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Uranium Carbene Complexes

Uranium–Carbon Multiple Bonding: Facile Access to the Pentavalent Uranium Carbene $[\mathrm{U\{C(PPh_2NSiMe_3)_2\}(Cl)_2(I)}]$ and Comparison of $\mathrm{U^{V}{=}C}$ and $\mathrm{U^{IV}{=}C}$ Bonds**

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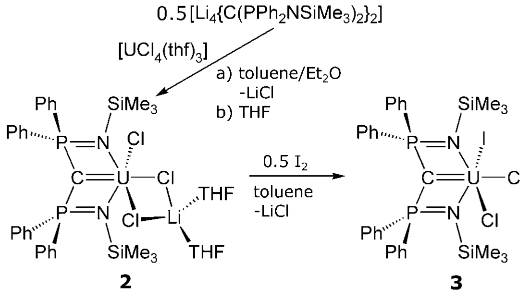
Compared to the extensive investigations of d-block metal–ligand multiple bonding and reactivity,[1] the corresponding field of f-block chemistry is underdeveloped.[2,3] For uranium, imido and oxo complexes dominate, yet there is a paucity of uranium carbenes that do not derive from neutral free carbenes.[3]

The first uranium carbenes, $[\mathrm{U(\eta^5\text{-}C_5H_5)_3(CHPMe_2R)}]$ (R = Ph, **I**; Me, **II**), were reported by Gilje et al.[4] Uranium carbenes have been detected in matrix isolation experiments,[5] and implicated in reactions of ketones with $\mathrm{UCl_4}$/Li(Hg).[6] Recently, Ephritikhine et al. reported a range of uranium carbenes, exemplified by $[\mathrm{U\{C(PPh_2S)_2\}(BH_4)_2(THF)_2}]$,[7] and, as part of a program studying f-block carbenes,[8] we reported the homoleptic uranium carbene $[\mathrm{U\{C(PPh_2NMes)_2\}_2}]$ (**1**, Mes = 2,4,6-trimethylphenyl).[9]

To date, all uranium carbenes with U−C multiple bonds incorporate uranium(IV). Higher-valence analogues are notable for their absence, which contrasts to the dominance of high-oxidation-state uranium oxo and imido complexes.[3,10] However, pentavalent uranium chemistry has been revitalized recently,[10] and encouraged by this and the absence of any uranium(V) carbenes we targeted a pentavalent uranium carbene by an oxidation strategy. Herein, we report the facile synthesis, structure, and reactivity of the first pentavalent uranium carbene, which permits direct comparisons between $\mathrm{U^{V}{=}C}$ and $\mathrm{U^{IV}{=}C}$ bonds for the first time.

Complex **1** was prepared from a disproportionation reaction between $[\mathrm{UI_3(thf)_4}]$ and $[\mathrm{Li_4\{C(PPh_2NMes)_2\}_2}]$.[9] We therefore employed $[\mathrm{UCl_4(thf)_3}]$ and treated it with $[\mathrm{Li_4\{C(PPh_2NSiMe_3)_2\}_2}]$[11] in toluene/$\mathrm{Et_2O}$ (Scheme 1). The uranium(IV) carbene $[\mathrm{U\{C(PPh_2NSiMe_3)_2\}(Cl)(\mu\text{-}Cl)_2Li(thf)_2}]$ (**2**) was isolated as yellow plates in 62% yield following workup and recrystallization from THF.[12]

The molecular structure of **2**, as determined by X-ray crystallography, is shown in Figure 1a with selected bond



Scheme 1. Synthesis of **2** and **3**.

