the course of the refinement of the data, disorder was noted with regard to atoms C(1) and C(2). On the basis of relative peak heights, initial occupancies of 0.75 were assigned to C(1) and C(2) and 0.25 to C(1)′ and C(2)′. These factors were refined for three cycles in the following manner: refinement of C(1) and C(2) (*x*, *y*, *z*) and *U*'s only, refinement of C(1)′ and C(2)′ only, and refinement of the occupancy factors only (the total was constrained to equal 1.0). This produced values of 0.75 (1) and 0.25 (1). C(1)′ and C(2)′ could not be refined with anisotropic thermal parameters. Final positional parameters are given in Table VI, and temperature factors are available elsewhere.[32]

Acknowledgment. We are grateful to the National Science Foundation and the University of Alabama School of Mines and Energy Development for support of this work.

Registry No. I, 81988-05-8; II, 81988-06-9.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, complete bond lengths and angles, and structure factors for I and II (19 pages). Ordering information is given on any current masthead page.

Monosubstituted Triazenido Complexes as Intermediates in the Formation of Amido Complexes from Hafnium Hydrides and Aryl Azides[†]

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$(\eta^5\text{-}C_5Me_5)_2HfH_2$, 1, has been shown to react smoothly with RN_3 (R = Ph, *p*-tolyl) to afford moderately stable triazenido complexes of hafnium, $(\eta^5\text{-}C_5Me_5)_2HfH(NHNNR)$, 2. Upon thermolysis at 80 °C, 2 loses dinitrogen to form hafnium arylamido complexes $(\eta^5\text{-}C_5Me_5)_2HfH(NHR)$, 4, which can alternatively be prepared from 1 and RNH_2. Treatment of 1, 2, or 4 with excess RN_3 results in rapid formation of $(\eta^5\text{-}C_5Me_5)_2Hf(NHR)_2$, which can also be prepared from 4 and RNH_2 at 80 °C.

Introduction

The reactions of organic azides, RN_3, with transition-metal complexes are varied, but usually result in the loss of molecular nitrogen and addition of the "RN" fragment to the metal's coordination sphere.[1] The "RN" moiety can be incorporated either as a coordinated nitrene (imido) ligand or as the product of a coupling or insertion reaction between "RN" and another coordinated ligand. Since organic azides are known to be excellent sources of free nitrenes ($R-\ddot{N}:$) in photoassisted and thermal reactions,[2] it is not surprising that early workers often attributed organometallic nitrene-like products to the interactions of free nitrenes with metal complexes.

$$R-\ddot{N}=\overset{+}{N}=\overset{-}{\ddot{N}}: \leftrightarrow R-\overset{-}{\ddot{N}}-\overset{+}{N}\equiv N: \xrightarrow[\Delta]{h\nu\text{ or }} R-\ddot{N}: + :N\equiv N:$$

Most nitrenes have triplet ground states and are extremely reactive.[2] It would be surprising if such species were particularly selective in their reactions with organometallic complexes. Indeed, evidence is compelling that rarely, if ever, are free nitrenes involved in reactions of metal complexes with organic azides. Instead, most of these reactions probably proceed via metal azide intermediates which subsequently lose dinitrogen.

Transition-metal hydrido complexes are often quite reactive toward these azides. In some instances unexpected products are obtained. For example, $RhH(dppe)_2$ is reported to react with tosyl azide to afford a dimeric diimide-bridged complex $[Rh(dppe)_2]_2(\mu\text{-TosNNTos})$,[3] while the same azide reacts with $OsH_4(PEtPh_2)_3$ to give the monomeric dinitrogen species $OsH_2(N_2)(PEtPh_2)_3$ and tosyl amine.[4] The most common products from the reactions of transition-metal hydrides with organic azides, however, are metal amido complexes, formally resulting from the insertion of the "RN" fragment of the azide into a metal–hydride bond. Typical examples include *trans*-$Pt(NHPh)Cl(PPh_3)_2$ from PhN_3 and $PtHCl(PPh_3)_2$,[5] $Re(NHC(O)Ph)(CO)_2(PPh_3)_2$ from benzoyl azide and $ReH(CO)_2(PPh_3)_3$,[1] $(\eta^5\text{-}C_5H_5)W(CO)_3(NHTos)$ from $(\eta^5\text{-}C_5H_5)WH(CO)_3$ and tosyl azide,[6] and $Os_3H(\mu\text{-NHTos})(CO)_{10}$ from tosyl azide and $Os_3H_2(CO)_{10}$.[7] Although several authors have speculated on the mechanisms by which these amido complexes form, no convincing evidence has been advanced to support any of the proposed mechanisms. The isolation of the monosubstituted triazenido complexes $W(NO)(NHNNTol)(CO)(PPh_3)_2$ and $Re(NHNNTol)(CO)_2(PPh_3)_2$ from the reactions of *p*-tolyl azide with $WH(NO)(CO)_2(PPh_3)_2$ and $ReH(CO)_2(PPh_3)_3$, respectively, suggested triazenido complexes might be reactive intermediates in the formation of amides from azides and metal hydrides.[8] It is known that free phenyltriazene, $PhN=N-NH_2$, decomposes above −20 °C to give aniline and dinitrogen quantitatively, an observation compatible with the suggestion that triazenido complexes might be unstable with respect to dinitrogen loss and

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[†] Contribution No. 6604.

