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ABSTRACT: The first thorium(IV) and uranium(IV) hydrocarbyl complexes of a \textit{trans}-calix[2]benzene[2]pyrrolide macrocycle can use ligand non-innocence to enable multiple C-H bond activation reactions at the metal. Both alkyl and alkynyl complexes supported by the (L) dianion and (L -2H) tetraanion are reported. The Th IV and UIV mono-alkyl -ate complexes \([M(L-2H)An(R)] (M = K for R = CH 2Ph, M = Li for R = Me, CH 2SiMe 3), in which the ligand aryl groups are metallated, add the C-H bonds of terminal alkynes across the metal and ligand, forming the An IV-alkynyl complexes \([(L)An(C≡CR') 2] (R' = SiMe 3, Si i Pr 3). This ligand reprotonation from \((L-2H) 4-\) to \((L) 2-\) is accompanied by a change in coordination mode of the ligand from \(\eta^5:\eta^5\) to \(\eta^1:\eta^6:\eta^1\). Alternatively, the original alkyl group can be retained if the ligand is reprotonated using \([Et_3NH][BPh 4], affording the Th IV cations \([(L)Th(R)][BPh 4] (R = CH 2Ph, N(SiMe 3) 2). Again, ligand rearrangement to the \(\kappa^1:\eta^6:\kappa^1:\eta^6\) coordination mode occurs. These complexes provide rare examples of bis(arene) actinide sandwich geometry. The two \(\eta^1\)-alkynides in \([(L)Th(C≡CSiMe 3) 2]\) rearrange upon coordination of \([Ni 0]\), forming \([(L)Th(C≡CSiMe 3) 2·Ni(PR'' 3)] (R'' = phenyl, cyclohexyl) – featuring the shortest yet reported distance between Th and Ni, and giving unprecedented insight into the changes in macroyclic ligand coordination between \(\kappa^1:\eta^6:\kappa^1:\eta^6\) and \(\eta^5:\eta^5\) coordination modes. A computational study of this conformational change demonstrates the \(\eta^5:\eta^5\) coordination mode to be the more stable in the Th/Ni bimetallics (and hypothetical Pt analogues), an observation rationalised by detailed analysis of the Kohn-Sham orbital structure of the \(\kappa^1:\eta^6:\kappa^1:\eta^6\) and \(\eta^5:\eta^5\) conformers. Although remarkably inert to even high-pressures of CO 2 at room temperature, the bis(alkynyl) complexes \([(L)An(C≡CSiMe 3) 2]\) completely cleave one CO bond of CO 2 when heated under a 1 bar pressure, resulting in the formation, and elimination from the metal, of a new, CO-inserted, bicyclic, carbonylated macrocycle with complete control over the C-C and C-N bond forming reactions.

INTRODUCTION

Organometallic f-block alkyl complexes show exciting reactivity in C-H bond activation. Examples include the uranium(III) mediated formation of both "tuck-in" and "tuck-over" products from intra- and inter-molecular pentamethylcyclopentadienyl (Cp*) C-H bond activation,\textsuperscript{2-4} C-H activation of typically inert carbocycles induced by steric crowding,\textsuperscript{5} or the addition of C-H bonds across f-block metal imido and nitrido bonds.\textsuperscript{6-10} This is important because C-H bond activation is a key step in the synthesis of a range of desirable organic products. In spite of the many successful examples of d-block hydrocarbon C-H bond activation, there are no reports of an economically viable, homogeneous, catalysed process.\textsuperscript{11-12}

Thorium(IV) and uranium(IV) coordination complexes have been studied for the last 60 years,\textsuperscript{13} showing not only some interesting C-H bond reactivity, for example the intramolecular C-H bond activation of the methyl group on bis(permethylycyclopentadienyl) (Cp*) C-H bond activation,\textsuperscript{2,4} C-H activation of typically inert carbocycles induced by steric crowding,\textsuperscript{5} or the addition of C-H bonds across f-block metal imido and nitrido bonds.\textsuperscript{6-10} The vast majority of studies of actinide alkyl reactivity have been carried out on complexes supported by the bis-Cp* ligand system, with the general formula [(Cp*) 2AnR 2]
(R = hydrocarbyl).\(^{25-28}\) We recently reported the synthesis of new trans-calix[2]benzene[2]pyrrole (L) complexes of U\(^{III}\), Th\(^{IV}\) (A in Scheme 1) and U\(^{IV}\) (B).\(^{29}\) The bis(pyrrole)-containing macrocycle (L)\(^{2-}\) commonly binds to the An\(^{IV}\) cations through η⁵-pyrpyridyl ligation, affording complexes reminiscent of the metallocene dialkyls [(Cp*)\(^2\)AnR\(^2\)].

However, L has a greater flexibility and range of binding modes than that available to the [(Cp*)\(^2\)AnR\(^2\)] complexes, including the facile conversion between η⁵- and η⁵-pyrpyridyl coordination, the ability to incorporate cations in the cavity between the arene rings of the macrocycle (bis(arene) pocket), and the ability to bind the arene in the macrocycle as an η⁵-aryl group, through further ligand deprotonation. Accordingly, we have studied the alkalylation chemistry of these An\(^{IV}\) complexes A and B, and report herein the synthesis and reactivity of the first thorium(IV) and uranium(IV) alkyl and alkynyl complexes supported by the non-innocent macrocyclic (L)\(^{2-}\), including rare examples of bis(arene) sandwich coordination of a thorium ion, the first structurally characterised thorium alkynyl complexes, and an unusual reversibility of the thorium-aryl interaction chemistry of these An\(^{IV}\) complexes A and B, and report herein the synthesis and reactivity of the first thorium(IV) and uranium(IV) alkyl and alkynyl complexes supported by the non-innocent macrocyclic (L)\(^{2-}\), including rare examples of bis(arene) sandwich coordination of a thorium ion, the first structurally characterised thorium alkynyl complexes, and an unusual reversibility of the thorium-aryl – thorium-arene bonding with a ligand that enables new hydrocarbon functional group interconversion at the active centre. Furthermore, we have isolated new bimetallic complexes of the form [(L)Th(C\(^5\)NMe\(^3\))\(^2\)Ni(PR''\(^3\))] (R'' = phenyl, cyclohexyl) gives insight into unprecedented changes in macrocyclic ligand coordination between η⁵-η⁵- and η⁵-η⁵ coordination modes. The latter mode is found by DFT calculations to be significantly more stable than the former in these bimetallic complexes, and analysis of the Kohn-Sham orbital structure provides a pleasing rationalisation of this energetic preference.

