

Cite this: *Chem. Sci.*, 2025, 16, 16101

All publication charges for this article have been paid for by the Royal Society of Chemistry

C–C bond cleavage and carbonylation enabled by an NNN-pincer uranium scaffold *via* metal–arene interaction†

Yue Pang,^a Thayalan Rajeshkumar,^b Rosario Scopelliti,^c Laurent Maron^{*b} and Marinella Mazzanti^{*a}

Metal–arene complexes have recently attracted an increasing interest in f-element chemistry, but the functionalization of arenes mediated by uranium–arene interactions is limited to a single example. Here, we report a new uranium–biphenylene complex supported by a bulky rigid trianionic NNN-pincer ligand in which the uranium–arene interaction is able to promote C–C bond cleavage and functionalization with CO under mild conditions to yield a U-bound 9-fluorenone. Reduction of the U(IV)-pincer complex [NNN-U(THF)Cl₂K(THF)₃]₂ (**1**) with KC₈, in the presence of biphenylene, results in the terminal arene complex [NNN-U(THF)(biphenylene)][K(THF)₅] (**3**). DFT studies of **3** indicate the presence of two unpaired electrons located at the uranium center, in line with a U(IV) and a biphenylene dianion. Complex **3** undergoes C_{aryl}–C_{aryl} bond cleavage of the biphenylene ligand, affording [NNN-U(THF)(2,2'-biphenyl)][K(THF)₂] (**4**). DFT studies indicated that, due to the interaction between the biphenylene dianion and the uranium, a concerted ring opening reaction can occur on the strained four members ring to yield **4** while the uranium center retains a +IV oxidation state. Complex **4** undergoes facile CO insertion into the U–C_{aryl} bond, followed by the C_{aryl}–C_{carbonyl} bond formation, yielding [NNN-U(THF)₂(fluorenone)][K(THF)₄] (**5**). This work demonstrates the potential of uranium–arene interactions to promote arene activation and functionalization.

Received 10th June 2025
Accepted 22nd July 2025

DOI: 10.1039/d5sc04248h

rsc.li/chemical-science

Introduction

Metal–arene complexes have recently attracted an increasing interest in f-element chemistry.^{1–13}

Notably, uranium–arene interactions have provided an important tool to investigate bonding modes,^{9,14–21} to stabilize very low oxidation states [U(II) and U(I)]^{12,22–26} and rare bonding motifs.²⁷ Following the seminal discovery by Diaconescu, Cummins *et al.*²⁸ of uranium inverse sandwich complexes featuring a U–arene–U core supported by δ -bonding interactions, several complexes were identified, presenting bridging arene moieties with different degrees of reduction.^{2,20,29–31} The electrons stored in the arene moieties become accessible to

different substrates in redox reactions, with concomitant release of the bridging arenes in the neutral form (Scheme 1a).^{28,30,32,33} In a few instances uranium–arene δ -bonding interactions were shown to lead to attractive magnetic properties³¹ and to enable rare catalytic activity.^{34–36} More recently, a unique case (**A**, Scheme 1b) of C–H bond oxidative addition of benzene was also reported for a heterometallic U–Pd cluster.³⁷ In contrast, there is only one previous example where uranium–arene interactions have resulted in arene functionalization in uranium inverse sandwich complexes (**B**, Scheme 1b).³⁸

Terminal actinide arenides^{9,19,39,40} are attractive candidates for promoting arene functionalization because they demonstrated relevant higher reactivity compared to bridging arenides⁴ but their chemistry remains poorly explored. We reasoned that bulky rigid pincer ligands⁴¹ should prevent the formation of inverse-sandwich complexes and therefore provide ideal ancillary scaffolds to isolate highly reactive terminally bound uranium arenides. We therefore set out to investigate the ability of the bulky triamide dihydroacridine-derived ligand (NNN^{3–}),^{42,43} which has not yet been used in uranium chemistry, to enable access to low oxidation states and to uranium–arene interactions.

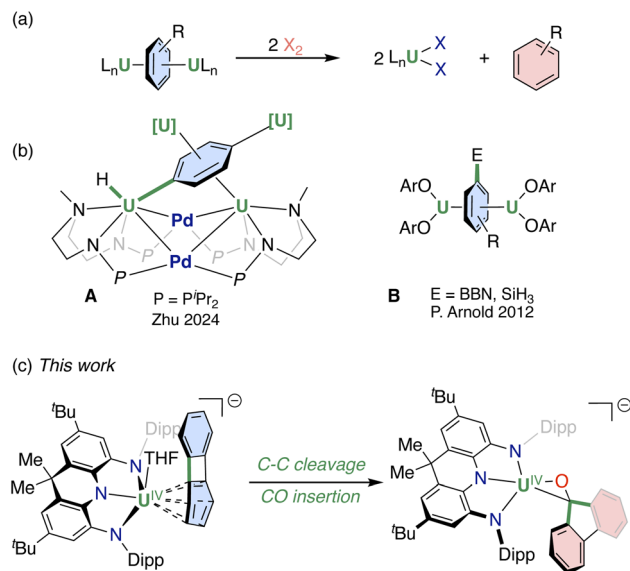
Here, we report a new terminal uranium–biphenylene complex supported by the bulky rigid trianionic NNN-pincer ligand^{42,43} in which the uranium–arene interaction is able to

^aGroup of Coordination Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. E-mail: marinella.mazzanti@epfl.ch

^bLaboratoire de Physique et Chimie des Nano-objets, Institut National des Sciences Appliquées, 31077 Toulouse, Cedex 4, France. E-mail: laurent.maron@irsamc.ups-tlse.fr

^cX-Ray Diffraction and Surface Analytics Platform, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

† Electronic supplementary information (ESI) available. CCDC 2392949, 2404451–2404454, 2442062 and 2457232. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5sc04248h>



Scheme 1 (a) Redox reactivities of uranium-arene inverse sandwich complexes; (b) examples of arene activation and functionalization enabled by uranium; (c) this work: C-C bond cleavage and carbonylation of biphenylene. Dipp = 2,6-diisopropylphenyl. The arene⁷⁻ and neutral arene are drawn in blue and red, respectively; bond cleavage and formation are drawn in bold green.

promote C-C bond cleavage and enable functionalization of the biphenylene moiety with CO under mild conditions (Scheme 1c).

