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Supporting Information

Functionalized saturated-backbone carbene ligands; yttrium and uranyl alkoxy-carbene complexes and bicyclic carbene-alcohol adducts

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Experimental and Crystallographic Details

General Procedures

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glove box unless otherwise stated. The solvents used (THF, diethyl ether, toluene, hexanes) were purified by passage through activated alumina towers and degassed prior to use. Benzene-d_6 and Pyridine-d_5 were refluxed over potassium and vacuum transferred prior to use.

N-substituted ethylenediamines,[1] $UO_2N''_2(THF)_2$ (N" = $N(SiMe_3)_2$),[2] KCH_2Ph [3, 4] were synthesised according to literature procedures. *N-iso*-propylethylenediamine and all other reagents were purchased from Aldrich or Strem and used as received.

^1H NMR spectra were recorded on Bruker arx250 MHz, avance360 MHz or av500 MHz spectrometers, and ^{13}C-{^1H} on the same spectrometers at 63, 90 and 125 MHz, respectively, at 300 K unless otherwise stated, and referenced internally to residual protio solvent. Chemical shift values are quoted in ppm. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University.

Preparations

Proligand synthesis: General procedure.

Proligands were synthesised via a combination and modification of literature procedures[5, 6] under ambient atmosphere. In a typical reaction, an *N*-substituted ethylenediamine was heated with an epoxide in a melt reaction in a sealed ampoule at 90 ºC for two days. The resulting oil was dissolved in diethyl ether and cooled to 0 ºC, acidified with a solution of anhydrous 2 M HCl in diethyl ether and stirred for 1 h at ambient temperature. Following filtration and drying *in vacuo*, the resulting yellow solid was combined with trimethylorthoformate in toluene and refluxed at 90 ºC for 2 h. The final workup procedure varied for each proligand.

$[H_2L^{i\text{-}Pr}]Cl$ $\mathbf{1^P}$

N-iso-propylethylenediamine (3.00 g, 29.35 mmol) and isobutylene oxide (2.12 g, 29.35 mmol) produced a yellow oil to which was added diethyl ether (50 ml) and HCl (2 M in ether, 14.60 ml, 29.35 mmol), furnishing a yellow solid. Toluene (50 ml) and trimethylorthoformate (13.01 g, 122.60 mmol) were added and after reflux, a brown oil settled from solution. The solvent was decanted and $\mathbf{1^P}$ dried *in vacuo* to yield a brown oil. (3.92 g, 60 %).

^1H NMR ($CDCl_3$); δ 9.71 (s, 1H, N-C*H*-N), 5.25 (s, 1H, O*H*), 4.33 (bm, 2H, N-CH_2-CH_2-N), 4.05 (bm, 2H, N-CH_2-CH_2-N), 4.05 (bm, 1H, N-C*H*-$(CH_3)_2$), 3.74 (s, 2H, N-CH_2-C), 1.46 (d, 6H, ^3J = 6 Hz, N-CH-$(CH_3)_2$), 1.36 (s, 6H, C$(CH_3)_2$). ^{13}C; 158.5 (N-*C*H-N), 70.3 (*C*-$(CH_3)_2$), 58.1 51.5 46.3 (N-*C*H_2), 50.8 (N-*C*H-$(CH_3)_2$), 27.7 (C-$(CH_3)_2$), 21.3 (CH-$(CH_3)_2$).

$[H_2L^{i\text{-}Pr}]I$ $\mathbf{1a^P}$

To a stirred solution of $\mathbf{1^P}$ (3.92 g, 17.75 mmol) in acetone (30 ml) at ambient temperature was added portionwise a solution of NaI (1.5 eq, 3.99 g, 26.63 mmol) in acetone (30 ml). A colorless precipitate formed immediately and the reaction was stirred for 2 h. Following filtration and removal of the volatiles, the residue was extracted into DCM (40 ml), filtered and the volatiles removed to yield $\mathbf{1a^P}$ as a viscous brown oil (5.07 g, 93 %).
Colourless crystals suitable for an X-ray diffraction study grew from the product oil after standing at room temperature for a number of weeks.