**RESULTS AND DISCUSSION**

**Synthesis of [M(L-2H)An(R)].** The syntheses of the chlorido-thorium complexes A and iodo-uranium complex B were reported previously, using a salt-metathesis strategy (Scheme 1).\(^{29}\) Using an analogous procedure, orange crystalline [(L)UCl\(^3\)] (t) (see SI Fig. S1 for molecular structure) is also accessible from UCl\(^3\)(thf)\(^{75}\) and potassium salt K\(^{-}\)(L) in 74% yield after work-up (see SI for solid-state structure). Characterisation of t by NMR spectroscopy and X-ray crystallography shows that t is isomorphous with A and B. With the aim of synthesising Th\(^{IV}\) and U\(^{IV}\) alkyl complexes, A and t were treated with three equivalents of MR (M = K for R = CH\(_2\)Ph, M = Li for R = Me, CH\(_3\)SiMe\(_2\)) in THF or toluene at ambient temperature over 18 hours (Scheme 2).

2). Following work-up to remove MX and HR, the product [M(L-2H)An(R)] was isolated arising from double aryl metallation to form the tetradentate (L\(^{2+}\))\(^{-}\) ligand, and coordination of a single alkyl ligand, with the alkali-metal counter-cation residing in the bis(arene) pocket. It is important to note the addition of two equivalents of MR to A or t results in analogous reactivity to that described in Scheme 2 with untreated A or t remaining.

**Scheme 2.** Syntheses of [L\(^{2+}\)]Th(R)] (R = Me (2), CH\(_3\)SiMe\(_2\) (3), CH\(_2\)Ph (4) and [M(L\(^{2+}\)]U(R)] (R = Me (5), CH\(_3\)SiMe\(_2\) (6), CH\(_2\)Ph (7)).

The new complexes are isolated as yellow solids (R = Me (2) in 93% yield, CH\(_3\)SiMe\(_2\) (3) in 73% yield, CH\(_2\)Ph (4) in 70% yield), and [M(L\(^{2+}\)]U(R)] as dark orange solids (R = Me (5) in 97% yield, CH\(_3\)SiMe\(_2\) (6) in 65% yield, CH\(_2\)Ph (7) in 46% yield). To our knowledge, complexes 2-7 are the first pyrrolic-macrocycle supported alkyl complexes of the actinides.

The 1H NMR spectra of 2-7 show that the macrocyclic ligand in the new complexes retains the C\(_n\) symmetry observed for A and B, where the methyl groups on the endo and exo faces of the macrocycle are represented by two singlets of equal integration. The ligand aryl deprotonation is characterised by the disappearance of the ipso-proton resonances in the 1H NMR spectra of 2-7 and the dramatic increase in the ipso-carbon chemical shift in the 1\(^{13}\)C\(_{\text{H}}\) NMR spectra from 121.6 ppm in A to 217.6, 213.6 and 215.8 ppm in 6, 3 respectively, and in complexes 5-7, the resonances are paramagnetically shifted and broadened due the U\(^{IV}\)\(^+\) ion. Single crystals suitable for X-ray diffraction studies were grown by vapour diffusion of hexane into saturated THF solutions of 2, 3, 4 and 6 at ambient temperature.

The molecular structures of 2 (Figure 1) and 4:THF (Figure 2) display the tetradentate η⁵-η⁵-η⁵-η⁵- binding mode analogous to that in the Th\(^{IV}\) amido complex, [K(L\(^{2+}\)]Th(N(SiMe\(_3\))\(_2\)] (C), previously reported by us.\(^{29}\) In 2, the lithium counter-ion occupies the cavity between the arene rings of the macrocycle. This motif is similar to that of 4:THF, where the potassium counter-ion is additionally coordinated to a THF molecule and the benzyl group of the adjacent complex. Although complexes 3 and 6 are synthesised using the procedure described in Scheme 2, X-ray quality crystals could not be obtained. Subsequent addition of one equivalent of LiCl to 3 and 6 facilitates salt-bridged dimerisation and the growth of X-ray quality crystals of 3·LiCl and 6-LiCl:THF (see SI Fig. S2 and S3 for molecular structures).
Figure 1. Solid state structure of 2 (thermal ellipsoids set at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 2: [Thi–Ci]avg 2.55, Thi–C1 2.65(2), Thi–C9 2.603(13), Thi–C29 2.603(11), Ct–Thi–Ct 172.26, C9–Thi–C29 129.9(4).

The Ct1–An–Ct2 (Ct = centroid) in the molecular structures of 2, 3·LiCl, 4·THF and 6·LiCl·THF are 172.26°, 168.48°, 170.16° and 172.03°, respectively; this is larger than that observed for A (163.60°) and 1 (164.97°). The C9–An–C29 angles are altered from A (120.50°) and 1 (120.88°) to 129.9(4)°, 120.95(14)°, 115.4(6)° and 124.33(12)° in 2, 3·LiCl, 4·THF and 6·LiCl·THF, respectively. These data indicate the flexibility of the macrocyclic ligand framework given varying sizes of both M⁺ and the R substituents. The Thi–C1 bond length in 2 is 2.65(2) Å, which is longer than that reported for Th IV–Me bond average (2.53 Å) in metallocene-like complexes.16, 18, 27, 30-36 The An–C1 bond lengths in 3·LiCl, average 2.532(5) Å, 4·THF, average 2.58(2) Å, and 6·LiCl·THF, 2.489(4) Å, are similar to literature values.4, 37-47

Figure 2. Solid state structure of 4·THF (thermal ellipsoids set at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 4·THF: [Thi–Ci]avg 2.53, Thi–C1 2.58(2), Thi–C9 2.55(3), Thi–C29 2.59(2), [Ct–Thi–Ct]avg 170.16, C9–Thi–C29 115.4(6).