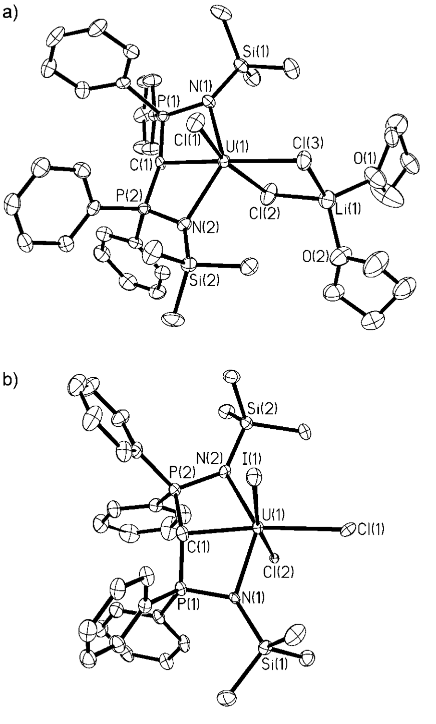


Figure 1. Molecular structures of a) **2** and b) **3**. Displacement ellipsoids set at 30% probability; hydrogen atoms and minor disorder components omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: U(1)–C(1) 2.310(4), U(1)–N(1) 2.371(4), U(1)–N(2) 2.374(4), U(1)–Cl(1) 2.6249(13), U(1)–Cl(2) 2.7041(14), U(1)–Cl(3) 2.7453(13), C(1)–P(1) 1.649(4), C(1)–P(2) 1.661(4), P(1)–N(1) 1.630(4), P(2)–N(2) 1.635(4); P(1)-C(1)-P(2) 164.8(3); **3**: U(1)–C(1) 2.268(10), U(1)–N(1) 2.282(7), U(1)–N(2) 2.268(8), U(1)–Cl(1) 2.711(2), U(1)–Cl(2) 2.710(2), U(1)–I(1) 2.9845(7), C(1)–P(1) 1.676(11), C(1)–P(2) 1.701(10), P(1)–N(1) 1.636(7), P(2)–N(2) 1.648(8); P(1)-C(1)-P(2) 154.5(6).

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Table 1: Selected experimental and computed data for **2** and **3**.[a]

	Bond lengths and indices			Atomic spin densities and charges			U=C σ-component[h]			U=C π-component[h]		
	U–C[b]	U–C[c]	BI[d]	m_U[e]	q_U[f]	q_C[g]	C [%]	U [%]	U 6d/5f	C [%]	U [%]	U 6d/5f
2	2.310(4)	2.313	1.43	2.24	2.30	−2.00	82.4	17.6	20.0:79.4	82.2	17.8	15.8:84.2
3	2.268(10)	2.267	1.54	1.25	2.53	−1.85	74.2	25.8	10.3:89.4	74.3	25.7	9.8:90.0

[a] Both molecules geometry-optimized without symmetry constraints at the spin-unrestricted BP TZP/ZORA level. [b] Experimental U–C distance [Å]. [c] Calculated U–C distance [Å]. [d] Nalewajski–Mrozek bond indices. [e] MDC-m α-spin density on uranium. [f] MDC-q charge on uranium. [g] MDC-q charge on carbene. [h] Natural bond orbital (NBO) analysis.

lengths and angles.[13] Complex **2** is monomeric and occludes a $\{ClLi(thf)_2\}$ fragment. The uranium center adopts a distorted octahedral geometry, the carbene is close to planar T-shaped $[\Sigma\measuredangle = 357.9(3)°]$,[14] and the CP_2N_2U ring is essentially flat. The U(1)–C(1) bond of 2.310(4) Å is short, and longer only than those in **I** and **II** [**I** = 2.293(2); **II** = 2.274(8) Å].[4]

We interrogated **2** with cyclic voltammetry in the potential range of −1.0 to +0.4 V vs. Fc^+/Fc and observed two oxidation processes at $E_p{}^a = -0.5$ V and $E_p{}^a = +0.27$ V.[12] The position of the first oxidation process, which has an associated reduction wave at $E_p{}^c = -0.9$ V, suggested that iodine would be capable of effecting the oxidation of tetravalent **2** to a potential pentavalent derivative, but also that it would be unable to oxidize **2** to a potentially hexavalent state.[15]

Straightforward addition of half a molar equivalent of iodine to **2** effected one-electron oxidation to afford the first pentavalent uranium carbene $[U\{C(PPh_2NSiMe_3)_2\}(Cl)_2(I)]$ (**3**) as red crystals in 45 % yield after workup and recrystallization from toluene. The characterization data support this formulation.[12] In particular, variable-temperature magnetic moment measurements on pentavalent **3** showed it to have a magnetic moment of 2.16 μ_B at 300 K that decreases to 0.9 μ_B at 1.8 K.[16] In contrast, the magnetic moment of **2** is 2.62 μ_B at 300 K, and this decreases to 0.34 μ_B at 1.8 K and clearly tends towards zero as expected for tetravalent uranium which has a singlet magnetic ground state.[16]