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Table I. Infrared and ^{1}H NMR Spectra

compd	IR, cm^{-1}	^{1}H NMR^{f} (multiplicity, rel ints, assignt)
Cp*$_2$HfH(NHNNPh), 2a	ν(NH) 3340^{a,b} ν(NNN) 1297^{c,d} ν(HfH) 1650 (br)	1.80 (s, 30 H, $C_5(CH_3)_5$), 7.1 (m, 5 H, NC_6H_5), 8.13 (br s, 1 H, NH),^{g} 11.20 (s, 1 H, HfH)
Cp*$_2$HfH(NHNNTol), 2b	ν(NH) 3343^{e} ν(NNN) 1302^{d} ν(HfH) 1635 (br)	1.83 (s, 30 H, $C_5(CH_3)_5$), 2.13 (s, 3 H, $C_6H_4CH_3$), 7.33 (AA'BB q, 4 H, $C_6H_4CH_3$), 8.07 (br s, 1 H, NH), 11.20 (s, 1 H, HfH)
Cp*$_2$HfH(NTolNNTol), 3 mol wt 683 (674 calcd)	ν(NNN) 1301^{d,e} ν(HfH) 1630 (br)	1.89 (s, 30 H, $C_5(CH_3)_5$), 2.13 (s, 3 H, $C_6H_4CH_3$), 2.20 (s, 3 H, $C_6H_4CH_3$), 7.13 (AA'BB' q, 4H, $C_6H_4CH_3$), 7.37 (AA'BB' q, 4 H, $C_6H_4CH_3$), 11.20 (s, 1 H, HfH)
Cp*$_2$HfH(NHPh), 4a	ν(NH) 3353^{a} ν(HfH) 1642 (br)	1.93 (s, 30 H, $C_5(CH_3)_5$), 4.27 (br s, 1 H, NH),^{h} 6.8 (m, 5 H, NC_6H_5), 11.60 (s, 1 H, HfH)
Cp*$_2$HfH(NHTol), 4b mol wt 484 (556 calcd)	ν(NH) 3350^{e} ν(HfH) 1640 (br)	1.93 (s, 30 H, $C_5(CH_3)_5$), 2.20 (s, 3 H, $C_6H_4CH_3$), 4.43 (br s, 1 H, NH), 6.70 (AA'BB' q, 4 H, $C_6H_4CH_3$), 11.40 (s, 1 H, HfH)
Cp*$_2$Hf(NHPh)$_2$, 5a	ν(NH) 3365^{e}	1.80 (s, 30 H, $C_5(CH_3)_5$), 4.83 (br s, 2 H, NH),^{i} 6.8 (m, 10 H, NC_6H_5)
Cp*$_2$Hf(NHTol)$_2$, 5b mol wt 596 (661 calcd)	ν(NH) 3365^{e}	1.82 (s, 30 H, $C_5(CH_3)_5$), 2.15 (s, 6 H, $C_6H_4CH_3$), 4.82 (br s, 2 H, NH), 6.70 (AA'BB' q, 8 H, $C_6H_4CH_3$)

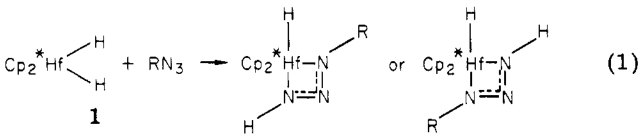
[a] Recorded in C_6D_6 solution. [b] 2a-γ-^{15}N, 3334 cm^{-1}. [c] 2a-α-^{15}N, 1276 cm^{-1}; 2a-γ-^{15}N, 1292 cm^{-1}. [d] Coupled strongly to ν(CN). [e] Recorded in Nujol mull. [f] Recorded in C_6D_6 solution, chemical shifts reported in δ from internal SiMe$_4$. [g] $^{1}J_{^{15}NH}$ = 74 Hz, $^{3}J_{^{15}NH}$ = 9 Hz. [h] $^{1}J_{^{15}NH}$ = 63 Hz. [i] $^{1}J_{^{15}NH}$ = 64 Hz.

