

CHEMISTRY A European Journal



Accepted Article

Title: Synthesis and Structure of Uranium-Silylene Complexes.

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202000214

Link to VoR: http://dx.doi.org/10.1002/chem.202000214

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Synthesis and Structure of Uranium–Silylene Complexes

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Abstract: While carbene complexes of uranium have been known for over a decade, there are no reported examples of complexes between an actinide and a "heavy carbene." Here we report the syntheses and structures of the first uranium–heavy tetrylene complexes: (CpSiMe₃)₃U–Si[PhC(NR)₂]R' (R = 'Bu, R' = NMe₂ 1; R = 'Pr, R' = PhC(N'Pr)₂ 2). Complex 1 features a kinetically robust uranium–silicon bonding interaction, while the uranium–silicon bond in 2 is easily disrupted thermally or by competing ligands in solution. Calculations reveal polarized σ bonds, but depending on the substituents at silicon a substantial π bonding interaction is also present. The complexes possess relatively high bond orders which suggests primarily covalent bonding between uranium and silicon. These results comprise a new frontier in actinide–heavy main group bonding.

Studies of the fundamental coordination chemistry of the actinide elements lag behind those of the transition metals.^[1] Recent experimental and computational investigations into the chemistry of the actinides incorporating new metal–element bonds have done much to challenge our understanding of actinide electronic structure. Despite the growing number of examples of bonds between actinides and heavy group 13,^[2–4] group 15,^[5] and group 16^[6] elements, there remain few structurally characterized examples of unsupported bonds between actinides and group 14 elements heavier than carbon.^[7–9]

In 2005, Ephritikhine and co-workers reported that tetramethyl imidazol-2-ylidene, an "Arduengo-type" Nheterocyclic carbene (NHC), was capable of preferential binding of uranium(III) complexes over isostructural cerium(III) analogs.^[10] The propensity for the NHC to bind uranium with modest selectivity over cerium was attributed to the "softness" of the NHC ligand,^[11] which has a greater capacity to interact with the diffuse and energetically accessible 5f orbitals of uranium than the core-like 4f orbitals of cerium.^[12] Such differentiation between trivalent 4f and 5f elements is of particular significance to the area of nuclear waste processing and remediation.[13] While further examples of actinide-carbene complexes have since emerged.^[14-16] species featuring bonds between actinides and a heavy 'tetrylene' - a formally divalent group 14 element heavier than carbon - have remained elusive. Since the heavier analogs of carbon should be "softer." we became interested in stabilizing bonds between actinides and heavy tetrylenes, as

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such bonding interactions may possess a higher degree of covalent character and could afford higher selectivity for trivalent 5f ions. Indeed, a recent theoretical study by Shi and co-workers predicted a series of polarized σ bonds between uranium and divalent heavy group 14 elements.^[17] We were particularly drawn to the amidinate-supported silylenes which have emerged in recent years. The 2010 discovery by Roesky and co-workers that amidinate-supported silylenes could be prepared in high yield through dehydrochlorination pathways has caused a surge of growth in their research and application;^[18,19] these silylenes have been bound to metals from nearly every group in the transition metal series^[20] as well as to lanthanides.^[21] The growing application of these silylenes is largely due to the ease with which the parent chlorosilylene Si[PhC(N/Bu)2]Cl can be derivatized to feature substituents such as alkoxy, amino, phosphino, and even alkyl groups, thus accessing an array of silylenes with varying steric and electronic properties.^[20,22,23]

In 2009, we showed that the uranium(III) complex (CpSiMe₃)₃U could be employed to generate species containing actinide–group 13 bonds with aluminum(I) and gallium(I).^[2] (CpSiMe₃)₃U has shown considerable versatility as a σ -acceptor and π -donor: this species was the first molecular uranium complex known to bind CO at room-temperature.^[24,25] Here we report the synthesis and characterization of the first actinide–heavy tetrylene complexes, obtained by reaction of (CpSiMe₃)₃U with amidinate-supported silylenes. These complexes address a gap in actinide–main group bonding and contribute to our growing understanding of covalent bonding in the actinides.



Scheme 1. Synthesis of complexes 1 and 2.

