

Isolation of a Uranium(III)-Carbon Multiple Bond Complex

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Abstract: Low-valent uranium-element multiple bond complexes remain scarce, though there is burgeoning interest regarding to their bonding and reactivity. Herein, isolation of a uranium(III)-carbon double bond complex $[(Cp^*)_2U(CDP)](BPh_4)$ (**1**) comprising a tridentate carbodiphosphorane (CDP) was reported for the first time. Oxidation of **1** afforded the corresponding U(IV) complex $[(Cp^*)_2U(CDP)](BPh_4)_2$ (**2**). The distance between U and C in **2** is 2.481 Å, indicating the existence of a typical U=C double bond, which is further confirmed by quantum chemical calculations. Bonding analysis suggested that the CDP also serves as both σ - and π -donor in complex **1**, though a longer U–C bond (2.666(3) Å) is observed. It implies that **1** is the first isolable mononuclear uranium(III) carbene complex. Moreover, these results suggest that CDPs are promising ligands to establish other low-valent *f*-block metal-carbon multiple bond complexes.

Molecular uranium carbon double bond complexes have been intensively probed concerning their bonding and reactivity, especially at a U(IV), U(V) and U(VI) center, over the past four decades.^[1] In the contrast, uranium carbenes comprising low-valent uranium, typically U(III), remained sparse. Although a few mononuclear U(III) N-heterocyclic carbene (NHC) adducts were synthesized, density functional theory (DFT) calculation and the single-crystal structural parameters suggest that the NHCs mainly act as a neutral two-electron σ donor in these complexes.^[2] For instance, Meyer et al.^[3] found that there is merely a weak π -bonding between C_{carbene} and U in the complex $U(N^{\prime})_3(IMe_4)$ (**I**) ($HN^{\prime}=HN(SiMe_3)_2$, $IMe_4=1,3,4,5$ -tetramethylimidazol-2-ylidene) (Scheme 1). The π -back donation was somewhat strengthened in an abnormal NHC–U(III) adduct **Ia** as reflected by a shorter U– C_{carbene} bond.^[4] Bis(imminophosphorano)methanediides ($BIPM^{2-}$)^[5] and bis(thiophosphorano)methanediide (SCS^{2-})^[6] are demonstrated to be efficient ligands in the construction of U(IV)/U(V)/U(VI)–C double bonds. Nonetheless, there have been few examples of U(III)–C double bonds supported by $BIPM^{2-}$ and SCS^{2-} .^[7] Very recently, Liddle and co-workers reported the preparation of a multinuclear mixed-valence uranium carbene complex **III** that comprises *formal* U(III) and U(IV) centers.^[8] Therefore, isolation of the authentic mononuclear U(III)–C double-bond-containing complexes is, to the best of our knowledge, still unknown.

Carbenes, in the form of $L \rightarrow C \leftarrow L$ (L is electron donor, such as PPh_3 , NHC, etc.), are divalent carbon(0) species.^[9] Most remarkably, carbene features a central carbon atom that retains two lone-pairs, which has been verified both by the unique reactivities^[10] and DFT calculations.^[11] While there are various compounds in which carbenes bind to two acceptors,^[12] carbenes which act as both σ and π donors to the same atom simultaneously remained rare, especially to metal atoms.^[13] Some of us have demonstrated that both monodentate and tridentate carbodiphosphoranes (CDPs) are efficient supporting ligands to establish polarized U(IV)–C double bond, involving the two lone pairs at the C_{carbene} center.^[13e] Furthermore, CDPs are much softer compared to the $BIPM^{2-}$. In this context, we are curious about the capacity of CDPs in the construction of low-valent uranium carbon multiple bonds. Herein, we present the synthesis and isolation of the first U(III)–CDP adduct (**1**). Further oxidation of **1** afforded its U(IV) analogue **2**. The identical coordination configuration of **1** and **2** allows assessments of the impact of the uranium oxidation state on the nature of U–C bonding. Characterizations in combination with quantum chemical calculations confirmed that **1** is an unprecedented mononuclear uranium(III)-carbon multiple bond complex.

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Our initial attempts to reduce pincer-type CDP–UCl₄^[13e] with KC₈ did not give the target complex CDP–UCl₃ due to the ligand dissociation under such a harsh condition. Alternatively, a proper U(III) precursor, [(Cp*)₂U(BPh₄)], was chosen owing to the facile cleavage of BPh₄ anion from the uranium center. Reaction of [(Cp*)₂U(BPh₄)] with tridentate CDP gives [(Cp*)₂U(CDP)](BPh₄) (1), Scheme 2. Two equivalents of CDP are required to attain a moderate yield. Complex 1 was isolated as dark green blocks in 48% yield after work-up and recrystallization from THF. Notably, similar reaction employing monodentate CDP, hexaphenylcarbodiphosphorane, did not give the desired unsupported analogue. Thus, the pyridyls should play important roles in stabilizing 1, which is confirmed by DFT calculations as well (see below). The treatment of 1 with one equivalent of ferrocenium afforded the corresponding U(IV) complex, [(Cp*)₂U(CDP)](BPh₄)₂ (2), which was obtained as dark-red blocks in 43% crystalline yield. Notably, oxidation of 2 with stronger oxidants, such as Ag⁺ and (NO)⁺, did not afford the U(V) analogue or carbon centered radicals.^[14]

