C−H Activation at a Cationic Platinum (II) Center: A Quantum Chemical Investigation

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The elementary steps of a recently reported methane activation reaction involving a platinum complex with a bidentate nitrogen ligand have been investigated using quantum chemical methods based on density functional theory. Our findings support a reaction mechanism involving formation of a σ-complex followed by oxidative addition.

1. Introduction

On a worldwide basis, it is recognized that natural gas is a more abundant resource than crude oil, and hence, selective conversion of methane to value-added products, such as methanol and other oxygenated liquids, will be of increasing importance. Alkanes are, however, practically inert to many reagents, a fact that is readily explained by its electronic structure.[1] Despite this, there has been a growing interest in C−H activation of alkanes using organometallic compounds.[1,2] Especially, the work of Shilov[3] has led to a significant interest in the use of compounds with an electrophilic metal center in general[4−6] and platinum complexes in particular.[7−11] Among the many recent reports on C−H activation with platinum complexes, we have found the work by Bercaw and co-workers to be of special interest.[7] This group has been able to activate methane by using a platinum complex, (tmeda)Pt$(CH_3)_2$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). To produce an active complex, $[H(S)_n]^+[BAr_f]^-$ ($BAr_f^- = B(3,5\text{-}(CF_3)_2{-}C_6H_3)_4$)[12] (S = OEt_2, NC_5F_5) was added to a solution of the (tmeda) complex, resulting in the formation of [(tmeda)Pt(CH_3)(S)]-[BAr_f]. When using diethyl ether as solvent, the ether adduct proved unstable with respect to internal C−H activation. On the other hand, intermolecular C−H activation was observed in pentafluoropyridine (PFP), as this solvent has no C−H bonds to activate. Thus, under 30 bar of $^{13}CH_4$, (tmeda)Pt$(^{13}CH_3)$-$(NC_5F_5)^+$ is observed, indicating activation of a C−H bond in methane. Further, the authors suggest that the reaction goes through an oxidative addition step, yielding a five-coordinated Pt(IV) cationic intermediate. Other possible reaction mechanisms include σ-bond metathesis and solvent abstraction of a hydrogen atom from a σ-complex between methane and the cation. The latter mechanism has been suggested for the Shilov reaction.[3,13] However, in that reaction water is the solvent, and the polarity and proton affinity thereof are described as crucial. Quantum chemical studies of methane activation at electrophilic late transition metal centers include those of Siegbahn and Crabtree,[13] Horsley et al.,[14] Mylvaganam et al.,[15] Su and Chu,[16] and Hill and Puddephatt.[17] All of these studies include interactions with solvents with some capability of solvating protons. To investigate the oxidative addition hypothesis, we have undertaken quantum chemical studies of the reaction between (tmeda)-Pt$(CH_3)^+$ and methane. In some cases (tmeda) has been replaced by a smaller model ligand. We also include studies of explicit inclusion of a solvent molecule.

2. Computational Details

The DFT calculations were carried out using the program system ADF developed by Baerends et al.[18] The frozen-core approximation was used for all atoms except hydrogen, keeping the orbitals up to and including 4f, 1s, 1s, and 1s frozen in their atomic shapes for Pt, C, N, and F, respectively. The orbitals were described by Slater-type orbital (STO) basis sets. The number of valence basis functions, in order of increasing angular momentum, is (5,3,3) for Pt, (2,2,1) for C, N, and F, and (2,1) for H, yielding TZV quality for the metal and DZVP for the other atoms. Slater exchange and the VWN parametrization of the LDA correlation energy,[19] with the gradient corrections of Becke[20] for exchange and of Perdew[21] for correlation, were used for the exchange-correlation energies, and the gradient corrections were added self-consistently. The accuracy of the numerical integration was set to $10^{-6.0}$.[22] Relativistic effects were taken into account through the quasirelativistic Pauli formalism.[23] For the stationary points of the unsolvated (eda) system, vibrational spectra were computed in order to ensure that the correct number of imaginary frequencies were at hand and for zero-point energy (ZPE) corrections. All systems for which results are reported here have a charge of +1.

