Mechanism and Energetics for Dehydrogenation of Methane by Gaseous Iridium Ions

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Ir^+ has been observed as the most efficient transition-metal ion for dehydrogenation of CH_4 in the gas phase. We carried out theoretical studies of the complete reaction profile for this process and find three salient factors responsible for the high reactivity: (i) the ability of Ir^+ to change spin easily, (ii) the strength of the Ir–C and Ir–H bonds, and (iii) the ability of Ir^+ to form up to four covalent bonds. We show that among transition-metal ions Ir^+ is unique in best possessing all three characteristics. The combination of these factors leads to a global minimum for the singlet $Ir(H)_2(CH_2)^+$ structure, which plays an important role in the activation. On the basis of these results, we suggest solution-phase analogues that may also activate CH_4.

1. Introduction

Because of the enormous worldwide reserves of methane (CH_4) and the difficulty associated with its transportation, there is a great deal of interest in finding catalysts to convert this most abundant natural gas to easily transportable liquid fuels. Current techniques generally involve the heterogeneous production of syngas (a mixture of CO and H_2) by reaction of CH_4 and H_2O at high temperatures (>800 °C) over a variety of metal-based catalysts.[1] Further reaction of this syngas over various additional metal catalysts leads to the desired products of either methanol (CH_3OH) or higher hydrocarbons. Despite significant advances, this process is not yet economical and a more direct synthesis route is desired.

Progress on alkane activation and functionalization has been made by organometallic chemists.[2] Development of solution-phase catalysts capable of breaking C–H bonds has proceeded on a number of fronts. The mechanisms of these catalysts generally fall into the categories of σ-bond metathesis, electrophilic displacement, and oxidative addition. Of these, electrophilic displacement reactions involving electron-deficient complexes of Pt(II), for example, are particularly notable in their ability to convert CH_4 to methanol. Unfortunately, these reactions generally lead to low yields and difficulties in making the process catalytic. However, the recent report of an $Hg(II)/H_2SO_4$ catalyst appears to represent a significant advance in this field.[3] The younger field of oxidative-addition-based catalysis involving coordinatively unsaturated Ir(I) complexes (among others) shows promise in the functionalization of alkanes, yet success has so far been limited.[4]

Of primary importance to the development of new heterogeneous and homogeneous catalysts is the understanding of the various factors which contribute to reactivity. For this purpose, studies in the gas phase are useful in providing information on the intrinsic properties of bare metal atoms in the absence of solvent and stabilizing ligands or metal support and surface effects. Under the low-pressure conditions of a Fourier-transform ion cyclotron resonance (FTICR) spectrometer, Irikura and Beauchamp[5] showed that the third-row transition-metal cations are generally much more reactive toward CH_4 in the gas phase than their first- and second-row counterparts. In particular, they found that Ir^+ is 70% efficient in the dehydrogenation of CH_4, whereas the next best ions are Pt^+ (40%), Ta^+ (30%), Os^+ (30%), and W^+ (10%). While the majority of transition metals have been observed to react spontaneously with larger alkanes[6] (for instance, Rh^+ can dehydrogenate C_2H_6 and larger alkanes[7] and Co^+ can dehydrogenate and demethanate C_3H_8 and larger alkanes[8]), the only non-third-row transition metal observed to react with CH_4 under ICR conditions is Zr^+, and the efficiency of this reaction is quite small (1%).[9] The high reactivity of Ir^+ is noteworthy, since this metal has been at the focus of research on alkane activation via oxidative addition.[4]

To garner better insight into such reactions, we carried out theoretical studies of the various steps involved in

$$Ir^+ + CH_4 \rightarrow H_2 + IrCH_2^+ \qquad (1)$$

An understanding of the nature of the potential energy surface makes it clear why Ir^+ is better than any other transition-metal cation at dehydrogenating CH_4. Many of the qualitative features of this potential energy surface

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have been independently verified by Musaev and Morokuma[10] and can be contrasted with the recent study of the $Rh^+ + CH_4$ potential energy surface.[11]

2. Calculational Details

Energetics were obtained using the modified coupled pair functional (MCPF) method[12] for geometries optimized at the Hartree–Fock (HF) level with analytic gradients. A relativistic effective core potential[13] was used to replace all but the valence and 5s/5p outer core electrons of Ir^+ (thus 16 electrons of Ir^+ are considered explicitly). The basis sets were uniformly of triple-ζ plus double-polarization quality. The Ir^+ basis set was from Perry *et al.*,[14] supplemented with two sets of f polarization functions ($\alpha = 0.60$ and $\alpha = 0.20$). The tighter function was optimized for the ^3F (d^8) state of Ir^+ at the Hartree–Fock times singles plus doubles (HFSD) level, while the more diffuse function was optimized for the ground state of IrH^+ at the generalized valence bond (GVB) level. The (11s7p/5s3p) basis set of Huzinaga[15] was used for C, supplemented with two sets of d polarization functions ($\alpha = 0.75$ and $\alpha = 0.08$), the more diffuse function optimized for the polarizability of CH_4. The (6s/3s) basis set of Dunning[16] was used for H, supplemented with two sets of p polarization functions ($\alpha = 1.407$ and $\alpha = 0.388$).[17] For the HF geometry optimization, the Ir^+ f functions were removed, as they have only a minor effect on the uncorrelated wave function.

We find that for stable organometallic complexes the HF wave function leads to optimum geometries in reasonable agreement with experiment. However, HF is poor at describing geometries of transition states. Therefore, we determined transition-state geometries using MCPF wave functions which build in all pairwise electron correlations self-consistently. These transition states correspond to the first and second C–H insertions (structures c and f′ of Figure 1) and were calculated using the following procedure. The newly breaking C–H bond length was fixed at various values, and all other coordinates were optimized at the HF level. (These C–H bond lengths were fixed to 1.3, 1.5, and 1.7 Å for transition state c and 1.5, 1.7, and 1.9 Å for transition state f′.) MCPF calculations were carried out for each of these geometries, and the maximum was identified as the transition state. The singlet–triplet crossings (structures e and g) were found in a similar manner. Since the optimum geometries are different for the singlet and triplet, we determined the weighting of these geometries which leads to the lowest crossing (for e, this is 70% singlet and 30% triplet; for g, only the pure singlet geometries were used).