Complexes 1 and 2 exhibit a sharp singlet at –7.1 and –6.7 ppm in the ¹¹B NMR spectra respectively, which can be assigned to the free BPh₄ counter anion (signal related to [Cp*₂U(BPh₄)] appears at –45.4 ppm in C₆D₆). This is indicative of the coordination of CDP to the U center. Crystalline 1 and 2 would gradually decompose in common solvents (DCM, MeCN), thus reliable ¹H and ¹³C{¹H} NMR spectra could not be attained. Fortunately, ³¹P{¹H} NMR spectra of both complexes were recorded though resonances relative to protonated CDP always exhibit. The ³¹P chemical shift of 2 appears at –246.5 ppm as a singlet in the ³¹P{¹H} NMR spectrum, which is comparable to that of CDP–UCl₄ (–234.5 ppm),^[13e] while the ³¹P signal of 1 was further up-field shifted to –315.8 ppm. These results suggested that the coordination of CDP to U center should be in a meridional configuration.

The solid structures of both complexes were determined by single crystal X-ray diffraction analysis (Figure 1). The uranium centers are in the same coordination environments: CDP ligates to [Cp*₂U] moiety in a NCN configuration, forming two five-membered rings. The distance between U1 and C1 in 1 is 2.666(6) Å, which is comparable to other U(III)–NHC species, for

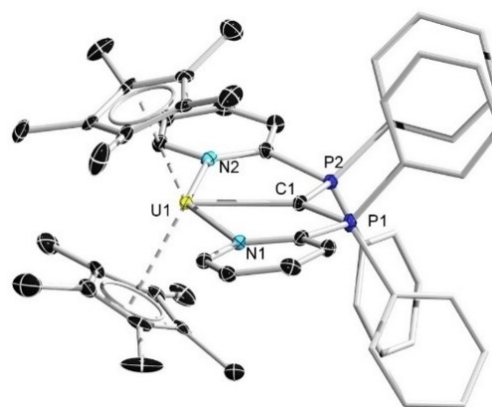
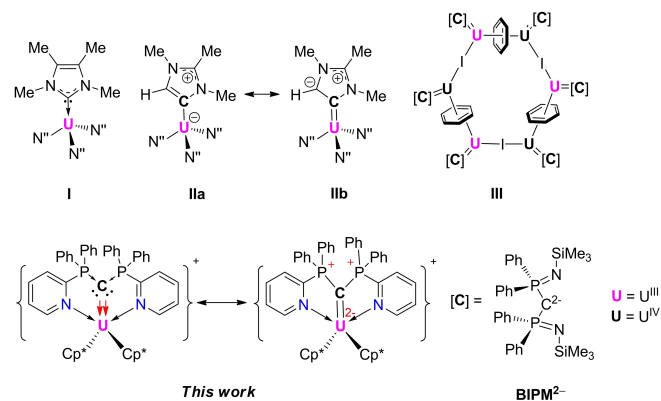
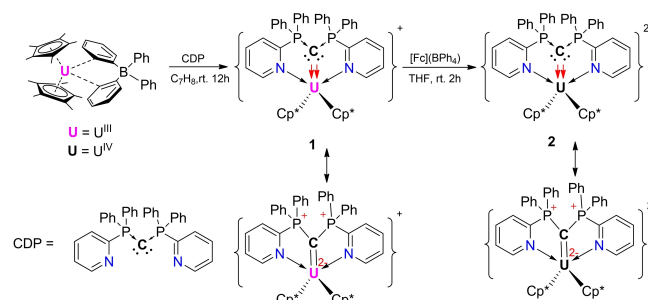


Figure 1. ORTEP drawing of [(Cp*)₂U(CDP)]ⁿ⁺ at 50% level. Hydrogens, solvents and BPh₄ anions were omitted for clarity. Selected bond length (Å) and angle (°) for 1 (n = 1): U1–C1 2.666(3), U1–N1 2.584(3), U1–N2 2.627(3), C1–P1 1.684(3), C1–P2 1.694(3), U1–Cp*_{cent} 2.570/2.570, P1–C1–P2 121.07(18); for 2 (n = 2): U1–C1 2.481(3), U1–N1 2.566(3), U1–N2 2.552(3), C1–P1 1.704(3), C1–P2 1.716(3), U1–Cp*_{cent} 2.517/2.523, P1–C1–P2 118.73(19).

