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Preparation and Reactions of Base-Free Bis(1,2,4-tri-*tert*-butylcyclopentadienyl)uranium Methylimide, Cp′$_2$U=NMe, and Related Compounds

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The uranium metallocenes [η^5-1,3-(Me$_3$E)$_2$C$_5$H$_3$]$_2$UMe$_2$ (E = C, Si) react with NH$_3$ to give the dimers {[η^5-1,3-(Me$_3$E)$_2$C$_5$H$_3$]$_2$U}$_2$(μ-NH)$_2$ (E = C (**1**), Si (**2**)) but with *p*-toluidine to give the monomeric diamides [η^5-1,3-(Me$_3$E)$_2$C$_5$H$_3$]$_2$U(NH-*p*-tolyl)$_2$ (E = C (**3**), Si (**4**)). The diamides [η^5-1,3-(Me$_3$E)$_2$C$_5$H$_3$]$_2$U(NH-*p*-tolyl)$_2$ (E = C (**3**), Si (**4**)) do not eliminate *p*-toluidine but sublime intact at 140 °C in a vacuum. The uranium metallocene [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UMe$_2$ reacts with RNH$_2$ to yield [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(NHR)$_2$ (R = Me (**8**), PhCH$_2$ (**9**), *p*-tolyl (**10**)), which are isolated as crystalline solids. In benzene solution these diamides are in equilibrium with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NR, which may be isolated pure when R is Me (**11**) or *p*-tolyl (**12**), and the primary amine. The monomeric imide [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**) reacts with R′C≡CR′ to yield the cycloaddition products [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U-[N(Me)C(R′)=C(R′)] (R′ = Me (**15**), Ph (**16**)), which react with excess MeNH$_2$ to regenerate the diamide [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(NHMe)$_2$ (**8**) and MeN=C(R′)CH(R′). The methylimide, [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**), does not react with Me$_3$SiX reagents; a model is proposed that rationalizes this reactivity pattern.

Introduction

Several substituted cyclopentadienyl uranium-imido derivatives of the type (η^5-C$_5$Me$_5$)$_2$U(NAr)$_2$, (η^5-C$_5$Me$_5$)$_2$U-(NAr)(O), (η^5-MeC$_5$H$_4$)$_3$U=NPh, and (η^5-C$_5$Me$_5$)$_2$U=NAr have been prepared.[1−10] When the arylamine has sterically bulky substituents such as i-Pr and t-Bu in the 2,6-positions,[3,4] the (η^5-C$_5$Me$_5$)$_2$U=NAr derivatives are generally prepared by reaction of (η^5-C$_5$Me$_5$)$_2$UMe$_2$ with 1 equiv of a primary arylamine, which presumably forms (η^5-C$_5$Me$_5$)$_2$U(Me)(NHAr), which eliminates methane, forming the imidometallocene.[3,4] When the substituents are somewhat less bulky, for example, 2,6-dimethylaniline, the bis-amide derivative is formed, which thermally eliminates the amine, forming (η^5-C$_5$Me$_5$)$_2$U(NAr)(thf).[8,9] However, the least bulky arylamine, aniline, yields (η^5-C$_5$Me$_5$)$_2$U(NHPh)$_2$, which is stable to elimination of aniline.[4] The primary alkylamines EtNH$_2$ and Me$_3$CNH$_2$ behave similarly.[8] Thus, formation of decamethylmetalloceneuranium imides depends in a very sensitive way on the steric bulk and, perhaps, on the electronic effects of the substituents on the primary amine. The formation of a metallocene imide from a metallocene bis(amide) is an important reaction since it is postulated to be a key step in the catalytic hydroamination of terminal acetylenes reported by Eisen.[10]

The decamethylmetalloceneuranium fragment[11] is essential for the preparation of these monomeric f^2-imido derivatives (with or without a coordinated Lewis base), since for example, imides derived from (η^5-MeC$_5$H$_4$)$_2$U or [(Me$_3$Si)$_2$N]$_2$U fragments yield dimeric derivatives, (η^5-MeC$_5$H$_4$)$_4$U$_2$(μ-NR)$_2$[12] or [(Me$_3$Si)$_2$N]$_4$U$_2$-(μ-NR)$_2$.[13] Thus, steric effects seem to play a dominant role in determining the degree of association of the uranium imide.

The bulky 1,2,4-(Me$_3$C)$_3$C$_5$H$_2$ cyclopentadienyl ligand has been shown to yield the base-free oxo and *p*-tolylimido uranium derivatives, [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=O (monomeric in the gas phase) and [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=N(*p*-tolyl) (**12**) (monomeric in the gas and solid phase), respectively.[14] In this paper, we show that the [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U fragment yields a monomeric methylimido derivative that undergoes irreversible cycloaddition reactions with internal

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(1) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514.

(2) Arney, D. J. S.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068.

(3) Arney, P. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840.

(4) Arney, P. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448.

(5) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959.

(6) Peters, R. G.; Warner, B. P.; Scott, B. L.; Burns, C. J. *Organometallics* **1999**, *18*, 2587.

(7) Peters, R. G.; Warner, B. P.; Burns, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 5585.

(8) Straub, T.; Frank, W.; Reiss, G. J.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.* **1996**, 2541.

(9) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773.

(10) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017.

(11) Fagan, P. J.; Manriquez, J. M.; Maata, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

(12) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1988**, *110*, 4554.

(13) Stewart, J. L.; Andersen, R. A. *New J. Chem.* **1995**, *19*, 587.

(14) Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251.

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acetylenes. In addition, we report that the less heavily substituted derivatives derived from 1,3-$(Me_3E)_2C_5H_3$ (E = C, Si) do not yield monomeric imido metallocenes.

Results and Discussion

Imides $\{[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U\}_2(\mu\text{-}NH)_2$ and Amides $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U(NH\text{-}p\text{-}tolyl)_2$. Addition of an excess of ammonia to a solution of either $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2UMe_2$[15] or $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2UMe_2$[15] in diethyl ether results in evolution of a gas, presumably methane, and formation of red-purple precipitates, eq 1. The precipitates are insoluble in hexane, sparingly soluble in toluene, but soluble in THF, from which they may be crystallized as red-purple or purple blocks, $\{[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U\}_2(\mu\text{-}NH)_2$ (E = C (**1**), Si (**2**)). The ammonia reaction is similar to the reaction of $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2UMe_2$ with water that yields the oxo-bridged dimers $\{[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U\}_2(\mu\text{-}O)_2$ (E = C, Si).[16-18] The imido derivatives **1** and **2** do not melt up to 300 °C, but both yield dimeric molecular ions in their mass spectra. Thus, the isoelectronic functional groups O and NH yield dimeric metallocene derivatives, which presumably have similar structures.

$$2[1,3\text{-}(Me_3E)_2C_5H_3]_2UMe_2 + 2NH_3 \rightarrow \{[1,3\text{-}(Me_3E)_2C_5H_3]_2U\}_2(\mu\text{-}NH)_2 + 4CH_4 \quad (1)$$
$$E = C\ (\mathbf{1}),\ Si\ (\mathbf{2})$$

The ^1H NMR spectra of the imido dimers **1** and **2** are similar to each other and to those of the oxo-bridged dimers.[16,19] Thus, at room temperature the Me_3C or Me_3Si resonances appear as two equal area resonances and the ring-CH resonances appear as a pair of A_2B resonances; see Experimental Section for details. A structure in which the rings on each metallocene fragment are inequivalent and the metallocene fragments in the dimer are related so that the dimer has averaged C_{2h} symmetry at this temperature is consistent with the ^1H NMR spectra. Increasing the temperature results in coalescence of the two Me_3Si resonances and the pair of A_2B subspectra in **2**, with a barrier ($\Delta G^{\ddagger}$ at $T_c = 100$ °C) of 16.9 kcal mol^{-1}. This barrier is similar to that found in the analogous oxo-bridged dimer.[16] The Me_3C resonances in **1** do not coalesce by 100 °C, although the resonances are moving toward each other. An intramolecular process that is responsible for the site exchange is Cp-ring oscillations about their pseudo-C_5 axes, generating a dimer with time-averaged D_{2d} symmetry, as suggested for the oxo- and fluoride-bridged dimer.[19]

Two equivalents of p-toluidine react rapidly with $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2UMe_2$ (E = C, Si)[15] in hexane to yield the red diamide metallocenes $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U(NH\text{-}p\text{-}tolyl)_2$ (E = C (**3**), Si (**4**)), which may be crystallized from pentane, eq 2. Using 1 equiv of p-toluidine results in a ^1H NMR spectrum that consists of the diamide **3** or **4** and unreacted $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2UMe_2$, implying that $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U(Me)(NH\text{-}p\text{-}tolyl)$ disproportionates. The diamides **3** and **4** melt without decomposition about 150 °C, sublime without decomposition in a vacuum in the temperature range 130−140 °C, and give a molecular ion in their mass spectra.

$$[1,3\text{-}(Me_3E)_2C_5H_3]_2UMe_2 + 2p\text{-}tolylNH_2 \rightarrow [1,3\text{-}(Me_3E)_2C_5H_3]_2U(NH\text{-}p\text{-}tolyl)_2 + 2CH_4 \quad (2)$$
$$E = C\ (\mathbf{3}),\ Si\ (\mathbf{4})$$

