Synthesis and electronic structure analysis of the actinide allenylidenes, $[[\text{NR}_2]_3\text{An(CCCPh}_2)]^-$ (An = U, Th; R = SiMe$_3$)$^\dagger$

Gregory T. Kent,$^{a,b}$ Xiaojuan Yu,$^{a,b}$ Guang Wu,$^a$ Jochen Autschbach$^{a,b}$ and Trevor W. Hayton$^{a,b}$

The reaction of $[\text{AnCl(NR}_2]_3$ (An = U, Th, R = SiMe$_3$) with in situ generated lithium-3,3-diphenylcyclopropene results in the formation of $[[\text{NR}_2]_3\text{An(CH}==\text{C}==\text{CPh}_2)]$ (An = U, 1; Th, 2) in good yields after work-up. Deprotonation of 1 or 2 with LDA/2.2.2-cryptand results in formation of the anionic allenylidene, $[\text{Li}(2.2.2\text{-cryptand})][[\text{NR}_2]_3\text{An(CCCPh}_2)]$ (An = U, 3; Th, 4). The calculated $^{13}$C NMR chemical shifts of the C$_\alpha$, C$_\beta$, and C$_\gamma$ nuclei in 2 and 4 nicely reproduce the experimentally assigned order, and exhibit a characteristic spin–orbit induced downfield shift at C$_\alpha$ due to involvement of the 5f orbitals in the Th–C bonds. Additionally, the bonding analyses for 3 and 4 show a delocalized multi-center character of the ligand π orbitals involving the actinide. While a single–triple–single-bond resonance structure (e.g., An–C==C–CPh$_2$) predominates, the An==C==C==CPh$_2$ resonance form contributes, as well, more so for 3 than for 4.

Because of the requirement for heteroatom substituents, no isolable “Schock-type” actinide allylidenes, i.e., An==CR$_2$ (R = H, alkyl, aryl), are known,$^{7,9,12}$ although they have been observed in inert gas matrices.$^{16–22}$ Even vinylidene and allenylidene complexes, which should be less reactive than allylidenes, are unknown, in part due to the lack of viable synthetic routes. Allylidenes are especially informative in this regard, as they are typically made by H$_2$O elimination from a propargyl alcohol – a route that is problematic for actinide organometallics given their high sensitivity to water.$^{7,13–24}$

Herein, we report the synthesis of the actinide allyl complexes $[[(\text{NR}_2]_3\text{An(CH}==\text{C}==\text{CPh}_2)]$ (An = U, 1; Th, 2), formed via salt metathesis with lithium-3,3-diphenylcyclopropene. Subsequent deprotonation of 1 and 2 results in the formation of the actinide allenylidene complexes, $[\text{Li}(2.2.2\text{-cryptand})][[(\text{NR}_2]_3\text{An(CCCPh}_2)]$ (An = U, 3; Th, 4). Significantly, 3 and 4 represent the first complexes with An–C multiple bonds that do not feature heteroatom stabilization.

Synthesis and characterization

Drawing inspiration from the groups of Hashmi and Binger,$^{25,26}$ we sought to synthesize an An–cyclopropenyl complex, which we hypothesized could undergo thermal ring opening to form an An–allenyl complex. In fact, addition of in situ generated lithium-3,3-diphenylcyclopropene to an Et$_2$O solution of $[\text{UCl(NR}_2]_3$ (R = SiMe$_3$) does result in formation of the allenyl complex, 1, which can be isolated as dark-brown blocks in 72% yield after work up (Scheme 1).$^{28}$ The thorium analogue 2 can be prepared in a similar fashion in 62% yield, via the reaction of $[\text{ThCl(NR}_2]_3$ with 1 equiv. of lithium-3,3-diphenylcyclopropene.

---

*Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106, USA. E-mail: hayton@chem.ucsb.edu

†Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260, USA. E-mail: jochen@buffalo.edu

‡ Electronic supplementary information (ESI) available: Experimental procedures, computational results, and spectral data for complexes 1–4. CCDC 2098903–2098906. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc04666g

† G. T. K. and X. Y. contributed equally to this work.