Considering the minimal steric encumbrance of the dimethylamido substituent, we targeted the silylene Si[PhC(N^tBu)₂](NMe₂) as an ideal candidate for bindina (CpSiMe₃)₃U. Mixing room-temperature hexane solutions of (CpSiMe₃)₃U and Si[PhC(N⁴Bu)₂](NMe₂) yielded a dark purple solution. Concentration and cooling to -40 °C overnight afforded burgundy crystals of analytically pure (CpSiMe₃)₃U-Si[PhC(N^tBu)₂](NMe₂) (1) in 93% yield (Scheme 1). An X-ray diffraction study on single crystals of 1 revealed a uraniumsilicon bond length of 3.1637(1) Å (Figure 1). While this distance is longer than the sum of the covalent radii of uranium and silicon as tabulated by Pyykkö (2.86 Å)^[26] or Alvarez (3.07 Å),^[27] bond lengths between *f*-elements and heavy main group atoms have often exceeded the sums of the relevant covalent radii, [3,28-^{30,21]} suggesting that these radii may not be the best predictor of main group element-f element bond length.[31] Compared to its 'base-free' solid state structure, [32] the (CpSiMe₃)₃U subunit has

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Figure 1. Crystal structure of **1** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances and angles are tabulated in the Supporting Information (Table S1).

reorganized to minimize unfavorable steric interactions: the trimethylsilyl (TMS) groups on the cyclopentadienyl rings of $(CpSiMe_3)_3U$ are oriented away from the fourth ligand, an arrangement that has only been observed previously in some dimeric structures containing bridging ligands.^[33–35] The bond lengths and angles of the Si[PhC(N'Bu)₂](NMe₂) fragment are largely unchanged upon coordination (Table S1),^[36] although the *tert*-butyl groups are angled further away from the silicon center (C(3)–N(2)–C(10) 129.8(2), C(3)–N(3)–C(14) 129.5(3)), likely as a result of steric interactions.

The room-temperature ¹H NMR spectrum of **1** shows Si[PhC(N'Bu)₂](NMe₂) resonances shifted well out of their usual diamagnetic region (Figure S1). Variable-temperature (VT) ¹H NMR did not reveal free Si[PhC(N'Bu)₂](NMe₂) upon heating to 84 °C, indicative of a remarkably stable and persistent bonding interaction with (CpSiMe₃)₃U (Figure S3). The ²⁹Si(¹H} NMR spectrum of **1** shows a sharp resonance for the cyclopentadienyl-based TMS groups at -170 ppm, shifted upfield ~5 ppm from their value in (CpSiMe₃)₃U (Figure S2). The resonance corresponding to the silicon center of the Si[PhC(N'Bu)₂](NMe₂) subunit, typically located around -2.6 ppm,^[36] was not observed between 200 and -400 ppm due to its proximity to the paramagnetic uranium(III) center.

The room-temperature electronic absorption spectrum of **1** shows high energy charge-transfer (CT) bands around 460 and 500 nm; these transitions are red-shifted relative to the analogous CT bands in the spectrum of isolated (CpSiMe₃)₃U (Figure S11). Additionally, the region between 600 and 1500 nm reveals a series of Laporte-forbidden *f*-*f* transitions that are characteristic of uranium(III) (Figure 2).^[31,37] The energies of these transitions differ considerably from those of 'base-free' (CpSiMe₃)₃U even at low concentrations (2 mM), consistent with the lower symmetry of **1** and suggestive of an A + B \rightleftharpoons AB equilibrium that heavily favors the products side in solution.

Having isolated a uranium-silylene complex using the sterically accessible Si[PhC(N'Bu)₂](NMe₂) silylene, we sought to investigate the influence of increasing steric encumbrance on the U-Si bond properties. A second example of a uranium-silylene complex (2) derived from the bulkier silylene Si[PhC(N'Pr)₂]₂ was prepared similarly in 99% yield and

structurally characterized (Scheme 1, Figure S16). Interestingly, and in contrast to its adducts with Lewis-acidic boron, aluminum, and transition metal compounds,^[38] the Si[PhC(N[/]Pr)₂]₂ fragment in **2** has retained one monodentate amidinate ligand, likely to minimize steric strain.



