



### From a mercury(II) bis(yldiide) complex to actinide yldiides†

Cite this: *Chem. Commun.*, 2024, 60, 3190

Received 10th November 2023,  
Accepted 19th February 2024

DOI: 10.1039/d3cc05553a

rsc.li/chemcomm

Mike Jörges,<sup>ab</sup> Alexander J. Gremillion,<sup>ab</sup> Daniel Knyszczek,<sup>id b</sup> Steven P. Kelley,<sup>id a</sup> Justin R. Walensky<sup>id \*a</sup> and Viktoria H. Gessner<sup>id \*b</sup>

The bis(yldiide) mercury complex, (L–Hg–L) [L = C(PPh<sub>3</sub>)P(S)Ph<sub>2</sub>], is prepared from the corresponding potassium yldiide and used to access the first substituted yldiide actinide complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(L)(Cl)] (An = U, Th) via salt metathesis. Compared to previously reported phosphinocarbene complexes, the complexes exhibit long actinide–carbon distances, which can be explained by the strong polarization of the π-electron density toward carbon.

Actinide–carbon multiple bonding has attracted attention in the past decade due to efforts to better understand actinide–ligand bonding and differences in coordination chemistry and reactivity between actinides and the rest of the periodic table.<sup>1</sup> Actinide carbene and carbene-like complexes have been reported with different ligand systems including widely used singlet carbenes<sup>2–13</sup> carbodiphosphoranes,<sup>14–17</sup> as well as highly nucleophilic methandiides (e.g. in A and B, Fig. 1A),<sup>18–22</sup> which exhibited most different bonding situations and reactivities depending on the substituents at the carbon atom and the metal oxidation state.<sup>23</sup> In recent years, yldiides (as their alkali metal complexes) have emerged as a further class of di-substituted carbon ligands (Fig. 1B)<sup>24</sup> which have particularly been applied for the synthesis of main group complexes leading to seminal contributions in structure, bonding, and reactivity.<sup>25–29</sup> Analogous complexes with transition metals are rare,<sup>30–33</sup> but have demonstrated the unusual donor strength of the respective phosphonio-carbene/yldiide ligands.<sup>34–36</sup> Likewise phosphonio-carbene complexes of the actinides have been reported, but only with the parent phosphoranomethylide ligand (C and D),<sup>37–40</sup> which was synthesized in the coordination sphere of the metal and was shown to produce short actinide–carbon bonds with some degree of

multiple bonding character. Albeit in the meantime various yldiides have been isolated,<sup>41–44</sup> no actinide complexes have been prepared from these precursors, so that the impact of the substitution pattern on the bonding situation remains completely unclear.

Previous attempts by our group to close this gap with various transition metal precursors remained unsuccessful, which we attributed to the reducing power of the alkali metal yldiides. Therefore, we turned our attention towards a milder method for introducing yldiide ligands and selected metathesis via a mercury compound as an alternative strategy. Herein, we report the first examples of substituted yldiide actinide complexes, which were prepared through the salt metathesis between the bis(yldiide) mercury complex, [Hg{C(PPh<sub>3</sub>)(SPPH<sub>2</sub>)<sub>2</sub>}], and [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>AnCl<sub>2</sub>] (Scheme 1).

Due to the intrinsic ability of organomercury compounds to undergo transmetalation under mild conditions, we targeted the synthesis of an yldiide mercury complex. To date, only one