Introduction

Despite the significant advancements made in actinide–carbene chemistry in the past decade,$^{1–6}$ every example reported thus far has relied on ancillary chelators or heteroatom-containing substituents to stabilize the An–C multiple bond.$^{7–10}$ For example, the groups of Ephrussi and ZI employed a pincer-type ligand to form $[\text{U}[\text{C(PPh}_2\text{S})_2][\text{BH}_4]_2(\text{THF})_2]$ and $[\text{Th}[\text{C(PPh}_2\text{S})_2]_2(\text{DME})_2]$, respectively,$^{11,12}$ where two thiophosphinoyl pendant arms support the An–carbene interaction. In addition, Liddle et al. isolated the silyl-phosphino-carbene $[\text{Li}(2.2.2\text{-cryptand})][\text{U}[\text{C}[\text{SiMe}_3][\text{PPh}_2]][\text{BIPM}^{\text{TMRS}}][\text{Cl}]$ (BIPM$^{\text{TMRS}}$ = $\text{C}[\text{PPh}_2][\text{SiMe}_3])$, whose U–C bond is stabilized by a P(n) substituent.$^{13}$ Similarly, the uranium[nv] arsionium-carbene complex $[\text{U}[\text{Tren}^{\text{TIPS}}][\text{CHAsPh}_3]]$ (Tren$^{\text{TIPS}}$ = $\text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}_3)_3$) features stabilization by an As(n) substituent.$^{14}$ These heterocarotenophospholes help dissipate the negative charge at the carbene carbon caused by the weak An==C π-bond, which itself results from the energetic mismatch between actinide and carbon valence orbitals combined with the relatively small $r_{\text{max}}$ of the 5f orbitals.$^{15}$ Without these substituents, the An==C bond would likely be too reactive to isolate.
in Et₂O. We hypothesize that the ring opening occurs after salt metathesis.

The ¹H NMR spectrum of complex 1 in C₆D₆/THF-d₈ features a resonance at −174.8 ppm assigned to the proton attached to the Cₐ carbon (Fig. S4†). The ¹H NMR spectrum of 2 in C₆D₆/THF-d₈ displays a resonance at 5.77 ppm assigned to the same ligand environment (Fig. S5†). Additionally, the ¹³C{¹H} NMR spectrum of 2 features resonances at 139.4, 204.7, and 1934 ppm assigned to the proton attached to the same ligand environment, respectively (Fig. S6†). For comparison, the Cₐ and Cₐ NMR shifts of 1,1-diphenylallene are 78.2 and 210.0 ppm, respectively, whereas the Cₐ, Cₐ, and Cₐ NMR shifts of [OsCl₂(NO)(CH=CH₂)(PPr₃)₂] are 79.1, 199.1, and 101.0 ppm, respectively. We attribute the large Cₐ shift of 2 to spin–orbit coupling (SOC) effects (see below for more discussion). Finally, the IR spectra of 1 and 2 exhibit C–C and C=O stretching modes at 1934 and 1871 cm⁻¹, respectively, in their IR spectra (Table 1). These vibrational frequencies are consistent with those previously reported for transition metal allenyl complexes. Furthermore, the An–Cₐ–Cₐ angles (1: 133.2(2); 2: 132.0(4), 128.6(4)°) confirm that Cₐ is sp² hybridized, consistent with our proposed formulation. Notably, 1 and 2 are the first reported f element allenyl complexes.

Given the low proton affinity at Cₐ, we hypothesized that addition of base to 1 or 2 would yield an actinide–allenylidene. Gratifyingly, addition of 1 equiv. of LDA and 2.2.2-cryptand to 1 in Et₂O results in the formation of 3, which can be isolated as dark purple blocks in 54% yield after work-up (Scheme 1). The thorium analogue 4 can be prepared in a similar fashion, via the reaction of 2 with 1 equiv. of LDA and 2.2.2-cryptand, in 46% yield as deep orange-red solid. Complexes 3 and 4 are the first reported f element allenylidenes and are the first An=C complexes that do not employ heteroatoms or ancillary chelators to stabilize the An=C interaction.

