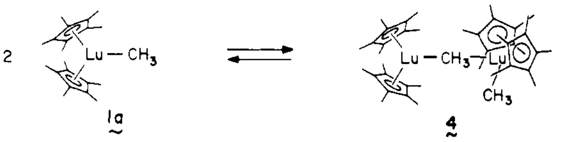
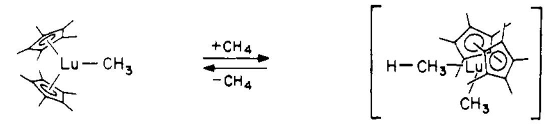
involve intermediate **3**[22,23] or metalated dimers derived from **4** by loss of CH_4.

Both the lutetium and yttrium methyl complexes $M(\eta^5\text{-}C_5Me_5)_2CH_3$ (**1a**, M = Lu; **1b**, M = Y) exist as asymmetric dimers in the solid state. Dimeric structure **4** (shown in eq 5)



(5)



(6)

is confirmed by the solid-state ^{13}C NMR spectra (for M = Lu, Y)[24] and X-ray crystallography (for M = Lu).[25] In hydrocarbon solution the dimers dissociate rapidly and reversibly (eq 5, fast on the NMR time scale above −40 °C), providing measurable concentrations of the coordinatively unsaturated monomers. Monomer **1a** was shown to be the reactive species in olefin insertion chemistry[26,27] and C–H activation reactions.[1] Features pertinent to reactivity are the following: (1) Steric bulk of the $M(\eta^5\text{-}C_5Me_5)_2$ unit prevents formation of a more stable, symmetrical dimer with both methyl groups bridging as in $Ln[(\eta^5\text{-}C_5H_5)_2CH_3]_2$.[28] (2) The monomers are strong Lewis acids and electron density requirements can be satisfied either by coordination of Lewis bases[27] or via three-center interactions with σ-CH bonds.[29] The structural analogy between bridging coordination of a methyl group as in the dimer and weak initial coordination of a hydrocarbon such as methane (eq 6) should be emphasized. (3) For d_0 metals such as lutetium and yttrium, oxidative addition and reductive elimination sequences would generate intermediates in unreasonable oxidation states (e.g., +5 or +1) and are considered unlikely.

Other hydrocarbons, such as ethane and propane, also react with **1a** and **1b** but the products decompose via β-hydrogen elimination. The kinetic advantage of methane over the solvent cyclohexane-d_{12} in these experiments is probably both steric and isotopic in origin.

In conclusion, alkane activation in these systems probably depends on the electrophilicity of the metal center. The C–H bond(s) of the substrate alkane initially acts as an electron donor, a source of electron density. This type of interaction is structurally and spectroscopically characterized in intramolecular transition-metal complexes.[30] Having demonstrated the alkane exchange reaction for both lanthanide and group 3 metals, we expect reactivity with other electron-deficient, coordinately unsaturated organometallic species and are currently investigating reaction mechanisms for the isostructural series $M(\eta^5\text{-}C_5Me_5)_2CH_3$.

Acknowledgment. The excellent technical assistance of W. Dietrich and B. Dunn is gratefully acknowledged. Discussions with G. W. Parshall, F. N. Tebbe, and D. C. Roe are most appreciated as are the efforts of R. Farlee in obtaining solid-state ^{13}C NMR spectra.

Registry No. 1a, 85962-87-4; **1b**, 87136-56-9; $Lu(\eta^5\text{-}C_5Me_5)_2{}^{13}CH_3$, 87136-57-0; $Y(\eta^5\text{-}C_5Me_5)_2{}^{13}CH_3$, 87136-58-1; $^{13}CH_4$, 6532-48-5; CH_4, 74-82-8.

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(22) Such an intermediate was previously invoked. Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–6473.

