

Methane activation by tris(imido) complexes: the effect of metal, ligand and d orbital occupation

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Abstract

An effective core potential (ECP) and molecular mechanics (MM) study of methane activation by tris(imido) complexes is presented. The effects of metal, ligand, and d-orbital occupation on the potential energy surface are determined for d^0 systems $M(=NH)_3$ ($M = Mo, W$), $[M(=NH)_3]^-$ ($M = Ta$), and $[M(=NH)_3]^+$ ($M = Tc, Re$), and for d^2 systems $[M(=NH)_3]^-$ ($M = Tc$) and $M(=NH)_3$ ($M = Os$). The d^2 (20 electron) tris(imido) complexes are planar, while d^0 (18 electron) complexes are pyramidal, except for $[Ta(=NH)_3]^-$, which is planar. Methane activation is more exothermic for neutral, tris(imido) complexes than related bis(imido) and mono(imido) complexes. For a series of tris(imido) complexes the reaction enthalpy is more sensitive to d orbital occupation than metal or overall charge on the complex. The enthalpic barrier to methane elimination (microscopic reverse of methane activation) is strongly dependent on the extent of π -loading in the product. Methane elimination barriers (ΔH_{elim}^\ddagger) to form tris(imido) complexes are much higher than ΔH_{elim}^\ddagger to form bis(imido) complexes and mono(imido) complexes. Activation barriers for $[2_\sigma + 2_\pi]$ CH activation (ΔH_{act}^\ddagger) of methane by d^2 imidos are considerably larger (≈ 50 kcal mol⁻¹) than activation by d^0 analogues, owing primarily to overcoming a repulsive methane-complex interaction. The methane-complex interaction increases upon going from anion to cation, $[Ta(=NH)_3]^- < W(=NH)_3 < [Re(=NH)_3]^+$, with $\Delta H_{add} = -8.3, -15.6,$ and -26.3 kcal mol⁻¹, respectively. For this isoelectronic series more negative ΔH_{add} correlate with larger ΔH_{act}^\ddagger . A combination of ECP and MM calculations suggests that an alkane adduct of $[Tc(NAr)_3]^+$ (and its Re analogue) is a plausible experimental target.

Keywords: *Ab-initio*; Catalysis; Transition metals; Imidos; Methane; Bond activation

1. Introduction

Selective CH activation is the first and perhaps most important step in catalytic conversion of methane and other petrochemical feedstocks into functionalized derivatives [1]. Activation of methane and other alkanes by well-characterized organometallics has attracted considerable recent interest [2]. Imido complexes ($L_nM = NR$) have been successfully employed in activation of hydrocarbons including methane. Bergman et al. have demonstrated that zirconocene imidos can CH activate benzene and chlorinated arenes [3]. Wolczanski et al. have extensively probed CH activation by three-coordinate, imido transients such as $(OSi')_2Ti = NSi'$, $(NHSi')_2Zr = NSi'$ and $(NHSi')Ta(=NSi')_2$, $Si' = Si'Bu_3$ [4–6]. Horton et al. have investigated the reactivity of a V analogue of the latter complex,

$(NHSi')V(=NSi')_2$ [7]. Each of the three-coordinate imidos has been shown to CH activate methane [4–7]. Wigley has observed CH activation of terminal alkynes by a PMe_3 adduct of $W(=NAr)_3$, $Ar = 2,6-C_6H_3Pr_2$ [8]. Bercaw et al. have observed methane activation by cationic $[Cp_2^*Ta=N-t-Bu]^+$, $Cp^* = \eta^5-C_5Me_5$ [9]. This experimental research has added much to our understanding of selective hydrocarbon CH activation, although much remains to be done to achieve an intimate knowledge of how modifications to the chemical environment affect the potential energy surface for this important reaction. To this end we have instituted computational investigations of the bonding, structure and reactivity of imido complexes in order to complement current experimental research [10–18].

1.1. Imido bonding

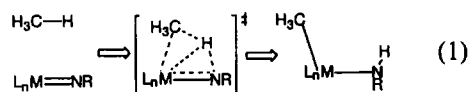
Our earliest studies concentrated on bonding in transition metal (TM) imidos [10]. Using a simple technique

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for extracting resonance structures from a molecular orbital wavefunction the description of the metal–imido bond is seen to be much more complex than previously discussed. To describe the metal–imido bond requires a minimum of eight resonance structures, some of which do not correspond to those previously discussed in the literature. Much of the analysis of the structure and reactivity of imidos has been couched in valence bond (i.e., resonance structure) terms so that calculations were valuable in showing how the description of the metal–imido linkage changed as a function of metal and ancillary ligands. More recently, a joint theory–experiment study of heavily π -loaded $\text{MX}(=\text{NR})_3$ complexes leads to the interesting conclusion that X exerts its influence on the bonding in $\text{MX}(=\text{NR})_3$ through the σ framework [12].

1.2. Mechanism of activation

Theory [10–18] and experiment [2–9] agree about the preferred mechanism for CH activation by imidos $[2_\sigma + 2_\pi]$ addition of C–H across a metal–imido π -bond to produce methyl(amido) (Eq. (1)). Computations clearly support a $[2_\sigma + 2_\pi]$ pathway as preferred over sigma-bond metathesis ($[2_\sigma + 2_\sigma]$) followed by rapid H transfer from an amino to an imido ligand [12,16,19]. Addition of H_2 across the metal–imido ($\text{Zr}=\text{NH}$) bond of $\text{Zr}(\text{NH}_2)_2(=\text{NH})$, a simple model of Wolczanski's Zr–imido transient, was found to have a barrier less than half that for H_2 activation across the metal–amido ($\text{Zr}-\text{NH}_2$) bond [12]. Additionally, computational studies of methane activation by Group VB bis(imido)amido ($\text{M}(=\text{NH})_2(\text{NH}_2)$, $\text{M} = \text{V}, \text{Nb}, \text{Ta}$) showed the $[2_\sigma + 2_\pi]$ pathway to be favored over $[2_\sigma + 2_\sigma]$ addition [16].



1.3. Methane adducts

Given the assumption of a preferred $[2_\sigma + 2_\pi]$ pathway, we have tried to understand the role of geometry, d orbital occupation, metal and coordination number on important points along the methane activation potential energy surface (PES), in particular weakly bound methane–imido adducts [14]. For three-coordinate TM imidos a pyramidal geometry is preferred over a planar geometry for methane coordination. Changes in the metal-based LUMO accompanying pyramidalization of the imido are crucial in making the activating complex more effective at “capturing” a substrate CH bond to form an adduct prior to CH scission. Calculations on

methane adducts also suggest that the bonding of methane to imido has a significant covalent contribution and is not entirely ion-dipole as might have been supposed given the TM's d^0 configuration.

1.4. d orbital occupation

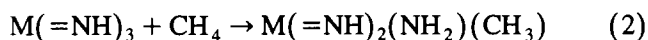
Effective core potential calculations were used to compare $[2_\sigma + 2_\pi]$ and oxidative addition of methane to a d^2 W-imido ($\text{W}(\text{OH})_2(=\text{NH})$) [17,20]. Analysis of the PES suggests that oxidative addition will be favored over $[2 + 2]$ addition for kinetic and thermodynamic reasons. The calculations also indicate a great degree of similarity between the two mechanisms in the early part of the reaction coordinate. Discrimination between the activation mechanisms does not occur until quite close to the transition state (TS).