To confirm the formulation of **3** we determined the structure by X-ray diffraction and this is illustrated in Figure 1b with selected bond lengths and angles.[12,13,17] Complex **3** is monomeric and the uranium center adopts a distorted octahedral geometry. The U(1)–C(1) bond of 2.268(10) Å is very short compared to all other uranium carbenes,[4,7,9,18] but it is essentially invariant to **II** and **2** which reflects the fact that an electron of essentially nonbonding f-character is removed on oxidation. The U–N bonds in **3** are contracted by 0.1 Å compared to **2**; however, the U–Cl bonds are 0.09 Å longer than the terminal U–Cl bond in **2**, perhaps reflecting greater steric congestion in **3**. This is also suggested by the geometry of the carbene center in **3** which is now slightly pyramidalized $[\Sigma\measuredangle = 345.7(5)°]$.

The electronic absorption spectrum of **3** is dominated by charge transfer in the UV/Vis/NIR regions and exhibits peaks characteristic of U^V.[12,16] A sharp peak at 6650 cm^{-1} is assigned as the pure electronic $\Gamma_7 \rightarrow \Gamma_7'$ transition and broad peaks at 8420–9400 cm^{-1} are assigned as vibronic transitions.[16a] Although **3** has approximately C_s symmetry which should enhance transition intensities compared to O_h, the observed NIR extinction coefficients of 35 $M^{-1} cm^{-1}$ are comparable to O_h UBr_6^- (22 $M^{-1} cm^{-1}$),[19] which is significantly lower than observed for the approximately C_s-symmetric metallocenes $[(\eta^5\text{-}C_5Me_5)_2U(X)(NAr)]$ (X = halide; Ar = bulky aryl; $\varepsilon = 200\text{–}400\ M^{-1} cm^{-1}$).[16c,d] This suggests an effective O_h local symmetry at uranium in **3**, and reduction of peak intensity by efficient coupling of the A_{1g} vibrational mode to electronic transitions. The energetic similarity of the bands observed for **3** to UX_6^- ions suggests that spin–orbit coupling is similar (ca. 2000 cm^{-1}).[16a]

Complexes **2** and **3** both possess octahedral geometry at uranium comprising the same chelating carbene ligand and meridional halide ligands. Thus, **2** and **3** present the first meaningful opportunity to directly compare U^V=C and U^{IV}=C bonds. Complexes **I** and **II** were not investigated computationally because the presence of only one carbene phosphorus substituent and cyclopentadienyl, rather than halide, co-ligands renders these systems incompatible for direct comparison to **2** and **3**. We therefore carried out unrestricted DFT calculations on **2** and **3** and pertinent data are compiled in Table 1.[12] The HOMO and HOMO−1 of **2** and the HOMO of **3** are each singularly occupied and are nonbonding, essentially pure f-orbitals. The computed uranium spin densities and Mulliken charges support the $^3H_4$ and $^2F_{5/2}$ formulations of **2** and **3**, respectively, and show significant charge donation from the carbene ligands to uranium in **2** and **3**. The calculated carbene charges are high, consistent with formally dianionic centers. The α-spin Kohn–Sham orbitals[12] show σ- and π-components of the U=C bonds in **2** and **3**,[12] and the Nalewajski–Mrozek bond indices show significant multiple bond character,[20] with the value for **3** greater than for **2**.