Even though these calculations include a high level of electron correlation and an extensive basis set, we estimate on the basis of even higher level calculations (on $Ir(CH_4)^+$ and $IrCH_2^+$) that the calculated bond energies are low by 5–10% per metal–ligand bond. Thus, to estimate the exact energies, we corrected the calculated energetics by 3 kcal/mol per metal–ligand bond. These corrections approximately account for the zero-point energy and are used for the potential energy surface of Figure 1.

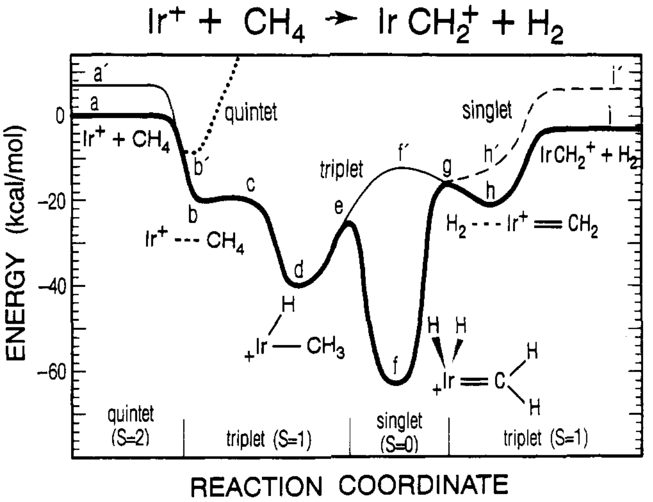

Figure 1. Potential energy surface for the dehydrogenation of CH_4 by Ir^+ (numbers from the last column of Table 1). The heavy solid line indicates the lowest energy pathway with spins as indicated at the bottom. Excited states are indicated with a solid line for triplet, a dashed line for singlet, and a dotted line for quintet.

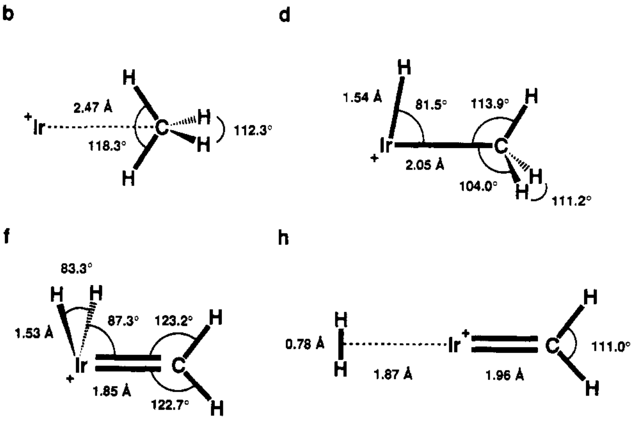

Figure 2. Optimized structures for various reaction intermediates: (b) $Ir(CH_4)^+$; (d) $Ir(H)(CH_3)^+$; (f) $Ir(H)_2(CH_2)^+$; (h) $Ir(H_2)(CH_2)^+$.

All calculations were performed using the MOLECULE/SWEDEN[18] and GVB[19] suites of programs on Alliant FX80/8, FPS 522, and Cray Y-MP computers.

3. Results

The reaction steps for the dehydrogenation of CH_4 are as follows (see Figures 1 and 2).

(i) Initial formation of an η^2-molecular complex, $Ir(CH_4)^+$ (structure b).

(ii) Oxidative addition of a single C–H bond to form the hydridomethyliridium complex, $Ir(H)(CH_3)^+$ (structure d).

(iii) Insertion into a second C–H bond to form the pyramidal dihydridomethylideneiridium complex, $Ir(H)_2(CH_2)^+$ (structure f).

(iv) Coupling of the H–H bond to form the planar (dihydrogen)methylideneiridium complex, $Ir(H_2)(CH_2)^+$ (structure h).

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[19] GVB is a suite of electronic structure programs written at the California Institute of Technology under the supervision of W. A. Goddard III, unpublished.

Table 1. Energetic Data[a] (in kcal/mol) for the Dehydrogenation of CH_4 by Ir^+ (See Figure 1)

point	structure	state	calcd D_e	est D_0
a	$Ir^+ + CH_4$	^5F:^1A_g	0.0	0
a′		^3F:^1A_g	−6.6	−7
		^1D:^1A_g	−26.3	−26
b	$Ir(CH_4)^+$	$^3B_2$	17.4[b]	20
b′		$^5B_1$	6.4	9
c	transition state b–d	$^3A'$	15	20
d	$Ir(H)(CH_3)^+$	$^3A''$	33.7	40
e	S–T crossing d–f	^3A–^1A	19	26
f	$Ir(H)_2(CH_2)^+$	$^1A'$	50.7	63
f′	transition state d–h	^3A	2	11
g	S–T crossing f–h	$^1A'$–$^3A'$	7	16
h	$Ir(H_2)(CH_2)^+$	$^3A_2$	11.9	21
h′		$^1A_1$	2.5	12
i	$H_2 + IrCH_2^+$	$^3A_2$:$^1\Sigma_g^+$	−2.9[c]	3
i′		$^1A_1$:$^1\Sigma_g^+$	−11.7	−6

[a] Total MCPF energies (in hartrees) are −144.260 96 for a and −144.256 35 for i. [b] Improvements in the geometry optimization lead to a calculated D_e = 20.4 kcal/mol. [c] Improvements in the level of electron correlation lead to a calculated D_0 = 2.7 kcal/mol.

(v) Elimination of H_2 (structure i).

