

Synthesis and Small Molecule Reactivity of Uranium(IV) Alkoxide Complexes with both Bound and Pendant N-heterocyclic Carbene Ligands

Polly L. Arnold,* Alexander J. Blake, and Claire Wilson^[a]

Abstract: The syntheses of two tetravalent uranium alkoxide-carbene complexes are reported, $[\text{U}(\text{L})_3]$, and $[\text{U}(\text{L})_4]$ where $\text{L} = \text{OCMe}_2\text{CH}_2[1-\text{C}(\text{NCHCHN}i\text{Pr})]$. The latter shows dynamic behaviour of the alkoxycarbene ligands in solution at room temperature, and the crystal structure of $[\text{U}(\text{L})_4]$ shows that one carbene group remains

uncoordinated. The unbound N-heterocyclic carbene group is trapped by a range of reagents such as 16-valence-electron metal carbonyl fragments and

Keywords: bifunctional catalysis • carbene ligands • heterometallic complexes • O ligands • uranium

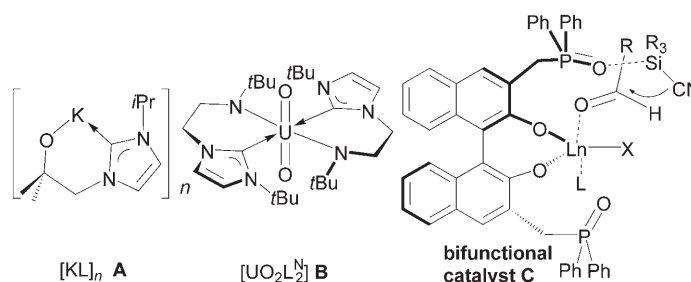
BH_3 moieties, forming, for example, $[\text{U}(\text{L})_3(\mu\text{-L})\text{W}(\text{CO})_5]$, $[\text{U}(\text{L})_2(\mu\text{-L})_2\text{Mo}(\text{CO})_4]$, and $[\text{U}(\text{L})_n(\text{L-BH}_3)_{4-n}]$ ($n=1-4$), demonstrating the potential for these hemilabile electropositive metal-carbene complexes to participate in the bifunctional activation of small molecules.

Introduction

N-heterocyclic carbenes (NHCs) are most well-known as strong σ -donor ligands for electronegative metals, providing stabilisation of the metal centre in many homogeneous catalysts based on ruthenium(II) and palladium(0).^[1] In contrast to alkyl phosphines, carbenes are also recognised now as effective ligands for high oxidation state metal complexes.^[2-5]

We have shown how the incorporation of an anionic functional group into an NHC-based ligand stabilises electropositive metal cations, and have made NHC complexes of potassium(I) (**A**) and uranium(VI) (**B**) cations using uninegative alkoxide-NHC-L (where $\text{L} = \text{OCMe}_2\text{CH}_2[1-\text{C}(\text{NCHCHN}i\text{Pr})]$) and amido-NHC ligands.^[6,7]

The U-C(carbene) bond in complex **B** is most simplistically viewed as a two-electron dative bond. Two trivalent and one tetravalent adduct of the simplest NHC, C-(NMeCMe)₂, have been reported recently, in which the NHC is used as a two-electron donor ligand to control the compounds' nuclearity.^[8,9] However, the potential for involvement of the NCN π system in additional bonding interactions with the metal has been suggested for some electropositive metal systems, by inspection of crystallographic data and some DFT calculations.^[10,11]