Result and discussion

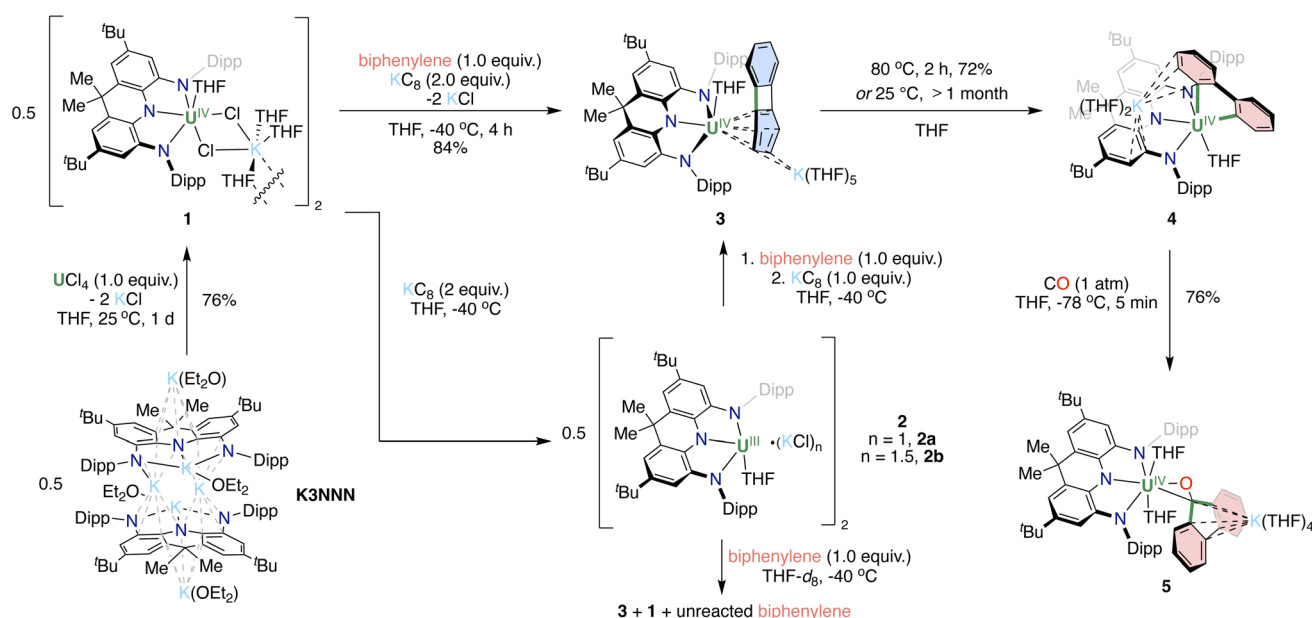
Uranium pincer complexes

The reaction of the potassium salt of the NNN pincer ligand (**K₃NNN**) with UCl_4 in a 1 : 1 ratio in THF at room temperature

yielded the U(IV) complex **1** that was isolated as a green solid in 76% yield from a Et_2O /hexane mixture (Scheme 2). Single crystals of **1** suitable for XRD analysis were obtained from a mixture of THF and *n*-hexane at -40°C . X-ray studies revealed that **1** has a dimeric structure in the solid state, where two monomeric $[\text{NNN-U(THF)}(\mu\text{-Cl})_2\text{K(THF)}_3]$ units are connected by two bridging THF molecules from two different moieties (Fig. 1). In complex **1**, each uranium center is hexa-coordinated by the three N atoms of the pincer ligand, one oxygen of THF and two chlorides bridging the uranium and the potassium cation. The U-N bond distances range from 2.266(3) to 2.304(3) Å and are similar to those reported for the U(IV) complex of NON (NON = [4,5-bis(2,6-diisopropylanilino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene]) rigid pincer system (2.297(4) and 2.306(4) Å).⁴⁴

With complex **1** in hand, we explored its reduction to investigate if the NNN pincer scaffold could support uranium in lower oxidation states. ^1H NMR spectroscopic studies showed that when **1** was treated with 2 equiv. of K^+C_8 in $\text{THF-}d_8$ at -40°C , full consumption of **1** was reached in 2 h, resulting in the formation of new species (Fig. S5†).

A mixture of dark purple and brown crystals was obtained upon addition of *n*-hexane to the concentrated THF filtrate of the reaction mixture at -40°C . XRD analysis of a dark brown single crystal showed the presence of a dimeric U(III) species, $[\text{NNN-U}^{\text{III}}\text{Cl(THF)}\text{K(THF)}_3]_2$ (**2a**), consisting of two $[\text{NNN-U}^{\text{III}}\text{(THF)}]$ units bridged by two KCl molecules (Fig. S26†), however, the poor quality of the single crystal prevents further discussion of the structure of **2a**. Furthermore, dark purple single crystals of $[\text{NNN-U}^{\text{III}}\text{(THF)}]_2(\text{KCl})_3(\text{THF})_2(\text{Et}_2\text{O})_2$ (**2b**) suitable for XRD analysis were obtained from a concentrated Et_2O solution of the isolated material at -40°C , showing the presence of a dimeric U(III) species bridged by three KCl molecules (Fig. 2). The U-N bond lengths in **2b** (2.385(10) to 2.417(9)



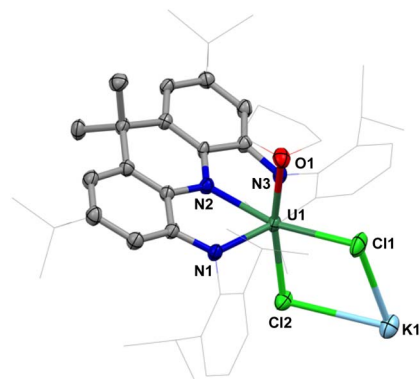


Fig. 1 Molecular structure of the fragment $[\text{NNN-U(THF)}(\mu\text{-Cl})_2\text{K}]$ in **1**; with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and potassium-bound solvent molecules are omitted for clarity; ^tBu and Dipp groups of the pincer backbones and uranium-bound THF molecules are drawn in a wireframe style (the figures below follow the same style).

Å) are significantly longer than those in **1** (2.266(3) to 2.304(3) Å), in accordance with the change of oxidation states from +IV (**1**) to +III (**2b**). Overall, the presence of variable numbers of bridging KCl molecules complicates the isolation and characterization of the U(III) species $[\text{NNN-U}^{\text{III}}(\text{THF})_2(\text{KCl})_n]$ (**2**) obtained from the reduction of **1**. ¹H NMR spectroscopic studies of THF-*d*₈ solutions of complex **2** showed that the complex decomposes slowly at −40 °C, but rapidly at room temperature.

We also attempted the direct synthesis of the U(III) pincer complex from $\text{U}(\text{THF})_4$ (Scheme S2†). The reaction of **K3NNN** with $\text{U}(\text{THF})_4$ is very slow and did not reach complete conversion after 2 weeks (Fig. S11†). Dark brown crystals were obtained from the reaction mixture, showing the presence of $\text{NNN-U}^{\text{III}}(\text{THF})_3$ (**2c**) (Fig. S27†). Complex **2c** decomposes rapidly at room temperature rendering difficult to increase the rate of its formation.

Uranium-terminal biphenylene complex

With the U(III) pincer complex in hand we set out to isolate a terminal arenide complex and pursued the reactivity of the U(III) species **2** with biphenylene. Notably, metalla-biphenylene

complexes provide an attractive target for C–C bond activation and functionalization, due to the weak character of the bond, which has resulted in a rich chemistry of transition-metal promoted C–C bond cleavage and functionalization,^{45,46} including a very recent example with rare-earth complexes⁴⁷ but has not been investigated in actinide chemistry.