The overall exothermicity of the reaction is calculated to be 3 kcal/mol. As indicated in Figure 1, the spin changes from $S = 2$ to $S = 1$ to $S = 0$ and back to $S = 1$ along the reaction path, reflecting the changing number of covalent bonds to Ir^+. This should be facilitated by the strong spin–orbit coupling of the heavy metal. Table 1 summarizes all calculated and corrected energetics. A detailed description of each stage of the reaction follows.

3.1. $Ir(CH_4)^+$. The ground state of Ir^+ is a spin quintet (^5F (s^1d^7)) with a low-lying triplet (^3F (d^8)) state[20] (experimentally, the splitting between the lowest J levels of these states is 6.5 kcal/mol;[21] we calculate a J-averaged splitting of 6.6 kcal/mol). Interaction of CH_4 with ground-state (quintet) Ir^+ leads to a weakly bound C_{2v} η^2-molecular complex (a to b′). However, the triplet and quintet curves cross near the bottom of the quintet well and the change of spin from $S = 2$ to $S = 1$ is expected to be facile and efficient. We calculate that the triplet η^2-molecular complex (C_{2v} $^3B_2$) b is bound by D_e = 17.4 kcal/mol with respect to ground-state $Ir^+ + CH_4$. A more complete geometry optimization (outlined in ref 22) increases the bond strength to D_e = 20.4 kcal/mol. On the other hand, the triplet η^3-molecular complex (C_{3v} ^3E) is 4.0 kcal/mol higher and the quintet (C_{2v} $^5B_1$) state is bound by only 9 kcal/mol.[23] Similar calculations on the $Co(CH_4)^+$ cluster lead to a bond strength of D_e = 21.4 kcal/mol for the $^3B_2$ ground state,[22] which can be compared to recent experimental measurements of $D_0 = 22.9 \pm 0.7$ kcal/mol[24] and $D_0 = 21.4 \pm 1.2$ kcal/mol.[25] The accuracy of the Co^+ cluster calculations suggest that the exact $Ir(CH_4)^+$ bond energy is $D_0 = 21 \pm 2$ kcal/mol.

3.2. $Ir(H)(CH_3)^+$. The second step in the reaction sequence involves oxidative addition to a C–H bond (b to d). This process is exothermic and effectively barrierless, resulting in the $^3A''$ state of the hydridomethyliridium complex (d). The structure is eclipsed (the trans conformer is 2.1 kcal/mol higher in energy) with $\theta_{H-Ir-C} = 81.5°$. It is bound by an estimated 40 kcal/mol with respect to the reactants (D_e = 33.7 kcal/mol, calculated) and ~20 kcal/mol with respect to the molecular complex (D_e = 16.3 kcal/mol, calculated), consistent with calculated Ir^+–H and Ir^+–CH_3 bond strengths of D_e = 74.9 kcal/mol and D_e = 70.3 kcal/mol, respectively.[26] The transition state c occurs at a C–H bond length of 1.5 Å and a calculated barrier of 2 kcal/mol relative to the molecular complex. We estimate that this barrier will disappear entirely with more complete calculations.

The formal oxidation state of Ir in $Ir(H)(CH_3)^+$ is Ir^{III}. However, we find that the Ir–H and Ir–CH_3 bonds are fairly covalent, involving hybridization of the metal 6s and 5d orbitals. Thus, one should interpret the Ir^{III} notation to mean that there are two covalent bonds to Ir^+. As described earlier,[14] hybridization of valence s and d orbitals is effective for the second- and third-row metals due to the similarity in the sizes of the orbitals. This hybridization increases the overlap of the metal orbitals with the ligands, thereby increasing the strengths of the bonds. Due to a large discrepancy in the sizes of the 4s and 3d orbitals of first-row metals such as Co^+, hybridization is much less efficient for these elements. Furthermore, the s^1d^7 state, used to form the strongest covalent bonds, does not require a promotion energy for Ir^+ (in contrast to Rh^+, which has a d^8 to s^1d^7 promotion energy of 49.0 kcal/mol). Both of these considerations make insertion into a C–H bond of CH_4 a much more exothermic process for Ir^+ than for its first- and second-row counterparts. These same considerations also explain why the $^1A'$ state of $Ir(H)(CH_3)^+$ is higher in energy than the $^3A''$ state by ~20 kcal/mol. The singlet state is derived from the d^8 excited state of the metal and has weaker d bonds (as compared to the sd bonds).

3.3. $Ir(H)_2(CH_2)^+$. The next step is insertion into a second C–H bond to form the dihydridomethylideneiridium complex (f). The resulting *singlet* species is the global minimum on the potential energy surface, bound by ~63 kcal/mol (D_e = 50.7 kcal/mol, calculated) and having a pyramidal structure with $\theta_{H-Ir-H} = 83.3°$ and $\theta_{H-Ir-C} = 87.3°$. A rotation of the methylene group by 90° about the Ir–C axis leads to a conformer which is 0.9 kcal/mol less stable. On the other hand, the planar structure is bound by only ~23 kcal/mol (calculated D_e = 11.1 kcal/mol), leading to an energy ~40 kcal/mol above f.

3.3.1. Singlet State. The GVB orbitals (Figure 3) show that the bonding in $Ir(H)_2(CH_2)^+$ involves a covalent double bond to CH_2 (a Schrock-like metal methylidene[27a,b]) plus covalent bonds to both H atoms. Thus, the quantum-mechanical calculations lead to an overall effective atomic valence configuration for $Ir(H)_2(CH_2)^+$ of s^1d^7, which allows a maximum of four bonds to the Ir^+ (using hybrids of the four singly occupied orbitals on the metal). The formal oxidation state of the metal is Ir^V; however, the chemistry and structure of the complex are much more easily understood in terms of bonding to the s^1d^7 configuration

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(20) For convenience and clarity we use Russell–Saunders term symbols. It should be kept in mind, however, that the spin-orbit coupling of the third-row transition metals is large.