example, [Cp*₂U(I)(IME₄)] (2.687(5) Å),^[2b] [U(N'')₃(IME₄)] (2.672(5) Å),^[3] and II [2.598(11) Å].^[4] The length of Cp*_{cent}–U1 is 2.570 Å, which is ca. 0.1 Å longer than that of [Cp*₂U(BPh₄)], indicating that the uranium center retains a +3 oxidation state.^[15] On the other hand, complex 2 possesses a remarkably shorter U1–C1 distance of 2.481(3) Å, which is comparable with those of the previously reported U(IV)–C double bond complexes, for instance CDP–UCl₄ (2.471(7) Å),^[13e] [(Cp*)₂U(SCS)] (2.396(4) Å)^[16] and [(Cp*)₂U(BIPM)] (2.351(2) Å),^[17] thus confirming the U=C double bond character. The average lengths of Cp*_{cent}–U1 (2.520 Å) and N_{py}–U1 (2.560 Å) bonds of 2 are shorter than those of 1, which implies a lower oxidation state of the uranium center in 1. The difference (ca. 0.18 Å) of the U–C bond in complex 1 and 2 can be ascribed to the decreased ionic radii of U^{III} and U^{IV} (ca. 0.14 Å),^[18] presumably implying the presence of double dative bond between U and C in complex 1. An alternative description of the bonding between U and C of both complexes was depicted in Scheme 2 as well, in which the CDP ligand was treated as methanediide. Bonding analysis suggests the double dative bond resonance dominates.



Scheme 1. Chemical structures of NHC- (I and II) and BIPM²⁻-ligated (III) U(III) complexes.



Scheme 2. Synthesis of 1 and 2. The counter ions are BPh₄ anions.

Generally, measurement of magnetic susceptibilities of uranium complexes is a powerful analytical method to support the assignment of oxidation states, especially at low temperature.^[19] Hence, temperature and field dependent magnetization data were collected (Figure S5, S6 and S7). The magnetic moments of complex **2** decrease with decreasing temperature from 300 to 2.0 K and approaching 0 ($0.54 \mu_B$ at 2.0 K). This is in line with the presence of a 3H_4 ground state $5f^2$ U(IV) ion in **2**.^[19] While magnetic moments of **1** follow a similar trend with decreasing temperature, a much higher value of $2.12 \mu_B$ was detected at 2.0 K, which is consistent with the $^4I_{9/2}$ ground state from the $5f^3$ configuration of the U(III) ion at low temperature.^[19] The different low-temperature behaviors of **1** and **2** unambiguously confirmed the oxidation states of uranium in both complexes. Furthermore, Field-dependent magnetization data is consistent with the assignment, with a value of $1.15 \mu_B$ for **1** and $< 0.1 \mu_B$ for **2** at 7 T (Figure 2).^[19,20]

The bonding nature between the U-center and the CDP ligand in **1** and **2** was then investigated by quantum chemical calculations (see Supporting Information for details). As detailed in Figure S8, the optimized structures of $[(Cp^*)_2U(CDP)]^+$ and $[(Cp^*)_2U(CDP)]^{2+}$ agree with the experimental data. The small differences between the computational and experiment values are within the range of solid-state effects and the accuracy of the methods. Calculations suggest that they have the electronic quartet and triplet ground state, respectively. We also plot the spin densities of the cation of 1^+ and 2^{2+} and find that the unpaired electrons are localized mainly at the uranium center (see Figure S9). This is in good agreement with the shape of the

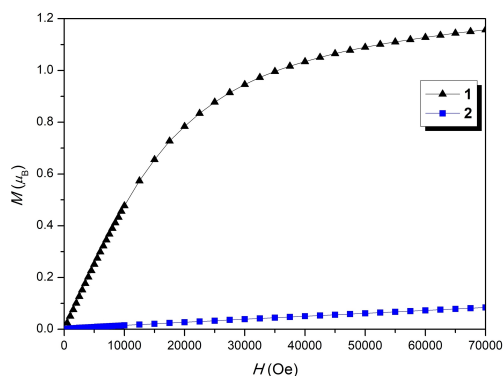


Figure 2. Field-dependent magnetic susceptibility of complex **1** and **2** at 2 K.

