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Methane Adducts of d^0 Transition Metal Imido Complexes

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Summary: Ab-initio results are presented for a series of methane adducts of d^0, three-coordinate imido complexes. The presence of weakly bound adducts on the reaction coordinate for CH activation has been inferred from kinetic and spectroscopic data, although their role, if any, in CH activation is not clear. Methane adducts of pyramidal $M(NH_2)({=}NH)_2$ ($M = Nb, Ta$) and $M({=}NH)_3$ ($M = Mo, W$) have appreciable calculated binding enthalpies ($\approx$11–16 kcal mol^{-1}), comparable to values measured for Kubas' H_2 complex. However, planar imidos ($(NH_2)_2M{=}NH$, $M = Ti, Zr$; $(OH)_2Ti{=}NH$) have much smaller binding enthalpies. The calculations suggest a significant covalent contribution to the bonding between substrate and the formally d^0 complex. Upon coordination there is weakening of methane CH bonds, charge transfer from methane to metal, and increased $C^{\delta-}H^{\delta+}$ polarization, all indicative of a role for the adduct in the all-important CH scission step to follow. The calculations suggest that a methane adduct of $Ta({=}NR)_2(NHR)$ or $W({=}NR)_3$ affords the best opportunity to have an appreciable lifetime and form in concentrations large enough to facilitate characterization, perhaps by methods similar to those used in agostic complexes, e.g. IR and NMR analyses of shifts in ν_{CH} and $^1J_{CH}$, respectively.

A detailed understanding of transition metal-mediated CH activation reaction surfaces is crucial to processes like catalytic methane conversion.[2] A growing body of data is available for hydrocarbon interaction with low-valent complexes.[3-5] However, CH activation is also effected by d^0 complexes.[6,7] Kinetic data for alkane activation by d^0 Zr– and Ta–imidos can be interpreted in favor of formation of weakly-bound alkane adducts.[8-10] We report here ab-initio[11-14] results for methane adducts of d^0 imido complexes. Adducts of group VB and VIB imidos have sizable binding enthalpies (>11 kcal mol^{-1}). Marked shifts in methane CH stretching frequencies occur upon adduct formation, suggesting potential experimental probes to elucidate their role in CH activation.

Target imidos are models of putative methane activators and related congeners, Figure 1.[9,15] Imido and methane are first optimized individually at the restricted Hartree–Fock (RHF) level. As found previously,[7c,14] agreement between calculated and experimental geometries is excellent at this level.[12] Optimized reactants are placed with a M···C distance of $\approx$2.75 Å, and the adduct is completely geometry optimized at the RHF level. Reactant fragments in adduct minima change little from isolated optimized geometries. Group IVB imidos distort slightly from trigonal planar (TP3) to pyramidal (PY3) upon methane coordination; group VB and VIB imidos, PY3 when isolated, maintain this geometry.[16] Coordination results in transfer of $\approx$0.1–0.3 electrons from substrate to metal and increased $C^{\delta-}H^{\delta+}$ polarization[17] (calculated from Mulliken population analyses).

Enthalpies of adduct formation (ΔH_{add}), calculated at RHF optimized geometries using MP2 energies, are given in Table I. Larger ΔH_{add} correlate with pyramidal geometries and greater charge transfer. Burkey[5] has measured alkane binding enthalpies for low-valent complexes as high as 17 kcal mol^{-1};[5] the estimated value for CpIr(CO) is 10 kcal mol^{-1}.[4a] A ΔH_{add} of *at least* 10 kcal/mol is estimated[10b] for Zn^+ and Mn^+. Thus, calculated ΔH_{add} values are in accord with experimental estimates. *Group VB and VIB imidos have ΔH_{add} > 11 kcal mol^{-1}, values which suggest that adduct formation may be exergonic even with an unfavorable $T\Delta S$ term.* Using

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[2] *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989.

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[9] Methane activation by bis(imido)amido Ta: Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.*, in press.

[10] (a) Perhaps the best "proof" of the viability of d^0 alkane adducts lies in isolation of *intramolecular* analogues, i.e. agostic complexes. Green, M. L. H.; Brookhart, M.; Wong, L. K. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Adducts between transition metal ions and methane have been studied in the gas phase. Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92.