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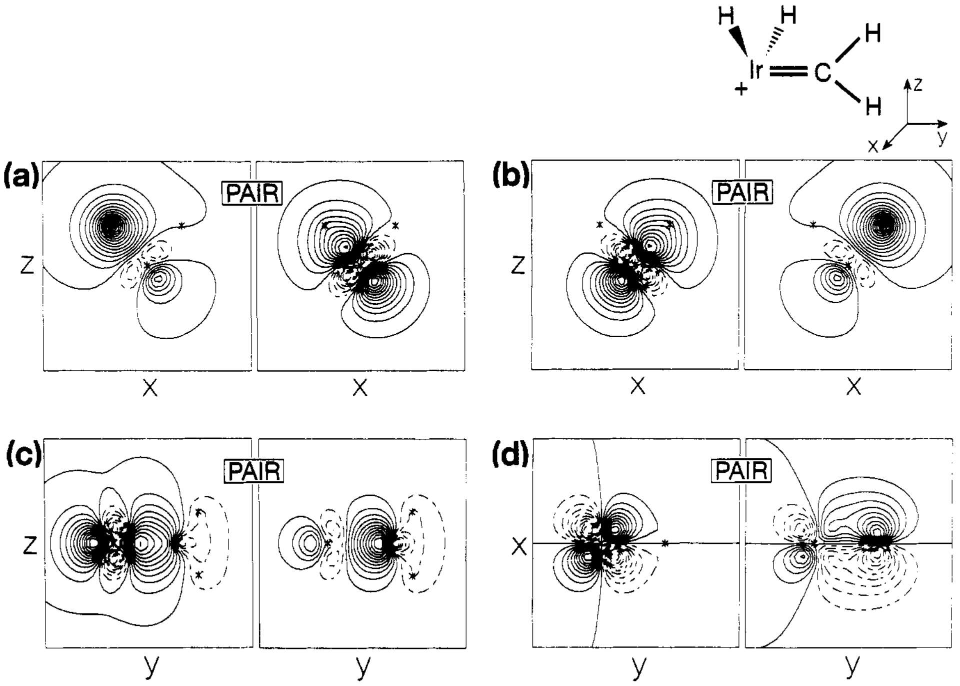

Figure 3. GVB-PP(8/8) orbitals for the $Ir(H)_2(CH_2)^+$ global minimum. The covalent nature of these bonds is evident in the orbitals of the (a, b) Ir^+–H bonds, (c) Ir^+–C σ bond, and (d) Ir^+–C π bond. Denoting the Ir–C axis as y and taking the z axis as bisecting the angle between the Ir–H bonds, the atomic configuration of the Ir^+ is $(s)^1(d_{x^2-z^2})^2(d_{yz})^2(d_{y^2})^1(d_{xy})^1(d_{xz})^1$. (a) and (b) are formed from $(s - d_{y^2}) \pm d_{xz}$, (c) is formed from $s + d_{y^2}$, and (d) is formed from d_{xy}.

of the metal rather than in terms of the d^4 configuration implied by the Ir^V notation.

To understand why the pyramidal structure is 40 kcal/mol better than the planar structure, it is important to consider the intraatomic repulsion and the nature of sd hybridization. An s^1d^7 configuration leads to two high-spin states, ^5F and ^5P, separated by ~30 kcal/mol. The ^5F atomic degeneracy is lifted when ligands are fixed in particular locations to overlap the orbitals, and the best single configuration (denoted $\sigma\delta$) has the d_{z^2} orbital and either the $d_{x^2-y^2}$ or d_{xy} orbital doubly occupied with the other s, d_{xz}, d_{yz}, and either the d_{xy} or $d_{x^2-y^2}$ orbitals singly occupied. This results in higher electron density along the z axis and in the xy plane, minimizing the intraatomic electron repulsions. The second-best configuration (denoted $\pi\delta$) has either the d_{xy} or $d_{x^2-y^2}$ orbital and either the d_{xz} or d_{yz} orbital doubly occupied and the other four singly occupied. This configuration is a mixture of 80% ^5F and 20% ^5P character and is 6 kcal/mol higher in energy than the $\sigma\delta$ configuration; it is also optimal for bonding to CH_2 and two H's.

With the Ir–C axis as the z axis and the Ir–H bonds in the xy plane, the bonding in the pyramidal structure arises as follows.

(a) The Ir–C σ bond is formed from an s + d_{z^2} hybrid orbital. This hybrid is polarized along the z axis.

(b) The Ir–H bonds are formed from the s − d_{z^2} hybrid and the d_{xy} orbital. The s − d_{z^2} hybrid is polarized in the xy plane and is ideal for forming bonds normal to the Ir–C bond, hence the pyramidal structure.

(c) The Ir–C π bond is formed from either the d_{xz} or d_{yz} orbitals, leading to the two nearly degenerate pyramidal structures. The staggered geometry is slightly more favorable (by 0.9 kcal/mol) than the eclipsed geometry due to a small amount of Ir $\sigma\delta$ character in the wave function, which is reflected in the smaller H–Ir–H angle for the staggered structure (83.3 vs 88.8°).

To form the planar structure of $Ir(H)_2(CH_2)^+$ requires a more highly excited atomic configuration of the metal (denoted $\sigma\pi$) with the d_{z^2} and d_{yz} orbitals doubly occupied (the molecule is in the xy plane, and the Ir–C bond is along the x axis). This configuration is 40% ^5F and 60% ^5P and is 18 kcal/mol higher in energy than the $\sigma\delta$ configuration. Thus, the planar structure is 12 kcal/mol higher in energy than the pyramidal structure just on the basis of the intraatomic repulsion. The remaining 28 kcal/mol of the 40 kcal/mol excitation energy between the pyramidal and planar structures is a consequence of the hybridization restrictions for the planar structure.

The bonding in the planar structure arises as follows.

(a) The Ir–C σ bond is formed from an s + $d_{x^2-y^2}$ hybrid. This hybrid is polarized along the x axis.

(b) The Ir–H bonds are formed from the s − $d_{x^2-y^2}$ hybrid and the d_{xy} orbital. The s − $d_{x^2-y^2}$ hybrid is polarized along the y axis, and this favors a large H–Ir–H bond angle (122.6°).