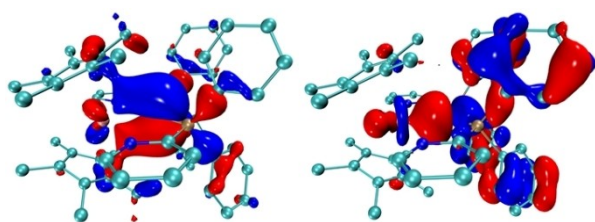
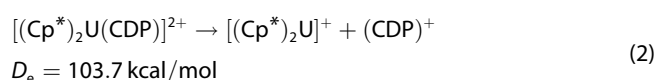
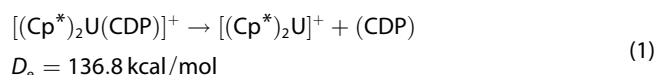


Figure 3. Shape of the HOMO-4 and the HOMO-7 of cation $[(Cp^*)_2U(CDP)]^+$ at the BP86+(D3BJ)/def2-TZVPP/SDD level. The isosurface value is $0.027 e/\text{\AA}^3$.

single occupied molecular orbitals (SOMO) as shown in Figure S10–S11 in Supporting Information. Figure 3 shows the occupied molecular orbitals HOMO-4 and HOMO-7 of cation $[(Cp^*)_2U(CDP)]^+$, which can be identified with the π and σ dative bonds of $\{[(Cp^*)_2U] \leftarrow CDP\}^+$. This is in contrast to uranium-mesoionic carbene complex **IIb** (Scheme 1), in which $U \rightarrow C$ one-electron π -back-donation exists in addition to $C \rightarrow U$ two-electron σ -donation, forming a Fisher-type $U=C$ carbene complex.^[4] The related MOs of cation $[(Cp^*)_2U(CDP)]^{2+}$ are similar and given in Figure S11.

The bond dissociation energies (BDEs, $D_e = 136.8$ and 103.7 kcal/mol) in reaction (1) and (2) suggested that the $U-C_{CDP}$ bond in cation of 1^+ and 2^{2+} is much stronger than the previous reported neutral complexes of UCl_4 with CDP ligands ($D_e = 70.8$ – 91.5 kcal/mol).^[13e]

More detailed information about the $U-C_{CDP}$ bonding nature in cations of 1^+ and 2^{2+} are available from the state-of-the-art energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV) calculations,^[21] by using the quartet $[(Cp^*)_2U(III)]^+$, triplet $[(Cp^*)_2U(IV)]^{2+}$ and singlet CDP with their frozen geometries of the complexes as interacting fragments. Further details about the method are given in the method section in Supporting Information. Table 1 shows the calculated numerical results.



The intrinsic interaction energy ΔE_{int} in $[(Cp^*)_2U(CDP)]^{2+}$ is clearly stronger than in $[(Cp^*)_2U(CDP)]^+$, which is due to the higher charge in the dication. The electrostatic and covalent orbital interactions are therefore bigger in the doubly charged species. Note that the dispersion term provides 12–15% of the total attraction, which is non-negligible. The most important information about the EDA-NOCV analysis comes from the breakdown of the total orbital interactions into pairwise orbital contributions.

The nature of the individual orbital interactions $\Delta E_{orb(1)} - \Delta E_{orb(5)}$ is revealed by the associated deformation densities $\Delta\rho_{(1)} - \Delta\rho_{(5)}$ and the connected fragment orbitals. Figure 4 shows the shape of the deformation densities $\Delta\rho_{(1)} - \Delta\rho_{(5)}$ of the cation 1^+ . The fragment orbitals belonging to $\Delta\rho_{(1)} - \Delta\rho_{(5)}$ of 1^+ are given in Figure S14 of Supporting Information. The deformation densities $\Delta\rho_{(1)} - \Delta\rho_{(5)}$ of the dication 2^{2+} and the connected fragment orbitals are displayed in Figures S15 and S16.

The strongest orbital term $\Delta E_{orb(1)}$ in 1^+ comes from the donation of the σ lone pair electrons of the divalent carbon atom of the CDP ligand towards uranium atom $[(Cp^*)_2U]^+ \leftarrow C^{CDP}(\sigma)$. The second strongest orbital interaction $\Delta E_{orb(1)}$ in 1^+ is due to the donation from the nitrogen lone-pair orbitals of the pyridine groups at CDP. Since the UHF calculation treats the α and β electrons separately, the consolidated term $\Delta E_{orb(2)}$ comprises donation from the $+, +$ in-phase combination of the nitrogen lone-pairs (σ donation) and the $+, -$ out-of-phase

Table 1. EDA-NOCV results of cations of 1^+ (i.e., $[(\text{Cp}^*)_2\text{U}(\text{CDP})]^+$) and 2^{2+} (i.e., $[(\text{Cp}^*)_2\text{U}(\text{CDP})]^{2+}$) using the quartet(Q), triplet (T) or singlet (S) fragments at the BP86 + (D3BJ)/TZ2P// BP86 + (D3BJ)/def2-TZVPP level of theory. Energy values are given in kcal/mol.