(23) Also, a η^6-$CH_2C_5(CH_3)_4$ complex of titanium has been isolated and characterized: McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

(24) NMR shows only dimers in solid state at 23 °C and in solution below −60 °C. Spectrum of **1a**: solid-state ^{13}C NMR 11.1, 11.7, 12.4 (ring CH_3, 1:2:1), 20, 24 ($LuCH_3$ very broad, 1:1) 114.4, 114.9, 119.6, 120.6 (ring C, 1:1:1:1), ppm; ^{13}C NMR (−80 °C, toluene) 119.4, 118.9, 114.2 (ring C, 1:1:2), 25.6, 20.6 ($LuCH_3$, 1:1), 12.0, 10.8, 10.7 (ring CH_3, 2:1:1). ^{13}C NMR of **1b** (−80 °C, toluene) 119.6, 119.0, 114.7 (ring C, 1:1:2), 22.0, 21.8 (YCH_3, 1:1, J_{YC} 42.7, 51.1 Hz, respectively), 12.0, 10.7 (ring CH_3, 1:1) ppm. ^1H NMR of **1a**: (−90 °C, toluene-d_8) δ −1.47, −0.30 ($LuCH_3$, 1:1), 1.76, 1.81, 2.22 (ring CH_3, 1:1:2); (20 °C, cyclohexane-d_{12}) δ 1.98 (s, ring CH_3), −1.00 (s, $LuCH_3$). ^1H NMR of **1b**: (−95 °C, toluene-d_8) δ −1.65, −0.41 (YCH_3, 1:1), 1.69, 1.74, 2.18 (ring CH_3, 1:1:2); (20 °C, cyclohexane-d_{12}) δ 1.97 (s, ring CH_3), −1.22 (br s, YCH_3).

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Experimental and Theoretical Evaluation of the Mechanism of HCN Formation in the Reaction between Carbon and Ammonia

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In a recent investigation of the reaction of atomic carbon with ammonia, we have reported that methyleneimine (**1**) and HCN are initial products.[1,2] Although it is reasonable to postulate that **1** arises via the series of reactions in eq 1, the mechanism of HCN

$$\mathrm{C} + \mathrm{NH_3} \rightarrow \underset{\mathbf{2}}{\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{N}}\mathrm{H_3}^{+}} \rightarrow \underset{\mathbf{3}}{\mathrm{H{—}C{—}NH_2}} \rightarrow \underset{\mathbf{1}}{\mathrm{H_2C{=}NH}} \qquad (1)$$

formation is not clear. The fact that carbon is an extremely high-energy species leads to the possibility that **1**, **2**, or **3** could be generated with sufficient excess energy to eliminate hydrogen. We now report a combined theoretical and experimental evaluation of the mechanism of HCN formation in which we reach the interesting conclusion that HCN is generated via elimination of H_2 from initial complex **2** followed by rearrangement of HNC to HCN.

In order to estimate the most plausible route to HCN in this system, we have calculated the relative energies of **1**, **2**, and **3** and the activation enthalpies for loss of hydrogen from each of these species. The geometries of all intermediates and transition states were initially optimized at the Hartee–Fock level with a 3-21G basis.[4] Energies were then calculated by the MP3/6-31G** method.[4] The energies of **1–3** were also calculated with a multiconfiguration approach (MCSCF).[5] The geometry of **2** was reoptimized with imposed C_{3v} symmetry by using a MCSCF wave function with a 3-21G basis[6] and the energy of this geometry calculated by the MCSCF/CI/6-31G** method.[7] Since the above geometry of **2** differs little when calculated by single

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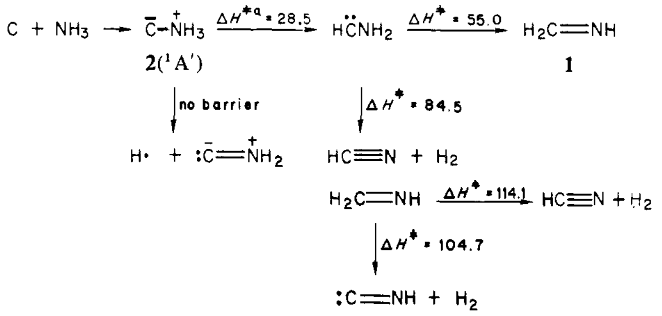
Scheme I



[a] Activation enthalpies are in kcal/mol.

configurational and multiconfigurational methods, the HF/3-21G geometries of **1** and **3** were used to calculate the energies of these species by the MCSCF/CI/6-31G** method.