The ^1H NMR spectra of the diamides **3** and **4** at 20 °C are well resolved; all of the expected resonances are observed and the doublet splitting between the ortho and meta protons on the p-tolyl groups are resolved. The observation of the coupling, along with the relative intensities, allows all of the resonances to be assigned, including a resonance tentatively assigned to the NH group. Thus, $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2U(NH\text{-}p\text{-}tolyl)_2$ (**3**) has two broadened absorptions of relative area 2 at −2.6 ($\nu_{1/2} = 8$ Hz) and −68 ppm ($\nu_{1/2} = 24$ Hz) due to either the Cp-ring CH or the NH groups, respectively. To distinguish between these two alternative assignments, the dibenzyl derivatives $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2U(CH_2Ph)_2$ (E = C (**5**), Si (**6**)) were prepared. The benzylic CH_2 groups in **5** and **6** and the p-tolylamido NH groups in **3** and **4** should have a similar chemical shift, since the origin of the chemical shifts in these f-element compounds is largely determined by the dipolar contribution; that is, those protons that have similar geometrical orientations relative to the paramagnetic center will have similar chemical shifts.[20-22] The dibenzyl derivatives **5** and **6** may be prepared from the benzyl-Grignard reagent and the dichlorides, $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_2UCl_2$ (E = C, Si);[15] see Experimental Section for details. The ^1H NMR spectra are well resolved, the couplings for the phenyl CH resonances allow them to be assigned, and the other resonances may be assigned on the basis of their relative intensities. In the spectrum of $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2U(CH_2Ph)_2$ (**5**), a resonance at −72 ppm ($\nu_{1/2} = 32$ Hz) is assigned to the benzylic CH_2 group, which by inference suggests that the resonance at −68 ppm in **3** is due to the NH group. Unfortunately, a resonance due to the benzylic CH_2 group in **6** cannot be observed, so the NH resonance at −34.7 ppm in **4** is only a tentative assignment.

The difference in behavior between ammonia and p-toluidine is rather striking and difficult to interpret, but several possible reasons may be suggested. The thermodynamics of imide formation from the diamide may be endoergic, the rates of elimination of CH_4 and RNH_2 may be greatly different, or the hypothetical p-tolylimide metallocenes may be unstable. The experiments described in the next section begin to address these differences.

Amides $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(HNR)_2$. The reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ with an excess of ammonia was shown recently to give the bis-amide $[\eta^5\text{-}$

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

[16] Lukens, W. W.; Beshouri, S. M.; Blosch, L. L.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 901.

[17] Zalkin, A.; Beshouri, S. M. *Acta Crystallogr.* **1988**, *C44*, 1826.

[18] Lukens, W. W.; Allen, P. G.; Bucher, J. J.; Edelstein, N. M.; Hudson, E. A.; Shuh, D. K.; Reich, T.; Andersen, R. A. *Organometallics* **1999**, *18*, 1253.

[19] Lukens, W. W.; Beshouri, S. M. Stuart, A. L.; Andersen, R. A. *Organometallics* **1999**, *18*, 1247.

[20] *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. D., Holm, R. H., Eds; Academic Press: New York, 1973; Chapters 4 and 13.

[21] *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds; D. Reidel: Dordrecht, 1979; p 337.

[22] *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds; D. Reidel: Dordrecht, 1985; p 229.

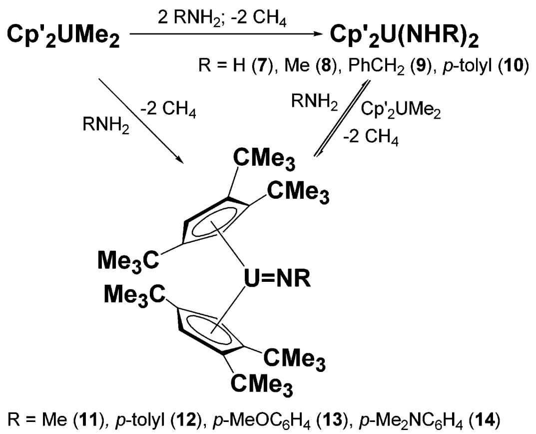
1,2,4-$(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (**7**).[14] Excess primary amines react with $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UMe_2$ to give the bis-amide metallocenes $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U(HNR)_2$ (R = Me (**8**), $PhCH_2$ (**9**), *p*-tolyl (**10**)), Scheme 1. The rates of the reaction qualitatively follow the order $MeNH_2$ > $PhCH_2NH_2$ ≫ *p*-tolylNH_2. Primary amines with bulky substituents, such as Me_2CHNH_2 or Me_3CNH_2, do not react with $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UMe_2$ even at 65 °C. All three bis-amides are soluble in pentane, from which they may be crystallized in colors that range from yellow (**8**) to red (**10**). The bis-amides have moderately high melting points, they do not sublime but decompose about 200 °C, and give $[M - NHR]^+$ molecular ions in their mass spectra. The latter data suggest that the metallocene imide derivatives are accessible, on a synthetic scale, by thermal loss of an amine. This inference is shown to be correct by the following experiments.

The ^1H NMR spectrum of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U$-(NH-*p*-tolyl$)_2$ (**10**) at 20 °C in C_7D_8 shows the Me_3C groups in a 2:1 relative area ratio, the ortho and meta tolyl CH resonances as a pair of doublets, and the methyl group as a singlet, Table 1. The Cp-ring CH and tolyl NH resonances are not apparent. The spectrum is consistent with a metallocene with time-averaged C_{2v} symmetry, as found in derivatives of the general formula $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UX_2$.[14] Increasing the temperature alters the appearance of the spectrum in the following manner. The chemical shifts of the Me_3C groups change slightly and a new set of resonances in a 2:1 relative area ratio appear upfield of the original set, which decreases in intensity such that the total intensity of both sets is constant. The new set of resonances is due to the Me_3C groups of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}N$(*p*-tolyl) (**12**).[14] Inspection of the spectrum at 100 °C shows the resonances due to the ortho and meta CH, and the *para*-Me groups on the tolyl groups of the diamide (**10**) and imide (**12**), but the resonances for free *p*-toluidine are not visible, perhaps due to the small amount formed or chemical exchange. At 100 °C, the ratio of **10** to **12** is approximately 6:1. Cooling to 20 °C yields the original spectrum without loss in absolute intensity. The reversibility of the ^1H NMR spectrum is consistent with the equilibrium shown in eq 3.

$$[1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHR)_2 \rightleftharpoons [1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}NR + H_2NR \quad (3)$$

The changes in the ^1H NMR spectrum on lowering the temperature are not so readily interpreted, since Me_3C resonances that appear in a 2:1 area ratio at 20 °C do not simply decoalesce into three equal area resonances as found in $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UX_2$.[14] The Me_3C resonance at −4.6 ppm of relative area 1 at 20 °C moves upfield and broadens, while the resonance at 2.5 ppm of relative area 2 broadens and disappears by −10 °C. By −50 °C, two broad, approximately equal area resonances emerge. On further cooling to −80 °C, the upfield resonance disappears and does not reappear, while the downfield resonance is very broad and appears to be on the verge of decoalescing into two equal-area resonances. During this process, neither the chemical shift of the *p*-Me resonance nor its line width changes much, suggesting that a single isomer is present but that the Cp rings are still related by a mirror plane of symmetry at −80 °C.

Scheme 1



The variable-temperature ^1H NMR behavior of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**) (labeled A in Figure 1) is similar to that of the *p*-tolyl derivative **10**. The chemical shifts of the Me_3C groups in relative ratio of 2:1 shift as a function of temperature, and by about 70 °C, the resonances due to the Me_3C groups of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11**) (labeled B in Figure 1) appear. Increasing the temperature to 100 °C changes the relative intensity of these resonances until the amide (**8**) to imide (**11**) ratio is approximately 4:1. Thus, the equilibrium illustrated by eq 3 also operates in this case. The low-temperature ^1H NMR spectrum of the diamide (**8**) is well behaved like the $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UX_2$ derivatives;[14] the Me_3C resonance of relative area 2 decoalesces into two equal-area reasonances and $\Delta G^{\ddagger}(T_c = -70\ °C) = 12$ kcal mol^{-1}, essentially identical to the values observed for $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UX_2$ (X = F, Cl, N_3).[14] In addition, the methyl resonance in the MeNH group broadens and disappears by −60 °C.