3. Results and Discussion

We have studied the reaction between a methane molecule and the (tmeda)Pt$(CH_3)^+$ cationic complex, in which platinum has a coordination number of 3. In the experimental work,[7] the fourth coordination site is occupied by a solvent molecule. We have not attempted to model the exchange of solvent and methane at this site. See, however, the discussion below on methane bonding to the starting complex.

First, we investigate the oxidative addition pathway with the full (tmeda) complex and a smaller model complex; thereafter, results for the σ-bond metathesis pathway will be described. Finally, we address solvent effects.

Two possible reaction pathways have been investigated, oxidative addition (OA) and σ bond metathesis (σBM). A third possibility, proton abstraction by a solvent molecule, has not

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TABLE 1: Relative Energies for Stationary Points on the Potential Energy Surface (kcal/mol), with Vibrational Zero-Point Energy[a] (ZPE) Corrections Included

system	σBM TS	σ-complex	OA TS	OA product
(eda)	+9.4	0	+3.6	+1.6
(tmeda)	not calculated	0	+3.7	+0.4
(eda) + NF_2H	+13.1[b]	0	+2.6	−14.8
(eda) + PFP	not calculated	0	not calculated	−13.3

[a] The ZPE's are taken from the (eda) calculations in all cases. [b] Approximate value; only NF_2H allowed to relax geometrically.

TABLE 2: Geometries (Ångströms and Degrees) for Critical Points on the Potential Energy Surface of the (eda) System[a]

	σBM TS	σ-complex	OA TS	OAP
R(H−Pt)	1.55	1.73	1.54	1.50
R(C′-H)	1.62	1.18	1.65	2.43
R(C′-Pt)	2.14	2.36	2.12	2.04
R(C−Pt)	2.14	2.05	2.05	2.04
R(N−Pt)	2.16	2.04	2.15	2.25
R(N′-Pt)	2.16	2.24	2.25	2.25
A(C′-Pt−H)	49	29	51	85
A(C−Pt−C′)	98	87	89	88
A(N−Pt−N′)	80	82	80	79
R(C′−plane)	0.03	0.35	0.74	0.01

[a] "σBM TS" = transition state for σ bond metathesis; "OA TS" = transition state for oxidative addition; "OAP" = oxidative addition product. C and C′ are the carbon atoms in the methyl group and incoming methane molecule, respectively, while N and N′ are the nitrogen atoms cis to C and C′, respectively. R(C′−plane) is the distance between the carbon atom of the incoming methane molecule and a plane spanned by the methyl group carbon and the two nitrogen atoms, indicating deviation from planarity of the four sites. H is the hydrogen atom leaving the methane molecule.

been considered as it necessitates the ability of the solvent to supply protons as well in order to complete the reaction under study.

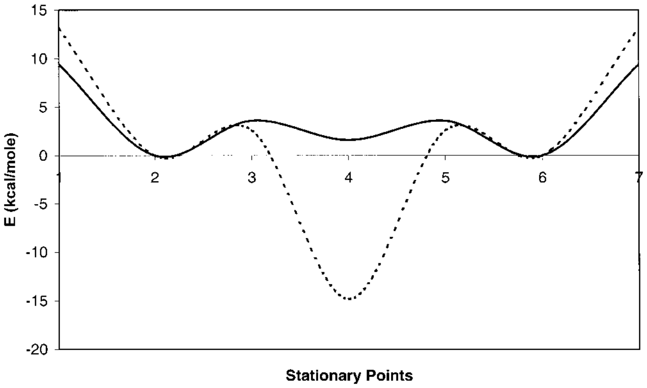
Initially, calculations on the OA pathway were carried out with two models: a simplified molecular model in which the methyl groups of the (tmeda) ligand were replaced by hydrogen, giving an (eda) ligand, and the (tmeda) complex itself. The largest differences introduced by using the (eda) rather than the (tmeda) ligand were found to be 0.03 Å and 3° in the geometries and 1.5 kcal/mol in the relative energies for oxidative addition, as can be seen from Table 1. After considering the very small discrepancies between the results obtained with the two systems for the OA pathway, the σBM pathway and solvent effects were investigated with the (eda) system only.