[11] GAMESS (General Atomic and Molecular Electronic Structure System): Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

[12] As in previous work,[7c14] we have employed relativistic effective core potentials (Krauss, M.; Stevens, W. J.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612) for heavy atoms (double- and triple-ζ valence basis sets for main group and transition metal atoms, respectively) and a −31G basis for H. Main group basis sets are augmented with d polarization functions.[13] Addition of polarization functions ($\xi_p = 1.1$) to H and diffuse functions to all ligand atoms[13] affects the geometry and binding enthalpy of $W({=}NH)_3{\cdots}CH_4$ only slightly.

[13] Pople, J. A.; Hehre, W. J.; Radom, L.; Schleyer, P. v. R. *Ab-Initio Molecular Orbital Theory*; Wiley: New York, 1986.

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[15] (a) Methane activation by $(amido)_2Zr$–imido: Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (b) Methane activation by a $(alkoxy)_2Ti$–imido: Wolczanski, P. T. Personal communication. (c) Wigley (Arizona) has observed CH activation by a $W({=}NR)_3{\cdot}PMe_3$ adduct (personal communication).

[16] When methane coordinates through a tetrahedral face, imaginary frequencies are found leading to η^2 coordination. Face coordinated structures are close in energy to η^2 minima ($\approx$2 kcal mol^{-1} higher at the RHF level).

[17] Increased polarization of CH is in line with the conclusions of Crabtree regarding increased acidity of the H in the CH bond upon adduct formation. This process should facilitate what is (in a formal sense) concerted, heterolytic CH cleavage. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245 (in particular eq 49 and the attendant discussion).

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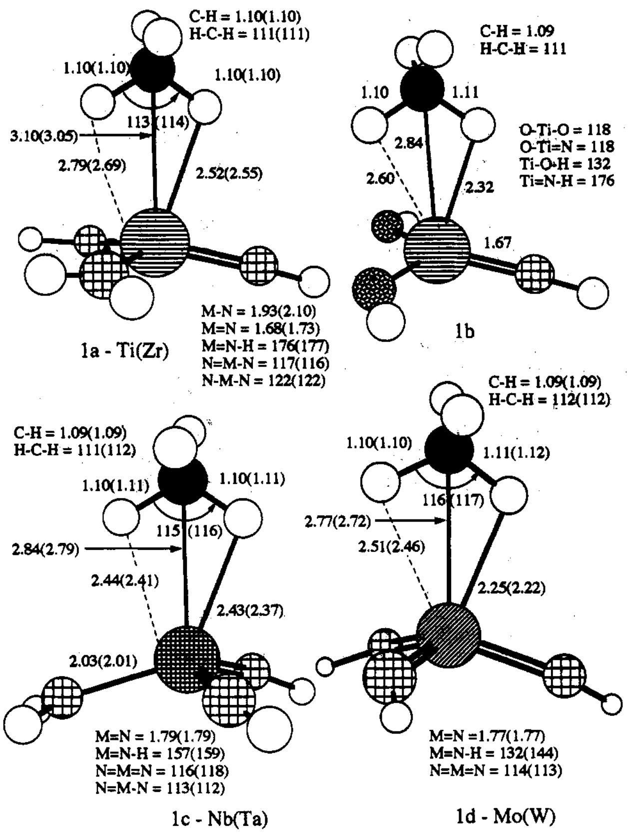


Figure 1. Pertinent metric data (bond lengths in Å; angles in deg) for calculated minima. Group IVB (Ti, Zr), group VB (Nb, Ta), and group VIB (Mo, W) metals are prepresented by circles with horizontal, meshed, and diagonal lines, respectively. Carbon, hydrogen, nitrogen, and oxygen are the shaded, open, cross-hatched, and speckled circles, respectively.