^{1}H NMR (CDCl$_3$); δ 9.00 (s, 1H, N-C*H*-N), 4.22 (bm, 2H, N-C*H*$_2$-CH$_2$-N), 4.00 (bm, 2H, N-CH$_2$-C*H*$_2$-N), 4.00 (bm, 1H, N-C*H*-(CH$_3$)$_2$), 3.68 (s, 2H, N-C*H*$_2$-C), 1.42 (d, 6H, ^{3}J = 6 Hz, N-CH-(C*H*$_3$)$_2$), 1.31 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C; 157.5 (N-*C*H-N), 71.1 (*C*-(CH$_3$)$_2$), 58.4 52.0 46.9 (N-*C*H$_2$), 51.2 (N-*C*H-(CH$_3$)$_2$), 28.0 (C-(*C*H$_3$)$_2$), 21.5 (CH-(*C*H$_3$)$_2$). Found: C 38.18, H 6.10, N 8.18. Calc. for $C_{10}H_{21}IN_2O$: C 38.47, H 6.79, N 8.97 %.

[H$_2$L^{Mes}]Cl 1^M

N-mesitylethylenediamine (4.00 g, 22.44 mmol) and isobutylene oxide (1.78 g, 24.68 mmol) produced a yellow oil to which was added diethyl ether (60 ml) and HCl (2 M in ether, 11.22 ml, 22.44 mmol), furnishing a yellow solid. Toluene (50 ml) and trimethylorthoformate (11.91 g, 112.20 mmol) were added and after reflux a yellow/ brown oil settled from solution. The volatiles were removed *in vacuo* giving a yellow solid which was suspended in acetone (50 ml) and sonicated briefly; filtration and drying yielded **1^M** as a cream solid (4.94 g, 74 %).

^{1}H NMR (CDCl$_3$); δ 9.33 (s, 1H, N-C*H*-N), 6.89 (s, 2H, Ar-C*H*), 5.20 (s, 1H, O*H*), 4.42 (bm, 2H, N-C*H*$_2$-CH$_2$-N), 4.13 (bm, 2H, N-CH$_2$-C*H*$_2$-N), 3.89 (bs, 2H, N-C*H*$_2$-C), 2.26 (bs, 9H, Ar-C*H*$_3$), 1.27 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C; 160.8 (N-*C*H-N), 140.6 135.6 131.2 (quaternary Ar-*C*), 130.4 (Ar-*C*H), 70.1 (*C*-(CH$_3$)$_2$), 57.9 52.4 51.4 (N-*C*H$_2$), 27.7 (C-(*C*H$_3$)$_2$), 21.4 18.4 (Ar-*C*H$_3$). Found: C 64.84, H 8.57, N 9.41. Calc. for $C_{16}H_{25}ClN_2O$: C 64.73, H 8.51, N 9.44 %.

[H$_2$L^{Mes}]I 1a^M

A similar anion exchange procedure to that already described was used. **1^M** (0.28 g, 0.94 mmol) and NaI (0.21 g, 1.42 mmol) in acetone (5 ml each) yielded **1a^M** as a yellow solid (0.33 g, 90 %).

^{1}H NMR (CDCl$_3$); δ 8.94 (s, 1H, N-C*H*-N), 6.89 (s, 2H, Ar-C*H*), 4.50 (m, 2H, N-C*H*$_2$-CH$_2$-N), 4.16 (m, 2H, N-CH$_2$-C*H*$_2$-N), 3.92 (s, 2H, N-C*H*$_2$-C), 3.63 (s, 1H, O*H*), 2.28 (s, 6H, Ar-ortho-C*H*$_3$), 2.25 (s, 3H, Ar-para-C*H*$_3$), 1.31 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C; 159.5 (N-*C*H-N), 140.7 135.6 130.9 (quaternary Ar-*C*), 130.4 (Ar-*C*H), 71.0 (*C*-(CH$_3$)$_2$), 58.2 52.9 51.4 (N-*C*H$_2$), 27.8 (C-(*C*H$_3$)$_2$), 21.4 18.8 (Ar-*C*H$_3$). Found: C 50.17, H 6.81, N 7.96. Calc. for $C_{16}H_{25}IN_2O$: C 49.49, H 6.50, N 7.22 %.