(c) The Ir–C π bond is formed from the d_{xz} orbital.

The hybridization in the pyramidal structure is an intrinsically more efficient scheme than that in the planar structure, leading to a greater overlap of the metal orbitals with the ligands and less repulsion between the bonds.

The doublet state of $Os(H)_2(CH_2)^+$ can also form pyramidal and planar geometries. While hybridization will still favor the pyramidal structure, the s^1d^6 configuration of the metal leads to the same intraatomic repulsion energy for both structures. Thus, the pyramidal structure should be more stable than the planar structure but the energy difference is expected to be smaller than for the Ir^+ complex.

3.3.2. Triplet State. For the *triplet* potential energy surface, a maximum of only two covalent bonds can be formed (as two of the four singly occupied orbitals must be high-spin). Thus, the triplet $Ir(H)_2(CH_2)^+$ conformer (f′) is unstable with respect to $Ir(H)(CH_3)^+$ and $Ir(H_2)$-

$(CH_2)^+$. It is, however, bound with respect to the reactants and can be thought of as having two covalent Ir–H bonds and a donor–acceptor Ir–CH_2 bond (Fischer carbene[27a,c]). This triplet transition state has a geometry similar to that of the singlet but with the second Ir–H bond not fully formed (the C–H bond length is 1.7 Å). This produces a barrier of ~29 kcal/mol (D_e = 32 kcal/mol, calculated) for the conversion of $Ir(H)(CH_3)^+$ to $Ir(H_2)(CH_2)^+$. This barrier is still ~11 kcal/mol (D_e = 2 kcal/mol, calculated) below the energy of the reactants and, thus, is a viable pathway for dehydrogenation. An attempt to find a lower barrier from a four-center transition state was unsuccessful. On the other hand, the crossing between the singlet and triplet surfaces for the insertion of the second C–H bond (e) was calculated to occur with the tilting of the methyl group and the stretching of the second C–H bond length to 1.3 Å. This produces a barrier of only ~14 kcal/mol with respect to $Ir(H)(CH_3)^+$ (~26 kcal/mol below the threshold energy (D_e = 19 kcal/mol, calculated)). Thus, under collisionless conditions (where reactive intermediates are not thermally stabilized), there is sufficient energy for dehydrogenation to proceed while remaining on the triplet surface (crossing the barrier f′); however, with spin–orbit coupling the preferred process is to form the singlet state f.

3.4. $Ir(H_2)(CH_2)^+$. The singlet and triplet curves cross again (g) with the formation of the H–H bond to produce (dihydrogen)methylideneiridium (III), $Ir(H_2)(CH_2)^+$. This crossing creates a barrier in the exit channel of ~5 kcal/mol for the back-reaction which could be observable as a broadening of the statistical kinetic energy release distribution (KERD).[28] The barrier results from the change in the H_2–Ir–CH_2 angle of 96° at the singlet–triplet crossing to 180° at the optimal triplet geometry of the $Ir(H_2)(CH_2)^+$ conformer (h). The resulting complex is planar and is bound by ~21 kcal/mol (D_e = 11.9 kcal/mol, calculated). A 90° rotation of the methylene group about the Ir–C bond leads to a conformer which is higher in energy by 4.6 kcal/mol. This is due to the fact that H_2 tends to coordinate to doubly occupied d_π orbitals and thus is more favorably oriented perpendicular to the Ir–C π-bond (i.e. a planar geometry). In contrast, the singlet state of the planar conformer is bound by only ~12 kcal/mol (D_e = 2.5 kcal/mol, calculated). As discussed below, there is some evidence to suggest that the crossing from the singlet to the triplet potential energy surface (g) is inefficient and the reaction proceeds directly from f to i′ with no change of spin.

Formally the metal in the triplet complex is Ir^{III}, yet again GVB calculations indicate that the metal is s^1d^7 and not d^6. With the complex in the *yz* plane, the bonding configuration is $\pi\delta$, with the d_{yz} and d_{xy} orbitals doubly occupied and the others ($s + d_{z^2}$, $s - d_{z^2}$, d_{xz}, and $d_{x^2-y^2}$) singly occupied. The Ir–C σ bond is formed from an $s + d_{z^2}$ hybrid, and the Ir–C π bond is formed from the d_{xz} orbital. The Ir–H_2 bond is dative, analogous to the Dewar–Chatt model for π complexes. Polarization of charge in the Ir–C σ bond increases the acidity of the Ir^+ on the side opposite to the bond; hence, H_2 prefers coordination to this site.

3.5. $H_2 + Ir(CH_2)^+$. With the MCPF method, the total reaction energy (a → i) is *endo*thermic by 2.9 kcal/mol (D_e). At this level, the product $IrCH_2^+$ ($^3A_2$) species has an Ir═C bond strength of D_e = 110.9 kcal/mol. However, with more extensive electron correlation,[29] the calculated bond strength increases to D_e = 116.5 kcal/mol. Including the estimated zero-point correction of 2 kcal/mol and using the experimental heat of reaction[30] for reaction 2 of ΔH

$$CH_4 \rightarrow CH_2 + H_2 \qquad (2)$$

= 111 kcal/mol lead to a total reaction *exo*thermicity for a → i of 3 kcal/mol at the higher level of theory. We still regard this as a lower bound. Our best estimate of the $IrCH_2^+$ ($^3A_2$) bond energy is D_0 = 119 ± 3 kcal/mol, leading to an exothermicity for a → i of 8 ± 3 kcal/mol. In addition, the $^1A_1$ state of $IrCH_2^+$ is calculated to be bound by D_e = 102.1 kcal/mol at the MCPF level. Our best estimate for the bond energy (singlet state) is D_0 = 110 ± 3 kcal/mol, suggesting that reaction a → i′ is endothermic by 1 ± 3 kcal/mol. In contrast, using the higher level of theory, we find that the bond strengths for $CoCH_2^+$ and $RhCH_2^+$ are D_e = 73.8 and 77.5 kcal/mol,[31] respectively. Thus, dehydrogenation reactions of Co^+ or Rh^+ with CH_4 are endothermic by 30–35 kcal/mol and are not observable under ICR conditions.