Imides $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NR$. The monomeric *p*-tolylimide, $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}N$(*p*-tolyl) (**12**), was originally prepared by reaction of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U$(bipy) with *p*-tolyl azide.[14] The imide **12** may also be prepared by two alternative synthetic methods, i.e., heating an equimolar mixture of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UMe_2$ and either $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U$-(NH-*p*-tolyl$)_2$ or *p*-toluidine in methylcyclohexane for periods of 3−4 days. For amines that are liquids or solids, the reaction of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UMe_2$ and the amine is the most convenient synthetic route. In this way, the *p*-substituted benzene derivatives, $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NR$ (R = *p*-$MeOC_6H_4$ (**13**), *p*-$Me_2NC_6H_4$ (**14**)), are prepared. When the amine is a gas, for example, $MeNH_2$, the best synthetic route is heating an equimolar mixture of $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UMe_2$ and $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**) at reflux in cyclohexane. When the amine is ammonia, exchange does not occur between $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2UMe_2$ and $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (**7**), as shown by monitoring the ^1H NMR spectrum, up to a temperature of 65 °C, or by heating an equimolar mixture of the two metallocenes at reflux in methylcyclohexane for 4 days. Furthermore, the amide $[\eta^5$-1,2,4-$(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (**7**) does not eliminate ammonia on heating in refluxing

Table 1. Physical Properties of $Cp'_2U(X)(Y)$, $Cp' = 1,2,4\text{-}(CMe_3)_3C_5H_2$

		^1H NMR (δ, 20 °C)[a]				
compound	mp (°C)	$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$	ring C*H*	other
$Cp'_2U(NHMe)_2$ (**8**)	144−146 (dec)	3.9 (3)	−1.6 (4)	−1.6 (4)	−14.9 (4)	N*H*, −87.8 (135) NCH_3, 36.9 (11)
$Cp'_2U(NHCH_2C_6H_5)_2$ (**9**)	160−162 (dec)	9.4 (6)	−2.1 (124)	−2.1 (124)	−43.0 (110)	$PhCH_2NH$ CH_2, 68.6 (300) *o*-C*H*, 7.2 (t, *J* = 7.5 Hz) *m*-C*H*, 5.9 (m) *p*-C*H*, 6.7 (t, *J* = 7.5 Hz) N*H*, −12.9 (330)
$Cp'_2U(NH\text{-}p\text{-tolyl})_2$ (**10**)	231−239 (dec)	2.5 (5)	2.5 (5)	−4.2 (3)	b	NH-*p*-tolyl *o*-C*H*,[c] 3.1 (d, *J* = 8 Hz) *m*-C*H*,[c] −16.2 (d, *J* = 8 Hz) CH_3, 3.3 (6) N*H*[b]
$Cp'_2U{=}NMe$ (**11**)	205−207	−8.0 (42)	−8.0 (42)	−19.1 (59)	b	NCH_3, 23.2 (275)
$Cp'_2U{=}N(p\text{-}C_6H_4OCH_3)$ (**13**)	192−194	−6.1 (146)	−6.1 (146)	−22.6 (97)	22.7 (170)	$N(p\text{-}C_6H_4OMe)$ *o*-C*H*,[c] 28.9 (13) *m*-C*H*[c] 24.2 (15) OCH_3, 11.7 (4)
$Cp'_2U{=}N(p\text{-}C_6H_4NMe_2)$ (**14**)	190−192	−6.2 (170)	−6.2 (170)	−22.6 (115)	23.0 (216)	$N(p\text{-}C_6H_4NMe_2)$ *o*-C*H*,[c] 29.0 (d, *J* = 5.1 Hz) *m*-C*H*,[c] 24.2 (d, *J* = 5.1 Hz) $N(CH_3)_2$, 12.1 (5)
$Cp'_2U[N(Me)C(Me){=}C(Me)]$ (**15**)	250−252	−2.6 (14)	−2.6 (14)	−3.8 (7)	−0.9 (73) −1.5 (90)	NCH_3, 58.8 (10) CH_3, 37.2 (7) CH_3, 17.1 (5)
$Cp'_2U[N(Me)C(Ph){=}C(Ph)]$ (**16**)	172−174	−0.8 (36)	−3.1 (400)	−7.4 (160)	15.9 (26) 15.8 (29)	NCH_3, 56.9 (41) phenyl (1) *o*-C*H* 11.2 (t, *J* = 7.5 Hz) *m*-C*H*, 7.0 (m) *p*-C*H*, 10.0 (t, *J* = 7.5 Hz) phenyl (2) *o*-C*H*, 0.9 (t, *J* = 7.2 Hz) *m*-C*H*, 1.2 (m) *p*-C*H*, 0.6 (t, *J* = 7.5 Hz)

[a] The chemical shifts are expressed in δ units with $\delta > 0$ to downfield in C_6D_6 or C_7D_8 at 20 °C. The values in parentheses are the full widths at half-maximum (Hz). [b] These resonances are not observed at room temperature. [c] The specific assignments are uncertain, although the chemical shift values are not.

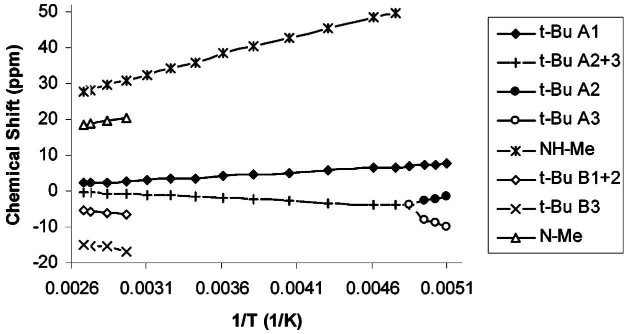


Figure 1. Plots of δ versus $1/T$ for $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**) in C_7D_8 (for Me_3C, NH-Me, and N-Me groups).

cyclohexane or toluene. Thus, the simplest imido cannot be made by these synthetic routes.

Formation of the imidometallocenes from the corresponding diamide derivatives by elimination of an amine, eq 3, is very dependent on the substituents on the cyclopentadienyl ring and on the amide group. When the cyclopentadienyl ligand is C_5Me_5, heating $(\eta^5\text{-}C_5Me_5)_2U(NHPh)_2$ does not yield an imide, whereas $(\eta^5\text{-}C_5Me_5)_2U(NH\text{-}2,6\text{-xylyl})_2$ does.[4,8] Thus, the thermal elimination pathway presumably has a high kinetic barrier that is lowered by increasing the steric bulk on the aromatic ring in these C_5Me_5 derivatives. In the metallocenes derived from $1,2,4\text{-}(Me_3C)_3C_5H_2$, amine elimination occurs for methyl- and phenyl-substituted amides, but not with the simplest amide, $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (**7**), which is consistent with the steric argument advanced above. When the number of Me_3C groups on the cyclopentadienyl ring is reduced, i.e., $[1,3\text{-}(Me_3C)_2C_5H_3]_2U(NH\text{-}p\text{-tolyl})_2$ (**3**), amine elimination does not occur because the intramolecular crowding is less and the elimination barrier is higher. This implies that the geometry of the transition state for the proton transfer is very sensitive to the intramolecular steric effects at uranium.

The imides are all dark brown-red, high melting solids that crystallize from pentane. They do not sublime, but they yield monomeric molecular ions in their mass spectra. The 20 °C ^1H NMR spectra of imide derivatives are well resolved, and all of the expected resonances, except those for ring CH's, are observed for metallocenes with C_{2v} symmetry, Table 1. However, their variable-temperature ^1H NMR spectra show that the cyclopentadienyl rings and the tolyl rings are fluxional.

The variable-temperature ^1H NMR spectra of the series $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}N(p\text{-}RC_6H_4)$ (R = Me (**12**), OMe (**13**), Me_2N (**14**)) are similar so only the Me_2N derivative, **14**, is described in detail. In general, at 20 °C the Me_3C resonances are in a 2:1 area ratio, and the Cp-ring CH resonances are observed, as are the ortho and meta benzene ring CHs' and para R groups' resonances, Table 1. In the case of R = NMe_2 (**14**), the methyl groups (NMe_2) appear as a single resonance, indicating that all of the cyclopentadienyl and the imido ligands are freely rotating and the molecule has aver-

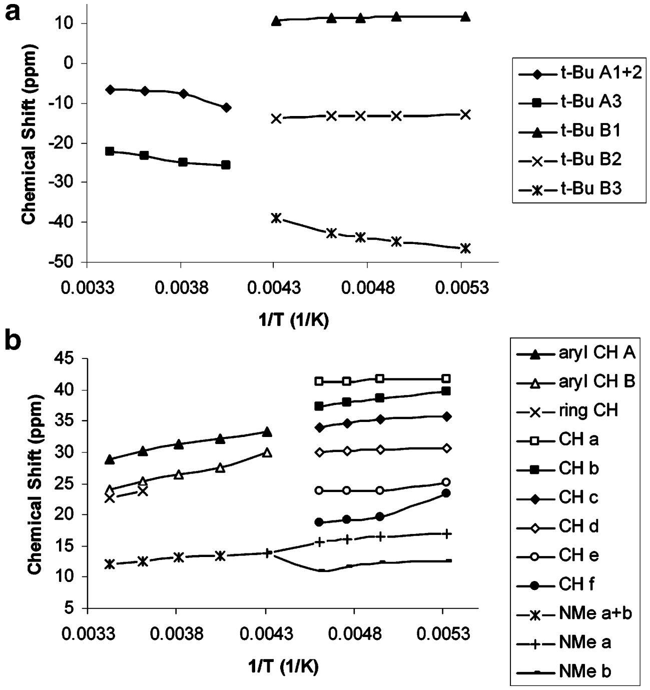


Figure 2. (a) Plots of δ versus 1/*T* for $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=N(}p\text{-Me}_2\text{NC}_6\text{H}_4)$ (**14**) in C_7D_8 (for Me_3C groups). (b) Plots of δ versus 1/*T* for $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=N(}p\text{-Me}_2\text{NC}_6\text{H}_4)$ (**14**) in C_7D_8 (for Me_2N, aryl, and Cp-ring CH groups).

aged C_{2v} symmetry. Increasing the temperature has the usual effect; that is, the chemical shifts of all of the resonances follow a Curie Law dependence. Lowering the temperature is, however, more informative. A plot of the chemical shift of the Me_3C and Me_2N resonances as a function of T^{-1} for $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=N(}p\text{-Me}_2\text{NC}_6\text{H}_4)$ (**14**) is shown in Figures 2a and 2b. On cooling from 20 °C to −10 °C, the Me_3C (labeled A in Figure 2a) and the Cp′-ring CH resonances broaden and disappear. By −40 °C, the Me_3C resonances emerge as three very broad equal-area resonances (labeled B in Figure 2a). By −60 °C, all of the resonances are visible and the Me_3C resonances are well defined; however, the three Me_3C resonances do not have a common parent, as illustrated in Figure 2a. At −60 °C and below, the Cp-ring and benzene-CH's are inequivalent, as are the NMe_2 resonances, as shown in Figure 2b. This behavior is consistent with a molecule with time-averaged C_s symmetry, where the plane of symmetry contains the $NC_6H_4NMe_2$ ligand in which the site exchange between the ortho and meta CH's and the NMe_2's is stopped. The time-averaged plane of symmetry interconverts the two $1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2$ rings, and these rings are still undergoing oscillations about their pseudo-C_5 axes, which is presumably the reason the Me_3C resonances do not have a common parent. Cooling to −85 °C broadens the Me_3C and Cp′-ring CH resonances further, consistent with slowing but not stopping the ring oscillations.

