

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: The Exceptional Diversity of Homoleptic Uranium-Methyl 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: Angew. Chem. Int. Ed. 10.1002/anie.202005138

Link to VoR: https://doi.org/10.1002/anie.202005138

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The Exceptional Diversity of Homoleptic Uranium-Methyl

Complexes

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Abstract: Homoleptic σ -bonded uranium-alkyl complexes have been a synthetic target since the Manhattan Project. The current study describes the synthesis and characterization of several unprecedented uranium-methyl complexes. Amongst these complexes, the first example of a homoleptic uranium-alkyl dimer, $[Li(THF)_4]_2[U_2(CH_3)_{10}]$, as well as a seven-coordinate uraniummethyl monomer, $\{Li(OEt_2)Li(OEt_2)_2UMe_7Li\}_n$ were both crystallographically identified. The diversity of complexes reported herein provides critical insight into the structural diversity, electronic structure and bonding in uranium-alkyl chemistry.

Spanning the early investigations of uranium enrichment technologies of the 1940s to the current interest of expanding the fundamental understanding of organoactinide chemistry, homoleptic actinide-alkyl and -aryl complexes have continued to be highly valued targets as model complexes for electronic structure and bonding studies.^[1–3] Early success in the synthesis of homoleptic transition-metal alkyl complexes for refining early bonding models sparked interest in extending to the f-block. For example, Wilkinson reported the synthesis of hexamethyltungsten (WMe₆) while also making note of a possible neutral hexamethyluranium complex (UMe₆), which was never structurally verified.^[4,5]

Akin to Wilkinson's method, we extended our approach in the synthesis of homoleptic iron-aryl species to the challenge of uranium-aryls.^[6] This resulted in the synthesis of a series of homoleptic uranium-aryl complexes containing sterically unencumbered aryl substituents (Ar = Ph, tolyl, and *p*-CI-Ph).^[7] This represented the first successful synthesis of homoleptic uranium-aryl complexes without the advantageous use of sterically bulky aryl ligands for kinetic stabilization. Prior to this report, homoleptic uranium-alkyl and -aryl complexes were made isolable by introducing large steric bulk to the corresponding alkyl or aryl substituents.^[7–14]

Homoleptic complexes of uranium bearing *simple* hydrocarbon substituents (i.e. Me, Et, etc.) have been extremely rare due to their inherent thermal instability and reactivity. To date, the only example is a hexamethyluranium(IV) complex, [(Li(TMEDA))₂U(CH₃)₆] (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA)).^[12] When compared with the homoleptic uranium-benzyl derivatized complexes, the homoleptic uranium-methyl complex does not benefit from additional stabilizing effects (i.e. interaction with the *ipso* carbon of the benzyl substituents), other than the use of the cation complexant TMEDA (Figure 1).^[12] In our

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iron work, additives such as *N*-methyl-2-pyrrolidone (NMP) also displayed a similar role as cation complexant.^[15,16] Without NMP, iron-alkyl clusters were observed, which displayed greatly lessened stability.^[15,17] This motivated exploration of reaction of MeLi with UCl₄ in the absence of TMEDA to evaluate uraniummethyl speciation. Herein, a collection of homoleptic uraniummethyl species are reported, the diversity of which demonstrates unique coordination and bonding previously unknown in organouranium chemistry.



Figure 1. Selected examples of homoleptic uranium-alkyl complexes.