4. Discussion

4.1. Gas-Phase Chemistry. 4.1.1. Comparison of Ir^+ Activation of CH_4 with Other Metals. The distinction of Ir^+ as the most efficient element at dehydrogenating CH_4 is due to the ability of Ir^+ (1) to form four covalent bonds (using the s^1d^7 configuration, a formal oxidation state of Ir^V), (2) to optimally hybridize valence 6s and 5d orbitals, thereby forming strong bonds to C and H (50–60% stronger than Co^+ and Rh^+), and (3) to change spin easily as bonds are broken and formed. The combination of these effects leads to $Ir(H)_2(CH_2)^+$ (f) as the global minimum.

It has previously been shown that the two strongest metal–hydride bonds are those of Ir^+–H and Pt^+–H.[32] Moreover, we calculate that the Ir^+–CH_3 bond is comparable in strength to that of the hydride (D_e = 70.3 kcal/mol and D_e = 74.9 kcal/mol, respectively) and expect the same to be true of Pt^+–CH_3. Various electronic structure considerations (promotion energy, 6s and 5d orbital sizes, and exchange energy loss)[5,33] suggest that Ir^+ and Pt^+ should also form the strongest bonds to methylene. This too is borne out by calculations.[34] The trends in these MCH_2^+ bond strengths are enough to explain the observed trends in the reactivities of the metals La^+–Ir^+. For instance, the $ReCH_2^+$ bond is 27 kcal/mol weaker than the $IrCH_2^+$ bond due to the large loss of exchange energy on the metal in forming the double bond ($2.5K_{sd} + 2K_{dd}$ = 58 kcal/mol for Re^+ vs $1.5K_{sd} + 1K_{dd}$ = 32 kcal/mol for Ir^+, where $K_{sd} \approx 12$ kcal/mol and $K_{dd} \approx 14$ kcal/mol).[33]

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(28) Beauchamp, J. L. Personal communication.

(29) These calculations used a CASSCF followed by multi-reference singles plus doubles configuration interaction (MRSDCI) including the Davidson correction.

(30) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*, No. 1.

(31) See also: Bauschlicher, C. W., Jr.; Partridge, H.; Sheehy, J. A.; Langhoff, S. R.; Rosi, M. *J. Phys. Chem.* **1992**, *96*, 6969. On the basis of their calculations, their best estimates for the $CoCH_2^+$ and $RhCH_2^+$ dissociation energies are D_0 = 79 ± 4 and D_0 = 84 ± 4 kcal/mol, respectively.

(32) (a) Ohanessian, G.; Brusich, M. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1990**, *112*, 7179. (b) A comparison of the MH^+ bond strengths for the complete transition series is given in: Ohanessian, G.; Goddard, W. A., III. *Acc. Chem. Res.* **1990**, *23*, 386.

(33) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1988**, *92*, 5679.

(34) Irikura, K. K.; Goddard, W. A., III. *J. Phys. Chem.*, submitted for publication.

Re^+ has not been observed to react with CH_4. However, $ReCH_2^+$ *does* lead to dehydrogenation of CH_4 (efficiency 20%).[5] The loss of exchange energy is significantly reduced by the presence of the CH_2 ligand; thus, a second methylidene bond is stronger than the first by an estimated 23 kcal/mol. $ReCH^+$ is even more reactive with CH_4 (40%), as the exchange energy loss is further reduced by 14 kcal/mol.

On the other hand, the $PtCH_2^+$ bond is 1 kcal/mol *stronger* than the $IrCH_2^+$ bond but Pt^+ is observed to react *less* efficiently with CH_4 than Ir^+ (40% vs 70%, respectively). Consideration of the complete potential energy surface for $Ir^+ + CH_4$ indicates that the difference between the two metals is kinetic. With a valence configuration of s^1d^8, Pt^+ is capable of forming only three covalent bonds (oxidation state IV). Thus, the doublet $Pt(H)_2(CH_2)^+$ conformer is unstable, being analogous to the triplet state of $Ir(H)_2(CH_2)^+$ (f′) rather than the stable singlet state (f). While dehydrogenation is expected to be a thermodynamically and kinetically allowed process for Pt^+, the efficiency of the reaction should be significantly reduced compared to that for Ir^+. Thus, Ir^+ is the most reactive ion for dehydrogenation of CH_4.

4.1.2. Reaction of $IrCH_2^+$ with CH_4. While dehydrogenation is an important process in the reaction of Ir^+ with CH_4, the ion product, $IrCH_2^+$, is itself an intermediate since it will react further with CH_4.

Reaction 1 is exothermic by 8 ± 3 kcal/mol to produce ground-state $IrCH_2^+$ ($^3A_2$) and thermoneutral (endothermic by 1 ± 3 kcal/mol) to produce excited-state $IrCH_2^+$ ($^1A_1$). Experiment indicates that $IrCH_2^+$ is actually formed in an excited state.[5] Our results suggest that this excited species is the $^1A_1$ state (i′), the spin-allowed product of reductive elimination of H_2 from $Ir(H)_2(CH_2)^+$ (f). As the singlet state of $IrCH_2^+$ is calculated to be 9 kcal/mol above the ground-state triplet and our best estimate of the triplet bond strength is $D_0 = 119 \pm 3$ kcal/mol, reaction 1 should be nearly thermoneutral for the production of the excited-state ion (an energy change of -1 ± 3 kcal/mol).