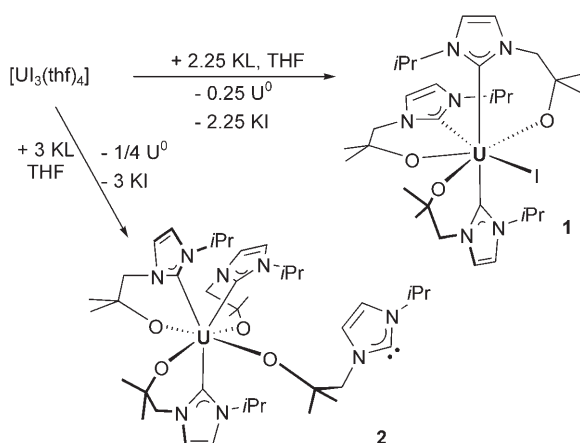
A small number of complexes of strongly Lewis acidic metals that contain an adjacent, hemilabile or uncoordinated Lewis base ligand, such as 3,3'-bis(phosphinoylalkyl)-1,1'-bi-2-naphtholate adducts of aluminium(III), titanium(IV), and lanthanide(III), **C** have been demonstrated to be active and selective bifunctional catalysts, capable of activating two different substrates.^[12-15] Since N-heterocyclic carbenes are very effective Lewis base catalysts,^[16] we have sought to identify whether Lewis acidic metals can be combined with suitably labile NHCs to provide a new class of bifunctional catalysts, especially since chiral L analogues can be made from enantiopure epoxides.^[17] To use the NHC reactivity in combination with the reactivity and variety of accessible oxidation states available to uranium coordination complexes, we have studied the complexation of the bidentate alkoxide-carbene L, where $\text{L} = \text{OCMe}_2\text{CH}_2[1-\text{C}(\text{NCHCHN}i\text{Pr})]$, to uranium cations. Herein, we present the synthesis of uranium(IV) complexes that contain both bound and free N-heterocyclic carbenes that are tethered by alkoxide functional

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groups, and the use of this hemilability to study the suitability of such combined Lewis acid–base systems for binding and functionalising small molecules.

Results and Discussion

The reaction of uranium triiodide with the potassium alkoxide-NHC (KL), affords two disproportionation products: a tetravalent uranium complex and one quarter molar equivalent of uranium metal. Thus the reaction using 2.25 equivalents of KL affords the uranium iodide tris(ligand) complex **1**, [U₄I₃], which is isolated as a dark golden-coloured powder in excellent yield (Scheme 1). The ¹H NMR spec-



Scheme 1.

trum of **1** is spread between $\delta = +10$ and -30 ppm, in agreement with the formulation of **1** as a uranium(IV) complex, and with elemental analysis data. However, the methyl group resonances are broadened (fwhm ~ 2000 Hz); this could be attributable to steric crowding at the tetravalent metal cation, or to a fluxional process. All single crystals of **1** grown for X-ray diffraction studies have so far been glassy, and afforded no diffraction pattern.

The reaction of uranium triiodide^[18] with three equivalents of KL gives a more unusual complex (Scheme 1). After work-up, an emerald green, toluene-soluble complex formulated as [U₄], **2**, is isolated in good yield. This is shown by NMR spectroscopy and crystallography to contain a seven-coordinate uranium(IV) centre, and one unbound NHC group. To the best of our knowledge, this is the first example of a metal complex that contains a free NHC group, and is surprising since the NHC group is such a strong nucleophile. Previously, from reactions of softer metal halides with sterically encumbered NHC ligands, we have isolated complexes that immediately abstract a proton from the solvent; for example [Ru(1-Me-4-*i*PrC₆H₄)[OCPh{CH₂[1-C(NCHCHN*t*Bu)]}{CH₂[1-CH(NCHCHN*t*Bu)]Cl}]Cl containing a pendant imidazolium cation rather than a free NHC group was isolable in

good yield from the reaction between [Ru(1-Me-4-*i*PrC₆H₄)Cl₂]₂ and the lithium alkyoxydicarbene [LiOCPh(CH₂[1-C(NCHCHN*t*Bu)])₂].^[3] The complex **2** crystallises readily as large, gem-like crystals; so far two morphologies have been crystallised, from toluene (see Figure 1) and benzene (see ESI) but in each case with the same general structure, and no measurable intermolecular contacts with the free NHC group.

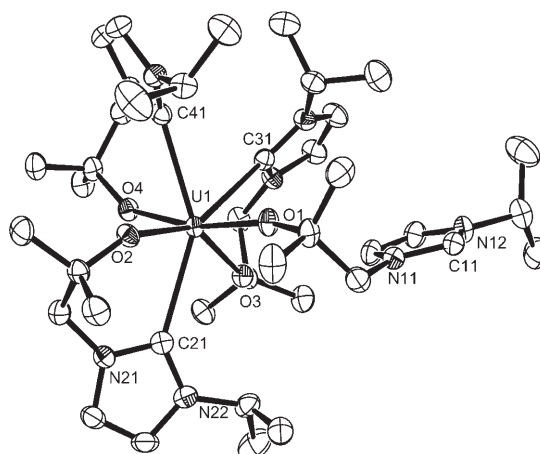


Figure 1. Displacement ellipsoid drawing of **2**. Hydrogen atoms and lattice solvent omitted for clarity. Selected distances [Å] and angles [°]: U1–O(av) 2.203, U1–C21 2.748(3), U1–C31 2.799(3), U1–C41 2.696(3), N11–C11 1.373(4), N21–C21 1.365(4); N12–C11–N11 101.3(2), N21–C21–N22 102.1(2).