The ¹H NMR spectrum of 3 in C₆D₆/THF-d₈ features a broad singlet at −1.60 ppm, assignable to the lone SiMe₃ environment (Fig. S7†). The ¹H NMR spectrum of 4 features a sharp singlet at 0.53 ppm, assignable to its SiMe₃ environment (Fig. S7 and S8†), whereas its ¹³C{¹H} NMR spectrum exhibits resonances at 205.4, 128.5, and 70.6 ppm. These resonances are assigned to the Cₐ, Cₐ, and Cₐ environments of the allenylidene ligand, respectively (Fig. S11†). Complexes 3 and 4 exhibit Cₐ–Cₐ and Cₐ–Cₐ stretching modes at 2050/1911 and 2044/1921 cm⁻¹, respectively, in their IR spectra (Table 1). These vibrational frequencies are higher than those observed for their respective precursors, suggesting an increase in both the Cₐ–Cₐ and Cₐ–Cₐ bond orders upon deprotonation. For further comparison, the

| Complex | v(Cₐ–Cₐ) (cm⁻¹) | v(Cₐ–Cₐ) (cm⁻¹) |
|---------|----------------|----------------|
| 1       | 1934           | 1871           |
| 2       | 1934           | 1869           |
| 3       | 2050           | 1911           |
| 4       | 2044           | 1921           |

Table 1. Selected IR spectral data for complexes 1–4.
Os allenylidene complex, [Os(CCCPh2)(CH3CN)3(IPr)(PiPr3)][BF4]2, features C–C distances of 1.246(8) and 1.362(9) Å, slightly shortened, whereas the C–C distances in [(C5Me5)2ThCl(CHPPh3)] and [Th(CHPPh3)(NR2)3] are 1.221(11) and 1.23(2) Å, respectively, whereas the Th–C distances in [(C5Me5)2ThCl(CPHPh3)] and [Th(CHPPh3)(NR2)3] are 1.325(5) and 1.362(2) Å, respectively.45

Compared to 1 and 2, the Cα-Cβ distances in 3 and 4 are slightly shortened, whereas the Cγ-Cδ distances are slightly elongated. The Cα-Cβ distances are similar to those observed for the An-acetylide complexes [Th(C==C)(NR2)3] (1.173(12) Å) and [(NN′)2U(CCCPh)] (1.212(5) Å, NN′ = N(CH2CH2-NSiBuMe3)3). However, the An-C distances in these examples are much longer, at 2.481(8) and 2.480(4) Å, respectively, reflecting their single bond character.47,48 The Cα-Cβ-Cγ angles in 3 and 4 remain unchanged, whereas the An-Cα-Cβ angles approach linear. In addition, the sum of angles around Cγ confirms that it is sp2 hybridized (Table 2). These metrical parameters are typical of the allenylidene ligand and can be rationalized by the contribution of resonance forms I and II to its electronic structure (Scheme 1, inset).49 For comparison, [Os(CCCPh3)(CH3CN)3(IPr)(PiPr3)][BF4]2 features Cα-Cδ and Cβ-Cγ distances of 1.246(8) and 1.362(9) Å, respectively.44

Electronic structure analysis

The An–allenylidene interaction in complexes 3 and 4 was analyzed via relativistic density functional theory (DFT).50 Complete computational details and results are provided in the ESI.† Based on Natural Localized Molecular Orbital (NLMO) analyses, complexes 3 and 4 exhibit strong π-delocalization (Fig. 3). Taking 4 as an example, the NLMO picture indicates triple bond character between Cα and Cπ corresponding to resonance structure (RS) II in Scheme 1. However, three-center...