Selective Ligand Reprotonation of [M(L⁻²An(R)]

The An–aryl bonds in the [M(L⁻²An(R)] complexes 2-7 provide a useful route to new hydrocarbon C–H bond reactivity pathways, exemplified by the reaction with terminal alkynes (Scheme 3). Two equivalents of HC≡CR' (R' = SiMe3, SiiPr3) were added to a suspension of 2 or 5 in hexanes at room temperature and stirred for 16 hours. Following work-up to remove the unusual by-product LiMe, the reprotonated (L)² complexes were isolated as pale yellow solids [(L)Th(C≡CSiMe3)] (8) and [(L)Th(C≡CSiPr3)] (9) or red solids [(L)U(C≡CSiMe3)] (10) and [(L)U(C≡CSiPr3)] (11) in 44%, 54%, 50% and 50% yield, respectively. The addition of an excess of HC≡CR' does not alter the outcomes or yields of these reactions.

Scheme 3. Syntheses of [(L)Th(C≡CSiMe3)] (8), [(L)Th(C≡CSiPr3)] (9), [(L)U(C≡CSiMe3)] (10) and [(L)U(C≡CSiPr3)] (11).

The C₂ᵥ symmetry in 8-11 is retained. The aryl ipso-proton resonances are observed in the ¹H NMR spectra and in the ¹³C{¹H} NMR spectra and are shifted from 217.6 ppm in 2 to 123.9 and 123.7 ppm in 8 and 9, respectively. Pale yellow single crystals of 8 and 9 were isolated from saturated benzene solutions. The synthesis of 8 and 9 was also attempted from 3, however the reactive by-product LiCH2SiMe3 has a very similar solubility to 8 and 9, preventing the isolation of pure material.

The molecular structures of 8, 9 and 11 (Figure 3 and SI Fig. S4 and S5 for 9, and 11) display bidentate η⁵:η⁵ binding, analogous to that of A. The Ct–An–Ct2 angles in 8, 9 and 11 are 169.49°, 169.43° and 170.44°, respectively; larger than in A (163.60°) and 1 (164.97°). This subtle change in geometry is likely to be the result of the smaller covalent radius of carbon compared to that of chloride.48

Although reactivity involving ThIV alkynyl complexes has been invoked,9-9 to the best of our knowledge 8 and 9 are the first crystallographically characterised thorium alkynyl complexes. A few uranium(IV) alkynyl complexes have been reported to date;48, 51-57 metallocene-like systems reported in the literature display similar U⁴-alkynyl bond lengths to the Ui–Cl/C3 average distance in 11, 2.408(9) Å.
Multiwavelength NMR spectroscopic analysis suggests that 12 and 13 are analogous, however X-ray quality single crystals of 12 could not be obtained and the coordination mode of (L)⁺ in 12 could not be determined.

Discussion of the Reversible Aryl Metallation. Evans showed that the addition of two equivalents of HC≡CPh to [(Cp*)₂U(Me)₂] results in the synthesis of [(Cp*)₂U(C≡CPh)₂] and methane elimination. A survey of
metallocene-like Th\textsuperscript{IV} and U\textsuperscript{IV} complexes shows that the bond dissociation energies of An–alkyl bonds are generally lower than those of An–aryl bonds.\textsuperscript{35-73} Interestingly, Marks showed that the U–alkynyl bond dissociation enthalpy in the complex [Cp\textsuperscript{′′},U(C≡CPh)] (Cp\textsuperscript{′′} = η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4}SiMe\textsubscript{3}) is nearly twice that of U–Me in the analogous methyl complex [Cp\textsuperscript{′′},U(Me)], however Marks did not make a direct comparison with U–aryl bond enthalpies.\textsuperscript{73} We have shown that An–arene bonds in complexes 2 or 5 can be reprotonated to give (L)\textsuperscript{+} by the alkynes HC=CR\textsuperscript{(R′)} (R\textsuperscript{′} = SiMe\textsubscript{3}, SiPr\textsubscript{3}) (pKa of acetylenes in DMSO: \textasciitilde28)\textsuperscript{74} or the weak acid [Et\textsubscript{3}NH][BPh\textsubscript{4}] (pKa in DMSO: 9).\textsuperscript{58} These findings suggest that the formation of 8–11 is in part driven by the formation of the stronger An–alkynyl bond. The synthesis of 12–13 is likely driven by the acidity of [Et\textsubscript{3}NH][BPh\textsubscript{4}].

**Reactivity of 2–13 Towards Small Molecules.**

Actinide complexes have been shown to effect unique small molecule transformations relative to d-block metals.\textsuperscript{75} Complexes 2–7 contain three actinide-carbon σ-bonds. The additions of small molecules such as CO, CO\textsubscript{2}, or \textsuperscript{14}BuNC with the aim of An–C bond insertion have been carried out to understand if selective insertion processes might be useful for ligand functionalisation prior to the selective reprotonation; the reactions are summarised in Scheme 5.

![Scheme 5: Reactions to target the insertion of small, unsaturated substrates into An–C bonds.](image)

**Scheme 6.** Proposed reaction path of ancillary ligand functionalisation and abstraction from the thorium-metal centres of complexes 8 or 9 to form LCO, 14.

Although the detailed mechanism of the formation of 14 has not been investigated, in the first step, shown in Scheme 6, CO\textsubscript{2} coordination to the metal centre is proposed, shown as intermediate i. The resulting steric crowding, in part due to the rigidity of the Th\textsuperscript{IV} alkynyl bonds, may then facilitate a ligand hapticity shift to pyrrolide κ\textsuperscript{i}-N coordination. It has been established that CO\textsubscript{2} can insert into actinide-nitrogen bonds to form carbamate;\textsuperscript{75-76} the suggested intermediate ii in Scheme 6. The non-innocence of this ligand system then allows for ipso-hydrogen migration to the pyrrolide, resulting in the formation of a demetallated derivative.