Once quenched to the triplet ground state by collision, $IrCH_2^+$ is capable of dehydrogenating CH_4 (reaction 3) with an efficiency of 30%. The structure of the product

$$IrCH_2^+ + CH_4 \rightarrow Ir(C_2H_4)^+ + H_2 \qquad (3a)$$

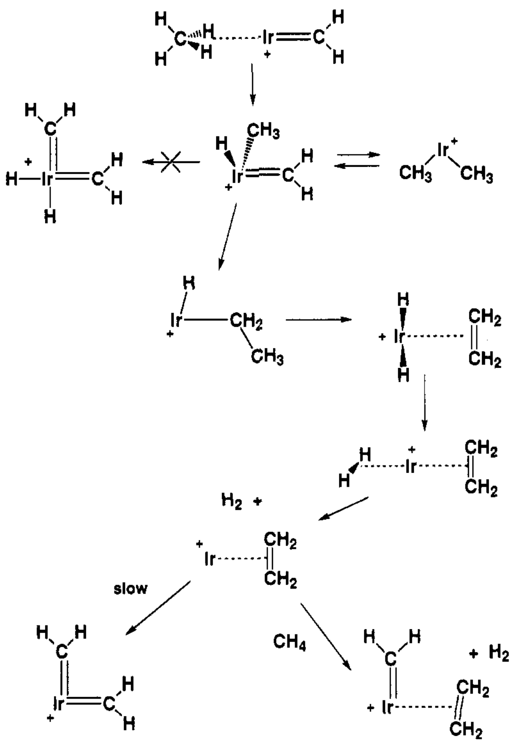
$$\rightarrow Ir(CH_2)_2^+ + H_2 \qquad (3b)$$

ion is unknown and could be either the ethylene π complex ($Ir(C_2H_4)^+$; reaction 3a) or the dimethylidene complex ($Ir(CH_2)_2^+$; reaction 3b).

We calculate that the $Ir(C_2H_4)^+$ bond strength is $D_e = 74.3$ kcal/mol.[23] (The calculations are similar to those of ref 22.) The ground state is triplet, derived from the d^8 state of the metal, and the bond is largely electrostatic (some metallacycle character is evident in that the C–C bond length increases by 0.07 Å, and the C–H bonds bend back out of plane by 9.3°). We expect that the error in the bond energy is small and estimate the exact number to be $D_0 = 76 \pm 2$ kcal/mol.

To bond two CH_2's to Ir^+, consider two σ bonds constructed from $s + d_{x^2-y^2}$ and $s - d_{x^2-y^2}$. This leads to one Ir–C bond along the x axis and the other along the y axis. We can then form the π bond to the first CH_2 with the xz orbital and the π bond to the second CH_2 with the yz orbital. The complex is then planar, and the nonbonding orbitals are $(d_{z^2})^2(d_{xy})^2$, giving a singlet ground state. Using our best estimate for the $IrCH_2^+$ bond strength of $D_0 = 119 \pm 3$ kcal/mol and accounting for exchange energy loss, we expect the second methylidene to be bound by $D_0 = 144$ kcal/mol (119 (first bond strength) + 32 ($1.5K_{sd} + 1K_{dd}$) − 7 ($0.5K_{dd}$) = 144 (second bond strength)). Siegbahn recently noted that bond energies can be significantly weakened as a result of rehybridization when numerous ligands are covalently bound to the metal.[35] For $Ir(CH_2)_2^+$, the two Ir–C σ bonds are formed from $sd_{x^2-y^2}$ hybrids, whereas for $Ir(CH_2)^+$ a single Ir–C σ bond is formed from an sd_{z^2} hybrid. Consequently, the $Ir(CH_2)_2^+$ complex may be destabilized by 5–10 kcal/mol due to the costs associated with rehybridization. A second bond strength of 137 ± 10 kcal/mol is then expected.

Scheme 1



Combining the predicted Ir^+ bond energies with the experimental heats of formation of C_2H_4 and CH_2 (12.5 and 93 kcal/mol, respectively)[30] indicates that the dimethylidene structure is more stable than the ethylene π complex by 7 ± 10 kcal/mol. On the basis of the potential energy surface for $Ir^+ + CH_4$, we expect that dehydrogenation of a second CH_4 to form $Ir(CH_2)_2^+$ requires a bound intermediate complex (whether a minimum or a transition state) with the structure $Ir(H)_2(CH_2)_2^+$. As this complex has a formal oxidation state of VII for Ir, it is clearly unstable and probably inaccessible (Re^+ is the only third-row metal for which this intermediate is likely to be stable). Thus, reaction 3b to form $Ir(CH_2)_2^+$ is kinetically disfavored. On the other hand, the reaction of a second CH_4 to form the higher energy ethylene π complex does not involve any kinetically unfavored steps (see Scheme 1). This has an exothermicity of 20 ± 4 kcal/mol. Our conclusion that (3a) gives the initially formed product is consistent with the observed kinetics, which indicate that the initially formed $Ir(C_2H_4)^+$ is reactive toward a third CH_4 but slowly converts to an unreactive form. We expect

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[35] Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993**, *115*, 4191.

that the triplet ethylene π complex would be reactive toward CH_4 but that the closed-shell dimethylidene complex would be inert. It is likely that this chemistry is unique to Ir^+ due to the large bond strengths for both the first and second methylidenes. For the other third-row metals (with the possible exception of Re^+), formation of the ethylene π complex should be both kinetically *and* thermodynamically favored.

4.2. Solution-Phase Chemistry. In many ways the chemistry of organometallic complexes in solution is far removed from that in the gas phase. The thermalizing conditions of the solvent and the steric hindrance of bulky ligands are especially notable perturbations to the chemistry of gaseous transition-metal ions. However, the electronic structural requirements for methane activation revealed in these gas-phase ion–molecule reactions should be intrinsic to the chemistry in the condensed phase. Thus, an understanding of how the energetics are modified by the presence on the metal of stabilizing ligands should be quite valuable in developing an analogous solution-phase catalyst.

