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Communication

Uranium Metalla-Allenes with Carbene Imido R₂C=U^{IV}=NR' Units (R=Ph₂PNSiMe₃; R'=CPh₃): Alkali-Metal-Mediated Push–Pull Effects with an Amido Auxiliary

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Abstract

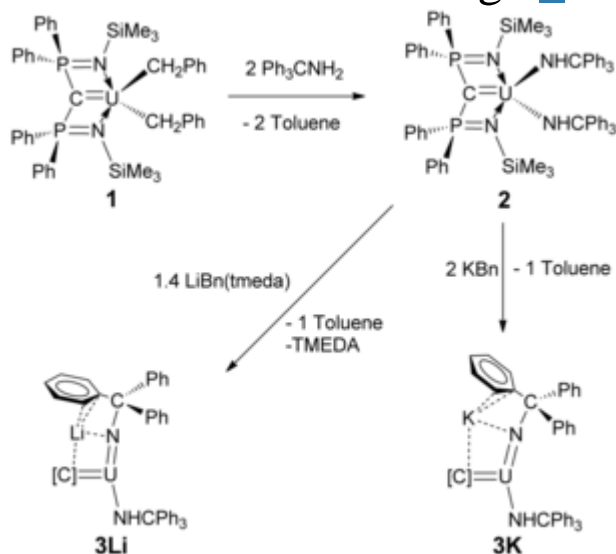
We report uranium(IV)-carbene-imido-amide metalla-allene complexes $[\text{U}(\text{BIPM}^{\text{TMS}})(\text{NCPH}_3)(\text{NHCPH}_3)(\text{M})]$ ($\text{BIPM}^{\text{TMS}}=\text{C}(\text{PPh}_2\text{NSiMe}_3)_2$; $\text{M}=\text{Li}$ or K) that can be described as $\text{R}_2\text{C}=\text{U}=\text{NR}'$ push–pull metalla-allene units, as organometallic counterparts of the well-known push–pull organic allenes. The solid-state structures reveal that the $\text{R}_2\text{C}=\text{U}=\text{NR}'$ units adopt highly unusual *cis*-arrangements, which are also reproduced by gas-phase theoretical studies conducted without the alkali metals to remove their potential structure-directing roles. Computational studies confirm the double-bond nature of the $\text{U}=\text{NR}'$ and $\text{U}=\text{CR}_2$ interactions, the latter increasingly attenuated by potassium then lithium when compared to the hypothetical alkali-metal-free anion. Combined experimental and theoretical data show that the push–pull effect induced by the alkali metal cations and amide auxiliary gives a fundamental and tunable structural influence over the $\text{C}=\text{U}^{\text{IV}}=\text{N}$ units.

The push–pull effect, first evoked by Pauling in the 1980s for carbenes and now a widely accepted concept, refers to mesomeric and inductive remote electronic properties of electron-donating/accepting substituents in conjugated systems.[[1](#)] Synthetic strategies based on this concept have yielded significant advances in push–pull carbenes[[2](#)] and allenes,[[3](#)] both of which are highly versatile in terms of reactivity and as key fundamental building blocks in organic synthesis. Metalla-allenes, that is, organometallic analogues of allenes with one carbon atom replaced by a transition-metal atom, form a class of organometallic compounds with intriguing structural features, rich and diverse reactivity and widespread applications in catalysis.[[4](#)] However, in contrast to the well-documented push–pull effect in organic allenes, the corresponding systematic study of push–pull effects in metalla-allenes is surprisingly absent. This is probably due to the intrinsic synthetic challenges, because there is a lack of methods to introduce varieties of electron-donors/acceptors into metalla-allene frameworks. The implementation of push–pull metalla-allenes, as an allene analogue, has the potential to boost the structural and reactivity profile of

this class of species, and to open up new areas of organometallic chemistry.