**Nickel Coordination to 8 and Ligand Fluxionality.**

The inertness of the An–C alkynyl bonds in [(L)Th(C≡CSiMe\textsubscript{3})\textsubscript{2}] (8) and [(L)Th(C≡CSiPr\textsubscript{3})\textsubscript{2}] (9), led us to explore the reactivity of their π-systems. It has been established that group 10 transition metals readily coordinate unsaturated complexes.\textsuperscript{77} Simple Group 14 [(Cp\textsubscript{2})\textsubscript{2}TM(C≡CMe\textsubscript{3})\textsubscript{2}] (TM = Ti or Zr) bis-alkynyl complexes have shown nickel coordination to the C≡C triple bonds that is accompanied by TM\textsuperscript{IV}–C activation and ligand rearrangement of the alkynyl groups.\textsuperscript{77} In order to establish whether this trend can be extended to Th\textsuperscript{IV}, [(L)Th(C≡CSiMe\textsubscript{3})\textsubscript{2}] (8) and [(L)Th(C≡CSiPr\textsubscript{3})\textsubscript{2}] (9), were treated with one equivalent of Ni(COD)\textsubscript{2} (COD = 1,5-cyclooctadiene) and PR\textsubscript{3} (R\textsuperscript{′} = cyclohexyl, phenyl) (Scheme 7). Complex 8 reacts readily and after work-up to remove volatiles, no bound COD remains, according to NMR spectroscopy, and dark orange-red X-ray quality single crystals of the new complexes [(L)Th(C≡CSiMe\textsubscript{3})\textsubscript{2}·Ni(PCy\textsubscript{3})\textsubscript{2}] (15a) (Figure 5) or [(L)Th(C≡CSiMe\textsubscript{3})·Ni(PPh\textsubscript{3})\textsubscript{2}] (16a) (see SI Fig. 5) were isolated from saturated hexane solutions in 7% and 18% crystalline, isolated yields, respectively. In the case of 9, no reaction occurs.
A survey of the available literature indicates that only one of which is a ThIV bis-Cp⁺ nickel phosphido complex [(Cp)₂Th(μ-Ph₃)₂Ni(CO)] (Th–Ni distance: 3.206(2) Å), where the authors suggest that an interaction between nickel and thorium exists.⁷⁹ The Th–Ni distances in complexes 15a (3.059(7) Å), 15b (3.053 Å) and 16 (3.068 Å) are notably shorter than those reported in the literature, and on average approximately 0.25 Å shorter than the sum of the covalent radii of nickel and thorium.⁸⁸

As an alternative crystallisation method for 15, hexane vapour was allowed to diffuse into a saturated THF solution of 15 yielding dark orange-red X-ray quality single crystals of [(L)Th(C≡CSiMe₃)₂(Ni(PCy₃))], 15b, the molecular structure of which is shown in Figure 6. Surprisingly, the two methods of crystallisation of 15 yield two different binding modes for L, shown in Figs 6 and 7. When crystallised from hexane the (L)₂- coordination mode is metalloocene-like (15a); when crystallised from THF, the (L)⁻ coordination mode is η⁶-C₆H₄-κ¹ (15b), like 13. Although THF is found co-crystallised in the lattice of 15b, computational analysis, discussed below, suggests that this is unlikely to affect ligand coordination.

A survey of the available literature indicates that only two heterobimetallic complexes featuring thorium and nickel adjacent to each other have been reported to date,⁷⁹

79 one of which is a ThIV bis-Cp⁺ nickel phosphido complex [(Cp)₂Th(μ-Ph₃)₂Ni(CO)] (Th–Ni distance: 3.206(2) Å), where the authors suggest that an interaction between nickel and thorium exists.⁷⁹ The Th–Ni distances in complexes 15a (3.059(7) Å), 15b (3.053 Å) and 16 (3.068 Å) are notably shorter than those reported in the literature, and on average approximately 0.25 Å shorter than the sum of the covalent radii of nickel and thorium.⁸⁸

The solid-state structures of 15 and 16 show that the interaction with the Ni⁺ centre is strong enough to reorganise the Th–C alkynyl groups from bis(η⁶) to η¹ to one metal and η¹ to the other. This asymmetry was previously observed in the solid state structure of [(Cp)₂TM(C≡CSiMe₃)₂(Ni(PCy₃))] (TM = Ti, Zr).⁸⁷

The solid-state structures of 15a, 15b and 16 display a very slight increase in C≡C bond lengths compared to that of free H≡C≡CTMS (1.194(8) Å).⁸⁰ There is also a small lengthening of the triple bonds of the alkynyl ligands upon nickel binding in [(Cp)₂TM(C≡CSiMe₃)₂[Ni(PCy₃)] (TM = Ti, Zr):
the IR stretching frequencies for these bonds are reported as 1780 and 1911 cm⁻¹ for the titanium complex and 1771 and 1876 cm⁻¹ for the zirconium complex.⁷ These data differ from those for 16, where the observed IR stretching frequencies are 2120 and 2071 cm⁻¹, indicating that only one C≡C stretch is notably shifted from the stretching frequency of the starting material (2140 cm⁻¹) as a result of interactions with the Ni centre.

Complexes 15 and 16 are stable in the solid state for a number of weeks, although decompose in solution over several days. To further stabilise these complexes, attempts were made to increase the electron count around the nickel metal centre by using a bidentate four electron phosphine donor dppf (dppf = 1,1'-ferrocenediyl-bis(diphenylphosphine)). No reaction was observed between Ni(dppf)(COD) and 8, Scheme 8, which may be caused by the bulk of the dppf ligand hindering the coordination of nickel to the alkynyl groups of 8.

Reactions were carried out to target platinum analogues of 15 and 16, 15 and 16, using Pt(nb)₃ (nb = norbornene). However, the reaction of 8 with Pt(nb)₃ in donor solvents such as THF resulted in the formation of a mixture of products (Scheme 8). The addition of donor molecules designed to stabilise the putative product such as PCy₃ or PPh₃ did not yield a clean product. In a similar manner to Ni(dppf)(COD) no reaction with Pt(dppf)(nb) was observed.

