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

Oliver J. Cooper, David P. Mills, Jonathan McMaster, Fabrizio Moro, E. Stephen Davies, William Lewis, Alexander J. Blake, and Stephen T. Liddle\*

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

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

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.<sup>[3,10]</sup> However, pentavalent uranium chemistry has been revitalized recently,<sup>[10]</sup> 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 U<sup>V</sup>=C and U<sup>IV</sup>=C bonds for the first time.

Complex **1** was prepared from a disproportionation reaction between  $[UI_3(thf)_4]$  and  $[Li_4\{C(PPh_2NMes)_2\}_2].^{[9]}$  We therefore employed  $[UCl_4(thf)_3]$  and treated it with  $[Li_4\{C(PPh_2NSiMe_3)_2\}_2]^{[11]}$  in toluene/Et\_2O (Scheme 1). The uranium(IV) carbene  $[U\{C(PPh_2NSiMe_3)_2\}(Cl)(\mu-Cl)_2Li-(thf)_2]$  (**2**) was isolated as yellow plates in 62 % yield following workup and recrystallization from THF.<sup>[12]</sup>

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

- [\*\*] We thank the Royal Society, the Engineering and Physical Sciences Research Council, the European Research Council, the University of Nottingham, and the UK National Nuclear Laboratory for funding this work.
  - Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201007675.



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**: <math>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).

Angew. Chem. Int. Ed. 2011, 50, 2383-2386

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

<sup>[\*]</sup> O. J. Cooper, Dr. D. P. Mills, Dr. J. McMaster, Dr. F. Moro, Dr. E. S. Davies, Dr. W. Lewis, Prof. A. J. Blake, Dr. S. T. Liddle School of Chemistry, University of Nottingham University Park, Nottingham, NG7 2RD (UK) Fax: (+44)115-951-3563 E-mail: stephen.liddle@nottingham.ac.uk

## Communications

Table 1:	Selected	experimental	and	computed	data	for <b>2</b>	and	<b>3</b> .[	a]

	Bond lengths and indices			Ato	Atomic spin densities		U=C $\sigma$ -component <sup>[h]</sup>			U=C $\pi$ -component <sup>[h]</sup>		
	U-C <sup>[b]</sup>	$U – C^{[c]}$	$BI^{[d]}$	$m_{U}^{[e]}$	$q_{\cup}^{[f]}$	9c <sup>[g]</sup>	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  $\alpha$ -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.<sup>[13]</sup> Complex **2** is monomeric and occludes a {ClLi(thf)<sub>2</sub>} fragment. The uranium center adopts a distorted octahedral geometry, the carbene is close to planar T-shaped  $[\Sigma \neq =357.9(3)^{\circ}]$ ,<sup>[14]</sup> and the CP<sub>2</sub>N<sub>2</sub>U 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].<sup>[4]</sup>

We interrogated **2** with cyclic voltammetry in the potential range of -1.0 to +0.4 V vs. Fc<sup>+</sup>/Fc and observed two oxidation processes at  $E_p{}^a = -0.5$  V and  $E_p{}^a = +0.27$  V.<sup>[12]</sup> 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.<sup>[15]</sup>

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<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>}(Cl)<sub>2</sub>(I)] (**3**) as red crystals in 45 % yield after workup and recrystallization from toluene. The characterization data support this formulation.<sup>[12]</sup> In particular, variable-temperature magnetic moment measurements on pentavalent **3** showed it to have a magnetic moment of 2.16  $\mu_B$  at 300 K that decreases to 0.9  $\mu_B$  at 1.8 K.<sup>[16]</sup> In contrast, the magnetic moment of **2** is 2.62  $\mu_B$  at 300 K, and this decreases to 0.34  $\mu_B$  at 1.8 K and clearly tends towards zero as expected for tetravalent uranium which has a singlet magnetic ground state.<sup>[16]</sup>

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.<sup>[12,13,17]</sup> 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,<sup>[4,7,9,18]</sup> 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 [ $\Sigma \neq = 345.7(5)^{\circ}$ ].