Table I. Methane Binding Enthalpies[a]

complex	d electron count	ΔH_{add} (kcal mol^{-1})	ΔG_{add} (kcal mol^{-1})	q (M)[b]	$q(CH_4)$[c]
$[Ti(NH_2)_2({=}NH)\cdots CH_4]$	d^0	−4.4	1.8	+1.08	+.13
$[Zr(NH_2)_2({=}NH)\cdots CH_4]$	d^0	−6.3	0.4	+1.62	+.15
$[Nb(NH_2)({=}NH)_2\cdots CH_4]$	d^0	−11.1	−4.0	+1.48	+.21
$[Ta(NH_2)({=}NH)_2\cdots CH_4]$	d^0	−13.6	−6.2	+1.55	+.27
$[Mo({=}NH)_3\cdots CH_4]$	d^0	−13.7	−5.8	+1.20	+.26
$[W({=}NH)_3\cdots CH_4]$	d^0	−15.6	−8.4	+1.48	+.31
$[Ti(OH)_2({=}NH)\cdots CH_4]$	d^0	−6.6	1.2	+1.36	+.20
$[W(OH)_2({=}NH)\cdots CH_4]$	d^2	0	8.3	+1.54	+.00
$[Os({=}NH)_2\cdots CH_4]$	d^2	0	5.6	+1.19	+.00

[a] Enthalpies (ΔH_{add}) and free energies (ΔG_{add}) of adduct formation relative to separated reactants were calculated using MP2 energies at RHF optimized geometries and are corrected to 298.15 K and for the zero point energy using methods outlined in ref 13 (pp 251–259). [b] These are the calculated Mulliken atomic charges for the metal in the reactant complex, i.e. before adduct formation. [c] These are the calculated Mulliken charges on the methane fragment in the adduct.

RHF vibrational frequencies to determine $T\Delta S_{add}$ shows that methane coordination is indeed exergonic for group VB bis(imido) and group VIB tris(imido) species, Table I.

We contend that methane–imido interaction is more than simply electrostatic or ion-dipole but that there is substantial covalency. If the bonding were primarily electrostatic or ion-dipole, one would expect better correlation between calculated metal charges and ΔH_{add}, which is not the case, Table I. More convincingly, d^2 electrophiles ($W(OH)_2({=}NH)$[18a] and $Os({=}NH)_3$[18b]) should have substantial ΔH_{add} values if methane–imido interaction were predominantly electrostatic or ion-dipole. This is clearly not so, as revealed by geometry optimization of d^2 adducts, which do not "converge" until M···C distances are >4 Å, and ΔH_{add} = 0 kcal mol^{-1}, indicative of repulsive substrate–complex interaction.

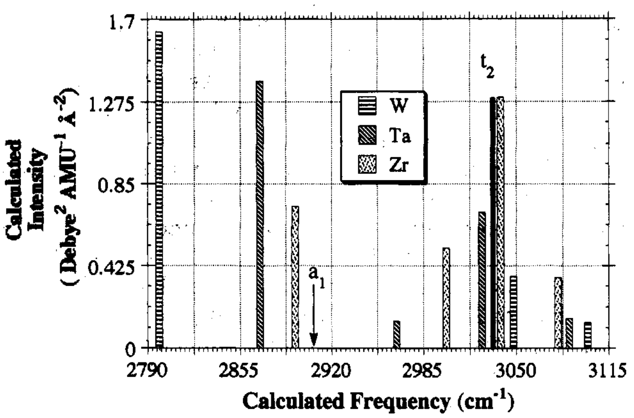
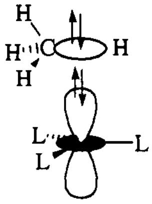


Figure 2. Calculated ν_{CH} (in cm^{-1}) and intensities (in D^2 amu^{-1} Å^{-2}) for methane adducts of $Zr(NH_2)_2({=}NH)$, $Ta({=}NH)_2(NH_2)$, and $W({=}NH)_3$. The arrow at 2908 cm^{-1} and the dark, vertical bar at 3037 cm^{-1} signify the calculated a_1 (intensity = 0) and t_2 stretches (intensity = 1.29) of free methane. One of the CH modes for the $W({=}NH)_3\cdots CH_4$ adduct (at 2972 cm^{-1}) has a calculated intensity of 0.003.

The origin of the repulsive interaction in d^2 adducts is between the filled, metal-based MO (a_1) and σ_{CH}, **1**. Conversely, a_1 is a low-energy acceptor orbital in the formally d^0 complexes,[19] available for bonding with σ_{CH}.



