- Supporting Information -

Actinide-Transition Metal Bonding in Heterobimetallic Uranium- and Thorium-Molybdenum Paddlewheel Complexes

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1. Experimental procedures

General Methods

All manipulations were carried out under an inert atmosphere of dinitrogen using Schlenk techniques or an MBraun UniLab glovebox. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors (with the exception of ethers that were stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze–pump–thaw cycles and stored under nitrogen. All other chemicals were purchased and all solid reagents were dried under vacuum for four hours and all liquid reagents were dried over 4 Å molecular sieves and distilled before use. UCl_4,[1] and $ThCl_4(DME)_2$,[2] were prepared according to published procedures. All other materials

were purchased from commercial sources and either used as received (^{n}BuLi) or dried prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6 and 162.0 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. 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. Data were measured on cooling from room temperature, and samples were immobilised in an eicosane matrix to prevent sample reorientation during measurements. Diamagnetic corrections were applied using tabulated Pascal constants and measured data were corrected for the effect of the blank sample holders (flame sealed Wilmad NMR tube and straw) and eicosane matrix. Elemental microanalyses were carried out by Dr. Tong Liu at the University of Nottingham.

Preparation of MesN(H)PPh$_2$

A solution of 2,4,6-trimethylaniline (6.76 g, 50.0 mmol) in Et_2O (100 ml) was cooled to 0 °C. To this was added Bu^{n}Li (22 ml, 2.5 M in hexanes, 55.0 mmol), the resulting solution was allowed to warm slowly to room temperature then heated to reflux (50 ºC) for 30 minutes. The resulting slurry was added to a stirring solution of PPh_2Cl (11.03 g, 50.0 mmol) in Et_2O (100 ml) at –78 °C. The solution was allowed to warm slowly to room temperature and stirred for a further hour where upon the solution turned pale yellow with a white precipitate. The reaction mixture was filtered away from the LiCl and the volatiles were removed *in vacuo* to afford MesN(H)PPh_2 as an analytically pure, pale yellow solid. Colourless crystals of MesN(H)PPh_2 suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et_2O solution at –30 °C for 72 hours. Yield: 13.73 g, 86 %. Anal. Calc'd for $C_{21}H_{22}NP$: C, 78.97; H, 6.94; N, 4.39 %. Found: C, 78.99; H, 7.09; N, 4.28 %. ^{1}H NMR (C_6D_6, 295 K): δ (ppm) 2.20 (6H, s, Mes-C*H*$_3$), 2.25 (3H, s, Mes-C*H*$_3$), 3.65 (1H, d, $^{2}J_{PH}$ = 8.0 Hz, N*H*), 6.86 (2H, s, Ar-C*H*), 7.19 (6H, m, Ar-C*H*), 7.60 (4H, m, Ar-C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ 19.07 (d, $^{4}J_{PC}$ = 6.20 Hz, Mes-*o*-*C*H$_3$), 20.53 (Mes-*p*-*C*H$_3$), 128.46 (d, $^{3}J_{PC}$ = 6.20 Hz), 128.74, 129.67, 130.70 (d, $^{2}J_{PC}$ = 3.40 Hz), 131.41, 131.69, 140.57 (d, J_{PC} = 14.65 Hz), 142.49 (d, $^{2}J_{PC}$ = 16.34 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 295 K): δ (ppm) 36.07 (s). FTIR ν/cm^{-1} (Nujol): 516 (w), 556 (m), 566 (m), 581 (m), 619 (w), 695 (s), 740 (s), 852 (m), 936 (w), 961 (w), 1067 (m), 1157 (m), 1180 (m), 1220 (m), 1246 (m), 1304 (m), 1365 (m), 1412 (s), 1480 (m).

Preparation of [Li(MesNPPh$_2$)(OEt$_2$)$_2$]

A solution of MesN(H)PPh$_2$ (7.25 g, 22.7 mmol) in Et$_2$O (75 ml) was cooled to –78 °C. To this was added Bu^{n}Li (10 ml, 2.5 M in hexanes, 25.0 mmol). The resulting yellow solution was allowed to warm slowly to room temperature and stirred for 3 hours. The reaction mixture was concentrated *in vacuo* and cooled to –30 °C to afford [Li(MesNPPh$_2$)(OEt$_2$)$_2$] as a colourless crystalline solid. Colourless crystals of [Li(MesNPPh$_2$)(OEt$_2$)$_2$] suitable for a single crystal X-ray diffraction study were obtained from storage of a concentrated Et$_2$O solution at –30 °C for 72 hours. Yield: 9.34 g, 79 %. Anal. Calc'd for $C_{29}H_{41}LiNO_2P$: C, 73.55; H, 8.73; N, 2.96 %. Found: C, 73.68; H, 8.65; N, 3.04 %. ^{1}H NMR (C_6D_6, 295 K): δ (ppm) 0.78 (12H, t, $^3J_{HH}$ = 8.0 Hz, Et$_2$O-C*H*$_3$), 2.22 (6H, s, Mes-C*H*$_3$), 2.33 (3H, s, Mes-C*H*$_3$), 3.00 (8H, q, $^3J_{HH}$ = 8.0 Hz, Et$_2$O-C*H*$_2$), 6.95 (2H, s, Ar-C*H*), 7.13 (2H, m, Ar-C*H*), 7.21 (4H, m, Ar-C*H*), 7.81 (4H, m, Ar-C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ (ppm), 13.95, 20.52, 21.34 (d, $^4J_{PC}$ = 3.35 Hz, Mes-*o*-*C*H$_3$), 65.08, 128.18, 128.6 (d, $^3J_{PC}$ = 6.70 Hz), 129.73, 132.2, 132.4, 133.4 (d, $^2J_{PC}$ = 6.20 Hz) 146.9 (d, J_{PC} = 22.3 Hz), 152.8. ^{31}P{^{1}H} NMR (C_6D_6, 295 K): δ (ppm) 45.03 (s). ^{7}Li{^{1}H} NMR (C_6D_6, 295 K): δ (ppm) 1.13 (s). FTIR *v*/cm^{-1} (Nujol): 535 (w), 578 (w), 614 (w), 625 (w), 698 (m), 739 (m), 749 (m), 856 (m), 924 (m), 965 (m), 1069 (m), 1090 (s), 1159 (m), 1230 (s), 1298 (m), 1414 (m), 1432 (m), 1501 (m).

Preparation of [ClU(MesNPPh$_2$)$_3$] (UCl)

THF (30 ml) was added slowly to a cold (–78 °C) stirring mixture of UCl$_4$ (1.90 g, 5.0 mmol) and [Li(MesNPPh$_2$)(OEt$_2$)$_2$] (7.10 g, 15.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed *in vacuo* and the resulting pale brown solid was extracted into toluene, concentrated to 15 ml and cooled to –30 °C to afford **3** as a brown crystalline solid. Brown crystals of **UCl** suitable for a single crystal X-ray diffraction study were obtained from storage of a toluene solution at –30 °C for 72 hours. Yield: 4.05 g, 66 % Anal. Calc'd for $C_{63}H_{63}ClN_3P_3U$ 0.35(C_7H_8): C, 62.35; H, 5.26; N, 3.33 %. Found: C, 62.43; H, 5.30; N, 3.42 %. ^{1}H NMR (C_6D_6, 295 K): δ (ppm) –11.41 (12H, s, br, Ar-C*H*), 5.58 (9H, s, Mes-C*H*$_3$), 7.44 (6H, s, Ar-C*H*), 7.89 (18H, s, Mes-C*H*$_3$), 11.20 (6H, s, br, Ar-C*H*), 11.73 (12H, s, br, Ar-C*H*). ^{31}P{^{1}H} NMR (C_6D_6, 295 K): No resonances observed. FTIR *v*/cm^{-1} (Nujol): 507 (s), 539 (s), 567 (w), 589 (m), 619 (w), 658 (s), 698 (s), 729 (m), 744 (s), 765 (s), 854 (m), 897 (m), 934 (m), 958 (m), 978 (m), 1000 (s), 1153 (w), 1188 (w), 1218 (s), 1247(w), 1301 (w), 1318 (m), 1434 (s). Magnetic moment (Evans method, C_6D_6, 298 K): μ_{eff} = 2.38 μ_B.

Preparation of [IU(MesNPPh$_2$)$_3$] (UI)

A solution of **UCl** (3.07 g, 2.5 mmol) in toluene (30 mL) was cooled to 0 °C. To this was added Me_3SiI (0.63 g, 0.45 ml 3.13 mmol). The resulting brown solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a pale brown solution and a green precipitate. The precipitate was isolated *via* filtration and washed with hexanes (3 × 20 ml) to yield **UI** as an analytically pure green powder. Green crystals of **UI** suitable for a single crystal X-ray diffraction study were obtained from storage of a toluene solution at –30 °C for 72 hours. Yield: 0.68 g, 72%. Calc'd for $C_{63}H_{63}IN3P3U$: C, 57.30; H, 4.81; N, 3.18 %. Found: C, 57.19; H, 4.80; N, 2.91 %. ^{1}H NMR (C_6D_6, 295 K): δ (ppm) –10.71 (18H, s-br, Mes-C*H*$_3$), 5.82 (9H, s, Mes-C*H*$_3$), 8.17 (12H, s, Ar-C*H*), 11.60 (6H, s, Ar-C*H*), 12.92 (12H, s, Ar-C*H*). ^{31}P{^{1}H} NMR (C_6D_6, 295 K): δ (ppm) 2048. FTIR (Nujol): ν̃ (cm-1) 507 (w), 538 (w), 567 (w), 589 (w), 658 (w), 699 (w), 743 (w), 763 (w), 854 (w), 897 (w), 959 (w), 1153 (w), 1182 (w), 1217 (w), 1303 (w), 1379 (w), 1434 (m). Magnetic moment (Evans method, C_6D_6, 298 K): μ_{eff} = 2.46 μ_B.

Preparation of [ClTh(MesNPPh$_2$)$_3$] (ThCl)

THF (30 ml) was added slowly to a cold (–78 °C) stirring mixture of $ThCl_4(DME)_2$ (0.55 g, 1.0 mmol) and [Li(MesNPPh$_2$)(Et$_2$O)$_2$] (1.42 g, 3.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. Volatiles were removed in *vacuo* and the resulting pale yellow solid was extracted into toluene and washed with Et_2O (3 × 10 ml) to afford **ThCl** as a colourless solid. Colourless crystals of **ThCl** suitable for a single crystal X-ray diffraction study were obtained from storage of an Et_2O solution at 25 °C for 24 hours. Yield: 0.81 g, 66 %. Anal. Calc'd for $C_{63}H_{63}ClN_3P_3Th$: C, 61.89; H, 5.19; N, 3.44 %. Found: C, 61.79; H, 4.98; N, 3.40 %. ^{1}H NMR (C_6D_6, 295 K): δ (ppm) 1.96 (18H, s, Mes-C*H*$_3$), 2.25 (9H, s, Mes-C*H*$_3$), 6.72 (6H, s, Mes-C*H*), 6.97 (18H, m, Ar-C*H*), 7.47 (12H, m, Ar-C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ (ppm), 20.65 (br, Mes-*C*H$_3$), 127.66 (Ar-*C*H), 127.89 (Ar-*C*H), 129.39 (Ar-*C*H), 129.61 (Ar-*C*H), 132.79 (Ar-*C*), 134.40 (Ar-*C*), 134.97 (Ar-*C*), 149.70 (Ar-*C*). ^{31}P{^{1}H} NMR (C_6D_6, 295 K): δ (ppm) 20.72 (s). FTIR *v*/cm^{-1} (Nujol): 514 (m), 540 (m), 566 (m), 590 (m), 618 (m), 661 (m), 695 (s), 741 (m), 767 (m), 856 (m), 893 (m), 959 (m), 1153 (m), 1216 (s), 1302 (m), 1435 (s).

