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# Diazoalkane Reduction for the Synthesis of Uranium Hydrazonido Complexes

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The reactivity of the uranium(III) alkyl $Tp^*_2UCH_2Ph$ (**1**) toward diazoalkanes is reported. Addition of 1 equiv. $N_2CPh_2$ produces 0.5 equiv. bibenzyl, along with $Tp^*_2U(N_2CPh_2)$ (**2**). This species is dynamic in solution at room temperature and rapidly interconverts between the $\eta^1$- and $\eta^2$ isomers as determined by variable-temperature $^1H$ NMR spectroscopy. X-ray crystallographic analysis at low temperature shows exclusively the $\eta^2$ isomer, which features a short U–N multiple bond analogous to an imido species. The $\eta^1$ isomer reacts quantitatively with aldehydes and ketones through multiple bond metathesis to produce $Tp^*_2U(O)$ and the corresponding ketazine. Treatment of **1** with $N_2CHSiMe_3$ generates 0.5 equiv. bibenzyl and the $\eta^1$ isomer $Tp^*_2U(N_2CHSiMe_3)$ (**3**). This species is unstable over the course of hours, and there is no spectroscopic evidence for the $\eta^2$ isomer. $Tp^*_2U(\eta^1\text{-}N_2CHSiMe_3)$ can be trapped by addition of phenylacetylene by a [2+2] cycloaddition to afford the uranium(IV) metallacycle $Tp^*_2U[(N\text{-}N = CHSiMe_3)CHCPh]$ (**4**). Crystallographic data for **4** are presented.

## Introduction

Diazoalkanes are versatile reagents as they are a convenient source of carbenes through loss of the dinitrogen fragment[1–3] or they serve as models for studying metal-mediated dinitrogen reduction when dinitrogen is retained.[4–6] These molecules are better ligands than nonpolar $N_2$ and offer multiple bonding modes. Although electron-rich transition metals are typically sought after for diazoalkane reduction because of their ability to engage in π backbonding, uranium is a highly reducing element as well, and thus a logical choice for the activation of these molecules.

Early studies of uranium demonstrated the synthesis of the diazoalkane adduct $(NN'_3)U(\eta^1\text{-}N_2CHSiMe_3)$ [$NN'_3$ = $N(CH_2CH_2NSiMe_2tBu)_3$], although no crystallographic evidence was provided for its structure.[7] Following this study, Meyer reported $[\{(tBuArO)_3tacn\}U^{IV}(\eta^2\text{-}NNCPh_2)]$ [$(tBuArO)_3tacn$ = trianion of 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane], which has a single electron delocalized over the C–N–N unit.[8] Use of the more sterically demanding adamantyl variant of the supporting ligand produced the end-on analogue $[\{(^{Ad}ArO)_3tacn\}U^{III}(\eta^1\text{-}NNCPh_2)]$. Migratory insertion of diphenyldiazomethane was observed by Kiplinger for actinide alkyl and aryl species to form the family of hydrazonato compounds $Cp^*_2An[\eta^2\text{-}(N,N')\text{–}R\text{–}N\text{–}N{=}CPh_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienide; An = Th, R = $CH_3$, $PhCH_2$, Ph; An = U, R = $CH_3$, $PhCH_2$).[9] The pincer bis(ligand) derivative $(PNP)_2UI$ {PNP = bis[2-(diisopropylphosphanyl)-4-methylphenyl]amido} in the presence of $KC_8$ and diphenyldiazomethane generates the first example of an actinide hydrazonido complex, $(PNP)_2U(\eta^2\text{-}N_2CPh_2)$.[10] Recently, Liddle has reported the reactivity of $[(tren^{TMS})UCl(THF)]$ [$tren^{TMS}$ = $N(CH_2CH_2NSiMe_3)_3$] with the lithiated diazoalkane $LiN_2CHSiMe_3$.[11] The product is not a diazoalkane species, but rather the isocyanotrimethylsilylamide dimer $[(tren^{TMS})U\{\mu\text{-}N(SiMe_3)NC\}]_2$.

Diazoalkanes are structurally similar to organic azides and access analogous resonance forms. Recent work from our laboratory has demonstrated that organic azides react with trivalent $Tp^*_2UCH_2Ph$ (**1**) to form the uranium(IV) imido species $Tp^*_2UNR$ [R = Ph, Ad, Mes (Mes = 2,4,6-trimethylphenyl)], with extrusion of bibenzyl, rather than insertion into the U–C bond.[12] We sought to determine whether analogous reactivity would occur for diazoalkanes given the structural similarities or whether migratory insertion would result as Kiplinger described.[9] Herein we present the results of a study focusing on the reactivity of both diphenyldiazomethane ($N_2CPh_2$) and trimethylsilyldiazomethane ($N_2CHSiMe_3$) with $Tp^*_2UCH_2Ph$. Characterization by $^1H$ NMR and IR spectroscopy as well as X-ray crystallography is presented.

## Results and Discussion

Initial studies explored the reactivity of diphenyldiazomethane with $Tp^*_2UCH_2Ph$ (**1**). Treatment of a THF solution of **1** with 1 equiv. $N_2CPh_2$ at room temperature resulted in an immediate color change from dark green to form a yellow–brown compound, **2** (Scheme 1). Analysis of

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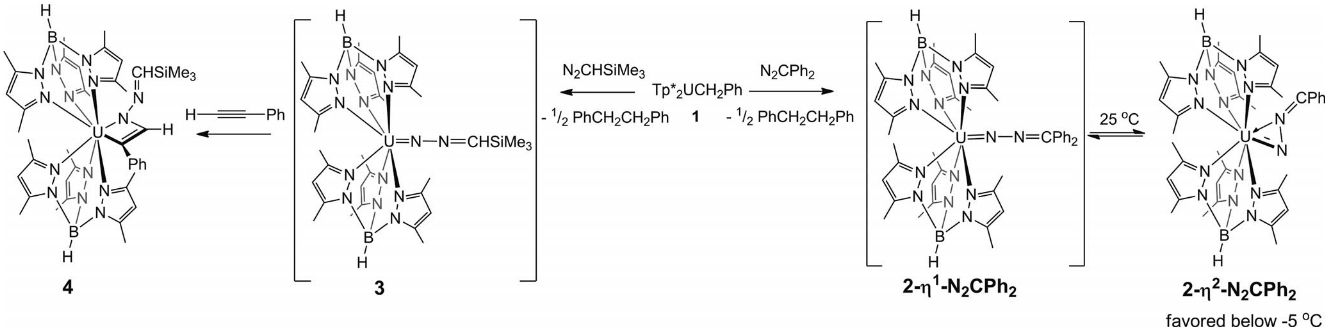


Scheme 1.