Table 2  Selected metrical parameters for Complexes 1–4

| Bond (Å, °) | 1 | 2 | 3·C5H12 | 4·C8H12 |
|------------|---------------|---------------|--------------|--------------|
| An–Cα      | 2.457(3)      | 2.529(5), 2.536(5) | 2.305(8) | 2.368(16) |
| Cα–Cβ      | 1.299(4)      | 1.292(7), 1.288(7) | 1.221(11) | 1.23(2)    |
| Cγ–Cδ      | 1.329(4)      | 1.327(7), 1.319(7) | 1.403(11) | 1.40(2)    |
| Cγ–Cπ      | 1.490(4), 1.474(4) | 1.492(7), 1.487(7), 1.497(7), 1.488(7) | 1.443(12), 1.468(12) | 1.47(2), 1.45(2) |
| Σ(ζ Cipso–ζ C–ζ Cipso) | 359.0 | 360.0/359.9 | 359.9 | 359.9 |

Fig. 2  Solid-state structure of [Li(2.2.2-cryptand)][(NR2)3]U(CCCPh2)] (3) shown with 50% probability ellipsoids. Hydrogen atoms, [Li(2.2.2-cryptand)], and pentane solvate omitted for clarity.

Fig. 3  Isosurfaces (±0.03 a.u.) of selected NLMOs for 3 and 4. The α spin NLMOs of 3 are shown, weight-% metal character and 6d vs. 5f contributions at U are averaged over spins.
character involving thorium, $C_{a}$, and $C_{b}$, denoted as $\pi(\text{Th}-C)$ in Fig. 3 and Table S1,† also reveals an important contribution from RS I. The calculated natural charges for Th, $C_{a}$, $C_{b}$, and $C_{c}$ are $1.52$, $-0.67$, $0.05$, and $-0.22$, respectively, whereas the averaged natural charge for three N atoms bound to Th is $-1.65$. The NLMO representing the lone pair (and negative charge) at $C_{b}$ is $\pi$-LP($C_{b}$), and is strongly delocalized over the phenyl groups, $C_{a}$, and even $C_{a}$ and Th (Fig. S3†). This delocalization further confirms that RS I contributes to the overall electronic structure. In addition, for complex 3, the Mulliken spin population of U is 2.3 (excess alpha over beta spin), beyond the two unpaired spins expected for the $f^6$ configuration, indicating preferential alpha spin electron donation from ligand to metal. The spin populations for $C_{a}$, $C_{b}$, and $C_{c}$ are $-0.08$, $0.02$, $-0.10$, respectively; the remaining spin density in the ligand is further delocalized.

An NLMO representing the $\pi$-component of an $\text{An}=$C double bond is clearly seen for both 3 and 4 (Fig. 3). This NLMO features multi-center character ($3: 31\% C_{a}$, $28\% C_{b}$, and $11\% U$; $4: 53\% C_{a}$, $37\% C_{b}$, and $7\% \text{Th}$), and indicates that RS I is an important contributor to the overall electronic structure of both complexes, more so for 3 than for 4; although the metal weight in 4 is still significant. The other $\pi$-bonding NLMO in either complex has only $5\%$ metal weight. Finally, the $\sigma(\text{An–C})$ bonds of 3 and 4 are represented by two-center two electron NLMOs with $20\%$ and $18\%$ total An weight for 3 and for 4, respectively (Fig. 3). These results are similar to the weights found in the uranium methanediide complex, $[[\text{C}(\text{PPh}_{3})_{2}][\text{U}(\text{BH}_{4})_{2}][\text{THF}]_{2}]$.

