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Methane Activation by Group VB Bis(imido) Complexes

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An effective core potential, parallel supercomputing study of methane activation by group VB bis(imido) complexes, $M(=NH)_2(NH_2)$ (M = V, Nb and Ta), is presented in order to probe the efficacy of π-loading (i.e., repeated coordination of strong π-bonding ligands such as imides to a metal) as a strategy for designing more potent methane activators. Several important conclusions were reached. An activation pathway involving C−H addition across the metal−amido bond (i.e., σ-bond metathesis) is disfavored relative to a pathway involving C−H addition across the metal−imido bond (i.e., $[2_\sigma + 2_\pi]$ addition). The $M(=NH)_2(NH_2)$ complexes possess substantially more pyramidal coordination geometries than group IVB imides, $M(NH_2)_2(=NH)$. Comparisons of metal−imido bond lengths for d^0 imido and bis(imido) complexes are consistent with weakening of the metal−imido linkage, an important component of the π-loading strategy. Calculated methane elimination barriers ($\Delta H^{\ddagger}_{\mathrm{elim}}$) also show reasonable agreement with experiment and reproduce trends as a function of the metal. Methane activation by $M(=NH)_2(NH_2)$ (M = V, Nb, Ta) is ~10 kcal mol^{-1} more exothermic, versus separated reactants, than the analogous reaction for $M(NH_2)_2(=NH)$ (M = Ti, Zr, Hf), a result consistent with the π-loading hypothesis. Despite a range of reaction enthalpies for methane activation by group VB bis(imido) and group IVB imido complexes there are only small changes in methane activation enthalpies ($\Delta H^{\ddagger}_{\mathrm{act}}$) for these reactions; the average $\Delta H^{\ddagger}_{\mathrm{act}}$ value for the complexes studied is 17.6 ± 2.5 kcal mol^{-1}, in line with limited enthalpic data for C−H activation by transition-metal−ligand multiple bonds. The insensitivity of the activation barrier to activation enthalpy is, of course, opposite to what is desired from the π-loading strategy.

Introduction

Selective C−H activation is of great importance in the continued search for an efficient methane conversion catalyst.[2] High-valent (d^0) complexes with transition-metal (TM)−nitrogen multiple bonds have recently demonstrated the ability to C−H activate hydrocarbons, including methane.[3−8] Wolczanski et al.[3] have observed methane activation by the group IVB imides $Ti(OSi')_2(=NSi')$ and $Zr(=NSi')(NHSi')_2$ ($Si' = Si(t\text{-}Bu)_3$). Bergman et al. have reported C−H activation of benzene and substituted benzenes by a zirconocene imide.[4] A computational study of H_2 and methane activation by group IVB imides has been published.[5] Experiment and calculation support activation by $[2_\sigma + 2_\pi]$ addition of C−H across a metal−imido π-bond (eq 1).

$$L_nM{=}NR + CH_4 \rightarrow L_nM(CH_3){-}N(H)R \qquad (1)$$

One tactic that has been explored in the search for improved methane activators is π-loading.[8] π-loading entails the use of strongly π-bonding ancillary ligands to reduce the π-bond energy (Π_{MN}) of the activating metal−imido bond. There are three components to the π-loading strategy. First, π-loading will significantly reduce Π_{MN}. Second, π-loading provides a greater driving force in reaction 1. The enthalpy of reaction 1 can be estimated from bond energies (eq 2). If one

$$\Delta H_{\mathrm{rxn}}(1) = \mathrm{BDE}_{M=N} + \mathrm{BDE}_{H_3C-H} - \mathrm{BDE}_{M-CH_3} - \mathrm{BDE}_{HN-H} - \mathrm{BDE}_{M-N} \qquad (2)$$

defines the difference between $\mathrm{BDE}_{M=N}$ and BDE_{M-N} as the MN π-bond energy, then eq 3 (methane and

$$\Delta H_{\mathrm{rxn}}(1) = \Pi_{MN} + 13 - \mathrm{BDE}_{M-CH_3} \qquad (3)$$

amide BDEs: 105 and 92 kcal mol^{-1}, respectively) leads to the reasonable conclusion that lowering Π_{MN} will

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[7] Methane activation by Ta−bis(imide): Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131.

[8] (a) Wigley et al., have observed C−H activation of terminal acetylenes by the PMe_3 adduct of $W(=NAr)_3$ (Ar = 2,6-diisopropylphenyl): Chao, Y. W.; Rodgers, P. M.; Wigley, D. E.; Alexander, S. J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 6326 and personal communication. (b) Smith, D. P.; Allen, K. A.; Carducci, M. D.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 1319. (c) The structural consequences of π-loading in poly(imido) complexes are explored in: Bryan, J. C.; Burrell, A. K.; Miller, M. L.; Smith, W. H.; Burns, C. J.; Sattelberger, A. P. *Polyhedron* **1993**, *12*, 1769.

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make eq 1 more exothermic.[9] The third and most crucial component to the π-loading strategy is that a more exothermic methane activation step will lower the C—H activation barrier, a hypothesis consistent with the well-known Hammond postulate.[10] Replacement of a univalent ancillary ligand (X) in d^0 group IVB imides ($X_2M{=}NR$) with the strong, π-bonding imide should make d^0 group VB bis(imido) complexes ($XM({=}NR)_2$) more π-loaded. Group VB bis(imido) complexes have been the subject of recent experiments.[6,7] Methane C—H activation by V and $Ta({=}NSi')_2(NHSi)$ has been reported by Horton et al.[6] and Schaller and Wolczanski, respectively.[7]

To better understand highly reactive group VB bis(imido) transients, we have undertaken a computational investigation of methane activation by models of the form $M({=}NH)_2(NH_2)$ (M = V, Nb, Ta) (eq 4).

$$M({=}NH)_2(NH_2) + CH_4 \rightarrow M(NH_2)_2({=}NH)(CH_3) \quad (4)$$

Two issues are of prime interest. Reaction surfaces will be compared for C—H addition across metal—imido and metal—amido linkages; the former and latter will be referred to as $[2_\sigma + 2_\pi]$ and σ-bond metathesis pathways, respectively. Additionally, comparison with group IVB imides[5a] ($M(NH_2)_2({=}NH)$) will help shed light on the efficacy of π-loading as a strategy for rational design of more potent methane functionalization catalysts.

Computational Methods

Calculations employ the computational chemistry program GAMESS.[11] An iPSC/860 (Oak Ridge National Laboratories), CM-5 (University of Tennessee—Knoxville), scalable cluster of RISC systems (SCRS), KSR-1, and SP-1 (all at Cornell National Supercomputer Facility), and parallel-RISC cluster (Computational Inorganic Chemistry Lab, University of Memphis) were used as parallel platforms. Calculations also employed vectorized GAMESS on the Cray Y-MP/464 at the National Center for Supercomputer Applications.