The reaction of 6 equiv of MeLi with UCl₄ in THF at low temperature was monitored by ¹H NMR revealing resonances consistent with [(Li(TMEDA))₂U(CH₃)₆] (Figure S1 and S2).^[12] Crystallization attempts to identify these uranium-methyl species were carried out by the addition of hexane following addition of MeLi to UCl₄ at -70 °C and storage of the resultant solution at -80 °C for 16 h. Light orange crystalline material formed and was identified by X-ray diffraction (XRD) the as hexamethyluranium(IV) complex, [Li(THF)₄][Li(THF)₂U(CH₃)₆] (1), in approximately 20% isolated yield. Complex 1 crystallizes in the monoclinic space group $P2_1/n$ (Figure 2) and is analogous to $[Li(TMEDA)]_2[U(CH_3)_6]$.^[12] Complex **1** exhibits a distorted octahedral coordination environment reflected in the U-C bond lengths and angles. The U-C distances of the terminal -CH₃ groups range from 2.500(5) to 2.533(5) Å while the lithium coordination to the methyl groups lengthens the corresponding U-C distances (U1-C5 = 2.615(5) Å and U1-C6 = 2.591(6) Å). Two examples of angular distortion due to Li coordination are the C4-U-C5 = 84.65(18)° and C4-U-C6 = 171.66(19)°. The effect of Li coordination is also reflected in the ¹H NMR of **1** in THF- d_8 , which displays two singlet resonances at -20.66 and -24.99 ppm with a relative ratio of 14:4 consistent with approximate C_{2v} symmetry with the principal axis intersecting the U and Li centers. (Figure S3). Both the U-C distances and ¹H NMR resonances are consistent with the previously reported [Li(TMEDA)]_2[U(CH_3)_6] (2.48(1)-2.600(9) Å and -19.92 ppm, respectively).^[12] Magnetic susceptibility measurements using Evans method NMR analysis determined complex **1** to have an effective magnetic moment (μ_{eff}) of 2.1(1) B.M. at -80 °C. This is consistent with previously reported values for homoleptic uranium(IV)-alkyl complexes.^[12] The synthesis of this monomeric species suggests that the addition of TMEDA only provides enhanced kinetic stabilization and does not drastically change the accessible uranium-methyl species.

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Figure 2. X-ray crystal structure of $[Li(THF)_4][Li(THF)_2U(CH_3)_6]$ (1) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1-C1 = 2.533(5), U1-C2 = 2.510(5), U1-C3 = 2.500(5), U1-C4 = 2.504(5), U1-C5 = 2.615(5), U1-C6 = 2.591(6), U1...Li1 = 3.136(8), C3-U1-C4 = 96.27(19), C3-U1-C2 = 85.60(19), C3-U1-C5 = 178.5(2), C2-U1-C1 = 173.63(18), C1-U1-C6 = 89.9(2).

The accessibility of similar monomeric species in Et₂O was explored as challenges to identify organouranium products were reported in this solvent as well.^[12] Similar to our efforts in THF, 6 equiv of MeLi was added to UCl₄ in Et₂O at -70 °C. After stirring for 10 min, pentane was added, and the mixture was filtered over a cold Celite plug. In addition to the dark filtrate, unreacted UCl₄ was observed in the filtrate. The resultant light-yellow solution was stored at -80 °C. After several days the heptamethyluranium(IV) complex, {Li(OEt₂)Li(OEt₂)₂UMe₇Li}_n (2), formed as a pale-green crystalline material (ca. trace) (Figure 3). Complex 2 crystallized in the monoclinic space group, P21. Comparison of complex 2 to a previously reported thorium analog shows a similar distribution of An–CH₃ (An = Th or U) bond lengths (2.519(6)-2.779(5) Å vs. 2.571(9)-2.765(9) Å, respectively).^[18] The carbon atoms C1, C3, C4, and C7 in complex 2 form a plane in which U1, C5 and C6 are positioned below and C2 above. Furthermore, unlike its thorium analog, 2 oligomerizes in the solid state in which C7 coordinates to Li1 of another molecule of 2 in the extended crystalline network (Figure S4). To the best of our knowledge, complex 2 also represents an unprecedented coordination environment for homoleptic U(IV) alkyls. Previous attempts to generate such species proved unsuccessful and coordination of six alkyl ligands was hypothesized to be an upper limit to the U(IV) coordination number.^[12] The formation of the 7-coordinate complex 2 may result from the high effective concentration of MeLi due to the inherent heterogeneity of the reaction in Et₂O. Unfortunately, due to low conversions from UCI₄, sufficient amounts of crystalline material were unable to be produced, limiting any further characterization.