**2** by $^1$H NMR spectroscopy shows 14 broad paramagnetic resonances ranging from –61.65 to 105.98 ppm, which could not be assigned. Concomitant formation of 0.5 equiv. bibenzyl was noted, as determined by integration against a ferrocene internal standard. It was determined that the same paramagnetic spectrum could be generated by using 3 equiv. of the diazoalkane with the uranium(III) species $Tp^*_2U(2,2'\text{-bpy})$, which has a monoanionic bipyridine ligand.[13] In this case, along with **2** and 2,2′-bipyridine was formed a small amount of the previously synthesized $Tp^*U(dmpz)_3$ (dmpz = 3,5-dimethylpyrazolide).[14] $Tp^*U(dmpz)_3$ was originally discovered by Takats as a byproduct from heating (Tp*)(κ$^2$-Tp*)UCp, who confirmed this structure by independent synthesis by salt metathesis of $Tp^*UCl_3(THF)$ with 3 equiv K(dmpz).[14] In our hands, thermal decomposition of bis-Tp* U$^{IV}$ complexes with uranium–nitrogen multiple bonds also produces $Tp^*U(dmpz)_3$. To confirm that this product arises from the thermal instability of **2** and is not formed during conversion from **1**, the crude reaction mixture was heated to 80 °C in toluene, which resulted in exclusive formation of $Tp^*U(dmpz)_3$.[14] Analysis by IR spectroscopy of a KBr pellet of **2** shows two B–H absorptions consistent with the intact bis-Tp* ligand framework at 2523 and 2552 cm$^{-1}$. Also isolated from the $Tp^*_2U(2,2'\text{-bpy})$ reaction is tetraphenylketazine, whose formation was confirmed by $^1$H NMR spectroscopy and by a comparison of the unit cell of an isolated crystal by X-ray crystallography.[15]

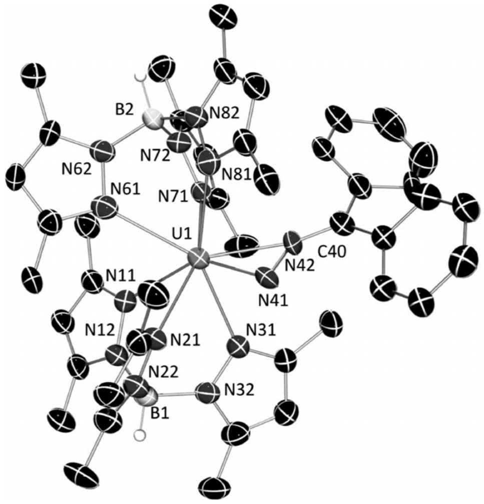


Figure 1. Molecular structure of **2** shown with 30% probability ellipsoids. Selected hydrogen atoms are omitted for clarity.

Table 1. Structural parameters for compounds **2** and **4**.

| Bond | **2** [Å] | **4** [Å] |
|---|---|---|
| U1–N11 | 2.739(8) | 2.523(7) |
| N1–N21 | 2.535(7) | 2.577(6) |
| U1–N31 | 2.666(8) | 2.636(7) |
| U1–N61 | 2.596(8) | 2.676(6) |
| U1–N71 | 2.536(8) | 2.568(6) |
| U1–N81 | 2.666(9) | 2.566(6) |
| U1–N41 | 2.146(9) | 2.348(6) |
| U1–N42 | 2.347(8) | – |
| U1–C45 | – | 2.372(8) |
| N41–N42 | 1.354(11) | 1.373(9) |
| N42–C40 | 1.283(13) | 1.380(11) |
| C44-C45 | – | 1.349(12) |

To further identify the structure of the organometallic product **2**, X-ray crystallography was employed. Single, brown crystals suitable for analysis were grown from a concentrated THF/pentane solution (1:4) at –35 °C. Refinement reveals an eight-coordinate uranium center with a molecule of diphenyldiazomethane coordinated in a η$^2$ fashion, $Tp^*_2U(\eta^2\text{-}N_2CPh_2)$ (**2**-η$^2$-$N_2CPh_2$) (Figure 1, Table 1). The molecular structure is a distorted dodecahedron defined by two trapezia containing N11–N61–N81–N31 and N42–N71–N21–N41. The trapezia intersect at an angle of 77.4°. The U–N distances for the hydrotris(3,5-dimethylpyrazolyl)borate ligand are consistent with those previously observed, and each ligand has one U–N distance that is elongated relative to the others.[12,13,16–18] Compound **2** features a short U1–N41 (diazomethane Nα) bond length of 2.146(7) Å, which is indicative of uranium–nitrogen multiple bonding. Uranium(IV) amide species, such as $Cp^*_2U(CCPh)(NPh_2)$ [2.298(4) Å][19] and $(CGC)U(NMe_2)_2$ [CGC = $Me_2\text{–}Si(\eta^5\text{-}Me_4C_5)(t\text{BuN})$; 2.207(4) Å $(NMe_2)_2$][20] commonly show longer U–N bonds. The bonding in **2** is more reminiscent of uranium imido species, in which U–N distances range from 1.85 to 2.05 Å.[21–27] In **2**, the imido moiety has an acute U–N–N angle of 80.8(5)° that prevents Nα nitrogen lone pair bonding typically seen in species with shorter distances, which creates a slightly longer U–N multiple bond. This angle is enforced by the uranium–Nβ-(diazoalkane) bond, U1–N42, which has a distance of 2.347(8) Å and shows dative uranium–nitrogen bonding. The structure of **2** is analogous to Kiplinger's $(PNP)_2U(\eta^2\text{-}N_2CPh_2)$,[10] which has a U–Nα bond of 2.097(5) Å, slightly shorter than that in **2**. The U–Nβ bond of $(PNP)_2U(\eta^2\text{-}N_2CPh_2)$ is 2.370(5) Å and is essentially the same as that for **2** within error. The N–N and C–N distances in compound **2** are 1.354(11) and 1.283(13) Å, respectively, and are statistically the same as those found in $(PNP)_2U(\eta^2\text{-}N_2CPh_2)$ [1.359(7) and 1.302(8) Å]. Distances for the same bonds in the uncoordinated diazoalkanes range from 1.130–1.145 Å (N–N) and 1.28–1.32 Å (C–N),[28–30] which indicates that the diazoalkane has been significantly reduced by interaction with the uranium center; a hydrazonido ligand, $[N_2CPh_2]^{2-}$, is formed.

