



Uranium-Carbene-Imido Metalla-Allenenes: Ancillary-Ligand-Controlled Cis-/Trans-Isomerisation and Assessment of Trans-Influence in the $R_2C=UIV=NR'$ Unit ($R = Ph_2PNSiMe_3$; $R' = CPh_3$)

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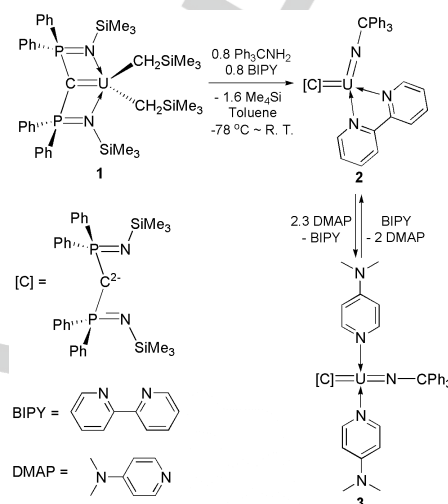


Uranium-Carbene-Imido Metalla-Allenes: Ancillary-Ligand-Controlled *Cis-/Trans*-Isomerisation and Assessment of *Trans*-Influence in the $R_2C=U^{IV}=NR'$ Unit ($R = Ph_2PNSiMe_3$; $R' = CPh_3$)

Erli Lu, Oliver J. Cooper, Floriana Tuna, Ashley J. Wooles, Nikolas Kaltsoyannis,* and Stephen T. Liddle*

Abstract: We report uranium(IV)-carbene-imido complexes $[U(BIPM^{TMS})(NCPH_3)(\kappa^2-N,N'-BIPY)]$ (**2**) ($BIPM^{TMS} = C(PPh_2NSiMe_3)_2$; $BIPY = 2,2$ -bipyridine) and $[U(BIPM^{TMS})(NCPH_3)(DMAP)_2]$ (**3**) ($DMAP = 4$ -dimethylaminopyridine) that contain unprecedented, discrete $R_2C=U=NR'$ units. These complexes complete the family of $E=U=E$ ($E = CR_2, NR, O$) metalla-allenes with feasible first row hetero-element combinations. Intriguingly, **2** and **3** contain *cis*- and *trans*- $C=U=N$ units, respectively, representing rare examples of controllable *cis*-/*trans*-isomerisation in *f*-block chemistry. This work reveals a clear-cut example of the *trans*-influence in a mid-valent uranium system, and thus a strong preference for the *cis*-isomer, which is computed in a co-ligand-free truncated model - to isolate the electronic *trans*-influence from steric contributions - to be more stable than the *trans*-isomer by ~ 12 kJ mol⁻¹ with an isomerisation barrier of ~ 14 kJ mol⁻¹.

Uranium metalla-allenes are a family of compounds containing the $(E=U=E)^{n+}$ unit where E or E' is a first-row dianionic group 14-16 element ligand (e.g. O²⁻, R₂C²⁻, RN²⁻; R = generic organo-group). The most well-known member of this family is uranyl(VI), $(O=U=O)^{2+}$,^[1] which is the most prevalent natural occurrence of uranium and is a crucial component of nuclear fuel recycling and waste remediation.^[2] Understanding the underlying electronic structure and bonding of this family of uranium metalla-allenes is of great scientific interest in terms of revealing the very essence of uranium-ligand multiple bonding and understanding the interplay of the *trans*-influence and specific to early actinides the inverse-*trans*-influence (ITI).^[3] However, despite the ubiquitous nature of uranyl,^[1g,4] the paucity of other members of the family reflects their underdeveloped nature and synthetic challenges to preparing them. For example, regarding homoleptic combinations the second largest family member after uranyl (>2900 CSD entries^[4]) is $RN=U=NR$ (~ 70 entries)^[5] and $R_2C=U=CR_2$ is even more elusive (5 entries).^[6] For heteroleptic variants there are eight $R_2N=U=O$ ^[7] and only four $R_2C=U=O$.^[7a,8] Where $R_2C=U=NR$ is concerned there are no examples of discrete units except for conceivably in $[U(BIPM^{TMS})(NMe_3)(O)(DMAP)]$ [$BIPM^{TMS} = C(PPh_2NSiMe_3)_2$; Mes = mesityl; DMAP = 4-dimethylaminopyridine]. However, this complex cannot be considered to contain a discrete $R_2C=U=NR$ unit due to extensive delocalisation and the clear structure-dictating role of the $RN=U=O$ unit.^[7a] Furthermore, in almost all complexes the uranium is high oxidation state (V, VI),^[9] and preparing mid-valent analogues represents a significant synthetic challenge because the combination of 5f² uranium(IV) with strongly electron-donating ligands renders the uranium(IV) centre electronically overburdened when compared with uranium(VI) congeners, and thus more liable to decompose.