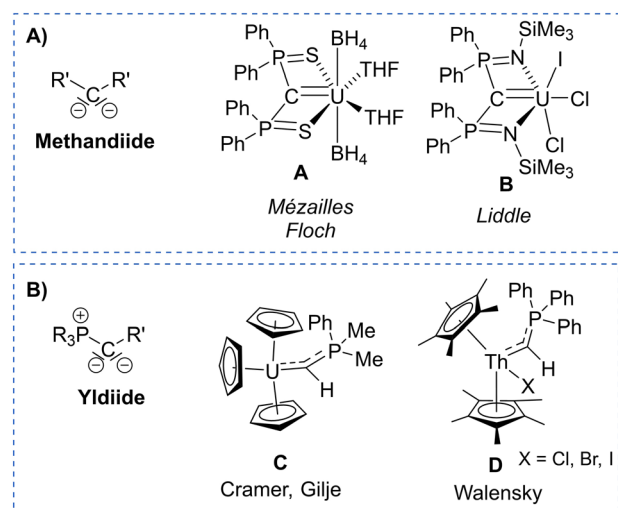


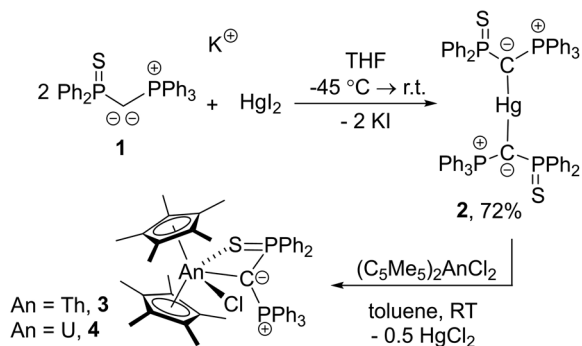
Fig. 1 Examples of reported actinide carbene complexes based on (A) methandiide and (B) yldiide ligands.

<sup>a</sup> Department of Chemistry, University of Missouri, Columbia, MO 65211, USA. E-mail: walenskyj@missouri.edu

<sup>b</sup> Faculty of Chemistry and Biochemistry, Ruhr-University Bochum, Bochum 44801, Germany. E-mail: viktorija.gessner@rub.de

† Electronic supplementary information (ESI) available: Experimental, spectroscopic, crystallographic, and computational details are given in the ESI. CCDC 2307044–2307048. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3cc05553a>





Scheme 1 Synthesis of bis(yldiide)mercury, **2**, and Th, **3**, and U, **4**, yldiide complexes.

mercury yldiide complex has been reported by Niecke and coworkers, but no reactivity studies were presented.<sup>45</sup> We selected the thiophosphinoyl-substituted potassium yldiide  $[\text{K}\{\text{C}(\text{PPh}_3)(\text{SPPH}_2)\}]$  (**1**) previously reported by us as a test system,<sup>46</sup> which we anticipated to form more stable complexes due to the potential additional coordination of the sulphur donor (for crystal structure of **1** see the ESI<sup>†</sup>). Treatment of  $\text{HgI}_2$  with two equivalents of **1** results in a shift in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum from  $-15.8$  and  $24.2$  ppm for the potassium yldiide to  $21.8$  and  $43.6$  ppm. The complete consumption of the starting materials and the appearance of a single set of signals suggested the formation of a symmetric bis-yldiide complex, which was confirmed by single crystal X-ray diffraction (sc-XRD) analysis (Fig. 2, top).

**2** crystallizes as a  $C_2$  symmetric complex with the expected linear geometry around mercury ( $\text{C-Hg-C}$  angle:  $178.3(7)^\circ$ ) and

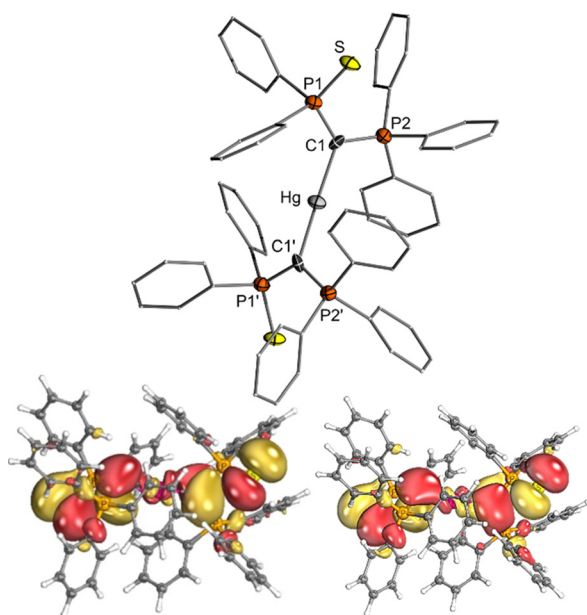


Fig. 2 (top) Crystal structure of mercury complex **2**. Ellipsoids are drawn at the 50% probability level. Important bond lengths and angles are given in Table 1. (bottom) Representations of the HOMO and HOMO-1 of **2** (isosurface value:  $0.2 \text{ e } \text{Å}^{-3}$ ).