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Perturbation from TP3 to PY3 will lower a_1 in energy as ligand σ donor orbitals move away from the d_{z^2} torus, making the complex a better Lewis acid.[20,21] Two interactions can arise in metal/CH bonding: donation from σ_{CH} to a vacant metal MO and back-donation from an occupied metal MO to σ^*_{CH}.[22] The latter is nonexistent for d^0 complexes. *The present results argue that if* $\sigma_{CH}{}^2 \rightarrow \sigma_M{}^0$ *donation is sizable, there can be an appreciable stabilizing interaction and significant* ΔH_{add} *values.*

Do calculations suggest an experimental probe for study of methane adducts? Agostic CH displays reduced IR

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(18) (a) Eppley, D. F.; Wolczanski, P. T.; Van Duyne, G. D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 584–585. (b) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

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(20) Pyramidalization is due to increased competition among the strongly π-bonding imido ligands for the vacant $d\pi$ orbitals on the metal. Similar arguments have been forwarded for the related polyoxo complexes. Holm, R. H. *Chem. Rev.* **1987**, 1401.

(21) Optimization of a $W({=}NH)_3\cdots CH_4$ adduct in which W is constrained to remain TP3 results in a binding energy of 10 kcal mol^{-1}, 5 kcal mol^{-1} less exothermic than for the PY3 minimum. Group IIIB tris(amido) complexes (D_{3h} minima) have $\Delta H_{add} \approx$ 2 kcal mol^{-1}.

(22) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

stretching frequencies (ν_{CH}) and NMR coupling constants ($^1J_{CH}$) versus "normal" CH bonds, indicating bond weakening.[23] Calculations using the present scheme reproduce ν_{CH} shifts for agostic versus normal CH in Ta–alkylidenes.[14e] The ν_{CH} shifts were calculated at the RHF level and scaled in the usual manner.[24] Calculated ν_{CH} values for a group IVB, VB, and VIB d^0 complex are plotted in Figure 2. Peaks derived from the methane t_2 stretch will probably be obscured by those from the free substrate. Adduct bands derived from the a_1 stretch ($\approx$2800–2900 cm^{-1}, Figure 2) are shifted significantly to lower values, have appreciable intensities, and will clearly be more intense than the IR inactive a_1 stretch of free CH_4.

Methane adducts with large enough ΔH_{add} values to result in appreciable lifetimes and concentrations may be amenable to IR characterization of ν_{CH} shifts (or NMR analysis of $^1J_{CH}$). The experimental H_2 binding energy for Kubas' complex (stable enough to be characterized by neutron diffraction) is $\approx$11 kcal mol^{-1}.[25] Calculations indicate a pyramidal, d^0, three-coordinate bis(imido)amido Ta[9] or tris(imido) W[15c] provides the best opportunity for isolation of a methane adduct of a d^0 complex and further elucidation of their importance in CH activation.

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(23) Schrock, R. R. *Acc. Chem. Res.* 1979, *12*, 98.

(24) (a) Vibrational frequencies for main group bonds can be accurately predicted at the RHF level (when scaled by $\approx$0.9 to account for electron correlation effects). Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. F.; Binkley, J. S.; Frisch, M. J.; Whiteside, R.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Proc. Sanibel Symp.* 1981, *15*, 269. (b) Calculated ν_{CH} shifts for methane are 3144 cm^{-1} (a_1) and 3283 cm^{-1} (t_2) using effective core potential methods outlined in the text, comparing favorably with all-electron values, e.g. 3197 cm^{-1} (a_1) and 3302 cm^{-1} (t_2) for RHF 6-31G*. Scaling the ECP results by 0.925 gives ν_{CH} shifts of 2908 cm^{-1} (a_1) and 3037 cm^{-1} (t_2), compared with experimental values of 2917 cm^{-1} (a_1) and 3019 cm^{-1} (t_2).[13] All ν_{CH} values for adducts are scaled by 0.925.

(25) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G. *Organometallics* 1992, *11*, 3390. Hay has calculated an H_2 binding energy of 17 kcal mol^{-1} for $W(CO)_3(PH_3)_2(H_2)$. Hay, P. J. *J. Am. Chem. Soc.* 1987, *109*, 705.