Scheme 1. Synthesis of complexes *cis*-**2** and *trans*-**3**.

Clearly, there remain significant knowledge gaps to be addressed: i) a discrete $R_2C=U=NR$ unit remains a ‘missing piece’; ii) very few heteroleptic combinations have been reported; iii) because in almost all cases uranium is in a high oxidation state (V, VI), mid-valent $(E=U^{IV}=E')^{0+}$ complexes are exceedingly rare, despite their obvious importance as potential models for 2-electron reduced uranyl $(O=U^{IV}=O)^{0+}$ which plays a key role in reductive uranyl functionalisation and environmental mobility.^[10]

Here, we report unprecedented heteroleptic mid-valent uranium(IV) *cis*- and *trans*-carbene-imido complexes, completing the uranium metalla-allene family. Both the molecular structures and theoretical calculations show an electronic preference for the *cis*-geometry, which is attributed to a *trans*-influence in mid-valent uranium systems, rather than the ITI found in high-valent uranium analogues where the $(E=U=E)^{n+}$ units are overwhelmingly *trans*. This work provides unambiguous experimental and theoretical support to the occurrence of the *trans*-influence in actinide chemistry.^[11] Lastly, we demonstrate that *cis*- and *trans*-isomers can be deliberately accessed, representing exceedingly rare examples of controllable *cis*-/*trans*-isomerisation in *f*-block chemistry.

Encouraged by prior work,^[6a,7a,8a,12] the uranium(IV)-carbene-bis-alkyl $[U(BIPM^{TMS})(CH_2SiMe_3)_2]$ (**1**)^[13] was used as a starting material. Seeking to effect α -abstraction of an intermediate metal-alkyl-amide, treatment of **1** with 0.8 equivalents of Ph_3CNH_2 and 0.8 equivalents of 2,2-bipyridine (BIPY) as an ‘external’ Lewis base produced the desired uranium(IV)-carbene-imide complex $[U(BIPM^{TMS})(NCPH_3)(\kappa^2-N,N'-BIPY)]$ (**2**) with elimination of $SiMe_4$ (Scheme 1). Complex **2** was obtained as a brown crystalline solid in 92% yield based on Ph_3CNH_2 and BIPY.^[13] The reaction must be carried out under highly-dilute conditions at low temperature with the optimised 0.8 sub-stoichiometric quantities of substrates or only the corresponding $BIPM^{TMS}$ -uranium(IV)-bis-amide is formed,^[14] and BIPY must be used to effect α -abstraction.

The ¹H NMR spectrum of **2** spans -35 to $+45$ ppm and the ³¹P NMR spectrum exhibits a broad resonance at -905 ppm. Weak *f* →

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f absorptions are observed across the visible and near-IR regions of the electronic absorption spectrum, consistent with the brown colour of this uranium(IV) complex. The magnetic moment of powdered **2** is $2.4 \mu_B$ at 298 K, decreasing slowly to $2.1 \mu_B$ at ca 60 K, after which the magnetic moment drops precipitously to $0.9 \mu_B$ at 2 K and is still decreasing. This suggests that the paramagnetic states are split into a low lying group populated even at low temperature, hence the high magnetic moment at 1.8 K,^[15] and a higher lying group that is not significantly populated up to 300 K, thus the small increase in magnetic moment at higher temperatures. This is characteristic of uranium(IV) with strongly donating multiply bonded ligands, and is usually observed in complexes with strong axial crystal fields;^[16] this suggests that the strong donor nature of the ligands is the key factor and symmetry is a secondary effect.

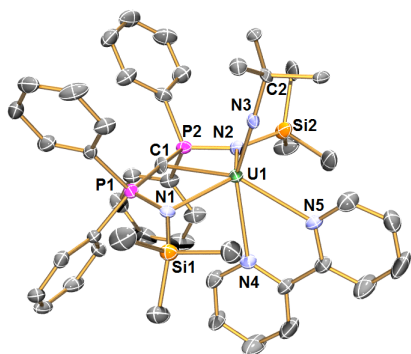


Figure 1. Solid state molecular structure of **2**. Displacement ellipsoids set at 40% probability. Hydrogen atoms, aromatic C-atoms in $-\text{CPh}_3$ group (except *ipso*-carbons), and any lattice solvents are omitted for clarity. Selected bond lengths [Å]: U1–C1 2.491(6), U1–N3 1.977(4), U1–N1 2.459(5), U1–N2 2.470(5), U1–N4 2.669(4), U1–N5 2.693(5). Selected bond angles [°]: C1–U1–N3 111.28(18), U1–N3–C2 173.9(4).

