

Dimethylplatinum(II) Complexes: Computational Insights into Pt–C Bond Protonolysis

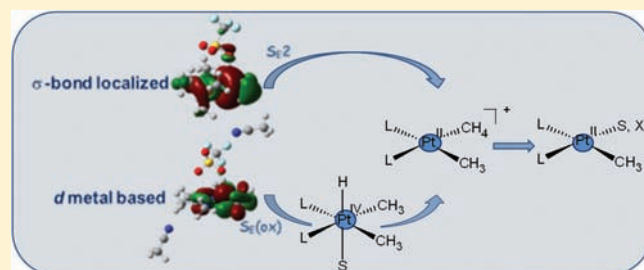
Gloria Mazzone, Nino Russo, and Emilia Sicilia*

Dipartimento di Chimica and Centro di Calcolo ad Alte Prestazioni per Elaborazioni Parallele e Distribuite-Centro d' Eccellenza MIUR, Università della Calabria, I-87036 Arcavacata di Rende, Italy

S Supporting Information

ABSTRACT: A detailed density functional theory (DFT) study of the protonation and subsequent methane elimination reactions of dimethylplatinum(II) complexes in presence of triflic acid in various solvents has been undertaken to contribute to the debate concerning the mechanism of the electrophilic cleavage of the Pt–C bond in Pt(II) complexes. Both mechanisms of direct one-step proton attack at the Pt–C bond (S_E2) and stepwise oxidative-addition on the central metal followed by reductive elimination ($S_E(ox)$) have been explored for a series of dimethylplatinum(II) complexes changing the nature of the ancillary ligands and the solvent. Theoretical calculations show that the most likely mechanism cannot be predicted on the basis of

spectator ligands donating properties only. A one-step protonolysis pathway is characteristic for complexes containing P based ligands, whereas for complexes containing N based and, in general, hard poor-donor ligands a common behavior cannot be indicated. Solvent nucleophilicity can influence the rate of the $S_E(ox)$ rate mechanism, whereas its steric hindrance can induce a change of the preferred mechanism. The hypothesis that five-coordinate methyl hydrido platinum(IV) intermediates might be formed along the $S_E(ox)$ pathway is not supported. Only six-coordinate Pt(IV) hydride complexes are calculated to be stable intermediates generated by direct protonation at the platinum center. Formation and experimental detection of six-coordinate Pt(IV) hydrides, nevertheless, cannot be considered a definite evidence that a $S_E(ox)$ mechanism is operative because such intermediates can be also generated by a hydrogen migration to Pt from the carbon atom of the σ -complex methane molecule formed by a S_E2 attack. For all the examined complexes methane loss occurs by an associative mechanism. Both solvent and anion of the acid can assist methane displacement. Calculations have been also carried out to probe whether the preference for a concerted or a stepwise mechanism should be predicted on the basis of two proposed criteria: metal-complex charge distribution as a consequence of the Pt–C bond polarization and the nature of the highest occupied molecular orbital (HOMO).



1. INTRODUCTION

Alkanes are the main constituents of oil and natural gas, and have been utilized as raw materials in industrial processes and for the production of energy for many decades. However, the possibility to selectively activate and functionalize saturated hydrocarbons to form more valuable products under mild conditions is one of the desirable goals of the current chemical research.¹

Extensive research over the past 40 years has discovered many examples of inter- and intramolecular C–H bond activation by homogeneous transition metal complexes, often under remarkably mild conditions.² A particular interest has been focused on Pt(II) square planar metal complexes that have proven to be good candidates as homogeneous systems able to activate alkane C–H bond in mild conditions.³ Since the early work by Shilov and coworkers established that a mixture of Pt(II) and Pt(IV) salts in aqueous solution is capable to convert alkanes (including methane) to mixtures of the corresponding alcohols and chlorides,^{3a,b} many studies on these and model systems have provided significant mechanistic details,^{1a,4} that have led to an

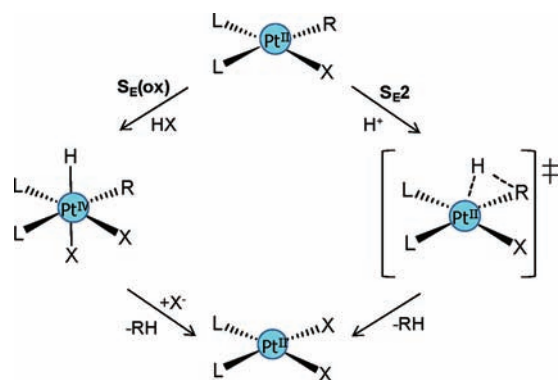
increased understanding of the reaction mechanism. Numerous experimental and theoretical studies have shown that of the three steps of the whole catalytic cycle proposed by Shilov and coworkers, the C–H activation step governs the overall rate as well as the selectivity of the catalytic cycle.⁵ Because of the inherent difficulties in studying C–H bond activation directly, much of the insight into alkane activation reactions has come from the investigation of the microscopic reverse reactions of the activation step, namely, protonolysis of well-defined model systems, such as alkylplatinum(II) complexes.⁶

Two alternative routes have been proposed in the literature^{1a,4a,7} for the electrophilic attack of the proton at alkylmetal complexes (as shown in Scheme 1 in the case of a Pt(II) complex): the direct protonation by a concerted attack at the platinum–carbon bond (S_E2 mechanism, the microscopic reverse of electrophilic C–H activation), or a stepwise prior oxidative addition on the central metal to generate a platinum(IV)-hydride followed by reductive

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Scheme 1. Alternative Reaction Pathways for the Protonolysis of Alkylplatinum(II) Complexes



elimination ($S_E(\text{ox})$ mechanism, the microscopic reverse of oxidative C–H cleavage). Both pathways involve the formation of a methane C–H σ -complex before the liberation of methane.^{2a,4a,8} Methane loss can occur through both either an associative or a dissociative substitution pathway.^{4a}

In spite of the numerous investigations on the protonolysis of alkyl- and arylplatinum(II) compounds, which have taken into account many parameters,⁹ whether the attack by the proton takes place on the metal center or directly on the Pt(II)-C bond is rather difficult to establish only on the basis of kinetic evidence. Very recently, Bercau et al. have suggested that kinetic isotope effect (KIE) behavior, consistent with tunnelling, can be an experimental indicator of the concerted S_E2 mechanism.¹⁰ The issue of the preferred protonation site has been for the first time theoretically investigate by Li et al.¹¹ for the benzene C–H bond activation mediated by a diimine Pt(II) complex.