The valence molecular orbitals of **2** and **3** are delocalized over the complexes. To obtain a localized and more chemically relevant description of the U=C bonds, we performed natural bond orbital (NBO) analyses which show polarized U=C bonds in each case. Upon oxidation from U^{IV} to U^V, the uranium character in the U=C bond increases by 8 % in both the σ- and π-components. Within the uranium contribution, a 50 % reduction in 6d character in the σ- and π-components occurs with a concomitant increase in 5f orbital participation. Thus, although the 6d orbitals are radially more expansive compared to the 5f orbitals, oxidation from U^{IV} to U^V apparently results in the 5f orbitals being better suited to the energetic and angular overlaps required to construct the U=C bond in **3**. It should be noted that the 5f orbital percentages in **2** and **3** are high compared to the 40 % 6d and 60 % 5f character of the 18 % uranium components of the U=

C bonds in $[U^{IV}\{C(PPh_2S)_2\}(BH_4)_2(thf)_2]$.[7] This shows that the carbene substituents, as well as the formal oxidation state of uranium, profoundly affects the extent of 6d and 5f orbital participation with ligand orbitals.

A preliminary investigation of the reactivity of **3** and **2** showed metallo-Wittig reactivity with 9-anthracene carboxaldehyde to quantitatively afford the yellow alkene $(Me_3SiNPPh_2)_2C{=}C(H)R$ (**4**, R = 9-anthracene, Figure 2a) in 41% yield.[12,13] This parallels other reports of uranium carbene reactivity,[7a] and confirms the U^V nature of **3**. In agreement with the cyclic voltammetric study of **2**, addition of half a molar equivalent of iodine to **3** does not afford oxidation of uranium to a hexavalent state and we are investigating the reactivity of stronger oxidants towards **2** and **3**. Instead, the uranium center in **3** is formally reduced to give tetravalent $[U\{C(I)(PPh_2NSiMe_3)_2\}(Cl)_{2.5}(I)_{0.5}]$ (**5**; Figure 2b) as yellow plates in 35% crystalline yield.[12,13] Addition of one molar equivalent of iodine to **2** also affords **5**, which suggests the reaction from **2** to **5** involves stepwise oxidation then reduction with **3** as an intermediate. However, we could not observe any intermediates when these reactions were monitored by ^1H NMR spectroscopy and **2** does not react with **5** to give **3**. Therefore, we can not rule out a concerted 1,2-addition of iodine across the $U^{IV}{=}C$ bond when the reaction is conducted in one-pot.

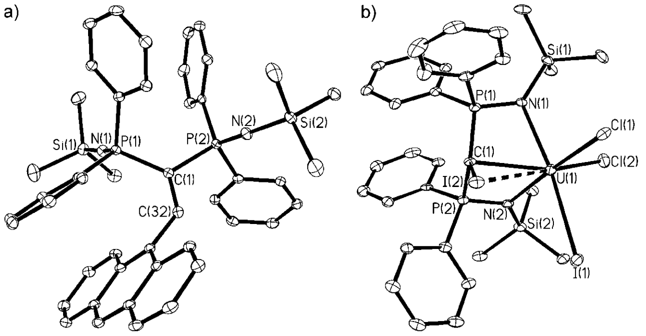

Figure 2. Molecular structures of a) **4** and b) **5**. Displacement ellipsoids set at 30% probability; hydrogen atoms and minor disorder components omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: C(1)–C(32) 1.346(3), C(1)–P(1) 1.821(2), C(1)–P(2) 1.848(2), P(1)–N(1) 1.528(2), P(2)–N(2) 1.525(2); P(1)-C(1)-P(2) 121.58(11); **5**: U(1)–C(1) 2.613(8), U(1)–N(1) 2.425(7), U(1)–N(2) 2.360(7), U(1)–Cl(1) 2.732(2), U(1)–Cl(2) 2.583(3), U(1)–I(1) 3.077(3), U(1)···I(2) 3.345(2) C(1)–P(1) 1.775(8), C(1)–P(2) 1.791(8), P(1)–N(1) 1.611(7), P(2)–N(2) 1.617(8); P(1)-C(1)-P(2) 125.3(5).

To conclude, we have prepared and characterized the first uranium(V) carbene by a simple oxidation strategy, and have confirmed its formulation by spectroscopic and reactivity studies. The isolation of structurally similar **2** and **3** has permitted a meaningful comparison of $U^{IV}{=}C$ and $U^V{=}C$ bonds for the first time. Computational analyses show that upon oxidation: 1) the uranium character of the U=C bond increases; 2) the 6d orbital contribution to the uranium component of the U=C bond halves; 3) the 5f character of the uranium component increases to compensate.