Calculated energies and geometry parameters of the different species under study are presented in Tables 1 and 2, respectively. In the following, energies and geometries will be for the (eda) system unless otherwise stated, and energies include zero-point energy corrections from vibrational spectra. The energy curve for the reaction with and without a solvent molecule (vide infra) is shown in Chart 1, and in the following, numerals in {curly braces} will denote species included in that chart.

Upon reacting methane with (eda)$PtCH_3^+$, a σ-complex {2} is formed. This complex has been proposed but not experimentally observed.[9] In fact, Crabtree,[24] in his 1993 review, states that no σ-complex of methane and a transition metal center in solution had been experimentally characterized until then. Only recently, experimental evidence for such a complex has been provided.[25,26] The σ-complex is depicted in Figure 1. One C−H bond is elongated by 0.08 Å compared to free methane, and the corresponding stretch frequency is shifted downward from 3081 cm^{-1} (free methane, asymmetric) to 2141 cm^{-1}. The coordination might be described as η^2-C,H.[27] The formation of the σ-complex seems to be unactivated in the gas phase; however, we cannot rule out the possibility of a small barrier of 1 kcal/mol or less. The possibility of more stable conformers of the σ-bonded complex was investigated by starting an optimization from a η^3 -H,H,H geometry; it converged to the η^2-C,H structure described above. The binding energy of methane to the starting (eda) complex is 21.9 kcal/mol. In the experimental situation, the solvation energy of methane in the solvent must be subtracted from this value. Test calculations on a several conformations of a methane−PFP adduct gives a binding energy of less than 1 kcal/mol, a result which may be inaccurate. This interaction is probably dominated by dispersion forces, which are not well described by the density functional in use. A quantitative estimate of the solvation energy would involve large-basis MP2 calculations on a system consisting of a methane molecule and several PFP rings, which is beyond our present computational reach. However, it must be kept in mind that the equilibrium between the σ complex and the corresponding complex with a solvent molecule is influenced by the solvation energies of the starting complex, methane, and PFP itself in the solvent, as well as PFP and methane binding energies to the starting complex. Again, a full investigation of these aspects is beyond the scope of the present study.

Starting with the σ complex, the further reaction was explored by using the distance between the methane carbon and the transferring hydrogen as the reaction coordinate. Along this path,

CHART 1: Potential Energy Curve for the Reaction between (eda)$PtCH_3^+$ and CH_4[a]



[a] Stationary points: 1,7, σ-bond metathesis transition state; 2,6, σ-complex; 3,5, oxidative addition transition state; 4, oxidative addition product. Full line, without coordinating NF_2H; dashed line, with coordinating NF_2H.

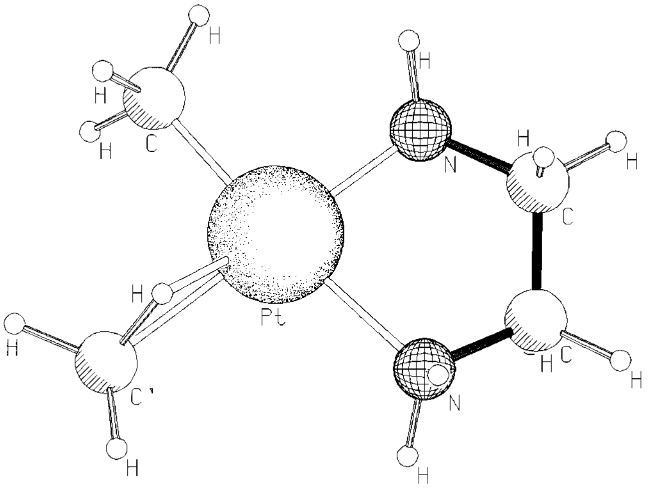


Figure 1. σ-Complex.