The ¹H NMR spectrum of **2** at room temperature contains only two very broad resonance signals of approximately equal intensity, centred at $\delta = 17$ ppm and $\delta = -6$ ppm. Cooling a [D₈]toluene solution of **2** to 228 K demonstrates that the presence of the two signals is due to a dynamic equilibrium process, and at 228 K, the sharp ¹H NMR spectrum anticipated for a U^{IV} complex is observed, spanning a wide (for U^{IV}) range of $\delta = 95$ to -60 ppm, assignable to four separate ligand environments. The fluxional process associated with this large change in chemical shift is assumed to be the exchange of free- for uranium-coordinated carbene groups. EI mass spectra of the complex show clean fragmentation patterns for the loss of imidazole-derived groups, and then complete L ligands.

Although uranium(IV) organometallic complexes with supporting cyclopentadienide ligands are common now,^[19] to the best of our knowledge, the only other crystallographically characterised uranium(IV) organometallic compound with four sigma-bound hydrocarbyl groups is [UMeBz₃-(Me₂PCH₂CH₂PMe₂)].^[20]

The most interesting feature of the structure of **2** is the unbound carbene group, which is tethered to the seven-coordinate metal centre through only the alkoxide group.

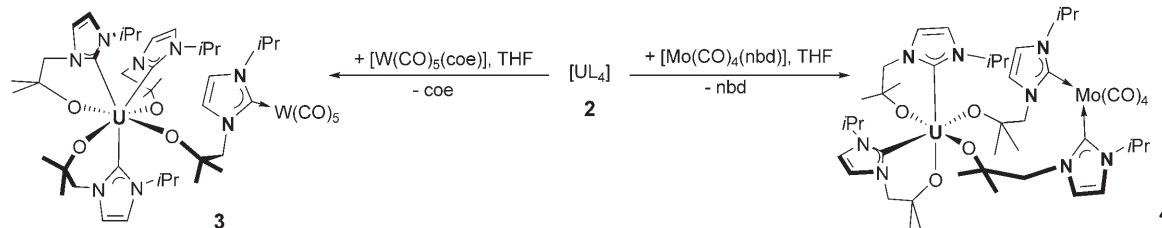
The coordination geometry about the uranium centre is pentagonal bipyramidal. The U–C(carbene) distances are

similar (av 2.75 Å), with no significant distortions in the M–CN₂ fragment away from the anticipated trigonal planar. The bite angles of the three bound ligands are 66.6, 69.7, and 73.1°. The average U–O distance of 2.203 Å is long—simple U^{IV}–O(alkoxide) distances are normally less than 2.1 Å.^[21–23] In the eight-coordinate tetrakis(hexafluoroacetylpyrazolido)uranium(IV) complex, the U–O distances are 2.24 Å.^[24] The U–C distance in **2** is significantly longer than that in the only other tetravalent uranium NHC adduct, [U(C₅Me₅)₂(=O)(C{NMeCMe}₂)], which has a U–C distance of 2.639(9) Å.^[9] All the U–C bonds in **2** are longer (within e.s.d.s) than those in the trivalent complex [U{N(SiMe₃)₂–C(NMeCMe)₂}] (2.672(5) Å), the U–C distance in the other trivalent complex, [U^{(Ad)Artacn}{C(NMeCMe)₂}], is 2.789(14) Å. Normal U^{IV}–C_{alkyl} distances are approximately 2.45 Å.^[25] There is no evidence of any interaction with lattice solvent or adjacent molecules in the structure.

We have studied some reactions to trap the free NHC to eliminate the dynamic equilibrium process, and to see if the NHC behaves as a simple carbene ligand to bring in potentially reactive fragments or molecules to the primary coordination sphere of the uranium cation.

