2269	1.1487	0.5617	0.069
H(7A)	0.4439	0.8954	0.5862	0.055
H(7B)	0.3554	0.8651	0.6112	0.055
H(7C)	0.4059	0.9981	0.6334	0.055
H(8A)	0.4463	1.1521	0.5001	0.065
H(8B)	0.3922	1.2251	0.5492	0.065
H(8C)	0.3567	1.2206	0.4685	0.065
H(9A)	0.4097	0.8545	0.3923	0.041
H(9B)	0.4361	0.9887	0.4321	0.041
H(10A)	0.3292	1.1015	0.3534	0.053
H(10B)	0.3948	1.0294	0.3129	0.053
H(11A)	0.3101	0.3603	0.2962	0.086
H(11B)	0.4062	0.3421	0.2828	0.086
H(11C)	0.3373	0.4229	0.2297	0.086
H(12A)	0.3811	0.4756	0.4373	0.080
H(12B)	0.4482	0.5941	0.4444	0.080
H(12C)	0.4763	0.4524	0.4228	0.080
H(13A)	0.5020	0.7089	0.3181	0.070
H(13B)	0.4665	0.6453	0.2448	0.070
H(13C)	0.5318	0.5653	0.3010	0.070
H(14A)	0.2094	0.7151	0.2412	0.043
H(14B)	0.2946	0.6634	0.2168	0.043
H(15A)	0.3674	0.8593	0.2522	0.042
H(15B)	0.2790	0.8950	0.2018	0.042
H(16A)	0.1088	0.6530	0.5825	0.036
H(17A)	0.2086	0.7987	0.5241	0.030
H(18A)	0.3429	0.6636	0.5102	0.034
H(19A)	0.3241	0.4298	0.5573	0.041
H(20A)	0.1826	0.4246	0.6047	0.043
H(21A)	0.1949	0.2776	0.4117	0.048
H(22A)	0.0602	0.3127	0.4655	0.042
H(23A)	-0.0110	0.5291	0.4224	0.040
H(24A)	0.0770	0.6299	0.3372	0.038
H(25A)	0.2054	0.4744	0.3300	0.041

S3. Computational Details

S3.1. General Methods and Discussion

Unrestricted geometry optimizations were performed for a model of **4** using coordinates derived from the X-ray crystal structure of **4**. The coordinate frame used for the calculations places the U atom at the origin, the z axis along the U-Re bond with x axis in the plane defined by the N(2), U and Re atoms. No constraints were imposed on the structures during the geometry optimizations. The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2007.01.^{1,2} The DFT geometry optimizations employed Slater type orbital (STO) triple- ζ -plus polarization 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.³ was used in all of the calculations. Gradient corrections were performed using the functionals of Becke⁴ and Perdew.⁵ The energy decomposition analysis (EDA) routine requires fragment files from restricted DFT calculations and therefore we used the FRAGOCCUPATIONS keyword to treat the $[(\text{Tren}^{\text{TMS}})\text{U}]^+$ fragment as if it were unrestricted. It has been recognized that the treatment of fragments in this way is not self-consistent, however it has been shown that this is a fair approximation that can provide significant insight into the chemical bonding between fragments.⁶ AOMIX⁷ was used to calculate Mayer bond orders and the program MOLEKEL⁸ was used to prepare the three-dimensional plot of the electron density.

Table 1 compares the structural data calculated for **4** with those of **4** obtained by X-ray crystallography. The calculated U(1)–Re(1) distance is *ca.* 0.01 Å longer, the average U(1)-

N(amide) distances are 0.04 Å longer and the U(1)-N(4) distance is 0.09 Å longer when compared to those of the experimental structure. The calculation reproduces the angles within the coordination sphere about the U(1) centre to within *ca.* 1° of those determined by X-ray crystallography. Thus, given the close similarities between the calculated and experimental geometries we conclude that the DFT calculations of **4** provide a reasonable, qualitative description of the electronic structure of this centre. Furthermore, analysis of calculations run at TZP BPE, and TZ2P VWN levels were in close agreement with negligible variation with respect to geometry optimization, breakdown of molecular orbitals, and energies.

Table 1 Selected bond lengths (Å) and angles (°) for **4** derived from X-ray crystallography and by DFT calculations.