The MCSCF calculations predict that the lowest singlet state of the carbon–ammonia complex **2** is ^1E in C_{3v} symmetry and lies 19.5 kcal/mol lower in energy than $C(^1D)$ and NH_3.[8] However, this species is not an energy minimum, as we calculate no barrier for its cleavage to $\cdot CNH_2$ and $H\cdot$ when the C_{3v} symmetry constraint is removed. Since the reaction of C with NH_3 is carried out on a matrix at 77 K, radical pair $\cdot CNH_2 + H\cdot$ trapped at this temperature could lead to both HNC and carbene **3** as shown in eq 2. A concerted 1,2-hydrogen migration in **2** to generate **3** is

$$\begin{array}{ccccc} \overset{-}{C}\text{-}\overset{+}{N}H_3^+ & \rightarrow & \cdot\overset{-}{C}{=}\overset{+}{N}H_2 + H\cdot & \rightarrow & H\ddot{C}NH_2 \\ 2 & & \downarrow & & 3 \\ & & C{=}NH + H_2 & & \end{array} \tag{2}$$

calculated to be a considerably higher energy process with $\Delta H^\ddagger = 28.5$ kcal/mol and is unlikely to compete with cleavage of **2**.

The energies of **3** and **1** were calculated by both the MCSCF/CI/6-31G** and the MP3/6-31G** methods. The MCSCF calculation indicate that **3** is 119.7 kcal/mol lower in energy than $C(^1D) + NH_3$ while **1** is 165.0 kcal/mol more stable than $C(^1D) + NH_3$.[8] The corresponding MP3/6-31G** calculations predict that **3** and **1** are 126 and 165 kcal/mol more stable than $C(^1D) + NH_3$.[9] The use of experimental heats of formation leads to the conclusion that **1** is generated from $C(^1D) + NH_3$ with the release of 162.5 ± 3.2 kcal/mol.[10]

Scheme I summarizes activation ethalpies for the formation of **3** and **1** and for elimination of hydrogen from **1**, **2**, and **3**. The geometries of the intermediates are depicted in Figure 1. In order to determine if hydrogen migration or loss of H_2 is the more favorable reaction of carbene **3**, we have calculated the activation enthalpies for both of these reactions. In the case of the rearrangement of **3** to methyleneimine (**1**) the geometry of the product was taken from the Quantum Chemistry Archive[11] and the energy calculated at MP3/6-31G** level. This procedure lead to a calculated barrier at 55 kcal/mol for rearrangement of **3** to **1**. The barrier for loss of H_2 from **3** was calculated to be 84.5 kcal/mol indicating that HCN formation from **3** is unlikely to compete with rearrangement to **1**.

Scheme I demonstrates that elimination of H_2 from **1** is also a high-energy process which is unlikely to occur. An α-elimination of H_2 to generate HNC has $\Delta H^\ddagger = 104.7$ kcal/mol while a β-elimination giving HCN has $\Delta H^\ddagger = 114.1$ kcal/mol. Thus the calculations indicate that the lowest energy pathway to HCN involves cleavage of an NH bond in **2**, a reaction that is likely to proceed via hydrogen isocyanide, HNC.

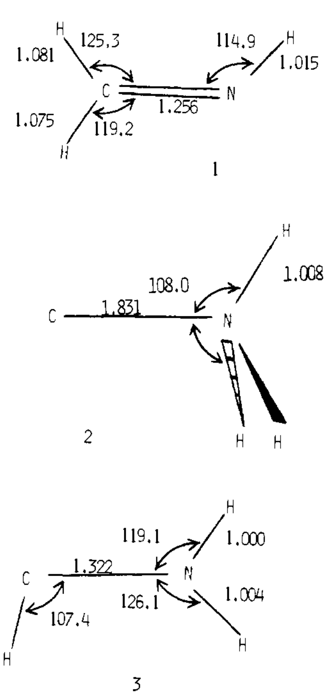
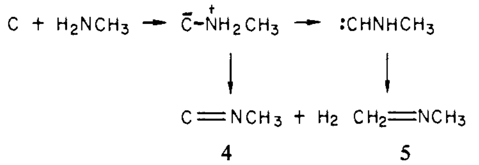


Figure 1. Geometries of relevant intermediate an transition states in the reaction of $C(^1D)$ with NH_3.