The variable-temperature ^1H NMR behavior of $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=NMe}$ (**11**) in C_7D_8 is qualitatively similar to that observed in the arylimide metallocenes. Thus, the Me_3C resonances broaden, disappear, and then reappear as three equal-area resonances, without a common parent, implying that the fluxional motion is not stopped by −80 °C. The MeN resonance disappears by −40 °C and does not reappear.

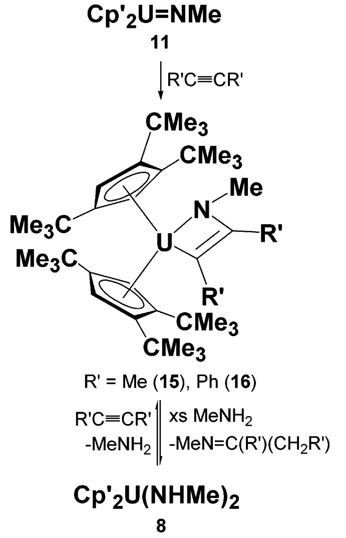
Reactions of $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=NMe}$ (11). Mixing experiments monitored by ^1H NMR spectroscopy at 20 °C were explored in order to compare the reaction patterns of the methylimide **11** with those of the oxometallocene $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$.[14] The methylimide **11** does not react with Me_3SiX (X = Cl, Br, I, CF_3) at 20 or 65 °C for time periods of up to 3 days. The lack of reaction is in contrast with the instantaneous reaction of the oxometallocene $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$ with these reagents. However, **11** reacts with Me_3SiN_3 to give small amounts (20%) of $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U(N}_3)_2$[14] over the course of 3 days at 65 °C. Imide **11** reacts instantaneously with SiF_4 or $BF_3(OEt_2)$ to give $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UF}_2$[14] as the only organometallic product observed in the ^1H NMR spectrum. The reactions of $SiCl_4$ or $SiBr_4$ are much slower; the final product in each case is $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UX}_2$[14] after 4 or 10 days when X = Cl or Br, respectively. A similar pattern is observed for the oxometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$,[14] but the rates for the methylimide are much slower. Thus, the nitrogen atom in **11** is a poorer nucleophile than is the oxygen atom in the oxometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$.

As observed previously, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=N(}p\text{-tolyl)}$ (**12**) reacts on mixing with Ph_2CO to give the oxometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$, and $Ph_2C{=}N(p\text{-tolyl})$.[14] The methylimide **11** behaves similarly, giving the oxometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$, and $Ph_2C{=}NMe$, eq 4. Addition of pyridine-*N*-oxide to **11** in C_6D_6 results in rapid disappearance of the resonances due to **11** and formation of resonances due to $(2,3,5\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2)_2$ in quantitative yield. A similar pattern is observed for the oxometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$, and the imido metallocene **12**.[14] The cyclopentadienyl ring coupling product was observed in the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U(NPh)(py)}$ with pyridine-*N*-oxide, which gives a mixture of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U(NPh)}_2$, $(C_5Me_5)_2$, and "UO_2".[4] However, the methylimide **11** does not react with Ph_3PE (E = O, S, Se) nor with pyridine, $4\text{-Me}_2\text{NC}_5\text{H}_4\text{N}$, or PhCl.

$$[1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=NMe} + \text{Ph}_2\text{CO} \rightarrow [1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO} + \text{Ph}_2\text{C=NMe} \quad (4)$$

Neither the *p*-tolylimidometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U=N(}p\text{-tolyl)}$ (**12**), nor the oxometallocene, $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{UO}$, reacts with diphenyl- or dimethylacetylene.[14] In contrast, the methylimide **11** reacts on time of mixing to form the cycloaddition products $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U[N(Me)C(R}')\text{=C(R}')]$ (R′ = Me (**15**), Ph (**16**)), Scheme 2. The silylacetylene, $Me_3SiC{\equiv}CSiMe_3$, does not change the chemical shifts of **11**, but phenylacetylene yields $(Me_3C)_3C_5H_3$. The cycloaddition products **15** and **16** may also be obtained by addition of the acetylenes to $[\eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2]_2\text{U(NHMe)}_2$ (**8**), a reaction that is consistent with the equilibrium illustrated in eq 3. The cycloaddition products **15** and **16** are soluble in pentane, and they may be crystallized from that solvent. They are high-melting solids, do not sublime, but yield molecular ions in their mass spectra. An ORTEP diagram of **15** is shown in Figure 3. The terminal MeN and MeC groups are disordered (the disorder model is described in the Experimental Section), but the crystal structure analy-

Scheme 2



sis shows that it is a cycloaddition product, not an acetylene adduct of the imide **11**.

The ^{1}H NMR spectrum of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$U-[N(Me)C(Me)=C(Me)] (**15**) at 20 °C in C_7D_8 shows the Me_3C groups in a 2:1 area ratio, but the Cp-ring CH groups are inequivalent, Table 1. The reason for this apparent contradiction is that the Me_3C resonance of relative area 2 is composed of two equal-area resonances that are accidentally degenerate at 20 °C. Increasing the temperature removes this degeneracy, and at 35 °C the Me_3C resonances appear as three equal-intensity resonances; the Cp-ring CH resonances are inequivalent, as are the CMe resonances. Thus, the cycloaddition product **15** has C_s symmetry, the MeC groups are not undergoing site exchange, but the Cp rings are undergoing rotation or oscillation about their pseudo-C_5 axes that generates a time-averaged plane of symmetry. Lowering the temperature results in disappearance of Cp-ring CH resonances as the Me_3C resonances broaden. Broadening of the latter resonances increases with decreasing temperature until three approximately equal area resonances appear with widely different line widths at −75 °C. The MeN resonance and both of the MeC resonances remain sharp, which implies that a single isomer is present, which further implies that the oscillations of the Cp rings about their pseudo-C_5 axes are slowed but not stopped at −75 °C.

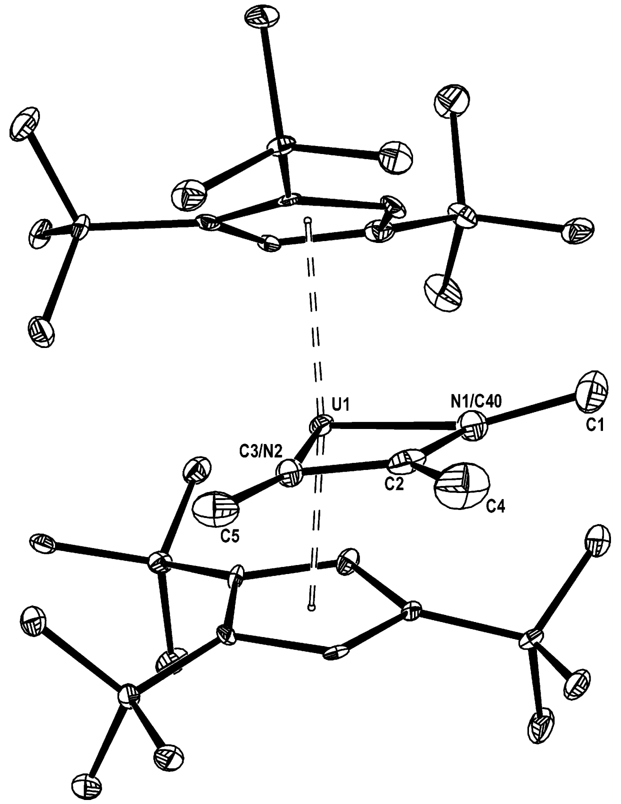


Figure 3. ORTEP drawing of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$U-[N(Me)C(Me)=C(Me)] (**15**) with 35% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Cp′(cent)−U1 2.55 and 2.56, U1−N1/C40 2.202(6), U1−C3/N2 2.270(6), C2−N1/C40 1.410(9), C2−C3/N2 1.390(9), Cp′(cent)−U1−Cp′(cent) 138.7, N1/C40−U1−C3/N2 65.1(2), N1/C40−C2−C3/N2 118.5(7).

