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Ring-opening of a Thorium Cyclopropenyl Complex Generates a Transient Thorium-bound Carbene

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The reaction of $[\text{Cp}_3\text{ThCl}]$ with *in situ* generated lithium-3,3-diphenylcyclopropene results in the formation of $[\text{Cp}_3\text{Th}(3,3\text{-diphenylcyclopropenyl})]$ (**1**), in good yields. Thermolysis of **1** results in isomerization to the ring-opened product, $[\text{Cp}_3\text{Th}(3\text{-phenyl-1H-inden-1-yl})]$ (**3**) via a hypothesized carbene intermediate. This transformation represents a new mode of reactivity of 3,3-diphenylcyclopropene with the actinides, improving our ability to use this reagent as a carbene source. A combined DFT and $^{13}\text{C}\{^1\text{H}\}$ NMR analysis of **1** shows a spin-orbit induced downfield shift at C_α due to participation of the 5f orbitals in the Th–C bond.

A large number of heteroatom-stabilized actinide carbene complexes have been reported in recent years,^{1–7} including $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{CHAsPh}_3)]$ ($\text{Tren}^{\text{TIPS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}^t_3)_3$),⁸ $[\text{U}\{\text{C}(\text{SiMe}_3)(\text{PPh}_2)\}(\text{BIPM}^{\text{TMS}})(\text{Cl})]^-$ ($\text{BIPM}^{\text{TMS}} = \text{C}(\text{PPh}_2\text{NSiMe}_3)_2$),⁹ and $[\text{An}(\text{CHPh}_3)(\text{NR}_2)_3]$ ($\text{An} = \text{Th}, \text{U}; \text{R} = \text{SiMe}_3$).^{10, 11} Yet, an isolable “Schrock-type” actinide alkylidene, which features no heteroatom stabilization, remains elusive. Their scarcity is likely due to a number of factors, but the high reactivity of the An=C linkage, a consequence of the weak An–C π bond, plays a significant role.⁸ Another important factor is the dearth of viable synthetic routes.^{12–14} For instance, in a seminal contribution, Kiplinger and co-workers found that reaction of $[\text{Cp}^*_2\text{U}(\text{NAr})]$ ($\text{Ar} = 2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$) with diphenyldiazoalkane did not result in N_2 elimination and carbene formation, but instead resulted in generation of the U(VI) hydrazone complex, $[\text{Cp}^*_2\text{U}(\text{NAr})(\text{N}_2\text{CPh}_2)]$.¹⁵ Several other groups have reported similar diazoalkane reactivity with the actinides.^{1, 16–19}

In an effort to find new routes to an actinide alkylidene, we turned our attention to 3,3-diphenylcyclopropene and its derivatives. This reagent has been successfully employed by

Binger,^{20, 21} and others,^{22–26} to generate transition metal vinyl carbenes and allenylidenes.^{27–29} For example, reaction of $[\text{Cp}_2\text{Ti}(\text{PMe}_3)_2]$ with 3,3-diphenylcyclopropene results in ring opening and formation of the vinyl carbene complex, $[\text{Cp}_2\text{Ti}(\text{C}(\text{H})\text{C}(\text{H})=\text{CPh}_2)(\text{PMe}_3)]$.²⁰ Similarly, reaction of $[\text{RuCl}_2(\text{PPh}_3)_4]$ with 3,3-diphenylcyclopropene results in formation of $[\text{Ru}(\text{C}(\text{H})\text{C}(\text{H})=\text{CPh}_2)\text{Cl}_2(\text{PPh}_3)_2]$.^{28, 30}

Drawing inspiration from this work, as well as recent results from Hashmi and co-workers,³¹ we began exploring the reactivity of 3,3-diphenylcyclopropene with the actinides. In particular, we found that reaction of 1-lithium-3,3-diphenylcyclopropene with $[\text{AnCl}(\text{NR}_2)_3]$ ($\text{An} = \text{Th}, \text{U}; \text{R} = \text{SiMe}_3$) resulted in the formation of the An-allenyl complexes $[\{(\text{NR}_2)_3\text{An}(\text{CH}=\text{C}=\text{CPh}_2)\}]$.³² Subsequent deprotonation resulted in the formation of the first An allenylidenes, $[\{(\text{NR}_2)_3\text{An}(\text{CCPh}_2)\}]^-$, which were also the first reported An carbenes that contain no heteroatom stabilization.