Although HNC has been observed as an interstellar molecule[12] and terrestrially as a transient species[13,14] little is known of its chemistry. A recent sophisticated molecular orbital calculation indicates that the barrier for the unimolecular rearrangement of HNC to HCN is 36.3 kcal/mol.[15] These data indicate that HNC is potentially trappable if it is generated at 77 K in the reaction between C and NH_3. However, it must be remembered that the reaction of C with NH_3 will generate HNC in the presence of a great deal of excess NH_3. This NH_3 would undoubtably bring about the rapid base-catalyzed conversion of HNC to HCN shown in eq 3 and prevent isolation of HNC. Thus, experimental confirmation of the theoretically predicted intermediacy of HNC in the C + NH_3 reaction is difficult and perhaps impossible. This reaction has been observed to generate both HCN and **1** in a 1.9:1 ratio.[2b]

$$HNC + NH_3 \rightarrow NH_4^+CN^- \rightarrow HCN + NH_3 \tag{3}$$

However, it is reasonable to assume that the reaction of carbon with methylamine will follow a pathway similar to that with NH_3 in which loss of H_2 generating methylisocyanide (**4**) will be competative with rearrangement to *N*-methylmethyleneimine (**5**).



The methylisocyanide does not have the base-catalyzed rearrangement shown in eq 2 available to it and should be isolable under the reaction conditions. Accordingly, we have reacted arc-generated carbon atoms with methylamine by cocondensing the two at 77 K. The results of this experiment demonstrate that loss of H_2 to generate **4** and hydrogen migration leading ultimately to *N*-methylmethyleneimine (**5**) both occur. Analysis of the reaction products reveals the presence of **4** and **5** in a 2:1 ratio.[16]

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[8] The energy of $C(^1D)$ and NH_3 was estimated in the MCSCF method by calculating the energy of these species at a distance of 50 Å.

[9] The fact that $C(^1D)$ is composed of both open- and closed-shell configurations makes calculation of the energy of this species by the Hartree–Fock method difficult. For this reason we have calculated the energy of $C(^3P)$ at the UMP3/6-31G** level and added the experimental $C(^1D)$ (^3P) energy difference of 30 kcal to obtain the energy of $C(^1D)$.

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These results confirm the theoretical prediction that loss of hydrogen occurs from an initial carbon-amine complex and is competative with N-H insertion.

Acknowledgment. We thank the Auburn University Computation Center for a generous allotment of computer time. M.L.M. thanks Auburn University of the award of a Grant-in-Aid (82-54). D.W.M. and P.B.S. gratefully acknowledge support of the experimental portion of this research by the National Science Foundation under Grant CHE-8103034.

Registry No. Carbon, 7440-44-0; ammonia, 7664-41-7; hydrocyanic acid, 74-90-8.

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(16) The *N*-methylmethyleneimine (**5**) was trapped as the aminonitrile by adding an excess of HCN at 77 K. The aminonitrile was hydrolyzed to the amino acid which was derivatized and analyzed by GC-MS. The methylisocyanide (**4**) was detected among the volatile products by IR spectroscopy and quantitated by GC. Products of hydrogen abstraction by carbon and of C-H insertion are also observed in this system.[2b]

Valence Electronic Structures of the Organouranium Complexes $(\eta^5\text{-}C_5H_5)_2UX_2$ (X = Cl, CH_3)

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In recent years there has been a tremendous growth in the synthesis and structural characterization of organothorium and organouranium complexes.[1] Of particular interest have been the bis(pentamethylcyclopentadienyl) complexes $(\eta^5\text{-}C_5Me_5)_2M(X)(Y)$ (M = Th or U; X, Y = halide, alkyl, or acyl), the chemistry of which has been extensively developed by Marks and co-workers.[2] Some of these have been shown to activate CO toward hydrogenation or coupling,[3] and they are structurally analogous to the well-known dicyclopentadienyl complexes of early transition metals such as Ti, Zr, and Mo.[4] With the exceptions of thorocene and uranocene,[5] however, comparatively little is known about either the bonding in or the electronic demands of organoactinide systems and, in particular, how these might be related to their chemical reactivity. Here we report the first quantitative molecular orbital descriptions of two model nonactinocene organoactinide complexes, viz., $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$, as calculated by the $X\alpha$-SW method[6] including relativistic corrections. The recent He(I) and He(II) photoelectron spectroscopic studies of $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5Me_5)_2UCl_2$[7] will be used as a gauge of the effectiveness of the relativistic $X\alpha$ method to calculate the electronic structure of organoactinide systems.