Fragments	$[(\text{Cp}^*)_2\text{U}(\text{CDP})]^+$ Orbital interactions	$[(\text{Cp}^*)_2\text{U}(\text{III})]^+(\text{Q})$ + CDP(S) $5f^2 6d^0 7s^0$ Dative bonding	$[(\text{Cp}^*)_2\text{U}(\text{CDP})]^{2+}$ Orbital interactions	$[(\text{Cp}^*)_2\text{U}(\text{IV})]^{2+}(\text{T})$ + CDP(S) $5f^2 6d^0 7s^0$ Dative bonding
ΔE_{int}		-159.7		-236.7
ΔE_{Pauli}		248.4		241.6
$\Delta E_{\text{disp}}^{[\text{a}]}$		-59.9(14.7%)		-58.6(12.3%)
$\Delta E_{\text{elstat}}^{[\text{a}]}$		-192.8(47.2%)		-204.1(42.7%)
$\Delta E_{\text{orb}}^{[\text{a}]}$		-155.5(38.1%)		-215.6(45.1%)
$\Delta E_{\text{orb}(1)}^{[\text{b}]}$	$[(\text{Cp}^*)_2\text{U}]^+ \leftarrow \text{C}^{\text{CDP}} \sigma$ donation	-35.1(22.6%)	$[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{C}^{\text{CDP}} \sigma$ donation	-54.4(25.2%)
$\Delta E_{\text{orb}(2)}^{[\text{b}]}$	$[(\text{Cp}^*)_2\text{U}]^+ \leftarrow \text{N}^{\text{CDP}} \sigma + \pi$ donation	-32.3(20.8%)	$[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{N}^{\text{CDP}} \sigma$ donation	-35.4(16.4%)
$\Delta E_{\text{orb}(3)}^{[\text{b}]}$	$[(\text{Cp}^*)_2\text{U}]^+ \rightarrow \text{CDP SOMO } \sigma$ back donation	-12.5(8.0%)	$[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{C}^{\text{CDP}} \pi$ donation	-22.3(10.3%)
$\Delta E_{\text{orb}(4)}^{[\text{b}]}$	$[(\text{Cp}^*)_2\text{U}]^+ \rightarrow \text{CDP SOMO } \pi$ back donation	-11.9(7.7%)	$[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{C}^{\text{CDP}} \pi$ donation	-16.9(7.8%)
$\Delta E_{\text{orb}(5)}^{[\text{b}]}$	$[(\text{Cp}^*)_2\text{U}]^+ \leftarrow \text{C}^{\text{CDP}} \pi$ donation	-10.9(7.0%)	$[(\text{Cp}^*)_2\text{U}]^{2+} \rightarrow \text{CDP SOMO } \delta$ back donation	-7.4(3.4%)
$\Delta E_{\text{orb}(\text{rest})}$		-52.8(34.0%)		-79.2(36.7%)

[a] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$. [b] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb} .

Table 2. Calculated NBO compositions of the U–C natural orbitals in 1^+ and 2^{2+} .

	σ -bond		C 2 s:2p		π -bond		U 7 s:7p:5f:6d	
	C%	U%			C%	U%		
1^+	82.8	17.2	41.9/57.9	9.9/1.0/60.9/28.1	92.1	7.9	0/100	0/0.1/45.5/54.4
2^{2+}	80.1	19.9	42.7/57.2	9.3/0.8/56.7/33.3	82.5	17.5	0/100	0.05/0.05/25.2/74.7