formation of metal amido species.[9] The above tungsten and rhenium triazenido complexes, however, have not been observed to readily lose dinitrogen. An interesting recent report describes the isolation and structural characterization of $Os_3H(NHNNPh)(CO)_{10}$ from the reaction of $Os_3H_2(CO)_{10}$ and phenyl azide; this compound decomposes upon thermolysis with extrusion of dinitrogen to give $Os_3H_2(CO)_9(\mu_3\text{-NPh})$ in moderate yield.[10]

Herein we report the results of our study of the interaction of phenyl and *p*-tolyl azides with $(\eta^5\text{-}C_5Me_5)_2HfH_2$ to give isolable, moderately stable monosubstituted aryltriazenido complexes of hafnium, $(\eta^5\text{-}C_5Me_5)_2$HfH(NHNNR). Upon thermolysis at 80 °C these triazenido complexes undergo an apparent hydrogen migration with loss of dinitrogen to cleanly yield the amido complexes $(\eta^5\text{-}C_5Me_5)_2$HfH(NHR). Reaction of either the triazenido complex or the amido complex with another equivalent of azide produces the bis(amido) complexes $(\eta^5\text{-}C_5Me_5)_2$Hf(NHR)$_2$.

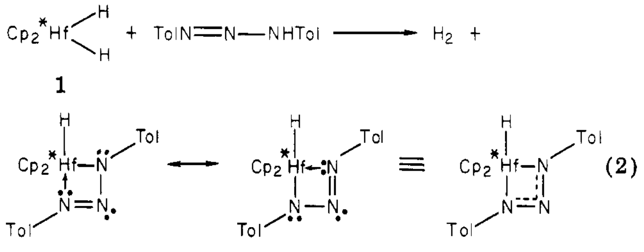
Results and Discussion

Phenyl and *p*-tolyl azides react with benzene solutions of Cp$_2$*HfH$_2$ (1),[11] (Cp* ≡ $\eta^5\text{-}C_5Me_5$) to give moderately stable monosubstituted triazenido complexes Cp$_2$*HfH(NHNNR) (2) (eq 1) as air-sensitive, light yellow crystalline materials. Labeling studies with Ph^{15}NNN and PhNN^{15}N clearly show that the γ-nitrogen atom of the azide formally inserts into a hafnium hydride bond: the ^{1}H NMR spectrum of 2a-γ-^{15}N (prepared from PhNN^{15}N) exhibits $J_{^{15}NH}$ = 74 Hz indicative of one-bond ^{15}NH coupling while the spectrum of 2a-α-^{15}N (prepared from Ph^{15}NNN) exhibits $J_{^{15}NH}$ = 9 Hz, consistent with three-bond ^{15}NH coupling.[12] Interestingly, the hydride ligand of **2a** is not coupled strongly ($^{2}J_{^{15}NH}$ < 1 Hz) to either the α- or γ-nitrogen atom. **1** reacts with 1,3-di-*p*-tolyltriazene, TolN=N—NHTol, with vigorous evolution of hydrogen to give bright orange, air-stable crystals of the di-*p*-tolyltriazenido analogue of **2**, Cp$_2$*HfH(NTolNNTol) (**3**), nearly quantitatively (eq 2).



1

2a, R = Ph
b, R = Tol



1

3

The formulation of **2** and **3** as monomeric, 18-electron species containing chelating (as opposed to monodentate or bridging) triazenido ligands is based on a molecular weight measurement and their infrared spectra. Both **2** and **3** exhibit strong bands at 1300 cm^{-1} associated with $\nu(N_3)$ of the triazenido ligands, but no bands at 1150 or 1210–1190 cm^{-1}, which Robinson has proposed as indicative of monodentate or bridging triazenido ligands, are observed.[13] There is some debate, however, concerning the validity of such assignments based on IR evidence alone.[14] It should be noted that while the band which appears at 1297 cm^{-1} in **2a** shifts to 1276 cm^{-1} in **2a**-α-^{15}N (Δ = 21 cm^{-1}), a much smaller isotopic shift is observed (1292 cm^{-1}, Δ = 5 cm^{-1}) in **2a**-γ-^{15}N, suggesting this band is a coupled mode containing a strong ν(CN) component in addition to $\nu(N_3)$. The solution infrared spectrum (C_6D_6) of **2** exhibits a single, sharp band at 3340 cm^{-1} for ν(NH). The hafnium–hydride stretching modes for both **2** and **3** appear as broad absorptions at ca. 1650 cm^{-1}. The

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[11] Abbreviations used: Cp* = $\eta^5\text{-}C_5(CH_3)_5$, dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, Et = CH_2CH_3, Me = CH_3, Ph = C_6H_5, Tol = *p*-$CH_3C_6H_4$, Tos = *p*-$CH_3C_6H_4SO_2$.