The preference for the $S_E(\text{ox})$ pathway has been considered plausible by the detection of Pt(IV)-H intermediates in the protonolysis of many alkylplatinum complexes. The mere observation of Pt(IV) hydrides does not definitively prove, however, that protonation occurs at the metal since, as underlined by Tilset's group,^{6d} only the thermodynamic site of protonation is identified. Unobserved kinetic products can be formed by a S_E2 attack that rapidly rearrange to give observed hydrides. The same authors have provided the first unambiguous evidence that the metal center of Pt(II) dialkyl complexes is also the kinetically preferred site of protonation. On the other hand, since the possibility to detect hydride intermediates is strongly dependent on many factors, failure to observe hydridoplatinum(IV) intermediates does not allow to definitely exclude their involvement.

After the isolation of some platinum(IV) aryl hydrido complexes in the early 1990s,¹² several research groups^{6a,7h,i,13} have observed formation of hydridoalkylplatinum(IV) intermediates under low-temperature protonation of alkyl Pt(II) complexes containing hard N-donor ligand or trans-activating groups supporting the hypothesis of an oxidative addition mechanism to be operative in such cases.

Evidence of this trend, has been presented more recently by Tilset and co-workers, which have carried out a detailed kinetic study of the protonolysis reaction of a (N–N)PtMe₂ complex (where N–N is the ArN=C(Me)-C(Me)=NAr diimine ligand with Ar = 2,6-Me₂C₆H₃) in MeCN/CH₂Cl₂ solvent mixtures and have indicated the $S_E(\text{ox})$ mechanism as the preferred one.^{6b} Even in absence of a direct evidence for the existence of a pentacoordinate hydrido dimethylplatinum(IV) intermediate,

the authors have assumed that the reaction proceeds via formation of such a complex. Nevertheless, the results of their analysis are equally consistent with a mechanism that involves protonation and acetonitrile ligation at Pt occurring in a concerted fashion.

This mechanism is not the preferred one for the protonolysis of the *cis*-dialkyl, *cis*- and *trans*-diarylplatinum(II) and mixed alkyl-aryl complexes containing phosphane, for which measured kinetic parameters provide strong evidence that the concerted attack at the Pt(II)-carbon bond is the most likely mechanism.^{6c} A detailed kinetic study of platinum(II) alkyl complexes of the type with monodentate and chelating phosphane ligands has demonstrated that the protonolysis occurs following a one-step mechanism of proton transfer.⁷

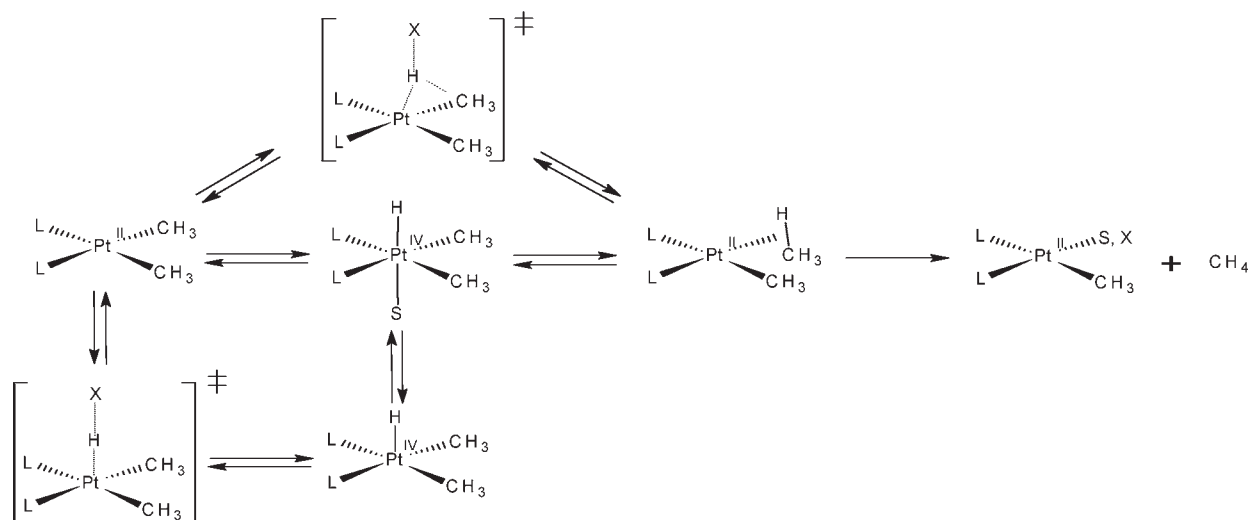
In view of the fundamental mechanistic relevance of the protonation of the Pt–C bond as the microscopic reverse of C–H bond activation by platinum complexes, we have considered of interest to probe how changes in the Pt(II) ligand environment affect the protonolysis process. With this aim, we have investigated the protonolysis reaction mechanistic details of two dimethylplatinum(II) complexes in presence of triflic acid in acetonitrile solvent. The former one is the model (N–N)Pt(Me)₂ complex, very similar to that studied by Tilset et al.,^{6b} where the diimine N–N is MeN=C(Me)–C(Me)=NMe, containing a hard nitrogen-donor ligand. The latter one is the platinum(II) complex *cis*-[Pt(Me)₂(PMe₃)₂] containing soft ligands as trimethylphosphine. We have used Density Functional Theory (DFT) calculations to gain useful insight and understanding of the factors that affect every step of the protonolysis process. Our aims are 4-fold: (i) to evaluate the influence of the change from hard poor- to soft good-donor ligands on the protonation step that could occur at Pt or at the methyl group; (ii) to assess the involvement of a pentacoordinate platinum(IV) hydrido intermediate in the multistep $S_E(\text{ox})$ mechanism; (iii) to address the issue of whether the reacting methane leaves (or enters) the coordination sphere by an associative or a dissociative mechanism; and, also connected to the previous topic, (iv) to establish which is the role of both the solvent and the anion of the acid that releases the proton. Special note should be made concerning the effect of the presence of an explicit solvent molecule and of the anion of the acid. A series of preliminary calculations carried out by using hard NH₃ and soft PH₃ ligands to reduce the computational cost have clearly shown that inclusion of solvent and anion species is mandatory to correctly reproduce both the mechanism and the energetics of the process.