Figure 2. Solution-state NIR absorption spectra of $(CpSiMe_3)_3U$ (blue) and $(CpSiMe_3)_3U$ –Si[PhC(N'Bu)₂](NMe₂) (1, green) in toluene, and the solid-state diffuse reflectance spectrum of $(CpSiMe_3)_3U$ –Si[PhC(N'Pr)₂]₂ (2, yellow). Since 1 and 2 are in equilibrium with their starting materials in solution, absorption spectra are reported on an arbitrary intensity scale. Furthermore, the spectra in Figure 2 have been scaled arbitrarily to highlight similarities and differences.

The room-temperature ¹H NMR spectrum of a dilute C₆D₆ solution of 2 shows only minor shifts and broadening of the starting material peaks, indicative of dynamic behavior in solution and an equilibrium that heavily favors the reactants side (Figure S5). At higher concentrations, however, the shifts and broadening effects become more dramatic (Figure S6). In the room-temperature ²⁹Si{¹H} NMR spectrum of **2**, the Cp-based TMS resonance was observed at -164.4 ppm (Figure S7), essentially unchanged from its value in the isolated uranium(III) starting material (-165 ppm).^[39] As with complex 1, a resonance attributable to the silvlene was not observed. To probe the temperature dependence of the solution equilibrium, we performed VT ¹H NMR spectroscopic studies on 2 from 23 to -80 °C (Figure S8). Resonances attributable to the isopropyl methyl and methyne groups of Si[PhC(N/Pr)₂]₂ broadened and shifted out of the diamagnetic region as the temperature was lowered, indicating closer contact with the paramagnetic uranium(III) center. However, more detailed analysis of the VT ¹H NMR data was obscured by the broadness of most signals at lower temperature, which may result from fluxionality not only between the starting materials and 2 but also between the mono- vs. bidentate binding modes of the amidinato ligands bound to Si[PhC(N/Pr)₂]₂.

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In contrast to 1, the room-temperature electronic absorption spectrum of 2 in solution is nearly identical to the summation of the spectra of the two starting materials (Figures S12), providing further evidence that the solution equilibrium between the reactants and 2 lies on the reactants side at room temperature. The diffuse reflectance spectrum of solid 2, on the other hand, bears an absorbance profile strikingly similar to the solutionstate NIR spectra of 1 (Figure 2), including prominent f-f transitions at approximately 920, 980, 1020, 1080, 1220, and 1335 nm. The close resemblance of the spectra suggests that, while 2 readily undergoes ligand dissociation in solution, the uranium-silylene interaction is less perturbed in the solid state yielding a complex that is very similar electronically to 1. Furthermore, the infra-red (IR) spectrum of 2 shows substantial differences relative to those of the starting materials (Figure S15); evidently, the uranium-silicon bonding interaction in 2 changes the electronic and vibrational nature of the Si[PhC(N/Pr)₂]₂ unit. further discounting the possibility that the uranium and silicon starting materials simply co-crystallized.

Magnetometric studies of **1** and **2** are ongoing. Preliminary results on the DC magnetic susceptibility of **2** are consistent with the trivalent oxidation state assignment for uranium (Figures S17-S18).^[40] Notably, the room-temperature $\chi_M T$ value of **2** is lower than that of 'base-free' (CpSiMe₃)₃U (Figure S17), which may reflect the stronger ligand-field splitting in **2**.

Accessing a third uranium-silylene complex via the widely utilized parent chlorosilylene, Si[PhC(N^tBu)₂]Cl, proved impossible under our conditions: reaction between Si[PhC(N/Bu)2]Cl and (CpSiMe3)3U resulted in conversion the complete to uranium(IV) chloride. (CpSiMe₃)₃UCl,^[41] and the bis(silylene), Si₂[PhC(N^tBu)₂]₂,^[42] as confirmed by ¹H NMR spectroscopy as well as unit cell checks of the crystalline products (Figure S10). Analogous reactivity toward Si[PhC(N^tBu)₂]Cl has been observed for a samarium(II) metallocene.^[21] The reduction from silicon(II) to silicon(I) highlights the well-known reducing power of uranium(III) organometallic complexes.