[H$_2$L^{Dipp}]Cl 1^D

N-(2,6-di-*iso*-propylphenyl)ethylenediamine (7.28 g, 33.00 mmol) and isobutylene oxide (2.50 g, 34.70 mmol) produced a yellow oil to which was added diethyl ether (25 ml) and HCl (2 M in ether, 9.60 ml, 19.11 mmol), furnishing a colorless solid. After drying under reduced pressure, toluene (30 ml) and trimethylorthoformate (10.14 g, 95.57 mmol) were added and the reaction mixture was refluxed for 2 days to afford a yellow solution. The volatiles were removed *in vacuo* giving a pale yellow solid which was washed with acetone (3 x 20 mL) and, following drying, yielded **1^D** as a colorless solid (3.89 g, 60 %).

^{1}H NMR (CDCl$_3$); δ 9.47 (s, 1H, N-C*H*-N), 7.40 (t, ^{3}J = 7 Hz, 1H, 4-Ar-C*H*), 7.21 (d, ^{3}J = 7 Hz, 2H, 3,5-Ar-C*H*), 5.18 (s, 1H, O*H*), 4.44 4.13 (m, 2H, N-C*H*$_2$-C*H*$_2$-N), 3.95 (s, 2H, N-C*H*$_2$-C), 2.88 (sept, ^{3}J = 2 Hz, 2H, Ar-C*H*(CH$_3$)$_2$), 1.30 (s, 6H, C(C*H*$_3$)$_2$), 1.27 (d, ^{3}J = 2 Hz, 6H, Ar-CH(C*H*$_3$)$_2$), 1.24 (d, ^{3}J = 2 Hz, 6H, Ar-CH(C*H*$_3$)$_2$). ^{13}C; 160.4 (N-*C*H-N), 146.5 (2-Ar-*C*), 131.0 (4-Ar-*C*), 130.0 (1-Ar-*C*), 124.8 (3,5-Ar-*C*), 69.7 (*C*-(CH$_3$)$_2$), 57.3 (N-*C*H$_2$-C), 53.1 51.7 (N-*C*H$_2$-*C*H$_2$-N), 28.8 (Ar-*C*H(CH$_3$)$_2$), 27.2 (Ar-CH(*C*H$_3$)$_2$), 25.0 (C-(*C*H$_3$)$_2$), 23.9 (Ar-CH(*C*H$_3$)$_2$. Found: C 67.29, H 9.30, N 8.28. Calc. for $C_{19}H_{31}ClN_2O$: C 67.33, H 9.22, N 8.27 %.

[H$_2$L^{Dipp}]I 1a^D

A similar anion exchange procedure to that already described was used. **1^D** (1.06 g, 3.13 mmol) and NaI (0.94 g, 6.26 mmol) in acetone (15 ml each) yielded **1a^D** as a colorless solid (1.00 g, 73 %).

^{1}H NMR (CDCl$_3$); δ 9.07 (s, 1H, N-C*H*-N), 7.40 (t, ^{3}J = 8 Hz, 2H, 3,5-Ar-C*H*), 7.20 (d, ^{3}J = 8 Hz, 1H, 4-Ar-C*H*), 5.18 (s, 1H, O*H*), 4.55 4.17 (m, 2H each, N-C*H*$_2$-C*H*$_2$-N), 4.00 (s, 2H, N-C*H*$_2$-C), 2.91 (sept, ^{3}J = 7

Hz, 2H, Ar-C*H*(CH$_3$)$_2$), 1.32 (s, 6H, C(C*H*$_3$)$_2$), 1.25 1.22 (d, ^{3}J = 2 Hz, 6H each, Ar-CH(C*H*$_3$)$_2$). ^{13}C; 157.7 (N-*C*H-N), 145.6 (2-Ar-*C*), 130.1 (4-Ar-*C*), 129.8 (1-Ar-*C*), 123.9 (3,5-Ar-*C*), 69.6 (*C*-(CH$_3$)$_2$), 56.5 (N-*C*H$_2$-C), 52.3 51.5 (N-*C*H$_2$-*C*H$_2$-N), 27.9 (Ar-*C*H(CH$_3$)$_2$), 26.3 (Ar-CH(*C*H$_3$)$_2$), 24.3 (C-(*C*H$_3$)$_2$), 23.1 (Ar-CH(*C*H$_3$)$_2$). Found: C 53.07, H 7.28, N 6.59. Calc. for $C_{19}H_{31}IN_2O$: C 53.03, H 7.26, N 6.57 %.