In order to make the calculation tractable, the $\eta^5\text{-}C_5Me_5$ ligands have been modeled with $\eta^5\text{-}C_5H_5$ ligands. Although the former have been used primarily to block formation of the tri- and tetracyclopentadienyl adducts, it is recognized that replacement of $\eta^5\text{-}C_5H_5$ by $\eta^5\text{-}C_5Me_5$ perturbs the electronic structure as well. The magnitude of this perturbation has been studied by ourselves[8] and others.[9] We find the effect to be small and uniform, and replacement of $\eta^5\text{-}C_5Me_5$ by $\eta^5\text{-}C_5H_5$ will not affect the conclusions presented here.

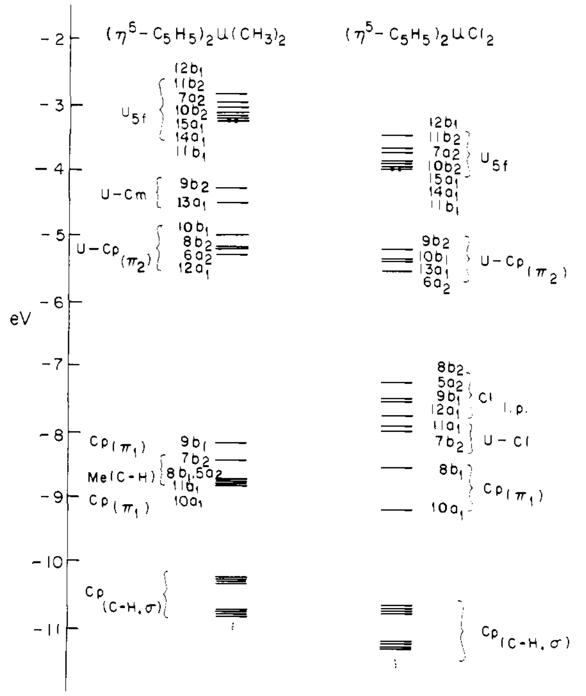

Figure 1. Converged $RX\alpha$ orbital energies for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$. The principal contribution to each orbital is indicated.

Atomic coordinates for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$ were taken from the crystal structures of the corresponding pentamethylcyclopentadienyl derivatives[10] and were idealized to C_{2v} symmetry. The calculations were first converged nonrelativistically via procedures analogous to other spin-restricted overlapping sphere $X\alpha$-SW calculations which we have reported.[11] The converged nonrelativistic potential was used as a starting point for the relativistic $X\alpha$ ($RX\alpha$) formalism of Wood and Boring.[12] This method, which includes the mass-velocity and Darwin terms of the Pauli Hamiltonian within a scattered-wave framework, was used to calculate orbital energies within the nonrelativistic single point group. Case and Yang have pointed out that the $RX\alpha$ method is generally a good approximation to a full Dirac-Slater treatment.[13] Spin-orbit splittings were not calculated for these molecules.

The valence orbital energies of $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$ are summarized in Figure 1. The bonding of the cyclopentadienyl ligands, both within the rings and to the uranium atom, is very similar in both compounds. The C-H and C-C σ bonds comprise a band of orbitals below −10 eV, and the totally symmetric π orbitals (π_1) are between −8.2 and −9.2 eV. None of these has a significant interaction with the uranium atom. Molecular orbitals that are bonding between the doubly degenerate π HOMO of $C_5H_5^-$ (π_2) and the U atom are clustered between −5.0 and −5.5 eV. These MO's contain from 12% to 26% U character with sizable contributions from both the 5f and 6d AO's of U. In the dimethyl complex, some of the C(Me)-H bonding levels are between −8.5 and −8.8 eV. The $9b_2$ and $13a_1$ MO's are the U-C(Me) bonds; these are the second- and third-highest occupied orbitals in the dimethyl complex and have energies of −4.3 and −4.5 eV, respectively. In the dichloro complex, four Cl lone pair levels appear at −7.5 to −7.8 eV, and the U-Cl σ bonds are slightly below these.

A comparison of the dimethyl and dichloro complexes leads to the expected conclusions that CH_3^- is a stronger σ donor than is Cl^- and that the U-C(Me) bonding orbitals have higher orbital

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