The salient aspect of the electronic states in the gas-phase reaction between Ir^+ and CH_4 which distinguishes the chemistry of this metal from others of the third row is the ability of the metal to change formal oxidation states from I to III to V concomitant with formation of the appropriate bonds. For bare metal ions, the energetics of these changes in electronic configuration depend on promotion energy and exchange energy loss. Ir^+ is the most efficient gas-phase ion for the methylene dehydrogenation reaction, in part because these energy costs are minimal and each oxidation state is easily accessible. These same factors of promotion and exchange energies also determine the accessibility of various oxidation states for ligated complexes. However, ligation alters the energetics such that a solution-phase Ir complex is not optimal for dehydrogenation of CH_4. In general, the effect of multiple X^- ligands (such as Cp^- or Cl^-) and L ligands (such a PPh_3 or CO) on a metal is to destabilize the valence s orbital and to favor lower spin states.[36] Thus, in the gas phase Ir^+ has a quintet s^1d^7 configuration, but in solution, the analogous 14-electron $(X)Ir(L)_2$ complex is expected to be low-spin d^8. This complex could react with CH_4 to form the 16-electron $(X)Ir(H)(CH_3)(L)_2$ complex, where the H and CH_3 each bond to a singly occupied d orbital (corresponding to triplet d^8). However, the X^- and L ligands make it most unfavorable to promote the Ir^+ to the s^1d^7 state required to form the 18-electron species $(X)Ir(H)_2(CH_2)(L)_2$ (oxidation state Ir^V).[37]

In order to obtain a solution-phase complex with chemistry analogous to gas-phase Ir^+, we need to remove two electrons. This suggests Re^+. Thus, $(X)Re(L)_3$ would have a d^6 configuration which, depending on the ligands, could be low-spin singlet (no unpaired orbitals), intermediate-spin triplet (two singly occupied orbitals), or high-spin quintet (four singly occupied orbitals). It then makes sense to consider reaction 4. Further reaction of the product species with a second methane can be envisioned from the model in the gas phase (Scheme 1). The desirable production of C_2 hydrocarbons could result, as in reactions 5–8.

$$(X)Re(L)_3 + CH_4 \rightarrow (X)Re(H)(CH_3)(L)_3 \rightarrow (X)Re(H)_2(CH_2)(L)_3 \quad (4)$$

$$(X)Re(H)_2(CH_2)(L)_3 \rightarrow (X)Re(CH_2)(L)_3 + H_2 \quad (5)$$

$$(X)Re(CH_2)(L)_3 + CH_4 \rightarrow (X)Re(H)(CH_3)(CH_2)(L)_3 \rightarrow (X)Re(H)(C_2H_5)(L)_3 \quad (6)$$

$$(X)Re(H)(C_2H_5)(L)_3 \rightarrow (X)Re(C_2H_6)(L)_3 \quad (7)$$

$$\rightarrow (X)Re(H)_2(C_2H_4)(L)_3 \quad (8)$$

It must be recognized, however, that reaction 6, to form the hydrido ethyl complex, may be kinetically less favorable than reaction 9 to form the dimethyl complex. In the gas

$$(X)Re(H)(CH_3)(CH_2)(L)_3 \rightarrow (X)Re(CH_3)_2(L)_3 \quad (9)$$

phase, the formation of the dimethyl structure is a dead end with no outlet for release of the heat of reaction. Consequently, the hydrido ethyl complex is formed, which leads to dehydrogenation and removal of the excess internal energy. In solution, solvation can stabilize the dimethyl complex; therefore, its formation must be considered as a possible reaction pathway. This is not an unfavorable situation, however, as many additional reactions of a dimethyl Re complex may be suggested.

Higher oxidation states are common for Re, and there are numerous examples of Re complexes with multiple hydride[38] and alkyl[39] bonds. In fact, the first step in reaction 4—the oxidative addition of a C–H bond—has already been demonstrated for 16-electron complexes of Re analogous to those of Ir.[40] These complexes tend to be more selective than the Ir complexes (for example, activating methane in preference to cyclohexane), and they also tend to lead to more intramolecular attack. Overcoming problems associated with competing reactions may be the most difficult task in developing a homogeneous organometallic complex capable of methane dehydrogenation, yet we believe that with appropriately labile ligands Re is the most likely candidate for such a catalyst.

Much of the work on alkane activation has concerned the chemistry of coordinatively unsaturated 16-electron Ir complexes. These complexes, such as (Cp*)Ir(L) (where L = PMe_3, CO), were the first observed to insert into unactivated C–H bonds, changing the oxidation state of the metal form I to III.[4a,b] As the resulting alkyl hydride complex satisfies the 18-electron rule, further reaction is not expected. The chemistry has been extended, however, by substitution of Cp* with an indenyl group (C_9H_7), since this ligand is capable of converting easily from η^5 to η^1 coordination. Foo and Bergman[4e,f] took advantage of this property to facilitate the migratory insertion of an associated CO ligand into the metal–alkyl bond of the alkane adduct. Still elusive are goals such as the oxidative addition of two methane C–H bonds. This would require

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(36) See for example: Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

(37) A notable example of an Ir complex in oxidation state V is $H_5Ir(P\text{-}i\text{-}Pr_3)_2$: Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(38) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558.

(39) Floë, M.; Hedtweck, E.; Wagner, W.; Kulpe, J.; Harter, P.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 787.

(40) (a) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856. (b) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358.

a 14-electron active complex with a metal capable of accessing the I, III, and V oxidation states. By the arguments given above, Re is a better candidate for such chemistry than Ir.

5. Conclusions

We show that Ir^+ has a unique capability of activating CH_4. The origins of this uniqueness involve the intrinsic strengths of the Ir–C and Ir–H bonds and the ability of the metals to change spin easily (due to strong spin–orbit coupling). Both of these traits are generally common to all of the third-row metals. Ir^+ is distinguished from La^+, Hf^+, and Pt^+, however, in its ability to form the stable intermediate $M(H)_2(CH_2)^+$ (requiring a formal oxidation state of V on the metal). This intermediate provides a lower energy pathway for dehydrogenation, thereby increasing the reaction efficiency. The other metals of the third row capable of forming such an intermediate (Ta^+–Os^+) experience greater loss of exchange energy in forming covalent bonds (W^+–Os^+) or have slightly weaker intrinsic MCH_2^+ bond strengths (Ta^+), leading to less stable intermediate and product species and reduced efficiencies for dehydrogenation. The reactivities of these metals may be improved, however, by appropriate ligands.

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