Our main approach to the challenges of computational d- and f-block chemistry is the design and testing of effective core potentials (ECPs).[12] Great savings in time, memory, and disk space are effected by replacing core electrons, and basis functions which describe them, with a small number of ECPs. Effective core potentials (ECPs) and valence basis sets are used for heavy atoms, and the −31G basis set is employed for H. ECPs replace the innermost core orbitals for the TMs and all core orbitals for main-group (MG) elements.[12a] Thus, *n*s, *n*p, *n*d, (*n* + 1)s, and (*n* + 1)p are treated explicitly for the d block; for the main group, *n*s and *n*p are treated explicitly.[12a] In the standard implementation, TM valence basis sets are quadruple and triple ζ for the sp and d shells, respectively, while main-group elements have a double-ζ valence basis.[12a] Basis sets for heavy, main-group elements are augmented with a d polarization function.[13] Relativistic effects are incorporated into ECP derivation. Transition metal ECPs are generated from all-electron, Dirac—Fock calculations and thus include Darwin and mass velocity effects, while spin—orbit coupling is averaged out in potential generation. From a chemical standpoint, ECPs afford great leeway in the choice of interesting problems, particularly with respect to assessing the role of the TM, since calculations on congeners within a triad are carried out with near-equal facility.

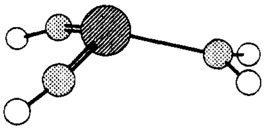
Geometries are optimized at the restricted-Hartree—Fock (RHF) level for closed-shell singlets. Bond lengths and angles for ground-state TM complexes are typically predicted to within several percent of experiment using the present scheme.[14] Electron correlation effects on calculated geometries were assessed in previous studies of H_2 and methane activation/elimination by d^0 imides.[5] A multiconfiguration self-consistent field (MCSCF) study found small changes in stationary point geometries (including TSs) versus the much less computationally demanding RHF wave function; calculated RHF and MCSCF intrinsic reaction coordinates are nearly identical.[5] These calculations point to the appropriateness of a single-determinant description of these and related potential energy surfaces for these d^0 complexes.

Vibrational frequencies are calculated at stationary points to identify them as minima (zero imaginary frequencies) or transition states (one imaginary frequency). Intrinsic stretching frequencies were calculated using the method of Boatz and Gordon.[15a] The intrinsic reaction coordination (IRC) is followed using the Gonzalez—Schlegel algorithm.[15b]

Although geometries are accurately predicted at the RHF level, energetics are expected to be poor if correlation is ignored. For species described well at the RHF level, the correlation contribution is a perturbation to the RHF energy and is calculated using the Møller—Plesset second-order perturbation theory (MP2).[13] An [RHF geometry/MP2 energy] scheme yields good agreement[5a] with experimental data[3] for methane elimination from group IVB methyl amido complexes. Enthalpic data are corrected (using RHF frequencies) for the zero-point energy and from absolute zero to the temperatures at which activation parameters are experimentally determined: 373.15 K (group IVB),[3b] 353.15 K (V),[6] and 453.15 K (Nb and Ta).[7]

Results and Discussion

1. Reactants. The reactants are C_s group VB bis(imido) complexes, $M({=}NH)_2(NH_2)$ (**1**; M = V, Nb, Ta).



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Coordination geometries of TMs in **1** are distorted from trigonal planar (TP3) toward pyramidal (PY3) (Table 1). The V complex is closer to TP3 (Table 1) than the Nb and Ta congeners but still substantially more pyramidal than group IVB imides ($M(NH_2)_2({=}NH)$). Pyramidalization is a soft mode; e.g., the C_s ground state of $Ta({=}NH)_2(NH_2)$ is only 3 kcal mol^{-1} lower (at the RHF level) in energy than the TP3 (C_{2v}) transition state. Structural data for $M(NH_2)({=}NH)_2$ suggest that π-load-

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[9] (a) Nitrogen—hydrogen bond energies for NH_x (x = 1—3) are reported in: Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 3008. (b) *CRC Handbook*, 64th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1983; p F-187. (c) Defining Π_{MN} as the difference between $BDE_{M=N}$ and BDE_{M-N} is somewhat simplistic, since the σ-bond will change as the bond length changes. Gas-phase data for metal—ligand bond energies of $M^+{-}NH_2$ and $M^+{=}NH$ (M = Ti, V) yield $\Pi_{MN} \approx 1.1$ eV;[9a] the paucity of thermochemical data does not allow one to infer how this might carry over to coordinatively saturated TM complexes.

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[14] Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879.

[15] (a) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 1819. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

Table 1. Bis(imido) Amido Reactants[a]

	$V(=NH)_2(NH_2)$	$Nb(=NH)_2(NH_2)$	$Ta(=NH)_2(NH_2)$
M=N (Å)	1.64	1.78	1.79
M−N (Å)	1.86	2.02	2.00
N=M=N (deg)	120	117	118
N−M=N (deg)	119	114	112
β^b (deg)	13	40	42
$q(M)^c$	+0.87	+1.48	+1.55
$q(=N)$	−0.57	−0.81	−0.85
$q(-N)$	−0.82	−0.95	−0.97
$\nu_{M=N}$ (cm^{-1}) ($k_{M=N}$ (mdyn Å^{-1}))^d	1094 (7.75)	1007 (7.26)	1016 (7.91)
ν_{M-N} (cm^{-1}) (k_{M-N} (mdyn Å^{-1}))	780 (3.93)	686 (3.38)	693 (3.68)

[a] Geometries of the complexes (**1**) were calculated at the RHF level as described in Computational Methods. [b] This is the acute angle subtended by the N=M=N plane and the M−N vector. For a perfectly trigonal-planar complex $\beta = 0°$; as β increases the metal coordination environment becomes more pyramidal. [c] These are Mulliken charges on the metal (q(M)), imide N (q(=N)) and imide N (q(−N)). [d] The intrinsic stretching frequencies (and the attendant force constants) were calculated using the method of Boatz and Gordon.[15a]

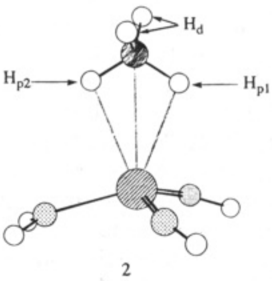
ing leads to greater pyramidalization at the TM in these three-coordinate transients (compare group IVB imido[5a] and group VB bis(imido) complexes), which can be beneficial for C—H activation by making the TM more accessible for substrate binding.[16] In a previous study of methane coordination by d^0 imides, pyramidalization was also found to produce beneficial electronic results—it makes the complex a better Lewis acid (by lowering in energy the metal-based lowest unoccupied molecular orbital which is d_{z^2} in character with some s and p character), crucial for coordination of a very weak Lewis base such as methane.[17]