[12] The $^{1}J_{^{15}NH}$ = 74 Hz for **2a** compares to $^{1}J_{^{15}NH}$ = 78.6 Hz for Ph^{15}NH$_2$ in CDCl$_3$. Although there are no reported through-nitrogen $^{3}J_{^{15}NH}$ (i.e., ^{15}NNNH) for comparison, the 6.6-Hz $^{3}J_{^{15}NH}$ for Ph^{15}NHN=C*H*Ph suggests the observed $^{3}J_{^{15}NH}$ = 9 Hz for **2a** is reasonable. See: Witanowski, M., Webb, G. A., Eds. "Nitrogen NMR"; Plenum Press: New York, 1973; p 263 and references therein.

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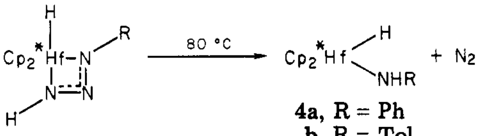
^1H NMR spectrum of **3** shows inequivalent tolyl resonances, consistent with either a chelate (eq 2) or monodentate structure for the $TolNNNTol^-$ ligand.

Crystals of **2** are stable for months at −20 °C under N_2; however, benzene solutions of **2** decompose slowly at room temperature and more rapidly (ca. 12 h) at 80 °C with concomitant dinitrogen evolution to afford the lemon yellow arylamido complexes $Cp_2^*HfH(NHR)$ (**4**), which can be prepared more conveniently by the reaction of the appropriate primary amine with **1** (eq 3 and 4). When

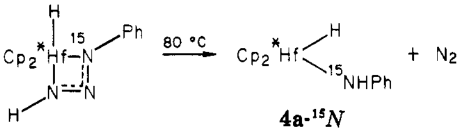


2 **4a**, R = Ph
b, R = Tol (3)

$$Cp_2^*HfH_2 + RNH_2 \xrightarrow{25\ °C} Cp_2^*HfH(NHR) + H_2 \qquad (4)$$

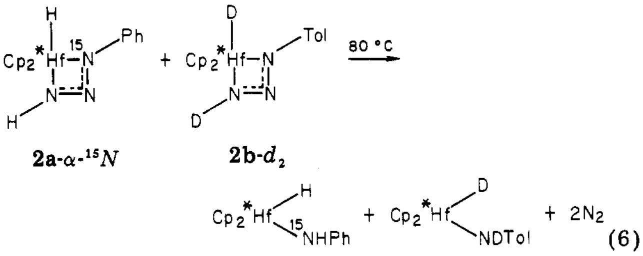
1 **4a,b**

reaction 3 is carried out with **2a**-α-^{15}N, the exclusive products are **4a**-^{15}N ($J_{^{15}NH}$ = 63 Hz) and $^{14}N{\equiv}^{14}N$ (mass spectrometry (eq 5)); likewise, thermolysis of **2a**-γ-^{15}N gives



2a-α-^{15}N **4a**-^{15}N (5)

only **4a**-^{14}N with liberation of $^{15}N{\equiv}^{14}N$. Although no detailed kinetic studies have been undertaken, the dinitrogen extrusion was shown to be an *intramolecular* process by a crossover experiment in which a mixture of **2b**-d_2, prepared from $Cp_2^*HfD_2$ (**1**-d_2) and $TolN_3$, and **2a**-α-^{15}N was observed to yield only **4b**-d_2 and **4a**-^{15}N upon thermolysis (eq 6). In contrast to **2**, solutions of **3** are



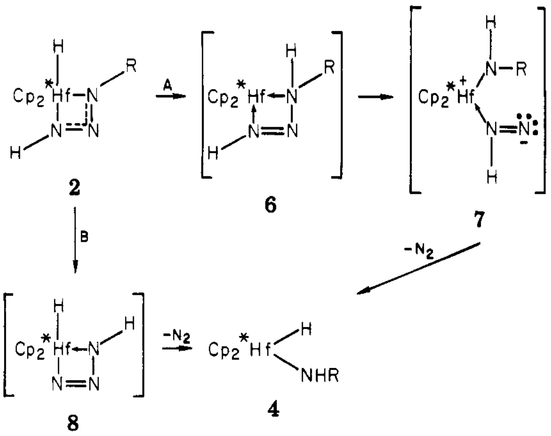
2a-α-^{15}N **2b**-d_2

4a-^{15}N **4b**-d_2 (6)

thermally stable with respect to nitrogen loss; **3** can be recovered quantitatively from benzene solutions after days at 150 °C.