The electronic structures of both silylene complexes have been investigated using density functional methods: natural bond orbital (NBO) analyses of geometry-optimized 1 and 2 reveal polarized σ bonds between uranium and silicon (Figure 3, Table S3). The Wiberg bond indices for 1 and 2 are relatively high (~0.7) compared to those calculated for other donoracceptor complexes containing the (CpSiMe₃)₃U fragment and suggest a primarily covalent single bond between uranium and silicon.^[2] In both complexes, the uranium hybrid acceptor orbital is of primarily d parentage (58%) but with substantial f-orbital contributions (12%) (Table S3). Similar f-orbital contributions were calculated for dative bonds between U(III) and the group 13 diyls AICp* and GaCp*.^[2] The silicon donor hybrids in both complexes are of primarily s character (73% s, 27% p), falling in the range of values reported for amidinato-silylene complexes of transition metals,^[43] while a substantially higher percentage of p character was calculated for the formally X-type group 14 ligands in (TIPSTREN)U-SnMe3 and the model complex H3Si-U(NH₂)₃.^[8,9] Consistent with our experimental observations in the ¹H NMR and UV/vis/NIR spectra of 1 and 2, complex 1 is calculated to have a BDE nearly twice that of complex 2. The



Figure 3. Kohn-Sham α -spin HOMO-4 of 1 showing the primary U–Si bonding orbital.

BDE for 1, at 11.9 kcal/mol, is remarkably high (cf. 13.1 kcal/mol for the model complex Cp₃U–pyridine).^[2] The stability of the uranium–silicon bond in 1 is further demonstrated by the low-lying nature of the bonding orbital (HOMO–4) which contrasts with the bonding orbital in 2 (HOMO); accordingly, the uranium–silicon bond in 1 should be less easily perturbed. Additionally, at the second order NBO level, a significant π backbonding contribution (10.3 kcal/mol) is present in 1, while the backbonding in 2 is less than half as strong (Table S3). The substantial backbonding in 1 contrasts with the NBO analysis performed on the theoretical complex (CpSiMe₃)₃U–Si(NCHMes)₂ investigated by Shi and co-workers, which found no U–Si π bonding character.^[17]

We have begun studies into the reactivity of these complexes with the aim of probing the nature of the U-Si interaction. Addition of 1 atm of CO to a benzene-d₆ solution of 1 resulted in an equilibrium between the CO and silvlene adducts of (CpSiMe₃)U, as monitored by ¹H NMR spectroscopy (Figure S4). The ¹H NMR spectrum of **1** after the addition of CO closely resembled the spectrum of isolated 1, indicating that the equilibrium was not dominated by (CpSiMe₃)₃U-CO.^[24] The spectrum of 1 could be recovered by freeze-pump-thawing the solution and replacing the CO atmosphere with dry N₂. Although qualitative due to the unknown concentration of CO in solution, the ability of Si[PhC(N'Bu)2](NMe2) to compete with CO for uranium binding further confirmed the kinetic persistence of the uranium-silylene interaction of 1 in solution, as the metal-ligand bond dissociation energy in (CpSiMe₃)₃U-CO has been estimated at 14.3 kcal mol^{-1.[25]} In contrast, addition of 1 atm of CO to a benzene-d₆ solution of 2 showed essentially complete conversion to (CpSiMe₃)₃U–CO and free Si[PhC(N/Pr)₂]₂ (Figure S9). These ligand substitution reactions highlight the dative bonding character of 1 and 2 while reaffirming that the U-Si bond of 1 is less easily perturbed than that of 2.

In conclusion, we have synthesized and characterized the first complexes containing actinide-heavy tetrylene bonds. Complex **1** possesses a remarkably stable uranium-silicon bonding interaction that can compete with strong π -acids such as CO, while complex **2** shows only a weak interaction in solution that can be stabilized by cooling or crystallization. These bonds can be described as polarized covalent σ bonds,

featuring high calculated bond orders and substantial f-orbital contributions to the bonding orbital. In the case of 1, a significant π backbonding contribution is present, contrasting theoretical expectations for uranium-silylene species^[17] and highlighting the importance of investigating actinide-heavy tetrylene bonds. Reaction of (CpSiMe₃)₃U with a chlorosilylene resulted in reduction to a silicon(I) dimer, emphasizing the importance of the silylene's supporting ligands to stabilizing uranium-silicon bonds. Current work is focused on the reactivity of 1 and 2, experimental determination of the thermodynamic parameters for uranium-silylene binding, and the synthesis of related actinide, lanthanide, and group 14 congeners.

Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry Program of the U.S. Department of Energy (DOE) at LBNL under Contract DE-AC02-05CH11231. I.J.B. acknowledges the U.S. DOE Integrated University Program for a graduate research fellowship. Collection and interpretation of the magnetic susceptibility data and near-IR spectra were supported by the National Science Foundation (NSF) under grant CHE-1800252to Prof. Jeffrey R. Long. M.A.B. acknowledges support from NSF GFRP No. DGE 1106400. We thank College of Chemistry's NMR facility staff for their assistance. NMR instruments are supported in part by National Institute of Health grant S10OD024998. We thank Drs. S. Minasian and M. E. Garner for helpful discussions.

Keywords: actinides · donor-acceptor interactions · heavy carbenes • silylenes • uranium

- S. T. Liddle, Angew. Chem. Int. Ed. 2015, 54, 8604-8641.
- S. G. Minasian, J. L. Krinsky, J. D. Rinehart, R. Copping, T. Tyliszczak, M. Janousch, D. K. Shuh, J. Arnold, *J. Am. Chem. Soc.* **2009**, *131*, [2] 13767-13783
- S. T. Liddle, J. McMaster, D. P. Mills, A. J. Blake, C. Jones, W. D. [3] Woodul, *Angew. Chem. Int. Ed.* **2009**, *48*, 1077–1080. A. B. Altman, A. C. Brown, G. Rao, T. D. Lohrey, R. D. Britt, L. Maron,
- [4]
- S. G. Minasian, D. K. Shuh, J. Arnold, *Chem. Sci.* **2018**, *9*, 4317–4324. S. P. Vilanova, J. R. Walensky, *Actinides: Pnictogen Complexes*. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*, R. A. Scott, [5] Ed.; Wiley: Hoboken 2018.
- M. Ephritikhine, Coord. Chem. Rev. 2016, 319, 35-62.
- [6] [7] M. Porchia, U. Casellato, F. Ossola, G. Rossetto, P. Zanella, R. Graziani, J. Chem. Soc. Chem. Commun. 1986, 1034-1035.
- P. L. Diaconescu, A. L. Odom, T. Agapie, C. C. Cummins, Organometallics **2001**, *20*, 4993–4995. M. S. Winston, E. R. Batista, P. Yang, A. M. Tondreau, J. M. Boncella, [8]
- [9] Inorg. Chem. 2016, 55, 5534-5539.
- T. Mehdoui, J.-C. Berthet, P. Thuéry, M. Ephritikhine, Chem. Commun. [10] 2005, 2860-2862.
- M.-T. Lee, C.-H. Hu, Organometallics 2004, 23, 976-983. [11]
- [12] K. L. Nash, Separation Chemistry for Lanthanides and Trivalent Actinides. In Handbook on the Physics and Chemistry of Rare Earths;
 K. A. Gschneidner Jr., L. Eyring, G. R. Choppin, G. H. Lander, Eds.;
 Elsevier Science, Amsterdam, 1994, vol. 18, 197–238.
 H. H. Dam, D. N. Reinhoudt, W. Verboom, *Chem. Soc. Rev.* 2007, *36*,
- [13] 367-377
- P. L. Arnold, S. T. Liddle, Chem. Commun. 2006, 3959–3971. [14]
- [15] S. Hameury, P. de Frémont, P. Braunstein, Chem. Soc. Rev. 2017, 46, 632-733.