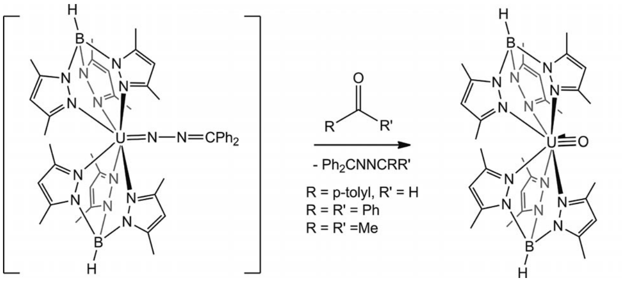
The $\eta^2\text{-}N_2CPh_2$ ligand in tetravalent $[\{(t\text{BuArO})_3\text{tacn}\}U(\eta^2\text{-NNCPh}_2)]$[8] differs from **2** in that its molecular structure has a U–Nα bond of 2.259(4) Å, longer than those observed for **2** or $(PNP)_2U(\eta^2\text{-}N_2CPh_2)$. This distance is more consistent with an amide linkage to the uranium center, while the U–Nβ distance of 2.582(4) Å shows dative coordination to uranium. Activation of the diazoalkane in $[\{(t\text{BuArO})_3\text{tacn}\}U(\eta^2\text{-NNCPh}_2)]$ is noted by the respective N–N and C–N distances of 1.338(5) and 1.333(6) Å. The formation of $[\{(t\text{BuArO})_3\text{tacn}\}U(\eta^2\text{-NNCPh}_2)]$ results from a one-electron reduction of diphenyldiazomethane by trivalent $[\{(t\text{BuArO})_3\text{tacn}\}U]$.

The $\eta^2$-hydrazonido uranium species can be contrasted with analogous examples involving transition metals. Bergman's $Cp^*_2Ti(\eta^2\text{-}N_2CHSiMe_3)$[31] displays single bond character between the titanium atom and both Nα and Nβ in the molecular structure. In this species, the N–N bond is elongated to 1.276(3) Å, which indicates that backbonding from the titanium to the N=N π* orbital occurs. The authors note that imide-like character may be present in solution. The bonding in $Ni(i\text{Pr}_2\text{Im})_2(\eta^2\text{-}N,N'\text{-}N_2CPh_2)$ ($i\text{Pr}_2\text{Im}$ = 1,3-diisopropylimidazol-2-ylidene)[32] and $Ni(t\text{BuNC})_2$(diazofluorene)[33] differs from the titanium example in that the Ni–N distances are intermediate of single and double bonds. The respective elongated N–N bonds of 1.266(3) and 1.245(4) Å in $Ni(i\text{Pr}_2\text{Im})_2(\eta^2\text{-}N,N'\text{-}N_2CPh_2)$ and $Ni(t\text{BuNC})_2$(diazofluorene) compare well with those in azobenzene (1.244 Å),[34,35] and, again, indicate that π backbonding is prevalent in both molecules.

The $^1$H NMR spectrum of **2** at 25 °C is extremely broad and shows resonances consistent with inequivalency throughout the molecule, but it is not useful for structural assignment. Thus **2** was analyzed by variable-temperature $^1$H NMR spectroscopy to determine if dynamic behavior on the NMR timescale is the origin for the broad lines at room temperature (Figure S1). As the sample is cooled to 5 °C and eventually to –5 °C, the resonances become very sharp and shift slightly from their values at 25 °C. At –5 °C, it is clear that there is inequivalency in the molecule, which supports the formation of the $\eta^2\text{-}N_2CPh_2$ species. The crystals obtained for **2** were grown at –35 °C, and the X-ray structured was determined at 150 K; thus the structural insights obtained from this analysis indicate that the low-temperature NMR spectroscopic data represents the side-on coordinated diazoalkane compound. Upon warming of the sample to 25 °C, the dynamic behavior is most likely a result of interconversion between the $\eta^2\text{-}N_2CPh_2$ (**2**-$\eta^2\text{-}N_2CPh_2$) and the $\eta^1\text{-}N_2CPh_2$ (**2**-$\eta^1\text{-}N_2CPh_2$) species (Scheme 1). Thus, the spectrum measured at ambient temperature is representative of either **2**-$\eta^1\text{-}N_2CPh_2$ or the time-averaged structure of the solution mixture of **2**-$\eta^2\text{-}N_2CPh_2$ and **2**-$\eta^1\text{-}N_2CPh_2$. The related family of linear uranium(IV) imidos, $Tp^*_2UNR$ (R = Ph, Ad, Mes), displays sharp resonances different from those observed for **2** at ambient temperature, which supports the notion that the observed spectrum for **2** is most consistent with the time-averaged mixture of **2**-$\eta^1\text{-}N_2CPh_2$ and **2**-$\eta^2\text{-}N_2CPh_2$ in solution.

Such dynamic behavior has previously been observed for the titanium diazoalkane species $Cp''_2Ti(N_2CPh_2)$ [$Cp''$ = $\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)$].[36] This species undergoes interconversion between the $\eta^1$ and $\eta^2$ isomers in solution at –20 °C. Similar to that of **2**, this species has a broad and featureless $^1$H NMR spectrum at ambient temperature that sharpens to display resonances for both isomers as the sample is cooled. Further support for the isomeric forms of **2** lies in the previous synthesis of the end-on $\eta^1$-diazoalkane uranium species, including Kiplinger's $Cp^*_2U(\eta^1\text{-}N_2CPh_2)_2$[10] and Burns' $Cp^*_2U(\eta^1\text{-}N_2CPh_2)[N(2,4,6\text{-}t\text{Bu}_3\text{Ph})]$.[37] Both of these species feature reduced $\eta^1\text{-}N_2CPh_2$ hydrazonido ligands with U–N bonds reminiscent of imido linkages, which indicates this isomeric form effectively supports the uranium centers. Diazoalkane ligands have also been shown to change hapticity on the uranium centers in the $[\{(^{Ad}\text{ArO})_3\text{tacn}\}U]$ system. Upon addition of $N_2CPh_2$ to this molecule, the end-on $\eta^1\text{-}N_2CPh_2$ uranium compound, $[\{(^{Ad}\text{ArO})_3\text{tacn}\}U(\eta^1\text{-NNCPh}_2)]$, is isolated.[8] Heating of the latter causes a shift of the diazoalkane hapticity from $\eta^1$ to $\eta^2$, which facilitates C–H activation of the phenyl ring to form the uranium(IV) indazole product $[\{(^{Ad}\text{ArO})_3\text{tacn}\}U^{IV}\{\eta^2\text{-3-phen(Ind)}\}]$.[8]