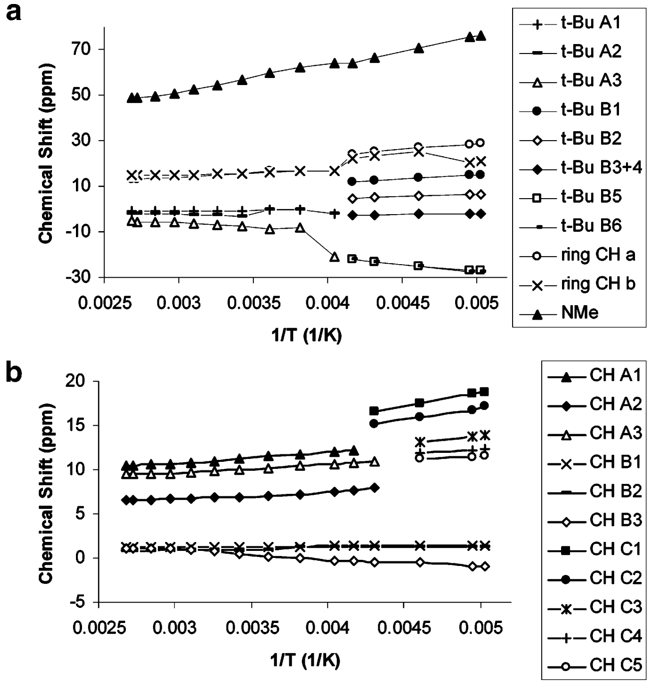


Figure 4. (a) Plots of δ versus 1/*T* for [η^5-1,2,4-$(Me_3C)_3$-$C_5H_2]_2$U[N(Me)C(Ph)=C(Ph)] (**16**) in C_7D_8 (for MeN, Me_3C, and Cp-ring CH groups). (b) Plots of δ versus 1/*T* for [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$U[N(Me)C(Ph)=C(Ph)] (**16**) in C_7D_8 (for phenyl CH groups).

The cycloaddition product **15** does not undergo intramolecular site exchange to 100 °C, since the individual MeC resonances do not coalesce. Intermolecular site exchange is also slow since addition of dimethylacetylene or diphenylacetylene does not lead to exchange up to 100 °C. Hence, the dynamic behavior described above is due to intramolecular fluxions of the cyclopentadienyl rings. This fluxional motion is clarified by examination of the low-temperature ^{1}H NMR spectrum of the diphenylacetylene cycloaddition product **16**.

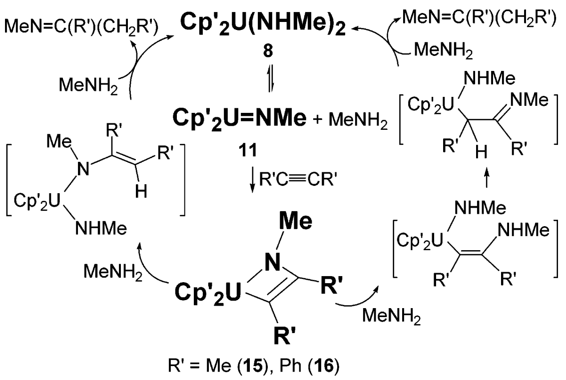
The 20 °C ^{1}H NMR spectrum of **16** in C_7D_8 shows three equal-area Me_3C resonances (labeled A in Figure 4a) and two inequivalent Cp-ring CH resonances. The two chemically inequivalent phenyl rings are freely rotating, since the ortho and meta CH's are equivalent; the chemical shifts are given in Table 1. On cooling, the three Me_3C resonances broaden and decoalesce, and by −80 °C, they appear as five resonances in a 9:9:18:9:9

area ratio (labeled B in Figure 4a). The ring CH resonances broaden, shift downfield, and emerge as a pair of broadened singlets with the relative area ratio 2:2, which implies that their chemical shift difference is small. This behavior is shown graphically in Figure 4a. The Cp rings are inequivalent, and only a single isomer is observed since the MeN resonance is a sharp singlet throughout the temperature study. The benzene ring CH groups are also resolved into eight resonances in a 1:1:1:1:1:1:2:2 area ratio by −80 °C (Figure 4b), consistent with a molecule without symmetry. Ten equal-area resonances should be observed, but two are accidentally degenerate. Thus, the diphenylacetylene cycloaddition product **16** is sufficiently sterically crowded that the intramolecular barriers to Cp-ring fluxions and C−Ph rotations are sufficiently high that these motions are stopped by −80 °C.

In summary, the different reactivity patterns observed for [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$[14] and [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11**) are striking, given the fact that O and NMe are isolobal, but with different electronegativities and steric effects. Steric differences should be minor, but this difference is difficult to evaluate and steric effects could be the principle reason that [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}N$(*p*-tolyl) (**12**) does not react with internal acetylenes whereas [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11)** does. Our current qualitative model traces the different reactivity patterns to the nature of the multiple bond between the metallocene uranium and the O/NMe fragments. The general reactivity pattern is that the oxometallocene, [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$, reacts rapidly with electron-poor substrates, such as Me_3SiX, to yield addition products, but does not react with internal acetylenes.[14] In contrast, the methylimidometallocene, [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11**), does not react with Me_3SiX (except Me_3SiN_3) but does react with more electron-rich reagents, such as internal acetylenes. A model that rationalizes this behavior is that the uranium−oxygen bond is better represented by the polar resonance structure $U^+{-}O^-$, which emphasizes the electronegativity of the oxygen atom and therefore nucleophilicity,[14] whereas the uranium−nitrogen bond is better represented by the double-bond resonance structure U=NMe, consistent with the lower electronegativity of the NMe group, and therefore lower nucleophilicity. These resonance structures emphasize the differences in local charges on the atoms in their ground states, but the general concept of atom electronegativity in conjugation with the electroneutrality principle[23] is a qualitatively useful model that accounts for the reactivity patterns observed for [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UE$ (E = O, NMe).

Hydroamination. In mixing experiments monitored by ^1H NMR spectroscopy at 20 °C, the resonances of the cycloaddition products [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U[N(Me)C(R')=C(R')]$ (R′ = Me (**15**), Ph (**16**)) disappear when excess $MeNH_2$ is added, while resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**) and the azomethine derivatives $MeN{=}C(R')CH_2R'$ (R = Me, Ph)[24,25] appear in the spectra. The azomethine derivatives result from the addition of methylamine to the cycloaddition product followed by two successive proton transfer reactions that liberate the azomethines and form [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**), Scheme 3. Since the diamide **8** is in equilibrium with the imide **11**, the diamide **8** is a catalyst for the hydroamination of an internal acetylene. This reaction pattern was discovered by Eisen, using (η^5-$Me_5C_5)_2U(NHR)_2$ and terminal acetylenes, though the cycloaddition product was not observed.[10] Replacing the (η^5-$Me_5C_5)_2U$ fragment with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$ yields the diamide (**8**), imide (**11**), and the cycloaddition products with RC≡CR (R = Me (**15**), Ph (**16**)) as isolable, crystalline solids. The essential steps in the hydroamination of internal acetylene are established by monitoring the ^1H NMR spectra of the isolated solid **8** as it proceeds to **11** and then to **15** and the azomethine. The suggested mechanism for the reaction of the cycloaddition product **15** with $MeNH_2$ is shown in Scheme 3. On the right-hand side is the pathway suggested by Eisen,[10] and on the left-hand side is a pathway originally suggested by Bergman for the catalytic reaction between (η^5-$C_5H_5)_2Zr(NHR)_2$ and an acetylene,[26] which is adapted for the uranium metallocenes. We have no information to distinguish between these two pathways since these intermediates are not observed in the ^1H NMR spectra. Unfortunately, the simplest diamide, [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (**7**), does not react with either acetylene, presumably because the equilibrium illustrated in eq 3 lies to the left.

Scheme 3



The compounds in brackets are not observed

Conclusions

Amine elimination occurs from [1,2,4-$(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**) and [1,2,4-$(Me_3C)_3C_5H_2]_2U(NH$-*p*-tolyl$)_2$ (**10**), while not from [1,2,4-$(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (**7**) and [1,3-$(Me_3C)_2C_5H_3]_2U(NH$-*p*-tolyl$)_2$ (**3**). These results show that formation of the imidometallocenes from the corresponding diamide derivatives by elimination of an amine is very sensitive to the intramolecular steric effects at uranium. The equilibrium illustrated in eq 3, which was discovered by examining the variable-temperature behavior of the ^1H NMR spectra of the diamides, is the key discovery, since it leads to a simple synthesis of the imide [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11**), which in turn leads to the development of the catalytic hydroamination of the internal acetylenes.[27]

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(23) Pauling, L. *The Nature of the Chemical Bond*; Connell University Press: Ithaca, NY, 1960; pp 64 and 172.

(24) Karabatsos, G. J.; Lande, S. S. *Tetrahedron* **1968**, *24*, 3907.

(25) Ahlbrecht, H.; Fischer, S. *Tetrahedron* **1970**, *26*, 2837.

(26) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708.

(27) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673, and references therein.

The methylimidometallocene [η^5-1,2,4-($Me_3C)_3$-$C_5H_2]_2U{=}NMe$ (**11**) does not show nucleophilic behavior, in contrast to [η^5-1,2,4-($Me_3C)_3C_5H_2]_2UO$,[14] but it does undergo cycloaddition reactions that [η^5-1,2,4-($Me_3C)_3$-$C_5H_2]_2UO$ does not.[14] This implies that the uranium−nitrogen bond is better represented by the double-bond resonance structure U=NMe, whereas the uranium−oxygen bond is better represented by the polar resonance structure $U^+{-}O^-$.[14] Further studies designed to test this model are underway.