Experimental Section

2: Diethyl ether (20 mL) and toluene (20 mL) were added to a precooled (−78 °C) mixture of $[UCl_4(thf)_3]$ (2.98 g, 5.00 mmol) and $[Li_2\{C(PPh_2{=}NSiMe_3)_2\}]_2$ (2.85 g, 2.50 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 72 h to give a brown suspension. Volatiles were removed in vacuo and the residue was recrystallized from THF (5 mL) layered with diethyl ether (5 mL) to afford **2** as yellow crystals. Several crops were obtained. Combined yield: 3.35 g, 62%. Elemental analysis calcd for $C_{39}H_{54}Cl_3LiN_2O_2P_2Si_2U$: C 44.51, H 5.17, N 2.66; found: C 41.93, H 5.15, N 2.68. ^1H NMR ($[D_8]$THF, 400.2 MHz, 298 K): $\delta = -14.33$ (br, 18H, $Si(CH_3)_3$), 1.79 (m, 8H, OCH_2CH_2), 3.64 (m, 8H, OCH_2CH_2), 8.78 (br, 4H, *p*-Ar-H), 9.18 (br, 8H, *m*-Ar-H), 14.55 ppm (br, 8H, *o*-Ar-H). $^7Li\{^1H\}$ NMR ($[D_8]$THF, 155.5 MHz, 298 K): $\delta = 6.93$ ppm. FTIR (Nujol): $\tilde{\nu} = 1587$ (w), 1344 (m), 1245 (m), 1109 (m), 1042 (br, s), 834 (s), 771 (m) 753 (m), 716 (m), 693 (m), 640 (m), 606 (m), 525 (m), 510 cm^{-1} (m).

3: Toluene (20 mL) was added to a precooled (−78 °C) mixture of **2** (1.05 g, 1.00 mmol). Iodine (0.13 g, 1.00 mmol) was then added and the mixture was allowed to slowly warm to room temperature with stirring over 18 h to afford a deep red solution. Volatiles were removed in vacuo and the resulting red solid was dissolved in toluene. Storage at 5 °C overnight gave a small crop (< 3% yield) of the compound identified as **3a** by X-ray diffraction. The mother liquor was decanted and stored at −30 °C to afford **3** as red crystals. Yield: 0.49 g, 45%. Elemental analysis calcd for $C_{31}H_{38}Cl_2IN_2P_2Si_2U \cdot {}^1/_2\, C_7H_8$: C 39.89, H 4.08, N 2.70; found: C 38.92, H 4.06, N 2.63. ^1H NMR ($[D_6]$benzene, 400.2 MHz, 298 K): $\delta =$ 1.77 (s, 8H, Ar-H), 1.09 (s, 4H, *p*-Ar-H), 0.10 (s, 8H, Ar-H), −0.07 ppm (s, 18H, $Si(CH_3)_3$). FTIR (Nujol): $\tilde{\nu} = 1589$ (w), 1402 (m), 1260 (m), 1109 (m), 1049 (m), 1024 (s), 842 (s), 736 cm^{-1} (m).