an almost perpendicular arrangement of the two ylide ligands ( $\text{P1-C1-C1'-P1}'$ :  $92.8(9)^\circ$ ) relative to each other. The Hg-C bond lengths amount to  $2.096(11) \text{ \AA}$  and are thus similar to those ( $2.051(4) \text{ \AA}$ ) reported by Niecke *et al.* for a bis(yldiide) complex with an  $\text{ArNP}(\text{Ar})=\text{C}(\text{H})$  ligand ( $\text{Ar} = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$ ).<sup>45</sup> This distance is in the range of reported Hg-C single bonds,<sup>47</sup> thus ruling out any double bond character. This is also reflected by the small Wiberg bond index (WBI) of only 0.46 suggesting a strong ionic contribution to the bonding situation. Nonetheless, the P-C bonds in the ylide ligands of **2** are distinctly elongated compared to those found in the potassium yldiide **1-K** indicating a still significant charge transfer from the yldiide ligand to mercury. This increase in bond distances is more pronounced for the C1-P2 bond to the phosphonium group which elongates by more than  $0.2 \text{ \AA}$ , indicating the presence of a single rather than an ylidic bonding due to the reduced negative natural charge at C1. This is further supported by density functional theory (DFT) studies (b3pw91/def2TZVP/MWB60) together with natural bond orbital (NBO) analyses, which revealed a decreased Wiberg bond index of this bond and a surprisingly high negative NBO charge at the ylidic carbon atom ( $-1.634 \text{ e}$ ). NBO analysis yields a fully ionic bonding situation with a mercury dication bonded by two anionic yldiide ligands. However, strong second-order perturbation interactions between the  $\sigma$ -symmetric lone pair at carbon and an empty orbital at mercury indicate a strong dative bonding in line with the increased C1-P distances. The  $\pi$  symmetric lone pair is only minimally involved in the Hg-C bonding as is also apparent from the two highest molecular orbitals (HOMO and HOMO-1), which represent the combination of the  $\pi$  symmetric lone pairs at the ylidic carbon atom, with little contribution of the metal center (Fig. 2).

Given the weak C-Hg interaction, we next tested the ability of **2** to form actinide phosphinocarbene complexes. To our delight, reaction of uranium and thorium precursors  $[(\text{C}_5\text{Me}_5)_2\text{AnCl}_2]$  ( $\text{An} = \text{Th}, \text{U}$ ) with half an equivalent of **2** led to clean conversion to new products and yielded the corresponding actinide yldiide complexes  $[(\text{C}_5\text{Me}_5)_2\text{An}\{\kappa^2\text{-}(\text{C},\text{S})\text{-C}(\text{PPh}_3)(\text{SPPH}_2)\}(\text{Cl})]$  ( $\text{An} = \text{Th}, \text{3}; \text{U}, \text{4}$ ) as colourless and orange solids in 36–38% yield.<sup>48</sup> The thorium complex features two doublets in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 20.5 and 9.45 ( $^2J_{\text{PP}} = 8.2 \text{ Hz}$ ) ppm, while the two signals for the paramagnetic uranium complex appear at  $-47.4$  and  $-506.9$  ppm. The signals for the central carbon atom in **3** (as well as in **2**) could only be detected for derivatives with a  $^{13}\text{C}$  labelled ylidic carbon atom. In the case of the diamagnetic Th(IV) complex **3**, this carbenic carbon atom was observed at 42.0 ppm as a doublet of doublets ( $^1J_{\text{CP}} = 38.2 \text{ Hz}, 16.5 \text{ Hz}$ ) in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. This signal appears in a similar range as the multiplet observed for **2** (43.9 ppm;  $^1J_{\text{CP}} = 79.4 \text{ Hz}, 67.1 \text{ Hz}$ ), but with markedly lower  $^1J_{\text{CP}}$  coupling constants. Notably, these  $^{13}\text{C}$  signals are down-field shifted compared to yldiide **1-K** (27.6 ppm; dd,  $80.6 + 77.6 \text{ Hz}$ ), but clearly high-field shifted compared to carbene complexes with  $\text{M}=\text{C}$  double bonds, suggesting a carbanionic character.<sup>39,40</sup>