Due to the intractability of reactions in Et₂O even with low temperature synthetic techniques, the use of crown ethers as complexants to facilitate the isolation of uranium-methyl species was explored.^[19] The common Li⁺ complexant, 12-crown-4 was added to the reaction following addition of MeLi to Ul₄(1,4-dioxane)₂. Orange microcrystalline material not suitable for XRD was obtained. Thus, 18-crown-6, was utilized instead. Upon addition of a solution of 18-crown-6, a light-yellow precipitate immediately formed. The reaction mixture was filtered, and the filtrate was re-dissolved in THF. After storage at -80 °C for a week, a dark red crystalline material formed which was identified as the hexamethyluranium(V) complex, [Li(18-crown-6)(THF)₂][UMe₆] (**3**) (<10% yield, Figure 4).

Complex **3** crystallizes in the triclinic space group *P*-1, and the Li atom disorder is modeled over three positions. The U-C distances are consistent with other reported homoleptic U(V)-alkyl

complexes and overall, complex **3** adopts a distorted octahedral geometry.^[13] The four equatorial U-C distances of 2.449(5) Å and 2.452(5) Å and the shorter axial U-C distances of 2.415(5) Å reflect this symmetry. Due to the increased difficulty of obtaining enough material for NMR analysis, the 10 K EPR spectrum of a solid sample of **3** was instead obtained and displayed a resonance at a g-value of 1.49 consistent with the U(V) oxidation state (Figure S5).^[20] We hypothesize that the formation of **3** under these highly reducing conditions is consistent with disproportionation of two U(IV) centers. However, a homolytic U-CH₃ cleavage and subsequent oxidation of a U(IV) center to yield U(V) could not be ruled out.



Figure 3. X-ray crystal structure of $\{Li(OEt_2)Li(OEt_2)_2 UMe_7 Li\}_n$ (2) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1-C1 = 2.588(5), U1-C2 = 2.692(5), U1-C3 = 2.779(5), U1-C4 = 2.593(5), U1-C5 = 2.554(5), U1-C6 = 2.594(5), U1-C7 = 2.519(6), C7-U1-C5 = 116.0(2), C7-U1-C1 = 76.65(19), C1-U1-C2 = 80.88(16), C1-U1-C4 = 144.96(15), C5-U1-C2 = 156.51(18). Note: Li1 is coordinated to C7 of another molecule of 2 in the extended crystalline network (Figure S4).

The modest change in reaction conditions which led to the isolation of 2 and 3 motivated us to explore the crystallization conditions previously utilized to isolate 1 to determine whether other uranium-methyl species were accessible. To our surprise, the modification of the crystallization conditions used for complex 1, by the significant decrease in the volume of hexane used as co-solvent (1.0 mL vs. 2.5 mL), led to the formation of an unexpected uranium-methyl dimer, [Li(THF)₄]₂[U₂(CH₃)₁₀] (4) as dark orange crystalline material in 20% isolated yield (Figure 5). Complex 4 crystallized in the trigonal space group R-3c. The asymmetric unit consists of one-sixth of the dinuclear uranium dianion and one-third of a [Li(THF)₄]⁺. The orientation of the hydrogen atoms could not be determined from the difference Fourier map, hence, no agostic interaction could be determined from the solid-state structure. The dianion of 4 consists of two uranium centers bound to seven and six methyl groups with capped octahedral and octahedral geometries, respectively. The asymmetric coordination environment of the dimer is reflected in the difference between the terminal U-CH₃ bonds of the two uranium centers with the 7-coordinate U center displaying a significantly shorter terminal U-CH₃ bond length of 2.481(6) Å for three of the four -CH3 groups compared to that of the 6-coordinate U center of 2.524(5) Å. The unique methyl substituent, C4, has a distinctly shorter bond length of 2.438(10) Å. This distance is reminiscent of previously reported homoleptic U(V)-C bond lengths.^[13] The bridging U-CH₃ bonds were expectedly the longest 2.658(3) Å. The U–U separation is comparable to other reported alkyl bridged complexes (3.6089(3) Å compared to the closest of 3.616 and 3.629 Å of previously reported complexes).^[21,22] The ¹H NMR of complex **4** in methylenechlorided₂ is associated with two broad singlet resonances centered at 4.29 and 1.90 ppm, consistent with the two distinct chemical