Complex **2** has been characterised by single crystal X-ray diffraction, and the molecular structure is shown in Figure 1. The salient structural features concern the $\text{C}=\text{U}^{\text{IV}}=\text{N}$ unit. The $\text{U}^{\text{IV}}=\text{N}$ [1.977(4) Å] and $\text{U}^{\text{IV}}=\text{C}$ [2.491(6) Å] bond lengths are similar to other terminal $\text{U}^{\text{IV}}=\text{N}$ bond lengths (1.95–2.04 Å)^[16,17] or $\text{U}^{\text{IV}}=\text{C}_{\text{carbene}}$ bond lengths (2.30 – 2.50 Å).^[18] For the latter, care should be taken when judging the nature of the interaction only by bond length, but multiple bond character is corroborated by computational analysis (*vide infra*). Multiple bond character of the $\text{U}^{\text{IV}}=\text{N}$ linkage is also suggested by the linear $\text{U}=\text{N}_{\text{imido}}-\text{CR}_3$ arrangement [173.9(4)°]. The most intriguing feature of **2** is the *cis*- $\text{C}=\text{U}^{\text{IV}}=\text{N}$ unit, with a $\text{C}_{\text{carbene}}=\text{U}=\text{N}_{\text{imido}}$ angle of 111.28(18)°. This is in sharp contrast to the overwhelmingly prevalent *trans*- $\text{E}=\text{U}=\text{E}'$ moieties, where $\angle \text{E}=\text{U}=\text{E}'$ is around 180°. The BIPY bond lengths are consistent with its neutral form, and the $\text{U}-\text{N}_{\text{BIPY}}$ bond lengths are long [2.669(4) and 2.693(5) Å], and thus dative.^[19]

The *cis*-geometry of **2** suggests the potential for a *trans*-influence. However, chelating BIPY would enforce this geometry, so whether the BIPY is coordinated because of the geometry or is driving it is a moot point. To probe this aspect we targeted a *trans*-analogue of **2**, and treated **2** with 2.3 equivalents of the strong donor 2,2-dimethylaminopyridine (DMAP) to give the *trans* complex $[\text{U}(\text{BIPM}^{\text{IMS}})(\text{NCPH}_3)(\text{DMAP})_2]$ (**3**). The reaction of **2** with 2.3 equivalents of DMAP was monitored by ^1H NMR spectroscopy, revealing an equilibrium ($K_{298\text{K}} = \sim 0.38$) within 1 hour (Scheme 1). Extending the reaction time or elevating the reaction temperature does not drive the equilibrium towards the formation of **3**, or leads to significant decomposition of **2** and **3**. Scale-up and repeated crystallisation yielded single crystals of **3**. The equilibrium means that an analytically pure sample cannot be

obtained (see SI), but the structure of **3** confirms its formulation and it can be identified by difference in ^1H NMR spectra.

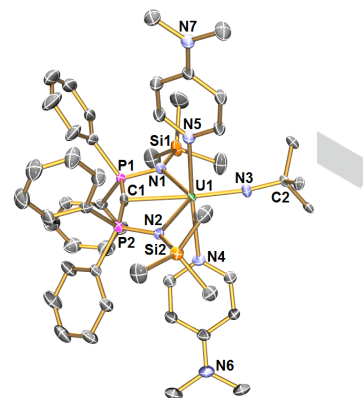


Figure 2. Solid state molecular structure of **3**. Displacement ellipsoids set at 40% probability. Hydrogen atoms, aromatic C-atoms in $-\text{CPh}_3$ group (except *ipso*-carbons), and any lattice solvents are omitted for clarity. Selected bond lengths [Å]: U1–C1 2.500(6), U1–N3 2.032(5), U1–N1 2.507(4), U1–N2 2.567(4), U1–N4 2.586(5), U1–N5 2.580(5). Selected bond angles [°]: C1–U1–N3 175.97(18), U1–N3–C2 171.6(4).

The molecular structure of **3** is shown in Figure 2. The *trans*-conformation of the $\text{N}=\text{U}=\text{C}$ unit is confirmed by the essentially linear $\text{C}_{\text{carbene}}=\text{U}=\text{N}_{\text{imido}}$ unit [175.97(18)°], some 64° more obtuse than the corresponding angle in **2**. The elongation of $\text{U}=\text{N}_{\text{imido}}$ bond from **2** [1.977(4) Å] to **3** [2.032(5) Å] is significant, although the apparent elongation of $\text{U}=\text{C}_{\text{carbene}}$ bond is not statistically meaningful [2.500(6) Å (**3**) vs 2.491(6) Å (**2**)]. These data suggest the validity of the *trans*-effect in mid-valent uranium system, and in the continued absence of a discrete *cis*-($\text{O}=\text{U}=\text{O}$)²⁺, **2** provides a unique opportunity to investigate the electronic structure and bonding of the $\text{C}=\text{U}^{\text{IV}}=\text{N}$ unit, which can be regarded as a 2-electron reduced heteroatomic *cis*-analogue of uranyl.