Reactivity studies with aldehydes and ketones also provide insight into the various isomeric forms of **2**. Addition of 1 equiv. *p*-tolualdehyde to a THF solution of **2** at 25 °C caused an immediate color change from yellow–brown to bright pink, which indicates the formation of the previously reported base-free uranium(IV) oxo species $Tp^*_2U(O)$,[18] as confirmed by $^1$H NMR spectroscopy [Equation (1)]. Simultaneous formation of the ketazine $Ph_2C{=}N\text{-}N{=}CH(p\text{-tolyl})$[38,39] was noted, supporting the reaction progresses through multiple bond metathesis. The same reactivity was observed for benzophenone and acetone, and ketazine products were identified by comparison to literature data.[40,41] Analogous reactivity with benzophenone has been observed for the uranium(IV) imido species $Cp'_2U\{N(p\text{-tolyl})\}$ [$Cp'$ = $\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2$][24] to form $Cp'_2U(O)$ and the corresponding imine product $Ph_2C[N(p\text{-tolyl})]$. Furthermore, treatment of $Tp^*_2UNR$ (R = Ph, Ad, Mes) with *p*-tolualdehyde also generates $Tp^*_2U(O)$ and $H(p\text{-tolyl})CNR$.[12] In contrast, addition of aldehydes or ketones to a solution of **2**-$\eta^2$-$N_2CPh_2$ at –35 °C resulted in no reaction. However, warming of this solution to room temperature started the reaction, which ultimately led to conversion of the products, presumably because of the accessibility of **2**-$\eta^1$-$N_2CPh_2$ at this temperature. These reactivity studies support that **2**-$\eta^2$-$N_2CPh_2$, which predominates at low temperature, does not perform metathesis chemistry. This most likely is a result of the dative coordination of Nβ, which prevents subsequent coordination of the carbonylated substrate. However, once the solution is warmed, $\eta^1$-$N_2CPh_2$ is present in solution, and the metathesis chemistry can proceed at the open coordination site. Attempts to freeze out the dynamic behavior and trap $\eta^1$-$N_2CPh_2$ with Lewis bases such as pyridine, DMAP, and isonitriles were unsuccessful, as no reaction was observed at room temperature.



(1)

With an understanding of compound **2** established, we turned our efforts to understanding the formation of 1 equiv. ketazine in the reaction from Tp*$_2$U(2,2′-bpy). Ketazine extrusion is not unique to this system and has been reported for transition metals. Recent work by Heyduk describes similar chemistry with [ONO$^{cat}$]TaCl$_2$(OEt$_2$) {[ONO$^{cat}$]H$_3$ = *N*,*N*-bis(3,5-di-*tert*-butyl-2-phenol)-amine}.[42] Addition of 30 equiv. $N_2CPh_2$ to this Ta$^V$ species catalytically forms $Ph_2CN{=}NCPh_2$, dinitrogen, and the new tantalum ketazine species [ONO$^{cat}$]TaCl$_2$($\eta^2$-$Ph_2CN{=}NCPh_2$). By performing the same reaction in neat styrene 1,1,2-triphenylcyclopropane is generated, and this is indicative of a transient tantalum alkylidene. Unlike the Heyduk system, compound **2** does not form tetraphenylketazine catalytically at any temperature. Furthermore, no cyclopropanation chemistry was observed upon addition of $N_2CPh_2$ to Tp*$_2$U(2,2′-bpy) in neat styrene, which indicates that a transient uranium alkylidene is not responsible for ketazine formation in this system.

The reactivity of trimethylsilyldiazomethane with **1** was also explored to determine how the steric and electronic variation in the diazoalkane changes the reactivity. Upon mixing 1 equiv. $N_2CHSiMe_3$ with **1** in thawing THF, a change from green to red–brown ensues immediately, and workup and isolation affords a brown–orange oil (**3**). The $^1$H NMR spectrum of **3** displays equivalent resonances for the Tp*-CH$_3$ groups pointing towards and away from the uranium center at –7.03 and 2.56 ppm, respectively. Additionally, resonances for the B–H and pyrazole C–H atoms of the two Tp* ligands are located at –21.78 and 17.00 ppm, respectively. The large peak for the protons of the SiMe$_3$ group is located downfield at $\delta$ = 35.98 ppm (9 H). Also visible by $^1$H NMR spectroscopy are the resonances for 0.5 equiv. bibenzyl. Infrared spectroscopy on a solid sample of recrystallized **3** shows two inequivalent B–H absorptions at 2529 and 2555 cm$^{-1}$, similar to those observed for complex **2** and as expected on the basis for other bis(Tp*) derivatives.[13,16–18] The symmetric nature of the $^1$H NMR spectrum and loss of N=N functionality by IR spectroscopy indicates that compound **3** is the linear hydrazonido product Tp*$_2$U($\eta^1$-$N_2CHSiMe_3$) (**3**), in analogy to **2**-$\eta^1$-$N_2CPh_2$. This species was found to be unstable upon storage and forms Tp*U(dmpz)$_3$, which prevents full characterization.

An experiment to trap unstable **3** was performed by repeating the synthesis reaction, with subsequent addition of excess phenylacetylene prior to warming of the mixture to room temperature. This procedure was accompanied by an immediate color change from green to orange–brown (Scheme 1). Analysis of this product, **4**, by $^1$H NMR spectroscopy reveals 25 paramagnetically shifted sharp resonances ranging from –32.18 to 163.14 ppm; no symmetry in the new product is seen. Notably, a large doublet present at –4.24 ppm corresponds to the protons of the –SiMe$_3$ group. Infrared spectroscopy shows loss of both the C≡C triple bond of phenylacetylene and the N=N double bond of free trimethylsilyldiazomethane. The two signature B–H stretches of the bis-Tp* ligand framework are also present (2521, 2553 cm$^{-1}$).

Small orange crystals of **4** were grown from a concentrated pentane/THF (6:1) solution and analyzed by X-ray crystallography. Following refinement of the data, compound **4** is assigned as the uranium(IV) metallacycle Tp*$_2$U-N(N=CHSiMe$_3$)CH=CPh (**4**) (Figure 1, Table 1), which features an eight-coordinate uranium atom in a distorted square-antiprismatic geometry. One face of the antiprism is made up of N61, N71, N81, and N41, while the other is composed of N21, N31, C45, and N11. The resulting structure of complex **4** has a U1–N41 bond length of 2.348(6) Å, indicative of a uranium(IV)–nitrogen(amide) bond.[43,44] Additionally, **4** has a new uranium–carbon bond of 2.372(8) Å, which is at the short end of the range for U–C σ bonds observed in uranium(IV) alkyl species (2.395–2.498 Å).[19,45–62] This is most likely due to increased s character at the U–C44 bond as a result of multiple bonding at the adjacent carbon–carbon bond (C44–C45). The former C≡C triple bond has been reduced to a double bond upon metallation, as supported by the lengthening of the bond to 1.349(12) Å (from 1.203 Å in acetylene). A new N–C bond has been formed between the Nα nitrogen atom and the carbon atom of phenylacetylene. This bond has an N41–C44 distance of 1.381(11) Å, which is intermediate of a carbon–nitrogen single and double bond. Finally, the U–N distances of the Tp* ligands are similar to those in **2**. Complex **4** is derived from $\eta^1$ coordination of the diazoalkane ligand with imido-type bonding through the terminal nitrogen atom in **3**, followed by [2+2] cycloaddition of phenylactylene (Figure 2). This serves to reduce the bond order of the N–N bond as well, which is now elongated to 1.373(9) Å. The new cyclometallated species is stable up to

80 °C. Attempts to elaborate the organic fragment with CO, $CO_2$, $H_2$, amines, hydrazines, or other diazoalkanes have been unsuccessful.