In contrast to well-established transition-metal metalla-allenes, f-block metalla-allenes are a poorly developed category. Based on previous work on f-block carbene chemistry,^[5] we now present the synthesis, structural and computational study of uranium metalla-allenes that can be rationalised using an approximate push–pull description. The push-pull effect is induced by pull–inductive (–I) and pull–resonance (–M) effects of alkali metal cations, and push–resonance (+M) and pull–inductive (–I) effects of an amido auxiliary. We find fundamental push–pull effects that are, considering in principle mainly electrostatic bonding, remarkably pronounced and exhibit an intriguingly tunable influence over the N=U^{IV}=C units. Combining 5 f² uranium with strong electron-donor carbene and imido ligands makes a mid-valent uranium(IV)-carbene-imido unit a significant synthetic challenge, because the electron-rich uranium centre is electronically overburdened in comparison to higher valent analogues.^[6] Encouraged by our prior work with the pincer–carbene ligand BIPM^{TMS},^[5a]–^[5f],^[5h],^[5i],^[5k],^[5m] the carbene dialkyl [U(BIPM^{TMS})(CH₂Ph)₂] (**1**)^[5d] was employed as a starting material. Treatment of **1** with two equivalents of Ph₃CNH₂ produces the uranium(IV)-carbene-*bis*(amide) [U(BIPM^{TMS})(NHCPh₃)₂] (**2**) in 67 % yield with concomitant elimination of toluene (Scheme 1).^[7] Uranium(IV)-carbene-alkyl-amide [U(BIPM^{TMS})(CH₂Ph)(NHCPh₃)] is a mixed alkyl-amide and thus part of a class of popular precursors to imido species obtained by α-

abstraction/intramolecular alkane elimination.[8] Attempts to prepare this alkyl-amide by treatment of **1** with just one equivalent of Ph_3CNH_2 resulted in a mixture of only **2** and unconsumed **1** in a 1:1 ratio. Complex **2** has a $\text{U}^{\text{IV}}=\text{C}$ linkage in the presence of two acidic NH-groups, which are liable to deprotonation by Brønsted bases to produce the desired $\text{U}^{\text{IV}}=\text{N}$ linkage.1



Scheme 1.

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Synthesis of complexes **2**, **3K** and **3Li**. Bn=benzyl; TMEDA= N',N',N'',N'' -tetramethylethylenediamine; $[\text{C}]=\text{C}(\text{PPh}_2\text{NSiMe}_3)_2$.

Treatment of brown-yellow **2** with two equivalents of benzyl potassium gives a brick red solid formulated as the uranium(IV)-carbene-imido-amide

$[\text{U}(\text{BIPM}^{\text{TMS}})(\text{NCPH}_3)(\text{NHCPH}_3)\text{K}]$ (**3K**) after work-up in 82 % yield (Scheme 1).[7] Use of a two-fold excess of benzyl potassium is necessary, probably due to the poor solubility of the materials in aromatic solvents, which renders the reaction somewhat heterogeneous.

Complex **3K** is stable as a solid at $-35\text{ }^\circ\text{C}$ for weeks, but standing at room temperature as a solid or in solution leads

to decomposition within two days. In crystalline form, **3κ** is essentially insoluble in aromatic/aliphatic solvents but decomposes in coordinating solvents. Encouraged by the straightforward preparation of **3κ**, but seeking a more soluble product, the lithium analogue [U(BIPM^{TMS})(NCPPh₃)(NHCPPh₃)Li] (**3Li**) was prepared from **2** and the benzyl lithium [LiBn(tmeda)], and was isolated in 83 % yield.^[7] As for **3κ**, an excess of benzyl lithium reagent was required to ensure a satisfactory yield of **3Li**. Complex **3Li** is much more soluble than **3κ**, facilitating spectroscopic characterisation. The characterisation data for **2**, **3Li** and **3κ** are consistent with their formulations. The presence of Li⁺ in **3Li** is confirmed by the ⁷Li NMR spectrum ($\delta=1.56$ ppm in C₆D₆). The ³¹P NMR spectra of **2** and **3κ** in C₆D₆ exhibit resonances at $\delta=-605$ and -630 ppm, respectively, whereas for **3Li** the ³¹P NMR resonance is found at much lower field ($\delta=-373$ ppm). The electronic absorption spectrum of **3Li** exhibits very weak f→f absorptions across the visible and near-IR regions and is dominated by a strong LMCT (ligand–metal charge transfer) absorption at low wavelength, which is responsible for the brick red colour of the complex. The optical spectrum of **3κ** cannot be considered reliable due to its poor solubility. The ATR-IR spectra of **3Li** and **3κ** are very similar, reflecting their structural similarity. The variable temperature solid state magnetic moments of **2** and **3Li/κ** measured by SQUID magnetometry corroborate the +4 oxidation state of uranium in all the three complexes,^[9] and are also informative regarding the electronic environment of the uranium ions in these complexes. The magnetic moment