Bicyclic carbene-alcohol adduct synthesis: General procedure.

To a Schlenk charged with a stirred mixture of KCH$_2$Ph and one equivalent of the appropriate proligand, at −78 °C, was added THF. The resulting dark orange solution/ suspension was allowed to warm slowly to ambient temperature overnight, furnishing a yellow/ green solution and fine precipitate. After filtration, the volatiles were removed and, in the case of HL$^{i\text{-Pr}}$ and HL$^{\text{Mes}}$, the residue was purified *via* short path distillation and the product isolated as a colorless oil. Compound HL$^{\text{Dipp}}$ was isolated as a green oily solid after removal of the volatiles, from which a small amount of colorless crystalline solid could be sublimed. Alternatively, one equivalent of Li^{n}Bu was added to a cooled (−78 °C) suspension of the proligand in hexanes or toluene, and the mixture allowed to warm to ambient temperature slowly overnight. The subsequent workup was the same as that just described, although no green color was observed in this case.

[HL$^{i\text{-Pr}}$] 2$^{\text{P}}$

1a$^{\text{P}}$ (3.00 g, 9.61 mmol) and KCH$_2$Ph (1.25 g, 9.61 mmol) with THF (30 ml) produced a pale yellow solution and colorless precipitate. After filtration and removal of the volatiles, the resulting yellow oil was distilled (10^{-1} mbar at 35-40 ºC) to yield **2$^{\text{P}}$** as a colourless oil (0.91 g, 51 %).

^{1}H NMR (C$_6$D$_6$); δ 5.47 (s, 1H, N-C(O)*H*-N), 3.13 2.85 2.64 2.63 (m, 1H each, N-C*H$_2$*-C*H$_2$*-N), 2.91 2.45 (d, 1H each, ^{2}J$_{\text{H-H}}$ 10.5 Hz N-C*H$_2$*-C), 2.85 (m, 1H, N-C*H*-(CH$_3$)$_2$), 1.24 1.16 (s, 3H each, C(*CH$_3$*)$_2$), 1.14 1.09 (d, 3H each, ^{3}J = 6 Hz, N-CH-(C*H*$_3$)$_2$). ^{13}C; 107.8 (N-*C*(O)H-N), 78.6 (*C*-(CH$_3$)$_2$), 65.6 54.4 47.9 (N-*C*H$_2$), 50.4 (N-*C*H-(CH$_3$)$_2$), 28.4 27.8 (C-(*C*H$_3$)$_2$), 22.6 21.6 (CH-(*C*H$_3$)$_2$). Found: C 65.13, H 11.06, N 15.19. Calc. for $C_{10}H_{20}N_2O$: C 65.16, H 10.96, N 15.20 %.

[HL$^{\text{Mes}}$] 2$^{\text{M}}$

1$^{\text{M}}$ (4.79 g, 16.14 mmol) and KCH$_2$Ph (2.10 g, 16.14 mmol) with THF (30 ml) produced a yellow/ green solution and fine colorless precipitate. After filtration and removal of the volatiles, the resulting yellow oil was distilled (10^{-1} mbar at 85 ºC) to yield **2$^{\text{M}}$** as a colorless oil (3.08 g, 73 %). This oil solidified slowly over time.

^{1}H NMR (C$_6$D$_6$); δ 6.80 (s, 2H, Ar-C*H*), 5.79 (s, 1H, N-C(O)*H*-N), 3.42 3.21 3.02 2.94 (m, 1H each, N-C*H$_2$*-C*H$_2$*-N), 2.90 (d, 1H, ^{2}J$_{\text{H-H}}$ 10.5 Hz, N-C*H*H-C(CH$_3$)$_2$), 2.52 (d, 1H, ^{2}J$_{\text{H-H}}$ 10.5 Hz, N-CH*H*-C(CH$_3$)$_2$, 2.39 (bs, 6H, Ar-ortho-C*H*$_3$), 2.14 (s, 3H, Ar-para-C*H*$_3$), 1.30 1.11 (s, 3H each, C(C*H*$_3$)$_2$). ^{13}C; 140.3 138.8 135.8 (quaternary Ar-*C*), 129.7 (Ar-*C*H), 108.6 (N-*C*(O)H-N), 77.5 (*C*-(CH$_3$)$_2$), 64.2 54.8 49.9 (N-*C*H$_2$), 29.4 28.0 (C-(*C*H$_3$)$_2$), 21.0 18.8 (Ar-*C*H$_3$). Found: C 73.90, H 9.36, N 10.63. Calc. for $C_{16}H_{24}N_2O$: C 73.79, H 9.31, N 10.76 %.