The electronic absorption spectrum of **3** is dominated by charge transfer in the UV/Vis/NIR regions and exhibits peaks characteristic of U<sup>V</sup>.<sup>[12,16]</sup> A sharp peak at 6650 cm<sup>-1</sup> is assigned as the pure electronic  $\Gamma_7 \rightarrow \Gamma_7'$  transition and broad peaks at 8420–9400 cm<sup>-1</sup> are assigned as vibronic transitions.<sup>[16a]</sup> Although **3** has approximately  $C_s$  symmetry which should enhance transition intensities compared to  $O_h$ , the

observed NIR extinction coefficients of  $35 \text{ m}^{-1} \text{ cm}^{-1}$  are comparable to  $O_h$  UBr<sub>6</sub><sup>-</sup>  $(22 \text{ m}^{-1} \text{ cm}^{-1})$ ,<sup>[19]</sup> which is significantly lower than observed for the approximately  $C_s$ -symmetric metallocenes [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(X)(NAr)] (X = halide; Ar = bulky aryl;  $\varepsilon = 200-400 \text{ m}^{-1} \text{ cm}^{-1}$ ).<sup>[16c,d]</sup> This suggests an effective  $O_h$  local symmetry at uranium in **3**, and reduction of peak intensity by efficient coupling of the A<sub>1g</sub> vibrational mode to electronic transitions. The energetic similarity of the bands observed for **3** to UX<sub>6</sub><sup>-</sup> ions suggests that spin–orbit coupling is similar (ca. 2000 cm<sup>-1</sup>).<sup>[16a]</sup>

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 UV=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.<sup>[12]</sup> 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 <sup>3</sup>H<sub>4</sub> and  ${}^{2}F_{5/2}$  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<sup>[12]</sup> show  $\sigma$ - and  $\pi$ -components of the U=C bonds in 2 and 3.<sup>[12]</sup> and the Nalewajski-Mrozek bond indices show significant multiple bond character,<sup>[20]</sup> 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  $\sigma$ - and  $\pi$ -components. Within the uranium contribution, a 50% reduction in 6d character in the  $\sigma$ - and  $\pi$ -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  $[U^{IV}{C(PPh_2S)_2}(BH_4)_2(thf)_2]$ .<sup>[7]</sup> 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



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)-C(1) 2.732(2), U(1)-C(2) 2.583(3), U(1)-I(1) 3.077(3),  $U(1)\cdots I(2)$  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).

41% yield.<sup>[12,13]</sup> This parallels other reports of uranium carbene reactivity,<sup>[7a]</sup> 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.<sup>[12,13]</sup> 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 <sup>1</sup>H 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<sup>IV</sup>=C bond when the reaction is conducted in one-pot.

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<sub>4</sub>(thf)<sub>3</sub>] (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 C39H54Cl3LiN2O2P2Si2U: C 44.51, H 5.17, N 2.66; found: C 41.93, H 5.15, N 2.68. <sup>1</sup>H NMR ([D<sub>8</sub>]THF, 400.2 MHz, 298 K):  $\delta = -14.33$  (br, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.79 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 3.64 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 8.78 (br, 4H, p-Ar-H), 9.18 (br, 8H, m-Ar-H), 14.55 ppm (br, 8H, o-Ar-H). <sup>7</sup>Li{<sup>1</sup>H} NMR ([D<sub>8</sub>]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),  $510 \text{ cm}^{-1}$  (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<sub>31</sub>H<sub>38</sub>Cl<sub>2</sub>IN<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>U<sup>.1</sup>/<sub>2</sub>C<sub>7</sub>H<sub>8</sub>: C 39.89, H 4.08, N 2.70; found: C 38.92, H 4.06, N 2.63. <sup>1</sup>H 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, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>). FTIR (Nujol):  $\tilde{\nu} = 1589$  (w), 1402 (m), 1260 (m), 1109 (m), 1049 (m), 1024 (s), 842 (s), 736 cm<sup>-1</sup> (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<sub>46</sub>H<sub>48</sub>N<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>: C 73.96, H 6.48, N 3.75; found: C 73.87, H 6.57, N 3.69. <sup>1</sup>H NMR ([D<sub>6</sub>]benzene, 400.2 MHz, 298 K):  $\delta = 0.09$  (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.40 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 6.58 (m, 4 H, 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,  $J_{\rm HH} = 8.80$  Hz, 2H, Ar-H-4,5), 7.77 (s, 1H, Ar-H-10), 8.20 (d,  $J_{\rm HH} =$ 9.20 Hz, 2H, Ar-H-1,8), 8.23 (m, 4H, o-Ph-H), 9.09 ppm (dd, <sup>3</sup>J<sub>PH</sub> = 39.62 Hz and 27.61 Hz, 1 H, ArCH=CP<sub>2</sub>).  $^{13}C{^{1}H}$  NMR ([D<sub>6</sub>]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<sub>PC</sub> = 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,  ${}^{4}J_{PC} = 3.02$  Hz, p-Ph-CH) 130.51 (d,  ${}^{4}J_{PC} = 3.02$  Hz, p-Ph-CH), 131.08 (Ar-C-11,14), 131.20 (d,  ${}^{2}J_{PC} = 11.07 \text{ Hz}, m$ -Ph-CH), 132.90 (d,  ${}^{2}J_{PC} = 11.07 \text{ Hz}, m$ -Ph-CH), 141.69 (d,  ${}^{1}J_{PC} = 73.97$  Hz, *ipso*-Ph-CH), 142.42 (d,  ${}^{1}J_{PC} = 73.97$  Hz, ipso-Ph-CH), 156.15 (m, CH=CP<sub>2</sub>), 191.26 ppm (br, CH=CP<sub>2</sub>). Ar-C-9 was not observed.  ${}^{31}P{}^{1}H{}$  NMR ([D<sub>6</sub>]benzene, 162.0 MHz, 298 K):  $\delta = -4.35$  (d,  ${}^{2}J_{PP} = 36.45$  Hz, C=CP<sub>2</sub>), 3.9 ppm (d,  ${}^{2}J_{PP} = 36.45$  Hz, C= CP<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR ([D<sub>6</sub>]benzene, 79.5 MHz, 298 K):  $\delta = -13.36$  (d,  $^{2}J_{PSi} = 22.34 \text{ Hz}, \text{ NSi}(CH_{3})_{3}), -12.47 \text{ ppm} (d, ^{2}J_{PSi} = 23.22 \text{ Hz}, \text{ NSi}$ (CH<sub>3</sub>)<sub>3</sub>). 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),  $698 \text{ cm}^{-1} \text{ (m)}.$ 