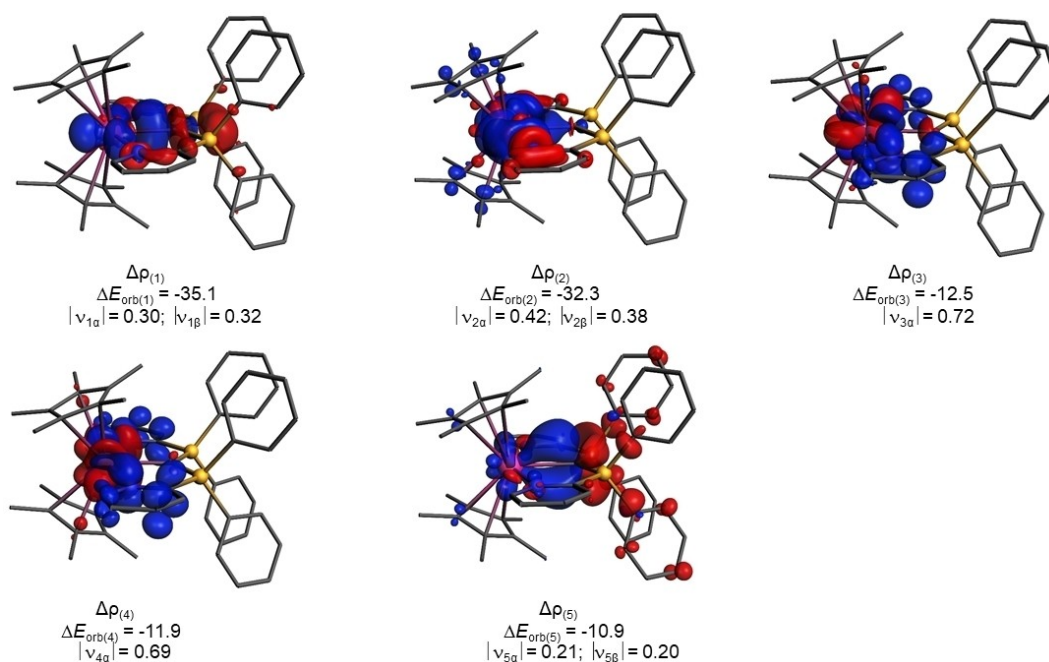


Figure 4. Plot of the deformation densities Δp of the five most important pairwise orbital interactions in cation 1^+ (i.e., $[(\text{Cp}^*)_2\text{U}(\text{CDP})]^+$) between the $[(\text{Cp}^*)_2\text{U}(\text{III})]^+$ and CDP fragments together with the associated interaction energies ΔE_{orb} (in kcal/mol). The charge eigenvalues v give an estimate of the relative size of the charge migration. The direction of the charge flow is red \rightarrow blue.

combination of the nitrogen lone-pairs (π donation) towards uranium atom $[(\text{Cp}^*)_2\text{U}]^+ \leftarrow \text{N}^{\text{CDP}} (\sigma + \pi)$. The orbital terms $\Delta E_{\text{orb}(3)}$ and $\Delta E_{\text{orb}(4)}$ are the σ and π backdonations from uranium to vacant π orbitals of the pyridine groups at the CDP ligand

$[(\text{Cp}^*)_2\text{U}]^+ \rightarrow \text{CDP SOMO } (\sigma, \pi)$. The orbital interaction $\Delta E_{\text{orb}(5)}$ comes from the donation of the π lone pair electrons of the divalent carbon atom of the CDP ligand towards uranium $[(\text{Cp}^*)_2\text{U}]^+ \leftarrow \text{C}^{\text{CDP}} (\pi)$. The clearly different and in each case quite

strong occurrence of the orbital terms $\Delta E_{\text{orb}(1)}$ and $\Delta E_{\text{orb}(5)}$ demonstrate the dual donor character of the carbene ligand in the cation 1^+ .

The orbital terms $\Delta E_{\text{orb}(1)} - \Delta E_{\text{orb}(5)}$ of the dication 2^{2+} exhibit similarities but also some distinctively different features compared with the cation 1^+ . The strongest interactions $\Delta E_{\text{orb}(1)}$ and $\Delta E_{\text{orb}(2)}$ are likewise due to $[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{C}^{\text{CDP}} \sigma$ donation and $[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{N}^{\text{CDP}} (\sigma + \pi)$ donation. They are stronger in 2^{2+} because the acceptor fragment is a dication. The orbital terms $\Delta E_{\text{orb}(3)}$ and $\Delta E_{\text{orb}(4)}$ come both from charge donation of the π lone pair of the divalent carbon atom to uranium $[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{C}^{\text{CDP}} (\pi)$. This is, because the acceptor orbital of the $[(\text{Cp}^*)_2\text{U}]^{2+}$ fragment is mainly the singly occupied SOMO (Figure S16), which means that $\Delta E_{\text{orb}(3)}$ and $\Delta E_{\text{orb}(4)}$ are actually 3-electron interactions. The $[(\text{Cp}^*)_2\text{U}]^{2+} \leftarrow \text{C}^{\text{CDP}} \pi$ donation in 2^{2+} is clearly stronger than the $[(\text{Cp}^*)_2\text{U}]^+ \leftarrow \text{C}^{\text{CDP}} \pi$ donation in 1^+ . The only reverse charge transfer in 2^{2+} is $\Delta E_{\text{orb}(5)}$, which is due to $[(\text{Cp}^*)_2\text{U}]^{2+} \rightarrow \text{CDP} \delta$ backdonation. It is as expected weaker than the backdonations $\Delta E_{\text{orb}(3)}$ and $\Delta E_{\text{orb}(4)}$ in 1^+ .

The numerical results of the NBO calculation are listed (Table 2), consistent with a U=C donor-acceptor interaction. The U—C σ - and π -bond in 1^+ are polarized with 83 and 91% at the carbon, which strongly supports that carbon serve as a double donor. This agrees very well with the NBO σ - and π -bond orbitals (see Figure S15). The uranium part of the U—C σ -bond has 61% *f* and 28% *d* character. The NBO data for 2^{2+} are similar.