Metal−imido bond lengths in **1** are 1.64 Å (V), 1.78 Å (Nb), and 1.79 Å (Ta); metal−amido bond lengths are 1.86 Å (V), 2.02 Å (Nb), and 2.00 Å (Ta) (Table 1). In $Ta(py)_2(Me)(=NSi')_2$,[7] Ta−imide = 1.81(1) and 1.82(1) Å, slightly longer than calculated, as expected given the increased coordination number of the bis(pyridine) adduct. The geometry of $Nb(=NH)_2(NH_2)$ is nearly identical with that of the Ta congener, as expected given the similar size and electronegativity of the elements.[18a] $Nb(=N\text{-}2,6\text{-}(i\text{-}Pr)_2C_6H_3)_2(Cl)(PMe_3)_2$ has been structurally characterized: Nb=N = 1.827(5) and 1.819(5) Å.[18b] An anionic bis(imido)vanadium species, $LiV(=NSiMe_3)_2(CH_3)_2$, has very long V−imido bonds (1.705(3) Å); however, the Li counterion interacts strongly with both imido N atoms, most certainly lengthening them versus hypothetical cation-free values.[6a] V−imido and V−amido bonds in four-coordinate $[(SiNH)(SiN)V\{\eta^1{:}\eta^3\text{-}CH_2C(Me)_2Si(t\text{-}Bu)_2NC(R')CHR'\}]$ are 1.676(3) and 1.883(4) Å, respectively, in excellent agreement with calculated values: V−imide = 1.64 Å and V−amide = 1.86 Å (Table 1).[6c]

It is interesting to compare calculated structural data for d^0 group VB bis(imido) and d^0 group IVB mono(imido) complexes. Metal−imido bond lengths for $M(NH_2)_2(=NH)$ are 1.66 Å (Ti), 1.83 Å (Zr), and 1.82 Å (Hf), and metal−amido bond lengths are 1.93 Å (Ti), 2.10 Å (Zr), and 2.07 Å (Hf), in good agreement with experiment.[14] The M−amido bond lengths in bis(imido) complexes **1** are 0.07 Å (Ti−V), 0.08 Å (Zr−Nb), and 0.07 Å (Hf−Ta), shorter than the M−amido bond lengths in their bis(amido) imido counterparts. Calculated differences in M−amido bond lengths are closer to the differences in their covalent radii ($R_{cov}(Ti) - R_{cov}(V) = 0.07$ Å; $R_{cov}(Zr) - R_{cov}(Nb) = 0.09$ Å; $R_{cov}(Hf) - R_{cov}(Ta) = 0.11$ Å[19]) than for the M−imido linkages: 0.02 Å (Ti−V), 0.05 Å (Zr−Nb) and 0.03 Å (Hf−Ta). The data are consistent with the hypothesis that replacing an amido (NH_2) with an imido (NH) ligand in these d^0 three-coordinate complexes leads to increased competition for M dπ−N$_{imido}$ pπ bonding between imido ligands and, hence, bonds in **1** which are longer than expected from consideration of relative covalent radii of the TMs. The calculated metric data are thus consistent with the notion that π-loading the metal center (in this case by going from $M(NH_2)_2(=NH)$ to $M(NH_2)(=NH)_2$) does work to weaken the metal−imido linkage. It seems reasonable to assume that the majority of these effects will be exerted on the metal−imido π-bond.[9c] An ECP study of TM−imido bonding[14] showed the π-bond to be much more susceptible to changes in the chemical environment than the σ-bond.

2. Initial Substrate−Complex Interaction. Weakly bound complexes between alkane substrates and C—H-activating complexes have been the subject of intense experimental investigation and speculation.[7,20] A computational investigation of methane adducts of d^0 imido complexes has been reported.[17] Alkane adducts are intermolecular analogues of agostic complexes[21] and thus can be envisaged as important intermediates along the C—H activation reaction path. The role, indeed the existence, of d^0 methane adducts is far from clear, making them ideal computational subjects.

Calculated minima for methane adducts of $M(NH_2)(=NH)$ are C_s (**2** and Table 2), with one C—H bond bisecting the N=M=N angle. There is little change in geometries of bis(imido) and methane fragments versus free compounds. The V coordination environment does



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[16] The powerful coordinating ability of the three-coordinate transients is clearly supported by their observed chemistry. The $V(=NSi')_2(NHSi')$ complex has only been isolated as an ether complex,[6b,c] while the larger Ta center allows its analogue to coordinate two pyridine ligands.[7] Wigley et al.[8] have characterized Nb and Ta bis(imido) complexes; in these cases the replacement of the Si′ substituent with less bulky 2,6-diisopropylphenyl groups allows for coordination of two amine ligands.

[17] (a) Cundari, T. R. *Organometallics* **1993**, *12*, 1998. (b) Methane binding enthalpies given here are slightly different than in ref 17a since they were calculated at a different temperature (298.15 K).

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Table 2. Methane Adducts[a,b]

	V	Nb	Ta
$\mathrm{M{\cdots}H_{p1}}$ (Å)	2.39	2.44	2.41
$\mathrm{M{\cdots}H_{p2}}$ (Å)	2.31	2.42	2.37
$\mathrm{M{\cdots}C}$ (Å)	2.76	2.84	2.785
$\mathrm{C-H_{p1}}$ (Å)	1.100	1.105	1.105
$\mathrm{C-H_{p2}}$ (Å)	1.104	1.103	1.106
$\mathrm{H_{p1}-C-H_{p2}}$ (deg)	114	115	116
$\mathrm{C-H_d}$ (Å)	1.095	1.095	1.094
$\mathrm{H_d-C-H_d}$ (deg)	111	111	112
M=N (Å)	1.63	1.79	1.79
M—N (Å)	1.86	2.03	2.01
N=M=N (deg)	116	116	118
N—M=N (deg)	114	113	112

[a] Geometries of methane adducts (**2**) were calculated at the RHF level. [b] Atom definitions for hydrogens (H_{p1}, H_{p2}, and H_d) are given in **2**.

Table 3. Calculated Reaction Energetics[a]

	V	Nb	Ta	Ti	Zr	Hf
ΔH_{add}	−13.2	−11.1	−13.1	−4.0	−6.0	−8.6
$\Delta H^{\ddagger}_{\mathrm{act}}[2_\sigma + 2_\pi]$	18.3	20.7	16.2	18.5	18.2	13.4
$\Delta H^{\ddagger}_{\mathrm{elim}}[2_\sigma + 2_\pi]$	23.6	38.6	42.9	23.3	33.9	38.3
$\Delta H_{\mathrm{rxn}}[2_\sigma + 2_\pi]$	−18.5	−28.5	−39.8	−8.9	−21.7	−33.4
$\Delta H^{\ddagger}_{\mathrm{act}}$[SBM]	21.7	26.2	26.4			
$\Delta H^{\ddagger}_{\mathrm{elim}}$[SBM]	22.6	27.4	29.6			
ΔH_{rxn}[SBM]	−14.1	−11.8	−16.3			

[a] Reaction enthalpies (in kcal $\mathrm{mol^{-1}}$) were determined using MP2 energies at RHF stationary points. Enthalpies are corrected for the zero-point energy and take into account the enthalpy change upon going from absolute zero to some finite temperature (see Computational Methods). ΔH_{add} is the binding energy of the methane adducts (**2**) relative to separated imido and methane reactants, $\Delta H^{\ddagger}_{\mathrm{act}}$ is the C—H activation barrier relative to the adduct, $\Delta H^{\ddagger}_{\mathrm{elim}}$ is the methane elimination barrier for **3** and **5a** and ΔH_{rxn} is the reaction enthalpy, versus separated reactants, for the $[2\sigma + 2\pi]$ and σ-bond metathesis (SBM) pathways.