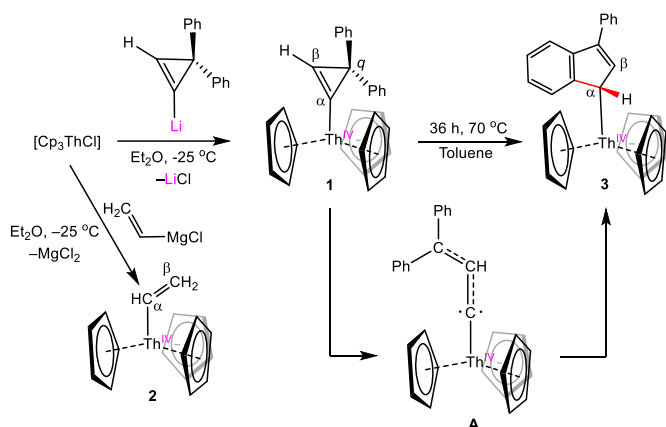
Given the rarity of An carbenes, and the promise of this new synthetic protocol for generating An=C bonds, we wanted to explore the generality of this approach. Herein we describe the synthesis and characterization of $[\text{Cp}_3\text{Th}(3,3\text{-diphenylcyclopropenyl})]$ (**1**), which was formed by reaction of $[\text{Cp}_3\text{ThCl}]$ with 1-lithium-3,3-diphenylcyclopropene. This complex isomerizes to $[\text{Cp}_3\text{Th}(3\text{-phenyl-1H-inden-1-yl})]$ (**3**) upon thermolysis. We propose that this transformation proceeds via a transient carbene intermediate.

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Addition of *in situ* generated 1-lithium-3,3-diphenylcyclopropene to an Et₂O solution of [Cp₃ThCl] results in the formation of the cyclopropenyl complex, [Cp₃Th(3,3-diphenylcyclopropenyl)] (**1**), which was isolated as colourless plates in 75% yield after work-up (Scheme 1). The ¹H NMR spectrum of **1** in THF-*d*₈ features diagnostic resonances at 6.17 ppm and 7.62 ppm, which are assignable to the Cp and H_β environments, respectively. The peaks are present in a 15:1 ratio, consistent with the proposed formulation. Additionally, the ¹³C{¹H} NMR spectrum of **1** features three cyclopropenyl environments at 177.4, 127.2, and 39.5 ppm, which are assignable to the C_α, C_β, and C_q (q = quaternary) positions, respectively (Figure S2).



Scheme 1. Synthesis of Complexes 1-3.

Complex **1** crystallizes in the orthorhombic space group *Pbca* and confirms the connectivity of the diphenylcyclopropenyl ligand (Figure 1). The Th–C bond distance is 2.52(1) Å and is within error of those reported for thorium allenyl or vinylic complexes, including [((NR₂)₃)Th(CH=C=CPh₂)] (R = SiMe₃, 2.529(5)/2.536(5) Å) and [η⁵-1,2,4-^tBu₃C₅H₂][η⁵-1,2-^tBu₂-4-(CH₂CMe₂)C₅H₂]Th[C(Ph)=CH(C₆H₁₁)] (2.480(6) Å).^{32–34} The C_α–C_β distance is 1.28(1) Å, consistent with its double bond character, whereas the C_α–C_q (1.47(1) Å) and C_β–C_q (1.56(1) Å) distances are assignable to C–C single bonds. Interestingly, the two C–C single bonds differ by ca. 0.1 Å, suggesting activation of the cyclopropenyl ring (see below). Hashmi and co-workers observed a similar level of activation in [((IPr)Au(3,3-diphenylcyclopropenyl))] complex (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene).³¹ Finally, the isolation of **1** supports our hypothesis that the ring opening required to form [((NR₂)₃)An(CH=C=CPh₂)] (An = Th, U) occurs after salt metathesis.³²

For further spectroscopic and structural comparison we independently synthesized and characterized the parent thorium vinyl complex [Cp₃Th(C(H)=CH₂)] (**2**) via reaction of [Cp₃ThCl] with [ClMg(C(H)=CH₂)] in Et₂O (Scheme 1). Complex **2** can be isolated in 80% yield as white needles after work-up. It represents the first reported thorium parent vinyl complex.^{33–35}