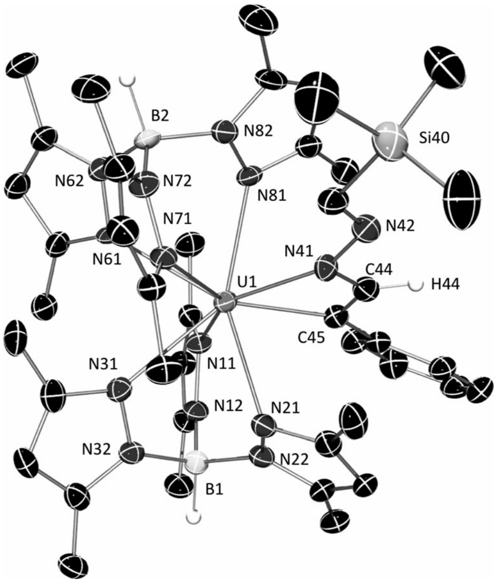


Figure 2. Molecular structure of **4** shown with 30% probability ellipsoids. Selected hydrogen atoms are omitted for clarity.

The cycloaddition chemistry observed for the formation of **4** is rare for diazoalkanes. Bergman previously reported analogous reactivity for $Cp^*_2Ti(\eta^2\text{-}N_2CHSiMe_3)$[31] with both acetylene and phenylacetylene to produce the corresponding metallacycles. Hillhouse observed similar metallacyclic products from the reaction of $Cp^*_2Zr(\eta^2\text{-}PhCCPh)$ and $N_2CPh_2$.[63] In both cases, no structural characterization for the cyclic products was presented, which makes that shown for **4** unique. The [2+2] cycloaddition chemistry is more common for transition-metal imido and hydrazido[64] species. For uranium, the reactivity observed for **4** parallels that found by Andersen,[24] who reported [2+2] cycloaddition of $Cp'_2U\{N(p\text{-tolyl})\}$ with phenylacetylene, which resulted in the analogous $U^{IV}$ metallacycle. This observation also supports the imido character proposed for **3**. The U–C and U–N bond lengths observed for $Cp'_2U{=}N(p\text{-tolyl})$ are the same within error [2.270(6) and 2.202(6) Å, respectively] and slightly shorter than those observed in **4**. The longer distances for **4** are most likely a result of steric congestion imparted by the bulky bis-Tp* ligand framework relative to that by the bis(Cp) framework.

## Conclusions

The reactivity of the uranium(III) alkyl species $Tp^*_2UCH_2Ph$ with $N_2CPh_2$ and $N_2CHSiMe_3$ is presented. In analogy to previous work with organic azides, the new uranium species exhibit structural features for uranium–nitrogen linkages consistent with imido functionalities with concomitant formation of 0.5 equiv. bibenzyl, as determined by $^1H$ NMR spectroscopy. In the case of $N_2CPh_2$, the diazoalkane ligand is dynamic and shifts between the $\eta^1$ and $\eta^2$ isomers in solution at ambient temperature. This has a profound effect on the reactivity, as the $\eta^1$ species can undergo metathesis with carbonylated small molecules, while the $\eta^2$ isomer cannot. Use of trimethylsilyldiazomethane results in the fleeting $\eta^1\text{-}N_2CHSiMe_3$ adduct, which can be effectively trapped by phenylacetylene to make the corresponding metallacycle.

Treatment of the uranium(III) alkyl species with diazoalkanes does not result in an alkylidene species by $N_2$ extrusion or by U–C insertion as previously observed.[9,65] Instead, the dinitrogen fragments are retained and reduced by two electrons to create stable uranium hydrazonido species containing U–N multiple bond linkages. This is in contrast to transition-metal reactivity, where a more charge-delocalized $N_2$ fragment, as a result of superior π backbonding by d-block metals, is common. Because the f-block elements typically do not engage in such activity to a significant extent, more π bonding from the nitrogen to the uranium occurs, which creates U–N multiple bonds.

## Experimental Section

**General Considerations:** All air- and moisture-sensitive manipulations were performed by using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a coldwell designed for freezing samples in liquid nitrogen and with two –35 °C freezers for cooling samples and for crystallization. Solvents for sensitive manipulations were dried and deoxygenated by using literature procedures with a Seca solvent purification system.[66] $[D_6]$Benzene and $[D_8]$toluene were purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles, and dried with 4-Å molecular sieves and sodium. Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN. Trimethylsilyldiazomethane (2.0 M in hexanes) was purchased from Sigma Aldrich and used as received. Phenylacetylene, *p*-tolualdehyde, and acetone were purchased from Sigma Aldrich, dried with calcium hydride, and distilled or vacuum transferred before use. Benzophenone was purchased from Sigma Aldrich, dried on a Schlenk line overnight, recrystallized from anhydrous diethyl ether at –35 °C, and dried under vacuum again. $Tp^*_2U(2,2'\text{-bipy})$,[13] $Tp^*_2UCH_2Ph$,[16] and $N_2CPh_2$[67] were prepared according to literature procedures.

$^1H$ NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts were reported relative to the peak for $SiMe_4$ by using $^1H$ (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained by using an acquisition time of 0.5 s, thus the peak widths reported have an error of ± 2 Hz. For paramagnetic molecules, the $^1H$ NMR spectroscopic data are reported with the chemical shift, followed by the peak width at half height in Hz, the integration value, and where possible, the peak assignment. Solid-state infrared spectra were recorded by using a Perkin–Elmer FTIR Spectrum RX I spectrometer. Samples were made by crushing the solids, mixing with dry KBr, and pressing into a pellet.

Single crystals for X-ray diffraction were coated with polybutene oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a

MicroMax002+ high intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with Cu-$K_\alpha$ radiation ($\lambda$ = 1.54184 Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified by using the program XPREP.[68] The structures were solved by using the structure solution program PATTY in DIRDIFF99.[69] Refinement was performed on a LINUX PC with SHELX-97.[68] The data were collected at a temperature of 150(1) K. CCDC-884974 and CCDC-884975 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.