become somewhat more pyramidal; Nb and Ta analogues which are quite pyramidal when isolated remain pyramidal in the adduct. Adducts **2** can be described as edge-coordinated, since the $\mathrm{M{\cdots}H_{proximal}}$ distances are nearly equivalent. Methane adducts of d^0 group IVB imido and group VIB tris(imido) complexes are more accurately described as η^2-CH coordinated, since they possess much different $\mathrm{M-H_{proximal}}$ distances.[17] However, in previous research it has been found that a variety of coordination modes of methane to metal complexes are very close in energy, so that a methane adduct can be expected to be quite fluxional.[17,22]

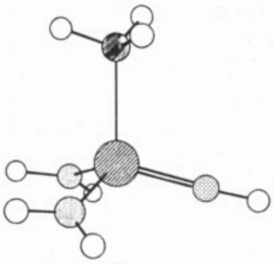
Enthalpies of adduct formation (ΔH_{add}) between $\mathrm{M(NH_2)({=}NH)_2}$ and methane are given in Table 3 for M = Nb, Ta,[17] along with the previously unpublished value for $\mathrm{V({=}NH)_2(NH_2)}$. Methane binding enthalpies are also given in Table 3 for Ti-triad bis(amido) imido complexes.[17] Calculated ΔH_{add} values are sizable for the pyramidal bis(imido) complexes, much larger than those found for trigonal-planar group IVB imides (Table 3). Calculated ΔH_{add} values range from −11.1 kcal $\mathrm{mol^{-1}}$ for $\mathrm{Nb({=}NH)_2(NH_2)}$ to −13.2 kcal $\mathrm{mol^{-1}}$ for $\mathrm{V({=}NH)_2(NH_2)}$, comparable to experimental estimates, e.g. 10 kcal $\mathrm{mol^{-1}}$ for CpIr(CO)−alkane adducts[20a] and ≥10 kcal $\mathrm{mol^{-1}}$ for $\mathrm{Zn^+}$ (and $\mathrm{Mn^+}$) and methane.[20c] The binding enthalpy of H_2 in Kubas' complex is estimated at ~15 kcal $\mathrm{mol^{-1}}$ from experiment and calculation.[23] Thus, ΔH_{add} values for $\mathrm{M({=}NH)_2(NH_2)}$ are consistent with such experimental estimates as are available. Furthermore, calculated ΔH_{add} values (Table 3) are exothermic enough to suggest that even with an unfavorable $T\Delta S$ term methane coordination to a d^0 group VB bis(imide) may be exergonic. Thus, the computations indicate that a search for an elusive d^0 methane adduct may be profitable for this family of bis(imido) complexes.[6,7]

Table 4. Bis(amido) Products[a]

	$\mathrm{V(NH_2)_2}$-$\mathrm{({=}NH)(CH_3)}$	$\mathrm{Nb(NH_2)_2}$-$\mathrm{({=}NH)(CH_3)}$	$\mathrm{Ta(NH_2)_2}$-$\mathrm{({=}NH)(CH_3)}$
M=N (Å)	1.60	1.75	1.75
M—N (Å)	1.85	2.01	1.99
M—C (Å)	2.03	2.21	2.20
C—M—N (deg)	105	107	107
C—M=N (deg)	103	106	107
N—M=N (deg)	112	110	116
N—M—N (deg)	118	116	110
q(M)	+0.33	+1.27	+1.27
q(=N)	−0.48	−0.75	−0.80
q(−N)	−0.79	−0.95	−0.98
$\nu_{\mathrm{M=N}}$ ($\mathrm{cm^{-1}}$) ($k_{\mathrm{M=N}}$ (mdyn $\mathrm{Å^{-1}}$))	772 (3.85)	694 (3.45)	691 (3.66)
$\nu_{\mathrm{M-N}}$ ($\mathrm{cm^{-1}}$) ($k_{\mathrm{M-N}}$ (mdyn $\mathrm{Å^{-1}}$))	1185 (9.09)	1088 (8.48)	1085 (9.01)

[a] Geometries, atomic charges, and intrinsic frequencies (force constants) were calculated in the same manner as described for the bis(imido) reactants (see Table 1).

3. Products. The product of $[2_\sigma + 2_\pi]$ C—H addition to a metal−imido bond in **1** is the methyl complex $\mathrm{M(NH_2)_2(CH_3)({=}NH)}$ (**3**). Calculated ground states for **3** are C_s. Pertinent metric data are collected in Table 4. The calculated Ta—C bond in $\mathrm{Ta(NH_2)_2({=}NH)(CH_3)}$ is 2.20 Å, in good agreement with the Ta—C value of 2.23(2) Å in $\mathrm{Ta({=}NSi)_2(Me)(py)_2}$.[7] The V—C distance in $\mathrm{V(NH_2)_2({=}NH)(CH_3)}$ is 2.03 Å; the structure of $\mathrm{LiV({=}NSiMe_3)_2(CH_3)_2}$ has been reported,[6a] with V—C bond lengths of 2.057(8) and 2.043(5) Å, in excellent agreement with calculation. It is of interest to compare the metal−imido and metal−amido bond lengths in reactants and products. Metal−imido bond lengths in products **3** are 1.60 Å (V), 1.75 Å (Nb), and 1.75 Å (Ta), or 0.03−0.04 Å shorter than metal−imido bond lengths in reactants despite the increased coordination number for products. Metal−amido bond lengths, on the other hand, differ little in reactants or products, indicating that the main M dπ−N pπ competition is between the imido ligands.



3

Comparison of calculated enthalpies for reactions 4 and 5 emphasize the effect of π-loading on the thermodynamics of methane activation. Calculated enthalpies

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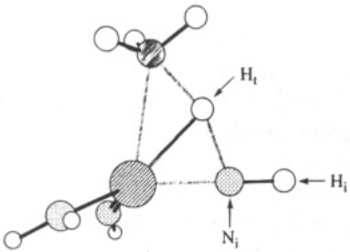
[22] This is most clearly demonstrated in: Koga, N.; Morokuma, K. *J. Chem. Phys.* **1990**, *94*, 5454.