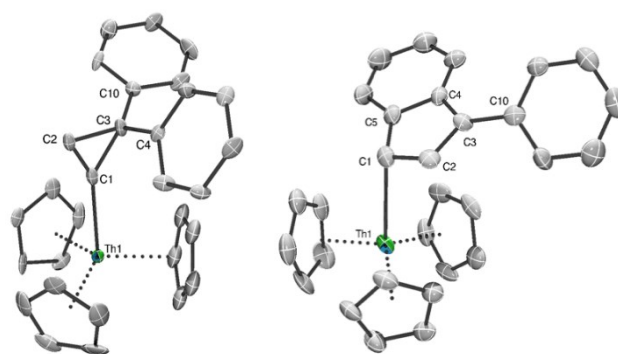


Figure 1. Solid-state molecular structures of **1** (left) and **3** (right); thermal ellipsoids set at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: **1**: Th1–C1 = 2.523(11), C1–C2 = 1.278(14), C1–C3 = 1.559(14), C2–C3 = 1.467(13), Th1–C1–C2 = 153.6(8), Th1–C1–C3 = 145.1(7), C2–C1–C3 = 61.3(7). **3**: Th1–C1 = 2.674(6), C1–C2 = 1.429(9), C1–C5 = 1.451(10), C2–C3 = 1.399(9), C3–C4 = 1.438(10), C4–C5 = 1.422(9), Th1–C1–C2 = 104.0(4), Th1–C1–C5 = 112.3(4), C1–C2–C3 = 109.7(7).

The ¹H NMR spectrum of **2** in C₆D₆ exhibits three vinyl environments at 8.19, 7.00, and 6.21 ppm, and one Cp environment at 5.96 ppm (Figure S3). These resonances are present in a 1:1:1:15 ratio. The ¹³C{¹H} NMR spectrum of **3** in C₆D₆ features resonances at 199.6, 134.3, and 116.7 ppm, which are assignable to the C_α, C_β, and Cp environments, respectively (Figure S4). The connectivity of **2** was further confirmed by X-ray crystallography (Figure S13).

In an effort to effect ring-opening, we heated a toluene solution of **1** for 36 h. Work-up of the resulting yellow-orange solution resulted in the isolation of the thorium indenyl complex, [Cp₃Th(3-phenyl-1H-inden-1-yl)] (**3**), in a 60% yield. Inspection of the crude reaction mixture by ¹H NMR spectroscopy reveals that **3** is the major Cp-containing product (Figure S7). A handful of minor species are also present in this sample, as evidenced by Cp signals at 6.03, 5.88, and 5.65 ppm; however, we were unable to determine their identities. The ¹H NMR spectrum of complex **3** in THF-*d*₈ features doublets at 7.57 (*J*_{HH} = 2.1 Hz) and 5.35 ppm (*J*_{HH} = 2.1 Hz), which are assignable to the H_α and H_β environments of the indenyl ring (Figure S5). The ¹³C{¹H} NMR spectrum of **3** in THF-*d*₈ features 14 resonances, consistent with the proposed structure. Notably, the C_α resonance (88.9 ppm) is downfield (less shielded) in comparison to the equivalent carbon resonance of 3-phenylindene, primarily due to metalation (Figure S6).^{36, 37} Complex **3** crystallizes in the monoclinic space group *P2₁/n* and its solid-state structure confirms the connectivity of the indenyl ligand (Figure 1). The Th–C distance is 2.674(6) Å, which is elongated in comparison to that of **1** on account of the weaker σ-donating ability of the indenyl ligand.

To account for the formation of **3**, we propose that thermolysis of **1** results in ring opening, forming a transient carbene intermediate **A** (Scheme 1), which activates an *ortho* C–H bond to form **3**. A similar transformation was observed by Hashmi upon thermolysis of [(IPr)Au(3,3-

diphenylcyclopropenyl)].³¹ Curiously, reaction of $[\text{ThCl}(\text{NR}_2)_3]$ with 1-lithium-3,3-diphenylcyclopropene does not generate the analogous indenyl complex, and instead results in isolation of $[\{(\text{NR}_2)_3\text{Th}(\text{CH}=\text{C}=\text{CPh}_2)]$, presumably via a 1,2-H-shift from an analogous carbene intermediate. Steric maps of the $[\{(\text{NR}_2)_3\text{Th}\}^+]$ and $[\text{ThCp}_3]^+$ fragments (Figure S12) demonstrate that the former is substantially more bulky than the latter,³⁸ suggesting that the *ortho* C–H bonds cannot approach the C_α carbene centre in $[\{(\text{NR}_2)_3\text{Th}(\text{CC}(\text{H})\text{CPh}_2)]$, leaving the 1,2-H-shift as the next best pathway for isomerization.