Two possible mechanisms for formation of **4** from **2** are illustrated in Scheme I. Pathway A requires the involvement of the hydride ligand of **2** to give a coordinated triazene intermediate **6**. Cleavage of the N–N single bond in **6** gives a diazo complex **7** which could undergo an α elimination to give **4** and dinitrogen. Two points argue against this pathway. First, the requirement of a hydrido triazenido complex is implied if N_2 loss is to occur. However, the addition of RN_3 to **4** to give the bis(amido) complexes $Cp_2^*Hf(NHR)_2$ (**5**) (see below) is not consistent with this notion. Second, compounds such as **7** would be expected to be stabilized with aryldiazo ligands (cf. $(\eta^5\text{-}C_5H_5)Mn(CO)_2(NPhN)^-$,[15] hence the much higher thermal

Scheme I



2 **6** **7** **8** **4**

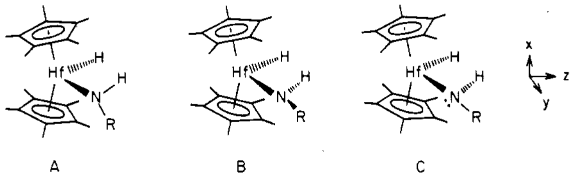


Figure 1. The three possible structural geometries of **4**. A represents the geometry required for effective π overlap between Hf d and N p orbitals; the amido substituents are ⊥ to the *yz* plane. B represents the sterically least crowded conformation. C has no Hf–N π interaction.

stability of **3** does not seem compatible with this mechanism.

Pathway B appears more likely. In **B**, the triazenido proton of **2** undergoes a 1, 3 hydrogen shift (perhaps via an α-N bound azide species) to give **8**, from which N_2 loss would clearly give **4**. If B represents an important mechanistic pathway for the **2** → **4** conversion, then the higher themal stability of **3** is not at all surprising.

It is interesting that while **2** is susceptible to thermal decomposition to give the amido complex, **4**, the monosubstituted triazenido complexes $W(NO)(NHNNTol)(CO)(PPh_3)_2$ and $Re(NHNNTol)(CO)_2(PPh_3)_2$ seem stable with respect to dinitrogen loss. The high activation energy expected for transformation from an octahedral d^6, 18-electron closed-shell configuration to a five-coordinate d^6, 16- or 18-electron configuration could well be responsible for their inertness. It is noteworthy that when $ReH(CO)_2(PPh_3)_3$ is treated with benzoyl azide (instead of aryl azide), the anticipated amido complex is indeed formed.[1]

The ^1H NMR spectrum of **4** is interesting in that the Cp* resonances are equivalent: **4b** exhibits a single resonance for all 30 Cp* protons even at −65 °C at 500 MHz. Effective π overlap between the $1a_1$ LUMO of $Cp_2^*MX_2$ compounds, which is directed in the *yz* plane between the rings (see Figure 1), and the amido nitrogen requires in **4b** that the amido proton be directed toward one ring and the tolyl group toward the other (formalism A in Figure 1), resulting in chemically inequivalent rings.[16] In light of the observed ring equivalence and barring accidental degeneracy, either the barrier to rotation about such a Hf–N multiple bond is very small (in contrast to typical values of ca. 10–15 kcal/mol for transition metal dialkylamides[17]) or, less likely, the amide does not donate a considerable amount of π-electron density to the metal and consequently acts merely as a σ "pseudohalogen" do-

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(16) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

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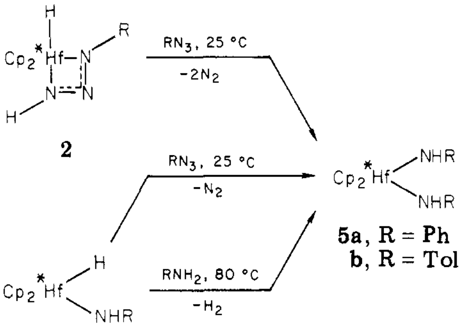
nor (formalism C in Figure 1).[18] Marks has reported that similar complexes, $Cp_2^*MCl(NMe_2)$ (M = Th, U),[19] likewise show equivalent Cp* resonances but inequivalent amido methyl resonances in their ^1H NMR spectra; f orbital participation in out-of-plane π bonding was invoked to explain these observations (corresponding to formalism B in Figure 1). The high solubility of 4 in most solvents (even in cold petroleum ether) has prevented isolation of crystals suitable for an X-ray study to elucidate the interesting metal–nitrogen bonding in 4, but we are pursuing this problem by using less sterically demanding amides, e.g., $Cp_2^*HfH(NHMe)$.