The structure of both actinide complexes was unambiguously elucidated by sc-XRD analysis (Fig. 3 and ESI<sup>†</sup>) and



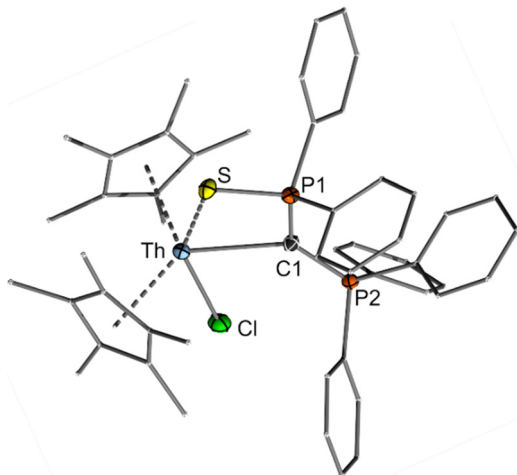


Fig. 3 Crystal structure of the thorium complex **3**. The uranium complex is isostructural (Fig. S24, ESI†). Important bond lengths and angles are given in Table 1.

confirms the expected carbene complex formation, with the ligand functioning as a bidentate C,S donor. Interestingly, both complexes feature distinct differences in the metal–carbon bond lengths relative to reported carbene and methandiide complexes, which argue for different bonding situations in these complexes. For example, the Th–C(yldiide) bond length of 2.6220(16) Å is long compared to those reported for Th–C(phosphonio-carbene) complexes (e.g. 2.3235(1)–2.299(6) Å in complexes **D**<sup>38,49,50</sup> or 2.362(2) Å in [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>Th(CHPhPh<sub>3</sub>)] or Th–C(methandiide) complexes (2.410(8)–2.489(14) Å).<sup>23</sup> Likewise, the U–C(yldiide) bond of 2.555(3) Å is long compared to U–C(methandiide) bonds (2.274(8)–2.393(2) Å),<sup>23</sup> but shorter than U(IV)–C(NHC) distances (2.573(5)–2.668(2) Å).<sup>7,51–53</sup> In contrast, the An–S bond lengths of 2.8885(4) and 2.8357(8) Å for **3** and **4**, respectively, are slightly shorter than the average An–S bond distances in dithiophosphate complexes (e.g. [An(S<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub>] with 2.907 Å for Th and 2.848 Å for U),<sup>54</sup> suggesting a strong covalent interaction. Comparison of the C–P distances in the yldiide ligands of **3** and **4** with the yldiide **1-K** and the mercury complex **2** was revealed to be highly informative regarding the bonding interaction. Both bond lengths in the actinide complexes are in between those found for **1-K** and **2**, indicating a high negative charge at the C1 carbon atom and hence a more ionic metal–carbon bond.

DFT calculations (see the ESI† for details and a more detailed discussion of the bonding situation in compounds **1–4**) were performed to obtain further insights into the bonding situation of **3** and **4**. Both complexes feature low Wiberg bond indices for the metal carbon bond, arguing for a single rather than a double bond, in line with the long metal carbon distances observed in the crystal structures (Table 1). This single bond character is further confirmed by atoms in molecules (AIM) calculations,<sup>55</sup> which in all cases yielded bond critical points (BCP) as a decisive criterion for the bonding interaction, but with ellipticity values close to zero as a result of the cylindrical symmetry of the M–C single bond. Natural bond

Table 1 Comparison of the crystallographic and computational parameters (WBIs and NPA charges); (b3pw91/def2TZVP/MWB60) of the yldiide **1-K** and yldiide complexes **2–4**