In summary, we have reported the synthesis and characterization of two carbodiphosphorane-supported uranocene complexes $[(\text{Cp}^*)_2\text{U} \leftarrow (\text{CDP})]^{n+}$ (1^+ : $n=1$; 2^{2+} : $n=2$) with the uranium centers in different formal oxidation states (1: +3, 2: +4). Quantum chemical calculations revealed that CDP served as a double donor towards uranium (both the U(III) and U(IV) cores), forming polarized σ and π dative bonds. Therefore, complex **1** represents the first example of authentic isolable mononuclear U(III)—C double bond complex. In addition, the isolation of CDP-supported U(III) carbene complex highlights the potential of CDPs as ideal ligands in the construction of other low-valent actinide-carbon multiple bond complexes.

Experimental Section

Full details of the synthesis, characterization, crystal structure determination and QC calculations can be found in the Supporting Information.

Deposition Number(s) 2053340 (for **1**), and 2053341 (for **2**·CH₂Cl₂) contain(s) 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.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbodiphosphorane · low-valent · multiple bond · quantum chemical calculation · uranium

- [1] a) R. E. Cramer, R. B. Maynard, J. C. Paw, J. W. Gilje, *J. Am. Chem. Soc.* **1981**, *103*, 3589–3590; b) R. E. Cramer, K. T. Higa, J. W. Gilje, *J. Am. Chem. Soc.* **1984**, *106*, 7245–7247; c) S. Fortier, J. R. Walensky, G. Wu, T. Hayton, *J. Am. Chem. Soc.* **2011**, *133*, 6894–6897; d) M. Ephritikhine, *C. R. Chim.* **2013**, *16*, 391–405; e) M. Gregson, A. J. Wooles, O. J. Cooper, S. T. Liddle, *Comments Inorg. Chem.* **2015**, *35*, 262–294; f) T. W. Hayton, *Chem. Commun.* **2013**, *49*, 2956–2973.
- [2] a) P. L. Arnold, I. J. Casely, *Chem. Rev.* **2009**, 3599–3611; b) T. Mehdoui, J.-C. Berthet, P. Thuéry, M. Ephritikhine, *Chem. Commun.* **2005**, 2860–2862.
- [3] H. Nakai, X. Hu, L. N. Zakharov, A. L. Rheingold, K. Meyer, *Inorg. Chem.* **2004**, *43*, 855–857.
- [4] A. Seed, M. Gregson, F. Tuna, N. F. Chilton, A. J. Wooles, E. J. L. McInnes, S. T. Liddle, *Angew. Chem. Int. Ed.* **2017**, *56*, 11534–11538; *Angew. Chem.* **2017**, *129*, 11692–11696.
- [5] selected references: a) O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2010**, *39*, 5074–5076; b) O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2011**, *50*, 2383–2386; c) D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2012**, *134*, 10047–10054; d) E. Lu, O. J. Cooper, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2014**, *53*, 6696–6700; e) M. Gregson, E. Lu, D. P. Mills, F. Tuna, E. J. L. McMaster, C. Hennig, A. C. Scheinost, J. McMaster, W. Lewis, A. J. Blake, A. Kerridge, S. T. Liddle, *Nat. Commun.* **2018**, *8*, 14137: 1–11; f) E. Lu, J. T. Boronski, M. Gregson, A. J. Wooles, S. T. Liddle, *Angew. Chem. Int. Ed.* **2018**, *57*, 5506–5511.
- [6] a) T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, *J. Am. Chem. Soc.* **2009**, *131*, 963–972; b) J.-C. Tourneux, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, M. Ephritikhine, *J. Am. Chem. Soc.* **2011**, *133*, 6162–6165; c) J.-C. Tourneux, J.-C. Berthet, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, *Dalton Trans.* **2010**, *39*, 2494–2496; d) J.-C. Tourneux, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, *Organometallics* **2011**, *30*, 2957–2971.
- [7] a) D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2011**, *3*, 454–460; b) O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2010**, *39*, 5074–5076.
- [8] A. J. Wooles, D. P. Mills, F. Tuna, E. J. L. McInnes, G. T. W. Law, A. J. Fuller, F. Kremer, M. Ridgway, W. Lewis, L. Gagliardi, B. Vlasisavljevich, S. T. Liddle, *Nat. Commun.* **2018**, *9*, 2097: 1–11.
- [9] a) F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539–3540; b) R. Tonner, G. Frenking, *Angew. Chem. Int. Ed.* **2007**, *46*, 8695–8698; *Angew. Chem.* **2007**, *119*, 8850–8853; c) C. A. Dyker, V. Lavallo, B. Donnadiou, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 3206–3209; *Angew. Chem.* **2008**, *120*, 3250–3253; d) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2008**, *47*, 3210–3214; *Angew. Chem.* **2008**, *120*, 3254–3258; e) O. Kauffhold, F. E. Hahn, *Angew. Chem. Int. Ed.* **2008**, *47*, 4057–4061; *Angew. Chem.* **2008**, *120*, 4122–4126; f) M. J. Goldfogel, C. C. Roberts, S. J. Meek, *J. Am. Chem.*