Compound 2 undergoes an immediate reaction at 25 °C with a second equivalent of azide with concomitant evolution of 2 equiv of dinitrogen to yield $Cp_2^*Hf(NHR)_2$ (**5**) as beautiful pale yellow crystals (eq 7). The reaction is complete in minutes in contrast to reaction 3 which requires hours at elevated temperatures to effect N_2 loss. The dramatic increase in the rate of nitrogen loss upon addition of the second equivalent of RN_3 suggests that an unobserved bis(triazenido) intermediate, $[Cp_2^*Hf(NHNNR)_2]$, which rapidly loses N_2 in a stepwise fashion, might be involved. It is possible that the triazenido ligand of 2 is stabilized by chelation, while the proposed intermediates $[Cp_2^*Hf(NHNNR)_2]$ and $[Cp_2^*Hf(NHR)(NHNNR)]$ must have at least one monodentate triazenido ligand which, in the absence of chelation, rapidly loses dinitrogen.[20] 3 *does not* react with RN_3 even at 80 °C although this might be due to steric factors. Alternatively, 4 might be an intermediate in reaction 7; if so, then the production of 4 from 2 must be catalyzed by RN_3 in some way. Treatment of 4 with an excess of aryl azide does result in immediate liberation of dinitrogen and quantitative production of 5 (eq 8). Labeling studies again show that only the α-nitrogens of the aryl azides are incorporated into the amido ligands of 5 ($J_{^{15}NH}$ = 65 Hz for **5a**-^{15}N). Finally, thermolysis (80 °C, 24 h) of 4 in the presence of aniline or p-toluidine results in the formation of 5 with evolution of an equivalent of hydrogen (eq 9).



2

4

5a, R = Ph
b, R = Tol

(7)

(8)

(9)

Conclusions

Although the reactions of organic azides with metal hydrides are known often to give metal amido species, little is known about how these interactions occur. In some cases, such as with tin hydrides, free radical mechanisms are implicated.[21] For the vast majority of the cases involving transition metals, a mechanism involving initial formation of a monosubstituted triazenido species followed by a formal hydrogen migration with N_2 loss is appealing. For the compounds *trans*-$Pt(NHPh)Cl(PPh_3)_2$, $(\eta^5-C_5H_5)W(CO)_3(NHTos)$, and $Re(NHC(O)Ph)(CO)_2(PPh_3)_2$, all produced from RN_3 and metal hydrides (see above), the corresponding diaryltriazenido analogues $Pt(NPhNNPh)Cl(PPh_3)_2$,[13] $(\eta^5-C_5H_5)W(CO)_2(NPhNNPh)$,[22] and $Re(NPhNNPh)(CO)_2(PPh_3)_2$[23] are known, suggesting similar monosubstituted triazenido intermediates are not unreasonable.

We consider it likely that the reaction of $Cp_2^*HfH_2$ with RN_3 is unusual only in that the initially formed $Cp_2^*HfH(NHNNR)$ has moderate kinetic stability, allowing its isolation. The reaction of other transition metal hydrides, M-H, with RN_3 is probably quite general to give monosubstituted triazenido (M–NHNNR) complexes, but most undergo a rapid decomposition to the thermodynamically favored amido complexes (M–NHR) and dinitrogen.

Experimental Section

General Considerations. Compounds were handled in an inert atmosphere glovebox and reactions effected by using high-vacuum techniques. Gas evolution measurements were performed by using standard Toepler techniques and the identities of the gases determined by mass spectrometry (DuPont 21-492 instrument) or by burning the gases over CuO with use of a Toepler pump for circulation. Rigorously anhydrous, oxygen-free solvents were vacuum transferred from green "titanocene"[24] and used throughout. Infrared spectra were recorded in Nujol and fluorinated hydrocarbon mulls or in C_6D_6 solution by using a Beckman 4240 spectrophotometer and were calibrated with a polystyrene film. Proton NMR spectra were recorded in C_6D_6 with an internal $SiMe_4$ reference by using a Varian Associates EM 390 (90 MHz) spectrometer. High-field, low-temperature proton spectra were obtained on a Bruker WM-500 (500-MHz) instrument in C_7D_8 solution. Open-faced, screw-capped 5-mm NMR tubes equipped with gas tight septa (Wilmad, Inc.) were used with a microliter syringe in the titration studies of $Cp_2^*HfH_2$ with RN_3. Elemental analyses and molecular weight measurements were performed by Alfred Bernhardt (West Germany) and Galbraith, Inc. (Knoxville, Tenn.).