1.5. Coordination number

Currently, we are probing methane activation by the four-coordinate, d^0 imido $\text{W}(\text{OH})_2(=\text{NH})_2$ [21]. Comparison of d^0 $\text{W}(\text{OH})_2(=\text{NH})_2$ with d^0 $\text{W}(=\text{NH})_3$ and d^2 $\text{W}(\text{OH})_2(=\text{NH})$ will assess the role of coordination number and d orbital occupation on methane activation. With a five-coordinate product (for which there are two low energy polytopes, trigonal bipyramidal and square pyramidal, with two inequivalent coordination sites) multiple paths are expected from $\text{W}(\text{OH})_2(=\text{NH})_2 + \text{CH}_4$ reactants to $\text{W}(\text{OH})_2(=\text{NH})(\text{NH}_2)(\text{CH}_3)$ product. The latter are expected to be close in energy although disparate in geometry. Thus, these studies should yield a detailed understanding of how geometry affects the methane activation PES.

An underlying theme to our research is the fact that studying catalytically important reactions can be used to assess improved computational methods and technology in inorganic chemistry. Catalysis has been labeled a “grand challenge” and “critical technology” to emphasize its importance [22,23]. A National Research Council report [24] states that computation must provide “a framework for understanding... catalyst composition, structure and performance”. Comparison with experiment is a necessary check on the accuracy of computational models. However, computation can provide a window on crucial portions of the catalytic cycle (e.g. transition states and reactive intermediates) not amenable to direct experimental observation. Ideally, computation can be used to predict and identify promising areas for further research, reducing time and cost. Vigorous experimental research in CH activation by imidos makes it most propitious to exploit theory–experiment synergism. A combination of computation and experiment provides a deeper understanding of promising systems than is possible from either acting alone.

In the present contribution previous work on methane activation by imido and bis(imido) complexes is extended to tris(imido) complexes (Eq. (2)) to assess the effect of π -loading on



methane activation PESs [15,16]. Also, this research will permit further probing of the effects of metal, d orbital occupation, and charge on the PES for $[2_\sigma + 2_\pi]$ CH activation by TM imidos.

2. Computational methods

2.1. Effective core potential methods

Our main approach to the challenges of computational TM chemistry entails design, testing and use of effective core potentials (ECPs) [25]. Great savings in time, memory and disk space are effected by replacing the many core electrons, and the basis functions describing them, with a small number of potentials. From a chemical standpoint, ECP methods afford great leeway in the choice of interesting problems, particularly with respect to assessing the role of the central metal, since calculations on congeners within a triad are carried out with near equal facility [26].

All the calculations described herein employ the GAMESS quantum chemistry program package [27]. For effective core potential research at the University of Memphis the following platforms were employed: iPSC/860 (Oak Ridge), Paragon (San Diego Supercomputer Center, SDSC), IBM SP1 and KSR-1 (both at Cornell Theory Center), CM-5 (University of Tennessee-Knoxville and National Center for Supercomputer Applications, NCSA), and the parallel IBM RS-6000 cluster (University of Memphis, Computational Inorganic Chemistry Lab) [28].

Effective core potentials (ECPs) and valence basis sets are used for all heavy atoms and the -31G basis set for H. The ECPs for the main group elements and transition metals are those derived by Stevens, Basch, Krauss and Jasien (SBKJ) [25]. ECPs replace the innermost core orbitals for the TMs and all core orbitals for main-group (MG) elements. Thus, the ns, np, nd, $(n+1)s$ and $(n+1)p$ are treated explicitly for the d-block; for the main-group ns and np are treated explicitly. Transition metal valence basis sets are quadruple and triple zeta for the sp and d shells, respectively, while main-group elements have a double-zeta valence basis. Basis sets for heavy, main-group elements are augmented with a d polarization function.

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 1–3% of experiment using the pre-

sent computational scheme involving complexes in a variety of geometries, formal oxidation states, and with metals from the entire transition series [26]. The energy Hessian is calculated at all stationary points to identify them as minima (zero imaginary vibrational frequencies) or transition states (one imaginary vibrational frequency). Calculation of intrinsic reaction coordinates (IRCs) utilized the Gonzalez–Schlegel algorithm [29].

Although geometries can be accurately predicted at the RHF level, energetics are expected to be poor if electron correlation is ignored. For species described well at the RHF level, the correlation contribution is a perturbation to the RHF energy, and can be calculated using Moller–Plesset second-order perturbation theory (MP2) [30]. Enthalpic data are determined using MP2 energies at RHF optimized geometries and corrected for zero point energy and from absolute zero to 298.15 K. An RHF geometry/MP2 energy scheme yields good agreement with experimental data for methane elimination from Group IVB and Group VB methyl complexes [15,16]. More importantly, an RHF geometry/MP2 energy scheme accurately predicts trends in methane elimination barriers as a function of metal. As the main goal is to understand trends among related complexes and reactions, the RHF geometry/MP2 energy scheme provides an attractive, computationally efficient choice for this research [15,16].

2.2. Molecular mechanics

An alternative approach to describing the structure of chemical systems is molecular mechanics (MM) [31]. Eq. (3) expresses the steric energy of a complex in terms of bond

$$U_{\text{steric}} = U_r + U_\theta + U_\tau + U_{\text{vdw}} \quad (3)$$

stretching (U_r), angle bending (U_θ), torsion about individual bonds (U_τ), and van der Waals interactions between non-bonded atoms (U_{vdw}). The calculations were done on a Macintosh LC 475 using CSC Chem3D Plus [32]. Stretch-bend, cubic, and quartic stretching corrections are ignored [31].

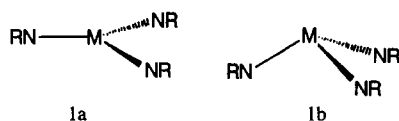
One can conceive of at least three approaches to coupling MM and ECPs as a way of addressing larger, more experimentally relevant organometallics. First, MM and ECPs can be “spliced” together so that parts of a molecule (e.g., the TM and its inner coordination sphere) can be treated quantum mechanically while other parts (e.g., peripheral organic substituents) are treated classically with MM. Second, small model complexes can be ECP optimized, large organic groups grafted on (e.g., $=NH \rightarrow NAr$) and then MM-optimized while other parts of the molecule are frozen at ECP determined values. Third, ECPs can be used to estimate parameters (force constants and equilibrium metric data) to use in a complete MM optimization. The third ap-

proach was used here due to its simplicity, and the success of the ECP scheme for predicting metric data [26].

There are two types of parameters: metal-independent and metal-dependent. For the former, standard MM2 force field parameters were used [31]. Technetium van der Waals parameters (U_{vdw}) are built into the standard force field [32] (essentially a slightly modified version of the MM2 force field [31]). For U_r in Tc-tris(imido) complexes the following scheme was used: X–Tc–Y–Z torsions were set to zero and Tc–X–Y–Z torsions were estimated with $C(sp^3)$ –X–Y–Z parameters. Both of these are frequent simplifications in MM applications for metal complexes [33]. Metal-dependent X–Tc–Y angle-bending parameters (U_θ) were estimated using ECP calculated bond angles and setting the force constant (k_θ) to 0.210 mdyn \AA^{-1} ; Tc–N_{imido}–C_{ipso} bending was described by setting the equilibrium angle to 170° (estimated from X-ray crystallographic analyses of TcR(=NAr)₃ complexes [11,34]) and $k_\theta = 0.10$ mdyn \AA^{-1} . In a previous study of MX(=NH)₃ complexes the present ECP scheme was found to reproduce subtle trends in angles about the metal which are primarily determined by electronic factors [11]. For Tc–ligand bonds ECP data was used to estimate equilibrium bond lengths and force constants. The only changeable parameters in the current MM scheme are k_θ .

