

Functionalised Saturated-Backbone Carbene Ligands: Yttrium and Uranyl Alkoxy–Carbene Complexes and Bicyclic Carbene–Alcohol Adducts

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Abstract: A new and modular route to bidentate ligands that combines an alkoxy with a saturated backbone N-heterocyclic carbene (NHC) is presented. The bi(heterocyclic) compounds are formally the addition product of a saturated NHC and the alcohol group of

the N-functionalised arm. Using these compounds, the synthesis and structural characterisation of the first electro-

positive metal complexes of saturated N-heterocyclic carbenes has been achieved, and examples structurally characterised for the yttrium(III) and the uranyl [UO₂]²⁺ cations.

Keywords: alkoxides • bicyclic • carbenes • uranium • uranyl • yttrium

Introduction

N-Heterocyclic carbenes (NHCs) of the form **A**, Figure 1, are undisputed as extremely strong σ -donor ligands, and now also as π -acceptors in appropriate situations.^[1, 2] Owing

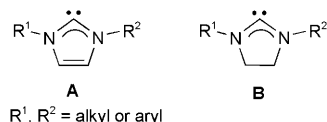


Figure 1. N-Heterocyclic carbenes (NHCs) **A** and **B**.

to an appreciation of the former property, and a desire to understand better the latter, they have been studied intensively as ligands for homogeneous transition metal catalysis.^[3–8] They have also been proven as active organocatalysts in their own right.^[9, 10]

As a part of efforts to tune the catalytic properties, the saturated analogue of the first generation NHC, **B** in Figure 1, has become the focus of much interest for late metal homogeneous catalysis. It should be noted, however, that saturated NHC complexes were also studied in Lappert's original

work on the synthesis of metal carbene complexes from electron-rich olefins, for example in the synthesis of *trans*-[PtCl₂[C(NPhCH₂)₂]PEt₃].^[11]

Nolan has examined the differences between saturated and unsaturated NHCs in Group 10 complexes by analysing the stretching frequency in [(NHC)Ni(CO)₃] adducts. He finds that within the group, the σ -donor properties of unsaturated and saturated NHCs are almost the same.^[12] Another study showed that the saturated NHCs are better acceptors of π -back-donation than the unsaturated analogues in Pt^{II} complexes, which contain a bonding contribution of about 10% from back-bonding.^[13] Most recently, studies on an iridium system that allows for a direct comparison of a wide range of monodentate carbenes, [Ir(NHC)(CO)₂Cl], have again concluded that the differences between the two types of NHC are very small, and the sterics of the ligands probably provide the greatest contribution to differences in the complexes formed.^[14]

A number of synthetic routes to substituted imidazolium proligands have been developed. These include a modular substituted diamine synthesis with subsequent ring closure,^[15] multicomponent synthesis by using a combination of amine, aldehyde, isocyanide and alkyl halide,^[16] the intramolecular “hydroamidinium” of alkenes,^[17] and a template synthesis with an azido isocyanide at a tungsten metal centre.^[18]

Late metal complexes containing alcohol and phenol-functionalised saturated NHC ligands have been reported, see Figure 2: Seeking an analogy with salicylaldimine ligands, Grubbs reported the synthesis of *o*-hydroxyaryl-substituted NHCs and showed that the Pd adducts **C** were stable.^[19] Hoveyda has used the BINOL-derived proligand

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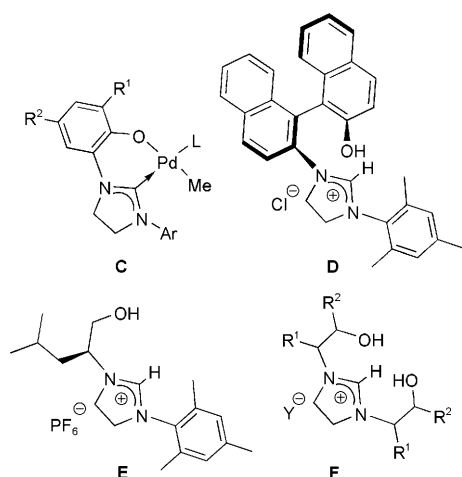


Figure 2. Functionalised, saturated NHC complex and imidazolium salts C–F.

D to make ruthenium catalysts for asymmetric alkene meta-thesis.^[20] Mauduit reported a five step route from β -aminoalcohols to chiral alkoxy-imidazolium salts **E**, which were highly active for copper-catalysed conjugate addition,^[21] and Wilhelm has shown that **F** is a good proligand for the enantioselective addition of ZnEt_2 to aldehydes.^[22]

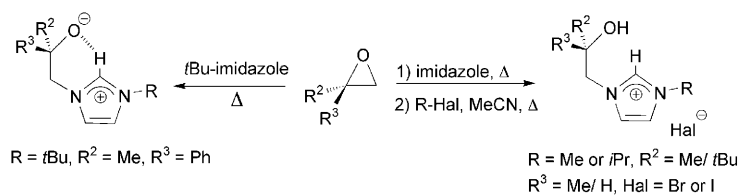
We have previously reported syntheses of unsaturated alcohol-carbene ligands,^[23,24] and their use in copper-catalysed asymmetric conjugate addition,^[25] lactide polymerisation,^[26] and Group 4^[27] and f-block organometallic chemistry.^[28, 29] We, like others, have found that the acidity of the protons of the carbene heterocyclic backbone can lead to unanticipated, and sometimes unwanted, ligand rearrangements.

Herein we report a modular synthesis of bidentate alkoxy-functionalised saturated NHC ligands and the first examples of early metal saturated carbene complexes; adducts of Y^{III} and the uranyl dication.