The addition of 1 equiv. biphenylene to a THF-*d*₈ solution of the *in situ* generated U(III) species **2** at −40 °C resulted in an immediate color change from dark purple to dark brown. The ¹H NMR spectrum of the reaction mixture showed the resonances assigned to the complex $[\text{NNN-U(THF)(biphenylene)}][\text{K(THF)}_5]$ (**3**), together with signals assigned to the U(IV) precursor **1** in a ratio of 1 : 1 and to signals of unreacted biphenylene (Scheme 2 and Fig. S10†). The addition of KC_8 (1 equiv.) to the reaction mixture led to the full conversion of **1** and biphenylene into complex **3**, as indicated by ¹H NMR spectroscopy (Scheme 2 and Fig. S8†). Dark brown needles of the complex $[\text{NNN-U(THF)(biphenylene)}][\text{K(THF)}_5]$ (**3**) were isolated in 76% yield on a preparative scale from the THF filtrate upon addition of *n*-hexane at −40 °C.

The formation of the terminally U-bound arenide **3** and of the U(IV) complex **1** from the reaction of the U(III) species **2** with biphenylene is the result of the two-electron reduction of biphenylene by two U(III) centers (Scheme S1†). The observed reactivity differs from previously reported reactions of U(III) complexes with arenes leading to inverse sandwich complexes of uranium involving different degree of arene reduction ranging from arene^{2−} to arene^{4−}.^{2,31,48} It is likely that, in the reaction of the U(III) species **2** with biphenylene, the bulky NNN ligand prevents the formation of an inverse sandwich complex and leads to a terminal $[\text{U(IV)-biphenylene}^{1−}]$ species that is rapidly reduced by a second uranium(III) complex to afford the final U(IV)-biphenylene^{2−}. It is worth noting that a few terminally bound arenides were previously reported for uranium.^{16,19}

Complex **3** can also be obtained in a similar yield by adding directly 2 equiv of KC_8 to a THF solution of complex **1** and 1 equiv. biphenylene at −40 °C (Scheme 2).

The solid-state molecular structure of **3** (Fig. 3) revealed the presence of a heterobimetallic complex where the biphenylene ligand binds a uranium center and a THF-solvated potassium

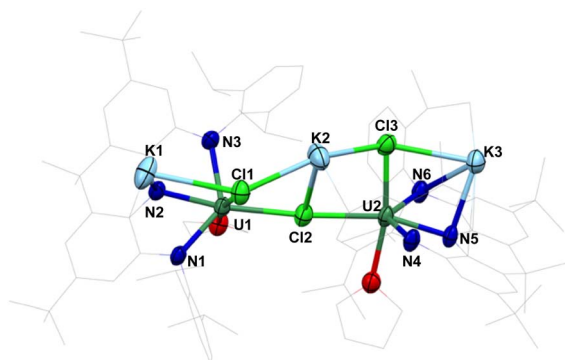


Fig. 2 Molecular structure of $[\text{NNN-U}^{\text{III}}(\text{THF})_2(\text{KCl})_3(\text{THF})_2(\text{Et}_2\text{O})_2]$, **2b**; with thermal ellipsoids drawn at the 50% probability level.

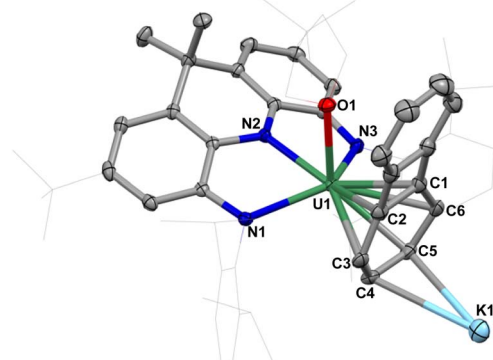


Fig. 3 Molecular structure of $[\text{NNN-U(THF)(biphenylene)}][\text{K(THF)}_5]$, **3**; with thermal ellipsoids drawn at the 50% probability level.

cation. In complex **3**, the uranium center is bound by three N atoms of the NNN ligand, one oxygen of THF and the biphenylene ligand in a η^6 fashion, with U–C_{aryl} bond distances ranging from 2.628(2) to 2.8089(19) Å. The solvated K⁺ is interacting with the C4 and C5 atoms of the coordinated phenyl ring. As a result, the coordinated phenyl ring is slightly folded towards the U center with an angle of 14.38° along C3–C6 axis. The bond lengths of C1–C2 (1.531(3) Å) and C4–C5 (1.461(3) Å) in the coordinated ring are noticeably longer than those in the uncoordinated ring (1.436(3) and 1.394(4) Å). These metrical parameters are comparable to those found in the previously reported heterometallic cluster with a [U(IV)–Pd(0)]₂[biphenylene] core,³⁷ suggesting the presence of a doubly reduced biphenylene with the uranium center in the +IV oxidation state. The U–N bond lengths in **3** (2.3355(15) to 2.3963(16) Å) are significantly longer than those in **1** (2.266(3) to 2.304(3) Å), but still in the range of U(IV)–N_{amido} distances reported for the U(IV) complexes supported by a sterically congested PNP scaffold (PNP = bis[2-(diisopropylphosphino)-4-methylphenyl]amido ligand) (2.343(7)–2.411(3) Å).⁴⁹ The lengthening of the U–N bond distances in **3** compared to **1** is probably due to the increased steric constraints imposed by the coordination of the biphenylene ligand rather than to the presence of a reduced uranium center. By sharp comparison to the flat pincer ligand in **1** (5.04°), the backbone in **3** is noticeably bent with an angle of 32.87°, thus minimizing the steric repulsion between two Dipp side arms and the coordinated biphenylene. This further suggests that the U–arene terminal binding mode in **3** is due to the bulky nature of the supporting NNN ligand.

C–C bond cleavage and carbonylation of the U-bound biphenylene

Considering the high reactivity of arenide complexes of uranium towards different substrates,^{2,19,28,32,33,38,50,51} we investigated the stability and reactivity of **3**.

Although **3** remained stable in a THF-*d*₈ solution at –40 °C for at least one week, it evolved slowly into a new species at room temperature, as monitored by ¹H NMR spectroscopy (Fig. S15†). When a THF-*d*₈ solution of **3** was heated at 80 °C, the complete conversion of **3** was achieved in 2 h, and the solution turned from dark brown to orange (Scheme 2 and Fig. S16†).