3. Results and discussion

3.1. Tris(imido) reactants



Model tris(imido) reactants are either planar (**1a**) or pyramidal (**1b**) complexes; geometric data are summarized in Table 1. Seven model tris(imido) complexes (Mo(=NH)_3 , W(=NH)_3 , $[\text{Ta(=NH)}_3]^-$, $[\text{Tc(=NH)}_3]^+$, $[\text{Re(=NH)}_3]^+$, $[\text{Tc(=NH)}_3]^-$, Os(=NH)_3) were investigated to probe the effects of metal, charge, and d orbital occupation on the PES for methane activation. Additionally, comparison with previous computations on methane activation by imido [15] and bis(imido) [16] complexes will yield further insight into the efficacy of π -loading as a strategy for designing more potent methane activators.

The bonding and structure of tris(imido) complexes have been discussed in a previous survey of TM imido complexes [10] and a joint theory–experiment study of tetrahedral tris(imido) complexes, MX(NR)_3 [11]. Previous studies show the ECP scheme employed here to be

Table 1
Tris(imido) reactants

Complex	Configuration ^a	M=N	BO(M=N) ^b	N=M=N	M=N–H
Mo(=NH)_3	d^0	1.77	1.96	114	133
W(=NH)_3	d^0	1.77	1.86	113	146
$[\text{Ta(=NH)}_3]^-$	d^0	1.85	1.74	120	149
$[\text{Tc(=NH)}_3]^+$	d^0	1.73	2.02	110	133
$[\text{Re(=NH)}_3]^+$	d^0	1.72	1.88	110	144
$[\text{Tc(=NH)}_3]^-$	d^2	1.77	2.00	120	124
Os(=NH)_3	d^2	1.72	1.88	120	137

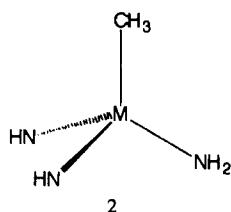
Optimized geometries (bond lengths in \AA ; bond angles in degrees) for the minima (**1**) were determined at the RHF level of theory using the methods outlined in Computational methods.

^a The electronic configuration at the metal (M^{+6}) makes the standard assumption of the imido ligand as NR^{2-} . The d^2 complexes are trigonal planar (C_{3h}) and the d^0 complexes are pyramidal (C_3). The only exception is $[\text{Ta(=NH)}_3]^-$, which is trigonal planar.

^b The metal–imido bond order, BO(M=N) , was determined using the method of Mayer [38].

capable of accurately describing the chemistry of tris(imido) complexes. A pair of three-coordinate, d^2 tris(imido) complexes (Os(NAr)_3 and $[\text{Re(NAr)}_3]^-$) have been characterized by X-ray crystallography [35,36]. In each case a planar geometry about the metal is observed. The preference for a planar geometry in d^2 tris(imido) complexes has been explained by Schrock et al. [35]. In the 20-electron d^2 tris(imido) complex (imido is formally NR^{2-} and a six-electron donor) a pair of electrons is located in a ligand-based nonbonding MO for a planar coordination geometry; hence, the preferred 18-electron arrangement about the metal is maintained. The d^0 complexes are 18-electron complexes thus, there is no impetus to remain planar and they can pyramidalize. One complex which falls outside the norm in terms of expected geometry is $[\text{Ta(=NH)}_3]^-$, **1-Ta**[–]. Although the electronic configuration at the metal is d^0 , **1-Ta**[–] is planar. Out-of-plane bending mode at the metal is quite soft; for example, $[\text{Ta(=NH)}_3]^-$ has an intrinsic frequency [37] for the out-of-plane bending mode of 95 cm^{-1} . As a comparison, the out-of-plane bending mode at boron in BH_3 is calculated at 1200 cm^{-1} using ECP methods. Analysis of the electronic structure of the tris(imido) reactants suggests that **1-Ta**[–] possesses the weakest metal–imido π -bond (as determined by calculation of a TaN bond order of 1.74) [38]. All other tris(imido) complexes (d^0 and d^2) have $M=N_{\text{imido}}$ bond orders of ≥ 1.86 (Table 1). Assuming that differences in the σ framework are minimal among the complexes, it seems reasonable to propose that if there is weaker π -bonding in a d^0 tris(imido), the electronic driving force for pyramidalization is lessened and steric preferences shift the energetic balance towards a planar geometry.

3.2. Bis(imido)amido(methyl) products



The product of $[2\sigma + 2\pi]$ addition to $M(=NH)_3$ is $M(=NH)_2(NH_2)(CH_3)$, **2**. Geometries of complexes **2** are pseudotetrahedral: see Table 2. Distortions from tetrahedral coordination are larger in d^2 than d^0 products (Table 2). The angles between the imido ligands is significantly larger than tetrahedral while the N–M–C angle is greatly reduced [39].

Structural consequences of π -loading in d^0 complexes are highlighted by comparing metal–imido bonds in **1** and **2**. For d^0 complexes, $M=N_{\text{imido}}$ bonds are shorter in four-coordinate, bis(imido) product than three-coordinate, tris(imido) reactant. Shortening of the $M=N_{\text{imido}}$ bond ranges from 0.03 Å (**2-W**, **2-Ta⁻**, **2-Re⁺**) to 0.05 Å (**2-Tc⁺**) for d^0 complexes (Table 2). Significant shortening of $M=N_{\text{imido}}$ bonds, despite an increase in coordination number, is strong indication of the competition for $d\pi$ – $p\pi$ bonding among the three imido ligands. Interestingly, d^2 products show opposite behavior; the $M=N_{\text{imido}}$ bond is longer in d^2 products (**2-Tc⁻** and **2-Os**) than reactants (**1-Tc⁻** and **1-Os**, respectively), but only by 0.01 Å. Metal–imido bond orders are higher (by roughly one-tenth of a bond; see Tables 1 and 2) in products than reactants for d^2 complexes, suggesting that metal–imido π -bonding is weaker in d^2 than d^0 complexes. The latter inference is reasonable since the metal-based frontier MOs (derived from the degenerate e pair in a tetrahedron) are metal–ligand π -antibonding.

One potentially useful parameter for comparing metal–ligand π -bonding in reactants and products is

$M=N_{\text{imido}}-H$. There has been much discussion about correlations between $M=N_{\text{imido}}$ bond lengths and $M=N_{\text{imido}}-R$ angles and its implication for the nature of the metal–imido bond [10,11,42]. Bent (**A**) and linear (**B**) coordination are often taken to represent metal–nitrogen double and triple bonds, respectively. However, close inspection of experimental [43] and computational [11] data suggests that correlations between $M=N_{\text{imido}}-R$ and $M=N_{\text{imido}}$ should be considered qualitative and not quantitative. In the case of the d^0 systems $M=N_{\text{imido}}-H$ angles increase by an average of 15° upon going from **1** to **2**; see Tables 1 and 2. For d^2 complexes, the trend is reversed with products having $M=N_{\text{imido}}-H$ angles $\approx 12^\circ$ less than reactants; see Tables 1 and 2.



Analysis of the molecular and electronic structure of the products (**2**) and comparison with ECP data for tris(imido) reactants (**1**) lead to two conclusions. First, metal–imido bonding in **2** is stronger than in **1**. Second, metal–imido bonding is stronger in d^0 than in d^2 complexes. Although one must consider both σ and π orbitals in describing the metal–imido bond it seems reasonable to propose that changes in electronic structure are more manifest in the π manifold [10]. It would be difficult to quantify these effects, although it seems clear that conversion of an imido ligand in the activating complex to an amido in the product reduces competition for $d\pi$ – $p\pi$ bonding. Thus, the calculations suggest that π -loading may provide extra driving force for methane activation not only by reducing the π -bond energy of the metal–imido bond in the reactant which cleaves the CH bond, but also by affording a relatively greater strengthening of spectator imido ligands in reactants.