4: Toluene (30 mL) was added to a precooled (−78 °C) mixture of 9-anthracene carboxaldehyde (0.21 g, 1.00 mmol) and **2** or **3** (1.00 mmol). The reaction mixture was allowed to slowly warm to room temperature with stirring over 16 h, forming a cloudy red reaction mixture. Volatiles were removed in vacuo and recrystallization from pyridine (2 mL) afforded **4** as yellow crystals (0.31 g, 42%). Elemental analysis calcd for $C_{46}H_{48}N_2P_2Si_2$: C 73.96, H 6.48, N 3.75; found: C 73.87, H 6.57, N 3.69. ^1H NMR ($[D_6]$benzene, 400.2 MHz, 298 K): $\delta = 0.09$ (s, 9H, $Si(CH_3)_3$), 0.40 (s, 9H, $Si(CH_3)_3$), 6.58 (m, 4H, *m*-Ph-H), 6.67 (m, 2H, Ar-H-3,6), 7.08 (m, 2H, Ar-H-2,7), 7.14–7.20 (m, 6H, *m*- and *p*-Ph-H), 7.29–7.39 (m, 6H, *o*- and *p*-Ph-H), 7.59 (d, $J_{HH} = 8.80$ Hz, 2H, Ar-H-4,5), 7.77 (s, 1H, Ar-H-10), 8.20 (d, $J_{HH} =$ 9.20 Hz, 2H, Ar-H-1,8), 8.23 (m, 4H, *o*-Ph-H), 9.09 ppm (dd, $^3J_{PH} =$ 39.62 Hz and 27.61 Hz, 1H, $ArCH{=}CP_2$). $^{13}C\{^1H\}$ NMR ($[D_6]$benzene, 100.6 MHz, 298 K): $\delta = 3.95$ (d, $J_{PC} = 3.02$ Hz, $Si(CH_3)_3$), 4.18 (d, $J_{PC} = 3.02$ Hz, $Si(CH_3)_3$), 125.00, (d, $J_{PC} = 26.67$ Hz, *o*-Ph-CH), 126.31, (d, $J_{PC} = 26.67$ Hz, *o*-Ph-CH), 126.56 (Ar-CH-1,8), 126.89 (Ar-CH-3,6), 127.46 (Ar-CH-2,7), 127.55 (Ar-CH-4,5), 128.33 (Ar-CH-10), 128.40 (Ar-C-12,13), 129.69 (d, $^4J_{PC} = 3.02$ Hz, *p*-Ph-CH) 130.51 (d, $^4J_{PC} = 3.02$ Hz, *p*-Ph-CH), 131.08 (Ar-C-11,14), 131.20 (d, $^2J_{PC} = 11.07$ Hz, *m*-Ph-CH), 132.90 (d, $^2J_{PC} = 11.07$ Hz, *m*-Ph-CH), 141.69 (d, $^1J_{PC} = 73.97$ Hz, *ipso*-Ph-CH), 142.42 (d, $^1J_{PC} = 73.97$ Hz, *ipso*-Ph-CH), 156.15 (m, $CH{=}CP_2$), 191.26 ppm (br, $CH{=}CP_2$). Ar-C-9 was not observed. $^{31}P\{^1H\}$ NMR ($[D_6]$benzene, 162.0 MHz, 298 K): $\delta = -4.35$ (d, $^2J_{PP} = 36.45$ Hz, $C{=}CP_2$), 3.9 ppm (d, $^2J_{PP} = 36.45$ Hz, $C{=}CP_2$). $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene, 79.5 MHz, 298 K): $\delta = -13.36$ (d, $^2J_{PSi} = 22.34$ Hz, $NSi(CH_3)_3$), −12.47 ppm (d, $^2J_{PSi} = 23.22$ Hz, $NSi(CH_3)_3$). FTIR (Nujol): $\tilde{\nu} = 1615$ (C=C, m), 1560 (w), 1261 (m), 1240 (m), 1100 (br, s), 1020 (m), 854 (m), 823 (m), 801 (m), 719 (m), 698 cm^{-1} (m).

5: Toluene (20 mL) was added to a precooled (−78 °C) mixture of **2** (1.05 g, 1.00 mmol). Iodine (0.26 g, 1.00 mmol) was then added and the mixture was allowed to slowly warm to room temperature with stirring over 18 h to afford a brown solution. Volatiles were removed in vacuo and the resulting brown solid was recrystallized from toluene (10 mL) to afford **5** as yellow crystals. Yield 0.39 g, 35%. Elemental analysis calcd for $C_{31}H_{38}Cl_{2.5}I_{1.5}N_2P_2Si_2U$: C 34.67, H 3.57, N 2.61; found: C 34.04, H 3.96, N 2.35. ^{1}H NMR ([D$_6$]benzene, 400.2 MHz, 298 K): $\delta = 1.77$ (s, 8H, Ar-H), 1.10 (s, 8H, Ar-H), −0.07 (s, 4H, *p*-Ar-H), −1.67 (s, 9H, Si(CH$_3$)$_3$, −1.78 ppm (s, 9H, Si(CH$_3$)$_3$). FTIR (Nujol): $\tilde{\nu} = 1588$ (w), 1438 (m), 1257 (m), 1161 (w), 1108 (s), 1049 (m), 1024 (m), 999 (m), 843 (s), 772 cm^{-1} (m).