As seen in Table S2,† the Wiberg Bond Order (WBO) analyses are consistent with the conclusions drawn from the NLMO picture. For example, the An–C$_{a}$, C$_{a}$–C$_{b}$, and C$_{b}$–C$_{g}$ WBOs are 0.91, 2.36, and 1.31, respectively, for 4, and 0.98, 2.40, and 1.28, respectively, for 3, further suggesting RS I is more important for 3 than for 4. Interestingly, the An–C$_{a}$ WBOs in 3 and 4 are notably larger than those of 1 (0.60) and 2 (0.57). The An–C$_{a}$ WBOs in 3 and 4 are also larger than those of the An($IV$) parent acetylenes, $[\text{An}=(\text{CCH})\{(\text{NR})_{2}\}]$ ($\text{An}=\text{Th}$, WBO = 0.67; U, WBO = 0.71).† Thus, the larger An–C$_{a}$ WBOs evident in 3 and 4 vs. $[[\text{NR}_{2}]\text{An}=(\text{CH})=\text{C}(\text{Ph}_{2})]$ vs. $[\text{An}=(\text{CCH})\{(\text{NR})_{2}\}]$ also supports the importance of resonance form I for these species, and confirms that they can be properly described as actinide carbenes.

An alternative way to examine the bonding in complexes 3 and 4 is offered by the quantum theory of atoms in molecules (QTAIM). This theory utilizes a variety of descriptors based on the topology of the electron density at a bond critical point (BCP).† QTAIM data (Table S4†) suggest that the An–C bonds in 3 and 4 are polarized towards the ligand but possess covalent character, and, for 3, the results are nearly identical to the data reported for $[[\text{BIPM}^\text{Mes}]\{(\text{Cl})_{2}][\text{THF}]_{2}]$ [BIPM$^\text{Mes}$ = $[[\text{C}(\text{PPh}_{3})_{2}\text{NMes}]_{2}]$].† Furthermore, the QTAIM data suggest that Th–C bond in 4 is somewhat less covalent than the U–C bond in 3, consistent with the NLMO analysis.

### 13C chemical shift analysis

An NLMO analysis of the $^{13}$C NMR shielding for complexes 2 and 4 was performed using the computational methods reported in ref. 50–52 and 54,55,63. Data reported here are from scalar relativistic and spin-orbit (SO) DFT calculations with the PBE functional. Additional data provided in the ESI† show that the calculated shifts do not vary strongly with the functional used in the calculations (Table S3†). We also performed a shielding analysis of allene ($\text{H}_{3}\text{C}=$C$=$CH$_2$), for comparison with complex 2. For all compounds, the diamagnetic and paramagnetic contributions to the shieldings were combined. We confirmed that the observed variations in the carbon shielding and chemical shift come from the (usually negative) paramagnetic shielding mechanism, involving magnetic coupling between occupied and unoccupied orbitals, along with SO effects. The diamagnetic shielding per carbon is essentially constant, as usual. More details are provided in the ESL†

Our calculated shielding constants for allene agree well with those reported by Wiberg et al. who analyzed the system in great detail (Table S3†).† Effects from SO coupling (SOC) are very minor, as expected for an organic molecule without a heavy element. $C_8$ is strongly deshielded, by almost 150 ppm, relative to the methylene carbons. The primary reason for this difference is a strong paramagnetic deshielding from both $\pi(\text{C}=$C) NLMOs for $C_8$ (Table S5†). Although, the $\sigma$-bond NLMOs also contribute somewhat to the large shielding difference between the central and terminal carbons.