![Scheme 8. Reactions to target platinum analogues of 15 and 16, platinum analogues of 15 and 16, R = cyclohexyl, phenyl, (L)Th[C≡CSiMe₃]₂][Pt(dppf)] (dppf = 1,1'-ferrocenediyl-bis(diphenylphosphine)) and [(L)Th[C≡CSiMe₃]₂][Ni(dppf)].](Image)

Analysis of the flexibility of the macrocycle and alkynide binding.

A combination of variable temperature NMR spectroscopy and DFT computational studies was undertaken to interrogate the ligand flexibility and dynamic equilibria. Given the low isolated yields of 15 and 15, and that computational analysis (discussed in detail below) shows that the Gibbs free energy difference between 15 and 16 is negligible (3.4 kJ mol⁻¹), the variable temperature NMR spectral study of just 16 was undertaken.

The ¹H NMR spectra of 15 and 16 at 298 K correspond to a molecule with overall C₂ᵥ symmetry, indicating a symmetrical bis(alkynide) coordination on the NMR timescale in solution, but this is lowered to C₃ᵥ as solutions are cooled to 190 K. Figure 7 shows the two halves of L in the a (me-tallocene) and b (bis arene) binding modes of 15/16 coloured blue and pink, that are inequivalent in the solid state structures, and at low temperatures in solution NMR spectroscopy, from the asymmetric alkynyl coordination.

![Figure 7. Plane of asymmetry introduced into 15 and 16 by alkynyl asymmetry in solid-state and low temperature solutions changes depending on coordination of (L)⁻. Hydrogens in one plane of symmetry are shown as blue and in the other plane as pink.](Image)

The flexibility of (L⁻) also offers other dynamic equilibria processes that decoalesce sequentially as the temperature of either THF-d₈ or toluene-d₈ solutions of 16 are warmed from 190 K.

Careful inspection of the spectra at 193 K in THF-d₈ shows that the two pyrrolide-H resonances of the macrocycle are doublets. These are closest to the alkynide ligands in the conformation a (Figure 7 LHS), in which the pyrrolide-hydrogens on the same ring are no longer equivalent, suggesting a low-temperature solution-state state structure consistent with 16a. The resonances of 16a, gradually coalesce to a single, average chemical shift from 200-230 K. This suggests there is sufficient flexibility in the ligand binding that even when the alkynyl ligands are bound asymmetrically (on the NMR timescale) the macrocycle can flex such that an average C₃ᵥ can be maintained.

For comparison, the coalescence temperature for the process that renders the SiMe₃ groups equivalent in [(Cp)₂Ti(C≡CSiMe₃)₂][NiPPh₃] is just above 190 K.⁷ The ¹H NMR spectra of the dichloride A show no dynamic processes; spectra in THF-d₈ are the same at 193 K and 298 K.

Computational Analysis of 15, 16 and Pt analogues.

In order to probe further the different conformations of the ancillary (L⁻) ligand in complexes 15 and 16, we turned to scalar relativistic, hybrid density functional theory. The hypothetical platinum analogues of these systems 15' and 16' have also been studied. The total SCF (E) and Gibbs (G) energies of the optimised geometries of the Th/Ni and Th/Pt systems are given in Tables S6 and S7 of the SI respectively, and the energy differences between the a (η⁶:η⁶) and b (η⁶:η⁶:η⁶:η⁶) forms of all four molecules are collected in Table 1. The negative numbers in Table 1 show that in all cases the a form is the more stable, with a greater preference for this conformation in the PPh₃ systems.

![Table 1: ΔE and ΔG values (kJ mol⁻¹) between the a (η⁶:η⁶) and b (η⁶:η⁶:η⁶:η⁶) forms of 15, 16, 15' and 16'.](Image)
By contrast to the data in Table 1, single point SCF energies of the [(L)ThIV]\(^{2+}\) fragment in geometry-optimised 15a and 15b show that this fragment is more stable, by 19.0 kJ mol\(^{-1}\), in the \(\eta^5:\eta^5\) conformation. The rest of 15 – i.e. the [(CCSiMe\(_3\))\(_2\)NiPCy\(_3\)]\(^{-}\) fragment – has almost exactly the same energy in 15a and 15b (1.0 kJ mol\(^{-1}\) difference). Hence, the energetic preference for the a form of the full molecules must arise from differences in bonding between the [(CCSiMe\(_3\))\(_2\)NiPCy\(_3\)]\(^{-}\) and [(L)ThIV]\(^{2+}\) fragments in the different L orientations. We assume that this is also the case for 16. That the energy differences between the a and b forms of both 15 and 16 are very similar for their Pt analogues, suggests the group 10 transition metal has little impact here, but the larger preference for the a conformation of the PPh\(_3\) systems hints at the R\(^{′′}\) group having a greater role.

To establish the origin of the energetic preference for the \(\eta^5:\eta^5\) bonding mode, we examined the valence Kohn-Sham molecular orbitals (MOs) of 15 and 16 to identify any with significant energy changes between the a and b conformations. Table S8 in the SI gives the energies of selected MOs for both compounds; the energies and isosurfaces for those of 15 are presented in Figure 8. The MOs labelled in red feature Ni–alkynyl interactions with an in-phase combination of Ni d and alkynyl π orbitals, the latter also being in phase with one another. For 15b, there is only one such orbital (MO 266), which has only small contributions from the LTh fragment, whereas there are two MOs with this character in 15a (MOs 267 and 255). This splitting of the Ni–alkynyl character in two 15a MOs arises because in this conformation it is similar in energy to a Th-pyrrolide bonding MO, and this generates in phase and out of phase combinations (MOs 255 and 267, respectively). The former is significantly stabilised vs MO 266 of 15b, while the latter is destabilised, albeit to a lesser extent.

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<th>(\Delta E)</th>
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<td>15a – 15b</td>
<td>–24.8</td>
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<tr>
<td>16a – 16b</td>
<td>–33.7</td>
</tr>
<tr>
<td>15a’ – 15b’</td>
<td>–25.6</td>
</tr>
<tr>
<td>16a’ – 16b’</td>
<td>–30.5</td>
</tr>
</tbody>
</table>

The MOs labelled in green (MO 265) also feature Ni–alkynyl bonding, but this time the π-orbitals of the two alkynyl ligands are out of phase with each other. MO 265 is more stable in 15b than in 15a, and its character doesn’t split from one conformation to the other. We attribute its destabilisation from b to a to a small admixture of L ring π-character. In 15b this comes from the arene rings while in 15a it is from the pyrrolides. In isolated (L)\(^{2+}\) fragments, these π MOs are 223.1 kJ mol\(^{-1}\) less stable in the pyrrolide rings, and so only a small admixture of this character into MO 265 will produce the 35.8 kJ mol\(^{-1}\) destabilisation from 15b to 15a.