We computed the full structures of **2** and **3** using DFT at the GGA (BP86) level, and the bond lengths and angles are reproduced within 0.08 Å and 3° of the experimental values. The multiple bond character of $\text{U}=\text{C}_{\text{carbene}}$ and $\text{U}=\text{N}_{\text{imido}}$ bonds are verified by the Kohn Sham, and Natural Bond orbital (Figure 3) representations, which show two- and three-fold bonding interactions, respectively. Also, topological Quantum Theory of Atoms-in-Molecules (QTAIM) analysis returns average values of 0.21 and 0.04 for the corresponding bond ellipticities that are characteristic of double and triple bond interactions, respectively.^[20] Significant differences in the bonding within the $\text{C}=\text{U}=\text{N}$ unit are observed on moving from *cis* **2** to *trans* **3**. Specifically, NBO analysis shows the uranium contributions to the σ - and π -components of the $\text{U}=\text{C}$ bond fall from 16 to 14 and 15 to 10%, respectively; the σ -component of the $\text{U}=\text{N}$ bond is returned as ionic so the uranium contribution is below the 5% NBO threshold, but for the two quasi-equivalent π -bonds the uranium contributions fall from 23 to 19%, respectively. In all uranium components of the $\text{U}=\text{C}$ and $\text{U}=\text{N}$ bonds 5f contributions dominate ($\sim 80\%$) with the remainder being 6d character. The reductions in uranium contributions to the $\text{U}=\text{C}$ and $\text{U}=\text{N}$ bonds from *cis* **2** to *trans* **3** are also reflected in the computed $\text{U}=\text{C}$ and $\text{U}=\text{N}$ bond lengths [and orders, respectively] for **2** (2.412, 1.994 Å [1.20, 2.59]) and **3** (2.437, 2.017 Å [1.17, 2.55]) that are clearly longer [lower] in *trans* **3** compared to *cis* **2**. These trends are also observed in the QTAIM analysis of these linkages; the bond critical point (BCP) ρ , $\nabla^2\rho$ and energy density [$H(r)$] terms vary from 0.085/0.130/-0.026 for **2** to 0.081/0.100/-0.024 for **3** ($\text{U}=\text{C}$), and 0.163/0.562/-0.085 for **2** to 0.155/0.481/-0.077 for **3** ($\text{U}=\text{N}$), respectively. Taken together, the computational data unequivocally produce the consistent picture

that on moving from *cis* to *trans* the U=C and U=N bonds weaken, consistent with a *trans*-influence.