To better understand the nature of the Th–C interactions in complexes **1–3**, as well as intermediate **A**, we analysed their electronic structures by relativistic density functional theory with different functionals. Complete computational details are given in the Supporting Information. The results obtained with the PBE0 functional are discussed here. Natural localized molecular orbital (NLMO)³⁹ analysis of **1** is indicative of a two-centre two-electron $\sigma(\text{Th}–\text{C})$ bond with 22% total thorium weight (8% 7s; 76% 6d; 16% 5f; Figure 2). The polarization toward C is typical, and reflective of the dative character of the bond. The An–C interaction in **2** is similar to that of **1**, with 23% total thorium weight (7% 7s; 79% 6d; 14% 5f). The NLMO analysis of complex **3** shows donation bonding via a delocalized π orbital evidencing the conjugation between the 5- and 6-membered rings of the ligand. The total Th contribution in this orbital is only 10%, indicating weaker donation bonding, which is consistent with the relatively long Th–C bond observed for this complex. The Th– C_α Wiberg bond orders (WBOs) are 0.68, 0.72, and 0.39 for **1**, **2**, and **3**, respectively, supporting the visual analysis of the orbitals. The combined Th–C WBOs for all carbons in the 5-membered ring of **3** is 0.59, which is still much below the WBOs of **1** and **2** and consistent with the increased distance. The total thorium weights calculated for **1** and **2** are slightly larger (ca. 5% points) than those calculated for $[\text{Th}\{\text{NR}_2\}_3(\text{CCH})]$ and $[\text{Th}\{\text{NR}_2\}_3(\text{CH}=\text{C}=\text{CPh}_2)]$,^{32, 40} but comparable overall. The DFT optimized structure of **A** is indicative of a triplet ground state for the carbene, which is lower by 4.9 kcal/mol than the singlet state (Figure S14). Most of its spin density (Figure 3) resides on C_α (1.26 electron spin population), with the remainder delocalized toward C_β and Th, the former arising from the π delocalization across C_α , C_β , and C_γ as revealed by NLMO analysis. The Th–C bond in **A** also has some, albeit weak, π -character (Figure S16).

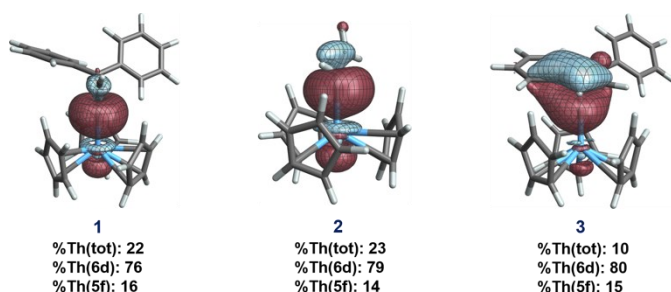
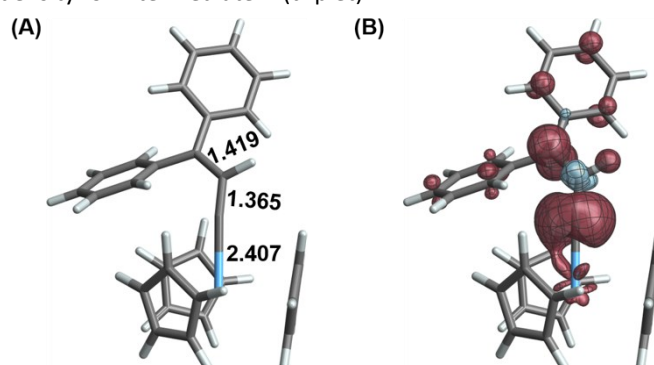


Figure 2. Isosurfaces (± 0.03 au) of the $\sigma(\text{Th}–\text{C})$ bonding NLMOs in **1–3**, along with total weight-% metal character and 6d vs 5f contributions at the metal.

Figure 3. (A) Optimized structure for intermediate **A** and selected bond lengths (\AA). (B) Isosurfaces (± 0.001 au) of the spin density for intermediate **A** (triplet).