Preparation of [ITh(MesNPPh$_2$)$_3$] (ThI)

To a cooled (0 °C) solution of **ThCl** (0.61 g, 0.5 mmol) in toluene (30 ml) was added Me_3SiI (0.11 g, 0.08 mL 0.55 mmol). The resulting pale yellow solution was allowed to warm slowly to room temperature and stirred for 18 hours to afford a colourless precipitate. The precipitate was

isolated by filtration and washed with hexane (3 × 10 ml) to afford **ThI** as a colourless solid. Colourless crystals of **ThI** suitable for a single crystal X-ray diffraction study were obtained from storage of a toluene solution at 0 °C for 48 hours. Yield: 0.57 g, 88 %. Anal. Calc'd for $C_{63}H_{63}IN_3P_3Th$: C, 57.58; H, 4.83; N, 3.20 %. Found: C, 57.17; H, 4.82; N, 2.94 %. ^{1}H NMR (C_6D_6, 295 K): δ (ppm) 1.96 (18H, s, Mes-C*H*$_3$), 2.22 (9H, s, Mes-C*H*$_3$), 6.70 (6H, s, Mes-C*H*), 6.96 (18H, m, Ar-C*H*), 7.53 (12H, m, Ar-C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ (ppm), 20.60 (Mes-*C*H$_3$), 20.96 (Mes-*C*H$_3$), 127.65 (Ar-*C*H), 127.95 (Ar-*C*H), 129.31 (Ar-*C*H), 129.65 (Ar-*C*H), 132.68 (Ar-*C*), 134.44 (Ar-*C*), 134.70 (Ar-*C*). ^{31}P{^{1}H} NMR (C_6D_6, 295 K): δ (ppm) 17.65 (s). FTIR *v*/cm^{-1} (Nujol): 658 (w), 696 (m), 743 (m), 765 (m), 959 (w), 1153 (w), 1184 (w), 1215 (m), 1302 (m), 1434 (m).

Preparation of [(Cl)U(MesNPPh$_2$)$_3$Mo(CO)$_3$] (UClMo)

Toluene (30 ml) was added to a stirring mixture of **UCl** (1.24 g, 1.0 mmol) and [Mo(CO)$_3$(NCMe)$_3$] (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Volatiles were removed *in vacuo* and the resulting orange solid was washed with hexanes (3 × 10 ml) to yield **UClMo** as an analytically pure powder. Orange crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **UClMo** at room temperature over 24 hours. Yield 1.24 g, 88 %. Anal. Calc'd for: $C_{66}H_{63}ClMoN_3O_3P_3U$ 0.4(C_7H_8): C, 57.03; H, 4.63; N, 2.92 %. Found: C, 57.00; H, 4.72; N, 2.92 %. ^{1}H NMR (C_6D_6 295 K): δ (ppm) 3.22 (12H, s, Ar-C*H*), 7.59 (6H, s, Ar-C*H*), 7.79 (12H, s, Ar-C*H*), 8.84 (9H, s, Mes-C*H*$_3$), 9.70 (6H, s, Ar-C*H*), 14.32 (18H, s, Mes-C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 295 K): No resonances observed. FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}): 519 (m), 542 (m), 579 (w), 601 (w), 661 (w), 697 (m), 722 (m), 745 (m), 762 (m), 800 (w), 854 (w), 897 (w), 959 (w), 1088 (m), 1144 (m), 1203 (m), 1307 (m), 1434 (m), 1891 (s), 1969 (s). Magnetic moment (Evans method, C_6D_6, 298 K): μ_{eff} = 2.25 μ_B.

Preparation of [(I)U(MesNPPh$_2$)$_3$Mo(CO)$_3$] (UIMo)

Toluene (40 ml) was added to a stirring mixture of **UI** (2.64 g, 2.0 mmol) and [Mo(CO)$_3$(NCMe)$_3$] (0.60 g, 2.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Upon cooling an orange microcrystalline solid precipitated from the reaction mixture, which was isolated *via* filtration and washed with hexanes (3 × 10 ml) to yield **UIMo** as an analytically pure powder. Orange crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **UIMo** at room temperature over 24 hours. Yield 1.86 g, 62 %. Anal. Calc'd for: $C_{66}H_{63}IMoN_3O_3P_3U$ 0.65(C_7H_8): C, 54.32; H, 4.66; N, 2.69 %. Found: C, 54.11; H, 4.66; N, 2.56 %. ^{1}H NMR (C_6D_6 295 K): δ (ppm) 3.54 (12H, s, Ar-C*H*), 7.94 (6H, s, Ar-C*H*),

8.25 (12H, s, Ar-C*H*), 9.28 (9H, s, Mes-CH_3), 11.32 (6H, s, Ar-C*H*), 22.54 (18H, s, Mes-CH_3 $^{31}P\{^1H\}$ NMR (C_6D_6, 295 K): No resonances observed. FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}): 518 (m), 541 (m), 578 (w), 600 (w), 660 (w), 696 (m), 724 (m), 745 (m), 761 (m), 800 (w), 854 (w), 895 (w), 959 (w), 1088 (m), 1142 (m), 1203 (m), 1307 (m), 1434 (m), 1893 (s), 1904 (s), 1969 (s). Magnetic moment (Evans method, C_6D_6, 298 K): μ_{eff} = 2.39 μ_B.

Preparation of [(Cl)Th(MesNPPh$_2$)$_3$Mo(CO)$_3$] (ThClMo)

Toluene (40 ml) was added to a stirring mixture of **ThCl** (1.22 g, 1.0 mmol) and [Mo(CO)$_3$(NCMe)$_3$] (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Upon cooling a yellow microcrystalline solid precipitated from the reaction mixture, which was isolated *via* filtration and washed with hexanes (3 × 10 ml) to yield **ThClMo** as an analytically pure powder. Yellow crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **ThClMo** at room temperature over 24 hours. Yield 0.51 g, 36 %. Anal. Calc'd for: $C_{66}H_{63}ClMoN_3O_3P_3Th$: C, 56.52; H, 4.53; N, 3.00 %. Found: C, 55.84; H, 4.68; N, 2.82 %. ^1H NMR (C_6D_6 295 K): δ (ppm) 2.03 (9H, s, Mes-CH_3) 2.14, (18H, s, Mes-CH_3), 6.66 (6H, s, Ar-C*H*), 6.95 (18H, m, Ar-C*H*), 7.81 (12H, m, Ar-C*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ (ppm) 20.23 (Mes-*C*H$_3$), 21.28 (Mes-*C*H$_3$), 127.48 (Ar-*C*H), 127.8 (Ar-*C*H), 129.07 (Ar-*C*H), 129.47 (Ar-*C*H), 131.06 (Ar-*C*), 134.08 (Ar-*C*), 142.41 (Ar-*C*), 142.84 (Ar-*C*). *C*O not observed due to low solubility. $^{31}P\{^1H\}$ NMR (C_6D_6, 295 K): δ (ppm) 46.18 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}): 522 (m), 542 (m), 581 (w), 606 (w), 665 (w), 697 (m), 744 (m), 765 (m), 854 (w), 899 (w), 959 (w), 1090 (m), 1144 (m), 1206 (m), 1305 (m), 1884 (s), 1896 (s), 1967 (s).

Preparation of [(I)Th(MesNPPh$_2$)$_3$Mo(CO)$_3$] (ThIMo)

Toluene (40 ml) was added to a stirring mixture of **ThI** (1.31 g, 1.0 mmol) and [Mo(MeCN)$_3$(CO)$_3$] (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Upon cooling a yellow microcrystalline solid precipitated from the reaction mixture, which was isolated *via* filtration and washed with hexanes (3 × 10 ml) to yield **ThIMo** as an analytically pure powder. Yellow crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **ThIMo** at room temperature over 24 hours. Yield 0.62 g, 41 %. Anal. Calc'd for: $C_{66}H_{63}IMoN_3O_3P_3Th$ 0.55(C_7H_8): C, 54.31; H, 4.40; N, 2.72 %. Found: C, 54.09; H, 4.70; N, 2.72 %. ^1H NMR (C_6D_6 295 K): δ (ppm) 2.02 (9H, s, Mes-CH_3) 2.17, (18H, s, Mes-CH_3), 6.71 (6H, s, Ar-C*H*), 6.93 (18H, m, Ar-C*H*), 7.82 (12H, m, Ar-C*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ (ppm) 20.29 (Mes-*C*H$_3$), 21.58 (Mes-*C*H$_3$), 127.48 (Ar-*C*H), 127.8 (Ar-*C*H), 129.09 (Ar-*C*H), 129.54 (Ar-*C*H),

131.48 (Ar-*C*), 134.23 (Ar-*C*), 142.13 (Ar-*C*), 142.57 (Ar-*C*). *C*O not observed due to low solubility. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 295 K): δ (ppm) 45.07 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}): 579 (w), 604(w), 663 (w), 696 (m), 745 (m), 763 (m), 854 (w), 902 (w), 960 (w), 1092 (m), 1144 (m), 1206 (m), 1305 (m), 1884 (s), 1898 (s), 1967 (s).

Preparation of [{(Cl)U(MesNPPh$_2$)}{μ-(MesNPh$_2$P)$_2$}Cr(CO)$_4$] (UCr)

Toluene (40 ml) was added to a mixture of **UCl** (0.20 g, 0.16 mmol) and [$Cr(CO)_6$] (179 mg, 0.81 mmol) in a Schlenk-type Quartz photolysis reactor. The light brown mixture was irradiated with a 125 W Hg UV-lamp for 3 h, upon which the colour changed to a light red. All volatiles were removed under vacuum and d_6-benzene (2 ml) was added to the resulting solid. The mixture was then filtered and concentrated under vacuum to *ca.* 1 ml. On standing red crystals of **UCr** suitable for a single crystal X-ray diffraction study were formed. Yield 25 mg (11%). ^{1}H NMR (C_6D_6 295 K): δ (ppm) 23.19 (2H, s, Ar-*H*), 14.17 (3H, s, Ar-*H*), 12.16 (2H, s, Ar-*H*), 9.35 (4H, s, Ar-*H*), 8.15 (3H, s, Ar-*H*), 7.61 (4H, s, Ar-*H*), 7.61 (4H, s, Ar-*H*), 7.03 (12H, s, Mes-C*H*$_3$), 6.63 (3H, s, Ar-*H*), 6.54 (2H, s, Ar-*H*), 6.12 (1H, s, Ar-*H*), 3.41 (2H, s, Ar-*H*), 2.31 (2H, s, Ar-*H*), 2.15 (2H, s, Ar-*H*), 2.05 (10H, s, Mes-C*H*$_3$ and Ar-H), -6.37 (2H, s, Ar-*H*), -17.55 (6H, s, Mes-C*H*$_3$), -63.81 (3H, s, Mes-C*H*$_3$). ^{31}P NMR (162 MHz, C_6D_6) δ 114.20, 99.67, 35.96. Magnetic moment (Evans method, C_6D_6, 298 K): μ_{eff} = 2.77 μ_B. FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}): 644 (s), 691 (s), 829 (m), 854 (m), 1086 (w), 1128 (w), 1433 (m), 1891 (s), 1916 (s), 1976 (w), 2013 (m), 3016 (w). There was insufficient material for further analysis.

Preparation of [{(Cl)U(MesNPPh$_2$)}{μ-(MesNPh$_2$P)$_2$}W(CO)$_4$] (UW)

Toluene (40 ml) was added to a mixture of **UCl** (0.70 g, 0.57 mmol) and [$W(CO)_6$] (1.00 g, 2.85 mmol) in a Schlenk-type Quartz photolysis reactor. The light brown mixture was irradiated with a 125 W Hg UV-lamp for 3 h, upon which the colour changed to a light red. All volatiles were removed *in vacuo* and d_6-benzene (2 ml) was added to the resulting solid. The mixture was then filtered and concentrated *in vacuo* to *ca.* 1 ml. On standing a small crop red crystals of **UW** suitable for a single crystal X-ray diffraction study were formed. Yield <20 mg (<3%). Upon dissolution of the red crystals, only diamagnetic decomposition products were observed *via* NMR spectroscopic studies.