$Cp_2^*HfH_2$ was prepared from $Cp_2^*HfCl_2$, *n*-BuLi, and H_2 and was recrystallized from petroleum ether.[25] $Cp_2^*HfD_2$ was prepared by stirring a toluene solution of $Cp_2^*HfH_2$ under 1 atm of D_2 for 48 h at ambient temperature. Phenyl and *p*-tolyl azides were prepared from the corresponding diazonium salts and sodium azide[26] and vacuum distilled under N_2 (PhN_3, 51 °C (10 torr); $TolN_3$, 53 °C (3 torr)). The resulting yellow oils were diluted with 30/60 petroleum ether or C_6D_6 to give ~2.5 M solutions and stored over 4-Å molecular sieves under N_2. Phenyl azide isotopically labeled with nitrogen-15 in the α-position ($Ph^{15}NNN$) was prepared similarly from $[Ph^{15}NN][BF_4]$, made by the diazotization of $Ph^{15}NH_2$ (99% ^{15}N, Stohler Isotope Chemicals). The resulting azide was diluted with C_6D_6 and dried over $MgSO_4$ and 4-Å sieves but was not distilled. Phenyl azide selectively labeled with nitrogen-15 in the γ-position ($PhNN^{15}N$) was prepared from phenylhydrazine and $Na^{15}NO_2$ (99% ^{15}N, Stohler Isotope Chemicals) in dilute HCl at −5 °C.[27] The labeled azide was extracted from

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[18] An editor suggested that the low barrier to rotation of the NHR ligand might be ascribed to formation of an intermediate $[Cp_2^*Hf(NH_2R)]$ in which the H's are in a nonclassical, semibridging position between Hf and N. To test this hypothesis, we prepared $Cp_2^*HfH(NDTol)$ (from $Cp_2^*HfH_2$ and $TolND_2$) but observed *no* H-D exchange between the hydride and the amide positions (<2 days, 25 °C), thus eliminating this mechanism for facilitating NHR rotation.

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the aqueous solution by using C_6D_6 and washed several times with H_2O to remove residual acid. The resulting solution was dried and stored over sieves but was not distilled. Technical grade *p*-toluidine (MCB) was sublimed prior to usage. 1,3-Di-*p*-tolyltriazene was prepared by the literature method.[28]

Preparation of Cp_2*HfH(NHNNTol), 2b. To a rapidly stirred solution of Cp_2*HfH_2 (0.30 g, 0.7 mmol) in 10 mL of toluene was added 0.95 equiv of $TolN_3$ (0.25 mL of a 2.45 M solution). The mixture was stirred at 0 °C for 15 min, then the volume of solvent was reduced under vacuum to ~2 mL, and petroleum ether (5 mL) was added to precipitate light yellow crystals of a 1:1 toluene solvate of **2b**. The precipitate was filtered cold and dried in vacuo to yield 0.24 g (62%) of unsolvated product. Anal. Calcd for $C_{27}H_{39}N_3Hf$: C, 55.52; H, 6.73; N, 7.19. Found: C, 55.79; H, 6.76; N, 7.18. Cp_2*HfH(NHNNPh), **2a**, was prepared analogously from phenyl azide.

Preparation of 2a-α-^{15}N and 2a-γ-^{15}N. The nitrogen-15 labeled phenyl azides were prepared in such small amounts that distillation and subsequent accurate standardization of the labeled azides were precluded. Consequently, the compounds Cp_2*HfH(^{15}NHNNPh), **2a**-γ-^{15}N, and Cp_2*HfH(NHN^{15}NPh), **2a**-α-^{15}N, were prepared by carefully titrating C_6D_6 solutions of Cp_2*HfH_2 with the appropriate labeled azide and following the titration by ^{1}H NMR. This was best accomplished by monitoring the Cp* methyl resonances upon addition of aliquots of the azides. Extreme care was exercised to avoid "over titrating" which would result in rapid production of the bis(amido) species.

Preparation of Cp_2*HfH(NTolNNTol), 3. To a stirred solution of 0.18 g (0.4 mmol) of Cp_2*HfH_2 in 5 mL of benzene was added, via an attached sidearm, 1.1 equiv (0.10 g) of 1,3-di-*p*-tolyltriazene. Immediate, vigorous evolution of gas was evident and ceased within 60 s (0.91 equiv of H_2/Hf). The volume of benzene was reduced to 2 mL, and petroleum ether was slowly added to precipitate orange prisms which were filtered and washed with cold petroleum ether to yield 0.27 g (91%). Anal. Calcd for $C_{34}H_{45}N_3Hf$: C, 60.57; H, 6.73; N, 6.23. Found: C, 60.29; H, 6.89; N, 6.22.