Treatment of **2** with one equivalent of [W(coe)(CO)₅] (coe = cyclooctene) results in the liberation of coe and a brown product, which contains carbonyl stretching frequencies in the FTIR spectrum at 2059 and 1908 cm⁻¹ consistent with the quantitative formation of the eighteen-electron tungsten complex [(OC)₃W{[1-C(NiPrCHCHN)]CH₂CMe₂O}]UL₃, [UL₃(μ-L)W(CO)₅] (**3**; Scheme 2). For comparison, the FTIR spectrum of the complex [W(CO)₅–C(NEtCH₂)₂] contains intense bands 2062 and 1919 cm⁻¹.^[26]

Similarly, the reaction of **2** with one equivalent of [Mo(nbd)(CO)₅] (nbd = norbornadiene) affords a paler green product after workup, formulated as the eighteen-electron molybdenum complex [(OC)₄Mo{[1-C(NiPrCHCHN)]CH₂CMe₂O}₂UL₂], [UL₂(μ-L)₂Mo(CO)₄] (**4**), in which the two NHC groups are mutually *cis* according to the FTIR spectrum. Carbonyl stretching frequencies are measured at 1986, 1868, 1847, and 1813 cm⁻¹; these are comparable with the values of 1993, 1870, 1862, and 1839 cm⁻¹ reported for *cis*-[Mo(CO)₄–C(NEtCH₂)₂].^[27,28] Both **3** and **4** lose all solubility in common organic solvents over time, so whilst combustion analysis can be obtained to confirm the formulation of **4**, no structural or clean solution NMR spectroscopic data can be obtained. A formulation for **4** is suggested in



Scheme 2.

Scheme 2, but presumably both products rearrange over time to form polymeric uranium isocarbonyl-containing compounds.^[29–32]

The reaction of **2** with the borane BH₃·SMe₂ affords the borane adduct, [UL₃{[1-CBH₃(NiPrCHCHN)]CH₂CMe₂O}], [U(L)₃(L-BH₃)] (**5**) [Eq. (1)], a less-soluble, paler grass green complex, which can be recrystallised from THF or toluene. The reaction is essentially quantitative, and there is no evidence of SMe₂ incorporation. Interestingly, a second equivalent of BH₃·SMe₂ reacts to afford a grass-green complex formulated as [UL₂{[1-CBH₃(NiPrCHCHN)]CH₂CMe₂O}₂], [UL₂(L-BH₃)₂] (**6**) [Eq. (1)]. Titration shows that up to four equivalents of BH₃·SMe₂ are consumed by **2**; the solubility of the product decreases with each BH₃ addition, so it is assumed that the homoleptic [U{[1-CBH₃(NiPrCHCHN)]CH₂CMe₂O}₄] is the final product. The solid-state molecular structure of the mono-BH₃ adduct, **5**, determined from a single-crystal diffraction study, is virtually identical to that of **2** (Figure 2). The ¹H NMR

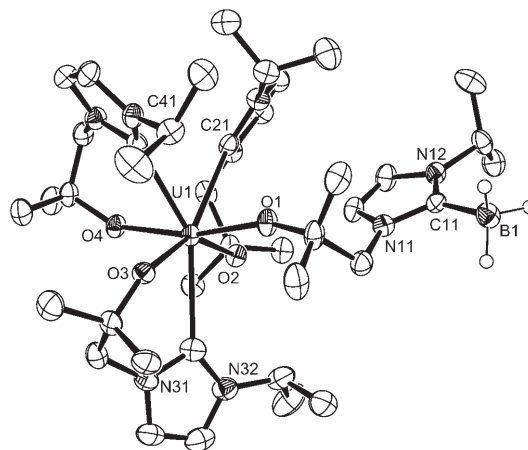
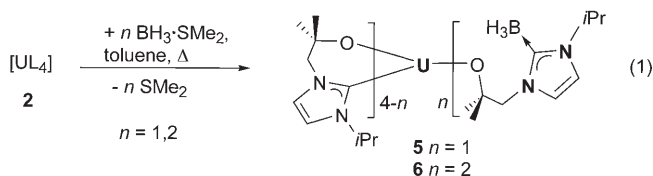


Figure 2. Displacement ellipsoid drawing of **5**. All except borane group hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: B1–C11 1.609(7), U1–O(av) 2.202, U1–C21 2.794(5), U1–C31 2.752(5), U1–C41 2.674(5), N11–C11 1.364(6), N41–C41 1.367(6); N12–C11–N11 104.5(4), N41–C41–N42 102.5(4).

spectra of **5** and **6** show no dynamic equilibria, but the ¹³C NMR spectra show neither a resonance for the borane-bound carbene carbon atom, nor any free or uranium-bound



carbene carbon atoms, due to coupling to the quadrupolar boron atom, and the paramagnetism of U^{IV} .

