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The Role of the Cyclopentadienyl Ligand in the *σ*-Bond Activation of Methane

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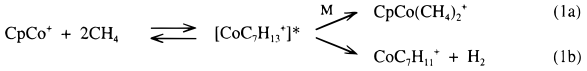
Chemists have long sought a way to selectively activate *σ* bonds in alkanes, especially the C−H bond in methane.[1] This interest is due, in part, to the need in the petroleum industry to transform methane into a transportable liquid feedstock. In addition, there is hope that such an activation process would allow alkanes, a generally unreactive class of compounds, to be utilized industrially as starting materials for more complex molecules. An equally important reason, however, for studying *σ*-bond activation in simple molecules such as methane is the insight it gives us into such fundamental concepts as chemical bonding and reactivity. Historically, transition-metal centers have been the primary templates for *σ*-bond activation. However, bare transition metal atoms, especially first row metals, are generally unreactive due to their repulsive occupied 4s orbital.[2] To make transition metals capable of activating *σ* bonds, chemists have traditionally coordinated them with oxidizing ligands to produce formal d^n metal centers.[3] Unfortunately, despite years of investigation, *controlled* activation of alkanes, especially methane, remains an elusive goal.

An alternative to oxidizing the neutral metal center with ligands is to start with singly charged metal ions,[4−6] thus jump-starting the oxidation process. Further, the reactivity of the metal ions can also be altered by ligation, often dramatically so.[7,8] The role of the ligand in ionic reactions is analogous to its role in neutral systems. In both cases, it alters the electronic structure of the metal center through oxidation and/or selective tuning of the reactive excited electronic states.

The cyclopentadienyl ligand (Cp = η^5-C_5H_5) is extensively used in organometallic chemistry involving *σ*-bond activation. It is believed to behave primarily as a "spectator" ligand in most organometallic reactions, serving only to oxidize the metal.[3] To our knowledge, there is no evidence, as yet, that the Cp ligand is directly involved in the chemistry of ionic systems. Here, we report novel experimental and computational evidence that the Cp ligand is directly involved in the mechanism of C−H bond activation in methane by $CoCp^+$.

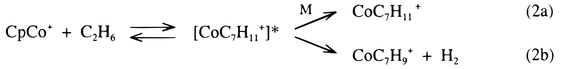
In thermal reactions with C_3H_8, bare Co^+ is able to activate both C−H and C−C *σ* bonds to produce H_2 and CH_4.[9] In contrast, bare Co^+ does not activate *σ* bonds in methane or ethane at thermal energies, even though the H_2 elimination channel with ethane is exothermic by about 11 kcal/mol. However, facile H_2 elimination from ethane is observed in thermal reactions with $CoCp^+$.[7d,10] Hence, we decided to explore the reactivity of $CoCp^+$ with methane. In thermal reactions between bare Co^+ and up to four CH_4 ligands, only cluster formation occurs.[11−13] Similarly, when $CoCp^+$ reacts with a single CH_4 ligand, only clustering is observed,[14] but when a second CH_4 is added, clustering (reaction 1a, where M is a stabilizing collision partner) and H_2 elimination (reaction 1b) are found to be competitive reaction channels.[14] We have termed processes such as reaction 1b "cluster-assisted *σ*-bond activation."[8,15]



$$CpCo^+ + 2CH_4 \rightleftharpoons [CoC_7H_{13}^+]^* \xrightarrow{M} CpCo(CH_4)_2^+ \quad (1a)$$

$$[CoC_7H_{13}^+]^* \rightarrow CoC_7H_{11}^+ + H_2 \quad (1b)$$

To investigate the structure of the $CoC_7H_{11}^+$ ion formed by reaction of $CoCp^+$ with methane, we performed metastable and collision-induced dissociation (CID) ion kinetic energy studies. The $CoC_7H_{11}^+$ ion was generated by two different methods: reaction 1b and by direct clustering with ethane (reaction 2). Ions were formed by electron impact in the source of a reverse-geometry double-focusing mass spectrometer (V. G. ZAB-2F),[16] accelerated to 8000 eV, and $CoC_7H_{11}^+$ was mass selected by the magnetic sector. Decomposition either occurred metastably or was induced by collision with helium in the field-free region between the magnetic and electric sectors. For $CoC_7H_{11}^+$ formed by either reaction 1b or 2, the only significant fragment produced under metastable conditions is $CoC_7H_9^+$, due to H_2 loss. However, more structural information can be gained by examining the CID spectra (Figure 1).