The situation is summarized in Scheme 2 that illustrates the explored alternative pathways. For both investigated model platinum(II) complexes calculated energy barriers have been compared with literature data for closely related compounds.^{6b,7} Moreover, in the effort to indicate the factors that could play a role in determining the site of attack, additional computations have been carried out for a series of platinum(II) complexes changing the nature of the solvent and of the ancillary ligands. It is worth mentioning that, for many systems examined here, simulation of the solvent effects does not reproduce the experimental conditions in terms of solvent characteristics and temperature.

2. COMPUTATIONAL DETAILS

All the electronic structure calculations involved in the protonolysis reaction of the *cis*-[PtMe₂(PMe₃)₂] and (N–N)PtMe₂ (N–N is

Scheme 2. Unified Scheme for Electrophilic Proton Attack at Dimethylplatinum(II) Complexes



MeN=C(Me)–C(Me)=NMe) complexes have been carried out using the Gaussian 03 program package¹⁴ at the DFT level by use of the hybrid exchange functional by Becke (B3)¹⁵ in combination with the Lee, Yang, and Parr (LYP) correlation functional.¹⁶

All equilibrium structures and transition states have been fully optimized using 6-311+G** standard basis sets for all atoms except the platinum atom, for which the double- ζ basis set LANL2DZ has been employed. The relativistic LANL2DZ pseudopotential is the typical basis set used for structural calculations of transition metal complexes, and it is known to give close agreement between optimized and experimentally determined structures for organoplatinum complexes.¹⁷

All stationary points have been characterized as minima or transition states by a vibrational analysis performed within the harmonic approximation at the same level of theory, ensuring that every transition state had only one imaginary frequency. The zero-point vibrational energy corrections have been included in all of the reported relative energies. The reaction pathways have been investigated more closely following the intrinsic reaction coordinate (IRC)^{18,19} starting from transition state structures and leading to the corresponding minima.

NBO charge analysis was carried out on the structures of some intercepted stationary points.²⁰

Single-point calculations on optimized structures have been also carried out to estimate the impact of the solvent employed in the experiments. Whereby, the acetonitrile environment has been modeled using the Conductor Polarized Continuum Model (CPCM)²¹ as implemented in Gaussian 03 and the UAHF set of radii has been selected to build up the cavity. Enthalpies and Gibbs free energies have been obtained at 298 K at 1 atm from total energies, including solvent, zero-point, and thermal corrections, using standard statistical procedures.²² However, such approach does not reflect the real entropic cost under catalytic conditions.²³ Following a common approach in theoretical catalysis, the solvation entropy has been estimated as two-thirds of its gas-phase value.^{23,24} Indeed, for catalytic reactions solvation entropy of the starting material and the adduct can be regarded as being similar. The difference in reaction entropy between the gas-phase and the condensed-phase is mainly due to substrate solvation. For polar solvents the entropic contribution of the substrate in solution is about two-thirds of the gas-phase value. Thus, it is reasonable to assume that the solvation entropy for catalytic systems is approximately two-thirds of the gas-phase value.

3. RESULTS AND DISCUSSION

3.1. Protonolysis of the Pt–C Bond of the (N–N)PtMe₂ Complex. The geometric structures of the Pt species (B3LYP optimized in the gas phase) which are stationary points along the pathway for the protonolysis reaction of the (N–N)PtMe₂ complex and selected geometrical parameters are reported in Supporting Information, Figures S2 and S3, respectively. The calculated potential energy surface (PES) for the protonolysis process is drawn in Figure 1, where relative energies in gas-phase and relative free energies in solution are calculated with respect to the sum of the energies of the separated reactants, that is (N–N)PtMe₂ complex, triflic acid, and one explicit molecule of acetonitrile solvent. Relative enthalpies (ΔH) at 298 K and free energies in MeCN (ΔG_{sol}) are provided. Unless otherwise noted, in what follows, the discussed energies are B3LYP free energies in MeCN. Both transition states for the proton transfer along the stepwise S_E(ox) pathway have been intercepted, whereas all the attempts to locate the transition state involved in the one-step S_E2 mechanism have failed. Protonation of the Pt–C bond of a Pt(II) alkyl complex takes place by oxidative addition on the central metal atom followed by reductive elimination. Geometrical structures reported in Supporting Information, Figure S2 show that the acetonitrile solvent molecule, which in the initial complex **I**_{ox} is far from the metal center of the complex, comes close in the transition state **TS1**_{ox} to assist the release of the proton from the acid. No stable minimum corresponding to the five-coordinate Pt(IV) hydrido complex has been intercepted, and the only calculated stable minimum is the six-coordinate platinum(IV) hydrido complex (**II**_{ox}) stabilized by the axial MeCN ligand. The barrier that is necessary to overcome to form the intermediate **II**_{ox} is 1.2 kcal/mol. The calculated imaginary frequency of 48i cm⁻¹ is mainly associated with the proton transfer from the oxygen atom of the acid to the Pt atom of the complex and the movement of the MeCN molecules that approaches the metal center. Full optimization in the solvent could clarify whether the **TS1**_{ox} really exists or the surface is very flat in this region of the energy profile. Intermediate **II**_{ox} is more stable than the first intermediate **I**_{ox} by 4.1 kcal/mol. Formation of the σ -methane complex **III**_{ox} takes place overcoming an energy barrier, corresponding to the **TS2**_{ox}