[23] (a) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G. *Organometallics* **1992**, *11*, 3390. (b) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (c) Calculation of relatively weak intermolecular interactions such as in these methane adducts can be affected by the so-called set superposition error. The counterpoise correction (Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553) can be applied, although its application to correlated wave functions can overcompensate for BSSE: *Methods in Computational Chemistry*; Wilson, S., Ed.; Plenum: New York, 1987; p 234.

$$M(NH_2)_2({=}NH) + CH_4 \rightarrow M(NH_2)_3(CH_3) \qquad (5)$$

for reaction 4 are −18.5 kcal mol^{-1} (V), −28.5 kcal mol^{-1} (Nb), and −39.8 kcal mol^{-1} (Ta) (Table 3). The paucity of experimental enthalpic data for TM systems makes it difficult to assess the accuracy of the calculated enthalpies for reaction 4. Using gas-phase data,[24] one can estimate the enthalpy of reaction for $V^+(NH) + CH_4 \rightarrow V^+(NH_2)(CH_3)$ as -11 ± 5 kcal mol^{-1}. Reaction enthalpies for reaction 5 are −8.9 kcal mol^{-1} (Ti), −21.7 kcal mol^{-1} (Zr), and −33.4 kcal mol^{-1} (Hf) (Table 3).[5a] Two trends in reaction enthalpies for methane activation are of importance. First, for group IVB imido and group VB bis(imido) systems the reaction became more exothermic as one descends to the heavier metals in a triad. Second, the group VB reactions are more exothermic than group IVB counterparts by 10 kcal mol^{-1} (Ti versus V), 8 kcal mol^{-1} (Zr versus Nb), and 7 kcal mol^{-1} (Hf versus Ta). Although it remains to be seen if greater driving force carries over into lower C−H activation barriers, the second observation is exciting, since greater exothermicity for the methane activation barrier with greater π-loading is the second component of the strategy.

4. Transition State. Experimental and computational evidence supports a mechanism of activation by d^0 transition-metal complexes which involves a four-center transition state comprising the C−H bond to be activated and the metal−ligand bond doing the activation.[25] Such a transition state is found for methane activation by group VB bis(imido) complexes (**4**), which entails addition of $H_3C{-}H$ to the $M{=}N_i$ (**4**) linkage (Table 5). Calculation of the energy Hessian reveals one and only one imaginary frequency; following the IRC[15b] shows that transition states **4** connect the appropriate reactants (methane adduct **2**) and products ($M(NH_2)_2({=}NH)(CH_3)$ (**3**)). The $M{-}N_i$ bond in **4** is significantly closer in length to the reactant metal−imido bond than the product metal−amido bond (Table 5). On the basis of an analysis of activation parameters, Schaller and Wolczanski[7] conclude that the TS for methane elimination from $Ta({=}NHSi')(NHSi')_2(CH_3)$ is late. Horton et al.[6c] have also deduced a late TS for methane elimination from $V({=}NHSi')(NHSi')_2(CH_3)$. Calculated metric data for the $[2_\sigma + 2_\pi]$ TSs thus support experimental conclusions[6,7] of a late TS for methane elimination to form group VB bis(imido) complexes and, hence, an early TS for the microscopic reverse, i.e. methane activation.



4

The angle about H_t (**4**) is large (Table 5), ranging from 154° (V) to 157° (Nb), leading to a short metal−H_t distance in the TS, the significance of which has been discussed elsewhere.[5,26] Performing an energetic decomposition[15a] of the imaginary frequency (Figure 1) for TSs **4** shows the main component to be $C{-}H_t$ bond stretching and $N_i{-}H_t$ bond compression. A large kinetic isotope effect has been measured ($k_H/k_D \geq 3.4$) experimentally[7] for methane elimination from $Ta(NHSi')_2({=}NSi')(Me)$, supporting a TS in which C−H bond breaking/making is occurring in the rate-determining step and an obtuse angle about the H is transferred in the transition state.[7]

Table 5. $[2_\sigma + 2_\pi]$ Methane Activation Transition State[a]

	V	Nb	Ta
$M{\cdots}C$ (Å)	2.23	2.42	2.41
$C{\cdots}H_t$ (Å)	1.43	1.43	1.41
$H_t{\cdots}N$ (Å)	1.41	1.44	1.47
$M{\cdots}N$ (Å)	1.69	1.85	1.84
$M{=}N$ (Å)	1.62	1.77	1.78
$M{-}N$ (Å)	1.85	2.02	2.00
$M{\cdots}H_t$ (Å)	1.71	1.90	1.91
$M{\cdots}N_i{-}H_i$ (deg)	153	157	159
$C{\cdots}M{\cdots}N$ (deg)	89	81	82
$M{\cdots}N{\cdots}H_t$ (deg)	66	69	70
$N{\cdots}H_t{\cdots}C$ (deg)	154	157	156
$H_t{\cdots}C{\cdots}M$ (deg)	50	52	53
$M{\cdots}H_t{\cdots}C$ (deg)	89.8	91.8	91.7
$\nu_i{}^b$ (cm^{-1})	1878 i	1902 i	1852 i

[a] The geometries of these transition states (**4**) were determined at the RHF level using the ECP and valence basis set scheme described in Computational Methods. [b] The frequency of the imaginary mode of the TS in cm^{-1}.

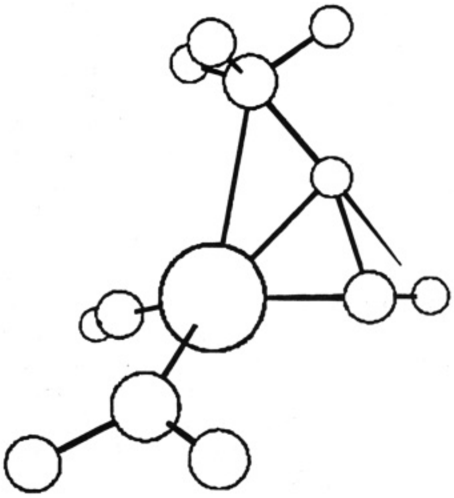


Figure 1. Plot of the imaginary frequency for the $[2_\sigma + 2_\pi]$ TS for methane C−H activation by $Ta({=}NH)_2(NH_2)$ leading to $Ta(NH_2)_2({=}NH)(CH_3)$. The imaginary modes for the V and Nb analogues are identical in composition.

Methane elimination barriers from $M({=}NSi')(NHSi')(CH_3)$ (M = V, Ta) have been reported: $\Delta H^{\ddagger}_{elim} = +29.4 \pm 1.9$ kcal mol^{-1} (M = V); $\Delta G^{\ddagger}_{elim} = 37.7$ kcal mol^{-1} (M = Ta).[7] Using the experimental[6c] $\Delta S^{\ddagger}_{elim}$ value of 9.1 ± 6.0 cal K^{-1} yields $\Delta G^{\ddagger}_{elim} \approx 26.2$ kcal mol^{-1} at 80 °C for the V complex. Calculated $\Delta H^{\ddagger}_{elim}$ values for $M(NH_2)_2({=}NH)(CH_3)$ (M = V, Ta) are 23.6 and 42.9 kcal mol^{-1}, respectively, in good agreement with experiment.[6,7] Methane elimination from $Zr(NHSi')_3(CH_3)$ has $\Delta G^{\ddagger}_{elim}$

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(24) (a) Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 208. (b) $D^0(V^+{=}NH) = 99(4)$ kcal mol^{-1}; $D^0(V^+{-}NH_2) = 73(2)$ kcal mol^{-1}; $D^0(V^+{-}CH_3) = 50(2)$ kcal mol^{-1}.

(25) Rothwell, I. P. In ref 2, p 151.

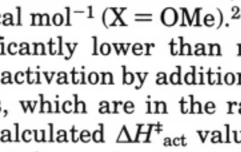
(26) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 4210.