**Synthesis of $Tp^*_2U(\eta^2$-*N,N*-$N_2CPh_2)$ (2):** A 20-mL scintillation vial was charged with $Tp^*_2UCH_2Ph$ (**1**) (0.100 g, 0.108 mmol), THF (approximately 5 mL), and a stirrer bar, and was cooled in a liquid-nitrogen coldwell for approximately 30 min. In a separate vial, 1 equiv. $N_2CPh_2$ (0.020 g, 0.101 mmol) was dissolved in THF (approximately 2 mL), and the solution was also cooled in the coldwell. After 30 min, the thawing solution of $N_2CPh_2$ was added dropwise to the thawing $Tp^*_2UCH_2Ph$ solution while stirring. The mixture was warmed to room temperature while stirring, and the volatiles were removed in vacuo. The brown–yellow oily residue was recrystallized from a concentrated diethyl ether/pentane solution (1:1), which resulted in the isolation of a brown solid (0.103 g, 0.100 mmol, 93%), assigned as **2**. X-ray quality crystals were grown from a concentrated mixture of THF and pentane (1:4) at –35 °C. $C_{43}H_{54}B_2N_{14}U$ (1026.64): calcd. C 50.31, H 5.30, N 19.10; found C 51.02, H 5.76, N 18.09. Elemental analysis results are reproducible over multiple independently synthesized samples; however, they are outside of the +/– 0.4% range because of the instability of this compound as mentioned in the text. Because of the broadness of the resonances of the $^1H$ NMR spectrum at 25 °C, chemical shifts are reported without decimal places and peak widths at half height are reported to two significant figures. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = –62 (660), –35 (740), –30 (180), –17 (770), –9 (280), –3 (450), 2 (110), 8 (260), 12 (250), 27 (110), 32 (240), 38 (620), 85 (430), 106 (700) ppm. $^1H$ NMR (300 MHz, $C_7D_8$, –5 °C): $\delta$ = –67.98 (211, 3 H, Tp*-C$H_3$), –66.56 (211, 3 H, Tp*-C$H_3$), –38.27 (197, 1 H, Tp*-C*H*), –33.95 (165, 2 H, Ph-C*H*), –19.99 (142, 3 H, Tp*-C$H_3$), –18.94 (129, 3 H, Tp*-C$H_3$), –17.77 (117, 3 H, Tp*-C$H_3$), –13.03 (110, 3 H, Tp*-C$H_3$), –11.11 (115, 3 H, Tp*-C$H_3$), –8.00 (94, 1 H, Tp*-C*H*), –7.83 (172, 2 H, B-*H*), –6.18 (92, 1 H, Tp*-C*H*), –4.16 (81, 1 H, Tp*-C*H*), –3.92 (67, 3 H, Tp*-C$H_3$), 3.10 (14, 3 H, Tp*-C$H_3$), 4.07 (8, 1 H, Tp*-C*H*), 8.83 (107, 3 H, Tp*-C$H_3$), 11.76 (64, 1 H, Tp*-C*H*), 12.36 (115, 2 H, Ph-C*H*), 29.43 (115, 1 H, Ph-C*H*), 34.16 (126, 2 H, Ph-C*H*), 40.75 (174, 2 H, Ph-C*H*), 41.87 (165, 1 H, Ph-C*H*), 93.05 (261, 3 H, Tp*-C$H_3$), 114.38 (305, 3 H, Tp*-C$H_3$) ppm. IR: $\tilde{\nu}$ = 2523, 2552 (B–H) cm$^{-1}$. The by-product in this reaction, bibenzyl, was observed by $^1H$ NMR spectroscopy as a singlet at $\delta$ = 2.78 ppm with multiplets in the aromatic region ranging from 7.01–7.23 ppm.

**Alternative Synthesis of $Tp^*_2U(\eta^2$-*N,N*-$N_2CPh_2)$ (2):** A 20-mL scintillation vial was charged with $Tp^*_2U$(2,2′-bipy) (0.100 g, 0.101 mmol), THF (approximately 5 mL) and a stirrer bar, and was cooled in a liquid-nitrogen coldwell for approximately 30 min. In a separate vial, 3 equiv. $N_2CPh_2$ (0.059 g, 0.303 mmol) were dissolved in THF (approximately 2 mL), and the solution was cooled in the coldwell. After 30 min, the thawing solution of $N_2CPh_2$ was added dropwise to the thawing uranium solution while stirring. The mixture was warmed to room temperature over 5 min, and the volatiles were then removed by vacuum. The brown–yellow oily residue was recrystallized from a concentrated diethyl ether solution, which resulted in isolation of **2** (0.080 g, 0.078 mmol, 77%).

**General Procedure for Addition of Carbonylated Substrates**

**Synthesis of $Tp^*_2U(O)$:** A 20-mL scintillation vial was charged with **2** (0.050 g, 0.049 mmol) and THF (approximately 3 mL). The solution was cooled in the coldwell until the THF was frozen. In a separate vial, 1 equiv. of a carbonylated organic (O=CR′R) was dissolved in diethyl ether [R = H, R′ = *p*-tolyl (6 µL, 0.051 mmol); R = R′ = Ph, (0.009 g, 0.049 mmol); R = R′ = Me (4 µL, 0.052 mmol)]. This colorless solution was added to the thawing uranium solution while stirring. No initial color change was observed; however, after the solution warmed to room temperature, it changed to bright pink. The uranium-containing product was isolated by removing the solvents in vacuo, and $^1H$ NMR spectroscopy confirmed the formation of $Tp^*_2U(O)$ in quantitative yield.[18] 1 equiv. of the corresponding ketazines, $Ph_2CNNCPh_2$,[41] $Me_2CNNCPh_2$,[41] and H(*p*-tolyl)$CNNCPh_2$,[38,39] were identified by comparison to literature data.

**Synthesis of $Tp^*_2U[\eta^1$-(*N*)=N–N=$CHSiMe_3]$ (3):** A 20-mL scintillation vial was charged with $Tp^*_2UCH_2Ph$ (**1**) (0.100 g, 0.108 mmol), THF (approximately 5 mL), and a stirrer bar, and was cooled in a liquid-nitrogen coldwell for approximately 30 min. In a separate vial, $N_2CHSiMe_3$ solution (51 µL, 0.108 mmol) was diluted with THF (approximately 3 mL) and cooled for 30 min in the coldwell. After this time, the thawing pale yellow solution of $N_2CHSiMe_3$ was added dropwise to the vial containing a thawing solution of $Tp^*_2UCH_2Ph$. No immediate color change was observed, but after stirring for 5 min, the solvents were removed in vacuo to leave a crude brown–orange oil, assigned as $Tp^*_2U[\eta^1$-(*N*)=N–N=$CHSiMe_3]$. The yield was determined by integration of the $^1H$ NMR spectrum against a ferrocene internal standard, (0.074 g, 0.079 mmol, 73%). $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = –21.78 (204, 2 H, B-*H*), –7.03 (8, 18 H, Tp*-C$H_3$), 2.56 (60, 18 H, Tp*-C$H_3$), 17.00 (11, 6 H, Tp*-C*H*), 29.98 (17, 1 H, C-*H*), 35.98 [7, 9 H, –Si(C$H_3)_3$] ppm. IR: $\tilde{\nu}$ = 2529, 2555 (B–H) cm$^{-1}$. The by-product in this reaction, bibenzyl, was observed by $^1H$ NMR spectroscopy as a singlet at $\delta$ = 2.78 ppm with multiplets in the aromatic region ranging from 7.01–7.23 ppm. Isolation and characterization of this species by elemental analysis was not possible because of instability.