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[12] Full details can be found in the Supporting Information.

[13] Crystal data for **2**: $C_{39}H_{54}Cl_3LiN_2O_2P_2Si_2U$, $M_r = 1052.28$, space group $P2_1/n$, $a = 12.6786(2)$, $b = 21.0589(3)$, $c = 17.1111(2)$, $\beta = 95.2915(11)$, $V = 4549.16(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.536$ g cm^{-3}; Cu$_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, $\mu = 13.094$ mm^{-1}, $T = 90$ K. 24272 data (8207 unique, $R_{int} = 0.046$, $\theta < 67.5°$). Data were collected on a Oxford Diffraction SuperNova Atlas CCD diffractometer and were corrected for absorption (transmission 0.22–0.69). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0843$, conventional $R = 0.0331$ for F values of 7085 with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.030$ for 485 parameters. Residual electron density extrema were 3.16 and −1.20 e Å^{-3}. Crystal data for **3**: $C_{38}H_{46}Cl_2IN_2P_2Si_2U$, $M_r = 1084.72$, space group $P2_1/c$, $a = 16.3721(3)$, $b = 11.6050(2)$, $c = 22.8223(4)$, $\beta = 98.1607(16)$, $V = 4292.29(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.679$ g cm^{-3}; Cu$_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, $\mu = 0.143$ mm^{-1}, $T = 90$ K. 15074 data (7159 unique, $R_{int} = 0.062$, $\theta < 67.5°$) Data were collected on a Oxford Diffraction SuperNova Atlas CCD diffractometer and were corrected for absorption (transmission 0.19–0.81).The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all to give $wR2 = 0.1560$, conventional $R = 0.0544$ for F values of 6640 with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.050$ for 428 parameters. Residual electron density extrema were 3.06 and −2.77 e Å^{-3}. Crystal data for **4**: $C_{46}H_{48}N_2P_2Si_2$, $M_r = 746.98$, space group $P2_1/n$, $a = 10.2019(11)$, $b = 22.108(2)$, $c = 18.280(2)$, $\beta = 100.901(2)$, $V = 4048.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.226$ g cm^{-3}; Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.201$ mm^{-1}, $T = 90$ K. 24918 data (9235 unique, $R_{int} = 0.048$, $\theta < 25°$) Data were collected on a Bruker SMART APEX CCD diffractometer and were corrected for absorption (transmission 0.61–0.75).The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all to give $wR2 = 0.1260$, conventional $R = 0.0516$ for F values of 6497 with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.020$ for 475 parameters. Residual electron density extrema were 0.57 and −0.31 e Å^{-3}. Crystal data for **5**: $C_{41.50}H_{50}Cl_{2.50}I_{1.50}N_2P_2Si_2U$, $M_r = 1212.42$, space group $P\bar{1}$, $a = 11.938(2)$, $b = 11.975(2)$, $c = 17.611(3)$, $\alpha = 81.020(3)$, $\beta = 71.561(3)$, $\gamma = 74.175(3)$, $V = 2291.0(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.758$ g cm^{-3}; Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 4.855$ mm^{-1}, $T = 90$ K. 18089 data (10202 unique, $R_{int} = 0.045$, $\theta < 25°$). Data were collected on a Bruker SMART APEX CCD diffractometer and were corrected for absorption (transmission 0.66–0.77). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all to give $wR2 = 0.1835$, conventional $R = 0.0684$ for F values of 7047 with $F_o^2 > 2\sigma(F_o^2)$, $S = 0.957$ for 459 parameters. Residual electron density extrema were 4.56 and −3.77 e Å^{-3}. CCDC 803695(**2**), 803696 (**3**), 803697 (**3a**), 803698 (**4**), and 803699 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[15] The formal potential for I_2 in acetonitrile is −0.14 V vs. Fc$^+$/Fc, see: N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877.

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[17] Yellow crystals of $[U\{CH(PPh_2NSiMe_3)_2\}(\mu\text{-}Cl)(Cl)(Cl)_{0.69}(I)_{0.31}]_2$ (**3a**, < 3 % yield) were also isolated from the reaction that produced **3**, which supports the carbene assignment of **3**. See Ref. [12] for full details.

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