= 28.5 kcal mol^{-1}, while the calculated $\Delta H^{\ddagger}_{\mathrm{elim}}$ for Zr(NH$_2$)$_3$(CH$_3$) is 33.9 kcal mol^{-1}.[5a] Note that $\Delta\Delta G^{\ddagger}_{\mathrm{elim}}$(Ta–Zr) = 9.2 kcal mol^{-1} (experimental), while $\Delta\Delta H^{\ddagger}_{\mathrm{elim}}$(Ta–Zr) = 9.0 kcal mol^{-1}. Calculated enthalpies and experimental free energies of activation show the same trend: Ta > Zr > Hf, although the experimental $\Delta G^{\ddagger}_{\mathrm{elim}}$ values place V and Zr much closer than the calculations do. However, as seen in group IVB imido studies,[5a] the computations reproduce trends in $\Delta H^{\ddagger}_{\mathrm{elim}}$ for related d^0 complexes, supporting the conclusion that the main energetic expense is the bond making/breaking of the M(C)—N(H) → M=N + C—H process[27] and giving added confidence in computational studies of the forward reaction.

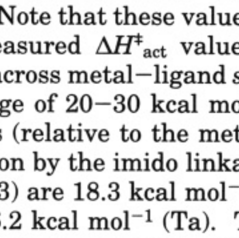
To our knowledge, the only measured activation barrier for C—H activation ($\Delta H^{\ddagger}_{\mathrm{act}}$) by a TM—ligand multiple bond is for intramolecular C—H activation by the Ta=C bond of a methyl groups on an ortho *t*-Bu group in Ta(O-2,6-(*t*-Bu)$_2$-4-X-C$_6$H$_2$)$_2$(CH$_3$)(=CH$_2$): $\Delta H^{\ddagger}_{\mathrm{act}}$ = 14.3 ± 1.0 kcal mol^{-1} (X = H) and $\Delta H^{\ddagger}_{\mathrm{act}}$ = 15.4 ± 1.0 kcal mol^{-1} (X = OMe).[25] Note that these values are significantly lower than measured $\Delta H^{\ddagger}_{\mathrm{act}}$ values for C—H activation by addition across metal—ligand *single* bonds, which are in the range of 20–30 kcal mol^{-1}.[25] The calculated $\Delta H^{\ddagger}_{\mathrm{act}}$ values (relative to the methane adduct) for methane activation by the imido linkage of bis(imido) complexes (Table 3) are 18.3 kcal mol^{-1} (V), 20.7 kcal mol^{-1} (Nb), and 16.2 kcal mol^{-1} (Ta). Thus, calculated $\Delta H^{\ddagger}_{\mathrm{act}}$ values are of a magnitude similar to that measured for the Ta–alkylidene system.[25]

5. Activation by C—H Addition across the Metal–Amido Bond. An alternative activation mechanism is σ-bond metathesis, i.e. C—H addition across the metal–amido linkage to yield M(NH$_3$)(=NH)$_2$(CH$_3$). This step would then be followed by a rapid H-transfer to yield M(NH$_2$)$_2$(=NH)(CH$_3$). Such α-H transfers from amine to imide are known in high-valent tungsten chemistry.[28] In this section we will deal with the σ-bond metathesis step.

The σ-bond metathesis products and transition states have the structures shown in **5a** and **5b**, respectively.



5a



5b

Table 6. Bis(imido) Methyl Amino Products[a]

	V	Nb	Ta
M=N (Å)	1.64	1.79	1.79
M←N (Å)	2.15	2.33	2.29
M—C (Å)	2.06	2.24	2.23
N=M=N (deg)	117	115	118
N=M←N (deg)	108	105	104
N=M—C (Å)	110	110	110
C—M←N (deg)	103	111	111

[a] These products (**5a**) of σ-bond metathesis were determined at the RHF level using the ECP and valence basis set scheme described in Computational Methods.

Table 7. σ-Bond Metathesis Transition State

	V	Nb	Ta
$\mathrm{M{\cdots}N_a}$ (Å)	1.98	2.15	2.12
$\mathrm{N_a{\cdots}H_t}$ (Å)	1.36	1.36	1.37
$\mathrm{H_t{\cdots}C}$ (Å)	1.43	1.44	1.44
$\mathrm{C{\cdots}M}$ (Å)	2.26	2.44	2.42
$\mathrm{M{\cdots}H_t}$ (Å)	1.87	2.06	2.04
$\mathrm{M{\cdots}N_a{\cdots}H_t}$ (deg)	65	67	68
$\mathrm{N_a{\cdots}H_t{\cdots}C}$ (deg)	159	162	160
$\mathrm{H_t{\cdots}C{\cdots}M}$ (deg)	55	57	58
$\mathrm{C{\cdots}M{\cdots}N_a}$ (deg)	80	74	75
$\mathrm{M{\cdots}H_t{\cdots}C}$ (deg)	85.6	86.6	86.0
M=N (Å)	1.63	1.78	1.79
N=M=N (deg)	117	117	120
β_{M}[b] (deg)	34	32	32
β_{Na} (deg)	19	19	20
ν_{i} (cm^{-1})	1965 i	1975 i	1969 i

[a] σ-bond metathesis transition states (**5b**) were calculated at the RHF level using the ECP and valence basis set scheme described in Computational Methods. [b] The flap angles β_{M} and β_{Na} are the acute angles between the M—N$_a$ bond and the N=M=N and H—N$_a$—H planes, respectively.

The σ-bond metathesis products and TSs have C_s symmetry (Tables 6 and 7). Metal–imido and metal–methyl bonds in **5a** (Table 6) remain in very good agreement with experimental models as discussed above. Calculated metal–amino bond lengths are 2.15 Å (V), 2.33 Å (Nb), and 2.29 Å (Ta). Dative Ta←N$_{\mathrm{py}}$ bond lengths in Ta(=NSi′)$_2$Me(py)$_2$ are 2.32(1) and 2.32(2) Å,[7] while the polymer [V(N)Cl$_2$(py)$_2$]$_\infty$ has dative V←N$_{\mathrm{py}}$ bond lengths of 2.135(6) Å.[29] Thus, dative metal–nitrogen bond lengths show good agreement with experimental values.

The amino methyl complexes **5a** are higher in energy than the [2$_\sigma$ + 2$_\pi$] products **3**. As one descends the triads, differences in energy between **5a** and **3** increase: −4.4 kcal mol^{-1} (V), −16.7 kcal mol^{-1} (Nb), −23.5 kcal mol^{-1} (Ta) (Table 3). Calculated reaction enthalpies versus separated reactants for σ-bond metathesis are significantly less exothermic than for the [2$_\sigma$ + 2$_\pi$] pathway: −14.1 kcal mol^{-1} (V), −11.8 kcal mol^{-1} (Nb), −16.3 kcal mol^{-1} (Ta). Thus, the σ-bond metathesis pathway provides less thermodynamic driving force than the [2$_\sigma$ + 2$_\pi$] pathway.