The complex [NNN-U(THF)(2,2′-biphenyl)][K(THF)₂] (**4**) was isolated as a brick-red microcrystalline solid on a preparative scale from a mixture of THF and *n*-hexane at –40 °C in 72% yield. As revealed by the X-ray determined solid-state molecular structure of **4**, the coordinated biphenylene in **3** undergoes C–C bond cleavage, affording the 9-uranafluorene derivative (Fig. 4). The resulting biphenyl ligand sits in a pocket between the two aryl substituents, to reduce steric hindrance. The U–C_{aryl} bond distances of 2.491(5) and 2.520(5) Å fall in the range of previously reported U(IV)–aryl and U(IV)–benzyne complexes (2.340(5) to 2.650(7) Å).^{52–55} The U–N bond distances in **4** (2.322(4) to 2.342(3) Å) are shorter than those found in complex **3** (2.3355(15) to 2.3963(16) Å), but longer than those in complex **1** (2.266(3) to 2.304(3) Å), manifesting the moderate steric hindrance of 2,2′-biphenyl in the coordination sphere of the uranium center. The solvated K⁺ binds to one of the phenyl

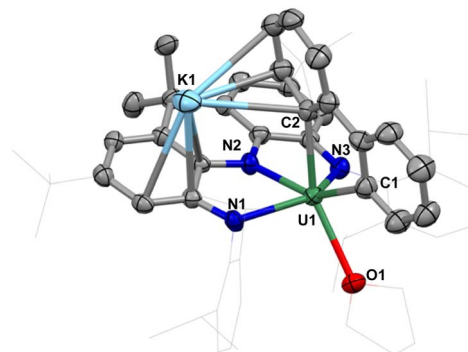


Fig. 4 Molecular structure of [NNN-U(THF)(2,2′-biphenyl)][K(THF)₂], **4**; with thermal ellipsoids drawn at the 50% probability level.

rings of the pincer backbone and to one of the phenyl rings in the biphenyl in η^3 fashion.

Actinide aryl complexes remain rare^{52–58} and most previously reported actinide aryl species display rather low thermal stability, due to the ionic nature of the An–C bonds. On the contrary, no decomposition was observed for complex **4** in THF-*d*₈ at room temperature over one week. The observed remarkable stability of the U–C bonds in **4** is probably the result of the chelating nature and steric shielding of the pincer scaffold.

The formation of complex **4** resembles an oxidative addition of the C–C bond of biphenylene to the metal center, but computational studies (see below) indicate that the cleavage of the C–C bond involves a concerted mechanism where the oxidation state of uranium remains unchanged. The C–C cleavage of biphenylene has not yet been reported for an actinide complex³⁷ but a relevant example of distal C–C cleavage has been recently reported by Hayton and coworkers for U(IV)- and Th(IV)-cyclopropyl complexes.^{59,60}

Since the insertion of small molecules into the highly reactive U–C bonds, such as CO, CO₂ and carbodiimides, is documented,^{56,61–65} we decided to investigate the possibility of functionalizing the bound 2,2′-biphenyl ligand.

A THF-*d*₈ solution of **4** was exposed to 1 atm atmosphere of CO at –78 °C, resulting in an immediate color change from orange to dark red (Scheme 2). The ¹H NMR spectrum of the reaction mixture showed the disappearance of the signals assigned to **4** and concomitant formation of a new species (Fig. S20†). The complex [NNN-U(THF)₂(fluorenone)][K(THF)₄] (**5**) was isolated as a dark red microcrystalline solid on a preparative scale from a mixture of THF and *n*-hexane at –40 °C in 76% yield. The solid-state molecular structure of **5** revealed the presence of a heterobimetallic complex with a 9-fluorenone ligand binding the K and U(IV) cations (Fig. 5). The uranium center in **5** is coordinated by the NNN pincer ligand, the anionic carbon and oxygen atoms of the 9-fluorenone ligand, and the oxygens of two THF. The oxidation state of the uranium centre remains unchanged. The 9-fluorenone is coordinated to the uranium center in a η^2 fashion, with the U1–O1 and U1–C1 bond lengths of 2.166(8) and 2.659(12) Å. The U1–C1 bond is significantly elongated compared to U–C_{aryl} bond distances found in **4** but still in the range of U(IV)–C bond distances found



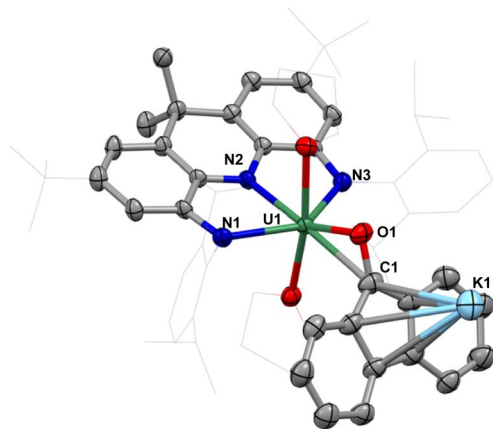


Fig. 5 Molecular structure of [NNN-U(THF)₂(fluorenone)][K(THF)₄], **5**; with thermal ellipsoids drawn at the 50% probability level.

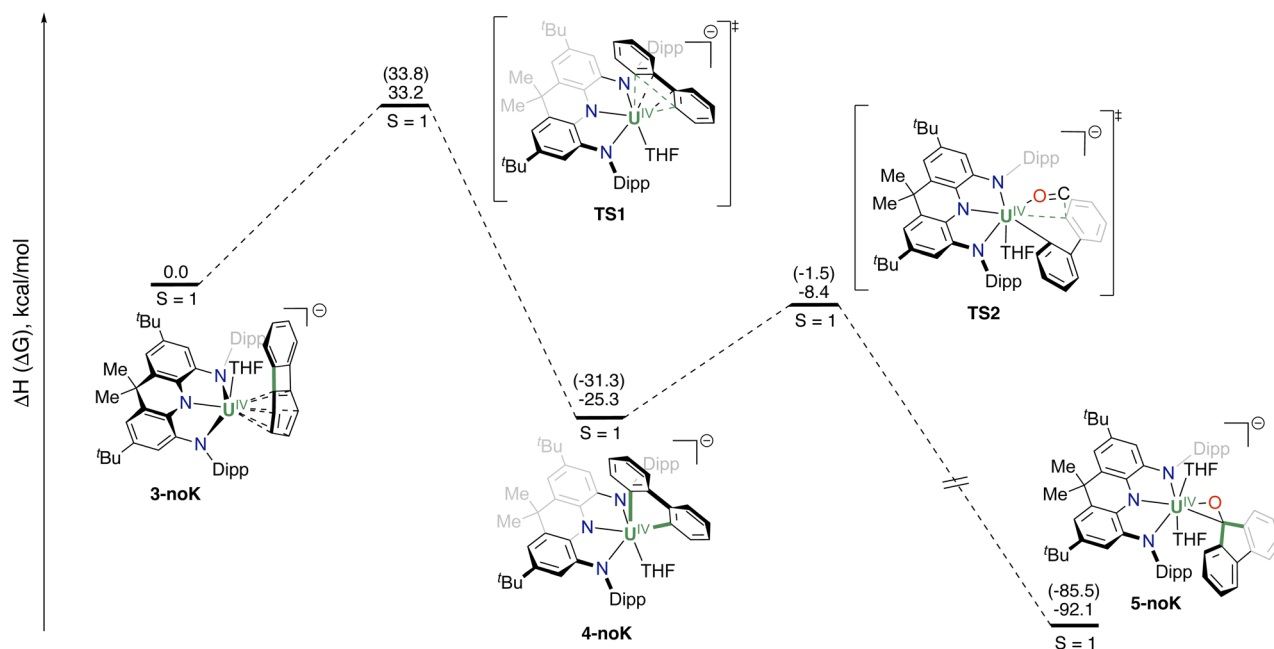
in previously reported U(IV) aryl complexes (2.340(5) to 2.650(7) Å).^{53,55} The C1–O1 bond distance of 1.392(15) Å is significantly longer compared to that found in the free 9-fluorenone (1.217(4) and 1.222(4) Å),⁶⁶ but comparable to the values found in metal-bound formyl groups (in [K₂{[U–OSi(O^tBu)₃]₂](μ-CH₂O)(μ-O)] (1.31(3) Å)⁶⁷ and [(1,2,4-(Me₃C)₃C₅H₂)₂Ce](μ-OCH₂) (1.39(1) Å),⁶⁸ suggesting the presence of a C–O single bond. Besides, the solvated K⁺ binds to the central five-membered ring in the 9-fluorenone in a η⁵ fashion.