The calculated chemical shifts for complex 2 agree reasonably well with the experimental data (Tables S3 and S6†). For example, the calculated $C_8$ shift for 2 is 144 ppm (expt. = 139.4 ppm). The replacement of $\text{C}_2\text{H}_4$ in allene by $\text{C}_2\text{Ph}_2$ in 2 and the bonding of $\text{C}_8$ to $\text{Th}$ has a noticeable effect on most of the NLMO shielding contributions, leading to an overall decrease of the $C_8$ and $C_7$ shielding, relative to allene, and a modest increase (13–17 ppm) of the $C_6$ shielding. The shielding patterns and contributions remain allene-like, however. This conclusion is further buttressed by the WBOs for $C_2$–$C_6$ (2.0) for $C_6$–$C_7$ (1.6). The former value corresponds exactly to the expected bond order, whereas the latter reflects the aforementioned delocalization of $\pi(C_6$–$C_7)$ onto $C_{ipso}$. The main difference to allene is the inequivalency of $C_8$ and $C_7$. The shielding difference is $-13$ ppm in the calculations without SOC, and is primarily caused by more negative contributions from $\sigma(C_8$–Th) and $\sigma(C_8$–H) to the $C_8$ shielding vs. the $\sigma(C_7$–$C_{ipso})$ contributions to the $C_7$ shielding, and a more negative contribution of $\sigma(C_7$–$C_6)$ to the $C_6$ shielding vs. $\sigma(C_6$–$C_5)$ contributing to the $C_5$ shielding. These differences are partially counteracted by a more positive allene-like $C_8$ shielding from $\sigma(C_8$–$C_9$) compared to the $C_8$ shielding from $\pi(C_8$–$C_9)$ (Table S6†). The delocalization onto $C_{ipso}$ (Fig. S3†) evidently enhances the $C_8$ paramagnetic deshielding relative to allene. With SOC effects included, the difference between the $C_8$ and $C_9$ shielding becomes $-39$ ppm, as a result of the Th 5f (and 6d) AO contributions in $\sigma(C_8$–Th) and an associated SOC deshielding in the $C_8$ core. The situation is reminiscent of the SOC effects on the shielding of nitrogen atoms bound to Th that we identified recently.†

The calculated $^{13}$C chemical shifts for complex 4 (Tables S3 and S7†) also agree reasonably well with the experimental data. For example, the calculated $C_8$ shift for complex 4 is 211 ppm
(expt. = 205.4 ppm). This value includes a 36 ppm deshielding contribution due to SOC, which is about 10 ppm larger in magnitude than that calculated for C\textsubscript{a} in complex 2 as a result of the stronger σ(An–C) covalency in 4. The calculations also reproduce the experimentally assigned chemical shift ordering C\textsubscript{a} > C\textsubscript{b} > C\textsubscript{y}, in 4, which is different from complex 2, for which the shifts are C\textsubscript{b} > C\textsubscript{y} > C\textsubscript{a}. The increased C\textsubscript{b} shielding (smaller chemical shift) in 4 compared to 2 partially reflects the formal C\textsubscript{a}–C\textsubscript{b} triple bond, according to RS II. However, C\textsubscript{b} in 4 is still substantially deshielded relative to C\textsubscript{b} in an authentic alkyne, such as PhCCH (77.2 ppm chemical shift),\textsuperscript{44} consistent with delocalization according to RS I. The different ordering is the result of two effects: (1) C\textsubscript{b} in 4 has triple bond character with a concomitant increase in magnetic shielding; and (2) the stronger C\textsubscript{a}–Th covalency lowers the shielding of C\textsubscript{a} in 4, compared to 2, via the combined effects of greater paramagnetic deshielding due to stronger Th–C bonding, and a stronger SOC deshielding (Tables S6 and S7). Finally, the SOC induced deshielding for C\textsubscript{a} in 4 (−9 ppm) is much larger than that calculated for complex 2 (−4 ppm), which shows independently from the NLMO analysis that the delocalization involves Th, where most of the SOC originates.

Conclusions

In summary, reaction of [AnCl(NR\textsubscript{2})\textsubscript{3}] with \textit{in situ} generated lithium-3,3-diphenylcyclopropene affords the first actinide–allenyl complexes, \{[((NR\textsubscript{2})\textsubscript{3}An(CH–≡C–CPh\textsubscript{2})] (An = U, Th). Subsequent treatment with LDA and 2.2.2-cryptand results in the formation of the actinide–allenylidene complexes, [Li(2.2.2-cryptand)[[(NR\textsubscript{2})\textsubscript{3}An(CCCPh\textsubscript{2})] (An = U, Th), which represent the first non-heteroatom supported carbene complexes of the actinides. Importantly, their isolation suggests that other actinide cumulene complexes could be isolable, provided a viable synthetic route is available. Quantum chemical calculations give a detailed picture of the actinide–allenylidene interaction, which features partial An–C double bond character. Additionally, the C\textsubscript{a} chemical shift in the two Th complexes exhibit SOC-induced deshielding due to 5f orbital participation in the Th–C bonds. The larger deshielding in the allenylidene complex vs. the allenyl is consistent with its greater Th–C covalency.