Table 2
Bis(imido)amido(methyl) products

Complex	M=N	M–C	M–N	BO(M=N)	BO(M–C)	BO(M–N)	N=M=N	M=N–H	N=M–N	N=M–C	N–M–C
Mo	1.73	2.15	1.96	2.09	1.12	1.06	115	153	112	104	101
W	1.74	2.16	1.96	1.98	1.15	1.11	116	156	111	104	109
Ta ⁻	1.82	2.26	2.05	1.83	0.99	0.86	119	157	110	105	106
Tc ⁺	1.68	2.13	1.88	2.23	1.01	1.33	114	154	116	100	108
Re ⁺	1.69	2.13	1.88	2.01	1.09	1.35	117	158	114	101	107
Tc ⁻	1.78	2.14	2.02	2.00	0.96	0.91	128	114 and 112	108 and 110	106 and 105	93
Os	1.73	2.10	1.93	2.01	1.08	1.18	123	124 and 124	114 and 110	105 and 108	90

Optimized geometries (bond lengths in Å; bond angles in degrees) are C_s RHF minima (**2**); see Computational methods. The C_s plane bisects the $N_{\text{imido}}=M=N_{\text{imido}}$ angle and contains the C–M– N_{amido} plane. The d^2 complexes deviate only slightly from ideal C_s symmetry, as evidenced by near equal $M=N_{\text{imido}}$ bond lengths (≤ 0.01 Å differences) and the small differences in $M=N_{\text{imido}}-H$, $N_{\text{imido}}=M-N_{\text{amido}}$ and $N_{\text{imido}}=M-C$ angles.

Table 3
Methane adducts of tris(imido) complexes

Complex	M...C	C-H _i	M=N	M...H _i	BO(M...C) ^a	BO(C-H _i)	BO(M...H _i)	q(CH ₄)	H _p -C-H _i	M=N-H	N=M=N	N=M...C	M...H _i -C
Mo	2.77	1.11	1.77	2.25	0.23	0.88	0.13	+0.25	116	132	114	104 ± 3	106
W	2.72	1.12	1.77	2.22	0.30	0.85	0.15	+0.31	117	144 ± 1	114	105 ± 3	104
Ta ⁻	3.03	1.10	1.85	2.51	0.13	0.93	0.06	+0.14	113	147 ± 1	118	99 ± 2	107
Tc ⁺	2.66	1.13	1.72	2.06	0.30	0.81	0.19	+0.35	117	130 ± 1	112	106 ± 6	109
Re ⁺	2.64	1.14	1.73	2.05	0.40	0.73	0.25	+0.47	119	142 ± 1	112	106 ± 6	109

Optimized geometries (bond lengths in Å; bond angles in degrees) for the C_v RHF minima (3) were determined as outlined in Computational methods. The d² tris(imido) complexes do not bind methane.

^a Bond orders were determined using the method of Mayer [38].

Table 4
[2_σ + 2_π] transition state

Complex	M...N _i	M...C	M...H _i	N _i ...H _i	C...H _i	M=N	N _i ...M...C	M...N _i ...H _i	M...C...H _i	N _i ...H _i ...C	M...N _i ...H _i	M=N-H
Mo	1.84	2.36	1.84	1.47	1.44	1.75 and 1.76	85	67	51	157	129	139 and 130
W	1.83	2.36	1.87	1.51	1.42	1.75 and 1.76	85	67	52	155	137	159 and 145
Ta ⁻	1.92	2.50	1.95	1.51	1.37	1.83 and 1.84	79	68	51	162	134	163 and 148
Tc ⁺	1.79	2.32	1.80	1.47	1.53	1.70 and 1.71	89	66	51	153	130	138 and 128
Re ⁺	1.79	2.32	1.83	1.52	1.52	1.71 and 1.72	90	67	52	151	139	157 and 143
Tc ⁻	1.91	2.51	2.03	1.36	1.35	1.76 and 1.79	72	75	54	156	120	125 and 110
Os	1.85	2.36	1.96	1.38	1.32	1.72 and 1.76	76	73	56	153	118	132 and 118

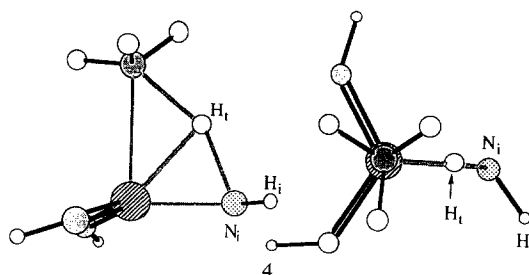
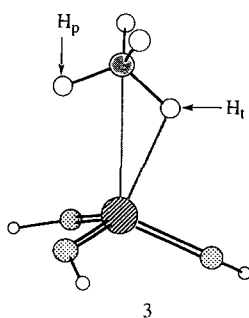
Optimized geometries (bond lengths in Å; bond angles in degrees) for the RHF transition states (4) were determined as outlined in Computational methods. An approximate C_s plane contains the CMN_iH_i plane, although M=N_{imido} bond lengths (0.01–0.04 Å) and M=N_{imido}-H angles (≈ 15°) are inequivalent.

3.3. Initial interaction between products and reactants

The Hoffmann–Saillard model [44] for CH bonding to metals describes the interaction as arising from a synergism between donation from σ_{CH} to a vacant metal-based orbital and backdonation from an occupied metal-based orbital to σ_{CH}^* . The best evidence for adducts between metal complexes and alkanes prior to CH activation is for late, low-valent complexes in which both interactions are present [45]. For d^0 complexes, backdonation is expected to be minimal or non-existent. One can thus ask for d^0 complexes: can σ_{CH} donation be made large enough, through the use of a suitably electrophilic complex, to give an appreciably bound alkane adduct? Model calculations on d^0 amido(imido) complexes [14] and kinetic studies for methane elimination from d^0 Zr complexes [46] suggests that the answer to this question may be yes.

The ECP calculations indicate that methane binding energies increase in the order Group IIIB $\text{M}(\text{NH}_2)_3 < \text{Group IVB } \text{M}(\text{=NH})(\text{NH}_2)_2 < \text{Group VB } \text{M}(\text{=NH})_2(\text{NH}_2) < \text{Group VIB } \text{M}(\text{=NH})_3$ for neutral, d^0 complexes [14]. The present calculations permit us to probe how charge and d orbital occupation modify methane–complex interaction. All d^0 tris(imido) complexes form methane adducts, **3**; Table 3. The geometries of **3** are best described as η^2 -CH coordinated since $\text{M}-\text{H}_p$ and $\text{M}-\text{H}_t$ distances differ by a large amount (≥ 0.2 Å). There are minimal changes in substrate and complex compared to isolated geometries. The most noticeable change is expansion of the $\text{H}_p-\text{C}-\text{H}_t$ angle from 109.5° (free methane) to 113° (**3-Ta⁻**) or 119° (**3-Re⁺**); Table 3. Non-coordinated CH bonds in **3** are 1.09–1.10 Å, thus nearly identical to free methane (1.10 Å).

The coordinated CH bond (CH_t) is 1.10 Å (**3-Ta⁻**) to 1.14 Å (**3-Re⁺**), suggestive of differing strengths of substrate–complex interaction. For the isoelectronic series CH_t bond lengths and H_pCH_t bond angles (see **3**) increase **3-Ta⁻** < **3-W** < **3-Re⁺**. Similarly, CH_t and H_pCH_t are larger for **3-Tc⁺** than **3-Mo**. It is also observed that $\text{H}_p-\text{C}-\text{H}_t$ and $\text{C}-\text{H}_t$ are larger for third row TMs (**3-W** and **3-Re⁺**) versus second row congeners (**3-Mo** and **3-Tc⁺**, respectively); Table 3.