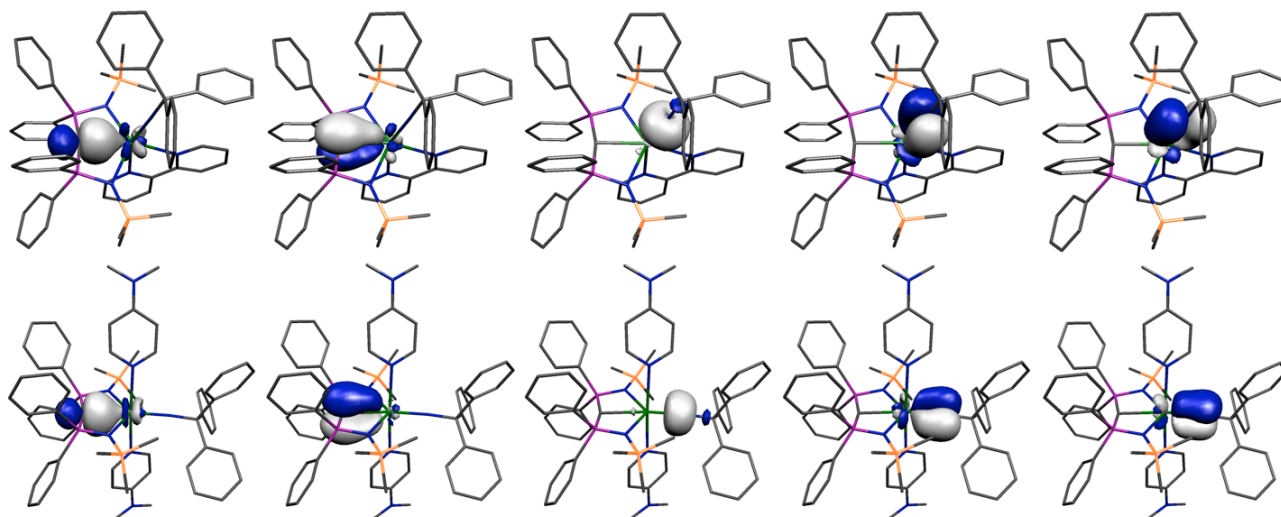


Figure 3. NBO representations of the σ - and π -interactions in the U=C and U=N bonds of *cis*-2 (top) and *trans*-3 (bottom). Left to right in each case: U=C σ -bond, U=C π -bond, U=N σ -bond, U=N π -bond, U=N π -bond. Hydrogen atoms are omitted for clarity.

To evaluate whether the *cis*-C=U=N arrangement is thermodynamically preferable over *trans*-C=U=N, or is a kinetic result stemming from the presence of the bidentate BIPY ligand inducing a cleft, we also computed the hypothetical model species 2-BIPY, $[\text{U}\{\text{C}(\text{PH}_2\text{NSiH}_3)_2\}(\text{NCH}_3)]$, in which the BIPY ligand was removed and the peripheral substituents were truncated to remove steric factors. These calculations were performed at the hybrid DFT (PBE0) level, as such an approach is known to give more reliable energetics than pure GGA functionals. It is significant that the geometry optimised 2-BIPY retains the *cis*-C=U=N arrangement ($\text{C}=\text{U}=\text{N} = 108.18^\circ$), and when the *trans*-C=U=N arrangement was used as a starting point the structure converged to the *cis* form when there is no obvious steric reason to do so. In order to probe further the *cis/trans* energetics we performed a constrained SCF energy surface scan of the C=U=N angle, incrementing from its optimised value in 5° steps to 178.18° whilst allowing all other geometric variables to relax at each point. The result is shown in Figure 4, which plots the SCF energy of 2-BIPY relative to its fully optimised geometry as a function of the C=U=N angle. The optimised *cis* form is 12.3 kJ mol^{-1} more stable than at $\text{C}=\text{U}=\text{N} = 178.18^\circ$, and the maximum of the energy profile (at 163.18°) is 14.2 kJ mol^{-1} above the global minimum.

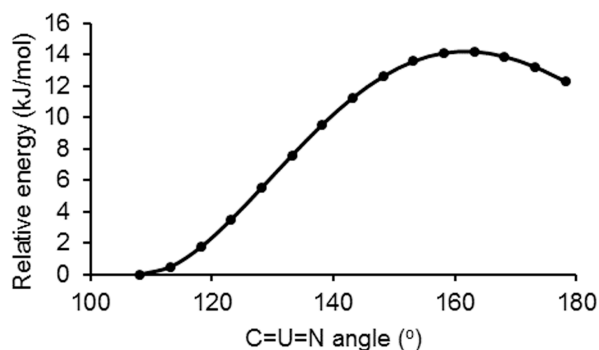


Figure 4. Constrained SCF energy surface scan of the N=U=C angle in 2-BIPY.

To probe the origin of the energetic preference for the *cis* geometry, we have calculated the electrostatic potential (ESP) of the $[\text{U}\{\text{C}(\text{PH}_2\text{NSiH}_3)_2\}]^{2+}$ unit in 2-BIPY. This is shown in the bottom image of Fig. S8, and clearly displays an asymmetry in the

positive ESP directed towards the *cis* position. This is the point of highest positive (repulsive) energy for an incoming positive charge, *i.e.* where a negatively charged ligand would most prefer to bind. Fig. S8 also shows how the ESP varies as a function of C-U distance; as this shortens from 6.429 \AA to its value in 2-BIPY the essentially spherical ESP around the U distorts to direct the imido ligand to the *cis* position.

By contrast to the calculations on the full systems 2 and 3, there is a much more significant lengthening ($\sim 0.11 \text{ \AA}$) of the U=C_{carbene} bond in 2-BIPY from the *cis* to the *trans* forms (*i.e.* the structure at $\text{C}=\text{U}=\text{N} = 178.18^\circ$ in the SCF energy surface scan), while the elongation of the U=N_{imido} distance is much more modest (Table S1). These changes are reflected in the QTAIM BCP metrics, and the QTAIM delocalisation index and Wiberg and bond order parameters, which are significantly reduced for the U-C interaction, but less so for the U-N (Table S1). NBO analyses of the *cis* and *trans* forms reveals that the only significant change is a reduction in the uranium contribution to the σ component of the U=C_{carbene} interaction, from 17 to 12%. It would therefore appear that, in the absence of neutral N-donor ancillary ligands, the *trans* influence manifests itself more as a weakening of the U=C_{carbene} bond than the U=N_{imido}. This seems reasonable given that the imido group would be expected to be the strongest donor, although we note that there is likely more flexibility in the simplified BIPM framework compared with the real version with sterically more demanding substituents, which permits greater changes in $r(\text{U}=\text{C}_{\text{carbene}})$.