Results and Discussion

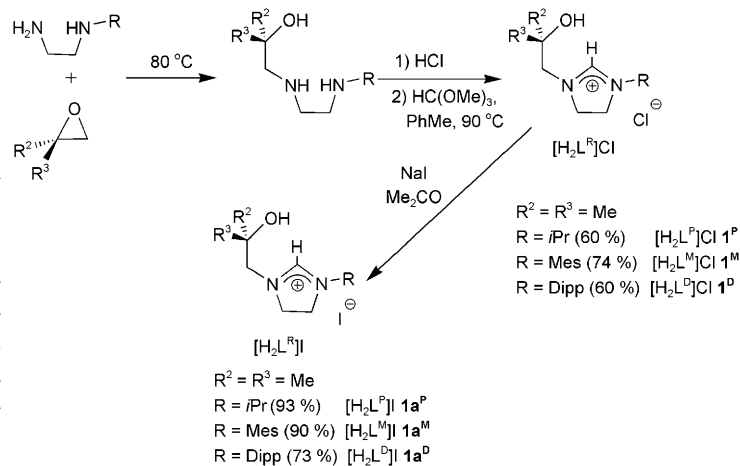
Synthesis of proligands: Our previous synthesis of unsaturated alkoxy-carbene ligands proceeded by means of the ring opening of an epoxide with either imidazole, followed by subsequent quaternization of the remaining imidazole nitrogen with an alkyl halide, or with a substituted imidazole to give a zwitterionic compound,^[23, 25] Scheme 1.

Hancock et al. previously reported that a primary amine will selectively ring open an epoxide in the presence of a



Scheme 1. Synthesis of unsaturated alkoxy-carbene proligands.

secondary amine, during the synthesis of hydroxyl substituted polyamine ligands.^[30] This result presented an opportunity for us to extend our straightforward modular unsaturated ligand synthesis to a range of saturated variants. Thus, the new imidazolium salts $[\text{H}_2\text{L}^{\text{R}}]\text{X}$, $[\text{HOCR}^2\text{R}^3\text{CH}_2(1\text{-CH}[\text{NCH}_2\text{CH}_2\text{NR}])]\text{Cl}$ ($\text{R} = i\text{Pr}$, denoted as **P**; $\text{R} = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6-(Mes)}$, denoted as **M**; $\text{R} = \text{C}_6\text{H}_3i\text{Pr}_2\text{-2,6-(Dipp)}$, denoted as **D**, $\text{X} = \text{Cl, I}$) are synthesised according to Scheme 2, through nucleophilic attack by a mono N-sub-



Scheme 2. Syntheses of saturated alkoxy-carbene proligands $[\text{H}_2\text{L}^{\text{R}}]\text{X}$ ($\text{X} = \text{Cl, I}$), **1^R** and **1a^R**.

stituted ethylene diamine on a substituted epoxide. Subsequent acidification and heating in trimethyl orthoformate furnishes the ring-closed alcohol-N-functionalised imidazolium chloride salts in yields of 60 to 74 %, as a viscous brown oil for $[\text{H}_2\text{L}^{\text{P}}]\text{Cl/I}$ (**1^P/1a^P**) and as colourless—or cream-coloured powders for $[\text{H}_2\text{L}^{\text{M}}]\text{Cl/I}$ (**1^M/1a^M**) and $[\text{H}_2\text{L}^{\text{D}}]\text{Cl/I}$ (**1^D/1a^D**). This simple modular approach allows for the incorporation of three different R groups, each close to a ligand donor atom, to yield proligands with a variety of steric and electronic profiles.

The identities of the imidazolium salts were confirmed by multinuclear NMR spectroscopy and combustion analyses (for all except **1^P**) of **1^P**, **1^M**, **1^D**; the iodide salts **1a^P**, **1a^M** and **1a^D** are readily made by treatment of $[\text{H}_2\text{L}^{\text{R}}]\text{Cl}$ with NaI in acetone. The ^1H NMR spectra of proligands **1^R** and **1a^R** show the characteristic highfield imidazolium resonance between $\delta = 8$ and 10 ppm, which are similar to those observed in the unsaturated analogues. In the ^{13}C NMR spectra, the imidazolium CH resonances lie in the range $\delta = 155$ to 160 ppm, as would be expected for the saturated cationic heterocycle, and lie approximately 20 ppm further downfield than in the unsaturated examples (range $\delta = 135$ to 141 ppm).

In addition, the conformation of **1a^P** and **1^D** were determined by single crystal X-ray diffraction studies on crystals grown from the dried crude product, which was an oil, and an acetone solution, respectively. The molecular structures

are shown in Figure 3 and selected distances and angles are displayed in Table 1.

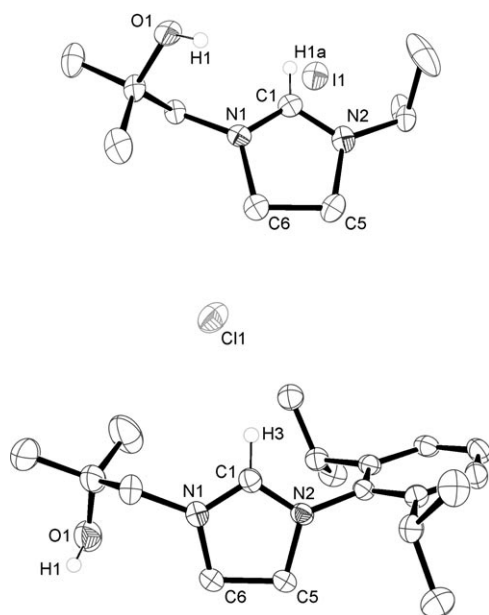


Figure 3. Displacement ellipsoid drawings (50% probability) of $[H_2L^P]I$ **1a^P** (top) and $[H_2L^D]Cl$ **1^D** (bottom).

Table 1. Selected distances (Å) and angles (°) for the molecular structures of proligands **1a^P** and **1^D**.

	1a^P Distance/angle	1^D Distance/angle
C1–N1	1.352(6)	1.305(3)
C1–N2	1.402(6)	1.317(3)
C2–N2	1.525(6)	1.438(3)
C5–N2	1.653(7)	1.481(3)
C5–C6	1.611(7)	1.527(3)
C1–Hal1*	3.462	3.438
O1–Hal1'*	3.771	3.100
O1–O1w'	–	2.853
N1–C1–N2	110.6(4)	113.7(2)
N2–C5–C6	98.7(4)	102.9(2)

* Hal = I (**1a^P**), Cl (**1^D**).