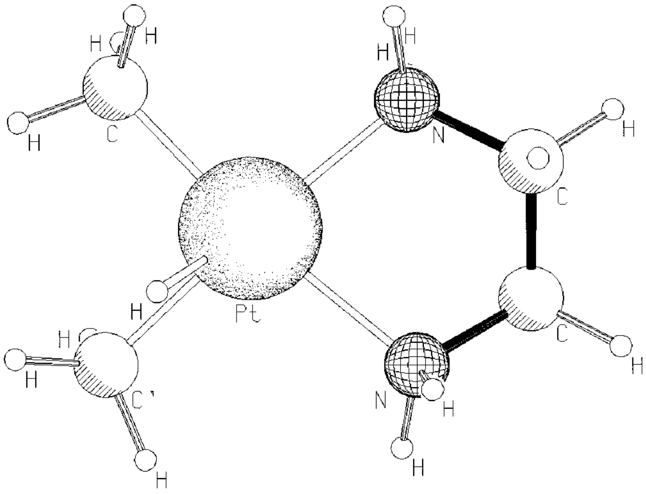


Figure 2. Oxidative addition transition state.

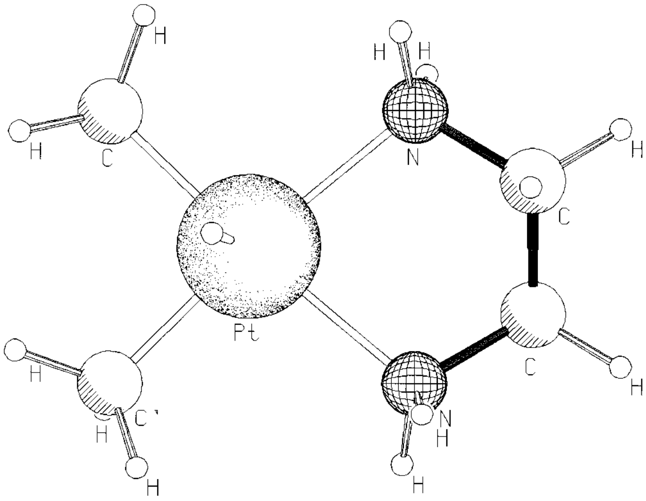


Figure 3. Oxidative addition product.

the energy rose towards a transition state (TS) {3}(Figure 2) before descending as the OA product (OAP) {4} was formed. The latter species, in which platinum is five-coordinated, is depicted in Figure 3.

The TS is characterized by a short Pt−H distance of 1.56 Å, while the C−H bond is almost fully broken at a length of 1.65 Å. The distance between the carbon atom of the reacting methane molecule and the plane spanned by the other three atoms coordinating to platinum grows to 0.61 Å, as the methyl group of the dissociating methane is bent away from the hydrogen and out of the plane. This is in contrast to the σ-complex and the OAP, which show much smaller deviations from planarity. The energy is 3.6 kcal/mol higher than for the σ-complex.

In the OAP, Pt(eda)$(CH_3)_2(H)^+$, platinum is five-coordinated, as can be seen from Figure 3. The structure is truncated octahedral, with the truncation trans to the position of the hydrogen ligand. It has no symmetry, but disregarding the hydrogen ligand it has something very close to a 2-fold axis through the platinum atom midway between the two nitrogen atoms and midway between the two methyl carbon atoms. Going from the σ-complex to the OAP, the Pt−N bond trans to the incoming methane is elongated by some 0.2 Å, which is reasonable in light of the stronger trans-effect of methyl compared to methane. The other Pt−N bond is virtually unchanged so that both nitrogen atoms are now 2.25 Å from platinum. At 1.50 Å, the Pt−H bond distance is very close to the 1.52 Å reported by Gropen et al.[28] for free PtH_2. The energy is 1.6 kcal/mol higher than for the σ-complex and hence 2.0 kcal/mol lower than for the TS.