of **2** is $2.35 \mu_B$ at 298 K, decreasing to 1.8 and finally $0.2 \mu_B$ at 2 K with a tendency towards zero; the decrease in magnetic moment in the 300–50 K window is not as monotonic as is usually the case for uranium(IV) but the fact that this complex is uranium(IV) is clear. In comparison, the data for **3 Li** and **3 K** are distinct from those of **2**. Specifically, the magnetic moments of **3 Li** and **3 K** are 2.4 and $2.5 \mu_B$, falling to 2.2 and $2.4 \mu_B$ by 50 K, and finally 0.9 and $0.8 \mu_B$ at 2 K, respectively. The magnetic moments of **3 Li** and **3 K** clearly remain higher over a larger temperature range than that of **2**. The low temperature magnetic moments of **3 Li** and **3 K** are also significantly greater than for **2**, whose low-temperature magnetic moment reflects a uranium(IV) ion in a magnetic singlet state at this temperature with temperature-independent paramagnetism.^[9] These data suggest that for **3 Li** and **3 K**, the paramagnetic manifold is split into a low-lying group populated even at low temperature and a higher-lying group that is not populated in the temperature range examined, hence the high magnetic moment at 2 K and 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.^[10] This suggests that the strong-donor nature of the ligands is the key factor and is certainly consistent with the presence of two multiply bonded groups at uranium in **3 Li** and **3 K**. Complexes **2**, **3 Li** and **3 K** have been characterised by single-crystal X-ray diffraction and their solid state molecular structures are shown in Figure 1.^[11] The salient structural features of **3 K/Li** are the C=U=N units. The $U^{IV}=N$ bond

lengths in 3K and 3Li are similar [$2.046(9)\text{ \AA}$, 3K ; $2.044(3)\text{ \AA}$, 3Li], compare well with other terminal $\text{U}^{\text{IV}}=\text{N}$ bond lengths ($1.95\text{--}2.04\text{ \AA}$) [[8](#), [10c](#), [12](#)] and are both much shorter than $\text{U}^{\text{IV}}-\text{N}_{\text{amide}}$ bonds in the same molecules [3K , $2.280(9)\text{ \AA}$; 3Li , $2.162(4)\text{ \AA}$] or in 2 [$2.211(4)/2.254(4)\text{ \AA}$]. The $\text{U}-\text{N}_{\text{imido}}-\text{C}_{\text{trityl}}$ angles in both 3K and 3Li approach linearity (3K , $174.4(7)^\circ$; 3Li , $169.1(3)^\circ$); these parameters are suggestive of a ‘terminal’ uranium–imido fragment, although with the presence of dative $\text{N}_{\text{imido}}\rightarrow\text{M}$ ($\text{M}=\text{Li}, \text{K}$) interactions. The $\text{U}^{\text{IV}}=\text{C}$ bond lengths in 3K [$2.527(10)\text{ \AA}$] and 3Li [$2.579(3)\text{ \AA}$] are closer to the high end of such bonding interactions, but this linkage is known to be quite variable because of the pincer framework. [[5](#)] Thus, judging the bonding solely on the basis of bond length is not necessarily reliable, but computational data suggest the presence of $\text{U}^{\text{IV}}=\text{C}$ bonding interactions in 3K/Li (vide infra). [[7](#)] The $\text{C}-\text{U}-\text{N}_{\text{imido}}$ angles in 3K/Li are surprisingly small (3K , $104.4(3)^\circ$; 3Li , $91.54(12)^\circ$), which is in sharp contrast to the prevalent *trans*- $\text{E}=\text{U}=\text{E}'$ moieties, where $\angle\text{EUE}'$ is around 180° , and they are thus *cis*-carbene-imido units. [1](#)