Experimental Section

General Procedures. All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and glovebox techniques. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. MeC≡CMe was freshly distilled from sodium immediately prior to use. Me_3SiX (X = Cl, Br, I, N_3) were distilled under nitrogen before using. PhC≡CPh, p-$MeC_6H_4NH_2$, p-$MeOC_6H_4NH_2$, and p-$Me_2NC_6H_4NH_2$ were sublimed before using. [η^5-1,3-($Me_3C)_2C_5H_3]_2UCl_2$,[15] [η^5-1,3-($Me_3Si)_2C_5H_3]_2$-UCl_2,[15] [η^5-1,3-($Me_3C)_2C_5H_3]_2UMe_2$,[15] [η^5-1,3-($Me_3Si)_2C_5H_3]_2$-UMe_2,[15] [η^5-1,2,4-($Me_3C)_3C_5H_2]_2UMe_2$,[14] and [η^5-1,2,4-($Me_3C)_3$-$C_5H_2]_2U(NH_2)_2$[14] (**7**) were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. used as received unless otherwise noted. Infrared spectra were obtained as Nujol mulls on CsI windows. ^{1}H NMR spectra were recorded on Bruker AVB-400, AVQ-400, and AV-300 spectrometers. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which are internal standards, for proton chemical shifts. Melting points were measured on a Thomas-Hoover melting point apparatus in sealed capillaries and are uncorrected. Electron impact mass spectra were recorded by the mass spectroscopy laboratory, and elemental analyses were performed by the analytical laboratories, both at the University of California, Berkeley.

Preparation of {[η^5-1,3-($Me_3C)_2C_5H_3]_2U\}_2(\mu$-NH$)_2$ (1). In a 250 mL flask, [η^5-1,3-($Me_3C)_2C_5H_3]_2UMe_2$ (1.0 g, 1.6 mmol) was dissolved in diethyl ether (50 mL). The headspace of the flask was evacuated and replaced with 1 atm of NH_3 (dried over sodium metal at −35 °C). During the course of the reaction, the color of the solution changed from red to brown-red and a purple-red precipitate formed. After the solution was stirred for 12 h at room temperature, the solvent was removed. The purple-red residue was extracted with tetrahydrofuran (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding purple-red microcrystals, which were isolated by filtration. Yield: 0.88 g (91%). ^{1}H NMR (C_6D_6): δ 35.5 (1H, $\nu_{1/2}$ = 110 Hz, ring C*H*), 33.2 (1H, $\nu_{1/2}$ = 100 Hz, ring C*H*), 20.0 (2H, $\nu_{1/2}$ = 45 Hz, ring C*H*), 10.0 (2H, $\nu_{1/2}$ = 50 Hz, ring C*H*), −10.9 (18H, $\nu_{1/2}$ = 25 Hz, ($CH_3)_3C$), −11.4 (18H, $\nu_{1/2}$ = 30 Hz, ($CH_3)_3C$); protons of N*H* were not observed. Mp: > 300 °C. EI-MS [M^+], *m/z* (calcd, found): 1213 (60, 58), 1214 (100, 100), 1215 (20, 18), 1216 (6, 4). IR: ν NH, 3321 (s) cm^{-1}. Anal. Calcd for $C_{52}H_{86}N_2U_2$: C, 51.4; H, 7.13; N, 2.31. Found: C, 51.2; H, 7.10; N, 1.98.

Preparation of {[η^5-1,3-($Me_3Si)_2C_5H_3]_2U\}_2(\mu$-NH$)_2$ (2). This compound was prepared as purple microcrystals from the reaction of [η^5-1,3-($Me_3Si)_2C_5H_3]_2UMe_2$ (1.0 g, 1.46 mmol) and excess NH_3 in diethyl ether (50 mL) by procedures similar to those used in the synthesis of {[η^5-1,3-($Me_3C)_2C_5H_3]_2U\}_2(\mu$-NH$)_2$ (**1**). Yield: 0.91 g (93%). ^{1}H NMR (C_6D_6): δ 40.5 (1H, $\nu_{1/2}$ = 72 Hz, ring C*H*), 33.1 (2H, $\nu_{1/2}$ = 59 Hz, ring C*H*), 23.0 (1H, $\nu_{1/2}$ = 62 Hz, ring C*H*), 15.0 (2H, $\nu_{1/2}$ = 85 Hz, ring C*H*), −9.78 (18H, $\nu_{1/2}$ = 43 Hz, ($CH_3)_3Si$), −11.6 (18H, $\nu_{1/2}$ = 48 Hz, ($CH_3)_3Si$); protons of N*H* were not observed. Mp: > 300 °C. EI-MS [M^+], *m/z* (calcd, found): 1342 (100, 100), 1343 (91, 92), 1344 (67, 55), 1345 (35, 29), 1346 (15, 11), 1347 (6, 4). IR: ν NH, 3335 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{86}N_2Si_8U_2$: C, 39.3; H, 6.45; N, 2.08. Found: C, 39.3; H, 6.15; N, 1.98.

Preparation of [η^5-1,3-($Me_3C)_2C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (3). To a hexane (30 mL) solution of [η^5-1,3-($Me_3C)_2C_5H_3]_2UMe_2$ (2.0 g, 3.2 mmol) was added a hexane (20 mL) solution of *p*-toluidine (0.69 g, 6.4 mmol) with stirring at room temperature. The solution was stirred for 12 h at room temperature and filtered. The volume of the filtrate was reduced to 5 mL and cooled to −80 °C, yielding orange-red microcrystals, which were isolated by filtration. Yield: 1.9 g (74%). The product sublimed at 145 °C in diffusion pump vacuum. ^{1}H NMR (C_6D_6): δ 5.2 (d, *J* = 7 Hz, 4H, tolyl *H*), 4.6 (6H, $\nu_{1/2}$ = 3 Hz, CH_3), 0.32 (36H, $\nu_{1/2}$ = 8 Hz, ($CH_3)_3C$), −2.6 (2H, $\nu_{1/2}$ = 8 Hz, ring C*H*), −14.2 (d, *J* = 7 Hz, 4H, tolyl *H*), −16.0 (4H, $\upsilon_{1/2}$ = 8 Hz, ring C*H*), −68.1 (2H, $\nu_{1/2}$ = 24 Hz, N*H*). Mp: 152−153 °C. EI-MS [M^+], *m/z* (calcd, found): 804 (100, 100), 805 (46, 39), 806 (10, 10). IR: ν NH, 3358 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{58}N_2U$: C, 59.7; H, 7.26; N, 3.48. Found: C, 59.4; H, 7.25; N, 3.25.

Preparation of [η^5-1,3-($Me_3Si)_2C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (4). This compound was prepared as orange-red microcrystals from the reaction of [η^5-1,3-($Me_3Si)_2C_5H_3]_2UMe_2$ (2.0 g, 2.9 mmol) and *p*-toluidine (0.62 g, 5.8 mmol) in hexane (50 mL) by procedures similar to those used in the synthesis of [η^5-1,3-($Me_3C)_2C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (**3**). Yield: 2.0 g (79%). ^{1}H NMR (C_6D_6): δ 4.5 (d, *J* = 7 Hz, 4H, tolyl *H*), 4.3 (6H, $\nu_{1/2}$ = 3 Hz, CH_3), 0.41 (36H, $\nu_{1/2}$ = 4 Hz, ($CH_3)_3Si$), −9.9 (2H, $\nu_{1/2}$ = 6 Hz, ring C*H*), −15.0 (4H, $\nu_{1/2}$ = 4 Hz, ring C*H*), −18.0 (d, *J* = 7 Hz, 4H, tolyl *H*), −34.7 (2H, $\nu_{1/2}$ = 19 Hz, N*H*). Mp: 156−158 °C. EI-MS [M^+], *m/z* (calcd, found): 868 (100, 100), 869 (62, 58), 870 (32, 28), 871 (11, 9), 872 (3, 2). IR: ν NH, 3358 (s) cm^{-1}. Anal. Calcd for $C_{36}H_{58}N_2Si_4U$: C, 49.7; H, 6.73; N, 3.22. Found: C, 49.5; H, 6.67; N, 3.15.