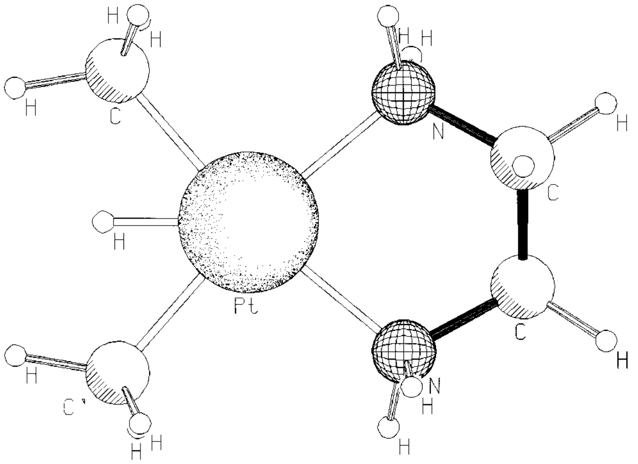


Figure 4. σ-Bond metathesis transition state.

To complete the exchange of carbon atoms, the hydrogen ligand must undergo a reductive elimination together with the original methyl ligand. We have not investigated this step explicitly, as it will be the reverse of the oxidative addition by something very close to symmetry. The second half of the energy curve in Chart 1 has been made by mirroring the first half. The rather shallow reaction profile is consistent with the facile isotopic exchange seen in the experimental work.

The Mulliken charge on the transferring hydrogen atom changes very little during the reaction, being close to zero all the way, indicating no great acidity. This is in line with Siegbahn and Crabtree's results for the Shilov reaction.[13]

The possibility of a σBM reaction path was explored applying the (eda) model. The σ-complex was taken as the starting point, and the angle θ, spanned by methyl carbon (as opposed to methane carbon), platinum, and dissociating hydrogen as reaction coordinate. This angle changes by only 2° during the OA reaction described above and should therefore be suitable for describing alternatives. Starting at $\theta = 86°$ (for the σ-complex), the energy rises by 13 kcal/mol at $\theta = 45°$, a point which, from inspection of the geometry, is still clearly on the reactant side of a possible TS. Further decreasing the angle brings the σBM reaction about, but stepping the same coordinate in reverse, we see a completely different energy curve. This phenomenon,[29] reminiscent of hysteresis, is an artifact caused by the fact that the chosen reaction coordinate diverges from the least energy path of the true reaction, which may be interpreted as an indication that the σBM path is unlikely. Upon placing H′ equidistant from C′ and C, and keeping it there during optimization by imposing C_2 symmetry, we arrive the a transition state depicted in Figure 4, with an energy 9.4 kcal/mol above the σ-complex. Its sole vibrational imaginary frequency mode links the reactant and product of a σ-bond metathesis. We infer that the σBM pathway is less favorable than OA in the nonsolvent approximation, as the OA TS energy is 3.6 kcal/mol.

We are not aware of any reports of methane activation by palladium complexes in solvents of very low proton affinity. The success of platinum and the failure of palladium systems in this type of reaction may be taken as further support for the OA pathway; for Pd, the OA will lead to a Pd(IV) intermediate, which is known to be energetically unfavorable.[30] A more quantum chemical view, put forth by Low and Goddard[31] and Siegbahn et al.[32] involves the preference of Pd for an atomic

d^{10} occupation, compared to the d^9s^1 occupation preferred by Pt. Further, we find that an attempt to optimize the OA structure of the analogous palladium system yields a σ-complex, indicating that the OA structure is not a minimum on the potential energy surface of the palladium system.[33,34] It should be mentioned that sulfuric acid appears to have sufficient proton affinity to act as a vehicle for proton transfer, as demonstrated by Hoarsley et al.[14] and Mylvaganam et al.[15] From the work of Sen et al.,[35] it appears that trifluoroacetic acid might not have the same capability. They reported methane activation in a system consisting of palladium diacetate solvated in trifluoroacetic acid. In later studies,[4,36] however, these results could not be reproduced. Eventually, it became clear that much of the reactivity reported in the original work was due to water, present as an impurity and leading to formation of methyltrifluoroacetate through decarbonylation of the presumed catalyst itself.[6]