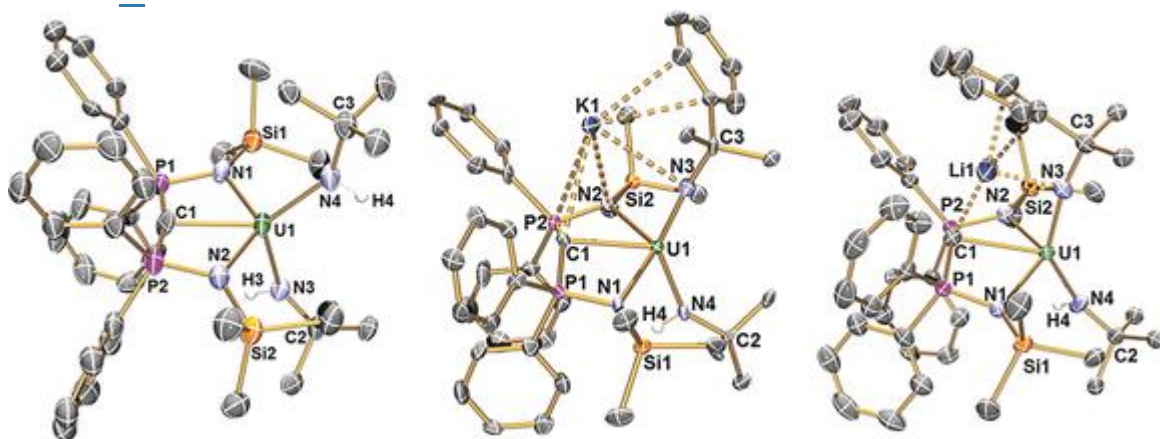


Figure 1.

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Solid-state molecular structures of **2** (left), **3κ** (middle) and **3Li** (right). Displacement ellipsoids set at 40 % probability. Hydrogen atoms (except amide hydrogens), aromatic C-atoms in trityl groups (except *ipso*-carbons and those in the phenyl rings interacting with alkali metal cations), any lattice solvents and minor disorder components are omitted for clarity. Selected bond lengths [Å]: **2**: U1–C1 2.367(5), U1–N4 2.254(4), U1–N3 2.211(4), U1–N1 2.425(5), U1–N2 2.384(5); **3κ**: U1–C1 2.527(10), U1–N3 2.046(9), U1–N4 2.280(9), K1–C1 3.156(10), K1–N3 3.048 (10), U1–N1 2.471(9), U1–N2 2.517(9); **3Li**: U1–C1 2.579(3), U1–N3 2.044(3), U1–N4 2.162(4), Li1–C1 2.162(8), Li1–N3 2.066(9), U1–N1 2.458(3), U1–N2 2.480(3). Selected bond angles [°]: **2**: U1–N3–C2 150.5(3), U1–N4–C3 146.0(4), C1–U1–N3 103.45(18), C1–U1–N4 134.00(19); **3κ**: U1–N3–C3 174.4(7), C1–U1–N3 104.4(3); U1–N4–C2 143.7(7); **3Li**: U1–N3–C3 169.1(3), C1–U1–N3 91.54(12), U1–N4–C2 153.6(3). Inspecting the metric parameters of **3κ/Li** in detail, and focussing on the Y-shaped C=U=N(–NH) core structures, we find invariant U^{IV}=N distances, but significant differences between the U–N_{amide} and U=C bond lengths, which can be rationalised as being mutually influenced by redistribution of charges under a push–pull effect mediated by the polarising power of Li⁺ and K⁺ (Figure [2](#)). Specifically, the more charge-dense Li⁺ interacts most strongly with the carbene, thus weakening the U=C bond to a greater extent than does K⁺. The U–N_{amide} distance in **3Li** then reduces by ~0.1 Å, compared with **3κ**, to compensate. This perhaps accounts for the greatly deshielded P-centres in **3Li** compared to **3κ** ($\Delta=257$ ppm) as suggested by the corresponding ³¹P NMR chemical shifts.[2](#)

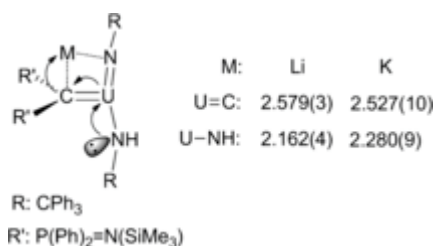


Figure 2.