**5**: Toluene (20 mL) was added to a precooled  $(-78 \,^{\circ}\text{C})$  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

Communications

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. <sup>1</sup>H NMR ([D<sub>6</sub>]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<sub>3</sub>)<sub>3</sub>, -1.78 ppm (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). FTIR (Nujol):  $\tilde{\nu} = 1588$  (w), 1438 (m), 1257 (m), 1161 (w), 1108 (s), 1049 (m), 1024 (m), 999 (m), 843 (s), 772 cm<sup>-1</sup> (m).

Received: December 7, 2010 Revised: January 6, 2011 Published online: February 14, 2011

**Keywords:** carbene ligands · f-block elements · metallo-Wittig reactivity · multiple bonding · uranium complexes

- [1] W. A. Nugent, J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, **1988**.
- [2] G. R. Giesbrecht, J. C. Gordon, Dalton Trans. 2004, 2387.
- [3] T. W. Hayton, Dalton Trans. 2010, 39, 1145.
- [4] a) R. E. Cramer, R. B. Maynard, J. C. Paw, J. W. Gilje, J. Am. Chem. Soc. 1981, 103, 3598; b) R. E. Cramer, M. A. Bruck, F. Edelmann, D. Afzal, J. W. Gilje, H. Schmidbaur, Chem. Ber. 1988, 121, 417.
- [5] J. T. Lyon, L. Andrews, H. S. Hu, J. Li, *Inorg. Chem.* 2008, 47, 1435.
- [6] C. Villiers, M. Ephritikhine, Chem. Eur. J. 2001, 7, 3043.
- [7] a) T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, J. Am. Chem. Soc. 2009, 131, 963; b) J. C. Tourneux, J. C. Berthet, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, Dalton Trans. 2010, 39, 2494.
- [8] a) S. T. Liddle, J. McMaster, J. C. Green, P. L. Arnold, *Chem. Commun.* 2008, 1747; b) D. P. Mills, O. J. Cooper, J. McMaster, W. Lewis, S. T. Liddle, *Dalton Trans.* 2009, 4547; c) A. J. Wooles, D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* 2010, *39*, 500; d) A. J. Wooles, O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* 2010, *29*, 2315.
- [9] O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* 2010, 39, 5074.
- [10] For reviews see: a) C. R. Graves, J. L. Kiplinger, *Chem. Commun.* 2009, 3831; b) S. Fortier, T. W. Hayton, *Coord. Chem. Rev.* 2010, 254, 197; c) P. L. Arnold, J. B. Love, D. Patel, *Coord. Chem. Rev.* 2010, 254, 19753.
- [11] a) A. Kasani, R. P. Kamalesh Babu, R. McDonald, R. G. Cavell, Angew. Chem. **1999**, 111, 1580; Angew. Chem. Int. Ed. **1999**, 38, 1483; b) C. M. Ong, D. W. Stephan, J. Am. Chem. Soc. **1999**, 121, 2939.
- [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  $P2_l/n$ , a = 12.6786(2), b = 21.0589(3), c = 17.1111(2),  $\beta = 95.2915(11)$ , V = 4549.16(9) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.536$  g cm<sup>-3</sup>; Cu<sub>K\alpha</sub> radiation,  $\lambda = 1.5418$  Å,  $\mu = 13.094$  mm<sup>-1</sup>, T = 90 K. 24272 data (8207 unique,  $R_{int} = 0.046$ ,  $\theta < 67.5^{\circ}$ ). 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<sup>-3</sup>. 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<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.679$  g cm<sup>-3</sup>; Cu<sub>K\alpha</sub> radiation,  $\lambda = 1.5418$  Å,  $\mu = 0.143$  mm<sup>-1</sup>, T = 90 K. 15074 data (7159 unique,