- Soc. **2014**, *136*, 6227–6230; g) C. C. Roberts, D. M. Matias, M. J. Goldfogel, S. J. Meek, *J. Am. Chem. Soc.* **2015**, *137*, 6488–6491; h) Y.-C. Hsu, J.-S. Shen, B.-C. Lin, W.-C. Chen, Y. -T. Chan, W.-M. Ching, G. P. A. Yap, C.-P. Hsu, T.-G. Ong, *Angew. Chem. Int. Ed.* **2015**, *54*, 2420–2424; *Angew. Chem.* **2015**, *127*, 2450–2454; i) C. Prancevicus, L. Liu, G. Bertrand, D. W. Stephan, *Angew. Chem. Int. Ed.* **2016**, *55*, 5536–5540; *Angew. Chem.* **2016**, *128*, 5626–5630; j) A. Krool, H. Steinert, L. T. Scharf, T. Scherpf, B. Mallick, V. H. Gessner, *Chem. Commun.* **2020**, *56*, 8051–8054.
- [10] a) M. Alcarazo, K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, *Chem. Commun.* **2013**, *49*, 3140–3142; b) M. Klein, X. Xie, O. Burghaus, J. Sundermeyer, *Organometallics* **2019**, *38*, 3768–3777; c) S. C. Böttger, C. Poggel, J. Sundermeyer, *Organometallics* **2020**, *39*, 3789–3793.
- [11] a) R. Tonnor, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem. Int. Ed.* **2006**, *45*, 8038–8042; *Angew. Chem.* **2006**, *118*, 8206–8211; b) R. Tonnor, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260–3272.
- [12] a) W. Petz, *Coord. Chem. Rev.* **2015**, *291*, 1–27; b) L. Zhao, M. Hermann, N. Holzmann, G. Frenking, *Coord. Chem. Rev.* **2017**, *344*, 163–204.
- [13] a) B. Inés, M. Partil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo, *Angew. Chem. Int. Ed.* **2011**, *50*, 8400–8403; *Angew. Chem.* **2011**, *123*, 8550–8553; b) M. A. Celik, G. Frenking, B. Neumüller, W. Petz, *ChemPlusChem* **2013**, *78*, 1024–1032; c) J. E. Münzer, P. Oña-Burgos, F. M. Arrabal-Campos, B. Neumüller, R. Tonner, I. Fernández, I. Kuzu, *Eur. J. Inorg. Chem.* **2016**, *24*, 3852–3858; d) N.-J. H. Kneusels, J. E. Münzer, K. Flosdorf, D. Jiang, B. Neumüller, Li. Zhao, A. Eichhöfer, G. Frenking, I. Kuzu, *Dalton Trans.* **2020**, *49*, 2537–2546; e) W. Su, S. Pan, X. Sun, S. Wang, L. Zhao, G. Frenking, C. Zhu, *Nat. Commun.* **2018**, *9*, 4997: 1–8; f) J. Walley, L. Warring, G. Wang, D. A. Dickie, S. Pan, G. Frenking, R. J. Gilliard, *Angew. Chem. Int. Ed.* **2020**, *60*, 6682–6690.
- [14] S.-C. Chan, P. Gupta, X. Engelmann, Z. Z. Ang, R. Ganguly, E. Bill, K. Ray, S. Ye, J. England, *Angew. Chem. Int. Ed.* **2018**, *57*, 15717–15722; *Angew. Chem.* **2018**, *130*, 15943–15948.
- [15] W. J. Evans, G. W. Nyce, K. J. Forrestal, J. W. Ziller, *Organometallics* **2002**, *21*, 1050–1055.
- [16] J.-C. Tourneux, J.-C. Berthet, T. Cantat, P. Thuery, N. Mezailles, F. P. Le, M. Ephritikhine, *Organometallics* **2011**, *30*, 2957–2971.
- [17] G. B. Ma, M. J. Ferguson, R. McDonald, R. G. Cavell, *Inorg. Chem.* **2011**, *50*, 6500–6508.
- [18] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751–767.
- [19] a) D. R. Kindra, W. J. Evans, *Chem. Rev.* **2014**, *114*, 8865–8882; b) I. Castro-Rodríguez, K. Meyer, *Chem. Commun.* **2006**, 1353–1368.
- [20] E. J. Schelter, D. E. Morris, B. L. Scott, J. D. Thompson, J. L. Kiplinger, *Inorg. Chem.* **2007**, *46*, 5528–5536.
- [21] L. Zhao, M. Hermann, W. H. E. Schwarz, G. Frenking, *Nat. Chem. Rev.* **2019**, *3*, 48–63.

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