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Illustration of the push–pull effect along the M···C=U–NH linkages. All bond lengths are in Å.

To investigate this push–pull phenomenon and the *cis*-geometries of these complexes, we performed a computational analysis.^[7] We computed the full structures of **3**_{Li}, **3**_K and the hypothetical anion of **3** (**3**[−]) to provide a benchmark and to isolate the effects of the alkali metal cations; bond lengths and angles are generally within 0.06 Å and 2° of the experimental structures where available.

We attempted experimentally to prepare separated ion pair species by abstracting the alkali metal cations with appropriate crowns and cryptands; although reactions clearly occurred, the resulting viscous oils could not be crystallised. However, given that **3**_{Li} and **3**_K are experimentally verified, this gives confidence in the calculated structure of **3**[−], and we thus conclude that the models provide a qualitative picture of the electronic structures of these complexes. In all cases, inspection of the Kohn–Sham or natural bond orbitals reveals U–N_{amide}, U=N and U=C interactions as anticipated, that is, covalent–single+dative, double-covalent+ dative, and double-covalent bond interactions, respectively.^[7] Analysis of the Nalewajski–Mrozek bond indices reveals the same push–pull trend suggested by the solid state data.

Specifically, **3**_{Li} exhibits the lowest U=C bond order

(0.99), whereas 3^- (1.03) and 3_K (1.04) are moderately larger. The changes are small but consistent with the ordering that would be anticipated for the most polarising Li, whereas K being so ionic, it is essentially the same as the anion. Conversely, 3_{Li} has the highest U–N_{amide} bond order (1.34) followed by 3_K (1.32), then 3^- (1.23). Again, the changes are small but entirely in-line with polarisation of the U=C bond being compensated for by greater donation by the auxiliary amide. Interestingly, although the solid state U=N bond lengths do not vary in a statistically meaningful way, the bond orders of 2.62 (3^-), 2.53 (3_K) and 2.44 (3_{Li}) show that the U=N bond is electronically weakened by the increasingly withdrawing effects of K and then Li. The picture that emerges is of a R'₂C=U=NR unit that redistributes electron density in response to the demands of the alkali metal, supplemented as necessary by the amide group, which is thus a true auxiliary electronic reservoir. Indeed, whereas 3^- can legitimately be claimed as a carbene-imido complex, 3_{Li} has disrupted the U=C bond to such an extent that it is at best a single U–C bond with a Li–C single bond as well. Complex 3_K sits in between these two extremes.

To further corroborate the idea of the alkali metal cation (M⁺) and anionic amide ligand (RNH⁻) acting as a push–pull pair along the R₂C=U=NR' unit, we examined the effect of varying M⁺ over the entire alkali metal series (Li–Cs) in silico to determine the effect over U=C and U–NH bond lengths in truncated 3_M model systems (Figure 3). Although the absolute values of $r(U=C)$ and $r(U-NH)$ in the truncated models differ from the experimentally determined equivalents in the full systems (which can be

attributed to the much reduced steric profiles of the models), the computational trends provide clear evidence of a push–pull effect that increases with the polarizability of M^+ . Thus, moving from Li^+ (the strongest polarising ability) to Cs^+ (the weakest), both the $U=C$ and $U-NH$ bond lengths (Figure 3) and Quantum Theory of Atoms-in-Molecules (QTAIM) delocalisation indices (for measures of bond order, see Figure S16 in the Supporting Information) are essentially perfectly linearly correlated. This very clear trend, in conjunction with the experimental structural metric parameters and the calculated results on the full systems, unequivocally provides a self-consistent picture of the tunable push–pull effect along this metalla-allene series.³

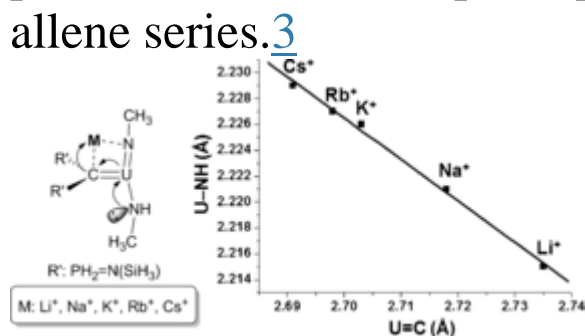


Figure 3.