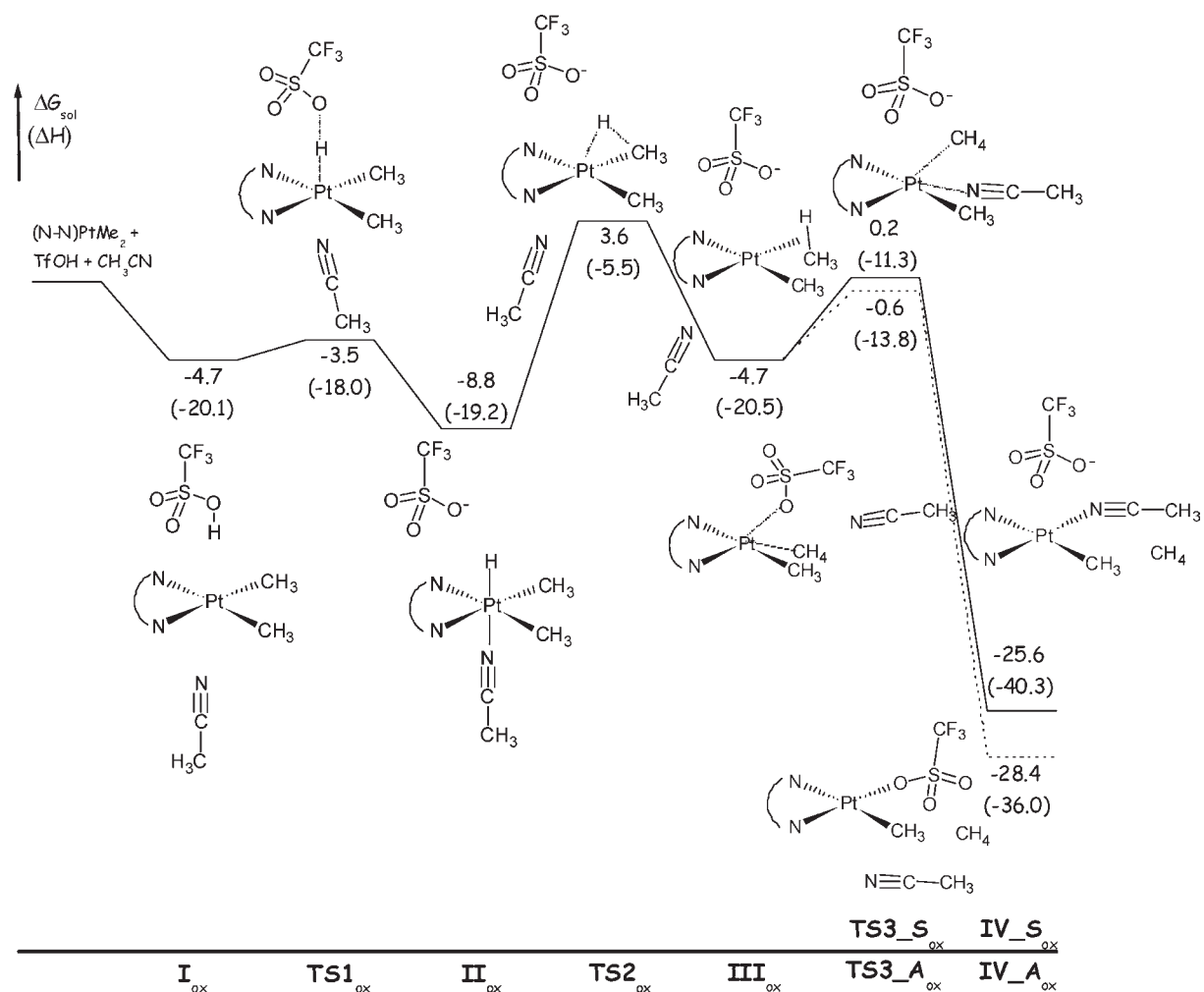


Figure 1. Calculated energy profile for the proton attack at the (N–N)PtMe₂ complex in presence of triflic acid in acetonitrile solvent leading to methane loss. Relative free energy in CH₃CN (ΔG_{sol}) and enthalpies (ΔH) at 298 K are reported. Relative energies are in kcal/mol.

transition state, of 12.4 kcal/mol. The normal mode associated to the imaginary frequency, calculated to be $567i \text{ cm}^{-1}$, corresponds to the proton transfer from the metal center to the carbon atom of one of the methyl groups. The MeCN molecule appears to be completely detached. Calculated values of the energy barriers for the model complex can be favorably compared with the experimental activation energies obtained for the specific complex used in ref 6b (3.6 and 18.2 kcal/mol for the first and the second step, respectively). For the metal-methane complex III_{ox} we have explored different coordination modes of the σ -CH₄ ligand. In analogy with previous investigations^{25a} only coordination corresponding to the so termed $\eta^2(\text{C,H})$ ^{25b,c} mode has been found as a stable minimum (see Figure 1) lying about 5 kcal/mol lower in energy with respect to separate reactants asymptote.

Concerning the methane loss we have investigated the two alternative scenarios corresponding to (a) a dissociative pathway involving formation of a coordinatively unsaturated 14-electron intermediate [(N–N)PtCH₃]⁺ followed by coordination of the solvent or the anion of the acid and (b) a solvent- or anion-assisted associative pathway that occurs by simultaneous departure of the leaving ligand and entering ligand approach to the platinum atom.

For the transition state of the associative mechanism, TS3_{ox} (corresponding to a five-coordinate platinum), we have considered

two different alternatives, one where the MeCN solvent molecule replaces methane (TS3_{S_ox}) and another where methane is replaced by the anion, OTf[−], of the acid (TS3_{A_ox}). In agreement with experimental findings, the square-planar complex [(N–N)Pt(MeCN)CH₃]⁺, named IV_{S_ox}, obtained in the former case is less stable than the square-planar complex (N–N)Pt(OTf)CH₃, named IV_{A_ox}, formed by methane replacement in the latter case. Gas-phase calculations are not able to reproduce this trend and a reversed ranking of IV_{S_ox} and IV_{A_ox} is obtained. The barriers that hamper the formation of the IV_{S_ox} and IV_{A_ox} complexes are comparable in solution. In addition, we have evaluated also the energy barrier for the transition state, TS4_{ox}, that should allow the interconversion between IV_{A_ox} and IV_{S_ox} complexes. The transition state between these two minima is 15.1 above the IV_{A_ox} least stable minimum, indicative of a slow process (see Supporting Information, Figure S4).