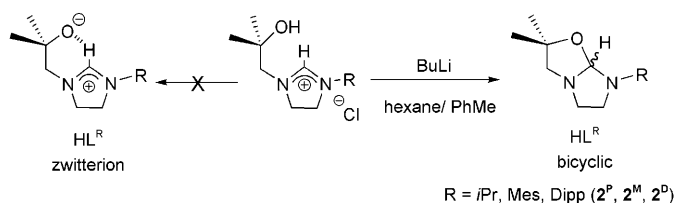
The structure of both **1a^P** and **1^D** show no unusual distances or angles. The imidazolium NC(H)N group is characterised by the C–N distances of 1.305(3) to 1.402(6) Å, consistent with the sp^2 character of each atom. A noticeable asymmetry is seen in the ring, with the C1–N1 bond next to the alcohol arm shorter than the C1–N2 bond in each case. The NCN angles of 110.6(4) and 113.7(2)° are approximately seven degrees wider than the NCN angle in imidazolium salts. The heterocycle rings in both are essentially planar.

The directionality towards lattice iodide ions of the alcohol and of the imidazolium group in **1a^P** both suggest the existence of hydrogen bonding interactions, but the distances are long; O–I = 3.771 Å in the former, and C–I = 4.306 Å in the latter.

The alcohol and imidazolium groups in **1^D** both participate in hydrogen-bonding networks within the structure, but

all are intermolecular, and involve the chloride counterion and a partial (60% present) molecule of water in the lattice. Thus the OH forms hydrogen bonds with a lattice water molecule and the imidazolium group forms a hydrogen bond with a chloride.

Deprotonation chemistry: Treatment of the $[H_2L^R]X$ salts with a single equivalent of base does not form zwitterionic or imidazolium salts as for the unsaturated analogues of these. Instead, $[H_2L^R]X$ reacts with benzyl potassium in THF, or with *Li*nBu in hexanes/toluene to afford the bicyclic products HL^R (**2^R**) in high yield (Scheme 3). Compounds HL^P (**2^P**) and HL^M (**2^M**) are colourless, distillable oils (40 °C at 10^{-1} mbar, 51% and 85 °C at 10^{-1} mbar, 73% respectively); compound HL^D (**2^D**) was isolated as a colourless powder and washed with hexanes, 97%.



Scheme 3. Bicyclic structure adopted by HL^R products **2^R**.

The 1H NMR spectra of these products confirm the presence of a single remaining acidic CH proton between $\delta = 5.47$ and 5.79 ppm, but the loss of the imidazolium CH resonance between $\delta = 8$ and 10 ppm. The spectra also show magnetically inequivalent *gem*-dimethyl and CH_2 arm and backbone resonances, consistent with an asymmetric structure for **2^R** in each case, as drawn in Scheme 3. A similar bicyclic structure **G** was recently reported from the annelation of a 1-substituted benzimidazole using α,β -acetylenic- γ -hydroxyacidnitriles (Figure 4).^[31] This compound exhibits a

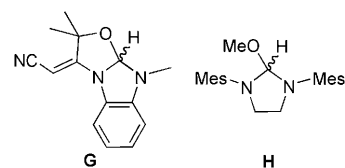


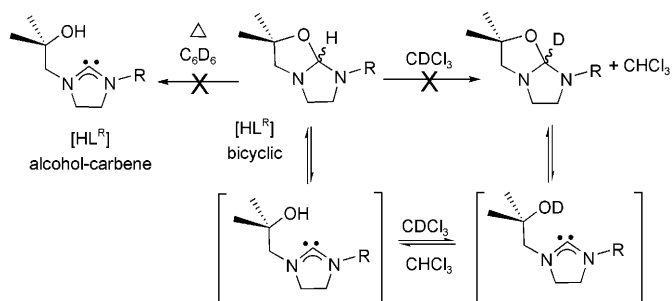
Figure 4. Alcohol adducts of NHCs.

characteristic CH resonance in the 1H NMR spectra as a singlet at $\delta = 6.28$ ppm, and in the $^{13}C\{^1H\}$ spectra at $\delta = 109$ ppm, respectively. These values are comparable to the chemical shifts of the NC(H)N proton in the 1H NMR spectra for **2^R**, considering the different arm substituents, at $\delta = 5.47$, 5.79 and 5.78 ppm and $\delta = 108$ –109 ppm in the $^{13}C\{^1H\}$ NMR spectra.

The bicyclic structures formed by compounds **2^R** are single-molecule analogues of the alcohol,^[10, 32] fluoro-phenyl,^[33] and chloroform^[32–34] adducts that have been used with great success as masked carbenes. For comparison, in

the compound (MeO)(H)C(NMe₃CH₂)₂, **H** in Figure 4, formed from the reaction between the free imidazolin-2-ylidines and methanol,^[10] the ¹H and ¹³C NMR chemical shifts of the NC(H)N fragment are δ =5.48 ppm and 104 ppm respectively. In the zwitterionic unsaturated analogue OCM₂CH₂[1-CHNCHN*i*Pr] reported by us,^[24] the ¹H and ¹³C NMR chemical shifts of the NC(H)N fragment are δ =7.77 ppm and 199 ppm, respectively, suggesting that adducts **2^R** do not exist as zwitterionic imidazolium alkoxides.

The addition products (X)(H)C(NMe₃CH₂)₂ (X=OtBu, OMe, C₆F₅, CCl₃) can be thermally converted to the free carbenes; the *tert*-butanol adduct spontaneously decomposes at room temperature^[32] and the methanol adduct reversibly eliminates methanol at 25 °C.^[10] Here, the bicyclic structure of **2^R** renders them more stable; heating a benzene solution of **2^P** to 70 °C in the NMR spectrometer does not show any evidence of a dissociated carbene-alcohol, Scheme 4.