2. Superconducting quantum interference device (SQUID) data

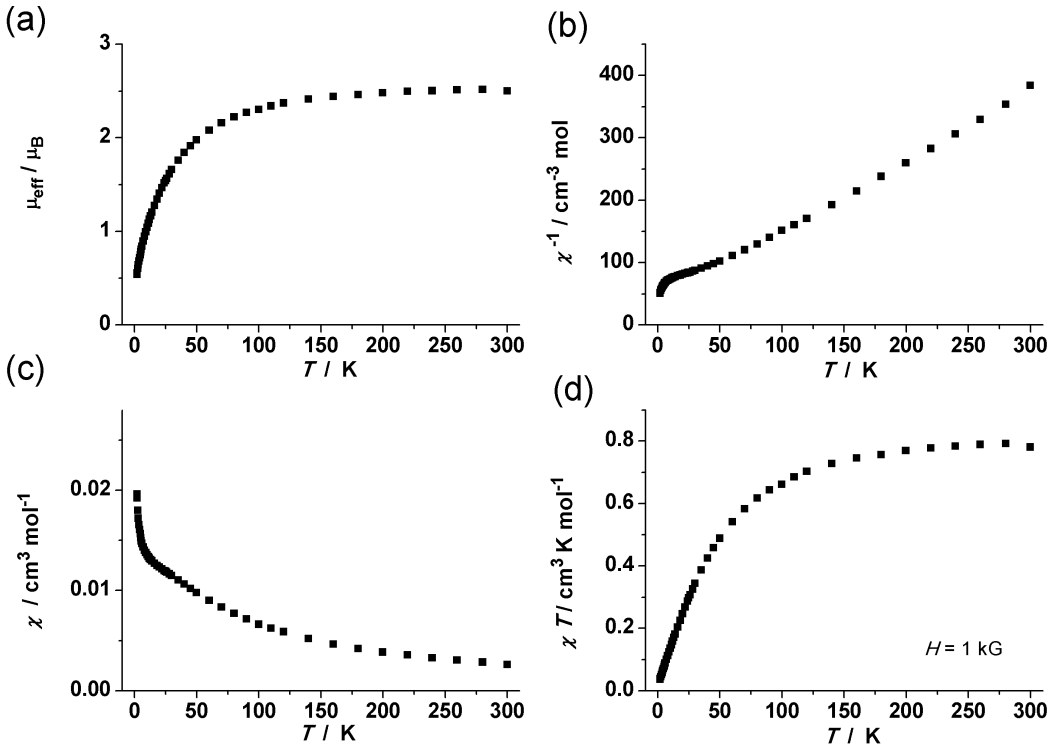

Figure S1. Variable temperature magnetism of **UClMo**. (a) μ_{eff} *vs* T. (b) $1/\chi$ *vs* T. (c) χ *vs* T. (d) χT *vs* T.

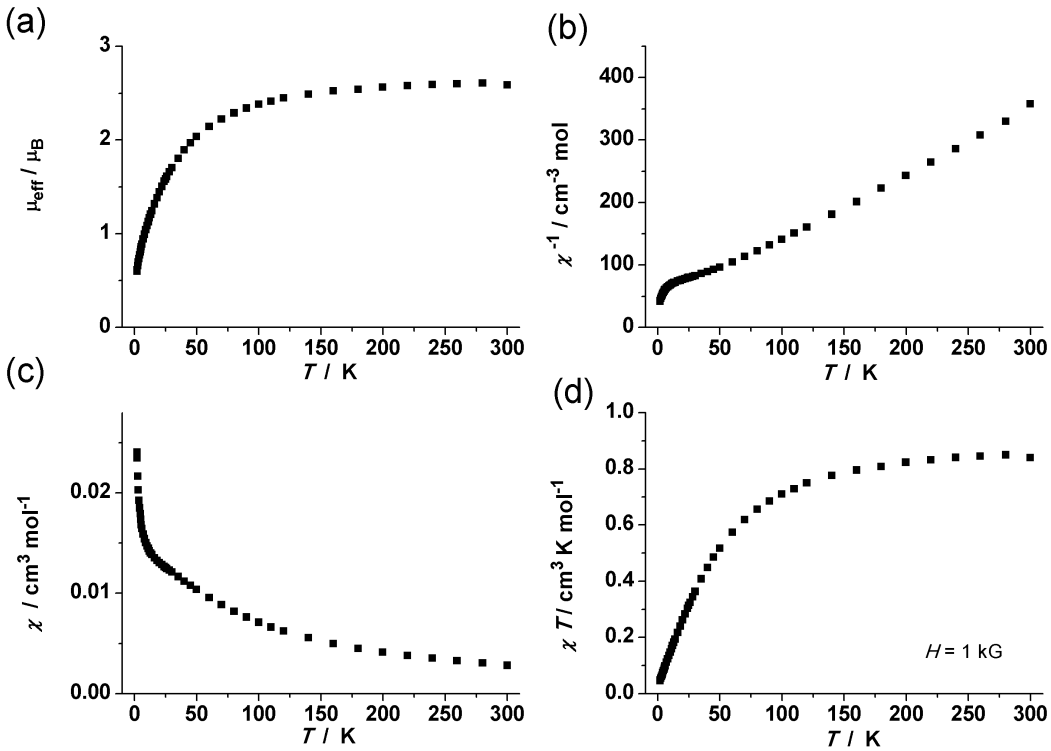

Figure S2. Variable temperature magnetism of **UIMo**. (a) μ_{eff} *vs* T. (b) $1/\chi$ *vs* T. (c) χ *vs* T. (d) χT *vs* T.

3. Single crystal X-ray diffraction (CCDC 1508432-1508441 and 1848240-1848241)

Crystals were examined variously using a) an Agilent Supernova diffractometer equipped with an Eos CCD area detector and a Microfocus source with Mo Kα radiation (λ = 0.71073 Å), b) an Agilent Supernova diffractometer, equipped with either an Atlas/AtlasS2 or TitanS2 CCD area detector and mirror-monochromated Cu Kα radiation (λ = 1.5418 Å), c) a Bruker SMART APEX diffractometer equipped with a CCD area detector with Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on narrow (0.3 or 0.5°) frames by *ω* rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Either Gaussian grid face-indexed or multi-scan absorption corrections with a beam profile correction were applied. The structures were solved by direct methods using either SHELXS or SHELXT,[3,4] and the datasets were refined by full-matrix least-squares on all unique F^2 values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; U_{iso}(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro,[5] SMART APEX and SAINT-PLUS[6] were used for control and integration, and SHELXL[7] and OLEX2[8] were employed for structure refinement. ORTEP-3[9] and POV-Ray[10] were employed for molecular graphics.

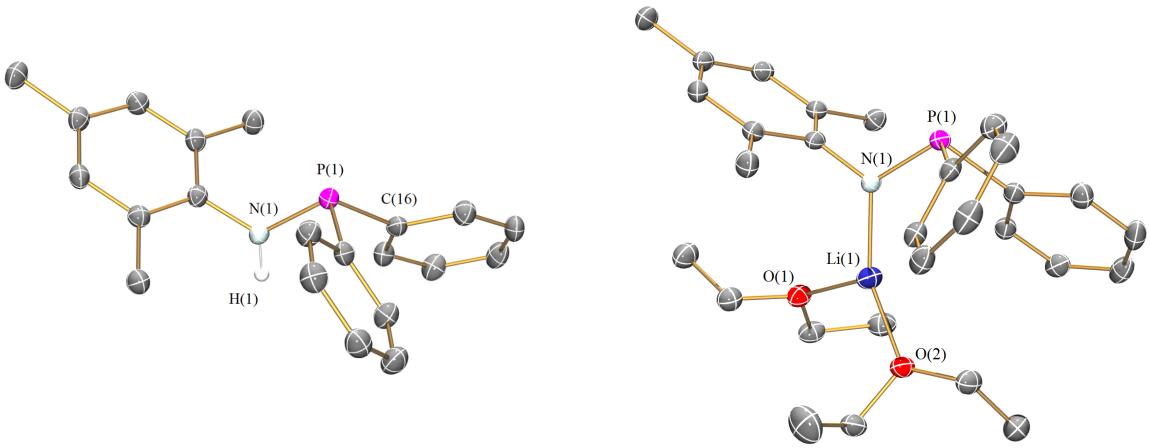

Figure S3. Molecular structures of $MesN(H)PPh_2$ and $[Li(MesNPPh_2)(OEt_2)_2]$.

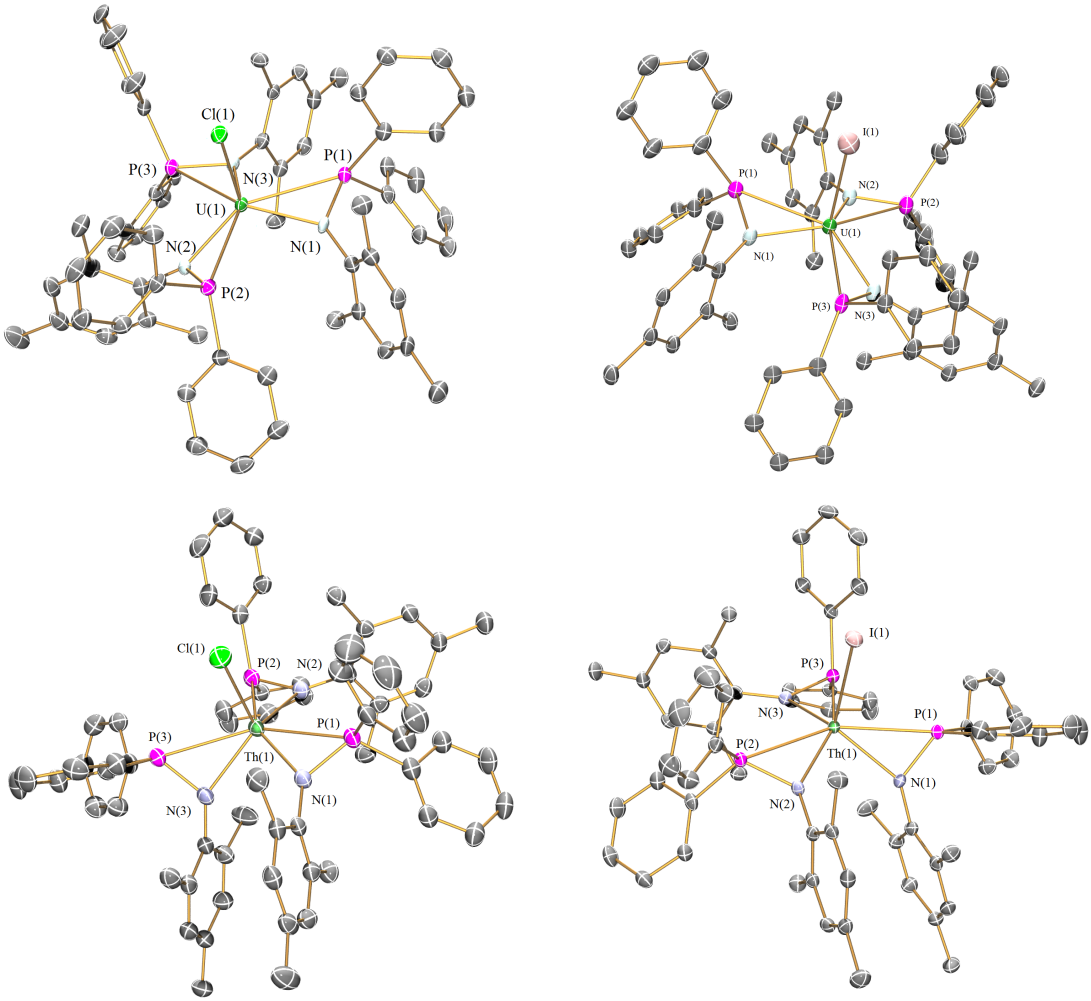

Figure S4. Top left to bottom right: Molecular structures of [ClU(MesNPPh$_2$)$_3$] (**UCl**), [IU(MesNPPh$_2$)$_3$] (**UI**), [ClTh(MesNPPh$_2$)$_3$] (**ThCl**), and [ITh(MesNPPh$_2$)$_3$] (**ThI**).