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Figure 4. X-ray crystal structure of $[Li(18-crown-6)(THF)_2][UMe_6]$ (3) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1-C1 = 2.449(5), U1-C2 = 2.452(5), U1-C3 = 2.415(5), C1-U1-C1A = 180.0, C1-U1-C2 = 87.36(17), C1A-U1-C2 = 92.64(17), C3-U1-C1 = 90.2(2), C3-U1-C2A = 88.08(17).

environments in the solid state (bridging and terminal -CH₃, respectively). Magnetic susceptibility measurements using Evans method determined **4** to have an effective magnetic moment of 3.9(4) B.M at -80 °C.

To our knowledge, complex 4 represents the first example of a homoleptic uranium-alkyl multimeric species. The ability to access multimeric uranium-alkyl species in the absence of the cation complexant TMEDA is highly consistent with the removal of cation-coordinating NMP from reactions of simple iron salts and Grignard reagents in which iron-alkyl clusters were observed. [15-^{17]} This result has led us to extend our working hypothesis that cation effects in homoleptic chemistry drastically shift metal speciation and nuclearity in d- and f-block metals. Similar to the homoleptic iron-alkyls we have previously characterized, the thermal stability of complexes 1-4 was extremely limited. As crystalline solids, all species are stable at -80 °C for at least several weeks, but readily decompose at elevated temperatures (-30 °C) within minutes. While the in situ thermal stability was found to be better for complexes 1 and 4, a tetrauranium-oxo cluster which incorporates ring-opened THF was obtained following prolonged stirring at elevated temperatures (see SI).^[23,24] This uranium-methyl cluster was assumed to form This uranium-methyl cluster was assumed to form similarly to previous reports of low-valent uranium reductive cleaving of C-O bonds in ethereal solvents.[25]

The analogous metal oxidation states in complexes 1 and 4 but distinct differences in nuclearity and coordination environments, led us to pursue computational studies in order to obtain additional insight into their electronic structures and metal-ligand bonding (see SI for computational details). Complete active space self-consistent field (CAS) calculations, augmented with a dynamic correlation treatment via second order perturbation theory (PT2), and treatment of the spin-orbit coupling (SOC) via state interaction, revealed complex, orbitally (near-)degenerate low-energy electronic structures for both 1 and 4, as detailed in Section 3 of the SI.

Despite the multiconfigurational GSs, geometrical parameters determined using density functional theory (DFT) were found to be in good agreement with the solid-state bond metrics, for both dianions of **1** and **4** (Figure S10). Furthermore, natural localized molecular orbital (NLMO) bonding analyses of the optimized and crystal structures displayed similar metal-ligand bonding. For the crystal structure, the NLMO bonding information is shown in Figure 6. The backbone of dianion **1** is maintained by six similar 2-center-2-electron σ (U-C) bonds with metal weights ranging from



Figure 5. X-ray crystal structure of the dianion $[Li(THF)_4]_2[U_2(CH_3)_{10}]$ (4) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and $[Li(THF)_4]^*$ cations are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1-C1 = 2.658(3), U1-C2 = 2.481(6), U1-C3A = 2.524(5), U1-C4 = 2.438(10), U1...U1A = 3.6089(3), C4-U1-C2 = 81.78(17), C4-U1-C1 = 132.75(6), C2-U1-C1 = 76.27(16), C3B-U1-C3A = 91.5(2), C2-U1-C1B = 145.39(18).