In the transformation from **4** to **5**, the insertion of CO into one of the U–C_{aryl} bonds is followed by the formation of the C_{aryl}–C_{carbonyl} bond, and the resultant dianionic 9-fluorenone fragment binds to the U(IV) center. Reactions of CO with metallafluorene complexes to yield 9-fluorenone were previously reported for a few transition-metal systems of Co, Rh, and more

recently, Au^{69–71} but required high CO pressure (*e.g.* 10 atm for Au⁷¹) and/or high temperatures (*e.g.* 120 °C for Co⁷⁰ and Rh^{69,70}).

Computational studies

DFT calculations (B3PW91 functional) were carried out to understand the formation of complex **3** from **1** and to gain more insights into the formation of complexes **4** and **5**, from complex **3**. The formation of the U(III) analog of complex **3** (Fig. S30†), that is a U(III) complex of the neutral biphenylene ligand, is almost athermic in Gibbs free energy (1.9 kcal mol^{−1}). The subsequent reduction of this U(III) intermediate is exergonic by 4.4 kcal mol^{−1}, making the overall transformation exothermic by 2.5 kcal mol^{−1}, and indicating that the formation of a U(III) intermediate is indeed plausible. Complex **3** was optimized without the potassium counterion (**3-noK**) and the obtained geometry is in good agreement with the experimental one. This complex has a triplet ground state, with two unpaired electrons located at the uranium center, in line with a U(IV) and a biphenylene dianion. Due to the interaction between the biphenylene dianion and the uranium (Scheme 3), a ring opening (RO) reaction can occur on the four-membered ring, which is the most strained one *via* **TS1**. The associated barrier is 33.2 kcal mol^{−1} in enthalpy (33.8 kcal mol^{−1} in Gibbs free energy) in line with a slow reaction at room temperature, but faster at 80 °C as carried out experimentally. **TS1** was located on the triplet PES and the two unpaired electrons were found to be located at the uranium center, in line with a U(IV) so that the RO is a concerted reaction. This can be explained by the presence of the dianionic charge of the biphenylene, where the two extra π electrons are used together with the two σ electron of the C_{aryl}–C_{aryl} bond to allow this RO reaction in a concerted manner. Following the intrinsic reaction coordinate, it yields the



Scheme 3 Computed enthalpy profiles (Gibbs free energy in brackets) for the formation of **4-noK** and **5-noK** from **3-noK**.

thermodynamically stable complex **4-noK** ($-25.3 \text{ kcal mol}^{-1}$ in enthalpy and $-31.3 \text{ kcal mol}^{-1}$ in Gibbs free energy), where two U-C_{aryl} bonds are formed, and the uranium remains in the +IV oxidation state. Complex **4-noK** can then react with CO *via* **TS2** with an associated barrier of $16.9 \text{ kcal mol}^{-1}$ in enthalpy ($29.8 \text{ kcal mol}^{-1}$ in Gibbs free energy), in line with a facile reaction. This reaction is the CO insertion into two U-C_{aryl} bonds. At the transition state, one of the U-C_{aryl} bonds is elongated and at the same time the C_{aryl}-C_{carbonyl} bond starts to be formed with the nucleophilic assistance of the oxygen interaction with the uranium center. Therefore, the carbon of CO displays a positive charge with an empty orbital. The latter can overlap with the π electron of the carbon of the second U-C_{aryl} bond. This explains why following the intrinsic reaction coordinate from **TS2**, the CO insertion is accompanied by a cyclization, directly yielding complex **5-noK**, which is thermodynamically highly favorable ($-66.8 \text{ kcal mol}^{-1}$ in enthalpy and $-54.2 \text{ kcal mol}^{-1}$ in Gibbs free Energy).

Conclusions

In summary, we have shown that the rigid bulky triamide pincer ligand **NNN**³⁻ allows to access a highly reactive uranium(III) complex **2** that readily reacts with biphenylene to yield a terminally-bound arenide complex **3**. Complex **3** can also be conveniently prepared by reacting the U(IV) chloride pincer complex **1** with excess KCl₈ and biphenylene. The electronic and molecular structure of **3** indicate the presence of uranium in the +IV oxidation state and of a doubly reduced biphenylene ligand. The coordinated biphenylene in **3** undergoes rapid C-C bond cleavage affording the 9-uranafluorene derivative **4**. DFT studies indicated that, due to the interaction between the biphenylene dianion and the uranium, a concerted ring opening reaction can occur on the strained four members ring that involves the two extra π electrons stored in the biphenylene to yield **4** while the uranium centre retains a +IV oxidation state. Complex **4** was found to react with CO in mild conditions *via* migratory insertion of CO into the U-C bonds to yield U-bound 9-fluorenone **5**. The observed reactivity provides the first example of C-C cleavage enabled by uranium-arene interactions. These results highlight the ability of the triamide pincer ligand to stabilize highly reactive uranium species and to enable the activation of unreactive bonds without accessing hard-to-handle low oxidation states. This work also demonstrates the potential of uranium-arene interactions to promote arene activation and functionalization.

Data availability

Synthetic details, analytical data including depictions of all spectra and coordinate data of all computationally optimised species, are documented in the ESI.† Crystallographic data is made available *via* the CCDC. The data that support the findings of this study are openly available in the Zenodo repository at DOI: <https://www.doi.org/10.5281/zenodo.16447740>.

Author contributions

Y. P. designed and carried out all the experiments and analyzed the data; M. M. designed and supervised the project; T. R. and L. M. carried out the computational study; R. S. measured and analyzed the X-ray data, Y. P. and M. M. wrote the manuscript with contributions of all authors, and all authors have given approval for the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge support from the Swiss National Science Foundation grant number 212723 and 236428 and the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Dr Andrzej Sienkiewicz for his assistance with EPR data collection, Dr Farzaneh Fadaei-Tirani for measuring and analyzing the structure of complex **3**. L. M. is a senior member of the Institut Universitaire de France. CalMip is acknowledged for a generous grant of computing time.