We also calculated the ^{13}C NMR chemical shifts of the α -carbon nuclei for complexes **1–3** using a variety of functionals, with and without SO coupling effects.^{41–43} We, and others, have previously used ^{13}C NMR chemical shifts to assess the covalency of An–C and Ln–C bonds.^{11, 44–50} The calculated chemical shifts are not strongly functional dependent; for convenience, we only discuss the PBE0/SO-PBE0 results. The calculated α -carbon shift for **1** is 179.9 ppm (expt. = 177.4 ppm) and includes a 20.8 ppm deshielding contribution due to SO effects. Complex **2** also exhibits good agreement between calculated (200.8 ppm) and experimental (199.6 ppm) α -carbon shifts, with 18.7 ppm deshielding due to SO effects. Complex **3** exhibits almost no SO effects on the calculated α -carbon shielding (4.7 ppm), likely for two reasons. First, the donation bonding is weaker, and second the relevant orbital is of local π symmetry at the carbon atoms, which does not support the effective transmission of isotropic SO effects to the ligand. The SO contributions observed for **1** and **2** are clear evidence of the covalent nature of the Th–C interactions, but they are smaller than those reported for other thorium organometallics,^{40, 49} even after controlling for the carbon 2s character and despite comparable bond orders and 5f contributions from Th. Because shielding is a magnetic response property, changes to the ancillary ligands at Th will modulate the magnitude of the spin density induced by the SO coupling and the external field, which in turn modulates the SO shielding effect. Therefore, care must be taken when comparing SO contributions between complexes with disparate ligand environments.

In summary, reaction of $[\text{Cp}_3\text{ThCl}]$ with *in situ* generated lithium-3,3-diphenylcyclopropene results in the formation of $[\text{Cp}_3\text{Th}(3,3\text{-diphenylcyclopropenyl})]$. This species undergoes ring opening upon thermolysis to generate the *ortho* C–H activated product, $[\text{Cp}_3\text{Th}(3\text{-phenyl-1H-inden-1-yl})]$. We propose that this transformation proceeds via a transient triplet carbene intermediate. Importantly, this work uncovers a new mode of reactivity of 3,3-diphenylcyclopropene with the actinides, improving our ability to use this reagent as a carbene source. Moving forward, we will continue to explore the reactivity of 3,3-diphenylcyclopropene, and its derivatives, with common actinide fragments in an effort to generate an elusive actinide Schrock-type carbene.

Conflicts of interest

There are no conflicts to declare.