Considering now the dissociative mechanism, the reaction should proceed by a tricoordinate transition state corresponding to methane bond breaking to generate a 14-electron intermediate with a vacant coordination site that should be occupied by the solvent or the anion. We have repeatedly tried to intercept the tricoordinate intermediate and the transition state leading to it, but without success. Owing to the lack of any stabilizing effect of

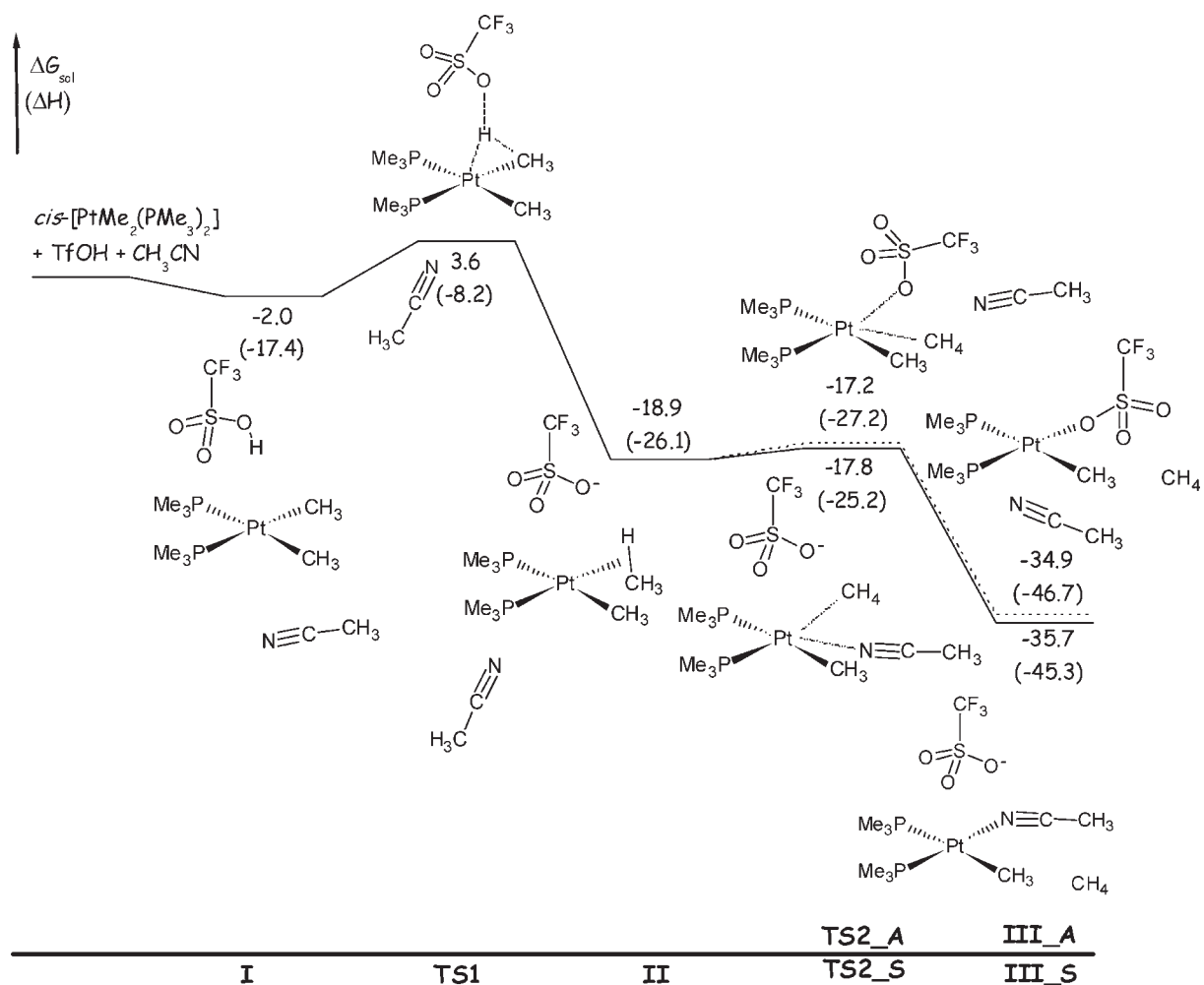


Figure 2. Calculated energy profile for the proton attack at the *cis*-[PtMe₂(PMe₃)₂] complex in presence of triflic acid in acetonitrile solvent leading to methane loss. Relative free energies in CH₃CN (ΔG_{sol}) and enthalpies (ΔH) at 298 K are reported. Relative energies are in kcal/mol.

the labile existence of these species, the empty site is immediately occupied by the incoming MeCN or OTf⁻ species. So this establishes that methane entering or leaving the coordination sphere is an assisted associative process.

From an examination of the energy profile in Figure 1 we conclude that the rate-determining step of the whole process is the reductive C–H coupling to the σ adduct, to which the highest energy barrier corresponds to.

3.2. Protonolysis of the Pt–C Bond of the *cis*-[PtMe₂(PMe₃)₂] Complex. Fully optimized structures of stationary points intercepted along the pathway for the protonolysis of the model *cis*-[PtMe₂(PMe₃)₂] complex and some selected geometrical parameters are reported in the Supporting Information, Figures S5 and S6, respectively. The corresponding energy profile is sketched in Figure 2 where relative enthalpies and relative free energies in acetonitrile solvent are calculated with respect to the sum of the energies of the complex, the triflic acid, and one solvent molecule. Discussed energy values are the B3LYP solvent free energies (ΔG_{sol}).

Even though the current literature strongly supports the hypothesis that phosphane trans-activating ligands promote the S_E2 mechanism, we have performed calculations aiming to locate minima and transition states along both stepwise and concerted mechanisms. Only the six-coordinate Pt(IV) hydride

intermediate involved in the S_E(ox) mechanism has been located, whereas along the one-step S_E2 protonation pathway the transition state has been easily intercepted. After formation of the first adduct I, protonation proceeds by a one-step electrophilic attack at the Pt–C bond with the formation of the σ methane adduct, that takes place overcoming a free energy barrier of 5.6 kcal/mol, corresponding to the transition state TS1. The imaginary frequency that characterizes this stationary point is calculated to be 1305i cm⁻¹ and corresponds to the transfer of the proton from the oxygen atom of the acid to the carbon atom of one of the methyl groups and the weakening of the Pt–C bond. As expected the explicit solvent molecule plays no role and can be considered one of the molecules of the solvent environment. The σ methane η^2 -bonded complex II is formed that is computed to be considerably more stable than the I complex.