The preference for *cis*- over *trans*-isomers in the present mid-valent uranium(IV) complexes contrasts with the prevalence of the ITI in high oxidation uranium(V/VI) systems.^[3,21] The ITI was first introduced by Denning *et al.*,^[3] who attributed the effect to hybridisation between the semi-core 6p orbitals and the valence 5f, an explanation largely supported by our later work.^[22] That the present lower oxidation state systems show behaviour typical of the regular *trans*-influence in d-block transition metal chemistry suggests that 6p/5f hybridisation is less likely in uranium(IV) than (VI). PBE0 calculations on U^{6+} and U^{4+} ions reveal a 6p/5f energy gap of 19.0 eV in the former and 22.9 eV in the latter (taken as ΔE of fully occupied β -spin 6p levels and the fully unoccupied 5f orbitals); an almost 4 eV increase in the 6p/5f energy gap should indeed lead to less 6p/5f hybridisation. That said, the nature, *i.e.* the polarising power, and combination, *i.e.* the relative polarising power of any strongly-donating *trans*-orientated ligands, coupled

to the oxidation state of the metal most likely combine in a complex interplay to determine whether the regular *trans*-influence or ITI operates.

In conclusion, we have reported two uranium(IV)-carbene-imido complexes that contain unprecedented, discrete $R_2C=U=NR'$ units and these complexes complete the currently feasible family of $E=U=E$ ($E = CR_2, NR, O$) metalla-allenes. Intriguingly, **2** and **3** contain *cis*- and *trans*- $C=U=N$ units, respectively, thus representing rare examples in f-block chemistry of targetable *cis/trans*-isomerisation with the same core $R_2C=U=NR'$ unit. This work reveals a clear-cut example of the *trans*-influence in a mid-valent uranium system where the preference for the *cis*-isomer can be clearly visualised in calculated electrostatic potentials. Thus, a strong preference for the *cis*-isomer emerges, which is computed in a co-ligand-free model - to isolate the electronic *trans*-influence from steric contributions - to be more stable than the *trans*-isomer by ~ 12 kJ mol⁻¹, with an isomerisation barrier of ~ 14 kJ mol⁻¹.

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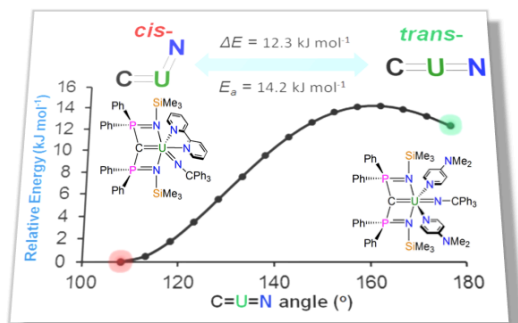
Keywords: uranium, *trans*-influence, metalla-allene, carbene, imido, DFT