[HL$^{\text{Dipp}}$] 2$^{\text{D}}$

To a cold (-78 °C) solution of **1$^{\text{D}}$** (6.47 g, 19.09 mol) in THF (30 mL) was added dropwise ^{n}BuLi (14.30 mL, 22.91 mol) to afford a colorless slurry. The reaction mixture was stirred for 2 h and then allowed to warm to room temperature, and stirred for a further 2 h. After filtration to remove precipitated salts, the volatiles were removed *in vacuo* from the filtrate to yield **2$^{\text{D}}$** as a colorless solid which was washed with hexane (3 x 10 mL) and dried. A second crop was afforded by precipitation from the washings at -78 °C (5.60 g, 97 %).

^{1}H NMR (C_6D_6); δ 7.28-7.04 (overlapping m, 3H, 3,4,5-Ar-C*H*), 5.78 (s, 1H, N-C(O)*H*-N), 4.09 (sept, ^{3}J = 7 Hz, 2H, Ar-C*H*$(CH_3)_2$), 3.53-2.95 (overlapping m, 4H, 2H, N-C*H*$_2$-C*H*$_2$-N), 3.36 (sept, ^{3}J = 7 Hz, 2H, Ar-C*H*$(CH_3)_2$), 2.91 2.52 (d, $^1J_{HH}$ = 11 Hz, ^{1}H each, N-C*H*$_2$-C), 1.42 1.30 (d, ^{3}J = 7 Hz, 2H each, Ar-CH(C*H*$_3$)$_2$), 1.30 (s, 3H, C(C*H*$_3$)$_2$), 1.18 1.14 (d, ^{3}J = 7 Hz, 3H each, Ar-CH(C*H*$_3$)$_2$), 1.11 (s, 3H, C(C*H*$_3$)$_2$). ^{13}C; 151.6 148.8 140.2 127.8 124.9 124.0 (Ar-*C*H), 109.4 (N-*C*(O)H-N), 77.6 (*C*$(CH_3)_2$), 63.9 (N-*C*H$_2$-C) 54.5 52.9 (N-*C*H$_2$-*C*H$_2$-N), 29.3 (Ar-*C*H$(CH_3)_2$), 28.3 (C(*C*H$_3$)$_2$), 27.9 (Ar-*C*H$(CH_3)_2$), 27.7 (C(*C*H$_3$)$_2$), 25.3 24.9 24.8 24.5 (Ar-CH(*C*H$_3$)$_2$). Found: C 75.51, H 10.07, N 9.20. Calc. for $C_{19}H_{31}N_2O$: C 75.45, H 10.00, N 9.26 %.

[$L^{i\text{-}Pr}YN''_2$] 3^P

In a Youngs tap NMR tube, C_6D_6 solutions of YN''_3 (46.4 mg, 0.08 mmol) and **2^P** (15.0 mg, 0.08 mmol) were combined and mixed well. The solution turned pale yellow and was heated to 85 ºC for 24 h.

^{1}H NMR (C_6D_6); δ 4.37 (sept, 1H, ^{3}J = 7 Hz, N-C*H*-$(CH_3)_2$), 2.97 (s, 2H, N-C*H*$_2$-C), 2.74 (m, 2H, N-C*H*$_2$-CH$_2$-N), 2.53 (m, 2H, N-CH$_2$-C*H*$_2$-N), 1.14 (s, 6H, C(C*H*$_3$)$_2$), 0.96 (d, 6H, ^{3}J = 7 Hz, N-CH-(C*H*$_3$)$_2$), 0.40 (s, 36H, N(Si{C*H*$_3$}$_3$)$_2$). ^{13}C; 212.3 (d, $^1J_{YC}$ = 46 Hz, N-*C*-N), 75.1 (*C*-$(CH_3)_2$), 63.3 53.2 51.5 (N-*C*H$_2$), 42.0 (N-*C*H-$(CH_3)_2$), 29.7 (C-(*C*H$_3$)$_2$), 21.5 (CH-(*C*H$_3$)$_2$), 5.9 (N(Si{*C*H$_3$}$_3$)$_2$).