Reaction of [η^5-1,3-($Me_3C)_2C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (3) or [η^5-1,3-($Me_3Si)_2C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (4) with Tetrahydrofuran or Me_3PO. NMR Scale. To an NMR tube charged with [η^5-1,3-($Me_3C)_2C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (**3**) or [η^5-1,3-($Me_3Si)_2$-$C_5H_3]_2U$(NH-*p*-tolyl$)_2$ (**4**) (15 mg) and C_6D_6 (0.5 mL) was added an excess of tetrahydrofuran or Me_3PO. In each case, the sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Preparation of [η^5-1,3-($Me_3C)_2C_5H_3]_2U(CH_2C_6H_5)_2$ (5). To a diethyl ether (100 mL) solution of [η^5-1,3-($Me_3C)_2C_5H_3]_2$-UCl_2 (3.0 g, 4.5 mmol) was added a diethyl ether (8.8 mL) solution of $PhCH_2MgCl$ (1.05 M in diethyl ether; 9.2 mmol) with stirring at room temperature. After the solution was stirred for 12 h at room temperature, the solvent was removed. The dark residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 25 mL and cooled to −80 °C, yielding black microcrystals, which were isolated by filtration. Yield: 2.2 g (64%). ^{1}H NMR (C_6D_6): δ 33.0 (2H, $\nu_{1/2}$ = 26 Hz, ring C*H*), 8.16 (t, *J* = 7 Hz, 4H, phenyl *H*), 2.08 (t, *J* = 7 Hz, 2H, phenyl *H*), 0.26 (36H, $\nu_{1/2}$ = 5 Hz, ($CH_3)_3C$), −2.56 (d, *J* = 7 Hz, 4H, phenyl *H*), −36.4 (4H, $\nu_{1/2}$ = 46 Hz, ring C*H*), −72.2 (4H, $\nu_{1/2}$ = 32 Hz, $PhCH_2$). Mp: 113−114 °C. EI-MS: *m/z* 683 [M − $PhCH_2]^+$. Anal. Calcd for $C_{40}H_{56}U$: C, 62.0; H, 7.28. Found: C, 61.9; H, 7.24.

Preparation of [η^5-1,3-($Me_3Si)_2C_5H_3]_2U(CH_2C_6H_5)_2$ (6). This compound was prepared as black microcrystals from the reaction of [η^5-1,3-($Me_3Si)_2C_5H_3]_2UCl_2$ (1.0 g, 1.37 mmol) and $PhCH_2MgCl$ (2.7 mL, 1.05 M in diethyl ether; 2.8 mmol) in diethyl ether (50 mL) by procedures similar to those used in the synthesis of [η^5-1,3-($Me_3C)_2C_5H_3]_2U(CH_2C_6H_5)_2$ (**5**). Yield: 0.62 g (54%). ^{1}H NMR (C_6D_6): δ 19.9 (4H, $\nu_{1/2}$ = 19 Hz, ring C*H*), 7.83 (t, *J* = 7 Hz, 4H, phenyl *H*), 0.40 (t, *J* = 7 Hz, 2H, phenyl *H*), −0.75 (36H, $\nu_{1/2}$ = 15 Hz, ($CH_3)_3Si$), −5.72 (d, *J* = 7 Hz, 4H, phenyl *H*), −37.0 (2H, $\nu_{1/2}$ = 35 Hz, ring C*H*); protons of $PhCH_2$ were not observed. Mp: 116−118 °C. EI-MS: *m/z* 747 [M − $PhCH_2]^+$. Anal. Calcd for $C_{36}H_{56}Si_4U$: C, 51.5; H, 6.73. Found: C, 51.2; H, 6.60.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (8). In a 250 mL flask, $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (1.0 g, 1.36 mmol) was dissolved in toluene (50 mL). The headspace of the flask was evacuated and replaced with 1 atm of $MeNH_2$ (dried over sodium metal at −5 °C). During the course of the reaction, the color of the solution changed from red to yellow. After the solution was stirred for 4 h at room temperature, the solvent was removed. The yellow residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding yellow crystals, which were isolated by filtration. Yield: 0.75 g (72%). EI-MS: *m/z* 734 $[M - CH_3NH]^+$. Anal. Calcd for $C_{36}H_{66}N_2U$: C, 56.5; H, 8.70; N, 3.66. Found: C, 56.2; H, 8.74; N, 3.37.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHCH_2C_6H_5)_2$ (9). $C_6H_5CH_2NH_2$ (0.30 mL, 2.72 mmol) was added to a toluene (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (1.0 g, 1.36 mmol) with stirring at room temperature. After the solution was stirred overnight at 40 °C in a water bath, the solvent was removed. The brown-yellow residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 5 mL and cooled to −20 °C, yielding brown-yellow crystals, which were isolated by filtration. Yield: 0.80 g (64%). EI-MS: *m/z* 811 $[M - C_6H_5CH_2NH]^+$. Anal. Calcd for $C_{48}H_{74}N_2U$: C, 62.9; H, 8.13; N, 3.05. Found: C, 62.6; H, 8.41; N, 2.98.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NH\text{-}p\text{-}tolyl)_2$ (10). To a hexane (30 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (2.0 g, 2.72 mmol) was added a hexane (20 mL) solution of *p*-toluidine (0.61 g, 5.7 mmol) with stirring at room temperature. The solution was heated at reflux for 1 day with stirring and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding red crystals, which were isolated by filtration. Yield: 1.6 g (65%). EI-MS: *m/z* 811 $[M - tolylNH]^+$. IR: ν NH, 3280 (s), 3260 (s) cm^{-1}. Anal. Calcd for $C_{48}H_{74}N_2U$: C, 62.9; H, 8.13; N, 3.05. Found: C, 62.7; H, 8.36; N, 3.21.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}NCH_3$ (11). To a cyclohexane (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (1.0 g, 1.36 mmol) was added a cyclohexane (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHCH_3)_2$ (**8**; 1.04 g, 1.36 mmol) with stirring at room temperature. After the solution was heated at reflux for 4 days with stirring, the solvent was removed. The dark brown residue was extracted with pentane (25 mL × 2) and filtered. The volume of the dark brown solution was reduced to 5 mL and cooled to −20 °C, yielding dark brown crystals, which were isolated by filtration. Yield: 1.4 g (70%). EI-MS $[M^+]$, *m/z* (calcd, found): 733 (100, 100), 734 (40, 38), 735 (8, 8), 736 (1, 2). Anal. Calcd for $C_{35}H_{61}NU$: C, 57.3; H, 8.38; N, 1.91. Found: C, 56.9; H, 7.99; N, 1.65.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}N(p\text{-}tolyl)$[14] (12). Modified Method A. To a methylcyclohexane (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (0.81 g, 1.1 mmol) was added a methylcyclohexane (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NH\text{-}p\text{-}tolyl)_2$ (**10**; 1.0 g, 1.1 mmol) with stirring at room temperature. After the solution was heated at reflux for 4 days with stirring, the solvent was removed. The dark brown residue was extracted with pentane (25 mL × 2) and filtered. The volume of the dark brown solution was reduced to 20 mL and cooled to −20 °C, yielding dark brown crystals, which were identified as **12** by ^1H NMR spectroscopy.[14] Yield: 1.0 g (56%).

Method B. $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (2.0 g, 2.72 mmol) and *p*-toluidine (0.28 g, 2.6 mmol) were heated together in methylcyclohexane (30 mL) as in the above method, which gave **12** in 68% yield (1.4 g).

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}N(p\text{-}C_6H_4OCH_3)$ (13). To a toluene (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (1.0 g, 1.36 mmol) was added a toluene (10 mL) solution of *p*-anisidine (0.16 g, 1.30 mmol) with stirring at room temperature. After the solution was heated at reflux for 4 days with stirring, the solvent was removed. The dark brown residue was extracted with pentane (25 mL × 2) and filtered. The volume of the dark brown solution was reduced to 20 mL and cooled to −20 °C, yielding dark brown crystals, which were isolated by filtration. Yield: 0.81 g (75%). EI-MS $[M^+]$, *m/z* (calcd, found): 825 (100, 100), 826 (47, 45), 827 (10, 10), 828 (2, 1). Anal. Calcd for $C_{41}H_{65}NOU$: C, 59.6; H, 7.93; N, 1.70. Found: C, 59.3; H, 8.00; N, 1.64.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}N(p\text{-}C_6H_4NMe_2)$ (14). This compound was prepared as dark brown crystals from the reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (1.0 g, 1.36 mmol) and $p\text{-}Me_2NC_6H_4NH_2$ (0.18 g, 1.32 mmol) in toluene (30 mL) by procedures similar to those used in the synthesis of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}N(p\text{-}C_6H_4OCH_3)$ (**13**). Yield: 0.77 g (70%). EI-MS $[M^+]$, *m/z* (calcd, found): 838 (100, 100), 839 (48, 48), 840 (11, 10), 841 (2, 2). Anal. Calcd for $C_{42}H_{68}N_2U$: C, 60.1; H, 8.17; N, 3.34. Found: C, 59.7; H, 8.36; N, 3.34.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U[N(Me)C(Me){=}C(Me)]$ (15). Method A. 2-Butyne (2.0 mL, 26 mmol) was added to a toluene (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**; 1.0 g, 1.3 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from yellow to brown-red. After the solution was stirred for 3 days at room temperature, the solvent was removed. The brown-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding brown-red crystals, which were isolated by filtration. Yield: 0.77 g (75%). EI-MS $[M^+]$, *m/z* (calcd, found): 787 (100, 100), 788 (44, 45), 789 (10, 10), 790 (1, 1); the parent ion is $[M - Me_2C_2]^+$. Anal. Calcd for $C_{39}H_{67}NU$: C, 59.5; H, 8.58; N, 1.78. Found: C, 59.3; H, 8.69; N, 1.71.

Method B. NMR Scale. To an NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of 2-butyne. The color of the solution immediately changed from dark brown to brown-red, and resonances due to **15** were observed by ^1H NMR spectroscopy (100% conversion).