The σ-bond metathesis TSs (**5b**) show some structural resemblance to the [2$_\sigma$ + 2$_\pi$] TSs (**4**); e.g., $\mathrm{C{\cdots}H_t}$ and $\mathrm{M{\cdots}C}$ distances are nearly equivalent (Table 7). Crabtree et al.[30] have defined a reaction coordinate for C—H activation based on a Bürgi–Dunitz analysis[31] of agostic complexes. The reaction coordinate r_{bp} is defined as eqs 6 and 7,

$$d_{\mathrm{bp}} = [d_{\mathrm{MH}}^{\;2} + r^2 d_{\mathrm{CH}} - r(d_{\mathrm{MH}}^{\;2} + d_{\mathrm{CH}}^{\;2} - d_{\mathrm{MC}}^{\;2})]^{1/2} \qquad (6)$$

$$r_{\mathrm{bp}} = d_{\mathrm{bp}} - r_{\mathrm{M}} \qquad (7)$$

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(27) Molecular mechanics studies of full Zr(NHSi′)$_3$(Me) models have shown that the path from ground to transition state is relatively open despite the bulk of the Si(*t*-Bu)$_3$ ligands. This gives added support to the importance of electronic over steric effects in determining the height of the methane activation and elimination activation barriers. Brown, T. L. (Chemistry, Illinois), personal communication.

(28) Chan, D. M. T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251.

(29) Critchlow, S. C.; Lerchan, M. E.; Smith, R. C.; Doherty, N. M. *J. Am. Chem. Soc.* **1988**, *110*, 8071.

(30) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

(31) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.

where d_{MH}, d_{CH}, and d_{MC} are the appropriate bond distances for the metal and C—H bonds being activated in the TS, $r = 0.28$ Å, and r_M is the covalent radius of the metal. Inserting the calculated data ($r_M = 1.22$ Å (V), 1.34 Å (Nb and Ta)) from Tables 5 and 7 into eqs 6 and 7 yields $r_{bp} = 0.54$ Å (V), 0.62 Å (Nb), and 0.62 Å (Ta) for the $[2_\sigma + 2_\pi]$ TSs (**4**) and $r_{bp} = 0.67$ Å (V), 0.73 Å (Nb), and 0.71 Å (Ta) for the σ-bond metathesis TSs (**5b**). Thus, $[2_\sigma + 2_\pi]$ and σ-bond metathesis transition states show r_{bp} in the expected range,[30] with the Burgi–Dunitz analysis indicating that the $[2_\sigma + 2_\pi]$ TSs are somewhat later.

Activation barriers for σ-bond metathesis, relative to the methane adduct, are 21.7 kcal mol^{-1} (V), 26.2 kcal mol^{-1} (Nb), and 26.4 kcal mol^{-1} (Ta), values consistent with experimental activation parameters for C—H addition across d^0 TM—ligand single bonds (*vide supra*).[25] It is expected that C—H addition across a TM—ligand single bond will provide less driving force than C—H addition across the related TM—ligand double bond, if one makes the reasonable assumption that a metal—ligand π-bond is weaker than the analogous σ-bond.[25] As with π-loading, it can be proposed that a lower driving force will yield a higher activation barrier. This assertion is supported by the experimental evidence (C—H activation of a methyl group on the alkoxide ligand by a Ta—C bond in $Ta(O\text{-}2,6\text{-}(t\text{-}Bu)_2C_6H_3)_2(CH_3)_3$ is 26.4 ± 1.0 kcal mol^{-1}, more than 10 kcal mol^{-1} higher (*vide supra*) than intramolecular C—H activation by Ta=C). The present calculations also support this contention; transition states for σ-bond metathesis (**5b**) are 3.4 kcal mol^{-1} (V), 5.5 kcal mol^{-1} (Nb), and 10.2 kcal mol^{-1} (Ta) higher in energy than the analogous $[2_\sigma + 2_\pi]$ TSs (**4**). Thus, the computations support an activation pathway involving methane activation by C—H addition across the metal—imido bond.

In a study of HX (X = H, CH_3, SiH_3, NH_2, Cl) elimination to form d^0 group IVB imides[26] it was found that, for a given metal, a shorter MH_t distance (and hence stronger interaction) in the TS correlated with a lower activation barrier. On the basis of this observation, and an anlaysis of the intrinsic reaction coordinate, it was concluded that MH_t interaction in the TS and along the reaction coordinate plays an important part in making the TS energetically accessible. The present study affords an excellent opportunity to further probe the importance of the MH_t interaction on the nature of the methane activation reaction coordinate. For the $[2_\sigma + 2_\pi]$ TSs (**4**) the MH_t distances are 1.71 Å (V), 1.90 Å (Nb), and 1.91 Å (Ta); these are much shorter than MH_t in the σ-bond metathesis TSs (**5b**): $MH_t = 1.87$ Å (V), 2.06 Å (Nb), 2.04 Å (Ta). If the structural and enthalpic data are coupled, once again[26] it is observed that a longer MH_t (**5b** > **4**) distance in the TS correlates with a higher activation barrier, providing further indications of the importance of the MH_t interaction in energetically modulating these TSs.[26]

Summary and Conclusions

In this paper the results of an effective core potential study of methane activation by group VB bis(imido) complexes, $M(=NH)_2(NH_2)$ (M = V, Nb, Ta), is presented. Several important conclusions were reached as a result of this research.

(1) As in previous research,[5,14,17,26] the present combination of effective core potentials and valence basis sets[12a] shows an excellent capacity for predicting the structure of a variety of organometallic complexes.

(2) The $M(=NH)_2(NH_2)$ complexes (**1**) have a substantially more pyramidal coordination environment about the metal than group IVB imides, $M(NH_2)_2(=NH)$. In a previous study of methane coordination to d^0 imides a pyramidal geometry was found to be crucial for forming a strongly bound methane adduct.[19] Although $V(=NH)_2(NH_2)$ is more planar than the Nb and Ta congeners (Table 1), pyramidalization is a soft mode for all bis(imido) complexes. Thus, even if the activating complex is not pyramidal, a strongly bound methane adduct can form if the complex can be easily perturbed in this fashion.

(3) Comparisons of metal—imido bond lengths for three-coordinate, d^0 group VB bis(imido) and d^0 group IVB mono(imido) complexes show weakening of the metal—imido bond caused by replacing a univalent ancillary ligand (NH_2 in the present case) with the strongly π-bonding imide. Thus, calculations are consistent with one phase of the π-loading strategy, i.e. weakening of the metal—imido linkage as additional imido ligands are coordinated to the metal.

(4) The exothermicity increases for methane addition across the metal—imido bond of the group VB bis(imido) complexes as one descends to heavier TMs in the triad, the same trend noted for group IVB imides.[5a] Also, methane activation by $M(=NH)_2(NH_2)$ is ~10 kcal mol^{-1} more exothermic, versus separated reactants, than the analogous reaction for $M(NH_2)_2(=NH)$ when transition metals in the same row are compared. Thus, the present calculations support the notion that greater driving force for methane activation is gained as one π-loads the metal center.