[$L^{Mes}YN''_2$] 3^M

In a Youngs tap NMR tube, C_6D_6 solutions of YN''_3 (43.8 mg, 0.08 mmol) and **2^M** (20.0 mg, 0.08 mmol) were combined and mixed well. The solution turned pale yellow after 5-10 minutes.

^{1}H NMR (C_6D_6); δ 6.75 (s, 2H, Ar-C*H*), 3.10 (s, 2H, N-C*H*$_2$-C$(CH_3)_2$), 2.85 (bs, 4H, N-C*H*$_2$-C*H*$_2$-N), 2.17 (s, 6H, Ar-ortho-C*H*$_3$), 2.14 (s, 3H, Ar-para-C*H*$_3$), 1.22 (s, 6H, C(C*H*$_3$)$_2$), 0.33 (s, 36H, N(Si{C*H*$_3$}$_3$)$_2$). ^{13}C; 215.5 (d, $^1J_{YC}$ = 44 Hz, N-*C*-N), 139.0 136.6 128.3 (quaternary Ar-*C*), 130.7 (Ar-*C*H), 74.3 (*C*-$(CH_3)_2$), 63.3 53.8 50.5 (N-*C*H$_2$), 29.3 (C-(*C*H$_3$)$_2$), 21.4 19.1 (Ar-*C*H$_3$), 5.7 (N(Si{*C*H$_3$}$_3$)$_2$).

[$L^{Dipp}YN''_2$] 3^D

To a solution of YN''_3 (0.47 g, 0.82 mmol) in THF (2 ml) was added a solution of **2^D** (0.25 g, 0.82 mmol) in THF (2 ml). The reaction mixture was stirred overnight at room temperature to afford a pale yellow solution. The volatiles were removed *in vacuo* and slow cool recrystallisation from toluene (~3 mL) at -30 ºC afforded **3^D** as colourless plates suitable for an X-ray diffraction study (0.30 g, 51 %).

^{1}H NMR (C_6D_6); δ 7.18 (m, 1H, 4-Ar-C*H*), 7.04 (m, 2H, 3,5-Ar-C*H*), 3.25 (s, 2H, N-C*H*$_2$-C), 3.15 (m, 2H, N-C*H*$_2$-CH$_2$-N), 3.09 (sept, ^{3}J = 7 Hz, 2H, Ar-C*H*$(CH_3)_2$), 2.90 (m, 2H, N-CH$_2$-C*H*$_2$-N), 1.44 (d, ^{3}J = 7 Hz, 6H, Ar-CH(C*H*$_3$)$_2$), 1.08 (d, ^{3}J = 7 Hz, 6H, Ar-CH(C*H*$_3$)$_2$), 0.39 (s, 36H, N(Si{C*H*$_3$}$_3$)$_2$). ^{13}C; 216.3 (d, $^1J_{YC}$ = 42 Hz, N-*C*-N), 147.4 (1-Ar-*C*), 136.3 (2,6-Ar-*C*), 129.8 (4-Ar-*C*H), 125.0 (3,5-Ar-*C*H), 73.5 (*C*-$(CH_3)_2$), 62.8, (N-*C*H$_2$-C)), 53.6 53.2 (N-*C*H$_2$-*C*H$_2$-N), 28.6 (C-(*C*H$_3$)$_2$), 28.3 (Ar-*C*H$(CH_3)_2$), 26.2 (Ar-CH(*C*H$_3$)$_2$), 24.7 (Ar-CH(*C*H$_3$)$_2$), 5.5 (N(Si{*C*H$_3$}$_3$)$_2$). Analysis. Found: C 52.27, H 9.28, N 7.73. Calc. for $C_{31}H_{65}N_4OSi_4Y$: C 52.36, H 9.21, N 7.88 %.

[$UO_2L_2^{Mes}$] 4^M

A solution of **2^M** (30.0 mg, 0.12 mmol) in benzene (2 ml) was carefully layered onto a red solution of $UO_2N_2''(THF)_2$ (42.3 mg, 0.06 mmol) in benzene (2 ml) and allowed to diffuse slowly overnight at room temperature. The solution turned yellow and **4^M** formed as yellow needles which were washed with benzene (3 x 1 ml) and dried *in vacuo* (24.0 mg, 52 %).