Preparation of Cp_2*HfH(NHTol), 4b. (a) To a stirred solution of Cp_2*HfH_2 (0.23 g, 0.5 mmol) in 10 mL of benzene was added 0.06 g (1.1 equiv) of *p*-toluidine via an attached side arm. Gas evolution commenced immediately and proceeded for about 5 min (0.84 equiv of H_2/Hf), at which time the solvent was removed and the resulting yellow oil was allowed to sit under a dynamic vacuum for 12 h. This allowed any residual toluidine to sublime from the product and yielded 0.25 g (88%) of a bright lemon yellow solid. Anal. Calcd for $C_{27}H_{39}NHf$: C, 58.32; H, 7.07; N, 2.52. Found: C, 58.40; H, 7.17; N, 2.25. Cp_2*HfH(NHPh), **4a**, was prepared analogously by using aniline instead of $TolNH_2$. (b) A 0.12-g (0.2-mmol) sample of **2b** was dissolved in 5 mL of toluene and placed in a thick-walled glass reaction vessel which was subsequently immersed in an 80 °C oil bath for 12 h. Afterward the solvent was removed and the gases were collected (0.81 equiv of N_2/Hf). The yellow residue was dissolved in C_6D_6 and identified as **4b** by ^{1}H NMR. Similar experiments conducted in sealed 5-mm NMR tubes showed the conversion of $2 \rightarrow 4$ to be nearly quantitative after 12 h at 80 °C for **2a**, **2a**-α-^{15}N, and **2a**-γ-^{15}N, producing **4a**, **4a**-^{15}N (with liberation of N_2-28 determined by mass spectrometry), and **4a** (with liberation of N_2-29), respectively.

Thermolysis of a Cp_2*HfH(NHN^{15}NPh)–Cp_2*HfD(NDNNTol) Solution. In an NMR tube were combined a C_6D_6 solution of Cp_2*Hf(NHN^{15}NPh), **2a**-α-^{15}N (prepared by titrating 0.012 g of Cp_2*HfH_2 with 1 equiv of Ph^{15}NNN), and 0.015 g of Cp_2*HfD(NDNNTol), **2b**-d_2 (prepared from Cp_2*HfD_2 and $TolN_3$). The tube was immersed in an 80 °C oil bath for 24 h and then examined by ^{1}H NMR. Within experimental limits (±5%), no crossover was observed, i.e., Cp_2*HfH(^{15}NHPh) and Cp_2*HfD(NDTol) were produced, but no signals due to ^{14}N–H amide products were present.

Preparation of Cp_2*Hf(NHTol)$_2$, 5b. (a) To a cooled (−78 °C) solution of 0.69 g (1.5 mmol) of Cp_2*HfH_2 in 20 mL of petroleum ether was added 2.2 equiv of $TolN_3$ (1.65 mL of a 2.05 M solution). Upon warming to 0 °C (ice bath), the solution began to evolve gas, and after it was stirred for 3 h at room temperature, a yellow precipitate had separated from the olive green solution. A Toepler measurement showed 1.84 equiv of N_2/Hf was produced. The volume of solvent was reduced to about 5 mL under vacuum, and then the reaction mixture was cooled to −78 °C to ensure complete precipitation of the product. The yellow, powdery material was washed repeatedly with cold petroleum ether and then dried in vacuo to yield 0.74 g (73%). When the reaction was conducted by titrating a C_6D_6 solution of Cp_2*HfH_2 with $TolN_3$ and following the course of the reaction by ^{1}H NMR, **2b** was formed immediately upon addition of 1 equiv of $TolN_3$, followed by rapid formation of **5b** upon addition of the second equivalent of $TolN_3$. Anal. Calcd for $C_{34}H_{46}N_2Hf$: C, 61.76; H, 7.01; N, 4.24. Found: C, 61.69; H, 7.21; N, 4.16. Cp_2*Hf(NHPh)$_2$, **5a**, and Cp_2*Hf(^{15}NHPh)$_2$, **5a**-^{15}N, were prepared analogously from PhN_3 and Ph^{15}NNN, respectively. (b) In a thick-walled glass reaction vessel were placed 0.15 g (0.27 mmol) of **4b**, 1.1 equiv (0.03 g) of *p*-toluidine, and 5 mL of toluene. The vessel was immersed in an 80 °C oil bath for 24 h, after which the reaction gases were collected (0.92 equiv of H_2/Hf) and the product was isolated by removal of solvent and addition of petroleum ether (−78 °C) to yield 0.13 g (73%). (c) To a solution of 0.025 g of **4b** in C_6D_6 was added 1 equiv of $TolN_3$ (0.017 mL of a 2.65 M solution in C_6D_6). Gas evolution was immediate and vigorous, and **5b** was quantitatively produced by ^{1}H NMR.

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Registry No. 1, 81956-87-8; **2a**, 81956-88-9; **2b**, 81956-89-0; **3**, 81956-90-3; **4a**, 81956-91-4; **4b**, 81956-92-5; **5a**, 81956-93-6; **5b**, 81956-94-7.

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