	<b>1-K</b>	<b>1<sub>2</sub>Hg (2)</b>	Th complex <b>3</b>	U complex <b>4</b>
<i>d</i> (P(S)–C) [Å]	1.664(3)	1.750(11)	1.706(2)	1.709(4)
<i>d</i> (PPh <sub>3</sub> –C) [Å]	1.607(3)	1.839(13)	1.699(2)	1.704(4)
<i>d</i> (P=S) [Å]	2.018(1)	1.994(4)	2.032(1)	2.031(1)
<i>d</i> (C–M) [Å]	—	2.096(11)	2.622(2)	2.555(3)
<i>d</i> (S–M) [Å]	3.157(1)	—	2.888(1)	2.836(1)
P–C–P [°]	141.3(2)	120.5(7)	123.7(1)	123.4(2)
WBI (C–M)	0.0180	0.4607	0.605	0.7229
WBI (C–P(S))	1.1775	0.9855	1.077	1.0857
WBI (C–PPh <sub>3</sub> )	1.3865	1.1642	1.1467	1.15
WBI (P=S)	1.1605	1.3118	1.0077	1.0464
<i>q</i> (C1) [e]	–1.556	–1.634	–1.488	–1.421
<i>q</i> (PPh <sub>3</sub> ) [e]	1.560	1.624	1.652	1.651
<i>q</i> (P(S)) [e]	1.395	1.383	1.515	1.492
<i>q</i> (M) [e]	0.876	1.249	0.755	0.575
<i>q</i> (S) [e]	–0.789	–0.661	–0.388	–0.389
Σ <i>q</i> (ligand)	–0.954	–0.625	–0.007	–0.011
ρ(BCP–MC)	0.014	0.126	0.062	0.069
ε(BCP–MC)	0.039	0.041	0.018	0.041

orbital (NBO)<sup>56</sup> analysis again resulted in an extreme bonding picture with two lone pairs remaining at the C1 carbon atom. The covalent bonding is solely expressed by strong second-order perturbation interactions between the σ-symmetric lone pair at carbon and empty metal orbitals. The π-symmetric lone pair at carbon shows again no or only a minimal interaction with metal orbitals. Overall, the bonding analysis argues for the presence of a M–C single bond in both complexes with a high ionic contribution. Accordingly, a high negative charge (approx. –1.4 for both actinide complexes) remains at the ylidic carbon centre. However, comparison of the overall charge of the yldiide ligand in the mercury complex **2** and the actinide complexes **3** and **4** revealed a significant charge transfer in the course of the transmetalation process from –0.625 e in **2** to almost zero in the thorium and the uranium complex. This net charge transfer mostly arises from the sulphur rather than from the carbon donor and is presumably the driving force of the transmetalation process. The calculated high ionic bonding character is commensurate with the long Th–C bond and upfield ylidic carbon resonances found in the solid-state structure and NMR spectrum, respectively. Hence, the trend of more downfield shifts in the <sup>13</sup>C NMR spectra equating to increased covalent character holds in this case.<sup>50,51</sup>

In conclusion, we report the first synthesis of yldiide actinide complexes *via* salt metathesis with a bis(yldiide) mercury complex, which showed promising capabilities as a yldiide transfer reagent also for broader applications. The obtained thorium and uranium complexes exhibit long metal carbon distances as a consequence of a highly ionic bonding situation. DFT studies confirm that only little electron density is shifted from the yldiide towards the metal centre resulting in a M–C single bond with high ionic contribution. This contrasts previously reported phosphino carbene actinide complexes, which implies that yldiides depending on the substituents at the carbon may form Schrock-type carbene, but also ionic bonding situations similar to methandiide ligands.