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Calculated M^+ -dependent $U=C$ and $U-NH$ bond lengths in truncated model systems $3_M(M=Li-Cs)$. $R^2=0.996$.

The push–pull effect is composed of mesomeric and inductive influences. In detail, there are four contributions: push-inductive (+I), pull-inductive (−I), push-resonance (+M) and pull-resonance (−M). Here, Li^+/K^+ have −I and −M effects, whereas RNH^- has major +M and minor −I effects. Based on those points, in $3_{Li/K}$, the mesomeric and inductive effects of the push–pull pair M^+/NH^- can be illustrated as the four resonance structures A–D (Figure 4). The metric parameters from the solid state structures,

together with the theoretical data, suggest that for 2Li , **D** is the major resonance structure, whereas for 3K , **A** dominates. This is supported by calculated atomic charges (both natural population and QTAIM approaches) in the truncated model systems (Figure 5 and Supporting Information), where charge distributions match the corresponding dominant resonances for Li^+ and K^+ structures.⁴⁵

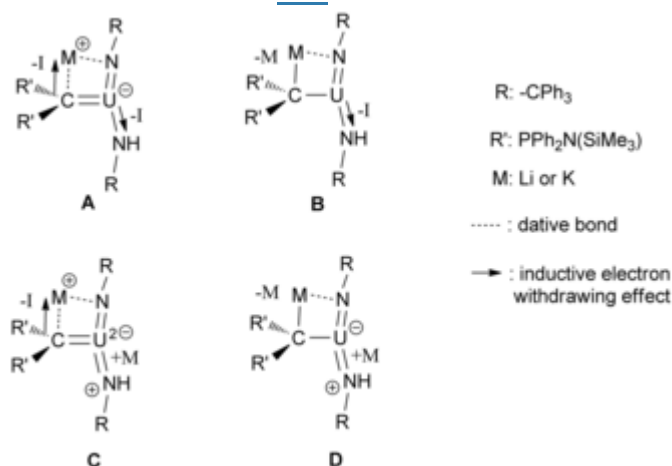


Figure 4.

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Resonance structures (**A–D**) illustrate inductive and mesomeric contributions of the push–pull pair M^+/RNH^- along the metallallene $\text{C}=\text{U}=\text{N}$ units in $3\text{Li}/\text{K}$. The inductive/mesomeric contributions are constituted by: 1) push-inductive (+I); 2) pull-inductive (-I); 3) push-resonance (+M); 4) pull resonance (-M).

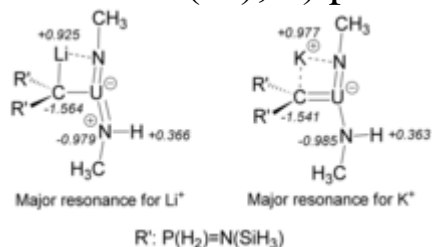


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Natural population analysis atomic charges (italic numbers) for U , M , $\text{C}_{\text{carbene}}$, N_{amido} and H_{amido} , and major resonances in truncated $3\text{Li}/\text{K}$.

To conclude, we report push–pull uranium metalla-allenes with alkali-metal cation and amide auxiliaries as push–pull pairs. The polarised multiple-bonding character of the U=C and U=N bonds and the push-pull effect in any metalla-allene are corroborated by structural, spectroscopic (³¹P NMR) and theoretical methods. The push–pull effect in these cases is tunable by changing the polarising power of the alkali metal cation, and the lone-pair on the N-atom of auxiliary amides acts as an electron density reservoir. This work extends the concept of the push–pull effect from organic allenes to metalla-allenes, suggesting the potential for unforeseeable and unique reactivity with this highly important organometallic moiety.

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