Bi-refringent yellow/ green crystals suitable for an X-ray diffraction study were grown from a 5:1 pyridine/benzene mixture via slow cooling of a hot solution to room temperature overnight.

^{1}H NMR (C_5D_5N); δ 6.82 (s, 2H, Ar-C*H*), 3.84 (bs, 2H, N-CH_2-C), 3.75 (bm, 2H, N-CH_2-CH_2-N), 3.64 (bm, 2H, N-CH_2-CH_2-N), 2.29 (bs, 6H, Ar-ortho-CH_3), 2.25 (s, 3H, Ar-para-CH_3), 1.45 (s, 6H, C(CH_3)$_2$). ^{13}C; 281.6 (N-*C*-N), 140.6 135.6 131.2 (quaternary Ar-*C*), 130.4 (Ar-*C*H), 83.7 (*C*-(CH_3)$_2$), 64.8 57.4 54.6 (N-*C*H_2), 33.1 (C-(*C*H_3)$_2$), 23.4 20.8 (Ar-*C*H_3). IR(nujol); ν = 851 cm^{-1} (O=U=O). Found: C 48.74, H 6.55, N 6.52. Calc. for $C_{32}H_{46}N_4O_4U$: C 48.72, H 5.89, N 7.10 %.

[$UO_2L_2^{Dipp}$] 4^D

A solution of **2**^{D} (32.9 mg, 0.10 mmol) in benzene (2 ml) was carefully layered onto a red solution of UO_2N_2''(THF)$_2$ (40.0 mg, 0.05 mmol) in benzene (2 ml) and allowed to slowly diffuse overnight at room temperature in the glovebox. The solution turned yellow and **4**^{D} formed as yellow needles which were washed with benzene (3 x 1 ml) and dried *in vacuo*.

^{1}H NMR (C_5D_5N); δ 7.43 (t, ^{3}J = 8 Hz, 1H, 4-Ar-C*H*), 7.27 (d, ^{3}J = 8 Hz, 2H, 3,5-Ar-C*H*), 3.94 3.87 (m, 2H each, N-CH_2-CH_2-N), 3.87 (s, 2H, N-CH_2-C), 3.43 (sept, ^{3}J = 7 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.31 (s, 6H, C(CH_3)$_2$), 1.28 1.17 (d, ^{3}J = 7 Hz, 6H each, Ar-CH(CH_3)$_2$). ^{13}C; 283.6 (N-*C*-N), 150.0 139.2 (quaternary Ar-*C*), 130.8 (4-Ar-*C*H), 126.4 (3,5-Ar-*C*H), 83.6 (*C*-(CH_3)$_2$), 64.6 (N-*C*H_2-C)), 57.3 57.0 (N-CH_2-*C*H_2-N), 32.4 (C-(*C*H_3)$_2$), 30.4 (Ar-*C*H(CH_3)$_2$), 27.6 26.2 (Ar-CH(*C*H_3)$_2$). IR(nujol); $\nu_{(asymm)}$ UO_2 = 853 cm^{-1}.

Crystallography

Crystallographic X-ray data were collected using Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart APEX CCD area detector diffractometer using ω, or ω and φ scans. Structure solution and refinement was carried out using the SIR program and the SHELXTL suite of programs, [7, 8] and graphics generated using Ortep-3.[9]

The ADPs for C(3) and C(4) (on the *iso*-propyl group) in **1a**^{P} were restrained to account for an unmodelled disorder, which results in close contacts between the hydrogen atoms placed upon these carbons. This is independent of the method used to place them (geometrically or by electron density). The hydroxyl hydrogen in **1a**^{P} was found in the electron difference map and restrained to lie approximately on the O(1)-I(1) axis.

Compound **1**^{D} contains 0.6 molecules of water in the lattice.

Compound **4**^{M} crystallised as a racemic mixture of the two enantiomers, with half of the molecule, and one molecule of benzene, present in the asymmetric unit. There is a superpositional disorder of the two enantiomers, which appear superimposed in the asymmetric unit; no higher symmetry or cell-doubling was found. The superpositional disorder has been modelled with a *trans*-L^D_2 geometry. Several anisotropic displacement parameter restraints, both spatial and rigid-rotor, were required to account for the superpositional disorder and also a disorder in the mesityl groups and co-crystallised benzene. There are several close crystallographic contacts between some hydrogen atoms as a result, and several carbon atoms still retain higher than desired thermal displacement parameters.