Whilst recognising that there are many other MOs in these compounds, those shown in Figure 8 change by the largest amount between the a and b forms; hence the likely driver for the greater stability of the \(\eta^5:\eta^5\) mode is the formation of MO 255.

The analogous MO diagram for 16 is shown in Figure 10. The orbitals labelled in red display very similar behaviour to those of 15a and 15b in Figure 8, as evidenced by their energy changes and isosurfaces (Fig. S13 of the SI).
Figure 9. Selected MOs of complexes 16a and 16b. Energies are plotted relative to MO 243 in the η^5-η η conformation. Hydrogens omitted for clarity. Isovalue = 0.025.

The orbitals labelled in green, however, show different behaviour from those in 15a and 15b. For 16b there are now two Ni–alkynyl bonding interactions in which the alkynyl ligands are out of phase with each other (MOs 250 and 251). This distribution over two MOs arises because these also feature contributions from π-orbitals on the Ph rings of the phosphine, character which obviously cannot be present in the saturated PCy3 system. The character of 16b’s MOs 250 and 251 is distributed amongst three MOs in 16a (245, 249 and 254). There is now only one MO with Ni-alkynyl character (MO 245 - still labelled in green). This is stabilised vs MOs 250 and 251 of 16b, and loses its contribution from the Ph rings. The latter character is now found in 16a MOs 249 and 254. These are labelled in black in Figure 9 to highlight that they have no Ni-alkynyl character, and are both destabilised vs MOs 250 and 251 of 16b.

As for compounds 15a and 15b, Figure 9 suggests that the driver for the greater stability of the η^5-η η mode in 16 is the formation of MO 243. It is also tempting to suggest that the slightly larger preference for the a conformation in the PPh3 system is a result of the different behaviour of the orbitals labelled in green in Figures 8 and 9.

Discussion of (L)^+ Ligand Conformation. The DFT calculations find that the a (η^5-η η) conformer is the more energetically favoured for both complexes 15 and 16. This is in agreement with low temperature NMR spectral studies on complex 16. We recalculated the energies presented in Table 1 for 15 and 16 in the presence of a continuum solvent of THF or hexane. These were found to differ from each other, and from the gas phase data in Table 1, by no more than 2.2 kJ mol⁻¹ for 15 and 1.6 kJ mol⁻¹ for 16, showing that the a conformer remains the more stable in solution, in agreement with the NMR data for 16.

It therefore remains unclear how structural isomer b forms. 15b may be a minor product in the reaction mixture that is not resolved in the NMR spectrum. 15b could also be the result of a packing effect imparted by lattice solvent and formed over several days in a slow rearrangement. Perhaps fluxionality would be promoted at higher temperatures, however complexes 15 and 16 readily decompose in solution when heated, precluding high temperature NMR studies.

CONCLUSIONS

A series of new Th IV and U IV complexes supported by a trans-calix[2]benzene[2]pyrrole ligand have been synthesised, enabling us to demonstrate the flexibility and range of binding modes available to this ligand system, which allows facile incorporation and abstraction of cations in the bis(arene) pocket. This ligand system has shown reversible C–H bond activation chemistry facilitated by its non-innocence and formed an excellent new route to new alkynyl complexes, and alkyl cations of Th IV. Additionally, interesting new bimetallic complexes incorporating nickel were isolated as two conformers a (η^5-η η) and b (η^5-κ η^3-κ η); the first instance of two structural isomers of (L)^+ in the same complex. No Th-Ni bond was sought in these ligand-bridged complexes, although the Th-Ni distances are the shortest yet reported, and are significantly shorter than the summed covalent radii.

In reactions with CO₂, the thorium bis(alkynyl) complex cleanly and quantitatively cleaves one CO bond of the small molecule, eventually releasing what is presumed to be thorium oxide, but showing a remarkably selective C-N and C-C bond formation in the insertion of the remaining CO atoms of CO₂ into the macrocycle.

DFT calculations show that the a (η^5-η η) bonding mode of the ancillary (L)^+ ligand is favoured, independent of the transition metal (Ni or Pt). Analysis of the Ni systems shows that this preference is due to favourable mixing of a Th-pyrrole π-bonding orbital with a Ni-alkynyl interaction; this is worth over 70 kJ mol⁻¹ in both 15 and 16. A more tentative orbital-based explanation for the slightly larger preference of the PPh3 system for the a conformation focuses on the involvement of Ph π-orbitals in the Ni-alkynyl interaction, a mixing which cannot occur in the PCy3 compounds.