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U[N(Me)C(Ph){=}C(Ph)]$ (16). Method A. To a toluene (10 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}NMe$ (**11**; 1.8 g, 2.45 mmol) was added a toluene (10 mL) solution of diphenylacetylene (0.44 g, 2.47 mmol) with stirring at room temperature. After the solution was stirred overnight at 40 °C in a water bath, the solvent was removed. The brown-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 15 mL and cooled to −20 °C, yielding brown-red microcrystals, which were isolated by filtration. Yield: 1.65 g (74%). EI-MS $[M^+]$, *m/z* (calcd, found): 911 (100, 100), 912 (56, 54), 913 (15, 15), 914 (3, 3); the parent ion is $[M - Ph_2C_2]^+$. Anal. Calcd for $C_{49}H_{71}NU$: C, 64.5; H, 7.85; N, 1.54. Found: C, 64.2; H, 8.14; N, 1.84.

Method B. NMR Scale. To an NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added diphenylacetylene (6 mg, 0.03 mmol). The color of the solution slowly (2 h) changed from yellow to brown-red at 40 °C, and resonances due to **16** were observed by ^1H NMR spectroscopy (100% conversion).

Reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U[N(Me)C(Me){=}C(Me)]$ (15) with $MeNH_2$. NMR Scale. To an NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U[N(Me)C(Me){=}C(Me)]$ (**15**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of $MeNH_2$. The color of the solution immediately changed from brown-red to yellow, and resonances due to $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NHMe)_2$ (**8**) along with $MeN{=}C(Me)(CH_2Me)$[24] were observed by ^1H NMR spectroscopy (100% conversion).

Reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U[N(Me)C(Ph){=}C(Ph)]$ (16) with $MeNH_2$. NMR Scale. To an NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U[N(Me)C(Ph){=}C(Ph)]$ (**16**; 18 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of $MeNH_2$. The color of the solution immediately changed from brown-red to yellow, and resonances due to $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3\text{-}$

C$_5$H$_2$]$_2$U(NHMe)$_2$ (**8**) along with MeN=C(Ph)(CH$_2$Ph)[25] were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U[N(Me)C(Me)=C(Me)] (15) or [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U[N(Me)C(Ph)=C(Ph)] (16) with RC$\equiv$CR (R = Me, Ph). NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U[N(Me)C(Me)=C(Me)] (**15**) or [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U[N(Me)C(Ph)=C(Ph)] (**16**) (16 mg) and C$_6$D$_6$ (0.5 mL) was added an excess of RC$\equiv$CR (R = Me, Ph). In each case, the sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with MeNH$_2$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added an excess of MeNH$_2$. The color of the solution immediately changed from dark brown to yellow, and resonances due to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(NHMe)$_2$ (**8**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=N(*p*-tolyl) (12) with *p*-Toluidine. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=N(*p*-tolyl) (**12**; 16 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added *p*-toluidine (2 mg, 0.02 mmol). The color of the solution immediately changed from dark brown to red, and resonances due to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(NH-*p*-tolyl)$_2$ (**10**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UMe$_2$ with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$(NH$_2$)$_2$ (7). NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UMe$_2$ (15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$(NH$_2$)$_2$ (**7**; 15 mg, 0.02 mmol). The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(NH$_2$)$_2$ (7) with RC$\equiv$CR (R = Me, Ph, Me$_3$Si). NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(NH$_2$)$_2$ (**7**; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added an excess of RC$\equiv$CR (R = Me, Ph, Me$_3$Si). In each case, the sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with PhC$\equiv$CH. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added an excess of PhC$\equiv$CH. The color of the solution immediately changed from dark brown to brown, and resonances due to (Me$_3$C)$_3$C$_5$H$_3$[14] and other unidentified uranium-containing compounds were observed by ^{1}H NMR spectroscopy.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with Ph$_2$C=O. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added benzophenone (3.6 mg, 0.02 mmol). The color of the solution immediately changed from dark brown to brown-red, and resonances due to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=O[14] along with Ph$_2$C=NMe[28] were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with Me$_3$SiC$\equiv$CSiMe$_3$, CH$_2$=CH$_2$, Me$_3$SiX (X = Cl, Br, I, CF$_3$), Ph$_3$PE (E = O, S, Se), Diethyl Ether, Tetrahydrofuran, Pyridine, 4-Me$_2$NC$_5$H$_4$N, or C$_6$H$_5$Cl. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added an excess of Me$_3$SiC$\equiv$CSiMe$_3$, CH$_2$=CH$_2$, Me$_3$SiX (X = Cl, Br, I, CF$_3$), Ph$_3$PE (E = O, S, Se), diethyl ether, tetrahydrofuran, pyridine, 4-Me$_2$NC$_5$H$_4$N, or C$_6$H$_5$Cl. In each case, the sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=N(*p*-tolyl) (12) with RC$\equiv$CR (R = Me, Ph, Me$_3$Si). NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=N(*p*-tolyl) (**12**; 16 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added an excess of RC$\equiv$CR (R = Me, Ph, Me$_3$Si). In each case, the sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with Pyridine-*N*-Oxide. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added pyridine-*N*-oxide (2 mg, 0.02 mmol). The color of the solution immediately changed from dark brown to black, and resonances due to (2,3,5-(Me$_3$C)$_3$C$_5$H$_2$)$_2$[14] were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with Me$_3$SiN$_3$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL) was added an excess of Me$_3$SiN$_3$, and resonances due to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(N$_3$)$_2$[14] (20% conversion) along with other uranium-containing unidentified compounds were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with SiF$_4$ or BF$_3$(OEt$_2$). NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg) and C$_6$D$_6$ (0.5 mL) was added an excess of SiF$_4$ or BF$_3$(OEt$_2$). The color of the solution immediately changed from dark brown to orange-red, and resonances due to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UF$_2$[14] were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with SiCl$_4$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg) and C$_6$D$_6$ (0.5 mL) was added an excess of SiCl$_4$. The color of the solution slowly (2 h) changed from dark brown to brown-red, and resonances attributable to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(N(Me)(SiCl$_3$))(Cl) (^{1}H NMR (C$_6$D$_6$): δ 51.8 (3H, NCH_3), 14.5 (18H, (CH_3)$_3$C), −4.8 (18H, (CH_3)$_3$C), −6.9 (18H, (CH_3)$_3$C); the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). This sample was maintained at 65 °C and monitored periodically by ^{1}H NMR spectroscopy. After 1 day, conversion to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UCl$_2$ was 30% complete, and after 4 days, conversion to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UCl$_2$ was complete.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (11) with SiBr$_4$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U=NMe (**11**; 15 mg) and C$_6$D$_6$ (0.5 mL) was added an excess of SiBr$_4$. The color of the solution slowly (4 h) changed from dark brown to brown-red, and resonances attributable to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U(N(Me)(SiBr$_3$))(Br) (^{1}H NMR (C$_6$D$_6$): δ 48.2 (3H, NCH_3), 15.8 (18H, (CH_3)$_3$C), −4.3 (18H, (CH_3)$_3$C), −6.8 (18H, (CH_3)$_3$C); the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). This sample was maintained at 65 °C and monitored periodically by ^{1}H NMR spectroscopy. After 2 days, conversion to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UBr$_2$ was 30% complete, and after 10 days, conversion to [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$UBr$_2$ was complete.

***X*-ray Crystallography.** Crystal data for [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$U[N(Me)C(Me)=C(Me)] (**15**): a red blocklike crystal (0.10 × 0.13 × 0.14 mm) was mounted from Paratone N oil onto a glass fiber and immediately placed on a Bruker SMART CCD diffractometer. A hemisphere of data was collected by using ω scans, with 10-s frame exposures and 0.3° frame widths. A total of 15 749 reflections were measured at T = 123 K in the 2θ range of 5.0−49.0°, of which 6277 were unique (R_{int} = 0.060); Mo Kα radiation (λ = 0.71069 Å). C$_{39}$H$_{67}$NU, M = 787.99, monoclinic, space group $P2_1/c$ (no. 14), a = 10.220(3) Å, b = 16.419(5) Å, c = 22.098(6) Å, β = 100.818(4)°, V =

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3642(1) Å^3, D_{calc} = 1.437 g cm^{-3}, Z = 4, $F(000)$ = 1600, μ(Mo Kα) = 44.83 cm^{-1}, F^2 refinement, R = 0.037, R_w = 0.041, R_{all} = 0.063, gof = 1.22, 4387 observed reflections ($I > 2.50\sigma(I)$), 361 parameters. The MeNC(Me)CMe ligand is disordered by an approximate 2-fold rotation, interchanging the terminal N and C atoms. The disorder was modeled with constrained C and N atoms in the two positions, refined with identical position and isotropic thermal parameters, and the sum of occupancies was constrained to equal 1.0. The majority occupancy refined to 0.70 rather than 0.50. N1, C2, and C3 form the majority backbone and C40, C2, and N2 form the minority backbone. The distances from C2 to the two terminal atoms are approximately equal, but the U−X distances are 2.202(6) Å to (N1/C40) and 2.270(6) Å to (C3/N2). The thermal parameters of the MeNC(Me)CMe ligand are substantially larger than those of the 1,2,4-$(Me_3C)_3C_5H_2$ ligands due to the cumulative effects of the disorder. Detailed information is available in the Supporting Information.

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Supporting Information Available: Crystallographic data (also deposited with the Cambridge Crystallographic Data Centre; copy of the data (CCDC 270596) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK; fax +44 1223 336033); labeling diagrams, tables giving atomic positions and anisotropic thermal parameters, bond distances, and angles, and least-squares planes for **15** are available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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