This project was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2033 – 390677874 – RESOLV and through research grant (DA 1402/6-1). J. R. W. gratefully acknowledges the Alexander von Humboldt Foundation for the award of a research fellowship and the Department of Energy, Office of Basic Energy Sciences, Heavy Element Program under Award DE-SC0021273. M. J. and A. J. G. thank the RUB research school for travel grants.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- 1 T. W. Hayton, *Chem. Commun.*, 2013, **49**, 2956–2973.
- 2 J. Warren, J. Oldham, S. M. Oldham, B. L. Scott, K. D. Abney, W. H. Smith and D. A. Costa, *Chem. Commun.*, 2001, 1348–1349.
- 3 H. Nakai, X. Hu, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Inorg. Chem.*, 2004, **43**, 855–857.
- 4 T. Mehdoui, J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Chem. Commun.*, 2005, 2860–2862.
- 5 W. J. Evans, S. A. Kozimor and J. W. Ziller, *Polyhedron*, 2004, **23**, 2689–2694.
- 6 D. Pugh, J. A. Wright, S. Freeman and A. A. Danopoulos, *Dalton Trans.*, 2006, 775–782.
- 7 P. L. Arnold, A. J. Blake and C. Wilson, *Chem. – Eur. J.*, 2005, **11**, 6095–6099.
- 8 S. A. Mungur, S. T. Liddle, C. Wilson, M. J. Sarsfield and P. L. Arnold, *Chem. Commun.*, 2004, 2738–2739.
- 9 P. L. Arnold, I. J. Casely, Z. R. Turner and C. D. Carmichael, *Chem. – Eur. J.*, 2008, **14**, 10415–10422.
- 10 (a) J. A. Seed, L. Vondung, R. W. Adams, A. J. Wooles, E. Lu and S. T. Liddle, *Organometallics*, 2022, **41**, 1353–1363; (b) E. Lu, J. T. Boronski, M. Gregson, A. J. Wooles and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2018, **57**, 5506.
- 11 J. A. Seed, M. Gregson, F. Tuna, N. F. Chilton, A. J. Wooles, E. J. L. McInnes and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2017, **56**, 11534–11538.
- 12 A. K. Maity, R. J. Ward, D. M. R. Y. P. Rupasinghe, M. Zeller, J. R. Walensky and S. C. Bart, *Organometallics*, 2020, **39**, 783.
- 13 J. F. DeJesus, R. W. F. Kerr, D. A. Penchoff, X. B. Carroll, C. C. Peterson, P. L. Arnold and D. M. Jenkins, *Chem. Sci.*, 2021, **12**, 7882–7887.
- 14 W. Fang, S. Pan, W. Su, L. Zhao, G. Frenking and C. Zhu, *CCS Chem.*, 2021, **3**, 2324.
- 15 W. Su, S. Pan, S. Wang, L. Zhao, G. Frenking and C. Zhu, *Nat. Commun.*, 2018, **9**, 4997.
- 16 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.
- 17 W. Su, Y. Ma, L. Xiang, J. Wang, S. Wang, L. Zhao, G. Frenking and Q. Ye, *Chem. – Eur. J.*, 2021, **27**, 10006–10011.
- 18 T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. L. Floch and N. Mézailles, *J. Am. Chem. Soc.*, 2009, **131**, 963–972.
- 19 J.-C. Tourneux, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, P. Le Floch and M. Ephritikhine, *Organometallics*, 2011, **30**, 2957–2971.
- 20 J.-C. Tourneux, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles and M. Ephritikhine, *J. Am. Chem. Soc.*, 2011, **133**, 6162–6165.
- 21 O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2011, **50**, 2383–2386.
- 22 O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Dalton Trans.*, 2010, **39**, 5074–5076.
- 23 O. J. Cooper, D. P. Mills, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, *Chem. Eur. J.*, 2013, **19**, 7071–7083.
- 24 L. T. Scharf and V. H. Gessner, *Inorg. Chem.*, 2017, **56**, 8599–8607.
- 25 A. Sarbajna, V. S. V. S. N. Swamy and V. H. Gessner, *Chem. Sci.*, 2021, **12**, 2016–2024.
- 26 T. Scherpf, K.-S. Feichtner and V. H. Gessner, *Angew. Chem., Int. Ed.*, 2017, **56**, 3275–3279.