$$CpCo^+ + C_2H_6 \rightleftharpoons [CoC_7H_{11}^+]^* \xrightarrow{M} CoC_7H_{11}^+ \quad (2a)$$

$$[CoC_7H_{11}^+]^* \rightarrow CoC_7H_9^+ + H_2 \quad (2b)$$

For $CoC_7H_{11}^+$ formed from $CoCp^+ + C_2H_6$ (reaction 2), the most significant ionic fragments produced upon CID are Co^+, $CoCp^+$, and $CpCo^+$-C_2H_4 (Figure 1a). This pattern is consistent with an ethane complex, $CpCo^+$-C_2H_6, for the structure of the $CoC_7H_{11}^+$ precursor ion. In contrast, the CID spectrum for $CoC_7H_{11}^+$ formed by sequential reaction of $CoCp^+$ with two CH_4 molecules followed by H_2 elimination (reaction 1b) shows the significant fragmentation pathways to be formation of Co^+ and $CoC_5H_7^+$, the latter ion due to C_2H_4 loss (Figure 1b). These results

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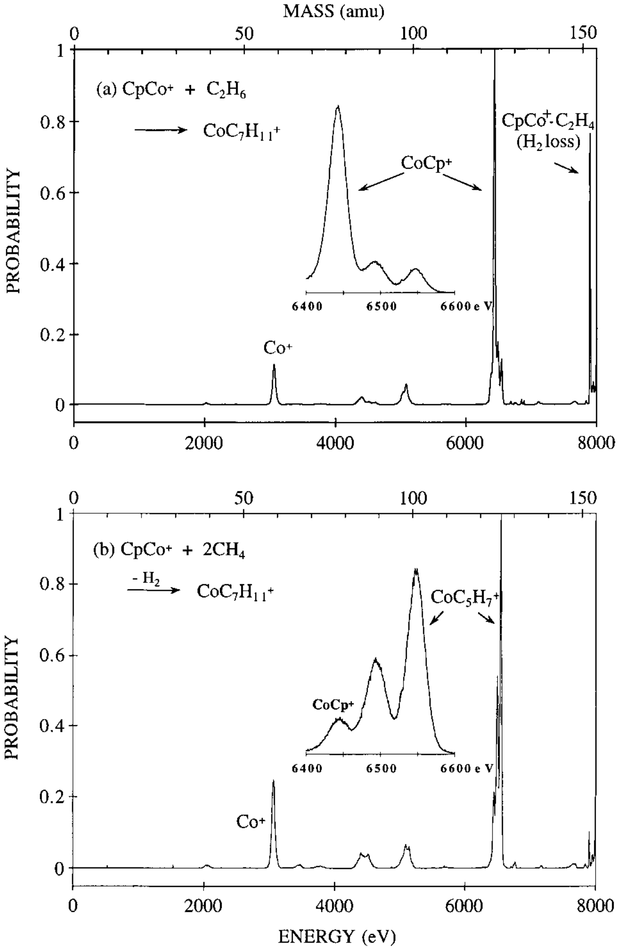


Figure 1. Kinetic energy/mass spectra for collision-induced dissociation of $CoC_7H_{11}^+$ formed by reaction of $CoCp^+$ with (a) C_2H_6 and (b) $2CH_4$ followed by H_2 elimination. Insets show an enlargement of each spectrum in an energy range of 6400−6600 eV.

strongly suggest the structures of the $CoC_7H_{11}^+$ ions formed by reactions 1b and 2 are different.

Ion equilibrium studies indicate that the first solvation shell of $CoCp^+$ can only accommodate either two H_2 or two CH_4 ligands.[14] Thus, it is probable that the intermediate $CoC_7H_{13}^+$ species leading to the formation of the products $CoC_7H_{11}^+$ and H_2 (reaction 1b) has at most three ligands coordinated to the cobalt ion. Because this intermediate eliminates dihydrogen, one of the ligands is most probably H_2. A second ligand must be a five-carbon ring species. Based on these assumptions, the two most reasonable structures for the $CoC_7H_{11}^+$ product ion formed in reaction 1b are $CpCo^+$-C_2H_6 and (c-C_5H_6)-Co^+-C_2H_5.[17] The ethane complex, $CpCo^+$-C_2H_6, can be ruled out by comparing the CID fragmentation patterns in Figure 1. The structure (c-C_5H_6)-Co^+-C_2H_5 is consistent with the experimental evidence (Figure 1b) because collisional activation of this ion would most likely result in loss of C_2H_4.