 $R_{\rm int} = 0.062, \ \theta < 67.5^{\circ}$ ) 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 = 0.0544for 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  $-2.77 \text{ e} \text{\AA}^{-3}$ . Crystal data for **4**: C<sub>46</sub>H<sub>48</sub>N<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>,  $M_r = 746.98$ , 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<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.226$  g cm<sup>-3</sup>; Mo<sub>Ka</sub> radiation,  $\lambda = 0.71073$  Å,  $\mu = 0.201$  mm<sup>-1</sup>, T = 90 K. 24918 data (9235 unique,  $R_{\rm int} = 0.048$ ,  $\theta < 25^{\circ}$ ) 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  $-0.31 \text{ e} \text{\AA}^{-3}$ . 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), a =81.020(3),  $\beta = 71.561(3)$ ,  $\gamma = 74.175(3)$ , V = 2291.0(8) Å<sup>3</sup>, Z = 2,  $\rho_{\text{calcd}} = 1.758 \text{ g cm}^{-3}$ ; Mo<sub>Ka</sub> radiation,  $\lambda = 0.71073 \text{ Å}$ ,  $\mu =$ 4.855 mm<sup>-1</sup>, T = 90 K. 18089 data (10202 unique,  $R_{int} = 0.045$ ,  $\theta < 25^{\circ}$ ). 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  $F_{0}^{2} > 2\sigma(F_{0}^{2}), S = 0.957$  for 459 parameters. Residual electron density extrema were 4.56 and  $-3.77 \text{ e} \text{ Å}^{-3}$ . 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.

- [14] a) D. P. Mills, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* **2009**, *28*, 6771; b) S. T. Liddle, D. P. Mills, B. M. Gardner, J. McMaster, C. Jones, W. D. Woodul, *Inorg. Chem.* **2009**, *48*, 3520.
- [15] The formal potential for I<sub>2</sub> in acetonitrile is -0.14 V vs. Fc<sup>+</sup>/Fc, see: N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877.
- [16] a) J. Selbin, J. D. Ortego, Chem. Rev. 1969, 69, 657; b) I. Castro-Rodriguez, K. Olsen, P. Gantzel, K. Meyer, J. Am. Chem. Soc. 2003, 125, 4565; c) C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, J. Am. Chem. Soc. 2007, 129, 11914; d) C. R. Graves, P. Yang, S. A. Kozimor, A. E. Vaughn, D. L. Clark, S. D. Conradson, E. J. Schelter, B. L. Scott, J. D. Thompson, P. J. Hay, D. E. Morris, J. L. Kiplinger, J. Am. Chem. Soc. 2008, 130, 5272; e) G. Nocton, P. Horeglad, J. Pécaut, M. Mazzanti, J. Am. Chem. Soc. 2008, 130, 16633; f) A. R. Fox, C. C. Cummins, J. Am. Chem. Soc. 2009, 131, 5716; g) D. D. Schnaars, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2009, 131, 17532; h) S. Fortier, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2010, 132, 6888.
- [17] Yellow crystals of [U{CH(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>}(µ-Cl)(Cl)-(Cl)<sub>0.69</sub>(I)<sub>0.31</sub>]<sub>2</sub> (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.</p>
- [18] As evidenced from a search of the Cambridge Structural Database (CSD version 1.11, date: 29/10/2010): a) F. H. Allen, *Acta Crystallogr. Sect. B* 2002, *58*, 380.
- [19] J. L. Ryan, J. Inorg. Nucl. Chem. 1971, 33, 153.
- [20] Nalewajski–Mrozek bond indices incorporate ionic and covalent components, see: A. Michalak, R. L. DeKock, T. Ziegler, J. Phys. Chem. A 2008, 112, 7256.