Solvent stabilization of the TS for a σBM reaction could involve a solvent molecule acting as a Brønsted base interacting with the transferring hydrogen. PFP, the solvent used in the experimental work,[7] has a very low proton affinity due to its strongly electronegative substituents.[37−39] For instance, it is not protonated by HCl or HBr in ethereal solution. On the other hand, a two-electron ligand coordinating to the vacant site of the OAP will effectuate a stabilization of the OAP, as has been shown experimentally for a related system by Wick and Goldberg.[10] It seems reasonable to assume that PFP is a better electron pair donor than a proton acceptor, as the fluorine atoms may back-donate electron density to the π-system of the ring. If this is the case, solvent effects most likely will stabilize the OA TS more efficiently than its σBM counterpart. This hypothesis has been tested by performing calculations on the OA and σBM reaction pathways including an NF_2H molecule, which has been chosen as a model for PFP for reasons of computational economy. This approximation was evaluated by optimizing PFP and NF_2H adducts to the σ-complex and OAP. The energy differences between σ-complex and OAP for the two Lewis bases is only 1.5 kcal/mol (see Table 1), resulting from a 0.3 kcal/mol difference in the coordination energy to the σ-complex and 1.8 kcal/mol to the OAP. Further studies of solvent effects were undertaken with NF_2H only. The single-molecule approach to solvent effects can, of course, only give semiquantitative results. However, it may provide insight as to the effect of a Lewis base coordinating to the metal complex.

NF_2H coordinates only weakly to the σ-complex. The most stable configuration, which was found after attempting several alternatives, involves the NF_2H molecule pointing the N atom lone pair toward the midpoint of a nitrogen−platinum bond. In the OAP, NF_2H fills the vacant site of the octahedral coordination around platinum and gives an 18-electron complex. The OAP is stabilized by 16.4 kcal/mol relative to the σ-complex by the Lewis base. Tracing the reaction path from the OAP, we arrive at the transition state, in which the NF_2H molecule has been pushed out close to the position that it occupies in the σ-complex. In accordance with this, the TS is only stabilized by 1.0 kcal/mol relative to the σ-complex compared to the nonsolvent case. From these results, it appears that an electron pair donor stabilizes the Pt(IV) complex much more than Pt(II) species.

In the σBM TS, platinum has a formal oxidation number of 2. It is dubious whether this TS exists at all if NF_2H is allowed to coordinate to platinum, with the accompanying stabilization of the OAP; this is supported by test calculations in which transition state searches invariably converge to the OAP. It appears reasonable to believe that in order to stabilize the σBM TS relative to the σ-complex, NF_2H must coordinate to the transferring hydrogen. We have not succeeded in optimizing a TS starting from the (eda)-only σBM TS with NF_2H coordination to the transferring hydrogen, directly opposite to platinum. An optimization in which all atoms except the solvent molecule are kept frozen gives an energy that is 13.1 kcal/mol higher than for the σ-complex, which is an upper limit to the true energy. The subsequent TS optimization, in which all geometrical degrees of freedom are released, shows numerically unstable behavior and eventually converges to the OAP. Preventing this by imposing symmetry restrictions is not possible, because NF_2H has no 2-fold axis. The relative energies of the other Pt(II) species under study are not strongly influenced by the presence of NF_2H, and there is no reason to believe that the σBM TS should behave differently. We conclude that the main effect of the solvent molecule is to stabilize the OAP, and, to a lesser extent, the OA TS.

4. Conclusions

We have investigated the mechanism of C−H activation at a cationic Pt(II) complex with a bidentate nitrogen ligand using quantum chemical DFT methods. The oxidative addition pathway suggested by experimentalists is supported by the present results. The main effect of a Lewis basic solvent is to stabilize Pt(IV) species relative to Pt(II). It is concluded that for the combination of platinum complex under study and a solvent of very low proton affinity, the existence of a favorable σ bond metathesis pathway is unlikely.

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