In analogy with the methane loss step from the [(N–N)Pt(CH₃)(CH₄)]⁺ adduct we have explored both dissociative and associative mechanisms and for the associative pathway the possibility that the substitution takes place by methane exchange for both a solvent molecule and the anion of the acid. It results that the methane displacement occurs by an associative mechanism that could involve as incoming species both the solvent and the anion. The calculated barrier for the methane removal from the coordination sphere of the metal is found in both cases to be

Table 1. Calculated NBO Charges for the Proton Attack at (N–N)PtMe₂, *cis*-PtMe₂(PMe₃)₂, (dmpe)PtMe₂, (tmeda)PtMe₂, and (COD)PtMe₂ Complexes in Acetonitrile Solvent, at (N–N)PtMe₂ and (PMe₃)₂PtMe₂ Complexes in Methanol Solvent, and at (N–N)PtMe₂ Complex in Ethyl Ether Solvent

solvent	complex	NBO charges						
		N	P	C _{COD}	Pt	H	C	X ^a
CH ₃ CN	(N–N)Pt(Me) ₂	–0.441			0.290	0.491	–0.813	–0.380
	<i>cis</i> -[PtMe ₂ (PMe ₃) ₂]		1.070		–0.293	0.508	–0.828	–0.367
	(tmeda)Pt(Me) ₂	–0.525			0.253	0.492	–0.800	–0.380
	(dmpe)Pt(Me) ₂		1.096		–0.319	0.516	–0.831	–0.386
	(COD)Pt(Me) ₂			–0.194	0.262	0.517	–0.806	–0.370
CH ₃ OH	(N–N)Pt(Me) ₂	–0.427			0.229	0.500	–0.813	–0.738
	<i>cis</i> -[PtMe ₂ (PMe ₃) ₂]		1.120		–0.331	0.505	–0.822	–0.732
(C ₂ H ₅) ₂ O	(N–N)Pt(Me) ₂	–0.418			0.306	0.502	–0.922	–0.614

^aX is the nucleophile atom of the solvent molecule: O for both CH₃OH and (C₂H₅)₂O solvent and N for CH₃CN solvent.

very low, less than 1 kcal/mol, indicating an almost barrierless process.

The overall process leads to the elimination of methane and formation of *cis*-[PtMe(MeCN)(PMe₃)₂]⁺, indicated as **III_S**, and *cis*-[PtMe(OTf)(PMe₃)₂], named **III_A**, square planar complexes is exothermic by 35.7 and 34.9 kcal/mol, respectively. The rate-determining step is the proton attack of the Pt–C bond, and the calculated energy barrier of 5.6 kcal/mol compares favorably with the experimental value of the enthalpy of activation of $\Delta H^\ddagger = 6.3$ kcal/mol obtained from the kinetic analysis of the protonolysis reaction of the *cis*-[PtMe₂(PET₃)₂] complex.⁷

Now, by the principle of microscopic reversibility, looking at the two energy profiles reported in Figures 1 and 2 from the right to the left side we can draw some conclusions on the relative efficiency of Pt(II) complexes containing N- and P-based ligands in activating C–H bonds. In presence of a soft P-donor ligand in trans position the first step of the C–H bond activation, that is coordination of CH₄ to the metal to form the σ -complex, occurs much more easily than in presence of a hard N-based ligand. However, the ease of access of the methane molecule to the coordination sphere of the metal is balanced by its much easier removal. Therefore, once the σ -complex is formed the phosphane complex is more likely to release the methane molecule than to proceed toward proton dissociation. The energetics, instead, are more favorable for the diimine complex (Figure 1) that, from the formed σ -complex, can proceed to transfer the proton to the metal center. The efficiency of diimine Pt(II) complexes in comparison with phosphane complexes in activating the C–H bond has been anticipated by Puddephatt et al.²⁶ and Romeo and D'Amico.⁷

3.3. Can the Preferred Protonolysis Mechanism Be Predicted? The preference for a stepwise oxidative route or a concerted one in the protonolysis of dialkylplatinum(II) complexes has been explained by invoking both the charge distribution⁷ and the character of the metal complex highest occupied molecular orbital (HOMO).²⁷

Regarding the first criterion, Romeo and D'Amico⁷ have proposed that the viability of a “one-step” electrophilic proton attack should increase with the increase of the electron donation from soft trans-activating groups because of an electron enrichment at the Pt-alkyl σ -bond of the four-coordinate starting complex combined with a significant L_nPt^{δ+}-C^{δ-} bond polarization.

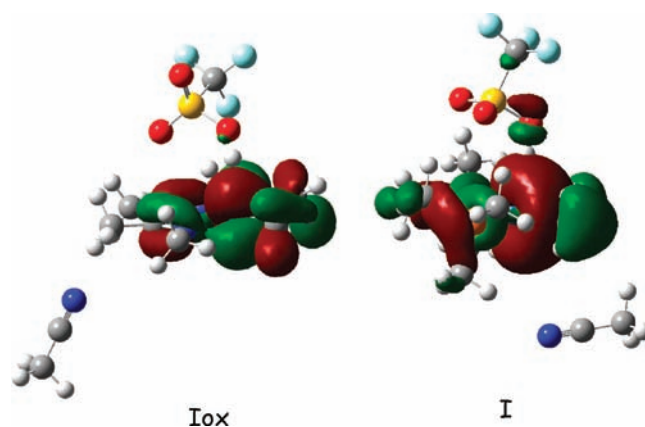


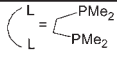
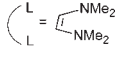
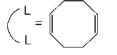
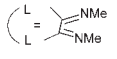
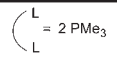
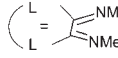
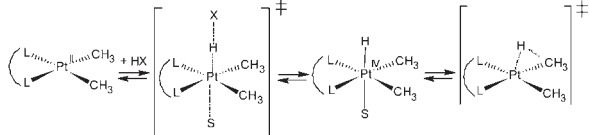
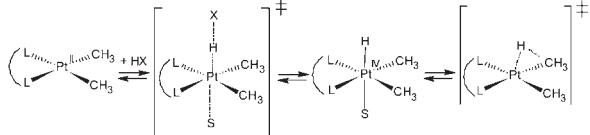
Figure 3. HOMO plot for (N–N)PtMe₂ (on the left) and *cis*-[PtMe₂(PMe₃)₂] (on the right) complexes in presence of triflic acid and an explicit acetonitrile solvent molecule.