The average U–C(carbene) bond length is 2.740 Å, compared with 2.747 Å in the two crystal structures of **2**. The average U–O bond length is unchanged from that in **2**.

The C(carbene)–B(borane) bond of 1.609(7) Å is comparable with that in the Lewis acid–base adduct 1-CBH₃-(NEtCMe)₂ of 1.604 Å.^[33] The borane hydrogen atoms were located in the difference Fourier map. Thus, the tethered carbene group has also facilitated the isolation of the first stable, neutral borane adduct of an f-element cation.^[34–36]

To conclude, the use of large metal cations has allowed the isolation of the first complexes to contain both bound and free NHC functional groups. In the tetrakis(carbene) complex, the fast exchange processes that interconvert free and bound NHC groups can be slowed by cooling, or stopped by complexation of a Lewis acid. For uranium(IV), the displacement of further carbenes is straightforward, and allows other metal fragments or functional groups to be brought into the coordination sphere of the uranium(IV) metal cation. We are currently investigating the reactivity of these systems and analogues with chiral alkoxycarbene ligands towards other small molecules and organic substrates.

Experimental Section

General details: All manipulations of air-sensitive materials were carried out under a dry, oxygen-free argon or dinitrogen atmosphere, using standard Schlenk techniques (rotary pump for vacuum 10^{−4} mbar) or in a glove box (Mbraun Unilab or Saffron) under dry dinitrogen. All NMR spectra were recorded on a Bruker DPX 300 spectrometer, operating frequency 300 MHz (¹H), 75 MHz (¹³C), variable temperature unit set to 300 K unless otherwise stated. Chemical shifts are reported in parts per million, and referenced to residual solvent proton resonances calibrated against external TMS. IR spectra were recorded in the range 400–4000 cm^{−1} on a Nicolet Avatar 360 FT-IR spectrometer as nujol mulls between KBr discs. Mass spectra (EI, ES and FAB) were run by Mr. Tony Hollingworth on a VG autospec instrument. Elemental analyses were determined by Dr. Stephen Boyer at London Metropolitan University. X-ray diffraction data were collected on a Bruker SMART1000 CCD area detector diffractometer. Structure solution and refinement were carried out using the SHELX suite of programs.

All solvents used (diethyl ether, tetrahydrofuran, hexane, toluene, dichloromethane, 1,2-dichloromethane, acetonitrile and pyridine) were purified by passage through activated alumina towers prior to use, and thoroughly degassed prior to use. NMR spectroscopic grade [D₆]benzene was dried over potassium metal, thoroughly degassed by the freeze–thaw method and transferred under reduced pressure before use.

Synthesis of [UL₄] (1): A cream solution of KL (82 mg, 0.346 mmol, 5 mL) in THF was added dropwise over 2 min to a cold, dark blue slurry of [UI₃(thf)₄] in THF (140 mg, 0.154 mmol, 10 mL, −30 °C), with stirring. The mixture was allowed to warm to room temperature over 16 h. After

this time, the brown supernatant was isolated from the grey precipitate by filtration. Concentration, then cooling of the brown solution to −30 °C, afforded an orange powder characterised as **1**, in 80.2% yield, 84 mg (based on calculated U^{IV}).

¹H NMR ([D₆]benzene, 300 MHz, 300 K): δ = 8.4 (br, 3H), 3.8 (br, 6H), −9.9 (br, 6H), −12.6 (br s, fwhm 2400 Hz, 18H), −25.0 ppm (br s, fwhm 1650 Hz, 18H); MS (EI): *m/z* (%): 532 ([ULI–CH₂]⁺, 10), 337 ([UOC–Me₂CH₂NCH]⁺, 4), 181 ([L]⁺, 30), 121 ([iPrNCCHCHNC]⁺, 100); elemental analysis calcd (%) for C₃₀H₅₁N₆O₃U: C 39.65, H 5.65, N 9.25; found: C 39.74, H 5.91, N 9.18.