17 to 18%. The U center involves in these bonds primarily with the 5f orbitals (50%) and secondarily with the 6d orbitals (34%). The U-C(alkv) bonding of 1 is therefore very similar to the recently reported U-C_(aryl) bonding (%U, %5f, %6d = 20, 47, 43) in the nearoctahedral $[U(p-Cl-Ph)_6]^{2^-}$ homoleptic complex.^[7] This similarity was expected since 1 and [U(p-Cl-Ph)612- also share similar U-C average bond distances (2.54 vs 2.53 Å). The molecular backbone of the dianion 4 obeys C_{3v} symmetry with the three-fold rotation axis defined by collinear U centers and a methyl C atom. The metal-ligand bonding in 4 is described by seven 2-center-2electron σ (U-C) bonds involving the peripheral methyl C atoms, and three 3-center-2-electron σ bonds involving the bridging methyl C atoms. In comparison to 1, the 2-center bonds of 4 show enhanced covalency, i.e. the corresponding NLMOs have between 20 and 25% metal contribution. The σ (U-C) bond along the C_3 axis has almost even contribution from the U 5f (44%) and 6d (43%) orbitals. The 2-center σ (U-C) bonds have larger contribution from the metal 6d (between 45 and 55%) than from the metal 5f (31%) orbitals. The 3-center NLMOs are delocalized over the two metal centers, with a combined 28% U contribution, and serve as linkers for the $U(CH_3)_4$ and $U(CH_3)_3$ molecular units. The U 5f and 6d orbital contributions in these 3-center orbitals are quite even. The 2-center U-C(alkyl) bonding in 4 is similar to the recently reported U-C_(aryl) bonding (%U=22–23%, %5f = 38–40%, %6d = 53–55%) in the $[U(Ph)_6]^{2^-}$ and $[U(p-tolyl)_6]^{2^-}$ homoleptic complexes. Again, this similarity was expected as the dianion of 4 and the aryl complexes share U(IV) metal centers with similarly distorted ligand coordination and similar average metal-ligand bond distances (2.50 Å U-C_{(alkyl)} in 4 vs. 2.52-2.53 Å U-C_{(aryl)} in the homoleptic aryl complexes)

The identification of complexes **1–4** addresses the challenge of synthesizing and handling highly unstable homoleptic uranium alkyl complexes, which has plagued the f-element community

[U(CH ₃) ₆] ²⁻ (1)			H ₃) ₁₀] ²⁻ (4)		
%U(tot): 18	25	25	15; 13	20	
%U(6d): 34	44	55	52; 45	45	
%U(5f) 50	43	31	41.47	31	



since the Manhattan Project. As described herein, by utilizing lowtemperature synthesis and cryogenic handling techniques, novel organouranium compounds are isolable. In particular, complex **4** represents an unprecedented uranium-alkyl species which changes the paradigm of homoleptic uranium-alkyl chemistry to now include multimeric uranium-alkyl complexes. Additionally, theoretical insight into electronic structure and bonding for complexes **1** and **4** demonstrates the distinct difference in 6d and 5f atomic orbital participation in distorted ligand coordination environments for homoleptic uranium-alkyls. Altogether, this report is indicative that after 70 years of research interest, we are still only at the tip of the iceberg of uranium-alkyl chemistry.

Acknowledgements

M.L.N. acknowledges support for this work from the U.S. Department of Energy, Office of Science, Early Career Research Program under Award DE-SC0016002. D.C.S. and J.A. acknowledge support from the U.S. Department of Energy, Office of Basic Energy Sciences, Heavy Element Chemistry program, under grant DE-SC0001136. We thank the Center for Computational Research (CCR) at the University of Buffalo for providing computational resources and the NSF for support for the acquisition of an X-ray diffractometer (CHE-1725028).