According to the second criterion,²⁷ the favored protonolysis mechanism should be equally well predicted on the basis of the relative accessibility of metal-based (nonbonding) and M–C σ -bonding orbital electron density. That is, for complexes having a HOMO with M–C σ -bonding character cleavage of this bond occurs according to the S_E2 mechanism, whereas complexes having the HOMO with nonbonding d orbital character typically follow the two step mechanism (S_E(ox)).

Aiming to prove whether one of these two criteria or both could be used to indicate which is the most likely pathway, NBO charge distribution and frontier molecular orbitals examination have been carried out on the optimized geometrical structures of (N–N)Pt(Me)₂ and *cis*-[PtMe₂(PMe₃)₂] model complexes. NBO charge analysis and molecular plots for both complexes are reported in Table 1 and Figure 3, respectively.

The first investigated model complex (N–N)Pt(Me)₂ is characterized by a d metal-based HOMO and, hence, a stepwise oxidative S_E(ox) mechanism is predicted to be the preferred one. NBO charge analysis shows that the presence of the hard N–N diimine ligand causes a Pt^{δ+}-C^{δ-} bond polarization. This information can be interpreted assuming that poor electron-donor ancillary ligands reinforce the Pt–C bond and favor the concerted protonation/solvent coordination on the metal center.

Table 2. Calculated Activation Energies (kcal/mol) for the Proton Attack at (dmpe)PtMe₂, (tmeda)PtMe₂, and (COD)PtMe₂ Complexes in Acetonitrile Solvent, at (N–N)PtMe₂ and *cis*-PtMe₂(PMe₃)₂ Complexes in Methanol Solvent, and at (N–N)PtMe₂ Complex in Ethyl Ether Solvent^a

Solvent	Complex	E	ΔE^\ddagger
CH ₃ CN		$E = 0$	$\Delta E^\ddagger = 10.4$
		$E = 0$	$\Delta E^\ddagger = 14.6$
		$E = 0$	$\Delta E^\ddagger = 13.9$
(C ₂ H ₅) ₂ O		$E = 0$	$\Delta E^\ddagger = 15.9$
		$E = 0$	$\Delta E^\ddagger = 10.0$
CH ₃ OH		$E = 0$	$\Delta E^\ddagger = 3.1$
			$\Delta E = 3.8$
			$\Delta E^\ddagger = 16.4$

^a HX is the triflic acid and S is the methanol solvent.

The second model system *cis*-[PtMe₂(PMe₃)₂] has a σ -bond localized HOMO (see Figure 3) and, in fact, a direct M–C bond electrophilic displacement, S_E2, has been observed. NBO analysis shows (see Table 1) that the soft character of strong donor phosphine ligands induces formation of partial negative charges on both carbon and platinum atoms weakening the Pt^{δ-}–C^{δ-} bond. Bond weakening is supported by the difference in Pt–C bond distances calculated for I (2.113 Å) and I_{ox} (2.056 Å) complexes (see the Supporting Information, Tables S3 and S6). The carbon atom becomes the favorable site of protonation.

It is worth underlining that, although the calculated charge distribution does not follow the surmised behavior,⁷ the ensuing polarization of the Pt–C bond can be used to discriminate between alternative, S_E(ox) and S_E2, protonolysis pathways, at least for both complexes considered so far in presence of triflic acid and acetonitrile.

To provide further mechanistic insights into the key step of the protonolysis process of dimethylplatinum(II) complexes and the extent to which a change in solvent and coordinative environment can promote a mechanism change, other spectator ligands and solvents with different, either electronic or steric, characteristics have been investigated. The same tools, NBO charge distribution and HOMO analysis, have been used. NBO charges are reported in Table 1 and HOMO plots in the Supporting Information, Figure S7.

The dimethylplatinum(II) complexes ligand environment has been changed with *N,N,N',N'*-tetramethylethylenediamine (tmeda), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,5-cyclooctadiene (COD) ligands in the same acetonitrile solvent. Additional calculations for (N–N)Pt(Me)₂ in methanol and

ether and for *cis*-[PtMe₂(PMe₃)₂] in methanol have been carried out. For all the investigated systems both direct and stepwise protonation mechanisms have been considered viable and the corresponding pathways explored. Activation energies calculated for the proton attack are schematically summarized in Table 2. The energies reported in this table are the relative ZPE corrected electronic energies (ΔE) obtained at the same level of theory of previous calculations.

As it clearly appears at a first glance from Table 2, only for the (N–N)Pt(Me)₂ complex in MeOH solvent have both transition states along the stepwise S_E(ox) pathway been located. According to calculations in acetonitrile solvent, no stationary points along the concerted pathway have been intercepted. This is the expected behavior on the basis of nonbonding d orbitals character of the HOMO (see Supporting Information, Figure S7) and NBO calculated charges (Table 1). Comparison between the calculated energy barriers in gas-phase for the protonation at the metal center (3.1 kcal/mol in MeOH vs 3.6 kcal/mol in CH₃CN) and the reductive coupling (16.4 in MeOH vs 12.8 kcal/mol in CH₃CN) indicates that acetonitrile solvent better assists the protonolysis reaction than methanol. Since the oxygen atom of methanol bears a negative charge greater than the negative charge on the nitrogen atom of acetonitrile, the energetic cost of the solvent nucleophile molecule release during the shift of the proton from the metal to the carbon atom should be consequently higher. In an analogous way the protonolysis reaction of the *cis*-[PtMe₂(PMe₃)₂] complex assisted by a solvent methanol molecule proceeds following the S_E2 concerted mechanism. The Pt–C σ -bonding nature of the HOMO (Supporting Information, Figure S7) and the bond polarization