Synthesis of [UL₄] (2): A cream solution of KL (1.819 g, 8.1 mmol, 20 mL) in THF was added dropwise over 10 min to a cold, dark blue slurry of [UI₃(thf)₄] in THF (2.50 g, 2.7 mmol, 20 mL, −78 °C), with stirring. The mixture was allowed to warm to room temperature over 16 h. After this time, the brown supernatant was isolated from the grey precipitate by filtration, and volatiles were removed under reduced pressure. Extraction with toluene, followed by concentration, then cooling of the brown solution to −30 °C, afforded a green microcrystalline solid characterised as **2**, in 78.2% yield, 2.008 g (based on calculated U^{IV} maximum). Single crystals suitable for X-ray analysis were grown from a saturated toluene solution of **2** at −5 °C. Another set of single crystals were grown from a saturated benzene solution of **2** at 20 °C.

¹H NMR ([D₈]toluene, 300 MHz, 300 K): δ = 17 (br, 36H), −6 ppm (br, 32H); ([D₈]toluene, 300 MHz, 228 K): δ = 4.7, 4.1, 3.6, −0.2 (s, 6H each, Me₂), 38.5, 35.4, 33.9, 31.3, −7.5, −10.8, −18.6, −27.5 (s, 3H each, Me), 10.9, 10.0, −5.7, −6.1 (s, 2H each, CH₂), 48.2, 44.1, 42.4, 39.0, 9.0, 8.7, 6.3, −1.4, −9.7, −12.9, −50.8, −64.2 ppm (s, 1H each, CH); μ_{eff} = 2.72 BM (300 K, [D₆]benzene solution, Evans method); MS (EI): *m/z* (%): 963 ([M+H]⁺, 16), 781 ([M–L]⁺, 70), 616 ([M–L+O]⁺, 68), 165 ([L–O]⁺, 100); elemental analysis calcd (%) for C₄₀H₆₈N₈O₄U: C 49.89, H 7.12, N 11.63; found: C 49.83, H 6.83, N 11.65.

Synthesis of [UL₄(W(CO)₃] (3): A colourless solution of [W(CO)₃(coe)], (coe = cyclooctene) (72 mg, 0.165 mmol, 5 mL) in toluene was added dropwise over two minutes to a green slurry of [UL₄] in toluene (159 mg, 0.165 mmol, 2 mL), with stirring. The mixture was stirred for 16 h. After this time, the green supernatant was isolated from a small quantity of brown oil by filtration, and volatiles were removed under reduced pressure to yield a khaki solid characterised as **3**, in 54% yield, 114 mg. Once isolated the solid is virtually insoluble in all common aprotic solvents.

FTIR (nujol mull): $\tilde{\nu}$ = 2058.5 (s), 1908.4 cm^{−1} (s); MS (EI): *m/z* (%): 1245 ([M–iPr+H]⁺, 5), 1171 ([M–2iPr–CO+H]⁺, 7), 1022 ([UL₂(OC–Me₂CH₂NC)W(CO)₃]⁺, 3), 588 ([U(L–iPr)W(CO)]⁺, 20).

Synthesis of [UL₄(Mo(CO)₄] (4): A very pale green solution of freshly sublimed [Mo(CO)₄(nbd)], (nbd = norbornadiene) (27 mg, 0.089 mmol, 5 mL) in toluene was added dropwise over two minutes to a green solution of [UL₄] in toluene (86 mg, 0.089 mmol, 10 mL), with stirring. The mixture was stirred for 16 h, during which time, a yellow-green precipitate formed in the green solution, which lightened. After removal of volatiles under reduced pressure, extraction of the pale sparingly soluble green solid with THF, followed by cooling to −30 °C, afforded a green powder characterised as **4**, in 63% yield, 66 mg. Once isolated the solid is virtually insoluble in all common aprotic solvents.

FTIR (nujol mull): $\tilde{\nu}$ = 1985.7 (s), 1868.0 (sh), 1846.7 (s), 1813.4 cm^{−1} (s); MS (EI): *m/z* (%): 515 ([U(L–iPr)₂+H]⁺, 100), 481 ([Mo(CO)₄(L–Me₂O)₂]⁺, 14), 424 ([Mo(CO)₂(L–Me₂O)₂]⁺, 25).