Notes and references

- 1 J. D. Cryer and S. T. Liddle, *Arene Complexes of the Actinides in Comprehensive Organometallic Chemistry IV*, Elsevier, 2022.
- 2 S. T. Liddle, Inverted sandwich arene complexes of uranium, *Coord. Chem. Rev.*, 2015, **293**, 211–227.
- 3 F. G. N. Cloke and N. Tsoureas, *Arene Complexes of the Group 3 Metals and Lanthanides*, Elsevier, 2022.
- 4 F. C. Hsueh, T. Rajeshkumar, B. Kooij, R. Scopelliti, K. Severin, L. Maron, I. Zivkovic and M. Mazzanti, Bonding and Reactivity in Terminal versus Bridging Arenide Complexes of Thorium Acting as Th^{II} Synthons, *Angew Chem. Int. Ed. Engl.*, 2023, **62**, e202215846.
- 5 M. Liu, Y. C. Chen, A. Mondal, H. Wang, M. L. Tong, R. A. Layfield and F. S. Guo, η^6 -Benzene Tetra-Anion Complexes of Early and Late Rare-Earth Metals, *J. Am. Chem. Soc.*, 2025, **147**, 11359–11367.
- 6 G. M. Richardson, T. Rajeshkumar, F. M. Burke, S. A. Cameron, B. D. Nicholls, J. E. Harvey, R. A. Keyzers, T. Butler, S. Granville, L. J. Liu, J. Langley, L. Lim, N. Cox, N. F. Chilton, J. Hicks, N. Davis, L. Maron and M. D. Anker, Four-electron reduction of benzene by a samarium(II)-alkyl without the addition of external reducing agents, *Nat. Chem.*, 2025, **17**, 20–28.
- 7 C. Deng, Y. Wang and W. L. Huang, f-Block Metal-Arene Interactions, *Chin. J. Org. Chem.*, 2025, **45**, 56–85.
- 8 F. I. Delano and S. Demir, Stabilization of the Compressed Planar Benzene Dianion in Inverse-Sandwich Rare Earth Metal Complexes, *Angew Chem. Int. Ed. Engl.*, 2025, **64**, e202417217.
- 9 J. Murillo, R. Bhowmick, K. L. M. Harriman, A. Gomez-Torres, J. Wright, P. Miró, A. Metta-Magaña, M. Murugesu, B. Vlaisavljevich and S. Fortier, Actinide arene-metalates: 2.



- A neutral uranium bis(anthracenide) sandwich complex and elucidation of its electronic structure, *Chem. Commun.*, 2022, **58**, 9112–9115.
- 10 C. A. Gould, J. Marbey, V. Vieru, D. A. Marchiori, R. D. Britt, L. F. Chibotaru, S. Hill and J. R. Long, Isolation of a triplet benzene dianion, *Nat. Chem.*, 2021, **13**, 1001–1005.
 - 11 R. P. Kelly, L. Maron, R. Scopelliti and M. Mazzanti, Reduction of a Cerium(III) Siloxide Complex To Afford a Quadruple-Decker Arene-Bridged Cerium(II) Sandwich, *Angew Chem. Int. Ed. Engl.*, 2017, **56**, 15663–15666.
 - 12 M. Keener, R. A. K. Shivaraam, T. Rajeshkumar, M. Tricoire, R. Scopelliti, I. Zivkovic, A. S. Chauvin, L. Maron and M. Mazzanti, Multielectron Redox Chemistry of Uranium by Accessing the +II Oxidation State and Enabling Reduction to a U(I) Synthron, *J. Am. Chem. Soc.*, 2023, **145**, 16271–16283.
 - 13 Y. Wang, R. Sun, J. F. Liang, Y. R. Zhang, B. W. Tan, C. Deng, Y. H. Wang, B. W. Wang, S. Gao and W. L. Huang, Synthesis and Stabilization of a Benzene Dianion with a Triplet Ground State and Baird Aromaticity, *J. Am. Chem. Soc.*, 2025, **147**, 7741–7748.
 - 14 J. Murillo, C. A. P. Goodwin, L. Stevens, S. Fortier, A. J. Gaunt and B. L. Scott, Synthesis and comparison of iso-structural f-block metal complexes (Ce, U, Np, Pu) featuring η^6 -arene interactions, *Chem. Sci.*, 2023, **14**, 7438–7446.
 - 15 S. R. Chowdhury, C. A. P. Goodwin and B. Vlasisavljevic, What is the nature of the uranium(III)-arene bond?, *Chem. Sci.*, 2024, **15**, 1810–1819.
 - 16 C. Deng, X. C. Xu, R. Sun, Y. Wang, B. W. Wang, H. S. Hu and W. L. Huang, Topology-Dependent Synthesis, Structures, and Bonding Interactions of Uranium Polyarene Complexes, *Organometallics*, 2024, **43**, 174–190.
 - 17 X. H. Dan, J. Z. Du, S. H. Zhang, J. A. Seed, M. Perfetti, F. Tuna, A. J. Wooles and S. T. Liddle, Arene-, Chlorido-, and Imido-Uranium Bis- and Tris(boryloxide) Complexes, *Inorg. Chem.*, 2024, **63**, 9588–9601.
 - 18 N. R. Andreychuk, B. Vidjayacoumar, J. S. Price, S. Kervazo, C. A. Peeples, D. J. H. Emslie, V. Vallet, A. S. P. Gomes, F. Réal, G. Schreckenbach, P. W. Ayers, I. Vargas-Baca, H. A. Jenkins and J. F. Britten, Uranium(IV) alkyl cations: synthesis, structures, comparison with thorium(IV) analogues, and the influence of arene-coordination on thermal stability and ethylene polymerization activity, *Chem. Sci.*, 2022, **13**, 13748–13763.
 - 19 J. Murillo, R. Bhowmick, K. L. M. Harriman, A. Gomez-Torres, J. Wright, R. W. Meulenberg, P. Miro, A. Metta-Magana, M. Murugesu, B. Vlasisavljevic and S. Fortier, Actinide arene-metalates: ion pairing effects on the electronic structure of unsupported uranium-arenide sandwich complexes, *Chem. Sci.*, 2021, **12**, 13360–13372.
 - 20 C. Camp, V. Mougél, J. Pecaut, L. Maron and M. Mazzanti, Cation-Mediated Conversion of the State of Charge in Uranium Arene Inverted-Sandwich Complexes, *Chem.-Eur. J.*, 2013, **19**, 17528–17540.
 - 21 B. Vlasisavljevic, P. L. Diaconescu, W. L. Lukens Jr, L. Gagliardi and C. C. Cummins, Investigations of the Electronic Structure of Arene-Bridged Diuranium Complexes, *Organometallics*, 2013, **32**, 1341–1352.
 - 22 H. S. La Pierre, A. Scheurer, F. W. Heinemann, W. Hieringer and K. Meyer, Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding, *Angew Chem. Int. Ed. Engl.*, 2014, **53**, 7158–7162.
 - 23 B. S. Billow, B. N. Livesay, C. C. Mokhtarzadeh, J. McCracken, M. P. Shores, J. M. Boncella and A. L. Odom, Synthesis and Characterization of a Neutral U(II) Arene Sandwich Complex, *J. Am. Chem. Soc.*, 2018, **140**, 17369–17373.
 - 24 C. Deng, J. F. Liang, R. Sun, Y. Wang, P. X. Fu, B. W. Wang, S. Gao and W. L. Huang, Accessing five oxidation states of uranium in a retained ligand framework, *Nat. Commun.*, 2023, **14**, 4657.
 - 25 M. D. Straub, E. T. Ouellette, M. A. Boreen, R. D. Britt, K. Chakarawet, I. Douair, C. A. Gould, L. Maron, I. Del Rosal, D. Villarreal, S. G. Minasian and J. Arnold, A Uranium(II) Arene Complex That Acts as a Uranium(I) Synthron, *J. Am. Chem. Soc.*, 2021, **143**, 19748–19760.
 - 26 R. A. K. Shivaraam, M. Keener, D. K. Modder, T. Rajeshkumar, I. Zivkovic, R. Scopelliti, L. MaronMaron and M. Mazzanti, A Route to Stabilize Uranium(II) and Uranium(I) Synthons in Multimetallic Complexes, *Angew Chem. Int. Ed. Engl.*, 2023, **62**, e202304051.
 - 27 A. J. Wooles, D. P. Mills, F. Tuna, E. J. L. McInnes, G. T. W. Law, A. J. Fuller, F. Kremer, M. Ridgway, W. Lewis, L. Gagliardi, B. Vlasisavljevic and S. T. Liddle, Uranium(III)-carbon multiple bonding supported by arene δ -bonding in mixed-valence hexauranium nanometre-scale rings, *Nat. Commun.*, 2018, **9**, 2097.
 - 28 P. L. Diaconescu, P. L. Arnold, T. A. Baker, D. J. Mindiola and C. C. Cummins, Arene-bridged diuranium complexes: Inverted sandwiches supported by δ backbonding, *J. Am. Chem. Soc.*, 2000, **122**, 6108–6109.
 - 29 M. J. Monreal, S. I. Khan, J. L. Kiplinger and P. L. Diaconescu, Molecular quadrangle formation from a diuranium μ - η^6 , η^6 -toluene complex, *Chem. Commun.*, 2011, **47**, 9119–9121.
 - 30 P. L. Diaconescu and C. C. Cummins, Diuranium inverted sandwiches involving naphthalene and cyclooctatetraene, *J. Am. Chem. Soc.*, 2002, **124**, 7660–7661.
 - 31 D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, A delocalized arene-bridged diuranium single-molecule magnet, *Nat. Chem.*, 2011, **3**, 454–460.
 - 32 W. J. Evans, C. A. Traina and J. W. Ziller, Synthesis of Heteroleptic Uranium (μ - η^6 : η^6 -C₆H₆)²⁻ Sandwich Complexes via Facile Displacement of (η^5 -C₅Me₅)¹⁻ by Ligands of Lower Hapticity and Their Conversion to Heteroleptic Bis(imido) Compounds, *J. Am. Chem. Soc.*, 2009, **131**, 17473–17481.
 - 33 W. J. Evans, S. A. Kozimor, J. W. Ziller and N. Kaltsoyannis, Structure, reactivity, and density functional theory analysis of the six-electron reductant, [(C₅Me₅)₂U]₂(μ - η^6 : η^6 -C₆H₆),