- [1] a) S. T. Liddle, *Angew. Chem. Int. Ed.* **2015**, *54*, 8604; b) H. S. La Pierre, K. Meyer, *Prog. Inorg. Chem.* **2014**, *58*, 303; c) M. B. Jones, A. J. Gaunt, *Chem. Rev.* **2013**, *113*, 1137; d) T. W. Hayton, *Chem. Commun.* **2013**, *49*, 2956; e) T. W. Hayton, *Dalton Trans.* **2010**, *39*, 1145; f) A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341; g) M. Ephritikhine, *Dalton Trans.* **2006**, 2501.
- [2] a) M. B. Andrews, C. L. Cahill, *Chem. Rev.* **2013**, *113*, 1121; b) T. K. Tokunaga, Y. Kim, J. Wan, *Environ. Sci. Technol.* **2009**, *43*, 5467; c) B. De Vivo, F. Ippolito, G. Capaldi, P. R. Simpson, *Uranium geochemistry, mineralogy, geology, exploration and resources*, Springer Netherlands, Houten, **1984**.
- [3] a) R. G. Denning, *J. Phys. Chem. A* **2007**, *111*, 4125; b) R. G. Denning, *Struct. Bonding (Berlin)* **1992**, *79*, 215; c) J. M. Bartleet, R. G. Denning, I. D. Morrison, *Mol. Phys.* **1992**, *75*, 601; d) K. Tatsumi, R. Hoffmann, *Inorg. Chem.* **1980**, *19*, 2656.
- [4] A search in the Cambridge Structure Database (CSD) (Ver. 5.37, Update 2, Feb. 2016) with $O=U=O$ leading to 2901 structures, which takes >50% portion among all uranium-containing structures (5303) in the database.
- [5] For recent representative examples see: a) L. Maria, I. C. Santos, V. R. Sousa, J. Marçalo, *Inorg. Chem.* **2015**, *54*, 9115; b) N. H. Anderson, S. O. Odoh, Y. Yao, U. J. Williams, B. A. Schaefer, J. J. Kiernicki, A. J. Lewis, M. D. Goshert, P. E. Fanwick, E. J. Schelter, J. R. Walensky, L. Gagliardi, S. C. Bart, *Nature Chem.* **2014**, *6*, 919; c) S. J. Kraft, P. E. Fanwick, S. C. Bart, *Organometallic* **2013**, *32*, 3279; d) L. P. Spencer, P. Yang, S. G. Minasian, R. E. Jilek, E. R. Batista, K. S. Boland, J. M. Boncella, S. D. Conradson, D. L. Clark, T. W. Hayton, S. A. Kozimor, R. L. Martin, M. M. MacInnes, A. C. Olson, B. L. Scott, D. K. Shuh, M. P. Wilkerson, *J. Am. Chem. Soc.* **2013**, *135*, 2279; e) D. P. Cladis, J. J. Kiernicki, P. E. Fanwick, S. C. Bart, *Chem. Commun.* **2013**, *49*, 4169; f) R. E. Jilek, L. P. Spencer, R. A. Lewis, B. L. Scott, T. W. Hayton, J. M. Boncella, *J. Am. Chem. Soc.* **2012**, *134*, 9876; g) L. A. Seaman, S. Fortier, G. Wu, T. W. Hayton, *Inorg. Chem.* **2011**, *50*, 636.
- [6] a) O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2010**, *39*, 5074; b) J. -C. Tourneux, J. -C. Berthet, P. Thuéry, N. Mézailles, P. Le Floch, M. Ephritikhine, *Dalton Trans.* **2010**, *39*, 2494; c) T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, *J. Am. Chem. Soc.* **2009**, *131*, 963.
- [7] a) 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; b) R. E. Jilek, N. C. Tomson, R. L. Shook, B. L. Scott, J. M. Boncella, *Inorg. Chem.* **2014**, *53*, 9818; c) K. C. Mullane, A. J. Lewis, H. Yin, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* **2014**, *53*, 9129; d) S. Fortier, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2010**, *132*, 6888; e) T. W. Hayton, J. M. Boncella, B. L. Scott, E. R. Batista, *J. Am. Chem. Soc.* **2006**, *128*, 12622; f) D. R. Brown, R. G. Denning, R. H. Jones, *Chem. Commun.* **1994**, 2601; g) D. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* **1993**, *115*, 9840.
- [8] a) 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; b) J. -C. Tourneux, J. -C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, M. Ephritikhine, *J. Am. Chem. Soc.* **2011**, *133*, 6162.
- [9] The only exceptions to high valent species are the $C=U^{IV}=C$ metalla-allenes in reference [6].
- [10] Representative recent examples of uranyl reductive functionalisation: a) J. J. Kiernicki, J. S. Harwood, P. E. Fanwick, S. C. Bart, *Dalton Trans.* **2016**, *45*, 3111; b) J. J. Kiernicki, D. P. Cladis, P. E. Fanwick, M. Zeller, S. C. Bart, *J. Am. Chem. Soc.* **2015**, *137*, 11115; c) P. L. Arnold, A. -F. Pécharman, R. M. Lord, G. M. Jones, E. Hollis, G. S. Nichol, L. Maron, J. Fang, T. Davin, J. B. Love, *Inorg. Chem.* **2015**, *54*, 3702; d) E. A. Pedrick, G. Wu, T. W. Hayton, *Inorg. Chem.* **2015**, *54*, 7038; e) E. A. Pedrick, G. Wu, N. Kaltsoyannis, T. W. Hayton, *Chem. Sci.* **2014**, *5*, 3204.
- [11] Although not formally described as a *trans*-influence, a pyrazole *trans* to an imido group exhibits a statistically longer U-N bond distance compared to the other two pyrazole U-N distances in the same molecule, see: E. M. Matson, W. P. Forrest, P. E. Fanwick, S. C. Bart, *Organometallics* **2013**, *32*, 1484.
- [12] a) M. Gregson, E. Lu, F. Tuna, E. J. L. McInnes, C. Hennig, A. C. Scheinost, J. McMaster, W. Lewis, A. J. Blake, A. Kerridge, S. T. Liddle, *Chem. Sci.* **2016**, doi: 10.1039/c6sc00278a; b) O. J. Cooper, D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2014**, *43*, 14275; c) E. Lu, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2014**, *53*, 9356; d) O. J. Cooper, D. P. Mills, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Chem. Eur. J.* **2013**, *19*, 7071; e) M. Gregson, E. Lu, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2013**, *52*, 13016; f) 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.
- [13] See Supporting Information for full details.
- [14] E. Lu, F. Tuna, W. Lewis, N. Kaltsoyannis, S. T. Liddle, *Angew. Chem. Int. Ed.* submitted.
- [15] The low temperature magnetic moment of uranium(IV) tends to be ca 0.3-0.5 μ_B due to temperature independent paramagnetic effects. See: D. R. Kindra, W. J. Evans, *Chem. Rev.* **2014**, *114*, 8865.
- [16] a) B. M. Gardner, G. Balázs, M. Scheer, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2015**, *7*, 582; b) D. P. Halter, H. S. La Pierre, F. W. Heinemann, K. Meyer, *Inorg. Chem.* **2014**, *53*, 8418; c) D. M. King, J. McMaster, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2014**, *136*, 5619; d) D. Patel, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2013**, *52*, 13334; e) J. L. Brown, S. Fortier, R. A. Lewis, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2012**, *134*, 15468; f) D. Patel, F. Moro, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2011**, *50*, 10388.
- [17] a) E. M. Matson, M. G. Crestani, P. E. Fanwick, S. C. Bart, *Dalton Trans.* **2012**, *41*, 7952; b) R. E. Jilek, L. P. Spencer, D. L. Kuiper, B. L. Scott, U. J. Williams, J. M. Kikkawa, E. J. Schelter, J. M. Boncella, *Inorg. Chem.* **2011**, *50*, 4235; c) 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; d) G. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen, R. A. Andersen, *Organometallics* **2005**, *24*, 4251; e) D. S. Arney, C. J. Burns, *J. Am. Chem. Soc.* **1995**, *117*, 9448.
- [18] M. Gregson, A. J. Wooles, O. J. Cooper, S. T. Liddle, *Comments on Inorganic Chemistry* **2015**, *35*, 262.
- [19] S. Fortier, J. Veleta, A. Pialat, J. Le Roy, K. B. Ghiassi, M. Olmstead, A. Metta-Magaña, M. Murugesu, D. Villagrán, *Chem. Eur. J.* **2015**, *22*, 1931.
- [20] R. F. W. Bader, T. S. Slee, D. Cremer, E. J. Kraka, *J. Am. Chem. Soc.* **1983**, *105*, 5061.