For all cases, the calculated charge [47] on methane (q_{MeH}) is positive ($+0.14 e^-$ (**3-Ta⁻**) to $+0.47 e^-$ (**3-Re⁺**)) and shows very strong linear correlations with $\text{H}_p-\text{C}-\text{H}_t$ and $\text{C}-\text{H}_t$; as the charge on methane becomes more positive $\text{C}-\text{H}_t$ and $\text{H}_p-\text{C}-\text{H}_t$ increase. The $\text{M}\cdots\text{H}_t$, $\text{M}\cdots\text{C}$, and $\text{C}-\text{H}_t$ bond orders in the adduct also show a strong linear correlation with q_{MeH} . As q_{MeH} becomes increasingly positive, $\text{M}\cdots\text{H}_t$ and $\text{M}\cdots\text{C}$ bond orders increase and $\text{C}-\text{H}_t$ bond orders decrease. The $\text{M}\cdots\text{C}$ and $\text{M}\cdots\text{H}_t$ bond orders as well as q_{MeH} increase **3-Ta⁻** < **3-W** < **3-Re⁺** and **3-Mo** < **3-Tc⁺**. The $\text{C}-\text{H}_t$ bond order decreases **3-Ta⁻** > **3-W** > **3-Re⁺** and **3-Mo** > **3-Tc⁺**. The $\text{M}\cdots\text{C}$ and $\text{M}\cdots\text{H}_t$ bond orders are larger for third row tris(imido) complexes than second row congeners, while the $\text{C}-\text{H}_t$ bond order is smaller in the adduct of the heavier metal.

The combination of metric and wavefunction data suggests that methane will coordinate more strongly to a heavier transition metal (third transition series) and a complex with a positive charge. As seen previously [14], d^2 tris(imido) complexes do not bind methane although the metal is highly electrophilic (as evidenced by a large positive charge on the metal [14]). Substrate–complex interaction is repulsive for d^2 imidos, consistent with significant covalent contribution to complex–methane bonding. However, the present study indicates that ion–dipole interactions play a role and can yield an adduct which is more tightly bound and a methane more significantly perturbed from its normal ground state electronic and vibrational structure, properties which could aid experimental characterization of a d^0 methane adduct.

3.4. Transition states

Based on previous computational studies a four-centered, $[2_\sigma + 2_\pi]$ transition state is expected [12,13,15–18]. Indeed, such a transition state, **4**, is found for the systems being studied; Table 4. The transition states all have the general structure shown in **4** (the view on the left is normal to the $\text{MN}_i\text{H}_t\text{C}$ plane; the view on the right is along the MC bond axis).

Transition states **4** show the structural characteristics expected for $[2_\sigma + 2_\pi]$ transition states (Table 4) with

interesting variations due to metal, charge or d orbital occupation. For d^0 complexes, the $M \cdots N_i$ bond in TS **4** is closer in length to a metal–imido bond of tris(imido) reactant (**1**) than the metal–amido bond of the product (**2**). For **4-Mo**, **4-W** and **4-Ta⁻** the $M \cdots N_i$ bond is roughly one-third of the way between $M=N$ in **1** and $M-N$ in **2**. A positive charge moves the imido further (by $\approx 8\%$) towards the metal–amido bond length. For d^2 TSs, $M \cdots N_i$ is relatively longer, being \approx two-thirds of the way towards $M-N$ in the product. The $M \cdots C$ bond in the d^0 (d^2) TSs are $\approx 9\%$ (13%) longer than metal–methyl bonds in product **2**; see Tables 2 and 4.

The lengthening of $C \cdots H_t$ and $N_i \cdots H_t$ bonds versus normal single-bond lengths ($C-H \approx 1.10$ Å, $N-H \approx 1.01$ Å) can be analyzed as a measure of the extent to which CH activation has proceeded in the TS. As $C-H$ lengthens and $N-H$ decreases, the CH activation event can be said to be further along in the TS, i.e. the TS is “later” on the PES. Upon comparing second- and third-transition series analogues (**4-Tc⁺** \rightarrow **4-Re⁺** and **4-Mo** \rightarrow **4-W**) it is seen that $N_i \cdots H_t$ increases and $C \cdots H_t$ decreases, indicating the heavier metals have relatively earlier TSs than lighter congeners. Comparing an isoelectronic series shows the $N_i \cdots H_t$ bond to remain roughly the same while $C \cdots H_t$ lengthens considerably (**4-Ta⁻** (1.37 Å) $<$ **4-W** (1.42 Å) $<$ **4-Re⁺** (1.52 Å)); Table 4. The $N_i \cdots H_t$ bond in **4-Mo** is identical to that in **4-Tc⁺** (1.47 Å) while the $C \cdots H_t$ bond is ≈ 0.1 Å longer for the cation. Thus, metric data for $N_i \cdots H_t$ and $C \cdots H_t$ indicate that a positive charge moves the TS later on the PES. The evidence is less conclusive for d^0 and d^2 analogues (**4-Tc⁺** \rightarrow **4-Tc⁻** and **4-W** \rightarrow **4-Os**) since both $N_i \cdots H_t$ and $C \cdots H_t$ are smaller in the d^2 TSs.

Analysis of the metric data for TSs suggests the following trends as a function of metal, charge and d orbital occupation. First, methane activation TSs are earlier for third row TM complexes compared to second row analogues (**4-Mo** vs. **4-W** and **4-Tc⁺** vs. **4-Re⁺**). Second, a positive charge moves the methane activation TS later on the PES (**4-Mo** vs. **4-Tc⁺** and **4-Ta⁻** vs. **4-W** vs. **4-Re⁺**). It should be noted that the trend is not so clear-cut for **4-Ta⁻** and neutral **4-W** as it is for the isoelectronic neutral and cationic systems. Third, analysis of the TS data is inconclusive about the effect of going from a d^0 tris(imido) to d^2 analogue (**4-Tc⁺** vs. **4-Tc⁻** and **4-W** vs. **4-Os**). In both cases, $C \cdots H_t$ bond lengths are shorter for the d^2 complex, suggestive of an earlier TS for the d^2 complexes. However, $N_i \cdots H_t$ bonds are also shorter for the d^2 complex, suggestive of a later TS for d^2 complexes.

3.5. Energetics

Analysis of the molecular and electronic structure has indicated a variety of trends as a function of metal,

Table 5
Calculated enthalpic data

Complex	ΔH_{add}	$\Delta H_{\text{act}}^\ddagger$	$\Delta H_{\text{elim}}^\ddagger$	ΔH_{rxn}	$\Delta H_{\text{rxn}} - \text{add}$
Mo	-13.7	21.1	55.8	-48.4	-34.7
W	-15.6	16.9	61.6	-60.3	-44.7
Ta ⁻	-8.3	8.1	57.2	-57.4	-49.1
Tc ⁺	-25.7	22.6	64.6	-67.7	-42.0
Re ⁺	-26.3	21.4	68.2	-73.1	-46.8
Tc ⁻	0.0	54.7	52.1	2.5	2.5
Os	0.0	59.5	60.5	-1.0	-1.0

Calculated enthalpic data (in kcal mol⁻¹) for methane activation by tris(imido) complexes. See Scheme 1 for definitions. Data were calculated using MP2 energies at RHF optimized stationary point geometries. Energetic differences are corrected using RHF vibrational frequencies for zero point energy and a temperature above absolute zero (298.15 K).

ligand and d orbital occupation. It will be of great interest to see if differences in structure translate into energetic differences. There are five energetic parameters of potential interest: Scheme 1: ΔH_{rxn} (reaction enthalpy, **1** + $\text{CH}_4 \rightarrow$ **2**), ΔH_{add} (methane adduct binding enthalpy, **1** + $\text{CH}_4 \rightarrow$ **3**), $\Delta H_{\text{act}}^\ddagger$ (enthalpy of activation, **3** \rightarrow **4**), $\Delta H_{\text{elim}}^\ddagger$ (enthalpy of elimination, **2** \rightarrow **4**), and $\Delta H_{\text{rxn}} - \text{add}$ (reaction enthalpy versus adduct, **3** \rightarrow **2**). Calculated enthalpic data are collected in Table 5.