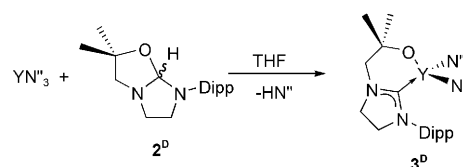
Scheme 4. Transient formation of alcohol-carbene compound from **2^R**.

Dissolution of **2^P** in CDCl₃ does not form any chloroform addition product, but a slow H/D exchange of the oxazolidine proton and the chloroform becomes apparent in the solution after a few hours at room temperature. Since a direct H/D exchange of the proton in the bicyclic structure is presumed to be not possible under these reaction conditions, the simplest exchange mechanism, shown also in Scheme 4, involves the transient generation of the free carbene in an equilibrium with the inter and intra-molecular addition product.

The suggestion of transient carbene formation in these systems has led us to explore their protonolysis chemistry with representative early transition metal and f-block metal complexes.

Yttrium complexes: Treatment of YN''₃ (N''=N(SiMe₃)₂) with an equivalent of **2^P** in THF affords a yellow-coloured solution and, after recrystallisation from toluene, colourless L^PYN''₂ **3^P** can be isolated in 51 % yield (Scheme 5).

Compound **3^P** is immediately identifiable by the yttrium-carbene ¹J_{YC} coupling of 42 Hz for the carbene carbon resonance at δ =216.3 ppm in the ¹³C{¹H} NMR spectrum. This is at a higher frequency than observed for unsaturated yttrium-carbene complexes, and compares with δ =186.3 (¹J_{YC}=53 Hz) in [Y(L){N(SiMe₃)₂}], L=N*t*Bu[CH₂CH₂[1-C(NCHCHN*t*Bu)]]^[35] δ =194.3 ppm (¹J_{YC}=48 Hz) in



Scheme 5. Synthesis of the yttrium(III) complex **3^P**.

[Y(L){N(SiMe₃)₂}Cl], L=N[CH₂CH₂[1-C(NCHCHNMe₃)]]₂,^[36] and δ =194.0 ppm in [Y{N(SiHMe₂)₂}₃[C(NMeCH)₂]]₂.^[37]

The ¹H NMR spectrum is simplified upon breaking the doubly five-membered bicyclic ring system into the six-membered ring-containing yttrium-alkoxide carbene; the alkoxide arm CH₂ protons are a singlet at δ =3.25 ppm. NMR spectroscopic-scale reactions between HL^R and YN''₃ for R=*i*Pr and Mes show that the analogous yttrium complexes **3^P** and **3^M** can be made as readily. The one-bond yttrium-carbene coupling constants for these two complexes are 46 and 44 Hz respectively, seen in the carbene chemical shifts of δ =212.3 and 215.5 ppm respectively.

Single crystals of **3^P** suitable for X-ray structural analysis were grown from a saturated toluene solution cooled to -30 °C; the molecular structure is shown in Figure 5, and selected distances and angles are collected in Table 2.

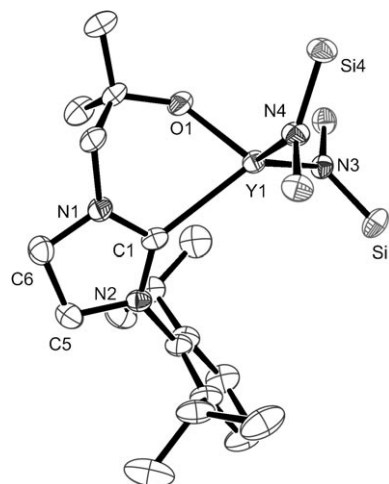


Figure 5. Displacement ellipsoid drawing (50% ellipsoid probability) of **3^P**. Hydrogen atoms and Si-bound methyl groups omitted for clarity.

The yttrium cation in **3^P** is distorted away from pseudo-tetrahedral, as the angle between the carbene and the two silylamido groups is widened to accommodate the large *N*-Dipp substituent, for example, C1-Y1-N4=122.55(6)°. There are two silylamido silicon atoms relatively close to the yttrium cation, with Y-Si distances of 3.1957(7) and 3.3268(7) Å. The yttrium carbene distance is 2.599(2) Å. This is long compared with Y-C distances in unsaturated carbene complexes; in these the distances are 2.501(5) Å in [Y(L){N(SiMe₃)₂}], L=N*t*Bu[CH₂CH₂[1-

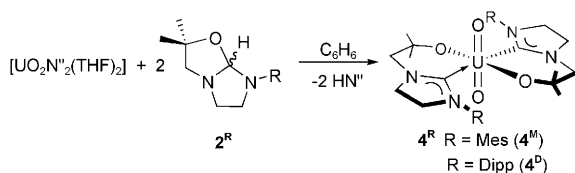
Table 2. Selected distances (Å) and angles (°) for the molecular structures of complexes **3^D**, **4^M**, and **4^D**

	3^D		4^M	4^D
C1–Y1	2.599(2)	U1–C1	2.580(4)	2.612(2)
N3–Y1	2.2654(17)	U1–C1	2.596(4)	–
N4–Y1	2.2613(16)	U1–O1	1.7978(18)	1.7984(16)
O1–Y1	2.0314(15)	U1–O2	2.161(3)	2.1538(16)
C1–N1	1.331(3)	C1–N1	1.298(17)	1.336(3)
C1–N2	1.347(3)	C1–N2	1.343(6)	1.338(3)
C2–N2	1.432(3)	O1–U1–O1	180.0(2)	180.00(11)
C5–N2	1.478(3)	O1–U1–O2	85.81(12)	89.83(7)
C5–C6	1.515(3)	O2–U1–C1	72.28(14)	72.46(6)
O1–Y1–C1	77.88(6)	O1–U1–C1	89.16(11)	87.58(7)
N1–C1–Y1	112.40(14)	N1–C1–U1	118.3(6)	117.23(15)
N2–C1–Y1	140.55(15)	N2–C1–U1	132.3(3)	132.38(15)
N4–Y1–C1	122.55(6)			
N1–C1–N2	107.0(2)	N1–C1–N2	108.9(7)	108.0(2)
N2–C5–C6	102.32(17)	N2–C5–C6	101.5(9)	102.0(2)