Synthesis of [UL₄(BH₃] (5): A colourless solution of BH₃·SMe₂ (119.5 μL, 0.239 mmol, 2 mL) in toluene was added by syringe to a green solution of [UL₄] in toluene (230 mg, 0.239 mmol, 5 mL). The mixture was heated to 60 °C for four hours during which time a paler grass green precipitate formed. Extraction with THF, followed by filtration and cooling to −30 °C afforded a grass green powder characterised as **5**, in 80% yield, 227 mg.

¹H NMR (THF/[D₆]benzene, 300 MHz, 300 K): δ = 2.6, −6.9 (18H), −15.3, 6.0, 5.8 (1H), 25.1, 8.6, 3.6, (6H), 23.9, −1.9, −15.5 (3H), 3.1 ppm (2H); BH₃ not observed; MS (EI): *m/z* (%): 977 ([M+H]⁺, 10), 869 ([UL₅(BH₃)(OCMe₃)H]⁺, 40), 795 ([M–L]⁺, 100), 640 ([UL₂–

(BH₃(CN))⁺, 66); elemental analysis calcd (%) for C₄₀H₇₁N₈O₄UB: C 49.17, H 7.33, N 11.47; found: C 48.99, H 7.22, N 11.31.

Synthesis of [UL₄(BH₃)₂] (6): A colourless solution of BH₃·SMe₂ (100 μL, 0.204 mmol, 2M) was added by syringe to a green solution of [UL₄] in toluene (97.8 mg, 0.102 mmol, 5 mL). The mixture was heated to 60 °C for four hours during which time a paler, grass green precipitate formed. Extraction with THF, followed by filtration and cooling to -30 °C afforded a pale green powder characterised as **6**, in 94% yield, 95 g.

¹H NMR ([D₆]benzene, 300 MHz, 300 K): δ = 30.4, 29.2, -4.1, -5.2, -15.5, -15.8, -16.3 (1H), 24.3, 23.0, -2.2 (6H), 6.5, -2.2 ppm (2H); BH₃ not observed; MS (EI): *m/z* (%): 992 ([M+H]⁺, 6), 869 ([M-N₂(CH)₂PrCBH₃+H]⁺, 35), 795 ([UL₃BH₃]⁺, 100), 673 ([UL₂OCMe₃]⁺, 66), 617 ([UL₂O+H]⁺, 46).

Crystallography: Single crystals of 2-C₆H₅CH₃, **2** and 5-C₆H₆ were grown from solutions of the complexes in toluene, benzene, and benzene, respectively. In turn, a crystal was mounted in a film of RS3000 perfluoropolyether on a dual-stage glass fibre and transferred to the diffractometer.

Complex 2: 0.24 × 0.22 × 0.19 mm, monoclinic, *P*₂₁/*n*, *a* = 11.3130(8), *b* = 22.619(2), *c* = 19.842(2) Å, *V* = 5034.6(8) Å³, ρ = 1.392 Mg m⁻³, 53°, MoK_α, ω scans, 150(2) K, 31 771, 11 790, 9594 (measured, independent, observed) reflections, *I* > 2σ(*I*), multi-scan (μ, 0.823 < *T* < 1.0), Shextl direct methods, 542 parameters, H atoms placed and riding, *R*[*F*² > 2σ(*F*²)] = 0.029, 0.066, 1.02, Δρ_{max}, Δρ_{min} = 1.32, -0.34 e Å⁻³.

Complex 5: 0.16 × 0.15 × 0.14, monoclinic, *P*₂₁/*n*, *a* = 11.2723(8), *b* = 22.4216(15), *c* = 20.4644 (14) Å, *V* = 5106.0(6) Å³, ρ = 1.372 Mg m⁻³, 53°, MoK_α, ω scans, 150(2) K, 31 744, 11 652, 8470 (measured, independent, observed) reflections, *I* > 2σ(*I*), Multi-scan (μ, 0.631 < *T* < 1.0), Shextl direct methods, 500 parameters, H atoms placed and riding, *R*[*F*² > 2σ(*F*²)] = 0.041, 0.099, 1.01, Δρ_{max}, Δρ_{min} = 1.56, -0.85 e Å⁻³. CCDC-268230 (**2**), CCDC-268231 (2-C₆H₅CH₃), and CCDC-268232 (**5**) contain the supplementary crystallographic data for this paper. These can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the EPSRC and the Royal Society for funding.

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Received: April 28, 2005
Published online: July 29, 2005