Going forward, we plan to explore the reactivity of our actinide allenylidene for comparison with the late transition metal allenylidenes, which will provide further insight into their electronic structure and potentially uncover new modes of allenylidene reactivity. The latter point is significant because the polarity of the carbon atoms within the actinide allenylidene unit is reversed relative to that observed in the late transition metals (\textit{e.g.}, resonance form III, Scheme 1).\textsuperscript{2,3,24,61}

Data availability

Raw experimental and computational data will be made available free of charge upon request.

Author contributions

G. T. K., G. W., and T. W. H. performed the experimental synthesis, characterization, and analysis of the data. X. Y. and J. A. performed the theoretical calculations and analyzed the data. All authors jointly wrote the manuscript. J. A. and T. W. H. secured the funding for the research.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division under Contract DE-SC-0001861. J. A. acknowledges support for the theoretical component of this study by the U.S. Department of Energy, Office of Science, Heavy Element Chemistry program, grant DE-SC0001136. We thank the Center for Computational Research (CCR) at the University of Buffalo for providing computational resources.

References

1 S. Fortier, J. R. Walensky, G. Wu and T. W. Hayton, \textit{J. Am. Chem. Soc.}, 2011, 133, 6894–6897.
2 O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake and S. T. Liddle, \textit{Angew. Chem., Int. Ed.}, 2011, 50, 2383–2386.
3 O. J. Cooper, D. P. Mills, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, \textit{Chem.–Eur. J.}, 2013, 19, 7071–7083.
4 D. E. Smiles, G. Wu, P. Hrošík and T. W. Hayton, \textit{Organometallics}, 2017, 36, 4519–4524.
5 P. Rungthanaphatsophon, P. Huang and J. R. Walensky, \textit{Organometallics}, 2018, 37, 1884–1891.
6 P. Rungthanaphatsophon, A. Bathelier, L. Castro, A. C. Behrle, C. L. Barnes, L. Maron and J. R. Walensky, \textit{Angew. Chem., Int. Ed.}, 2017, 56, 12925–12929.
7 S. T. Liddle, \textit{Angew. Chem., Int. Ed.}, 2015, 54, 8604–8641.
8 M. Gregson, A. J. Wooles, O. J. Cooper and S. T. Liddle, \textit{Comments Inorg. Chem.}, 2015, 35, 262–294.
9 T. W. Hayton, \textit{Dalton Trans.}, 2010, 39, 1145–1158.
10 J. T. Boronski, J. A. Seed, A. J. Wooles and S. T. Liddle, \textit{Chem. Commun.}, 2021, 57, 5090–5093.
11 W. Ren, X. Deng, G. Zi and D.-C. Fang, \textit{Dalton Trans.}, 2011, 40, 9662–9664.
12 T. Cantat, T. Arliguie, A. Noël, P. Thuery, M. Ephritikhine, P. L. Floch and N. Mézailles, \textit{J. Am. Chem. Soc.}, 2009, 131, 963–972.
13 E. Lu, J. T. Boronski, M. Gregson, A. J. Wooles and S. T. Liddle, \textit{Angew. Chem., Int. Ed.}, 2018, 57, 5506–5511.
14 J. A. Seed, H. R. Sharpe, H. J. Futcher, A. J. Wooles and S. T. Liddle, \textit{Angew. Chem., Int. Ed.}, 2020, 59, 15870–15874.
15 M. B. Jones and A. J. Gaunt, \textit{Chem. Rev.}, 2013, 113, 1137–1198.