- synthesized via a new mode of $(C_5Me_5)_3M$ reactivity, *J. Am. Chem. Soc.*, 2004, **126**, 14533–14547.
- 34 D. P. Halter, F. W. Heinemann, J. Bachmann and K. Meyer, Uranium-mediated electrocatalytic dihydrogen production from water, *Nature*, 2016, **530**, 317–321.
 - 35 D. P. Halter, F. W. Heinemann, L. Maron and K. Meyer, The role of uranium-arene bonding in H_2O reduction catalysis, *Nat. Chem.*, 2018, **10**, 259–267.
 - 36 D. P. Halter, C. T. Palumbo, J. W. Ziller, M. Gembicky, A. L. Rheingold, W. J. Evans and K. Meyer, Electrocatalytic H_2O Reduction with f-Elements: Mechanistic Insight and Overpotential Tuning in a Series of Lanthanide Complexes, *J. Am. Chem. Soc.*, 2018, **140**, 2587–2594.
 - 37 W. Fang, Y. F. Li, T. Z. Zhang, T. Rajeshkumar, I. del Rosal, Y. Zhao, T. W. Wang, S. O. Wang, L. Maron and C. Q. Zhu, Oxidative Addition of E-H (E=C, N) Bonds to Transient Uranium(II) Centers, *Angew Chem. Int. Ed. Engl.*, 2024, **63**, e202407339.
 - 38 P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, Spontaneous reduction and C-H borylation of arenes mediated by uranium(III) disproportionation, *Nat. Chem.*, 2012, **4**, 668–674.
 - 39 I. Korobkov, S. Gambarotta and G. P. A. Yap, Amide from dinitrogen by in situ cleavage and partial hydrogenation promoted by a transient zero-valent thorium synthon, *Angew Chem. Int. Ed. Engl.*, 2003, **42**, 4958–4961.
 - 40 I. Korobkov, S. Gambarotta and G. P. A. Yap, The first thorium arene complex: A divalent synthon, *Angew Chem. Int. Ed. Engl.*, 2003, **42**, 814–818.
 - 41 P. Hayes, C. S. MacNeil and T. K. K. Dickie, *Pincer Compounds*, Elsevier, 2018.
 - 42 M. K. Mondal, L. Zhang, Z. T. Feng, S. X. Tang, R. Feng, Y. Zhao, G. W. Tan, H. P. Ruan and X. P. Wang, Tricordinate Nontrigonal Pnictogen-Centered Radical Anions: Isolation, Characterization, and Reactivity, *Angew Chem. Int. Ed. Engl.*, 2019, **58**, 15829–15833.
 - 43 A. J. King, J. Abbenseth and J. M. Goicoechea, Reactivity of a Strictly T-Shaped Phosphine Ligated by an Acridane Derived NNN Pincer Ligand, *Chem.-Eur. J.*, 2023, **29**, e202300818.
 - 44 B. Vidjayacoumar, S. Ilango, M. J. Ray, T. Chu, K. B. Kolpin, N. R. Andreychuk, C. A. Cruz, D. J. H. Emslie, H. A. Jenkins and J. F. Britten, Rigid NON- and NSN-ligand complexes of tetravalent and trivalent uranium: comparison of $U-OAr_2$ and $U-SAr_2$ bonding, *Dalton Trans.*, 2012, **41**, 8175–8189.
 - 45 J. M. Parr and M. R. Crimmin, Carbon-carbon bond activation by Mg, Al, and Zn complexes, *Chem. Sci.*, 2023, **14**, 11012–11021.
 - 46 L. Soullart and N. Cramer, Catalytic C-C Bond Activations via Oxidative Addition to Transition Metals, *Chem. Rev.*, 2015, **115**, 9410–9464.
 - 47 M. M. Zhu, Z. Q. Chai, Z. J. Lv, T. Y. Li, W. Liu, J. N. Wei and W. X. Zhang, Selective Cleavage of the Strong or Weak C-C Bonds in Biphenylene Enabled by Rare-Earth Metals, *J. Am. Chem. Soc.*, 2023, **145**, 6633–6638.
 - 48 V. Mougel, C. Camp, J. Pecaut, C. Coperet, L. Maron, C. E. Kefalidis and M. Mazzanti, Siloxides as Supporting Ligands in Uranium(III)-Mediated Small-Molecule Activation, *Angew Chem. Int. Ed. Engl.*, 2012, **51**, 12280–12284.
 - 49 T. Cantat, B. L. Scott, D. E. Morris and J. L. Kiplinger, What a Difference a 5f Element Makes: Trivalent and Tetravalent Uranium Halide Complexes Supported by One and Two Bis 2-(diisopropylphosphino)-4-methylphenyl amido (PNP) Ligands, *Inorg. Chem.*, 2009, **48**, 2114–2127.
 - 50 W. J. Evans, S. A. Kozimor and J. W. Ziller, $[(C_5Me_5)_2U][(\eta-Ph)_2BPh_2]$ as a four electron reductant, *Chem. Commun.*, 2005, 4681–4683.
 - 51 P. L. Diaconescu and C. C. Cummins, $\mu-\eta^6, \eta^6$ -Arene-Bridged Diuranium Hexakis(ketimide) Complexes Isolable in Two States of Charge, *Inorg. Chem.*, 2012, **51**, 2902–2916.
 - 52 L. A. Seaman, E. A. Pedrick, T. Tsuchiya, G. Wu, E. Jakubikova and T. W. Hayton, Comparison of the Reactivity of 2-Li- $C_6H_4CH_2NMe_2$ with MCl_4 (M = Th, U): Isolation of a Thorium Aryl Complex or a Uranium Benzyne Complex, *Angew Chem. Int. Ed. Engl.*, 2013, **52**, 10589–10592.
 - 53 N. J. Wolford, D. C. Sergentu, W. W. Brennessel, J. Autschbach and M. L. Neidig, Homoleptic Aryl Complexes of Uranium (IV), *Angew Chem. Int. Ed. Engl.*, 2019, **58**, 10266–10270.
 - 54 E. A. Pedrick, L. A. Seaman, J. C. Scott, L. Griego, G. Wu and T. W. Hayton, Synthesis and Reactivity of a U(IV) Dibenzene Complex, *Organometallics*, 2016, **35**, 494–502.
 - 55 O. Ordonez, X. J. Yu, G. Wu, J. Autschbach and T. W. Hayton, Homoleptic Perchlorophenyl “Ate” Complexes of Thorium(IV) and Uranium(IV), *Inorg. Chem.*, 2021, **60**, 12436–12444.
 - 56 M. A. Boreen, B. F. Parker, T. D. Lohrey and J. Arnold, A Homoleptic Uranium(III) Tris(aryl) Complex, *J. Am. Chem. Soc.*, 2016, **138**, 15865–15868.
 - 57 T. J. Marks and A. M. Seyam, Stable uranium(IV) alkyl and aryl complexes, *J. Am. Chem. Soc.*, 1972, **94**, 6545.
 - 58 M. A. Boreen, C. S. Z. Ye, A. Kerridge, K. N. McCabe, B. A. Skeel, L. Maron and J. Arnold, Does Reduction-Induced Isomerization of a Uranium(III) Aryl Complex Proceed via C-H Oxidative Addition and Reductive Elimination across the Uranium(II/IV) Redox Couple?, *Inorg. Chem.*, 2022, **61**, 8955–8965.
 - 59 O. Ordoñez, G. T. Kent, M. A. Schuerlein, G. Wu and T. W. Hayton, Ring-Opening in the Actinide Cyclopropyl Complexes $[Cp_3U(2,2\text{-Diphenylcyclopropyl})]^{n-}$ ($n = 0, 1$), *Organometallics*, 2023, **42**, 2347–2352.
 - 60 G. T. Kent, X. J. Yu, G. Wu, J. Autschbach and T. W. Hayton, Ring-opening of a thorium cyclopropenyl complex generates a transient thorium-bound carbene, *Chem. Commun.*, 2022, **58**, 6805–6808.
 - 61 R. E. Cramer, R. B. Maynard, J. C. Paw and J. W. Gilje, Carbon-monoxide insertion into a uranium carbon double-bond - The structure of $(\eta^5-C_5H_5)_3U(\eta^2-OCCH)P(CH_3)(C_6H_5)_2$, *Organometallics*, 1982, **1**, 869–871.
 - 62 G. Paolucci, G. Rossetto, P. Zanella, K. Yunlu and R. D. Fischer, Facile insertion of carbon-monoxide into the U-C and U-N bonds of some tris(cyclopentadienyl)