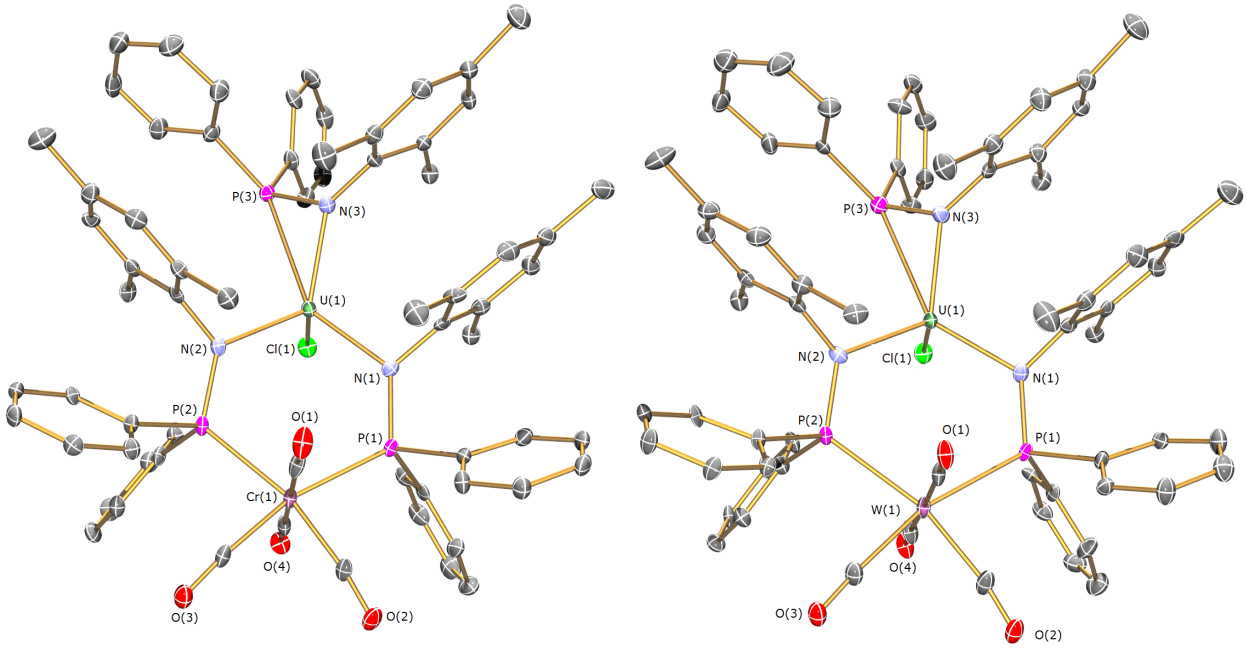

Figure S5. Molecular structures of [{(Cl)U(MesNPPh$_2$)}{μ-(MesNPh$_2$P)$_2$}Cr(CO)$_4$] (**UCr**) and [{(Cl)U(MesNPPh$_2$)}{μ-(MesNPh$_2$P)$_2$}W(CO)$_4$] (**UW**).

Table S1. Crystallographic data.

	MesNHPPh$_2$	LiMesNPPh$_2$(OEt$_2$)$_2$	**UCl**	**UI**
Formula	$C_{21}H_{22}NP$	$C_{29}H_{41}LiNO_2P$	$C_{77}H_{79}ClN_3P_3U$	$C_{77}H_{79}IN_3P_3U$
Fw, g mol^{-1}	319.36	473.54	1412.82	1504.27
Cryst size, mm	0.33 x 0.26 x 0.11	0.13 x 0.12 x 0.09	0.40 x 0.25 x 0.22	0.26 x 0.08 x 0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2$_1$/c	*P*2$_1$/c	*P*2$_1$/n	*P*2$_1$/n
Collection Temperature (K)	90(2)	90(2)	90(2)	90(2)
a, (Å)	14.1544(12)	19.3727(19)	15.9544(3)	12.496(3)
b, (Å)	4.5958(4)	9.1104(9)	22.7597(4)	39.078(9)
c, (Å)	26.774(2)	16.2220(16)	18.2868(3)	13.949(3)
α, (°)				
β, (°)	96.0990(10)	105.113(2)	96.5882(19)	91.079(5)
γ, (°)				
V, (Å^3)	1731.8(3)	2764.0(5)	6596.4(2)	6810(3)

Z	4	4	4	4
ρ_{calc} g cm-^{3}	1.225	1.138	1.423	1.467
μ, mm^{-1}	0.158	0.124	8.330	2.952
No. of reflections measured	14154	16708	29230	32237
No. of unique reflections, R_{int}	3886, 0.0348	6308, 0.0186	13076, 0.0427	11630, 0.1340
No. of reflections with $F^2 > 2s(F^2)$	3239	5744	11780	6785
Transmission coefficient range	0.78- 0.86	0.65-0.75	0.16-0.48	0.28-0.43
R, R_w[a] ($F^2 > 2s(F^2)$)	0.0395, 0.0977	0.0396, 0.1020	0.0379, 0.0995	0.1384, 0.2624
R, R_w[a] (all data)	0.0496, 0.1036	0.0439, 0.1058	0.0434, 0.1035	0.2084, 0.2898
S[a]	1.031	1.072	1.065	1.178
Parameters, Restraints	214, 0	314, 0	777, 0	777, 1257
Max.,min. difference map, e Å^{-3}	0.472, -0.278	0.350, -0.274	1.887, -1.244	8.172, -2.915

	ThCl	**ThI**	**UClMo**	**UIMo**
Formula	$C_{63}H_{63}ClN_3P_3Th$	$C_{63}H_{63}IN_3P_3Th$	$C_{80}H_{79}ClMoN_3O_3P_3U$	$C_{73}H_{71}IMoN_3O_3P_3U$
Fw, g mol^{-1}	1222.56	1314.01	1592.79	1592.10
Cryst size, mm	0.24 x 0.06 x 0.05	0.16 x 0.13 x 0.09	0.10 x 0.08 x 0.05	0.14 x 0.08 x 0.03
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	P-1
Collection Temperature (K)	120(2)	120(2)	120(2)	120(2)
a, (Å)	13.04797(8)	13.05887(12)	12.2335(2)	12.6048(5)
b, (Å)	25.46193(15)	25.3036(3)	13.3432(2)	13.3050(5)
c, (Å)	16.86018(11)	17.01612(16)	21.8523(4)	21.6579(10)
α, (°)			89.2225(14)	89.180(3)
β, (°)	97.4230(6)	96.6633(9)	74.9637(18)	75.294(4)
γ, (°)			89.8281(15)	88.901(3)
V, (Å^3)	5554.46(6)	5584.76(10)	3444.58(11)	3512.4(3)
Z	4	4	2	2
ρ_{calc} g cm-^{3}	1.462	1.563	1.536	1.505

μ, mm^{-1}	10.234	14.079	9.473	12.355
No. of reflections measured	83099	23954	43652	13805
No. of unique reflections, Rint	11261, 0.0579	11115, 0.0239	13636, 0.0531	12381, 0.0898
No. of reflections with $F^2 > 2s(F^2)$	10585	10426	12578	10599
Transmission coefficient range	0.65 – 1.00	0.98-0.99	0.66-0.81	0.049-1.00
R, $R_w{}^a$ ($F^2 > 2s(F^2)$)	0.0240, 0.0614	0.0226, 0.0528	0.0363, 0.0877	0.1542, 0.3786
R, $R_w{}^a$ (all data)	0.0258, 0.0626	0.0248, 0.0540	0.0407, 0.0901	0.1663, 0.3836
S^a	1.044	1.046	1.020	1.189
Parameters, Restraints	649, 0	649, 0	905, 399	841, 1381
Max.,min. difference map, e Å^{-3}	1.064, -1.043	1.470, -0.917	2.036, -1.286	8.965, -4.259

	ThClMo	**ThIMo**	**UCr**	**UW**
Formula	$C_{80}H_{79}ClMoN_3O_3P_3Th$	$C_{73}H_{71}IMoN_3O_3P_3Th$	$C_{67}H_{63}ClCrN_3O_4P_3U$	$C_{67}H_{63}ClN_3O_4P_3UW$
Fw, g mol^{-1}	1586.80	1586.11	1392.59	1524.44
Cryst size, mm	0.06 x 0.05 x 0.05	0.08 x 0.06 x 0.03	0.159 x 0.09 x 0.07	0.167 x 0.092 x 0.034
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
Collection Temperature (K)	120(2)	120(2)	150(2)	150(2)
a, (Å)	12.3260(6)	12.7259(5)	13.7659(6)	13.6390(17)
b, (Å)	13.3087(4)	13.3141(6)	14.4077(5)	14.6571(18)
c, (Å)	21.9496(10)	21.7153(10)	16.5607(7)	16.721(2)
α, (°)	88.897(3)	88.662(4)	76.698(3)	76.466(10)
β, (°)	74.385(4)	75.262(4)	89.117(3)	88.965(10)
γ, (°)	89.611(3)	88.660(3)	67.671(4)	67.082(12)
V, (Å^3)	3467.1(3)	3556.7(3)	2947.3(2)	2983.4(7)
Z	2	2	2	2
ρ_{calc} g cm-^{3}	1.520	1.481	1.569	1.697
μ, mm^{-1}	9.758	12.539	3.107	4.814
No. of reflections measured	24004	26816	46071	22831
No. of unique reflections, Rint	12669, 0.1140	13995, 0.0945	11171, 0.0946	10523, 0.0933

No. of reflections with $F^2 > 2s(F^2)$	9296	10758	9764	6399
Transmission coefficient range	0.64-0.73	0.68-0.85	0.98-0.99	0.790-0.933
R, $R_w{}^a$ ($F^2 > 2s(F^2)$)	0.0806, 0.1664	0.1262, 0.3284	0.0506, 0.1099	0.0725, 0.1055
R, $R_w{}^a$ (all data)	0.1147, 0.1849	0.1497, 0.3409	0.0605, 0.1167	0.1355, 0.1237
S^a	1.073	1.124	1.115	1.025
Parameters, Restraints	980, 1835	770, 790	730, 0	730, 758
Max.,min. difference map, e Å^{-3}	3.074, -1.503	6.943, -3.950	2.080, -1.543	2.076, -1.540

Table S2. Selected bond lengths (Å) and angles (°).