	Exptl 4	Calc 4		Exptl 4	Calc 4
U(1)-Re(1)	3.0475(4)	3.062	U(1)-N(3)	2.241(6)	2.292
U(1)-N(1)	2.282(6)	2.322	U(1)-N(4)	2.680(6)	2.766
U(1)-N(2)	2.274(6)	2.307			
N(2)-U(1)-N(1)	107.1(2)	106.0	N(4)-U(1)-N(2)	69.6(2)	68.6
N(3)-U(1)-N(1)	112.6(2)	112.4	Re(1)-U(1)-N(2)	119.06(15)	120.3
N(4)-U(1)-N(1)	69.4(2)	68.6	N(4)-U(1)-N(3)	69.5(2)	68.3
Re(1)-U(1)-N(1)	110.72(15)	111.7	Re(1)-U(1)-N(3)	101.83(16)	102.7
N(3)-U(1)-N(2)	105.4(2)	103.9	Re(1)-U(1)-N(4)	169.74(14)	169.3

The results of a Mulliken population analysis are given in Table 2. The spin density on the U(1) atom is slightly above that for a formal U(IV) 5f² centre and this, together with the negative spin densities across the N and Re(1) atoms within **4** is consistent with spin polarization that accompanies charge donation from the ligands. A spin density lower than 2 for U(1) would indicate metal to ligand charge transfer so we can effectively rule out π -type back donation in **4**. The Mulliken charge is considerably less than +4 expected for a formal U(IV) centre indicating that there is significant charge donation from the ligands within the co-ordination sphere of the U(1) centre. The Mulliken charge at the Re(1) centre in **4** (-

0.0634, Table 2) is considerably lower than that for Re(1) centre (0.2650) in the [Cp₂Re]⁺ fragment at the geometry of this unit in **4**, consistent with charge donation by the [Cp₂Re]⁺ fragment to the [(Tren^{SiMe₃})U]⁺ [Tren^{SiMe₃} = N(CH₂CH₂NSiMe₃)₃] fragment

Table 2 Mulliken Population Analysis

Atom	Mulliken Charge	Spin Density	Atom	Mulliken Charge	Spin Density
U(1)	2.2041	2.2710	N(3)	-0.9781	-0.0414
N(1)	-0.9683	-0.0437	N(4)	-0.5818	-0.0172
N(2)	-0.9707	-0.0594	Re(1)	-0.0634	-0.1175

The Mayer bond orders for the bonds within the co-ordination sphere of U(1) reveal a U(1)-Re(1) bond order (0.896, Table 3) that is larger than those of the U(1)-N(1), U(1)-N(2) and U(1)-N(3) bonds (average 0.732) and which is significantly greater than that for U(1)-N(4) (0.241, Table 3) that lies trans to the U(1)-Re(1) bond.

Table 3 Mayer bond orders for the bonds in the co-ordination sphere about U(1) in **4**.

Bond	Mayer Bond Order	Bond	Mayer Bond Order
U(1)-Re(1)	0.896	U(1)-N(3)	0.687
U(1)-N(1)	0.755	U(1)-N(4)	0.241
U(1)-N(2)	0.753		

We examined the nature of the U(1)-Re(1) interaction in **4** using the energy decomposition analysis (EDA) that is incorporated within the ADF code. In using this approach, the bonding energy ΔE_{bond} between two fragments is decomposed into $\Delta E_{\text{bond}} = \Delta E_{\text{steric}} + \Delta E_{\text{oi}}$, where ΔE_{steric} is the steric interaction energy between the two fragments in geometries that are identical to those in the parent molecule and ΔE_{oi} is the orbital contribution to the bonding energy. ΔE_{steric} comprises the destabilizing repulsive interactions between occupied MOs (ΔE_{Pauli}) and the classical electrostatic interaction (ΔE_{elstat}) between the fragments; ΔE_{oi} accounts for electron pair bonding, charge transfer, and orbital polarization. In order to

perform the EDA analysis we constructed $[(\text{Tren}^{\text{TMS}})\text{U}]^+$ [$\text{Tren}^{\text{TMS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3$] and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}]^-$ fragments in identical geometries to those in complex **4** noting the requirement for restricted calculations on fragments. The results of the EDA analysis for the U(1)-Re(1) interaction in **4** are shown in Table 4 and reveal that while there is a strong electrostatic contribution to the U(1)-Re(1) interaction there is also a significant orbital contribution to the U(1)-Re(1) bond. Taken as percentages of the total attractive interaction, the electrostatic and orbital interactions contribute 68 and 32%, respectively. The vacant orbital which corresponds to the anti-bonding partner of the occupied weak π -bonding orbital (215a) was identified as orbital 232a.