3.5.1. Reaction enthalpies

The enthalpy for reaction 2 can be estimated from bond dissociation energies, Eq. (4).

$$\Delta H_{\text{rxn}} = \text{BE}_{\text{CH}} + \text{BE}_{\text{M=N}} - \text{BE}_{\text{NH}} - \text{BE}_{\text{M-N}} - \text{BE}_{\text{MC}} \quad (4)$$

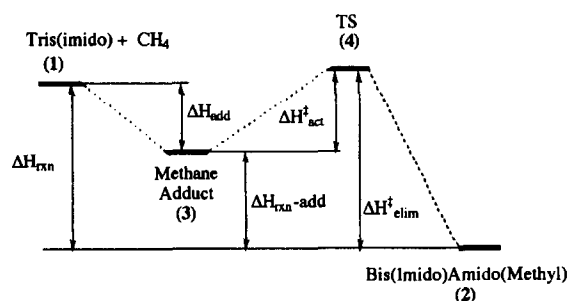
One can define the difference ($\text{BE}_{\text{M=N}} - \text{BE}_{\text{M-N}}$) as a metal–nitrogen π -bond energy (Π_{MN}) (Eq. 5).

$$\Delta H_{\text{rxn}} \approx \text{BE}_{\text{CH}} + \Pi_{\text{MN}} - \text{BE}_{\text{NH}} - \text{BE}_{\text{MC}} \quad (5)$$

Since BE_{CH} and BE_{NH} are constants, the differences among methane activation reactions are the differences in metal–nitrogen π -bond energies and metal–carbon single bond energies (Eq. 6).

$$\Delta \Delta H_{\text{rxn}} \approx \Delta \Pi_{\text{MN}} - \Delta \text{BE}_{\text{MC}} \quad (6)$$

Methane activation becomes more exothermic (whether or not enthalpy of adduct formation is included) for the heaviest member of a series of related d^0 systems which differ only by the metals which are

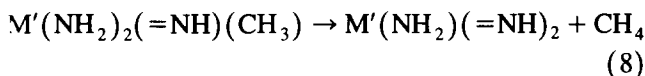
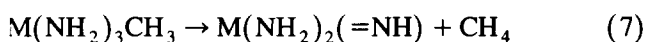


Scheme 1. Qualitative reaction coordinate for **1** + $\text{CH}_4 \rightarrow$ **3** \rightarrow **4** \rightarrow **2**.

members of a TM triad; Table 5. A similar trend has been seen in previous ECP studies of methane activation by TM imidos [15,16], and holds for neutral Mo and W-tris(imido) complexes as well as cationic Tc and Re systems. Two rationalizations for this observation seem plausible. First, M–C bond strengths increase as one goes down a triad. Second, π -bonding becomes weaker as one goes down a triad. Gas- and solution-phase data seem to support the former supposition [48,49]; there is too little evidence about metal–ligand π -bond energies, experimental or theoretical, to assess the latter. Indirect evidence on π -bond energies (e.g., percent lengthening of metal–imido versus metal–amido bond lengths and ratios of metal–imido to metal–amido force constants [15,16,50]) suggests that π -bonding changes little within a triad. Methane activation by d^2 -[Tc(=NH)₃][–] and d^2 -Os(=NH)₃ is close to thermoneutral, and hence much more endothermic than for d^0 analogues. For d^2 complexes, the adduct binding energy is zero so $\Delta H_{\text{rxn}} = \Delta H_{\text{rxn}} - \text{add}$. The paucity of experimental and computational data for trends in metal–ligand bond energies as a function of d orbital occupation does not allow us to make any conclusions at this time.

3.5.2. Methane elimination barriers

Elimination barriers are less sensitive to metal, charge and d orbital occupation ($\Delta H_{\text{elim}}^\ddagger \approx 60 \pm 5 \text{ kcal mol}^{-1}$) than the other enthalpic quantities in Scheme 1 for tris(imido) systems although interesting trends can still be seen; Table 5. Elimination barriers are $\approx 5 \text{ kcal mol}^{-1}$ higher for W and Re⁺ as compared to lighter congeners Mo and Tc⁺, respectively, a trend seen previously in comparing relative methane elimination barriers [15,16]. For example, methane elimination barriers to form imido and bis(imido) complexes (Eqs. (7) and (8)) increase as the metal becomes heavier



within a triad ($\Delta H_{\text{elim}}^\ddagger$ increases M = Ti < Zr < Hf for reaction 7 and M' = V < Nb < Ta for reaction 8). Methane elimination barriers for experimental systems and computational models show close correspondence to theory in terms of relative elimination barriers as a function of TM [5–7]. In terms of absolutes previous work, using the present computational scheme, suggests that calculated $\Delta H_{\text{elim}}^\ddagger$ are high by $\approx 4\text{--}6 \text{ kcal mol}^{-1}$, although going to higher levels of theory reduces $\Delta H_{\text{elim}}^\ddagger$, making them closer to experiment [12–17].

In the analysis of methane elimination barriers reaction 8 always has a higher barrier than reaction 7 for complexes with metals in the same transition series ($\Delta H_{\text{elim}}^\ddagger$ for M = Ti < M' = V, M = Zr < M' = Nb and

M = Hf < M' = Ta), a result consistent with experimental observation [4–7]. The same trend is seen in $\Delta H_{\text{elim}}^\ddagger$ since methane elimination to form Mo and W(=NH)₃ (Table 5) has a higher barrier ($\approx 20 \text{ kcal mol}^{-1}$) than methane elimination to form Nb and Ta(=NH)₂(NH₂), respectively [16]. Schaller and Wolczanski [6] suggest that larger methane elimination barriers for Ta(NHSi')₂(=NSi')Me versus Zr(NHSi')₃Me are due to increased π -loading in the product of the Ta reaction (Ta(=NSi')₂(NHSi')) destabilizing it and giving a higher elimination barrier versus the Zr complex. Extending this logic from methane elimination to form bis(imido) complexes to methane elimination to form tris(imido) complexes should then yield even more π -loading in the product of the latter reaction and an even larger elimination barrier. The ECP calculations support the prediction (Table 5) and hence the proposal of Schaller and Wolczanski [6].

3.5.3. Methane binding energies and CH activation barriers

As seen in a study [17] of W(OH)₂(=NH), d^2 complexes have very large ($\geq 50 \text{ kcal mol}^{-1}$) barriers to [$2\sigma + 2\pi$] CH activation. One can hypothesize that the large barrier to methane CH activation in d^2 complexes is due primarily to overcoming the repulsive methane– d^2 imido interaction to bring the reactants together and permit CH activation. As a simple probe of the preceding hypothesis, **3-Tc⁺** was reduced by two electrons to give “**3-Tc[–]**”. Activation TSs can be considered as generally “early” (a result supported by experimental evidence for methane elimination [5–7], the microscopic reverse of methane activation) and near to an adduct if one is formed. Without allowing the geometry to relax, **3-Tc[–]** is 72 kcal mol^{-1} higher in energy than isolated methane and [Tc(=NH)₃][–] at the MP2 level of theory. Methane and [Tc(=NH)₃][–] in **3-Tc[–]** are 2 kcal mol^{-1} and 19 kcal mol^{-1} , respectively, higher in energy than their ground state equilibrium geometries. If one assumes that $(72 - 2 - 19 =) 51 \text{ kcal mol}^{-1}$ is a measure of an intrinsic electronic barrier to CH activation by d^2 imidos (in addition to energetic contributions from bond breaking and bond making in the [$2\sigma + 2\pi$] TS), then the largest component of the activation barrier is due to repulsion between the methane substrate and the d^2 complex.