**Synthesis of $Tp^*_2U$–N(N=$CHSiMe_3$)CH=CPh (4):** A 20-mL scintillation vial was charged with $Tp^*_2UCH_2Ph$ (**1**) (0.100 g, 0.108 mmol) and THF (approximately 5 mL) and was cooled in the coldwell until frozen. In a separate vial, 1 equiv. $N_2CHSiMe_3$ (54 µL, 0.108 mmol) was dissolved in THF and cooled until frozen. The thawing diazoalkane solution was added dropwise to the green uranium solution as it thawed, which resulted in a change to red–brown. The vial was stored in the coldwell for approximately 10 min to ensure complete reaction at low temperature. After this time, excess phenylacetylene was added to the solution, which resulted in an orange–brown solution. After stirring for 5 min, the volatiles were removed under reduced pressure. Product **4** was isolated in moderate yields (0.072 g, 0.062 mmol, 57%) by recrystallization from a concentrated diethyl ether/pentane (1:2) solution at –35 °C. Orange X-ray quality crystals were grown from a concentrated solution of diethyl ether/pentane (1:1) at –35 °C. $C_{42}H_{60}B_2N_{14}SiU$ (1048.76): calcd. C 48.10, H 5.77, N 18.70; found C 48.28, H 5.82, N 18.68. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = –32.18 (23, 3 H, Tp*-C$H_3$), –30.43 (23, 3 H, Tp*-C$H_3$), –24.21 (82, 2 H, B-H), –20.21 (23, 1 H, Tp*-C*H*), –12.01 (17, 3 H, Tp*-C$H_3$), –11.75 (21, 3 H, Tp*-C$H_3$), –8.45 (17, 3 H, Tp*-C$H_3$), –6.37 (16, 3 H, Tp*-C$H_3$), –5.75 (21, 3 H, Tp*-C$H_3$), –4.24 (d, *J* = 11.4 Hz, 9 H, Si(C$H_3)_3$), –2.21 (20, 1 H, Tp*-C*H*), 0.91 (10, 1 H, Tp*-C*H*), 1.15 (16, 3 H, Tp*-C$H_3$), 1.31 (7, 3 H, Tp*-C$H_3$), 1.64 (6, 1 H, Tp*-C*H*), 2.38 (3, 1 H, Tp*-C*H*), 3.29 (16, 3 H, Tp*-C$H_3$), 9.09 (21, 3 H, Tp*-C$H_3$), 11.27 (15, 3 H, Tp*-C$H_3$), 11.79 (3, 1 H, Tp*-C*H*), 16.56 (14, 1 H, Tp*-C*H*), 21.08 [15, 1 H, C(SiMe$_3$)*H*], 25.53 (23, 1 H, phenyl-C*H*), 45.54 (27, 2 H, phenyl-C*H*), 63.96 (35, 2 H, phenyl-C*H*), 163.14 (50, 1 H, olefin-*H*) ppm. IR: $\tilde{\nu}$ = 2521, 2553 (B–H) cm$^{-1}$.

**Alternative Synthesis of Tp*$_2$U–N(N=CHSiMe$_3$)CH=CPh (4):** A 20-mL scintillation vial was charged with Tp*$_2$U(2,2′-bipy) (0.100 g, 0.101 mmol), THF (approximately 2 mL), and 1.3 equiv. phenylacetylene (0.020 g, 0.130 mmol). To an additional vial, 1 equiv. N$_2$CHSiMe$_3$ (50 µL, 0.101 mmol) was added by microsyringe and diluted with THF (2 mL). This pale yellow solution was cooled for 30 min in the coldwell. The thawing diazomethane solution was added dropwise to the original brown–red uranium solution. An immediate color change to brown–orange was observed. The volatiles were immediately removed, and the resulting residue was washed with cold pentane. After drying, the resulting oil was dissolved in diethyl ether and filtered, and the resulting filtrate evaporated to dryness (0.100 g, 0.096 mmol, 89%).

**Supporting Information** (see footnote on the first page of this article): $^1$H NMR spectra of the compounds are presented.