- uranium(IV)-alkyl and tris(cyclopentadienyl)uranium(IV)-dialkylamide derivatives, *J. Organomet. Chem.*, 1984, **272**, 363–383.
- 63 W. J. Evans, J. R. Walensky, J. W. Ziller and A. L. Rheingold, Insertion of Carbodiimides and Organic Azides into Actinide-Carbon Bonds, *Organometallics*, 2009, **28**, 3350–3357.
- 64 E. Mora, L. Maria, B. Biswas, C. Camp, I. C. Santos, J. Pécaut, A. Cruz, J. M. Carretas, J. Marçalo and M. Mazzanti, Diamine Bis(phenolate) as Supporting Ligands in Organoactinide(IV) Chemistry. Synthesis, Structural Characterization, and Reactivity of Stable Dialkyl Derivatives, *Organometallics*, 2013, **32**, 1409–1422.
- 65 K. G. Moloy, T. J. Marks and V. W. Day, Carbon monoxide activation by organoactinides. η^2 -Acyl-carbon monoxide coupling and the formation of metal-bound ketenes, *J. Am. Chem. Soc.*, 1983, **105**, 5696–5698.
- 66 H. R. Luss and D. L. Smith, Crystal and molecular structure of 9-fluorenone, *Acta Crystallogr. B*, 1972, **B28**, 884–889.
- 67 M. Falcone, R. Scopelliti and M. Mazzanti, CO₂ and CO/H₂ Conversion to Methoxide by a Uranium(IV) Hydride, *J. Am. Chem. Soc.*, 2019, **141**, 9570–9577.
- 68 E. L. Werkema, L. Maron, O. Eisenstein and R. A. Andersen, Reactions of monomeric [1,2,4-(Me₃C)₃C₅H₂]₂CeH and CO with or without H₂: An experimental and computational study, *J. Am. Chem. Soc.*, 2007, **129**, 2529–2541.
- 69 C. N. Iverson and W. D. Jones, Rhodium-catalyzed activation and functionalization of the C-C bond of biphenylene, *Organometallics*, 2001, **20**, 5745–5750.
- 70 C. Perthuisot, B. L. Edelbach, D. L. Zubris and W. D. Jones, C-C activation in biphenylene. Synthesis, structure, and reactivity of (C₅Me₅)₂M₂(2,2'-biphenyl) (M=Rh, Co), *Organometallics*, 1997, **16**, 2016–2023.
- 71 J. A. Cadge, P. J. Gates, J. F. Bower and C. A. Russell, Migratory Insertion of CO into a Au-C Bond, *J. Am. Chem. Soc.*, 2022, **144**, 19719–19725.