Complex **4**^{D} contains two molecules of benzene in the unit cell, disordered about a special position. This disorder was not modelled, however, resulting in short C-C bonds across the special position.

Experimental Crystallographic Details

Compound	**1a**^{P}	**1**^{D}	**3**^{D}	**4**^{M}	**4**^{D}
Crystal data					
Chemical formula	$C_{10}H_{21}IN_2O$	$C_{19}H_{31}ClN_2O$.$H_{1.2}O_{0.6}$	$C_{31}H_{65}N_4OSi_4Y$	$C_{44}H_{58}N_4O_4U$	$C_{38}H_{58}N_4O_4U$.$C_{12}H_{12}$
M_r	312.19	349.72	711.14	944.97	1029.13

Cell setting, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/C$	Triclinic, P-1	Triclinic, P-1
Temperature (K)	150 (2)	150 (2)	150 (2)	150 (2)	150 (2)
a, b, c (Å)	9.916 (3), 11.780 (3), 11.387 (3)	11.9968 (3), 11.2624 (3), 14.8437 (4)	20.3348 (16), 10.6423 (9), 20.1193 (16)	7.7547 (2), 12.0229 (3), 12.3593 (3)	10.1261 (7), 10.4437 (7), 11.7599 (8)
α, β, γ (°)	90.00, 90.00, 90.00	90.00, 94.715 (2), 90.00	90.00, 112.017 (4), 90.00	68.6800 (10), 75.4660 (10), 83.0090 (10)	93.023 (3), 92.881 (4), 101.057 (3)
V (Å^3)	1330.1 (6)	1998.79 (9)	4036.5 (6)	1038.50 (4)	1216.56 (14)
Z	4	4	4	1	1
D_x (Mg m^{-3})	1.559	1.162	1.170	1.511	1.405
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.38	0.20	1.59	3.95	3.38
Crystal form, colour	Cube, colourless	Slab, colourless	PLATES, colourless	Block, yellow	Irregular, colourless
Crystal size (mm)	0.61 × 0.54 × 0.50	0.4 × 0.2 × 0.17	0.83 × 0.57 × 0.1	0.50 × 0.26 × 0.25	0.41 × 0.38 × 0.29
Data collection					
Diffractometer	Brucker SMART APEX CCD area detector	Bruker SMART APEX CCD area detector	Bruker SMART APEX CCD area detector	Brucker SMART APEX CCD area detector	Bruker SMART APEX CCD area detector
Data collection method	ω scans	ω scans	ω and phi scans	ω scans	phi and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.584	0.634	0.512	0.804	0.779
T_{max}	1.000	0.746	0.746	1.000	1.000
No. of measured, independent and observed reflections	15127, 3263, 3223	20598, 5212, 4360	69743, 12185, 8188	14300, 5762, 5762	17211, 6730, 6725
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.037	0.042	0.091	0.031	0.032
θ_{max} (°)	34.0	29.7	30.6	30.6	30.5
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.078, 1.12	0.081, 0.173, 1.19	0.049, 0.119, 1.06	0.023, 0.054, 1.09	0.025, 0.061, 1.07

No. of relections	3263 reflections	5212 reflections	12185 reflections	5762 reflections	6730 reflections
No. of parameters	132	232	388	479	274
H-atom treatment	Riding	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Riding	Riding
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.682P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 2.3483P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.1912P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0346P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	<0.0001	0.004	0.013	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.99, –1.40	0.40, –0.36	0.95, –0.63	1.97, –1.29	1.88, –0.99
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881				
Flack parameter	0.03 (3)				
Rogers parameter					

Computer programs: *SMART (Siemans, 1993*; *SMART* (Siemens, 1993); *SMART* (Siemans, 1993); *SAINT* (Siemans, 1995); *SAINT* (Siemens, 1995); *SIR-92* (Giacovazzo, 1994); *SHELXL-97* (Sheldrick, 1997); *ORTEP* (Farrugia, 1997); *enCIFer* (Allen et al., 2004).

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