C(NCHCHN*t*Bu)]],^[35] 2.574(3) and 2.565(3) Å in [Y(L){N-(SiMe₃)₂Cl}, L = N[CH₂CH₂{1-C(NCHCHN*t*Bu)}]₂]^[36] and 2.560(9) and 2.55(1) Å in [Y{N(SiHMe₂)₂}{C(NMeCH)₂}]₂].^[37] Here, the Y–C bond is only slightly longer than the average Y–C single bond in the CS Database (version 1.10), which is 2.49 Å, and compares with longer Y-alkyl bonds, such as the average Y–C distance in bridging methyl groups of 2.55 Å in [Y(C₅Me₅)(μ-CH₃)₂]₃.^[38] The ligand bite angle is 77.88(6)°.

The N–C–N angle of the coordinated carbene group is now 107.0(2)°, which is smaller than the 113.7(2)° angle in the imidazolinium proligand **1^D** as would be expected for the high degree of σ-character in the Y–C_{carbene} bond. Other distances and angles are within accepted ranges.

Uranyl complexes: Mixing benzene solutions of [UO₂N''₂-(THF)₂] and two equivalents of **2^M** results in the deposition of pale yellow crystals of a new compound over a period of minutes (Scheme 6). The compound was identified as the poorly benzene-soluble *trans*-bis(L^M) adduct [UO₂(L^M)₂] **4^M**, by elemental analysis, multinuclear NMR spectroscopy and a single crystal X-ray diffraction study, and isolated in 52 % yield.

Scheme 6. Synthesis of the uranyl complexes **4^M** and **4^D**.

An NMR spectroscopic-scale reaction between two equivalents of HL^D and [UO₂N''₂(THF)₂] shows that the analogous uranyl complex **4^D** is also straightforwardly accessible (Scheme 6).

The most interesting feature of complexes **4^M** and **4^D** is the extraordinarily high chemical shift exhibited by the carbene carbon in the ¹³C{¹H} NMR spectrum, of δ = 281.6 and

283.6 ppm respectively. To our knowledge, these are the highest frequency carbene resonances exhibited by a metal carbene (NHC) compound.

A particularly high carbene chemical shift of δ = 255.5 ppm was reported for the open-chain bis(*diiso*-propyl)-carbene (N,N,N',N'-tetra *iso*-propylformamidinylidene), and the high value attributed to the wide NCN bond angle. Likewise, its complexes exhibit chemical shifts at values δ = 30–40 ppm higher frequency than the corresponding unsaturated NHC analogues.^[39]

In carbene complexes, the highest chemical shifts yet reported have been in uranyl systems. For example δ_{carbene} = 262.8 ppm for *trans*-[UO₂(L^N)₂] (L^N = N*t*BuCH₂CH₂{1-C(NCHCHN*t*Bu)}].^[40]

The asymmetric OUO stretch, ν_{asym}(OUO), is observed in the FTIR spectrum at ν̃ = 851 cm^{−1}, indicating a relatively strong binding of the two alkoxy-carbene ligands in the equatorial plane, which serves to weaken the UO₂ stretching energy. For comparison, ν_{asym}(OUO) in the analogous uranyl complex *cis*-[UO₂(O*t*Bu)₂(OPPh₃)₂] is ν̃ = 861 cm^{−1}, and in [UO₂N''₂(OPPh₃)₂] it is ν̃ = 901 cm^{−1}.^[41] This ligand set also weakens the UO₂ bonding more than in the complexes [UO₂(L^N)₂], in which the average ν_{asym}(OUO) = 931 cm^{−1}. We can conclude from these comparisons that the alkoxides are the dominating factor in the ability of the equatorial donor set to weaken the UO₂ stretch, but that the carbenes are stronger ligands than phosphine oxides.

The molecular structures of **4^M** and **4^D** were determined by single crystal X-ray diffraction and are shown in Figure 6a and b, respectively. Selected distances and angles are in Table 2.

The UO₂²⁺ uranyl unit in each is rigorously linear as expected and the compounds are four-coordinate in the equatorial plane, in which the two bidentate OC ligands adopt a perfectly symmetrical *trans*-geometry about the metal, enforced by a crystallographic C₂ axis. Most uranyl compounds are between five and seven-coordinate in the equatorial plane. Additionally, in **4^M** there is a disorder in the crystal, which superimposes two crystallographically independent molecules; only one is shown in Figure 6a.

In both structures, the alkoxy-carbene ligands twist out of the equatorial plane to accommodate the bulky aryl groups, with a ligand bite angle of 72°, smaller than in **3^D** by approximately 6°. The carbene ring is tilted with respect to the UC₂O₂ equatorial plane by 11° in **4^M** and 22° in **4^D**; this brings the arene rings out of the ligand plane in the same direction as the substituents on the alkoxide of the opposite ligand.

The U–C_{carbene} distances of 2.580(4) Å in **4^M** and 2.612(2) Å in **4^D** are shorter than in the six-coordinate [UO₂L₂], L = N*t*Bu[CH₂CH₂{1-C(NCHCHN*t*Bu)}] (2.640(5) Å) and L = N*t*Bu[CH₂CH₂{1-C(NCHCHN*t*Bu)}] (2.633(7) Å),^[40] and [UO₂Cl₂{C(NMeCH)₂}]₂ (2.626(7) Å).^[42] The U–OC distances of 2.161(3) Å in **4^M** and 2.154(2) Å in **4^D** are comparable to that in *cis*-[UO₂(O*t*Bu)₂(OPPh₃)₂] in which the average is 2.149 Å.^[41] The N–C–N angle of the coordinated carbene group is now