$MesNHPPh_2$			
P1-N1	1.7011(13)	N1-C1	1.4313(18)
P1-C10	1.8268(15)	N1-H1	0.85(2)
P1-C16	1.8375(14)	N1-P1-C16	103.51(6)
N1-P1-C10	102.90(7)	P1-N1-H1	116.1(12)
C10-P1-C16	101.51(6)	C1-N1-H1	116.7(12)
C1-N1-P1	118.78(10)		
$LiMesNPPh_2(OEt_2)_2$			
P1-N1	1.6580(10)	P1-C10	1.8523(12)
P1-C16	1.8642(13)	O1-Li1	1.930(2)
O2-Li1	1.932(2)	N1-C1	1.4191(14)
N1-Li1	1.922(2)	N1-Li1-O1	113.46(11)
N1-P1-C10	102.22(5)	N1-P1-C16	106.45(5)
C10-P1-C16	95.79(5)	C26-O1-Li1	122.95(10)
C22-O2-Li1	126.79(10)	C28-O1-Li1	118.27(10)
C1-N1-Li1	117.48(10)	C24-O2-Li1	118.78(10)
P1-N1-Li1	125.77(9)	C1-N1-P1	115.79(8)
O1-Li1-O2	107.68(11)	N1-Li1-O2	135.88(12)
UCl			
U1-Cl1	2.5967(11)	U1-P1	2.9486(11)
U1-P2	2.8786(11)	U1-P3	2.9334(12)
U1-N1	2.261(4)	U1-N2	2.287(3)
U1-N3	2.256(4)	P1-N1	1.693(4)
P1-C10	1.831(5)	P1-C16	1.833(5)
P2-N2	1.688(4)	P2-C31	1.836(5)
P2-C37	1.824(5)	P3-N3	1.697(4)
P3-C52	1.833(5)	P3-C58	1.844(5)
N1-C1	1.431(6)	N2-C22	1.431(6)
N3-C43	1.438(6)	N2-U1-P1	148.97(10)
Cl1-U1-P1	94.69(3)	Cl1-U1-P2	95.05(3)

Cl1-U1-P3	90.59(3)	P2-U1-P1	117.14(3)
P2-U1-P3	122.68(3)	P3-U1-P1	119.13(3)
N1-U1-Cl1	103.00(10)	N1-U1-P1	34.87(10)
N1-U1-P2	82.55(10)	N1-U1-P3	150.52(10)
N1-U1-N2	114.82(14)	N2-U1-Cl1	101.69(10)
N2-U1-P3	87.13(10)	N3-U1-Cl1	104.95(10)
N3-U1-P1	85.66(10)	N3-U1-P2	148.49(9)
N3-U1-P3	35.20(10)	N3-U1-N1	115.33(13)
N3-U1-N2	114.65(13)	N2-U1-P2	35.90(10)
UI			
U1-I1	2.980(2)	U1-P1	2.949(6)
U1-P2	2.932(5)	U1-P3	2.941(6)
U1-N1	2.288(17)	U1-N2	2.309(17)
U1-N3	2.280(17)	P1-N1	1.685(18)
P1-C10	1.82(3)	P1-C16	1.80(3)
P2-N2	1.695(17)	P2-C31	1.84(2)
P2-C37	1.85(2)	P3-N3	1.703(17)
P3-C52	1.81(3)	P3-C58	1.81(2)
N1-C1	1.44(3)	N2-C22	1.44(3)
N3-C43	1.41(3)	N3 -U1- N2	112.0(6)
P1 -U1- I1	95.35(14)	P2 -U1- I1	95.66(13)
P2 -U1- P1	118.84(16)	P2 -U1- P3	119.73(15)
P3 -U1- I1	90.78(14)	P3 -U1- P1	120.04(15)
N1 -U1- I1	102.5(5)	N1 -U1- P1	34.7(4)
N1 -U1- P2	148.5(5)	N1 -U1- P3	85.8(4)
N1 -U1- N2	113.4(6)	N2 -U1- I1	111.0(5)
N2 -U1- P1	85.3(4)	N2 -U1- P2	35.3(4)
N2 -U1- P3	145.6(5)	N3 -U1- I1	100.3(5)
N3 -U1- P1	150.1(5)	N3 -U1- P2	84.9(4)
N3 -U1- P3	35.3(4)	N3 -U1- N1	116.2(6)
ThCl			
Th1- Cl1	2.6686(6)	Th1-P1	2.9612(6)
Th1-P2	2.9469(6)	Th1-P3	2.8700(6)
Th1-N1	2.345(2)	Th1-N2	2.335(2)
Th1-N3	2.356(2)	P1-N1	1.687(2)
P1-C10	1.831(3)	P1-C16	1.826(3)
P2-N2	1.685(2)	P2-C31	1.822(3)
P2-C37	1.832(3)	P3-N3	1.680(2)
P3-C52	1.826(3)	P3-C58	1.822(3)
N1-C1	1.431(3)	N2-C22	1.429(3)
N3-C43	1.433(3)	N3-Th1-P3	35.83(5)
Cl1-Th1-P1	101.26(2)	Cl1-Th1-P2	92.68(2)
Cl1-Th1-P3	89.15(2)	P2-Th1-P1	121.887(18)
P3-Th1-P1	85.541(18)	P3-Th1-P2	151.408(18)
N1-Th1-Cl1	108.56(5)	N1-Th1-P1	34.66(5)
N1-Th1-P2	87.38(5)	N1-Th1-P3	118.98(5)
N1-Th1-N3	122.22(7)	N2-Th1-Cl1	101.45(5)
N2-Th1-P1	147.98(5)	N2-Th1-P2	34.83(5)

N2-Th1-P3	117.04(5)	N2-Th1-N1	115.54(7)
N2-Th1-N3	88.51(7)	N3-Th1-Cl1	117.19(5)
N3-Th1-P1	100.78(5)	N3-Th1-P2	121.93(5)
ThI			
Th1-I1	3.08187(19)	Th1-P1	2.9618(6)
Th1-P2	2.8612(6)	Th1-P3	2.9454(7)
Th1-N1	2.342(2)	Th1-N2	2.351(2)
Th1-N3	2.332(2)	P1-N1	1.692(2)
P1-C10	1.824(3)	P1-C16	1.826(3)
P2-N2	1.680(2)	P2-C31	1.824(3)
P2-C37	1.819(3)	P3-N3	1.688(2)
P3-C52	1.829(3)	P3-C58	1.831(3)
N1-C1	1.431(3)	N2-C22	1.432(3)
N3-C43	1.433(3)	N3-Th1-N2	88.93(8)
P1-Th1-I1	101.748(13)	P2-Th1-I1	88.652(14)
P2-Th1-P1	83.764(18)	P2-Th1-P3	152.240(17)
P3-Th1-I1	93.628(14)	P3-Th1-P1	122.576(17)
N1-Th1-I1	108.64(5)	N1-Th1-P1	34.79(6)
N1-Th1-P2	117.59(6)	N1-Th1-P3	87.85(6)
N1-Th1-N2	121.43(8)	N2-Th1-I1	116.82(5)
N2-Th1-P1	99.00(6)	N2-Th1-P2	35.94(5)
N2-Th1-P3	122.25(6)	N3-Th1-I1	101.79(6)
N3-Th1-P1	148.32(5)	N3-Th1-P2	117.66(5)
N3-Th1-P3	34.92(5)	N3-Th1-N1	116.31(7)
UClMo			
U1-Mo1	3.1682(4)	U1-Cl1	2.5535(15)
U1-N2	2.290(4)	U1-N1	2.278(3)
Mo1-P1	2.6354(11)	U1-N3	2.283(3)
Mo1-P3	2.6068(11)	Mo1-P2	2.6398(11)
Mo1-C65	2.001(5)	Mo1-C64	1.997(5)
P1-N1	1.683(4)	Mo1-C66	1.997(5)
O1-C64	1.136(6)	O2-C65	1.139(6)
O3-C66	1.137(6)	P2-N2	1.681(4)
P3-N3	1.676(4)	P1-U1-Mo1	49.83(2)
Cl1-U1-Mo1	171.79(4)	N1-U1-Cl1	90.19(10)
P3-U1-Mo1	49.19(2)	N1-U1-N3	122.51(13)
N1-U1-Mo1	81.85(10)	N2-U1-Cl1	103.47(11)
N1-U1-N2	109.67(13)	N3-U1-Cl1	101.69(10)
N2-U1-Mo1	81.24(10)	P1-Mo1-U1-	63.45(2)
N3-U1-Mo1	81.12(9)	P2-Mo1-U1	64.33(3)
N3-U1-N2	121.17(14)	P3-Mo1-P1	104.02(3)
P1-Mo1-P2	100.25(4)	C64-Mo1-U1	131.58(16)
P3-Mo1-U1	63.89(2)	C64-Mo1-P2	85.92(15)
P3-Mo1-P2	101.94(3)	C64-Mo1-C65	84.0(2)
C64-Mo1-P1	87.59(14)	C65-Mo1-U1	130.43(13)
C64-Mo1-P3	164.37(16)	C65-Mo1-P2	90.79(14)
C64-Mo1-C66	82.54(19)	C66-Mo1-U1	127.58(13)
C65-Mo1-P1	165.62(13)	C66-Mo1-P2	167.49(13)

C65-Mo1-P3	82.41(14)	C66-Mo1-C65	83.25(19)
C66-Mo1-P1	84.11(13)	C66-Mo1-P3	88.21(13)
UIMo			
U1-Mo1	3.159(2)	U1-I1	2.972(3)
U1-N1	2.30(3)	U1-N2	2.26(2)
U1-N3	2.29(2)	Mo1-P1	2.625(8)
Mo1-P2	2.627(8)	Mo1-P3	2.600(8)
Mo1-C64	2.01(3)	Mo1-C65	2.06(3)
Mo1-C66	2.03(3)	O1-C64	1.13(3)
O2-C65	1.06(4)	O3-C66	1.12(4)
I1-U1-Mo1	169.71(8)	N1-U1-I1	88.9(7)
N1-U1-Mo1	81.8(7)	N2-U1-I1	106.0(6)
N2-U1-Mo1	81.3(6)	N2-U1-N1	108.4(9)
N2-U1-N3	122.9(9)	N3-U1-I1	100.4(6)
N3-U1-Mo1	81.0(6)	N3-U1-N1	122.0(9)
P1-Mo1-U1	63.46(18)	P1-Mo1-P2	100.1(3)
P2-Mo1-U1	64.94(18)	P3-Mo1-U1	63.84(17)
P3-Mo1-P1	103.6(2)	P3-Mo1-P2	103.1(2)
C64-Mo1-U1	129.2(8)	C64-Mo1-P1	166.9(8)
C64-Mo1-P2	89.8(8)	C64-Mo1-P3	82.1(8)
C64-Mo1-C65	83.5(12)	C64-Mo1-C66	84.8(12)
C65-Mo1-U1	132.7(9)	C65-Mo1-P1	88.8(9)
C65-Mo1-P2	85.3(9)	C65-Mo1-P3	163.3(9)
C66-Mo1-U1	127.3(9)	C66-Mo1-P1	83.6(9)
C66-Mo1-P2	166.8(9)	C66-Mo1-P3	88.1(10)
C66-Mo1-C65	82.1(13)		
ThClMo			
Th1-Mo1	3.2986(11)	Th1-Cl1	2.640(3)
Th1-N1	2.322(9)	Th1-N2	2.314(9)
Th1-N3	2.342(9)	Mo1-P1	2.629(3)
Mo1-P2	2.635(3)	Mo1-P3	2.610(3)
Mo1-C64	1.941(13)	Mo1-C65	2.002(13)
Mo1-C66	2.011(14)	O1-C64	1.202(17)
O2-C65	1.113(16)	O3-C66	1.095(16)
Cl1-Th1-Mo1	172.18(8)	P1-Th1-Mo1	47.59(6)
P2-Th1-Mo1	48.04(6)	P3-Th1-Mo1	47.43(6)
N1-Th1-Mo1	77.7(2)	N1-Th1-Cl1	107.3(3)
N1-Th1-P1	30.1(2)	N1-Th1-N3	119.5(3)
N2-Th1-Mo1	79.0(2)	N2-Th1-Cl1	93.5(2)
N2-Th1-N1	109.9(3)	N2-Th1-N3	118.1(3)
N3-Th1-Mo1	77.6(2)	N3-Th1-Cl1	104.3(2)
P1-Mo1-P2	101.11(10)	P1-Mo1-Th1	64.54(7)
P3-Mo1-Th1	64.01(7)	P2-Mo1-Th1	63.39(7)
P3-Mo1-P2	103.42(10)	P3-Mo1-P1	102.04(9)
C64-Mo1-P1	85.3(4)	C64-Mo1-Th1	130.8(5)
C64-Mo1-P3	165.0(5)	C64-Mo1-P2	87.7(4)
C64-Mo1-C66	84.2(6)	C64-Mo1-C65	82.5(5)
C65-Mo1-P1	166.7(4)	C65-Mo1-Th1	128.1(4)