- 27 C. Mohapatra, L. T. Scharf, T. Scherpf, B. Mallick, K.-S. Feichtner, C. Schwarz and V. H. Gessner, *Angew. Chem., Int. Ed.*, 2019, **58**, 7459–7463.
- 28 C. Mohapatra, H. Darmandeh, H. Steinert, B. Mallick, K.-S. Feichtner and V. H. Gessner, *Chem. – Eur. J.*, 2020, **26**, 15145.
- 29 T. Stalder, F. Krischer, H. Steinert, P. Neigenfind and V. H. Gessner, *Chem. – Eur. J.*, 2022, **28**, e202104074.
- 30 W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer and W. D. Korte, *J. Am. Chem. Soc.*, 1974, **96**, 2847–2854.
- 31 X. Li, A. Wang, L. Wang, H. Sun, K. Harms and J. Sundermeyer, *Organometallics*, 2007, **26**, 1411–1413.
- 32 (a) X. Li, M. Schopf, J. Stephan, K. Harms and J. Sundermeyer, *Organometallics*, 2002, **21**, 2356–2358; (b) S. Yogendra, T. Weyhermüller, A. W. Hahn and S. DeBeer, *Inorg. Chem.*, 2019, **58**, 9358.
- 33 A. Y. Khalimov, E. M. Leitao and W. E. Piers, *Organometallics*, 2012, **31**, 5634–5637.
- 34 R. Zurawinski, C. Lepetit, Y. Canac, M. Mikolajczyk and R. Chauvin, *Inorg. Chem.*, 2009, **48**, 2147–2155.
- 35 S. Lapointe, P. Duari and V. H. Gessner, *Chem. Sci.*, 2023, **14**, 3816–3825.
- 36 R. Taakili, C. Barthes, C. Lepetit, C. Duhayon, D. A. Valyaev and Y. Canac, *Inorg. Chem.*, 2021, **60**, 12116–12128.
- 37 R. E. Cramer, R. B. Maynard, J. C. Paw and J. W. Gilje, *J. Am. Chem. Soc.*, 1981, **103**, 3589–3590.
- 38 S. Fortier, J. R. Walensky, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 6894–6897.
- 39 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.
- 40 W. Mao, L. Xiang, L. Maron, X. Leng and Y. Chen, *J. Am. Chem. Soc.*, 2017, **139**, 17759–17762.
- 41 T. Scherpf, R. Wirth, S. Molitor, K.-S. Feichtner and V. H. Gessner, *Angew. Chem., Int. Ed.*, 2015, **54**, 8542–8546.
- 42 C. Schwarz, L. T. Scharf, T. Scherpf, J. Weismann and V. H. Gessner, *Chem. – Eur. J.*, 2019, **25**, 2793–2802.
- 43 H. Darmandeh, T. Scherpf, K.-S. Feichtner, C. Schwarz and V. H. Gessner, *Z. Anorg. Allg. Chem.*, 2020, **646**, 835–841.
- 44 M. Jörges, R. M. Gauld, H. Steinert, L. Kelling, V. S. V. S. N. Swamy, A. Kroll, B. Mallick and V. H. Gessner, *Chem. – Eur. J.*, 2023, **29**, e202300504.
- 45 T. Baumgartner, B. Schinkels, D. Gudat, M. Nieger and E. Niecke, *J. Am. Chem. Soc.*, 1997, **119**, 12410–12411.
- 46 M. Jörges, F. Krischer and V. H. Gessner, *Science*, 2022, **378**, 1331–1336.
- 47 J. G. Melnick and G. Parkin, *Science*, 2007, **317**, 225–227.
- 48 The Th complex contained residual toluene, which was difficult to remove without decomposition. Therefore, the actual yield of the complex is slightly lower (see ESI<sup>†</sup>).
- 49 P. Rungthanaphatsophon, P. Huang and J. R. Walensky, *Organometallics*, 2018, **37**, 1884–1891.
- 50 D. E. Smiles, G. Wu, P. Hrobárik and T. W. Hayton, *Organometallics*, 2017, **36**, 4519–4524.
- 51 W. J. Evans, S. A. Kozimor and J. W. Ziller, *Polyhedron*, 2004, **23**, 2689–2694.
- 52 D. Pugh, J. A. Wright, S. Freeman and A. A. Danopoulos, *Dalton Trans.*, 2006, 775–782.
- 53 J. F. DeJesus, R. W. F. Kerr, D. A. Penchoff, X. B. Carroll, C. C. Peterson, P. L. Arnold and D. M. Jenkins, *Chem. Sci.*, 2021, **12**, 7882–7887.
- 54 A. C. Behrle, A. Kerridge and J. R. Walensky, *Inorg. Chem.*, 2015, **54**, 11625–11636.
- 55 R. F. A. Bader, *Chem. Rev.*, 1991, **91**, 893–928.
- 56 E. D. Glendenning, J. K. Badenhop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis and F. Weinhold, *NBO 7.0.*, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2018.