Deposition Number 1995366-1995370 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Keywords: uranium • organometallic • homoleptic • synthesis

- H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, J. F. Nobis, J. R. Thirtle, H. L. Yale, F. A. Yoeman, *J. Am. Chem. Soc.* **1956**, *78*, 2790–2792.
- [2] A. E. Gebala, M. Tsutsui, J. Am. Chem. Soc. 1973, 95, 91– 93.
- [3] T. J. Marks, A. M. Seyam, J. Organomet. Chem. **1974**, 67, 61–66.
- [4] A. J. Shortland, G. Wilkinson, J. Chem. Soc., Dalton Trans. 1973, 872–876.
- [5] A. L. Galyer, G. Wilkinson, J. Chem. Soc., Dalton Trans. 1976, 2235–2238.
- [6] S. H. Carpenter, T. M. Baker, S. B. Muñoz, W. W. Brennessel, M. L. Neidig, *Chem. Sci.* 2018, 9, 7931–7939.
- [7] N. J. Wolford, D.-C. Sergentu, W. W. Brennessel, J. Autschbach, M. L. Neidig, *Angew. Chem. Int. Ed.* 2019, 58, 10266–10270.
- [8] S. A. Johnson, S. C. Bart, *Dalt. Trans.* **2015**, *44*, 7710–7726.
- [9] M. A. Boreen, B. F. Parker, T. D. Lohrey, J. Arnold, J. Am. Chem. Soc. 2016, 138, 15865–15868.
- [10] W. G. Van der Sluys, C. J. Burns, A. P. Sattelberger, Organometallics 1989, 8, 855–857.
- [11] L. A. Seaman, J. R. Walensky, G. Wu, T. W. Hayton, *Inorg. Chem.* 2013, 52, 3556–3564.
- [12] S. Fortier, B. C. Melot, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2009, 131, 15512–15521.
- [13] S. Fortier, J. R. Walensky, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2011, 133, 11732–11743.
- [14] S. A. Johnson, J. J. Kiernicki, P. E. Fanwick, S. C. Bart, Organometallics 2015, 34, 2889–2895.
- [15] J. D. Sears, S. B. Muñoz III, S. L. Daifuku, A. A. Shaps, S. H. Carpenter, W. W. Brennessel, M. L. Neidig, *Angew. Chem. Int. Ed.* **2019**, *58*, 2769–2773.
- [16] S. B. Muñoz III, S. L. Daifuku, J. D. Sears, T. M. Baker, S. H. Carpenter, W. W. Brennessel, M. L. Neidig, Angew. Chem.

Int. Ed. 2018, 57, 6496-6500.

- [17] S. B. Muñoz, S. L. Daifuku, W. W. Brennessel, M. L. Neidig, J. Am. Chem. Soc. 2016, 138, 7492–7495.
- [18] H. Lauke, P. J. Swepston, T. J. Marks, J. Am. Chem. Soc. 1984, 106, 6841–6843.
- [19] C. J. Pedersen, J. Am. Chem. Soc. **1967**, 89, 2495–2496.
- [20] W. W. Lukens, N. M. Edelstein, N. Magnani, T. W. Hayton, S. Fortier, L. A. Seaman, J. Am. Chem. Soc. 2013, 135, 10742–10754.
- [21] I. Korobkov, S. Gambarotta, *Inorg. Chem.* **2010**, *49*, 3409–3418.
- [22] B. Kosog, C. E. Kefalidis, F. W. Heinemann, L. Maron, K. Meyer, J. Am. Chem. Soc. 2012, 134, 12792–12797.
- [23] L. R. Avens, D. M. Barnhart, C. J. Burns, S. D. McKee, *Inorg. Chem.* **1996**, *35*, 537–539.
- [24] C. Boisson, J. C. Berthet, M. Lance, M. Nierlich, M. Ephirtikhine, *Chem. Commun.* **1996**, 2129–2130.
- [25] C. P. Larch, F. G. N. Cloke, P. B. Hitchcock, Chem. Commun. 2008, 82–84.

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10.1002/anie.202005138

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Herein, a diverse group of homoleptic uranium-methyl complexes is presented. The addition of MeLi to UCl₄ at low temperature yields an unprecedented homoleptic uranium-methyl dimer. Overall this complex as well as several other monomeric uranium-alkyl complexes demonstrate the rich coordination and electronic structure and bonding of homoleptic uranium-alkyl complexes with sterically unencumbered alkyl substituents such as -CH₃.

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