C65-Mo1-P3	88.6(4)	C65-Mo1-P2	83.8(4)
C66-Mo1-Th1	131.0(3)	C65-Mo1-C66	82.6(5)
C66-Mo1-P2	164.9(3)	C66-Mo1-P1	90.8(3)
C66-Mo1-P3	82.7(4)		
ThIMo			
Th1-Mo1	3.310(2)	Th1-I1	3.030(2)
Th1-N1	2.337(19)	Th1-N2	2.312(19)
Th1-N3	2.311(19)	Mo1-P1	2.597(6)
Mo1-P2	2.623(6)	Mo1-P3	2.612(6)
Mo1-C64	2.01(2)	Mo1-C65	1.96(2)
Mo1-C66	1.98(2)	O1-C64	1.13(3)
O2-C65	1.18(3)	O3-C66	1.16(3)
I1-Th1-Mo1	170.81(6)	N1-Th1-I1	103.7(5)
N1-Th1-Mo1	78.0(5)	N2-Th1-I1	109.0(5)
N2-Th1-N1	120.6(7)	N3-Th1-I1	93.3(5)
N3-Th1-Mo1	78.0(5)	N3-Th1-N1	116.6(7)
N3-Th1-N2	109.5(7)	N2-Th1-Mo1	77.1(5)
P2-Mo1- Th1	64.75(14)	P1-Mo1- Th1	63.83(13)
C64-Mo1-Th1	130.0(6)	P3-Mo1- Th1	63.47(13)
C64-Mo1-P2	90.8(6)	C64-Mo1-P1	82.0(6)
C65-Mo1-Th1	128.5(7)	C64-Mo1-P3	165.8(6)
C65-Mo1-P2	165.8(8)	C65-Mo1-P1	89.2(8)
C65-Mo1-C64	83.0(9)	C65-Mo1-P3	83.9(7)
C66-Mo1-Th1	131.8(7)	C65-Mo1-C66	81.8(10)
C66-Mo1-P2	84.9(7)	C66-Mo1-P1	164.1(7)
C66-Mo1-C64	83.9(9)	C66-Mo1-P3	88.8(7)
UCr			
U1-Cl1	2.6149(15)	U1-P3	2.8990(16)
U1-N1	2.236(5)	U1-N2	2.221(5)
U1-N3	2.259(5)	U1-C22	2.946(6)
Cr1-P1	2.4017(17)	Cr1-P2	2.3939(18)
Cr1-C64	1.904(7)	Cr1-C65	1.848(7)
Cr1-C66	1.856(6)	Cr1-C67	1.878(7)
O1-C64	1.144(7)	O2-C65	1.162(8)
O3-C66	1.159(7)	O4-C67	1.155(7)
Cl1-U1-P3	84.61(5)	Cl1-U1-C22	105.90(13)
P3-U1-C22	120.37(12)	N1-U1-Cl1	105.24(13)
N1-U1-P3	101.24(13)	N1-U1-N3	120.06(18)
N1-U1-C22	129.48(17)	N2-U1-Cl1	97.52(13)
N2-U1-P3	147.70(13)	N2-U1-N1	109.12(18)
N2-U1-N3	115.42(18)	N2-U1-C22	28.14(17)
N3-U1-Cl1	106.39(12)	N3-U1-P3	35.39(12)
N3-U1-C22	87.30(17)	P2-Cr1-P1	110.53(6)
C64-Cr1-P1	87.77(18)	C64-Cr1-P2	88.37(18)
C65-Cr1-P1	83.04(19)	C65-Cr1-P2	166.15(19)
C65-Cr1-C64	89.4(3)	C65-Cr1-C66	83.4(3)
C65-Cr1-C67	93.1(3)	C66-Cr1-P1	166.3(2)
C66-Cr1-P2	82.9(2)	C66-Cr1-C64	90.2(3)

C66-Cr1-C67	92.3(3)	C67-Cr1-P1	90.32(19)
C67-Cr1-P2	89.7(2)	C67-Cr1-C64	176.6(3)
UW			
U1-Cl1	2.606(3)	U1-P3	2.911(3)
U1-N1	2.267(9)	U1-N2	2.243(10)
U1-N3	2.270(9)	U1-C22	2.970(12)
W1-P1	2.528(3)	W1-P2	2.521(3)
W1-C64	2.004(13)	W1-C65	2.065(13)
W1-C66	2.015(12)	W1-C67	1.986(12)
O1-C64	1.146(13)	O2-C65	1.122(14)
O3-C66	1.123(13)	O4-C67	1.174(13)
Cl1-U1-P3	83.44(10)	Cl1-U1-C22	104.1(3)
P3-U1-C22	117.8(2)	N1-U1-Cl1	105.9(3)
N1-U1-P3	95.9(3)	N1-U1-N3	114.1(3)
N1-U1-C22	136.9(3)	N2-U1-Cl1	95.7(3)
N2-U1-P3	143.9(2)	N2-U1-N1	118.8(3)
N2-U1-N3	113.8(4)	N2-U1-C22	27.4(3)
N3-U1-Cl1	105.5(3)	N3-U1-P3	34.7(3)
N3-U1-C22	86.3(3)	P2-W1-P1	112.23(10)
C64-W1-P1	165.7(4)	C64-W1-P2	81.9(3)
C65-W1-P1	86.6(4)	C65-W1-P2	88.0(3)
C65-W1-C64	91.4(5)	C65-W1-C66	88.7(5)
C65-W1-C67	174.6(5)	C66-W1-P1	81.7(4)
C66-W1-P2	165.5(3)	C66-W1-C64	84.1(5)
C66-W1-C67	95.6(5)	C67-W1-P1	90.8(4)
C67-W1-P2	88.5(3)	C67-W1-C64	92.2(5)

4. Density Function Theory Data

General

Unrestricted and restricted geometry optimisations were performed as appropriate for the full models of **UClMo**, **UIMo**, **ThClMo**, and **ThIMo** using coordinates derived from the X-ray crystal structures. No constraints were imposed on the structures during the geometry optimisations. The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2012.01.[11,12] 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*[13] was used in all of the calculations. Gradient corrections were performed using the functionals of Becke[14] and Perdew.[15] MOLEKEL[16] was used to prepare the three-dimensional plots of the

electron density. Natural Bond Order (NBO) analyses were carried out with NBO 5.0.[17] The Atoms in Molecules analysis was carried out with Xaim-1.0.[18-20]

Table S3. Final coordinates and single point energy for the geometry optimised structure of UClMo

1.C	-1.466116	-1.861496	-5.988364
2.C	-1.470524	-3.192377	-5.559596
3.C	0.405670	3.643143	-5.545656
4.C	1.254669	2.535111	-5.431955
5.C	-1.186414	-0.830224	-5.086312
6.C	-0.730869	3.724099	-4.737666
7.C	0.971666	1.524902	-4.511554
8.C	-1.192853	-3.486875	-4.220849
9.C	-1.015494	2.710079	-3.814632
10.C	-0.895486	-1.117606	-3.739803
11.C	-0.161846	1.605372	-3.682009
12.C	-0.902632	-2.456684	-3.323634
13.C	-4.077458	-0.874973	-3.117207
14.C	-5.482652	1.078245	-2.512523
15.C	-4.214074	0.475579	-2.467913
16.C	-7.144583	2.925306	-2.003192
17.C	1.972803	-1.807054	-2.373984
18.C	1.965886	4.775871	-2.007973
19.C	-5.758494	2.328784	-1.959385
20.C	2.834680	0.659034	-2.087172
21.C	0.475494	-6.436815	-1.654735
22.C	-3.156032	1.161040	-1.818115
23.C	2.850784	5.686596	-1.422497
24.C	1.661848	-5.716302	-1.467552
25.C	1.679503	3.568671	-1.365305
26.C	-0.721782	-5.933205	-1.142076
27.C	-4.694830	3.003604	-1.350412
28.C	-3.416881	2.446855	-1.267826
29.C	1.643459	-4.498951	-0.786724
30.C	-0.740605	-4.712679	-0.454692
31.C	3.435083	5.386274	-0.187414
32.C	-2.341329	3.216950	-0.551955
33.C	0.438302	-3.974906	-0.282085
34.C	-3.407745	-2.462624	-0.196309
35.C	2.257276	3.255565	-0.127477
36.C	3.340376	-1.144772	-0.212003
37.C	3.137570	4.183388	0.460469
38.C	4.545954	1.408182	1.167075
39.C	-3.185290	-2.973194	1.199562
40.C	-0.073797	4.925940	1.341651
41.C	-4.204925	-3.708613	1.806670
42.C	5.717444	1.290353	1.914883

43.C	3.290897	1.489000	1.801469
44.C	-2.002612	-2.658408	1.925413
45.C	1.604573	-2.919815	2.038932
46.C	1.563550	-4.249816	2.498072
47.C	0.007900	4.176153	2.648695
48.C	2.423725	-2.000246	2.708162
49.C	0.164022	2.771208	2.758997
50.C	-4.129514	-4.126550	3.141418
51.C	5.659505	1.249839	3.313589
52.C	3.244510	1.462738	3.201401
53.C	-1.935872	-3.017169	3.292025
54.C	-5.253950	-4.904228	3.782468
55.C	2.324310	-4.641146	3.603015
56.C	-0.148564	4.937584	3.818168
57.C	-2.994272	-3.752829	3.856086
58.C	3.184158	-2.390576	3.813508
59.C	4.420891	1.338605	3.951744
60.C	0.022177	2.176488	4.041688
61.C	3.137298	-3.713661	4.263757
62.C	-0.044399	0.682769	4.206968
63.C	-0.833731	-2.603377	4.232520
64.C	-0.191134	4.375625	5.094415
65.C	-0.129289	2.981008	5.175462
66.C	-0.312273	5.237778	6.329278
67.H	-1.676310	-1.618890	-7.031203
68.H	-1.676552	-3.996756	-6.268181
69.H	0.627925	4.434271	-6.263969
70.H	2.142424	2.456346	-6.060220
71.H	-1.194298	0.199582	-5.442033
72.H	-1.410745	4.572826	-4.824831
73.H	1.634841	0.663517	-4.448158
74.H	-3.761470	-0.778932	-4.167565
75.H	-1.175916	-4.520272	-3.873018
76.H	-5.043770	-1.395937	-3.111785
77.H	-6.291988	0.522021	-2.992910
78.H	-1.922348	2.777038	-3.218188
79.H	1.507873	4.991559	-2.973773
80.H	-7.186629	3.797567	-2.674041
81.H	-3.336873	-1.506493	-2.620577
82.H	-7.881187	2.194353	-2.360129
83.H	0.488763	-7.387610	-2.190496
84.H	-0.655316	-2.707424	-2.293429
85.H	3.090664	6.622094	-1.931453
86.H	2.606054	-6.101174	-1.854372
87.H	1.009617	2.857739	-1.846062
88.H	-1.651402	-6.491607	-1.262818
89.H	-7.461670	3.265951	-1.007223
90.H	-4.864978	3.984548	-0.899018
91.H	-1.359943	3.103827	-1.031568