EXPERIMENTAL SECTION

General Procedures and Techniques. Standard high-vacuum Schlenk-line techniques and Vac and Mbraun glove boxes were used to manipulate and store air- and moisture-sensitive compounds under an atmosphere of dried and deoxygenated di-nitrogen. All gases were supplied by BOC gases UK. All glassware was dried in an oven at 160 °C, cooled under 10⁻³ mbar vacuum and then purged with nitrogen. Prior to use, all Fisherbrand 1.2 μm retention glass microfiber filters and cannulae were dried in an oven at 160 °C overnight and all Celite 545 filter aid was flame dried under vacuum. All solvents for use with air- and moisture-sensitive compounds were stored in ampoules containing pre-dried 4 Å molecular sieves from the Vac Atmospheres solvent tower drying system, where they had been passed over a column of molecular sieves for 24 hours prior to collection. They were then degassed prior to use and subsequent storage. The solvents benzene-d₆, toluene-d₈, THF-d₈ and pyridine-d₅ were heated under reflux over the appropriate drying agent for 24 hours, vacuum transferred into ampoules and stored under an atmosphere of nitrogen prior to use. All solvents were purchased from Sigma-Aldrich or Fisher Scientific. All NMR spectroscopic analyses were recorded at 298 K using Bruker Avance III 500.12 MHz spectrometers with 1H NMR spectra run at 500.12 MHz, 13C NMR spectra at 125.77 MHz, 1H Li NMR spectra run at 194.41 MHz, 1H B NMR spectra at 160.49 MHz and 29Si NMR spectra at 99.37 MHz. SiMe₄, BF₃·(OEt₂) and LiCl were used to externally reference the relevant spectra. The 1H NMR and 13C[1H] NMR spectra were referenced internally to residual protio solvent (δ H= 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were performed by Mr. Stephen Boyer at the London Metropolitan University. All FTIR spectra were recorded using JASCO 410 or JASCO 460 plus spectrometers. The compounds KCH₂Ph,²⁶ LiCH₂SiMe₃,²⁵ KN,²³ ThCl(DME),²⁴ trans-calix[2]benzene[2]pyrrole (H₅L),²⁸ K₃,²⁹ LiCl,²⁹ [LiThCl₄] (A)³⁰ K₃SiMe₃,²⁶ were synthesised according to literature procedures.

[(L)UCl₃]⁺ (1). A Teflon-valved ampoule with a magnetic stirrer bar was charged with UCl₄(THF)₀.₇₅ (0.601 g, 1.38 mmol) and K₃ (0.730 g, 1.38 mmol). THF (40 ml) was added, and the reaction was then stirred and heated at 80 °C for 48 hours. The resulting dark orange solution was cannula-filtered to remove KCl and the vola-
ticles were subsequently removed under reduced pressure. The sol-
dium was washed with hexane (3 x 10 ml) and dried under vacuum
to yield 1 as an orange solid. Single crystals suitable for X-ray
were grown by vapour diffusion of hexane into a saturated solution of
1 in THF at ambient temperature. Yield: 0.772 g (1.02 mmol), 74%.

\[ \text{Li[(L-2H)U(CH$_2$SiMe$_3$)] (6).} \]

A Teflon-valved ampoule with a magnetic stirrer-bar was charged with 1 (0.030 g, 0.039 mmol) and LiMe (3eq, 0.041 g, 0.80 mmol). Benzene-\( d_6 \) was added (1 ml), the reaction sonicated for 20 minutes and left to react for 16h. The resulting dark brown solution was centrifuged and glass-filtered to remove LiCl and the volatiles were removed under reduced pressure. The solids were dried under vacuum to yield 6 as a dark orange solid. Single crystals suitable for X-ray were grown in the presence of LiCl by vapour diffusion of hexane into a satu-
rated THF solution of 7 at ambient temperature. Yield: 0.020 g (0.026 mmol), 65%. H NMR (benzene-\( d_6 \)): \( \delta \) 88.7 (s, 4H, pyridine CH$_2$), 85.8 (s, 12H, CH$_2$), 2.60 (s, 12H, CH$_2$), -3.93 - -8.17 (m, 6H, \( \text{Si(CH$_3$)$_3$} \)), \( \text{C}^7\text{Li}\{1H\} NMR (benzene-\( d_6 \)): \( \delta \) 151.1 (s, 4H, \( \text{Si(CH$_3$)$_3$} \)), \( \text{C}^2\text{Li}\{1H\} NMR (benzene-\( d_6 \)): \( \delta \) 12.4 (s, 12H, CH$_3$), 14.3 (s, 12H, CH$_3$). Resonance could not be found. \( \text{C}^7\text{Li}\{1H\} NMR (benzene-\( d_6 \)): \( \delta \) -52.7. Analysis (%) calc. for \( \text{C}_{126}\text{H}_{137}\text{N}_8\text{Li}_2\text{U} \): C 55.48; H 5.63; N 3.71.

\[ \text{K[(L)Th(C}_3\text{SiMe$_3$)$_2$]} (8). \]

A Teflon-valved ampoule with a magnetic stirrer-bar was charged with 2 (1.000 g, 1.12 mmol) and KCH$_2$Ph (3eq, 0.041 g, 0.396 mmol). Toluenes was added (20 ml) and the reaction sonicated for 15 minutes and stirred for 16 hours. The resulting dark brown solution was centrifuged and glass-filtered to remove KLi and the volatiles were removed under reduced pressure. The solids were washed with hexane (3 x 5 ml) and then dried under vac-
uum to yield 7 as a pale yellow solid. Single crystals suitable for X-
ray were grown in the presence of LiCl by vapour diffusion of hexane into a satu-
rated THF solution of 8 at ambient temperature. Yield: 0.050 g (0.061 mmol), 46%. H NMR (benzene-\( d_6 \)): \( \delta \) 97.8 (s, 4H, pyridine CH$_2$), 28.6 (s, 12H, CH$_2$), 11.2 (s, 2H, para-CH$_2$), -4.42 (s, 4H, meta-CH$_2$), -4.76 (s, 2H, meta-CH$_2$), -5.62 (m, 4H, ortho-CH$_2$) and meta-CH$_2$, -6.98 (s, 12H, CH$_2$), -57.8 (v br s, 2H, U-CH$_2$). \( \text{C}^7\text{Li}\{1H\} NMR (benzene-\( d_6 \)): \( \delta \) 225.8 (quaternary aromatic), 144.6 (aromatic), 142.0 (aromatic), 128.8 (aromatic), 128.6 (aromatic), 126.2 (aromatic), 122.7 (aromatic), 133.3 (aromatic), 67.1 (quater-
nary aliphatic), 38.2 (CH$_3$), 30.0 (CH$_3$), 25.5 (U-CH$_3$). One aromatic resonance is obscured by the solvent peak and could not be assigned. Analysis (%) calc. for \( \text{C}_{126}\text{H}_{137}\text{N}_8\text{K}_2\text{ThU} \): C 57.48; H 5.07; N 3.44, found C 57.60; H 5.00; N 3.34.

\[ \text{Li[(L)Th(C}_3\text{SiMe$_3$)$_2$]} (8). \]

