**Supporting Information**

**X-ray Data Collection, Structure Solution, and Refinement of [$\eta^5$:$\kappa^1$-$C_5Me_4SiMe_2CH_2C(^tBu)N]_2U$, 2.** A red crystal of approximate dimensions 0.07 x 0.14 x 0.52 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0510 and Goof = 1.028 for 370 variables refined against 8250 data (0.76Å), R1 = 0.0202 for those 7297 data with $I > 2.0\sigma(I)$.

**X-ray Data Collection, Structure Solution, and Refinement of $(C_5Me_4SiMe_3)_2U(C{\equiv}CPh)_2$, 4.** A red crystal of approximate dimensions 0.04 x 0.13 x 0.26 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned

and later determined to be correct. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0473 and Goof = 1.048 for 402 variables refined against 8689 data (0.76Å), R1 = 0.0191 for those 8094 data with $I > 2.0\sigma(I)$.

**Table 1.** X-ray Data Collection Parameters for $[\eta^5:\kappa^1\text{-}C_5Me_4SiMe_2CH_2C(^tBu)N]_2U$, **2** and $(C_5Me_4SiMe_3)_2U(C{\equiv}CPh)_2$, **4**.

| Empirical Formula | **2** | **4** |
|---|---|---|
| | $C_{34}H_{58}N_2Si_2U$ | $C_{40}H_{52}Si_2U$ |
| Formula weight | 789.03 | 827.03 |
| Temperature (K) | 153(2) K | 153(2) K |
| Crystal system | Monoclinic | Triclinic |
| Space Group | $P2_1/c$ | $P\bar{1}$ |
| a (Å) | 14.345(4) | 9.9155(4) |
| b (Å) | 14.466(4) | 10.5054(4) |
| c (Å) | 17.331(5) | 18.6237(7) |
| α (deg) | 90 | 89.5796(5) |
| β (deg) | 98.946(3) | 84.8150(5) |
| γ (deg) | 90 | 74.9561(5) |
| Volume ($Å^3$) | 3552.8(16) | 1865.55(13) |
| Z | 4 | 2 |
| $\rho_{calcd}$ ($Mg/m^3$) | 1.475 | 1.472 |
| μ ($mm^{-1}$) | 4.660 | 4.440 |

| | | |
|---|---|---|
| R1[a] (I □ 2.0σ(I)) | 0.0202 | 0.0191 |
| wR2[b] (all data) | 0.0510 | 0.0473 |

**Table 2.** Selected bond distances (Å) and angles (deg) for $[\eta^5:\kappa^1\text{-}C_5Me_4SiMe_2CH_2C(^tBu)N]_2U$, **2**.

| Bond Distances and Angles | **2** |
|---|---|
| U1-(C1-C5)$_{centroid}$ | 2.473 |
| U1-(C18-C22)$_{centroid}$ | 2.482 |
| U1-N1 | 2.173(2) |
| U1-N2 | 2.173(2) |
| N1-C13 | 1.264(3) |
| N2-C30 | 1.268(3) |
| (C1-C5)$_{centroid}$-U1-(C18-C22)$_{centroid}$ | 139.7 |
| (C1-C5)$_{centroid}$-U1-N1 | 100.7 |
| U1-N1-C13 | 152.64(2) |
| U1-N2-C30 | 152.47(2) |
| N1-U1-N2 | 110.06(7) |

**Table 3.** Selected bond distances (Å) and angles (deg) for $(C_5Me_4SiMe_3)_2U(C{\equiv}CPh)_2$, **4**.

| Bond Distances and Angles | **4** |
|---|---|
| U1-(C1-C5)$_{centroid}$ | 2.448 |
| U1-(C13-C17)$_{centroid}$ | 2.451 |
| U1-C25 | 2.390(2) |
| U1-C33 | 2.369(3) |

| | |
|---|---|
| C25-C26 | 1.214(3) |
| $(C1\text{-}C5)_{centroid}$-U1-$(C13\text{-}C17)_{centroid}$ | 143.8 |
| $(C1\text{-}C5)_{centroid}$-U1-C25 | 104.0 |
| C25-U1-C33 | 101.39(9) |

**References**


1. APEX2 Version 2.2-0 Bruker AXS, Inc.; Madison, WI 2007.
2. SAINT Version 7.46a, Bruker AXS, Inc.; Madison, WI 2007.
3. Sheldrick, G. M. SADABS, Version 2008/1, Bruker AXS, Inc.; Madison, WI 2008.
4. Sheldrick, G. M. SHELXTL, Version 6.12, Bruker AXS, Inc.; Madison, WI 2001.
5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.


**Definitions:**

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2] ]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.