92.H	-4.214068	-3.016207	-0.692907
93.H	-2.510929	-2.532986	-0.822681
94.H	2.578229	-3.957667	-0.641244
95.H	-2.574692	4.288277	-0.523913
96.H	-1.676420	-4.360235	-0.030461
97.H	4.127740	6.089150	0.277894
98.H	-3.709913	-1.402752	-0.173102
99.H	4.612910	1.447937	0.079978
100.H	-0.165354	4.258217	0.484198
101.H	-2.256306	2.903714	0.504449
102.H	0.815046	5.552260	1.178501
103.H	3.596884	3.971990	1.426045
104.H	-5.096965	-3.941643	1.218884
105.H	-0.947234	5.593653	1.358118
106.H	6.677553	1.229816	1.401896
107.H	0.934757	-4.985663	1.996091
108.H	2.488860	-0.971969	2.355798
109.H	-5.475526	-5.825797	3.223774
110.H	-6.180889	-4.311632	3.809386
111.H	-0.257667	6.020534	3.708624
112.H	6.575865	1.155922	3.899346
113.H	0.683783	0.153032	3.580096
114.H	2.296386	1.564778	3.719963
115.H	2.282140	-5.676704	3.944163
116.H	-0.104542	-1.944105	3.759714
117.H	-1.046299	0.317970	3.930589
118.H	3.825702	-1.660295	4.307088
119.H	-5.007215	-5.186110	4.814062
120.H	-0.289937	-3.477097	4.619907
121.H	-2.919498	-4.022156	4.913683
122.H	4.359571	1.323808	5.041091
123.H	3.739743	-4.023495	5.119772
124.H	-1.266931	-2.077875	5.096254
125.H	0.134171	0.389957	5.249373
126.H	-1.029236	6.056383	6.177530
127.H	-0.220065	2.494597	6.150005
128.H	0.654823	5.696434	6.587931
129.H	-0.642982	4.651792	7.196383
130.Cl	-3.077794	0.764707	1.998817
131.Mo	1.624274	-0.442710	-0.950296
132.N	-1.856883	0.593393	-1.551908
133.N	-0.981485	-1.889562	1.243367
134.N	0.375032	1.891740	1.629393
135.O	2.361719	-2.498388	-3.229765
136.O	3.673996	1.153440	-2.734049
137.O	4.381723	-1.607484	0.044231
138.P	-0.507653	0.214794	-2.500405
139.P	0.531525	-2.359471	0.631858
140.P	1.793865	1.665028	0.715004

141.U -0.983774 0.319397 0.581792
Energy: –894.70447696 eV

Table S4. Final coordinates and single point energy for the geometry optimised structure of UIMo

1.C	0.071238	-0.416735	-6.670371
2.C	1.048864	0.357909	-6.033472
3.C	-1.082532	-0.776558	-5.970766
4.C	0.875476	0.755383	-4.707544
5.C	-1.259424	-0.375028	-4.640046
6.C	-1.253788	4.637140	-4.095404
7.C	0.778542	-3.722687	-4.070831
8.C	1.370054	-4.988317	-4.009180
9.C	-7.254104	0.096023	-3.670658
10.C	-0.276499	0.383207	-3.988904
11.C	-1.112884	3.269943	-3.843422
12.C	-0.827638	5.576903	-3.150049
13.C	-5.869768	0.218527	-3.080107
14.C	1.904283	-5.442240	-2.799068
15.C	0.730799	-2.917102	-2.930914
16.C	-5.055904	-0.904171	-2.890781
17.C	-5.348152	1.450670	-2.689856
18.C	-0.543473	2.823263	-2.635985
19.C	2.598876	-0.493760	-2.405832
20.C	-3.763414	-0.805092	-2.371017
21.C	-4.053986	1.605912	-2.163776
22.C	-0.257683	5.141412	-1.949694
23.C	-3.221562	0.467759	-2.046945
24.C	-3.000892	-2.069138	-2.097381
25.C	1.845728	-4.638792	-1.655928
26.C	1.258462	-3.361429	-1.710380
27.C	-3.683691	2.985676	-1.685911
28.C	-0.116858	3.773974	-1.698550
29.C	2.490571	1.997228	-1.546382
30.C	-1.526543	-4.853058	-0.971335
31.C	3.571532	0.106864	-0.033679
32.C	3.780184	-3.002404	0.418539
33.C	-1.679322	-4.569095	0.499247
34.C	2.438144	-3.079953	0.833879
35.C	3.617835	4.902195	0.949214
36.C	2.772680	5.983731	1.226825
37.C	-2.480513	-5.459941	1.233410
38.C	3.139683	3.595527	1.045950
39.C	4.792282	-3.615405	1.158286
40.C	-1.082783	-3.473772	1.173359
41.C	1.452289	5.741210	1.610892
42.C	-2.332026	3.360860	1.418945
43.C	1.805036	3.341188	1.417824

44.C	0.971756	4.428781	1.710819
45.C	2.132105	-3.811072	1.990621
46.C	4.480589	-4.324833	2.324871
47.C	-2.711984	-5.332850	2.602643
48.C	-1.296048	-3.340884	2.573097
49.C	3.148507	-4.424967	2.733711
50.C	-1.942991	3.075091	2.842239
51.C	2.439317	1.055174	2.916970
52.C	-3.600816	-6.299954	3.347946
53.C	2.822769	-0.286772	3.044602
54.C	-2.090604	-4.263298	3.256568
55.C	-0.990087	2.071735	3.167609
56.C	-0.719510	-2.182696	3.336898
57.C	2.894381	1.982121	3.873521
58.C	-2.606506	3.768194	3.859282
59.C	3.635373	-0.704119	4.101977
60.C	-0.811322	1.730054	4.531804
61.C	3.713826	1.567066	4.927591
62.C	4.085996	0.223591	5.046349
63.C	-2.396104	3.486536	5.212900
64.C	0.040150	0.588467	5.026001
65.C	-1.510252	2.452341	5.512884
66.C	-3.100282	4.261454	6.301482
67.H	0.207271	-0.729586	-7.707408
68.H	1.951370	0.654275	-6.569269
69.H	-1.862452	-1.363729	-6.458480
70.H	-1.697351	4.966340	-5.036359
71.H	0.370905	-3.346313	-5.009868
72.H	1.425832	-5.612726	-4.902955
73.H	-7.224195	0.172846	-4.769083
74.H	-1.450619	2.551876	-4.591260
75.H	1.640949	1.368987	-4.233709
76.H	-2.183335	-0.632729	-4.129799
77.H	-7.711618	-0.870849	-3.421975
78.H	-7.916503	0.891648	-3.304998
79.H	-0.929937	6.644473	-3.353848
80.H	-5.444073	-1.897052	-3.131293
81.H	2.373087	-6.425714	-2.739190
82.H	0.297489	-1.921438	-3.005836
83.H	-5.974862	2.343612	-2.769540
84.H	-3.638370	3.698872	-2.521592
85.H	-1.967094	-2.028609	-2.460404
86.H	-3.490878	-2.931315	-2.565031
87.H	-2.440973	-5.317279	-1.362170
88.H	0.096192	5.861697	-1.211066
89.H	-1.314021	-3.955137	-1.553324
90.H	-2.717712	3.007582	-1.180368
91.H	-0.699081	-5.554975	-1.151478
92.H	-4.449700	3.348211	-0.984989

93.H	2.262685	-5.015038	-0.721898
94.H	-2.963792	-2.270278	-1.013682
95.H	0.351441	3.450750	-0.770249
96.H	4.039006	-2.467436	-0.494146
97.H	-2.958320	-6.278945	0.688486
98.H	4.654165	5.073166	0.654636
99.H	3.145033	7.006981	1.150389
100.H	5.826925	-3.535619	0.822658
101.H	-1.487319	3.290339	0.724007
102.H	3.817290	2.767786	0.838891
103.H	-3.092060	2.634591	1.090192
104.H	-2.769141	4.362835	1.318629
105.H	0.786388	6.572568	1.848399
106.H	-0.047702	4.264273	2.046676
107.H	-4.219358	-6.885063	2.655514
108.H	1.098544	-3.930370	2.306870
109.H	2.500430	-1.016749	2.303794
110.H	5.272319	-4.801050	2.906268
111.H	-1.319883	-1.266042	3.184879
112.H	0.320451	-1.969728	3.058247
113.H	2.887858	-4.989146	3.630475
114.H	-3.008990	-7.009510	3.946380
115.H	-3.328547	4.538540	3.576629
116.H	-4.271756	-5.770218	4.038361
117.H	2.611560	3.032288	3.800990
118.H	-2.252038	-4.118168	4.327685
119.H	3.925262	-1.752894	4.173376
120.H	-0.745341	-2.371946	4.416326
121.H	0.423136	-0.030218	4.214398
122.H	4.061642	2.299866	5.657382
123.H	4.731479	-0.097342	5.866158
124.H	0.905378	0.954996	5.597027
125.H	-0.551512	-0.047658	5.700040
126.H	-4.055499	4.671310	5.948024
127.H	-2.485365	5.107706	6.646406
128.H	-1.357221	2.168073	6.558172
129.H	-3.302609	3.627715	7.175314
130.N	-1.875253	0.506862	-1.512468
131.N	-0.377938	-2.395715	0.519240
132.N	-0.321708	1.392031	2.075553
133.O	3.281866	-0.878660	-3.270265
134.O	3.054516	2.865994	-2.085407
135.O	4.703917	0.103187	0.256294
136.P	-0.426697	1.012929	-2.245322
137.P	1.142308	-2.262466	-0.215220
138.P	1.289520	1.558440	1.547616
139.Mo	1.736384	0.310588	-0.787563
140.I	-3.818241	-0.421038	1.648636
141.U	-1.050937	-0.178029	0.525883

Energy: –893.27421547 eV

Table S5. Final coordinates and single point energy for the geometry optimised structure of ThClMo

1.C	2.111604	-3.414663	-7.124091
2.C	1.653900	-2.665919	-5.895344
3.C	1.526731	-1.278187	-5.889880
4.C	-2.409149	2.336090	-5.445129
5.C	-1.967033	3.611883	-5.078871
6.C	1.086897	0.951340	-4.902046
7.C	1.062430	-0.551504	-4.778923
8.C	1.345790	-3.336532	-4.705552
9.C	-2.262042	1.258577	-4.566110
10.C	-4.890513	-2.672636	-3.667642
11.C	-3.577473	-3.130148	-3.795862
12.C	-1.377893	3.805370	-3.825414
13.C	0.879981	-2.662531	-3.574441
14.C	0.667648	-1.256208	-3.615365
15.C	-5.128429	-1.416360	-3.096082
16.C	-2.506709	-2.345084	-3.348241
17.C	-1.675082	1.445326	-3.300604
18.C	-1.240980	2.729446	-2.944269
19.C	-4.063029	-0.636604	-2.646368
20.C	-2.736198	-1.095936	-2.756119
21.C	0.677560	-3.441933	-2.304103
22.C	2.725549	2.054544	-2.126316
23.C	0.610699	5.955009	-1.125707
24.C	-0.623424	6.583921	-0.944086
25.C	4.887579	2.741447	-1.092696
26.C	3.544517	2.397731	-0.909230
27.C	0.851744	4.696251	-0.561106
28.C	7.186587	3.373047	-0.225352
29.C	-1.615909	5.949286	-0.186594
30.C	-2.958232	2.024708	-0.308818
31.C	-3.037759	-4.594843	-0.172842
32.C	5.730316	3.031401	-0.016827
33.C	-0.141719	4.046367	0.185372
34.C	-2.377964	-3.396748	0.113995
35.C	-1.376200	4.694026	0.374457
36.C	-3.489869	-0.458319	0.415205
37.C	2.987275	2.336429	0.399898
38.C	-3.158268	-5.580429	0.811925
39.C	0.872769	-4.919872	0.733607
40.C	5.166701	2.987903	1.260204
41.C	-1.825925	-3.164548	1.381581
42.C	3.825755	2.653189	1.502385
43.C	1.779715	-4.200272	1.698288
44.C	-2.616446	-5.358174	2.082840