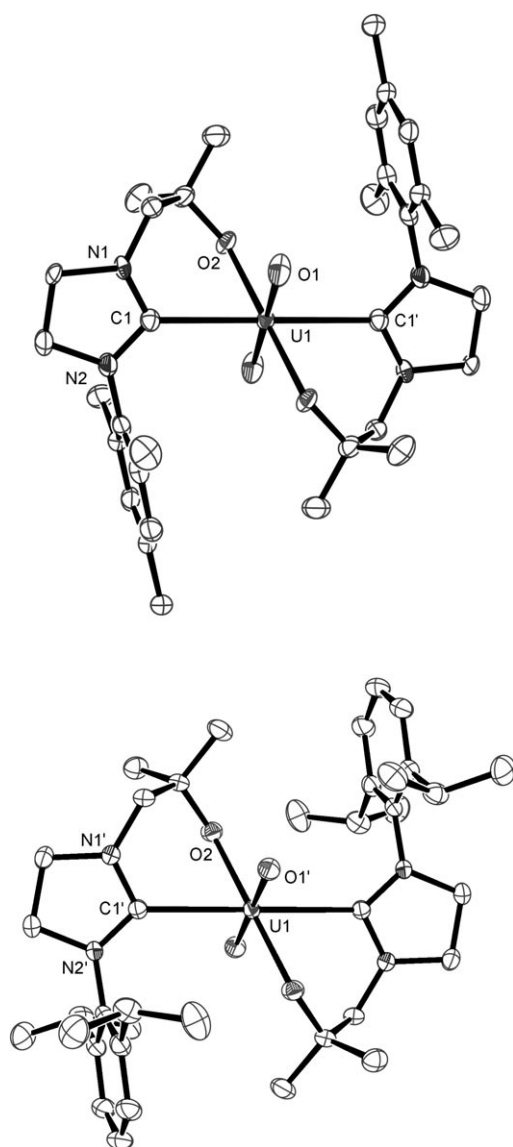


Figure 6. Displacement ellipsoid plot for **4^M** (top) and **4^D** (bottom) (50% probability). Hydrogen atoms omitted for clarity.

108.9(7)° (**4^M**) and 108.0(2)° (**4^D**). Other distances and angles are within standard ranges.

Conclusion

A new and modular route to proligands for bidentate, saturated backbone alkoxy-carbenes has been developed. The removal of one of the two acidic protons leads to the formation of bicyclic compounds that are formally the addition product of a saturated N-heterocyclic carbene (NHC) and the alcohol group of the functionalised arm. This is in contrast to the zwitterionic structures found for the unsaturated analogues. Despite this, the proligands are still reactive towards loss of the remaining acidic proton. Protonolysis chemistry with yttrium and uranyl amido complexes have af-

fected the first early transition metal, and the first f-block saturated carbene complexes.

Experimental Section

See the Supplementary Information for general synthetic and crystallographic details.

Proligand synthesis

General procedure: Proligands were synthesised through a combination and modification of literature procedures^[30,43] under ambient-atmosphere conditions. In a typical reaction, an N-substituted ethylenediamine was heated with an epoxide in a melt reaction in a sealed ampoule at 90°C for two days. The resulting oil was dissolved in diethyl ether and cooled to 0°C, acidified with a solution of anhydrous HCl (2M) 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°C for 2 h. The final workup procedure varied for each proligand. Iodide salts were formed by means of a standard anion exchange reaction with NaI in acetone.

[H₂L^{IPr}]Cl **1^P:** Brown oil (3.92 g, 60%). ¹H NMR (CDCl₃): δ = 9.71 (s, 1H; N-CH-N), 5.25 (s, 1H; OH), 4.33 (bm, 2H; N-CH₂-CH₂-N), 4.05 (bm, 2H; N-CH₂-CH₂-N), 4.05 (bm, 1H; N-CH-(CH₃)₂), 3.74 (s, 2H; N-CH₂-C), 1.46 (d, ³J = 6 Hz, 6H; N-CH-(CH₃)₂), 1.36 ppm (s, 6H; C-(CH₃)₂); ¹³C NMR (CDCl₃): δ = 158.5 ppm (N-CH-N).

[H₂L^{IPr}]I **1a^P:** Brown oil (5.07 g, 93%). Elemental analysis calcd (%) for C₁₀H₂₁IN₂O: C 38.47, H 6.79, N 8.97; found: C 38.18, H 6.10, N 8.18.

[H₂L^{Mes}]Cl **1^M:** Cream solid (4.94 g, 74%). ¹H NMR (CDCl₃): δ = 9.33 (s, 1H; N-CH-N), 6.89 (s, 2H; Ar-CH), 5.20 (s, 1H; OH), 4.42 (bm, 2H; N-CH₂-CH₂-N), 4.13 (bm, 2H; N-CH₂-CH₂-N), 3.89 (bs, 2H; N-CH₂-C), 2.26 (bs, 9H; Ar-CH₃), 1.27 ppm (s, 6H; C(CH₃)₂); ¹³C NMR (CDCl₃): δ = 160.8 ppm (N-CH-N); elemental analysis calcd (%) for C₁₆H₂₅ClN₂O: C 64.73, H 8.51, N 9.44; found: C 64.84, H 8.57, N 9.41.

[H₂L^{Mes}]I **1a^M:** Yellow solid (0.33 g, 90%). Elemental analysis calcd (%) for C₁₆H₂₅IN₂O: C 49.49, H 6.50, N 7.22; found: C 50.17, H 6.81, N 7.96.

[H₂L^{Dipp}]Cl **1^D:** Colourless solid (3.89 g, 60%). ¹H NMR (CDCl₃): δ = 9.47 (s, 1H; N-CH-N), 7.40 (t, ³J = 7 Hz, 1H; 4-Ar-CH), 7.21 (d, ³J = 7 Hz, 2H; 3,5-Ar-CH), 5.18 (s, 1H; OH), 4.44, 4.13 (m, 2H; N-CH₂-CH₂-N), 3.95 (s, 2H; N-CH₂-C), 2.88 (sept, ³J = 2 Hz, 2H; Ar-CH(CH₃)₂), 1.30 (s, 6H; C(CH₃)₂), 1.27 (d, ³J = 2 Hz, 6H; Ar-CH(CH₃)₂), 1.24 ppm (d, ³J = 2 Hz, 6H; Ar-CH(CH₃)₂); ¹³C NMR (CDCl₃): δ = 160.4 ppm (N-CH-N); elemental analysis calcd (%) for C₁₉H₃₁ClN₂O: C 67.33, H 9.22, N 8.27; found: C 67.29, H 9.30, N 8.28.