To determine if the proposed structures of reaction intermediates and products are energetically reasonable and to help understand the mechanism for dehydrogenation, we performed calculations using high-level density functional theory (DFT). Geometries were optimized at the Becke-3-LYP (B3LYP)/LACVP** level, and final energies were evaluated at the B3LPY/LACV3P**+ level using JAGUAR 3.5.[18] Parallel work being carried out by our group on the complexation of H_2 to $CoCp^+$ strongly suggests that the B3LYP functional is biased toward the high-spin quartet state and that the true ground state of $CoCp^+$ and its various complexes is a doublet state.[14] Thus, in this work we use the doublet potential energy surface for the reaction of $CoCp^+$ with two CH_4 molecules.

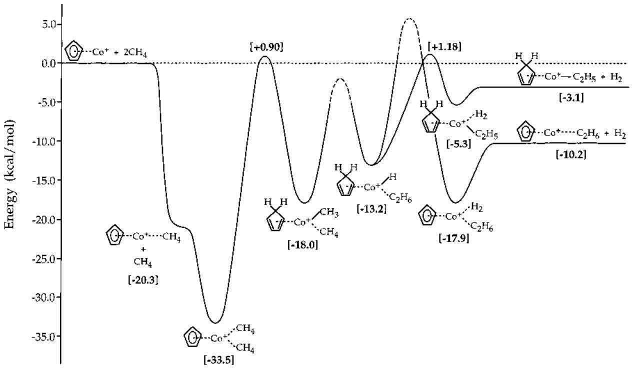
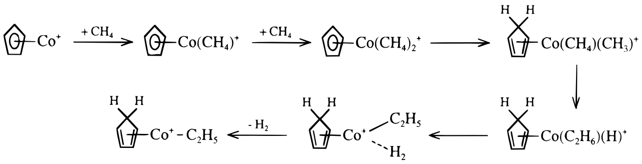


Figure 2. Schematic potential energy surfaces at 0 K for the dehydrogenation of methane by $CoCp^+$. Calculated relative energies (kcal/mol) are given in brackets below the stable species involved in the reaction and at the two transition states so far characterized. The barriers in the surfaces shown as dashed lines have not yet been characterized but their qualitative values can be inferred from the observed experimental results.

Scheme 1



The mechanism we propose is given in Scheme 1. The calculated energetics of the reaction intermediates and several key transition states are given in Figure 2, along with a schematic potential energy surface.

As shown in Figure 2, the molecular complexes $CpCo(CH_4)^+$ and $CpCo(CH_4)_2^+$ can form easily. In addition, the most stable product channel appears to be $CpCo^+$-C_2H_6 + H_2. However, because this channel has been ruled out by the CID experiments described above, we have also considered alternative reaction pathways including the possible formation of (c-C_5H_6)-Co^+-C_2H_5 + H_2, where a hydrogen is transferred to the Cp ligand. This channel is exothermic by 3.1 kcal/mol and the various intermediates from Scheme 1 that must lie along the reaction pathway to form (c-C_5H_6)-Co^+-C_2H_5 + H_2 all appear to be stable with respect to the $CoCp^+$ + $2CH_4$ asymptote. We also have located the initial and final transition states for this mechanism, with both occurring at energies only slightly above the reactant energy at this level of theory.[19] In contrast, theory indicated intermediates that might be expected in formation of the ethane complex, $CpCo^+$-C_2H_6, which do not involve hydrogen addition to the Cp ligand, such as $CpCo(CH_4)(CH_3)(H)^+$ and $CpCo(C_2H_6)(H)_2^+$, could not be converged and spontaneously reverted to corresponding stable species shown in Figure 2.

Finally, it should be emphasized that the Cp ligand must be transformed to c-C_5H_6 to allow the Co(II) center to form either Co−C or Co−H covalent bonds essential for the reaction to proceed. Both Cp and c-C_5H_7[17] ligands require cobalt to be oxidized to Co(IV) if covalent bonds are to be formed, an oxidation state far too high in energy for reaction to proceed at thermal energies. Hence, the active participation of the C_5-ring is essential.

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[17] Another possible $CoC_7H_{11}^+$ species is (c-C_5H_7)-Co^+-C_2H_4. However, after extensive theoretical efforts no transition state could be found allowing formation of the c-C_5H_7 ligand bound to Co although (c-C_5H_7)-Co^+-C_2H_6 and (c-C_5H_7)-Co^+-C_2H_4 were found to be stable minima.

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[19] The C−C coupling TS has not yet been located despite an extensive search. It is not clear if the problem is with the DFT method or if we have not yet found the correct configuration. Both experiment and theory indicate the proposed mechanism is viable and the C−C coupling TS must be at low energy. The search will continue and results will be presented in the full paper.