(5) Calculated TS geometries for $[2_\sigma + 2_\pi]$ pathways support experimental deductions[6,7] for the microscopic reverse of methane activation (i.e., methane elimination). The TS for elimination is late, hence the methane activation TS is early. High kinetic isotope effects are consistent with a rate-determining step in which C—H bond breaking/making is a prime contributor to the TS imaginary frequency and the large angles about the transannular hydrogen (H_t in **4**) in the TS.[7] Calculated methane elimination barriers ($\Delta H^{\ddagger}_{elim}$) also show reasonable agreement with experiment[6,7] and reproduce trends as a function of the metal.

(6) The σ-bond metathesis pathway yields the product $M(=NH)_2(NH_3)(CH_3)$, which is higher in energy than the $[2_\sigma + 2_\pi]$ product. σ-bond metathesis TSs are higher in energy than the TSs for $[2_\sigma + 2_\pi]$ pathways. Both results point to the favorability of the $[2_\sigma + 2_\pi]$ pathway over σ-bond metathesis. Calculated results also support experimental deductions[25] about relative activation barriers for C—H activation by analogous TM—ligand single and double bonds.

(7) As mentioned above, for a given set of complexes ($M(=NH)_2(NH_2)$ or $M(NH_2)_2(=NH)$) reaction enthalpies for eqs 4 and 5 are more exothermic as one descends a triad and for the more π-loaded group VB bis(imido) complexes. Note that if one takes into account the greater ΔH_{add} for bis(imido) complexes (Table 3), differences in driving force are less substantial when reactions between metals in the Ti and V triads are

compared (eqs 8 and 9):

$$[M({=}NH)(NH_2)_2{\cdots}CH_4] \rightarrow M(NH_2)_3(CH_3) \qquad M = \text{Ti triad} \quad (8)$$

$$[M({=}NH)_2(NH_2){\cdots}CH_4] \rightarrow M(NH_2)_2({=}NH)(CH_3) \qquad M = \text{V triad} \quad (9)$$

ΔH_{rxn}(vs adduct) = −4.9 kcal mol^{-1} (Ti), −5.3 kcal mol^{-1} (V), −15.7 kcal mol^{-1} (Zr), −17.4 kcal mol^{-1} (Nb), −24.8 kcal mol^{-1} (Hf), −26.7 kcal mol^{-1} (Ta). All six reactions still remain exothermic and are slightly more exothermic for the group VB bis(imido) species (eq 9). The general trend that driving force increases by ~10 kcal mol^{-1} as one descends a triad is unaffected by adduct formation, since ΔH_{add} values are similar within a triad.

The $\Delta H^{\ddagger}_{act}$ values for reaction 5 (C—H activation by group IVB imides) are 18.5 kcal mol^{-1} (Ti), 18.2 kcal mol^{-1} (Zr), and 13.4 kcal mol^{-1} (Hf).[5a] It remains, therefore, that despite reaction enthalpies which span a range of over 20 kcal mol^{-1} (whether or not adduct formation is taken into account) there are only small changes in $\Delta H^{\ddagger}_{act}$ for this family of related reactions; the average $\Delta H^{\ddagger}_{act}$ value for the six amido imido complexes studied here and elsewhere[5a] is 17.6 ± 2.5 kcal mol^{-1} (Table 3), in line with the admittedly limited enthalpic data[25] for C—H activation by TM—ligand multiple bonds. The insensitivity of the activation barrier to activation enthalpy is, of course, opposite to what is desired from the π-loading strategy.

Although there is no direct connection between reaction enthalpy and reaction barriers, such correlations have been successfully applied by chemists, for example the well-known Hammond postulate[10] and the Evans—Polanyi equation.[32] One caveat in applying such rules is that the reactions being compared must proceed by the same mechanism, which is certainly easier to confirm computationally. Linear relationships of the type shown in eq 10 have been used to rationalize large

$$\Delta H^{\ddagger}_{act} = \alpha(\Delta H_{rxn}) + \beta \qquad (10)$$

bodies of kinetic and thermodynamic data, particularly for radical reactions.[32,33] The parameter α has been interpreted as an indicator of the position of the TS—as α approaches 0, the transition state occurs earlier on the reaction coordinate. In Figure 2 we have plotted ΔH_{rxn} and $\Delta H^{\ddagger}_{act}$, both of them calculated versus a methane adduct. The best-fit line to the data in Figure 2 has a very small slope (α ≈ 0.17), although the low *R* value makes it unwise to overinterpret the α and β. However, inspection of Figure 2 makes it obvious that a linear correlation between increased driving force andactivation barrier for [$2_\sigma + 2_\pi$] C—H activation is poor.

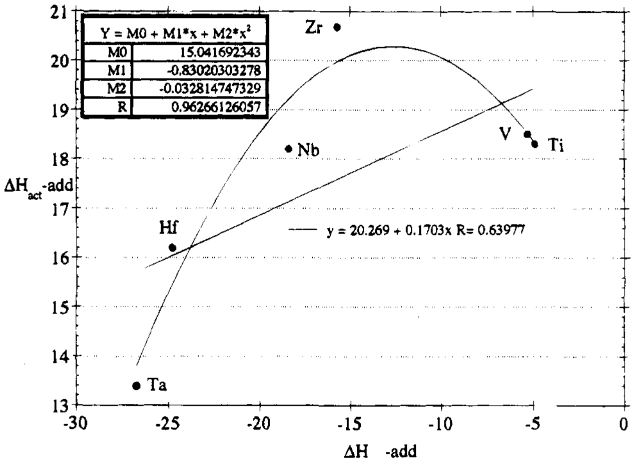

Figure 2. Plots of calculated activation and reaction enthalpies (in kcal mol^{-1}) for the processes $[M({=}NH)_2(NH_2){\cdots}CH_4] \rightarrow [M(NH_2)_2({=}NH)(CH_3)]$ (M = V, Nb, Ta) and $[M({=}NH)(NH_2)_2{\cdots}CH_4] \rightarrow [M(NH_2)_3(CH_3)]$ (M = Ti, Zr, Hf). The best-fit line and quadratic equation are shown.

This initial study of π-loading has yielded interesting insight into the nature of the methane activation potential energy surface and its response to modifications of the chemical environment. Efforts are underway in our laboratories to investigate methane activation by even more heavily π-loaded systems (i.e., tris(imido) complexes), and multiply bonded complexes other than imides ($X_2M{=}E$; E = O, CH_2), as well as degenerate methane-exchange reactions which will permit an analysis of the role of the metal while separating thermodynamic and kinetic factors. Clearly, more data for related methane activation reactions are desired to test correlations such as those in eq 10 and Figure 2 for this technologically important reaction.

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(32) *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vols. I and II.

(33) More sophisticated relationships between activation barriers and reaction energies have been proposed (Murdoch, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 1502), e.g. a quadratic equation. In Figure 2 it can be seen that a best-fit quadratic line correlates the data quite well. However, one would like to have additional data points before attributing extra significance to correlations between $\Delta H^{\ddagger}_{act}$ and ΔH_{rxn}.