The quantities ΔH_{add} and $\Delta H_{\text{act}}^\ddagger$ display a larger dependence on metal and charge for the d^0 complexes, in particular the latter quantity. As the metric data suggested (vide supra) methane–complex interaction increases (ΔH_{add} becomes more exothermic) in the order **1-Ta[–]** < **1-W** < **1-Re⁺**. Similarly, methane binds to **1-Tc⁺** $\approx 12 \text{ kcal mol}^{-1}$ more strongly than to **1-Mo**. Third-row TMs (**1-W** and **1-Re⁺**) are only slightly more tightly bound ($\approx 1\text{--}2 \text{ kcal mol}^{-1}$) than second-row

analogues (**1-Mo** and **1-Tc**⁺). Thus, the analysis based on structural data (in particular, C–H_t and H_p–C–H_t; Table 3) about trends in the strength of the substrate–complex interaction is supported by calculated ΔH_{add} .

What is fascinating is that tris(imido) reactants with the most exothermic ΔH_{add} have the largest $\Delta H_{\text{act}}^{\ddagger}$ (Table 5). For the isoelectronic Ta[−]/W/Re⁺ series ΔH_{add} and $\Delta H_{\text{act}}^{\ddagger}$ parallel each other: $\Delta H_{\text{add}}/\Delta H_{\text{act}}^{\ddagger}$ (kcal mol^{−1}) = −8.3/8.1 ([Ta(=NH)₃][−]), −15.6/16.9 (W(=NH)₃), −26.3/21.4 ([Re(=NH)₃]⁺) (Table 5). The energy of the [2_σ + 2_π] TS relative to separate reactants is roughly constant for the isoelectronic series while the adduct moves up in energy (neutral to anion) or down in energy (neutral to cation) relative to these points. The results suggest that a more positive charge on the activating complex allows it to bind methane more tightly, but that a positive charge does not aid in lowering the intrinsic enthalpic barrier to CH activation (i.e., the barrier relative to separated reactants). In other words, a positive charge makes the adduct a potential energy sink on the reaction coordinate prior to the TS. We propose that ion–dipole interactions are largely responsible for differences in methane binding enthalpy of anionic and cationic systems relative to neutral d⁰ tris(imido) analogues and that the interactions, although large, do not serve to activate methane in ways which facilitate CH activation. In support of the proposal, ECP calculations on a methane adduct of Li⁺ (assumed to be bound primarily through ion–dipole forces) show it to be tightly bound ($\Delta H_{\text{add}}(\text{Li}^+) = -10$ kcal mol^{−1}) compared to neutral TM imidos [51], but the methane fragment in [Li⁺ · CH₄] is negligibly perturbed from its ground state equilibrium structure. These results might be considered discouraging from the point of view of designing more potent methane activators through manipulation of the activating complex to give a more tightly bound adduct. However, results for cationic Tc- or Re-tris(imido) systems are very exciting since they suggest that a methane adduct of these complexes may have some stability (and hence an appreciable lifetime) since the enthalpic barriers from the adduct in the reverse (methane dissociation) and forward (methane CH activation) directions on the reaction coordinate are > 20 kcal mol^{−1}.

3.6. A molecular mechanics/ECP investigation of methane adducts of [M(NAr)₃]⁺

The molecular mechanics (MM) scheme outlined in Computational methods was calibrated against X-ray data for TcMe(NAr)₃ (Fig. 1) [11]. Differences between MM and X-ray data in heavy atoms (H atoms were not located in the experiment) average 0.04 Å (< 2.5%) for bond lengths, 2° for bond angles and 5° for torsional angles. Pertinent MM and experimental [11] data for the

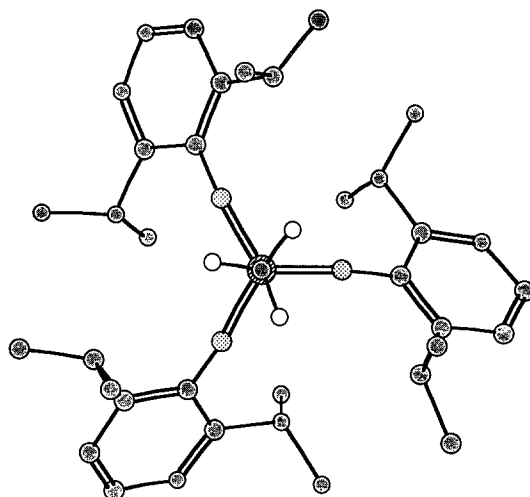


Fig. 1. Molecular mechanics optimized geometry of TcMe(NAr)₃ viewed along the Tc–CH₃ bond axis. Hydrogen atoms on Ar (= 2,6-C₆H₃Pr₂) substituents are removed for clarity.

TcMe(NAr)₃ calibration complex are: TcC = 2.136(17) Å (2.13 Å, MM); TcN = 1.738(11) Å–1.749(13) Å (1.74 Å, MM); CTcN = 101.4(6)–102.9(6)° (105–106°, MM); NTcN = 115.0(5)–116.6(6)° (112–114°); TcNC = 163.9(10)–168.0(9)° (163–166°). Metal-dependent metric parameters are predicted as accurately, if not more so, as those involving organic groups. Thus, the compact MM scheme is able to quickly and accurately reproduce the structure of TcMe(NAr)₃ [52].

As mentioned above, calculation of a large negative ΔH_{add} and a large positive $\Delta H_{\text{act}}^{\ddagger}$ for cationic, tris(imido) methane adducts (**3-Tc**⁺ and **3-Re**⁺) is very exciting, since it suggests adducts that are amenable to experimental study. Steric requirements in [Tc(NH)₃ ··· HCH₃]⁺ and [Tc(NAr)₃ ··· HCH₃]⁺ (and their Re analogues) are obviously very different, so it is reasonable to question whether methane can coordinate to a realistic experimental model such as [M(NAr)₃]⁺. After successfully modeling TcMe(NAr)₃ a methane adduct of [Tc(NAr)₃]⁺ was investigated. The approach used was to coordinate methane to Tc through a pseudo-atom at the centroid (Ct) of the coordinated CH bond. The majority of parameters are identical to those used in modeling TcMe(NAr)₃. Parameters used to describe the interaction of the coordinated CH bond with the metal were determined from the ECP calculation of the parent complex, [Tc(NH)₃ ··· HCH₃]⁺ (**3-Tc**⁺). The metal–centroid force constant was estimated by taking the average of the calculated Tc ··· C and Tc ··· H_t force constants in **3-Tc**⁺. The starting geometry was taken from ECP-optimized **3-Tc**⁺, imido Hs were replaced by Ar (i.e., 2,6-C₆H₃Pr₂, standard bond lengths and angles are used for the organic substituent), and then completely optimizing the structure using the modified MM force field. Parameters used in the MM analysis of

Table 6
Bond stretch and angle bending parameters

Bond ^a	K_r	r_0
C–Tc	1.95	2.14
C–Ct	9.20	0.52
H–Ct	9.20	0.52
N=Tc	6.98	1.73
Tc–Ct	1.45	2.31
Angle ^b	k_θ	θ_0
H–C–Tc	0.36	112.4
H–C–Ct	0.32	190.4
C'–N=Tc	0.10	170.0
C–Tc=N	0.21	100.5
N=Tc=N	0.21	116.8
N=Tc–Ct	0.21	112.0
C–Ct–H	2.00	180.0
C–Ct–Tc	0.30	120.0
H–Ct–Tc	0.20	60.0

These molecular mechanics parameters (in addition to standard force field parameters for organic systems) for bond angles were used in modeling of $\text{TcMe}(\text{NAr})_3$ and $[\text{Tc}(\text{MeH})(\text{NAr})_3]^+$. C = sp^3 or alkane carbon, C' = sp^2 or alkene C, Ct = centroid of coordinated CH bond, H = hydrogen attached to an electroneutral atom, Tc = Tc in a tetrahedral coordination environment, and N = imido N. Metal-dependent parameters were derived as described in Computational methods.