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[1] M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704.
[2] D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2002**, *124*, 9976.
[3] B. J. Anding, A. Ellern, L. K. Woo, *Organometallics*, *31*, 3628.
[4] M. Dartiguenave, J. M. Menu, E. Dyedier, Y. Dartiguenave, H. Siebald, *Coord. Chem. Rev.* **1998**, *178–180*, 623.
[5] Y. Mizobe, Y. Ishii, M. Hidai, *Coord. Chem. Rev.* **1995**, *139*, 281.
[6] S. K. Russell, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 36.
[7] P. Roussel, R. Boaretto, A. J. Kingsley, N. W. Alcock, P. Scott, *J. Chem. Soc., Dalton Trans.* **2002**, 1423.
[8] O. P. Lam, P. L. Feng, F. W. Heinemann, J. M. O'Connor, K. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 2806.
[9] T. Cantat, C. R. Graves, K. C. Jantunen, C. J. Burns, B. L. Scott, E. J. Schelter, D. E. Morris, P. J. Hay, J. L. Kiplinger, *J. Am. Chem. Soc.* **2008**, *130*, 17537.
[10] T. Cantat, C. R. Graves, B. L. Scott, J. L. Kiplinger, *Angew. Chem.* **2009**, *121*, 3735; *Angew. Chem. Int. Ed.* **2009**, *48*, 3681.
[11] B. M. Gardner, D. Patel, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2011**, *123*, 10624; *Angew. Chem. Int. Ed.* **2011**, *50*, 10440.
[12] E. M. Matson, M. G. Crestani, P. E. Fanwick, S. C. Bart, *Dalton Trans.* **2012**, *41*, 7952–7958.
[13] S. J. Kraft, P. E. Fanwick, S. C. Bart, *Inorg. Chem.* **2010**, *49*, 1103.
[14] M. A. Antunes, A. Domingos, I. Cordeiro dos Santos, N. Marques, J. Takats, *Polyhedron* **2005**, *24*, 3038.
[15] A. K. Saha, M. M. Hossain, D. S. Grubisha, D. W. Bennett, *J. Chem. Crystallogr.* **1995**, *25*, 383.
[16] E. M. Matson, W. P. Forrest, P. E. Fanwick, S. C. Bart, *J. Am. Chem. Soc.* **2011**, *133*, 4948.
[17] E. M. Matson, P. E. Fanwick, S. C. Bart, *Organometallics* **2011**, *30*, 5753.
[18] S. J. Kraft, J. Walensky, P. E. Fanwick, M. B. Hall, S. C. Bart, *Inorg. Chem.* **2010**, *49*, 7620.
[19] R. K. Thomson, C. R. Graves, B. L. Scott, J. L. Kiplinger, *Eur. J. Inorg. Chem.* **2009**, 1451.
[20] B. D. Stubbert, C. L. Stern, T. J. Marks, *Organometallics* **2003**, *22*, 4836.
[21] T. W. Hayton, *Dalton Trans.* **2010**, *39*, 1145.
[22] C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 11914.
[23] 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.
[24] G. Zi, L. L. Blosch, L. Jia, R. A. Andersen, *Organometallics* **2005**, *24*, 4602.
[25] D. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* **1995**, *117*, 9448.
[26] I. Castro-Rodriguez, K. Olsen, P. Gantzel, K. Meyer, *J. Am. Chem. Soc.* **2003**, *125*, 4565.
[27] S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein, K. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 12536.
[28] T. Iikubo, T. Itoh, K. Hirai, Y. Takahashi, M. Kawano, Y. Ohashi, H. Tomioka, *Eur. J. Org. Chem.* **2004**, 3004.
[29] P. J. Davis, L. Harris, A. Karim, A. L. Thompson, M. Gilpin, M. G. Moloney, M. J. Pound, C. Thompson, *Tetrahedron Lett.* **2011**, *52*, 1553.
[30] W. Sander, G. Bucher, P. Komnick, J. Morawietz, P. Bubenitschek, P. G. Jones, A. Chrapkowski, *Chem. Ber.* **1993**, *126*, 2101.
[31] J. L. Polse, A. W. Kaplan, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1998**, *120*, 6316.
[32] T. Schaub, U. Radius, *Z. Anorg. Allg. Chem.* **2007**, 2168.
[33] A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka, J. A. Ibers, *J. Am. Chem. Soc.* **1977**, *99*, 2108.
[34] C. J. Brown, *Acta Crystallogr.* **1966**, *21*, 146.
[35] C. J. Brown, *Acta Crystallogr.* **1966**, *21*, 153.
[36] T. E. Hanna, I. Keresztes, E. Lobkovsky, W. H. Bernskoetter, P. J. Chirik, *Organometallics* **2004**, *23*, 3448.
[37] J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Chem. Commun.* **2002**, 30.
[38] H. Heaney, K. G. Mason, J. M. Sketchley, *J. Chem. Soc. C* **1971**, 567.
[39] B. Krishnakumar, M. Swaminathan, *Catal. Commun.* **2011**, *16*, 50.
[40] E. C. K. Lai, D. MacKay, N. Taylor, K. N. Watson, *Can. J. Chem.* **1988**, *66*, 2839.
[41] J. Barluenga, S. Fustero, N. Gomez, V. Gotor, *Synthesis* **1982**, 966.
[42] R. A. Zarkesh, A. F. Heyduk, *Organometallics* **2009**, *28*, 6629.
[43] C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *Organometallics* **2008**, *27*, 3335.
[44] B. D. Stubbert, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 4253.
[45] W. J. Evans, N. A. Siladke, J. W. Ziller, *Chem. Eur. J.* **2010**, *16*, 796.
[46] W. J. Evans, S. A. Kozimor, W. R. Hillman, J. W. Ziller, *Organometallics* **2005**, *24*, 4676.
[47] W. J. Evans, J. R. Walensky, J. W. Ziller, A. L. Rheingold, *Organometallics* **2009**, *28*, 3350.
[48] K. C. Jantunen, C. J. Burns, I. Castro-Rodriguez, R. E. Da Re, J. T. Golden, D. E. Morris, B. L. Scott, F. L. Taw, J. L. Kiplinger, *Organometallics* **2004**, *23*, 4682.
[49] E. Barnea, T. Andrea, M. Kapon, J.-C. Berthet, M. Ephritikhine, M. S. Eisen, *J. Am. Chem. Soc.* **2004**, *126*, 10860.
[50] G. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen, R. A. Andersen, *Organometallics* **2005**, *24*, 4251.
[51] W. J. Evans, K. A. Miller, J. W. Ziller, A. G. DiPasquale, K. J. Heroux, A. L. Rheingold, *Organometallics* **2007**, *26*, 4287.
[52] S. Fortier, B. C. Melot, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2009**, *131*, 15512.
[53] W. J. Evans, J. R. Walensky, J. W. Ziller, *Organometallics* **2010**, *29*, 101.
[54] W. J. Evans, M. K. Takase, J. W. Ziller, A. L. Rheingold, *Organometallics* **2009**, *28*, 5802.
[55] G. Perego, M. Cesari, F. Farina, G. Lugli, *Acta Crystallogr., Sect. B* **1976**, *32*, 3034.

[56] K. C. Jantunen, F. Haftbaradaran, M. J. Katz, R. J. Batchelor, G. Schatte, D. B. Leznoff, *Dalton Trans.* **2005**, 3083.

[57] E. J. Schelter, J. M. Veauthier, C. R. Graves, K. D. John, B. L. Scott, J. D. Thompson, J. A. Pool-Davis-Tournear, D. E. Morris, J. L. Kiplinger, *Chem. Eur. J.* **2008**, *14*, 7782.

[58] E. M. Broderick, N. P. Gutzwiller, P. L. Diaconescu, *Organometallics* **2010**, *29*, 3242.

[59] W. W. Lukens Jr., S. M. Beshouri, L. L. Blosch, A. L. Stuart, R. A. Andersen, *Organometallics* **1999**, *18*, 1235.

[60] W. J. Evans, J. R. Walensky, F. Furche, J. W. Ziller, A. G. DiPasquale, A. L. Rheingold, *Inorg. Chem.* **2008**, *47*, 10169.

[61] P. L. Diaconescu, A. L. Odom, T. Agapie, C. C. Cummins, *Organometallics* **2001**, *20*, 4993.

[62] W. J. Evans, J. R. Walensky, J. W. Ziller, *Inorg. Chem.* **2010**, *49*, 1743.

[63] G. A. Vaughn, G. L. Hillhouse, A. L. Rheingold, *J. Am. Chem. Soc.* **1990**, *112*, 7994.

[64] A. D. Schofield, A. Nova, J. D. Selby, C. D. Manley, A. D. Schwarz, E. Clot, P. Mountford, *J. Am. Chem. Soc.* **2010**, *132*, 10484.

[65] J. L. Kiplinger, K. D. John, D. E. Morris, B. L. Scott, C. J. Burns, *Organometallics* **2002**, *21*, 4306.

[66] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.

[67] L. I. Smith, K. L. Howard, “Diphenyldiazomethane” in *Organic Syntheses, Collective Volume 3* (Ed. E. C. Horning), John Wiley and Sons, New York, **1955**, pp 351–352. .

[68] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[69] P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, *Crystallography Laboratory*, University of Nijmegen, The Netherlands, **2008**.

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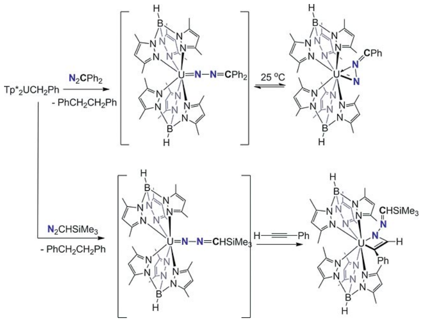
## Uranium Hydrazonido Complexes

Uranium hydrazonido complexes were synthesized by reduction of diazoalkanes by the uranium(III) alkyl Tp*$_2$UCH$_2$Ph with extrusion of bibenzyl.



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Diazoalkane Reduction for the Synthesis of Uranium Hydrazonido Complexes

**Keywords:** Uranium / Diazo compounds / Metallacycles / Tridentate ligands / Actinides