Table 4 Energy Decomposition Analysis (EDA) for the U(1)-Re(1) interaction in **4**.

Term	Energy /kJ mol ⁻¹
ΔE_{Pauli}	654.84
ΔE_{elstat}	-827.63
$\Delta E_{\text{steric}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}}$	-172.79
ΔE_{oi}	-388.52
ΔE_{bond}	-561.31

S3.2. Geometry Optimized Coordinates for **4**

```

U 0.0000 0.0000 0.0000
H 5.1149 1.6351 -2.9759
H 4.5107 0.0226 -3.3791
H 5.7479 0.8372 -0.1910
H 3.5231 1.4601 -3.7385
H 5.0532 -0.7907 -0.3728
H 3.9803 3.3822 -1.1256
H 4.5030 0.2663 0.9465
H 2.8389 -1.3116 -2.6712
H 1.3148 0.3672 -3.7295
H 3.0717 2.9338 0.3178
H 0.8441 -1.2989 -4.1401
H 2.2243 3.1420 -1.2354
H 1.4744 -1.9840 -1.7937
H 0.6582 -4.4515 -2.1276
H 1.8303 -3.4853 0.5763
H -0.2088 1.6954 -3.3410
H -0.0520 -5.8348 -1.2693

```

H -0.7735 -2.3150 -3.2147
H -0.2606 4.5468 -2.1163
H 1.0435 -4.8134 1.4491
H -1.5489 0.8369 -4.1582
H 0.7853 3.8499 0.7768
H -1.0761 -4.8167 -2.2960
H 0.7553 -3.1256 1.9545
H -2.1281 -1.2312 -3.6107
H -1.1285 5.7034 -1.0855
H -2.0190 4.7627 -2.2906
H -0.5081 4.6350 1.7020
H -2.3759 2.4913 -2.5538
H -0.2103 2.8890 1.9088
H -2.6062 -2.7233 -1.6559
H -2.8383 0.8898 -2.0117
H -2.6792 -1.0412 -1.1935
H -1.9074 -5.5573 1.0066
H -3.0096 -4.3998 0.2373
H -2.2706 -4.0126 1.8036
H -3.3874 4.6910 0.7455
H -3.9906 3.3865 -0.2968
H -3.4230 3.0182 1.3441
C 4.2068 1.0109 -3.0015
C 4.8167 0.2527 -0.1085
C 3.1431 2.7629 -0.7650
C 1.8709 -1.0441 -2.2143
C 0.9196 -0.5683 -3.3133
C -0.2358 -4.7942 -1.5837
C -1.0240 0.9763 -3.1904
C 0.9009 -3.7842 1.0845
C -1.3497 -1.4518 -2.8560
C -1.1965 4.7110 -1.5604
C -0.2326 3.7100 1.1710
C -1.9629 1.5552 -2.1366
C -1.9688 -1.8323 -1.5074
C -2.0839 -4.4842 0.8281
C -3.2281 3.6390 0.4571
Si 3.4711 0.9520 -1.2433
Si -0.5936 -3.7062 -0.0631
Si -1.4685 3.3860 -0.2186
N 1.9906 0.0000 -1.1651
N -0.4194 -0.2932 -2.7199
N -0.9108 -2.0424 -0.5022
N -1.2460 1.7615 -0.8581
Re 0.0000 0.0000 3.0620
H 2.3091 -1.2299 1.4149
H 2.0519 1.4883 1.3250
H 2.0436 -1.9984 4.0089
H 1.6505 2.3816 3.8394
H 1.6804 0.2352 5.5009

H -2.1196 -1.7801 1.7351
H -2.3869 0.8933 1.3452
H -1.5927 -2.1966 4.3681
H -2.0093 2.1361 3.7305
H -1.5285 0.2218 5.5914
C 2.0368 -0.5860 2.2497
C 1.8999 0.8540 2.1979
C 1.9363 -0.9874 3.6298
C 1.7275 1.3406 3.5435
C 1.7778 0.2034 4.4193
C -1.9798 -1.0168 2.4918
C -2.0947 0.4056 2.2774
C -1.7099 -1.2330 3.8830
C -1.9156 1.0715 3.5452
C -1.6972 0.0508 4.5319

Energy = -468.05634906 eV

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