^a Bond stretching terms were described using a potential of the form $f_r \cdot K_r \cdot (r - r_0)^2$ where K_r is the bond force constant (in $\text{mdyn } \text{\AA}^{-1}$), f_r is a constant to convert the potential contribution to kcal mol^{-1} , r is the bond length and r_0 is the equilibrium bond length (both in \AA).

^b The functional form of the angle bending potential is similar to that for bond stretching, i.e. $f_\theta \cdot k_\theta (\theta - \theta_0)^2$ where k_θ is the angular force constant (in $\text{mdyn } \text{\AA} \text{ rad}^{-2}$), f_θ is a constant needed to convert the potential contribution to kcal mol^{-1} , θ is the bond angle and θ_0 is the equilibrium bond angle.

$\text{TcMe}(\text{NAr})_3$ and $[\text{Tc}(\text{MeH})(\text{NAr})_3]^+$ are given in Table 6.

Molecular modeling of the methane adduct $[\text{Tc}(\text{NAr})_3 \cdots \text{HCH}_3]^+$ is very interesting. Upon MM optimization of $[\text{Tc}(\text{NAr})_3 \cdots \text{HCH}_3]^+$ it is found that there are no close contacts between non-coordinated methane protons and the atoms in the Ar substituents. A space-filling model of the MM optimized methane adduct is shown in Fig. 2. A close contact is defined as

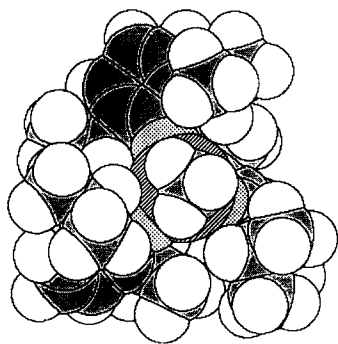


Fig. 2. Space filling model of optimized $[\text{Tc}(\text{MeH})(\text{NAr})_3]^+$.

two non-bonded atoms (not bonded to the same center) being within the sum of their van der Waals radii ($r_{\text{vdw}}(\text{C}) = 1.462$; $r_{\text{vdw}}(\text{H}) = 1.135$). Close contacts are usually taken as an indicator of steric congestion. Although the potential energy surfaces have not been exhaustively searched for $\text{Tc}(\text{NAr})_3$ complexes using molecular mechanics, the combination of ECP and MM results show that coordination of methane to a cationic tris(imido) complex of Tc is feasible from both an electronic and steric point of view. Given their similar properties, a related Re complex also would appear to be a worthwhile experimental target for a relatively stable d^0 methane adduct.

4. Summary and conclusion

A study of methane activation by tris(imido) complexes is reported. Analysis of a variety of tris(imido) complexes is used to probe the effect of metal, charge and d orbital occupation on methane CH activation. Additionally, comparison with previous results for methane activation by related imido [15] and bis(imido) [16] complexes is used to assess the effect of π -loading on the reaction. Several interesting conclusions resulted from this research and are summarized below.

(1) Methane activation is more exothermic for neutral, tris(imido) complexes than related bis(imido) and mono(imido) complexes. For a series of tris(imido) complexes the reaction enthalpy (ΔH_{rxn}) is more sensitive to d orbital occupation than the overall charge on the complex. Methane activation is close to thermoneutral for d^2 complexes studied here ($[\text{Tc}(\text{=NH})_3^-$ and $\text{Os}(\text{=NH})_3$) and highly exothermic for d^0 tris(imido) complexes. As seen previously, [15,16] when comparing complexes with a given triad (e.g., Mo vs. $\text{W}(\text{=NH})_3$) the reaction becomes more exothermic as one descends to heavier TMs in a triad. A thermochemical analysis suggests that differences in methane activation enthalpies are related to differences in metal–methyl and metal–nitrogen π -bond energies. However, more computational and experimental determination of these quantities is needed, in particular metal–ligand π -bond energies.

(2) Barriers to methane elimination, the microscopic reverse of methane activation, to form tris(imido) complexes depend very little on metal, charge and d orbital occupation. However, methane elimination barriers to form Group VIB tris(imido) complexes are significantly higher than those to form related Group VB bis(imido) [16] and Group IVB imido [15] complexes. Schaller and Wolczanski [6] have proposed for the latter two cases that higher methane elimination barriers are due to increased π -loading in the products as imido replaces amido ligands, destabilizing the product and driving the energy of the transition state higher. Computations sup-

port their contention and suggest that the Schaller–Wolczanski hypothesis can be extended to methane elimination to form tris(imido) complexes.

(3) Activation barriers for $[2_\sigma + 2_\pi]$ CH activation of methane by d^2 imidos are considerably larger (≈ 40 – 50 kcal mol $^{-1}$) than activation by analogous d^0 complexes. Calculations on methane adducts of d^0 -[Tc(=NH) $_3$] $^+$ and d^2 -[Tc(=NH) $_3$] $^-$ indicate that the largest part of the barrier is due to overcoming the repulsive methane–complex interaction when the complex has a d^2 configuration at the metal. The present calculations were important in outlining another important role for a methane adduct in CH activation (above and beyond roles described previously [10–18] such as orienting, polarizing and weakening the CH bond prior to activation). Adduct formation serves to get the substrate and complex close enough to react and minimizes the energetic expenditure needed to get reactants and products to a point on the PES close to the TS so CH activation can occur.

(4) Calculations show that methane can coordinate to a d^0 tris(imido) whether it is neutral, anionic or cationic, while interactions between d^2 imidos and methane are repulsive. Both results are consistent with previous conclusions regarding significant covalent contribution to the binding of methane to d^0 organometallic complexes [14]. Calculated metric and enthalpic data (ΔH_{add}) indicate that positive and negative charges strengthen and weaken, respectively, the bonding between methane and the d^0 -tris(imido). Analysis suggests that changes in ΔH_{add} as a function of charge are due to changes in ion–dipole interactions (which do not serve to activate methane and facilitate CH scission) while covalent interactions remain the same. For an isoelectronic series of complexes ([Ta(=NH) $_3$] $^-$, W(=NH) $_3$ and [Re(=NH) $_3$] $^+$) more negative ΔH_{add} (i.e., a more tightly bound adduct) correlate with larger $\Delta H_{\text{act}}^\ddagger$ (i.e., a larger CH activation barrier from adduct to $[2_\sigma + 2_\pi]$ TS). Hence in terms of facilitating CH activation it is desirable to increase the covalent contribution to methane–substrate bonding. Since a positive charge increases the strength of methane binding to the tris(imido) without a concomitant decrease in the CH activation barrier the adduct is in a potential energy well of > 20 kcal mol $^{-1}$ for cationic Tc and Re-tris(imido) complexes. A combination of ECP studies of the parent complexes and molecular mechanics study complexes suggests that a methane adduct of [Tc(NAr) $_3$] $^+$ (and its Re analogue) may be sufficiently stable, form in appreciable concentrations, and display substantial enough perturbations in the molecular, electronic and vibrational structure of coordinated methane to permit experimental characterization of an elusive methane adduct of a d^0 complex and further elucidation of the role of these transient species in methane activation.

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