45.C	1.733366	-2.810276	1.960722
46.C	2.776222	-4.977313	2.315945
47.C	-2.561525	1.251304	2.176192
48.C	-1.955742	-4.160147	2.368223
49.C	2.761033	-2.239801	2.764343
50.C	0.146008	2.925083	2.758264
51.C	2.879086	-0.750105	2.943173
52.C	3.369097	2.641771	2.935164
53.C	3.750436	-4.443012	3.155450
54.C	0.294038	4.269301	3.146084
55.C	3.728710	-3.056483	3.352758
56.C	4.805918	-5.310121	3.799208
57.C	-1.151490	-1.502374	3.537960
58.C	0.018749	1.949921	3.758122
59.C	-2.477279	-1.320982	3.975313
60.C	0.309239	4.620834	4.499870
61.C	-0.138925	-1.629454	4.498831
62.C	0.045689	2.297319	5.110410
63.C	-2.775501	-1.244334	5.335966
64.C	0.188173	3.637128	5.486253
65.C	-0.438509	-1.549292	5.865058
66.C	-1.754468	-1.351925	6.288643
67.H	2.661244	-2.758231	-7.811144
68.H	1.252731	-3.825392	-7.678165
69.H	2.764064	-4.258581	-6.861679
70.H	1.816798	-0.714761	-6.781348
71.H	-2.872825	2.174316	-6.419637
72.H	-2.089829	4.453582	-5.762918
73.H	0.326930	1.309563	-5.610947
74.H	2.067083	1.272387	-5.283260
75.H	-2.607385	0.270884	-4.872599
76.H	1.489002	-4.418620	-4.645148
77.H	-5.724434	-3.284851	-4.015849
78.H	-3.373231	-4.098844	-4.255238
79.H	0.903202	1.450964	-3.950017
80.H	-1.038248	4.795577	-3.519563
81.H	-6.147734	-1.041516	-2.996256
82.H	-1.492823	-2.706351	-3.491430
83.H	3.121275	2.552733	-3.019757
84.H	0.660047	-4.520622	-2.500817
85.H	-4.268565	0.341704	-2.211846
86.H	2.776231	0.973823	-2.365546
87.H	5.286780	2.755438	-2.110142
88.H	-0.805695	2.901239	-1.960943
89.H	1.673779	2.349781	-2.022634
90.H	1.399125	6.442935	-1.700829
91.H	-0.811493	7.564380	-1.385077
92.H	-0.252632	-3.181062	-1.785336
93.H	1.516074	-3.267782	-1.608291

94.H	7.642673	2.724572	-0.986001
95.H	-3.470526	-4.744552	-1.162646
96.H	7.309642	4.413025	-0.564945
97.H	1.829652	4.237274	-0.688249
98.H	-2.314533	-2.628569	-0.655580
99.H	-2.582180	6.431015	-0.032978
100.H	1.480522	-5.469764	0.000164
101.H	7.758341	3.259370	0.704600
102.H	-3.681095	-6.513522	0.593782
103.H	0.210348	-4.241423	0.194840
104.H	-2.154978	4.220785	0.970982
105.H	0.241247	-5.655382	1.252035
106.H	5.800221	3.200412	2.125494
107.H	2.790068	-6.049821	2.101789
108.H	3.373182	-0.287313	2.070602
109.H	0.397250	5.052316	2.395194
110.H	-2.706346	-6.119583	2.859160
111.H	5.817326	-4.950055	3.559824
112.H	2.901518	3.598863	3.210768
113.H	4.728763	-6.350320	3.457574
114.H	1.908362	-0.260111	3.077800
115.H	2.626704	1.862949	3.129988
116.H	-1.537445	-4.005564	3.363250
117.H	-3.286631	-1.245537	3.249477
118.H	4.226194	2.487187	3.603586
119.H	3.504403	-0.506551	3.810703
120.H	-0.128371	0.906387	3.483240
121.H	4.501841	-2.586907	3.966765
122.H	0.885670	-1.822100	4.194604
123.H	4.711903	-5.308814	4.895856
124.H	0.413989	5.670234	4.779871
125.H	-3.808963	-1.098053	5.651720
126.H	-0.067789	1.518809	5.865641
127.H	0.191752	3.914074	6.542195
128.H	0.366010	-1.653364	6.595052
129.H	-1.987053	-1.288990	7.353324
130.Cl	3.628898	-1.375504	-0.987420
131.Mo	-1.797207	0.596167	0.448887
132.N	0.150728	-0.623438	-2.418600
133.N	1.651836	1.804064	0.515254
134.N	0.774589	-1.904140	1.360322
135.O	-3.793353	2.762088	-0.667001
136.O	-4.552056	-0.934240	0.519349
137.O	-3.174650	1.691255	3.067660
138.P	-1.394302	0.029030	-2.128011
139.P	0.132751	2.388856	0.976225
140.P	-0.863686	-1.608258	1.703899
141.Th	1.278184	-0.364601	-0.346656

Energy: –894.68017762 eV

Table S6. Final coordinates and single point energy for the geometry optimised structure of ThIMo

1.C	0.322380	-2.643497	-6.152004
2.C	-0.864693	-2.011227	-5.761502
3.C	-0.194367	3.138426	-5.564432
4.C	1.499889	-2.386157	-5.447031
5.C	-0.802280	4.213481	-4.907329
6.C	0.094545	1.958922	-4.870654
7.C	-0.870974	-1.143418	-4.669587
8.C	7.011410	1.065920	-4.052730
9.C	1.495090	-1.510588	-4.352765
10.C	0.307885	-0.888964	-3.941794
11.C	4.744993	2.025463	-3.446676
12.C	5.638081	0.953598	-3.434883
13.C	-1.125848	4.100114	-3.551164
14.C	-0.229097	1.835200	-3.506722
15.C	2.631876	3.218100	-2.945292
16.C	3.447597	1.951369	-2.913795
17.C	5.207189	-0.225050	-2.818479
18.C	-0.846826	2.916744	-2.863039
19.C	0.866434	-4.901350	-2.373947
20.C	3.005635	0.727344	-2.350465
21.C	3.928922	-0.349469	-2.266112
22.C	-2.872177	0.541816	-2.073603
23.C	-2.149352	-2.001949	-1.983403
24.C	0.848287	-6.163407	-1.771804
25.C	0.442478	-3.778709	-1.657749
26.C	3.589334	-1.613097	-1.526048
27.C	-4.494394	4.126679	-0.851489
28.C	-3.903234	5.391105	-0.735774
29.C	0.404010	-6.293513	-0.451362
30.C	-3.841466	2.998592	-0.353138
31.C	-2.661217	5.514603	-0.108376
32.C	0.002120	-3.894960	-0.331843
33.C	-3.455360	-0.933761	0.026979
34.C	-0.016078	-5.169507	0.265238
35.C	1.520977	3.782378	0.263683
36.C	-2.582338	3.109992	0.264547
37.C	-2.006189	4.382111	0.392871
38.C	3.050163	-3.947573	0.882271
39.C	-2.822643	-3.739681	1.274934
40.C	1.224329	3.877462	1.736093
41.C	-1.651111	-3.177508	1.817104
42.C	2.685298	-3.412189	2.242641
43.C	-3.752238	-4.380556	2.094187
44.C	-2.977618	1.263049	2.350583
45.C	1.910305	4.832962	2.489802
46.C	0.306116	2.987249	2.362936

47.C	1.722727	-2.400964	2.475923
48.C	-3.831113	2.263847	2.850358
49.C	-3.007436	-0.004041	2.951020
50.C	3.414815	-3.921381	3.331579
51.C	-1.425700	-3.296604	3.195551
52.C	-3.528128	-4.477448	3.473368
53.C	-4.689689	1.995657	3.921570
54.C	1.740312	4.945112	3.873942
55.C	0.107177	3.102557	3.763282
56.C	1.608154	-1.867625	3.789575
57.C	-3.854334	-0.270087	4.029189
58.C	0.739073	-0.674790	4.074118
59.C	-2.361111	-3.938102	4.018195
60.C	-4.702116	0.730224	4.516585
61.C	2.521285	5.951731	4.683960
62.C	0.832517	4.072796	4.473663
63.C	3.261056	-3.459039	4.637161
64.C	-0.834731	2.243506	4.562653
65.C	2.357335	-2.408787	4.836167
66.C	4.038104	-4.053937	5.786911
67.H	0.326987	-3.325456	-7.004614
68.H	-1.791591	-2.195014	-6.306620
69.H	0.057147	3.213035	-6.623760
70.H	2.437374	-2.855139	-5.750668
71.H	-1.032574	5.131430	-5.451991
72.H	6.971010	0.897011	-5.140293
73.H	0.574392	1.135653	-5.399814
74.H	-1.802438	-0.652542	-4.389832
75.H	7.440919	2.064380	-3.894166
76.H	7.702672	0.325806	-3.629233
77.H	5.065622	2.980231	-3.873470
78.H	2.431376	-1.296282	-3.845436
79.H	3.270440	4.077408	-2.695377
80.H	2.211663	3.399892	-3.945160
81.H	1.191753	-4.785939	-3.408516
82.H	-1.612498	4.923688	-3.027481
83.H	5.891778	-1.073594	-2.742918
84.H	1.167373	-7.044011	-2.332632
85.H	1.793777	3.189053	-2.247213
86.H	4.272294	-2.427668	-1.796525
87.H	0.435002	-2.807309	-2.150411
88.H	-1.134164	2.832915	-1.815786
89.H	-5.467134	4.016147	-1.332242
90.H	-4.412790	6.273790	-1.127281
91.H	2.565655	-1.956601	-1.715275
92.H	3.703794	-1.459855	-0.438881
93.H	-4.323271	2.025611	-0.437751
94.H	-2.196798	6.495474	0.005889
95.H	0.629352	3.556665	-0.333986

96.H	0.381488	-7.274187	0.026907
97.H	1.948720	4.719816	-0.112426
98.H	2.295363	3.016942	0.055492
99.H	2.535355	-3.425275	0.075070
100.H	-3.009336	-3.685390	0.202857
101.H	4.134351	-3.846814	0.727798
102.H	2.803820	-5.015289	0.794331
103.H	-1.056596	4.504848	0.908926
104.H	-0.356987	-5.289733	1.294070
105.H	2.618818	5.489109	1.977989
106.H	-4.655369	-4.803462	1.652548
107.H	-3.833308	3.259288	2.406395
108.H	-2.379636	-0.804187	2.562139
109.H	4.152247	-4.703252	3.127633
110.H	-0.507447	-2.920308	3.636931
111.H	1.229456	0.256443	3.737432
112.H	-0.239605	-0.736756	3.585124
113.H	-5.351989	2.781875	4.287694
114.H	2.261386	6.983294	4.402966
115.H	-0.998245	1.265093	4.107860
116.H	3.603062	5.833805	4.525400
117.H	-4.256884	-4.976618	4.115097
118.H	-3.862563	-1.267384	4.470838
119.H	-1.821809	2.720830	4.653662
120.H	-5.378286	0.519945	5.347579
121.H	-2.161974	-4.021776	5.087974
122.H	0.572028	-0.558007	5.151883
123.H	4.949614	-4.555200	5.436695
124.H	0.682642	4.126734	5.555583
125.H	2.323796	5.836331	5.757292
126.H	-0.443721	2.100047	5.578629
127.H	2.243172	-1.978607	5.834339
128.H	3.436307	-4.802661	6.325674
129.H	4.329460	-3.284331	6.514728
130.I	3.966062	0.901384	1.758916
131.Mo	-1.701720	-0.454581	-0.807728
132.N	1.692948	0.534305	-1.763317
133.N	0.915733	-1.792857	1.433840
134.N	-0.251405	1.936077	1.541153
135.O	-3.639564	0.948024	-2.857429
136.O	-2.602880	-2.874670	-2.614518
137.O	-4.559250	-1.180996	0.316889
138.P	0.187164	0.310915	-2.523717
139.P	-0.466447	-2.374553	0.628435
140.P	-1.795528	1.570902	0.946127
141.Th	1.204676	0.366133	0.549290

Energy: –893.30190918 eV

Table S7. Selected QTAIM data for UClMo, UIMo, ThClMo, and ThIMo

Compound	$\rho(r)$	$\nabla^2\rho$	H(r)	$\varepsilon(r)$
UClMo	0.030	0.034	–0.005	0.112
UIMo	0.030	0.033	–0.005	0.087
ThClMo	0.040	0.048	–0.007	0.130
ThIMo	0.037	0.048	–0.008	0.110

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