- M. A. Boreen, J. Arnold, Multiple Bonding in Actinide Chemistry, In [16] Encyclopedia of Inorganic and Bioinorganic Chemistry, R. A. Scott, Ed.; Wiley: Hoboken 2018.
- X.-W. Chi, Q.-Y. Wu, J.-H. Lan, C.-Z. Wang, Q. Zhang, Z.-F. Chai, W.-[17] Q. Shi, Organometallics 2019, 38, 1963-1972
- S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, J. Am. Chem. [18] Soc. 2010, 132, 1123-1126.
- S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, Chem. Sci. 2012, 3, [19] 659-682
- [20] L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez, D. Polo, Coord. Chem. Rev. 2015, 300, 1-28.
- [21] R. Zitz, H. Arp, J. Hlina, M. Walewska, C. Marschner, T. Szilvási, B.
- Blom, J. Baumgartner, *Inorg. Chem.* **2015**, *54*, 3306–3315. R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *Organometallics* **2012**, *31*, 4588–4592. [22]
- R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, Chem. [23] Commun. 2012, 48, 4561-4563.
- [24] J. G. Brennan, R. A. Andersen, J. L. Robbins, J. Am. Chem. Soc. 1986, 108, 335-336.
- [25] L. Maron, O. Eisenstein, R. A. Andersen, Organometallics 2009, 28, 3629-3635
- [26]
- P. Pyykkö, M. Atsumi, *Chem. Eur. J.* 2009, *15*, 186–197.
 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* 2008, 2832–2838. [27] [28] M. T. Gamer, P. W. Roesky, S. N. Konchenko, P. Nava, R. Ahlrichs,
- Angew. Chem. Int. Ed. 2006, 45, 4447-4451. [29]
- W. J. Evans, J. M. Perotti, J. W. Ziller, D. F. Moser, R. West, Organometallics 2003, 22, 1160-1163.
- P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones, D. P. Mills, J. Am. [30] Chem. Soc. 2007, 129, 5360-5361.
- The uranium-silicon distances in 1 and 2 are significantly shorter (~80 [31] pm) than the sum of the van der Waals radii as estimated by Bondi (A. Bondi, J. Phys. Chem. 1964, 68, 441-451), suggesting a uraniumsilicon bonding interaction. It is also worth noting that the van der Waals radius for uranium estimated by Bondi is much shorter (>40 pm) than more recent estimates (see, for example, S. S. Batsanov, Inorg. Mat. 2001, 37, 871-885).
- A. Zalkin, J. G. Brennan, R. A. Andersen, Acta Crystallogr. C 1988, 44, [32] 2104-2106.
- [33] J.-C. Berthet, J.-F. Le Maréchal, M. Nierlich, M. Lance, J. Vigner, M. Ephritikhine, J. Organomet. Chem. 1991, 408, 335-341.
- [34] J.-C. Berthet, C. Villiers, J.-F. Le Maréchal, B. Delavaux-Nicot, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Organomet. Chem. 1992, 440, 53-65.
- [35] C. J. Windorff, M. R. MacDonald, K. R. Meihaus, J. W. Ziller, J. R. Long, W. J. Evans, *Chem. – Eur. J.* 2016, 22, 772–782.
 C.-W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T.
- [36] Gamer, P. G. Jones, S. Blaurock, J. Am. Chem. Soc. 2007, 129, 12049-12054.
- [37] L. R. Morss, N. M. Edelstein, J. Fuger, J. J. Katz, The Chemistry of the Actinide and Transactinide Elements., Springer, 2006. R. Tacke, T. Ribbeck, Dalton Trans. 2017, 46, 13628–13659.
- [38]
- C. J. Windorff, W. J. Evans, *Organometallics* **2014**, *33*, 3786–3791. D. R. Kindra, W. J. Evans, *Chem. Rev.* **2014**, *114*, 8865–8882. [39]
- [40] [41]
 - J. G. Brennan, R. A. Andersen, A. Zalkin, Inorg. Chem. 1986, 25, 1756-1760.
- [42] S. S. Sen, A. Jana, H. W. Roesky, C. Schulzke, Angew. Chem. Int. Ed. 2009, 48, 8536-8538.

[43] For examples of natural population analyses in amidinato-silylene transition metal complexes, see the following: [a] K. Junold, J. A. Baus, C. Burschka, T. Vent-Schmidt, S. Riedel, R. Tacke, Inorg. Chem. 2013, 52, 11593–11599

[b] B. Blom, S. Enthaler, S. Inoue, E. Irran, M. Driess, J. Am. Chem. Soc. 2013, 135, 6703-6713.

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