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References

- W. Ren, E. Zhou, B. Fang, G. Hou, G. Zi, D.-C. Fang and M. D. Walter, *Angew. Chem. Int. Ed.*, 2014, **53**, 11310-11314.
- P. Rungthanaphatsophon, A. Bathelier, L. Castro, A. C. Behrle, C. L. Barnes, L. Maron and J. R. Walensky, *Angew. Chem. Int. Ed.*, 2017, **56**, 12925-12929.
- P. Rungthanaphatsophon, P. Huang and J. R. Walensky, *Organometallics*, 2018, **37**, 1884-1891.
- T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. L. Floch and N. Mézailles, *J. Am. Chem. Soc.*, 2009, **131**, 963-972.
- M. Gregson, A. J. Wooles, O. J. Cooper and S. T. Liddle, *Comments Inorg. Chem.*, 2015, **35**, 262-294.
- G. Ma, M. J. Ferguson, R. McDonald and R. G. Cavell, *Inorg. Chem.*, 2011, **50**, 6500-6508.
- M. Gregson, E. Lu, D. P. Mills, F. Tuna, E. J. L. McInnes, C. Hennig, A. C. Scheinost, J. McMaster, W. Lewis, A. J. Blake, A. Kerridge and S. T. Liddle, *Nat. Commun.*, 2017, **8**, 14137.
- J. A. Seed, H. R. Sharpe, H. J. Fitcher, A. J. Wooles and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2020, **59**, 15870-15874.
- E. Lu, J. T. Boronski, M. Gregson, A. J. Wooles and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2018, **57**, 5506-5511.
- S. Fortier, J. R. Walensky, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 6894-6897.
- D. E. Smiles, G. Wu, P. Hrobárik and T. W. Hayton, *Organometallics*, 2017, **36**, 4519-4524.
- T. W. Hayton, *Dalton Trans.*, 2010, **39**, 1145-1158.
- S. T. Liddle, *Angew. Chem. Int. Ed.*, 2015, **54**, 8604-8641.
- J. H. Farnaby, T. Chowdhury, S. J. Horsewill, B. Wilson and F. Jaroschik, *Coord. Chem. Rev.*, 2021, **437**, 213830.
- J. L. Kiplinger, D. E. Morris, B. L. Scott and C. J. Burns, *Chem. Commun.*, 2002, 30-31.
- E. M. Matson, P. E. Fanwick and S. C. Bart, *Eur. J. Inorg. Chem.*, 2012, **2012**, 5471-5478.
- O. P. Lam, P. L. Feng, F. W. Heinemann, J. M. O'Connor and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 2806-2816.
- N. S. Settineri, A. A. Shiau and J. Arnold, *Chem. Commun.*, 2018, **54**, 10913-10916.
- T. Cantat, C. R. Graves, B. L. Scott and J. L. Kiplinger, *Angew. Chem. Int. Ed.*, 2009, **48**, 3681-3684.
- P. Binger, P. Müller, R. Benn and R. Mynott, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 610-611.
- P. Binger, P. Müller, F. Langhauser, F. Sandmeyer, P. Philipps, B. Gabor and R. Mynott, *Chem. Ber.*, 1993, **126**, 1541-1550.
- L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 8130-8145.
- B. T. Flatt, R. H. Grubbs, R. L. Blanski, J. C. Calabrese and J. Feldman, *Organometallics*, 1994, **13**, 2728-2732.
- F. J. de la Mata and R. H. Grubbs, *Organometallics*, 1996, **15**, 577-584.
- O. Fujimura, F. J. de la Mata and R. H. Grubbs, *Organometallics*, 1996, **15**, 1865-1871.
- J.-H. Huang, T.-Y. Lee, D. C. Swenson and L. Messerle, *Inorg. Chim. Acta*, 2003, **345**, 209-215.
- M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117-3179.
- S. T. Nguyen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, **114**, 3974-3975.
- P. Binger, P. Müller, R. Wenz and R. Mynott, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1037-1038.
- S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858-9859.
- F. F. Mulks, P. W. Antoni, F. Rominger and A. S. K. Hashmi, *Adv. Synth. Catal.*, 2018, **360**, 1810-1821.
- G. T. Kent, X. Yu, G. Wu, J. Autschbach and T. W. Hayton, *Chem. Sci.*, 2021, **12**, 14383-14388.
- B. Fang, L. Zhang, G. Hou, G. Zi, D.-C. Fang and M. D. Walter, *Chem. Sci.*, 2015, **6**, 4897-4906.
- B. Fang, G. Hou, G. Zi, W. Ding and M. D. Walter, *Organometallics*, 2016, **35**, 1384-1391.
- L. E. Schock, A. M. Seyam, M. Sabat and T. J. Marks, *Polyhedron*, 1988, **7**, 1517-1529.
- G. A. Taylor and P. E. Rakita, *Org. Magn. Reson.*, 1974, **6**, 644-647.
- T. Nakano, K. Endo and Y. Ukaji, *Chem. Asian J.*, 2016, **11**, 713-721.
- L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo, *Nat. Chem.*, 2019, **11**, 872-879.
- E. D. Glendening, C. R. Landis and F. Weinhold, *WIREs Comput Mol Sci*, 2012, **2**, 1-42.
- G. T. Kent, X. Yu, C. Pauly, G. Wu, J. Autschbach and T. W. Hayton, *Inorg. Chem.*, 2021, **60**, 15413-15420.
- J. Autschbach and E. Zurek, *J. Phys. Chem. A*, 2003, **107**, 4967-4972.
- J. Autschbach, *Mol. Phys.*, 2013, **111**, 2544-2554.
- S. K. Wolff, T. Ziegler, E. v. Lenthe and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 7689-7698.
- A. J. Lewis, P. J. Carroll and E. J. Schelter, *J. Am. Chem. Soc.*, 2013, **135**, 13185-13192.
- K. C. Mullane, P. Hrobárik, T. Cheisson, B. C. Manor, P. J. Carroll and E. J. Schelter, *Inorg. Chem.*, 2019, **58**, 4152-4163.
- E. A. Pedrick, P. Hrobárik, L. A. Seaman, G. Wu and T. W. Hayton, *Chem. Commun.*, 2016, **52**, 689-692.
- L. A. Seaman, P. Hrobárik, M. F. Schettini, S. Fortier, M. Kaupp and T. W. Hayton, *Angew. Chem. Int. Ed.*, 2013, **52**, 3259-3263.
- G. B. Panetti, D.-C. Sergentu, M. R. Gau, P. J. Carroll, J. Autschbach, P. J. Walsh and E. J. Schelter, *Nat. Commun.*, 2021, **12**, 1713.
- O. Ordoñez, X. Yu, G. Wu, J. Autschbach and T. W. Hayton, *Inorg. Chem.*, 2021, **60**, 12436-12444.
- O. Ordoñez, X. Yu, G. Wu, J. Autschbach and T. W. Hayton, *Chem. Eur. J.*, 2021, **27**, 5885-5889.