[H₂L^{Dipp}]I **1a^D:** Colourless solid (1.00 g, 73%). Elemental analysis calcd (%) for C₁₉H₃₁IN₂O: C 53.03, H 7.26, N 6.57; found: C 53.07, H 7.28, N 6.59.

Bicyclic carbene-alcohol adduct synthesis

General procedure: To a Schlenk charged with a stirred mixture of KCH₂Ph 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 a fine precipitate. After filtration, the volatiles were removed and, in the case of HL^{IPr} and HL^{Mes}, the residue was purified by means of a short path distillation and the product isolated as a colourless oil. Compound HL^{Dipp} was isolated as a green oily solid after removal of the volatiles, from which a small amount of colourless crystalline solid could be sublimed.

Alternatively, one equivalent of LinBu 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 colour was observed in these preparations.

[HL^{IPr}] **2^P:** Colourless oil (0.91 g, 51%). ¹H NMR (C₆D₆): δ = 5.47 (s, 1H; N-C(O)H-N), 3.13, 2.85, 2.64, 2.63 (m, 1H each; N-CH₂-CH₂-N), 2.91, 2.45 (d, ²J_{H-H} = 10.5 Hz, 1H each; N-CH₂-C), 2.85 (m, 1H; N-CH-

(CH₃)₂, 1.24, 1.16 (s, 3H each; C-CH₃)₂, 1.14, 1.09 ppm (d, ³J = 6 Hz, 3H each; N-CH-(CH₃)₂); ¹³C NMR (C₆D₆): δ = 107.8 ppm (N-C(O)H-N); elemental analysis calcd (%) for C₁₀H₂₀N₂O: C 65.16, H 10.96, N 15.20; found: C 65.13, H 11.06, N 15.19.

[HL^{Me}] **2^M**: Colourless oil (3.08 g, 73 %). This oil solidified slowly over time. ¹H NMR (C₆D₆): δ = 6.80 (s, 2H; Ar-CH), 5.79 (s, 1H; N-C(O)H-N), 3.42, 3.21, 3.02, 2.94 (m, 1H each; N-CH₂-CH₂-N), 2.90 (d, ²J_{H-H} 10.5 Hz, 1H; N-CHH-C(CH₃)₂), 2.52 (d, ²J_{H-H} 10.5 Hz, 1H; N-CHH-C(CH₃)₂), 2.39 (bs, 6H; Ar-ortho-CH₃), 2.14 (s, 3H; Ar-para-CH₃), 1.30, 1.11 ppm (s, 3H each; C(CH₃)₂); ¹³C NMR (C₆D₆): δ = 108.6 ppm (N-C(O)H-N); elemental analysis calcd (%) for C₁₆H₂₄N₂O: C 73.79, H 9.31, N 10.76; found: C 73.90, H 9.36, N 10.63.

[HL^{Dipp}] **2^D**: Colourless solid (5.60 g, 97 %). ¹H NMR (C₆D₆): δ = 7.28–7.04 (overlapping m, 3H; 3,4,5-Ar-CH), 5.78 (s, 1H; N-C(O)H-N), 4.09 (sept, ³J = 7 Hz, 2H; Ar-CH(CH₃)₂), 3.53–2.95 (overlapping m, 4H; 2H; N-CH₂-CH₂-N), 3.36 (sept, ³J = 7 Hz, 2H; Ar-CH(CH₃)₂), 2.91, 2.52 (d, ²J_{H-H} = 11 Hz, 1H each; N-CH₂-C), 1.42, 1.30 (d, ³J = 7 Hz, 2H each; Ar-CH(CH₃)₂), 1.30 (s, 3H; C(CH₃)₂), 1.18, 1.14 (d, ³J = 7 Hz, 3H each; Ar-CH(CH₃)₂), 1.11 ppm (s, 3H; C(CH₃)₂); ¹³C NMR (C₆D₆): δ = 109.4 (N-C(O)H-N); elemental analysis calcd (%) for C₁₉H₃₁N₂O: C 75.45, H 10.00, N 9.26; found: C 75.51, H 10.07, N 9.20.

[L^YYN³] **3^P**: NMR experiment: In a Youngs tap NMR tube, solutions of YN³ (46.4 mg, 0.08 mmol) and **2^P** (15.0 mg, 0.08 mmol) in C₆D₆ were combined and mixed well. The solution turned pale yellow and was heated to 85 °C for 24 h.

¹H NMR (C₆D₆): δ = 4.37 (sept, 1H; ³J = 7 Hz, N-CH-(CH₃)₂), 2.97 (s, 2H; N-CH₂-C), 2.74 (m, 2H; N-CH₂-CH₂-N), 2.53 (m, 2H; N-CH₂-CH₂-N), 1.14 (s, 6H; C(CH₃)₂), 0.96 (d, 6H; ³J = 7 Hz, N-CH-(CH₃)₂), 0.40 ppm (s, 36H; N(Si(CH₃)₃)₂). ¹³C NMR (C₆D₆): δ = 212.3 ppm (d, ¹J_{YC} = 46 Hz, N-C-N).

[L^{Me}YN³] **3^M**: NMR experiment: In a Youngs tap NMR tube, C₆D₆ solutions of YN³ (43.8 mg, 0.08 mmol) and **2^M** (20.0 mg, 0.08 mmol) were combined and mixed well. The resulting solution turned pale yellow after 5–10 minutes. ¹H NMR (C₆D₆): δ = 6.75 (s, 2H; Ar-CH), 3.10 (s, 2H; N-CH₂-C(CH₃)₂), 2.85 (bs, 4H; N-CH₂-CH₂-N), 2.17 (s, 6H; Ar-ortho-CH₃), 2.14 (s, 3H; Ar-para-CH₃), 1.22 (s, 6H; C(CH₃)₂), 0.33 ppm (s, 36H; N(Si(CH₃)₃)₂); ¹³C NMR (C₆D₆): δ = 215.5 ppm (d, ¹J_{YC} = 44 Hz, N-C-N).