A Teflon-valved ampoule with a magnetic stirrer-bar was charged with 2 (1.000 g, 1.43 mmol) and HCSiMe$_3$ (3eq, 0.280 g, 2.86 mmol). Hexane was added (30 ml) and the reaction was stirred for 5 hours. The hexane solution of 8 was filtered away from the solids, the volatiles were removed under reduced pressure and the solids were dried under vacuum to yield 8 as yellow solid. Single crystals suitable for X-ray were grown from a saturated solution of benzene at ambient tem-
perature. Yield: 0.544 g (0.622 mmol), 44%. H NMR (benzene-\( d_6 \)): \( \delta \) 7.96 (s, 2H, ipso-CH$_2$), 7.51 (s, 4H, pyridine CH$_2$), 7.09 (s, \( |\text{J}_{\text{HH}}| = 7.01 \) Hz, 2H, para-CH$_2$), 1.92 (s, 12H, CH$_3$), 1.51 (s, 12H, CH$_3$), 0.28 (s, 18H, Si(CH$_3$)$_3$).
was filtered away from the solids, the volatiles were removed under reduced pressure and the solids were then dried under vacuum to yield 9 as yellow solid. Single crystals suitable for X-ray were grown from a saturated solution of benzene at ambient temperature. Yield: 0.080 g (0.077 mmol), 53%. 1H NMR (benzene-

\[ \delta = 7.90 (s, 2H, ipso-C_6H_4), 7.33 (s, 4H, pyrrole CH), 7.10 (d, J_{HH} = 7.70 Hz, 4H, meta-C_6H_4), 7.02 (t, J_{HH} = 7.70 Hz, 2H, para-C_6H_4), 1.97 (s, 12H, CH_3), 1.02 (s, 12H, CH_3), 1.35 (d, J = 7.20 Hz, 36H, Si(CH_3)_2), 1.22 (septet, J_{HH} = 7.20 Hz, 6H, Si(CH_3)_3). \]

\[ \text{13C\{1H\} NMR (benzene-} \text{d}_6) \]

\[ \delta = 147.1 (ipso-C_6H_4), 123.3 (meta-C_6H_4), 121.9 (meta-C_6H_4), 115.7 (arene-CH), 112.5 (arene-CH), 107.4 (pyrrole CH), 42.7 (quaternary), 33.4 (CH_3), 29.3 (CH_3), 17.0 (CH_3). \]

\[ \text{31P\{1H\} NMR (benzene-} \text{d}_6) \]

\[ \delta = 13.9 (s, 88H, Si(\text{CH}_3)_3), -14.4 (s, 12H, C(CH_3)_3). \]

\[ \text{13C\{1H\} NMR (benzene-} \text{d}_6) \]

\[ \delta = 34.5. \] Analysis (%) calc. for \( \text{C}_9\text{H}_{12}\text{N}_2\text{Si}_2\text{Th}: \) C 64.26; H 6.34; N 3.55.

The reaction was stirred for 3 hours. The hexane solution of 9 was filtered away from the solids, the volatiles were removed under reduced pressure and the solids were then dried under vacuum to yield 9 as yellow solid. Single crystals suitable for X-ray were grown from a saturated solution of benzene at ambient temperature. Yield: 0.080 g (0.077 mmol), 53%. 1H NMR (benzene-

\[ \delta = 7.90 (s, 2H, ipso-C_6H_4), 7.33 (s, 4H, pyrrole CH), 7.10 (d, J_{HH} = 7.70 Hz, 4H, meta-C_6H_4), 7.02 (t, J_{HH} = 7.70 Hz, 2H, para-C_6H_4), 1.97 (s, 12H, CH_3), 1.02 (s, 12H, CH_3), 1.35 (d, J = 7.20 Hz, 36H, Si(CH_3)_2), 1.22 (septet, J_{HH} = 7.20 Hz, 6H, Si(CH_3)_3). \]

\[ \text{13C\{1H\} NMR (benzene-} \text{d}_6) \]

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\[ \text{31P\{1H\} NMR (benzene-} \text{d}_6) \]

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\[ \text{13C\{1H\} NMR (benzene-} \text{d}_6) \]

\[ \delta = 34.5. \] Analysis (%) calc. for \( \text{C}_9\text{H}_{12}\text{N}_2\text{Si}_2\text{Th}: \) C 64.26; H 6.34; N 3.55.
NMR (benzene-d6): δ 19.8 (quaternary aromatic), 152.0 (quaternary aromatic), 134.0 (para-C6H4), 130.0 (ipso-C6H4), 131.5 (meta-C6H4), 141.1 (pyridyl CH), 68.2 (C=C), 42.2 (CH2), 42.0 (quaternary), 36.6 (d, |J| = 12.7 Hz, P-C6H4), 33.8 (C=C), 30.8 (d, |J| = 13.4 Hz, P-C6H4), 29.3 (C=C), 28.0 (P-C6H4), 27.3 (P-C6H4), 25.6 (Si(CH3)3). 13Si{1H} NMR (benzene-d6): δ -7.16. 13P{1H} NMR (benzene-d6): δ 49.2. Analysis (%) calc for C60H87N2Si2PNiTh: C 59.35; H 5.81; N 2.34, found C 60.49; H 5.73; N 2.30. FTIR (cm⁻¹): 3027, 2927, 1601 (νC=O).

NMR (benzene-d6): δ 158.0 (quaternary aromatic), 134.0 (para-C6H4), 130.4 (ipso-C6H4), 131.5 (meta-C6H4), 141.1 (pyridyl CH), 68.2 (C=C), 42.2 (CH2), 42.0 (quaternary), 36.6 (d, |J| = 12.7 Hz, P-C6H4), 33.8 (C=C), 30.8 (d, |J| = 13.4 Hz, P-C6H4), 29.3 (C=C), 28.0 (P-C6H4), 27.3 (P-C6H4), 25.6 (Si(CH3)3). 13Si{1H} NMR (benzene-d6): δ -7.16. 13P{1H} NMR (benzene-d6): δ 49.2. Analysis (%) calc for C60H87N2Si2PNiTh: C 59.35; H 5.81; N 2.34, found C 60.49; H 5.73; N 2.30. FTIR (cm⁻¹): 3027, 2927, 1601 (νC=O).

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