- [21] a) H. S. La Pierre, M. Rosenzweig, B. Kosog, C. Hauser, F. W. Heinemann, S. T. Liddle, K. Meyer, *Chem. Commun.* **2015**, 51, 16671; b) A. J. Lewis, K. C. Mullane, E. Nakamura-Ogiso, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* **2014**, 53, 6944; c) A. J. Lewis, P. J. Carroll, E. J. Schelter, *J. Am. Chem. Soc.* **2013**, 135, 13185; d) D. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes, S. T. Liddle, *Angew. Chem. Int. Ed.* **2013**, 52, 4921; e) D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2013**, 5, 482; f) H. S. La Pierre, K. Meyer, *Inorg. Chem.* **2013**, 52, 529; g) O. P. Lam, S. M. Franke, H. Nakai, F. W. Heinemann, W. Heringer, K. Meyer, *Inorg. Chem.* **2012**, 51, 6190; h) B. Kosog, H. S. La Pierre, F. W. Heinemann, S. T. Liddle, K. Meyer, *J. Am. Chem. Soc.* **2012**, 134, 5284; i) A. Kovács, R. J. M. Konings, *ChemPhysChem* **2006**, 7, 455
- [22] E. O'Grady, N. Kaltsoyannis, *Dalton Trans.* **2002**, 1233.

COMMUNICATION

Cis- and *trans*-isomers of the same $R_2C=U=NR'$ ($R = Ph_2PNSiMe_3$; $R' = CPh_3$) metalla-allene unit are presented, together with an assessment of the *trans*-influence, which brackets this effect at $\sim 12 \text{ kJ mol}^{-1}$ with an isomerisation barrier of $\sim 14 \text{ kJ mol}^{-1}$.



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Uranium-Carbene-Imido
Metalla-Allene Mid-Valent
Uranyl Analogues: Ancillary-
Ligand-Controlled *Cis*-/*Trans*-
Isomerisation and Assessment
of *Trans*-Influence in the
 $R_2C=U^{IV}=NR'$ Unit ($R =$
 $Ph_2PNSiMe_3$; $R' = CPh_3$)