[L^{Dipp}YN³] **3^D**: To a solution of YN³ (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 cooling of a toluene solution (≈ 3 mL) to –30 °C afforded **3^D**, as colourless plates suitable for an X-ray diffraction study (0.30 g, 51 %). ¹H NMR (C₆D₆): δ = 7.18 (m, 1H; 4-Ar-CH), 7.04 (m, 2H; 3,5-Ar-CH), 3.25 (s, 2H; N-CH₂-C), 3.15 (m, 2H; N-CH₂-CH₂-N), 3.09 (sept, ³J = 7 Hz, 2H; Ar-CH-(CH₃)₂), 2.90 (m, 2H; N-CH₂-CH₂-N), 1.44 (d, ³J = 7 Hz, 6H; Ar-CH-(CH₃)₂), 1.08 (d, ³J = 7 Hz, 6H; Ar-CH(CH₃)₂), 0.39 ppm (s, 36H; N(Si(CH₃)₃)₂). ¹³C NMR (C₆D₆): δ = 216.3 ppm (d, ¹J_{YC} = 42 Hz, N-C-N); elemental analysis calcd (%) for C₃₁H₆₅N₄O₅Si₄Y: C 52.36, H 9.21, N 7.88; found: C 52.27, H 9.28, N 7.73.

[UO₂L^{Me}] **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 [UO₂N₂''(THF)₂] (42.3 mg, 0.06 mmol) in benzene (2 mL) and allowed to diffuse slowly overnight at room temperature. The resulting solution turned yellow and **4^M** formed as yellow needles which were washed with benzene (3 × 1 mL) and dried in vacuo (24.0 mg, 52 %). Bi-refrangent yellow-green crystals suitable for an X-ray diffraction study were grown from a 5:1 pyridine/benzene mixture by slow cooling of a hot solution to room temperature overnight. ¹H NMR (C₅D₅N): δ = 6.82 (s, 2H; Ar-CH), 3.84 (bs, 2H; N-CH₂-C), 3.75

Table 3. Selected crystallographic details

	1a^P	1^D	3^D	4^M	4^D
formula	C ₁₀ H ₂₁ IN ₂ O	C ₁₉ H ₃₁ ClN ₂ O·H _{1.2} O _{0.6}	C ₃₁ H ₆₅ N ₄ O ₅ Si ₄ Y	C ₄₄ H ₈₈ N ₄ O ₄ U	C ₃₈ H ₈₈ N ₄ O ₄ U·C ₁₂ H ₁₂
<i>M_r</i>	312.19	349.72	711.14	944.97	1029.13
crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
space group	<i>Pna</i> 2 ₁	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>T</i> [K]	150(2)	150(2)	150(2)	150(2)	150(2)
<i>a</i> [Å]	9.916(3)	11.9968(3)	20.3348(16)	7.7547(2)	10.1261(7)
<i>b</i> [Å]	11.780(3)	11.2624(3)	10.6423(9)	12.0229(3)	10.4437(7)
<i>c</i> [Å]	11.387(3)	14.8437(4)	20.1193(16)	12.3593(3)	11.7599(8)
α [°]	90.00	90.00	90.00	68.6800(10)	93.023(3)
β [°]	90.00	94.715(2)	112.017(4)	75.4660(10)	92.881(4)
γ [°]	90.00	90.00	90.00	83.0090(10)	101.057(3)
<i>V</i> [Å ³]	1330.1(6)	1998.79(9)	4036.5(6)	1038.50(4)	1216.56(14)
<i>Z</i>	4	4	4	1	1

(bm, 2H; N-CH₂-CH₂-N), 3.64 (bm, 2H; N-CH₂-CH₂-N), 2.29 (bs, 6H; Ar-ortho-CH₃), 2.25 (s, 3H; Ar-para-CH₃), 1.45 ppm (s, 6H; C(CH₃)₂). ¹³C NMR (C₅D₅N): δ = 281.6 ppm (N-C-N); IR(nujol): $\tilde{\nu}$ = 851 cm^{−1} (O=U=O); elemental analysis calcd (%) for C₃₂H₄₆N₄O₄U: C 48.72, H 5.89, N 7.10; found: C 48.74, H 6.55, N 6.52.

[UO₂L^{Dipp}] **4^D**: NMR experiment: A solution of **2^D** (32.9 mg, 0.10 mmol) in benzene (2 mL) was carefully layered onto a red solution of [UO₂N₂''(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 × 1 mL) and dried in vacuo. ¹H NMR (C₅D₅N): δ = 7.43 (t, ³J = 8 Hz, 1H; 4-Ar-CH), 7.27 (d, ³J = 8 Hz, 2H; 3,5-Ar-CH), 3.94, 3.87 (m, 2H each; N-CH₂-CH₂-N), 3.87 (s, 2H; N-CH₂-C), 3.43 (sept, ³J = 7 Hz, 2H; Ar-CH(CH₃)₂), 1.31 (s, 6H; C(CH₃)₂), 1.28 1.17 ppm (d, ³J = 7 Hz, 6H each; Ar-CH(CH₃)₂); ¹³C NMR (C₅D₅N): δ = 283.6 ppm (N-C-N); IR(nujol): $\tilde{\nu}$ = 853 cm^{−1} (asymm-UO₂).

Crystallography: Crystallographic X-ray data were collected by using MoK α radiation (λ = 0.71073 Å) on a Bruker Smart APEX CCD area detector diffractometer using ω , or ω and ϕ scans (Table 3). Structure solution and refinement was carried out using the SIR program, WinGX, and the SHELXTL suite of programs, and graphics generated using Ortep-3. 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*-L₂ 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.

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