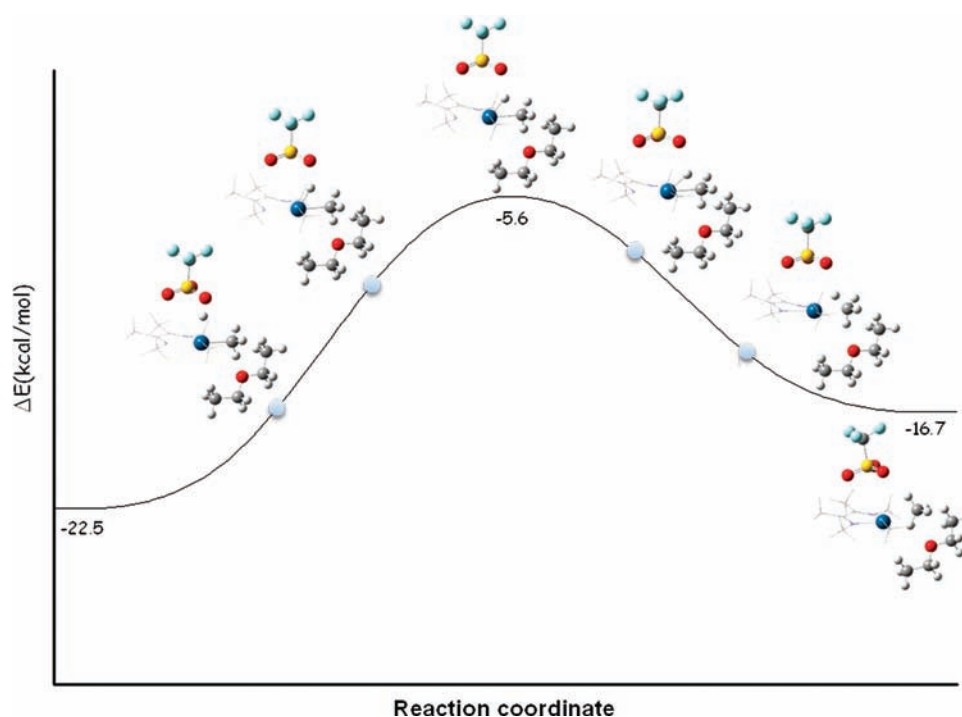


Figure 4. Schematic representation of the pathway for the conversion of the $(N-N)PtMe_2$ complex to the $[(N-N)Pt(CH_4)(CH_3)]^+$ σ -complex, in presence of triflic acid in ether solvent. Geometrical structures have been obtained by an intrinsic reaction coordinate calculation starting from the transition state structure.

remain unchanged, in accordance with the prediction of a single step protonolysis mechanism. Since the solvent does not play any role, the calculated barrier associated to the concerted transition state is nearly unchanged (10.0 in MeOH vs 9.0 in CH_3CN).

For the three $(dmpe)Pt(Me)_2$, $(tmeda)Pt(Me)_2$, and $(COD)Pt(Me)_2$ complexes in CH_3CN solvent the concerted proton attack at the Pt–C bond is the preferred one, although the inductive effects on the metal center are of different sort. In fact, from the electronic point of view, the complex containing the hard *tmeda* ligand is characterized by a $Pt^{\delta+}-C^{\delta-}$ bond polarization that should be a sign of a stepwise oxidative mechanism. On the basis of the σ -bonding character of the HOMO (Supporting Information, Figure S7), instead, a one-step proton transfer should be predicted. In fact, the transition state for the concerted hydrogen transfer has been intercepted and characterized as well as the six-coordinate Pt(IV)-hydrido complex. All attempts to intercept, instead, both transition states involved in a $S_E(ox)$ mechanism have been unsuccessful. Since $(tmeda)Pt(Me)_2$ protonolysis experimental findings^{4a} point to the formation of an observed alkylhydridoplatinum(IV) intermediate we have explored the hypothesis that a six-coordinate intermediate should be formed prior to methane loss from the σ -complex. A concerted transition state for the simultaneous shift of a methane hydrogen atom from carbon to the metal center and coordination of the anion of the acid should be intercepted. The results of our investigation are reported below.

The complex containing the *dmpe* soft donor ligand, as expected, is characterized by a $Pt^{\delta-}-C^{\delta-}$ charge distribution, which favors the direct formation of the σ -complex. In addition, also in this case, the HOMO character of such complex is that anticipated by the ligand nature, which is of σ -bonding type as reported in the Supporting Information, Figure S7.

The electron withdrawing nature of the third chelating ligand, COD, should favor the $S_E(ox)$ pathway. We have observed that, while the NBO calculations give a $Pt^{\delta+}-C^{\delta-}$ bond polarization, the HOMO (Supporting Information, Figure S7) is of σ -bond-localized type. Only the transition state corresponding to the concerted proton transfer to the substrate has been located and characterized according to the HOMO nature. In this case the steric hindrance of the ligand seems to play a role in directing the proton attack at the carbon atom.

Finally, a very interesting behavior is revealed by the $(N-N)Pt(Me)_2$ complex in ether solvent. In this solvent the complex shows the same $Pt^{\delta+}-C^{\delta-}$ charge distribution and HOMO character (Supporting Information, Figure S7) as in both CH_3CN and CH_3OH solvents. However, the Et_2O solvent molecule, because of its steric hindrance, can hardly have access to the metal center and the direct Pt–C bond protonation is the only observed pathway. This should represent the ideal situation for the formation of a five-coordinate intermediate. Nevertheless, as a consequence of the partial positive charge on the Pt center, transfer of the proton to the metal can occur only if it is assisted by the concomitant coordination of a nucleophile molecule. For this particular situation, the normal mode associated to the only imaginary frequency corresponding to the intercepted transition state seems to show a proton transfer from the Pt atom to the carbon atom of the methyl ligand. IRC calculations have been carried out to locate minima connected to the transition state. The analysis of the structures along the reaction coordinate from the transition state to the methane complex reveals that, as sketched in Figure 4, the proton is transferred first to the Pt atom and from this to carbon atom of the methyl ligand to form the product in one step. Only for the protonolysis of the $(N-N)Pt(Me)_2$ in ether solvent a disagreement is observed between the mechanism ($S_E(ox)$) that should be predicted on

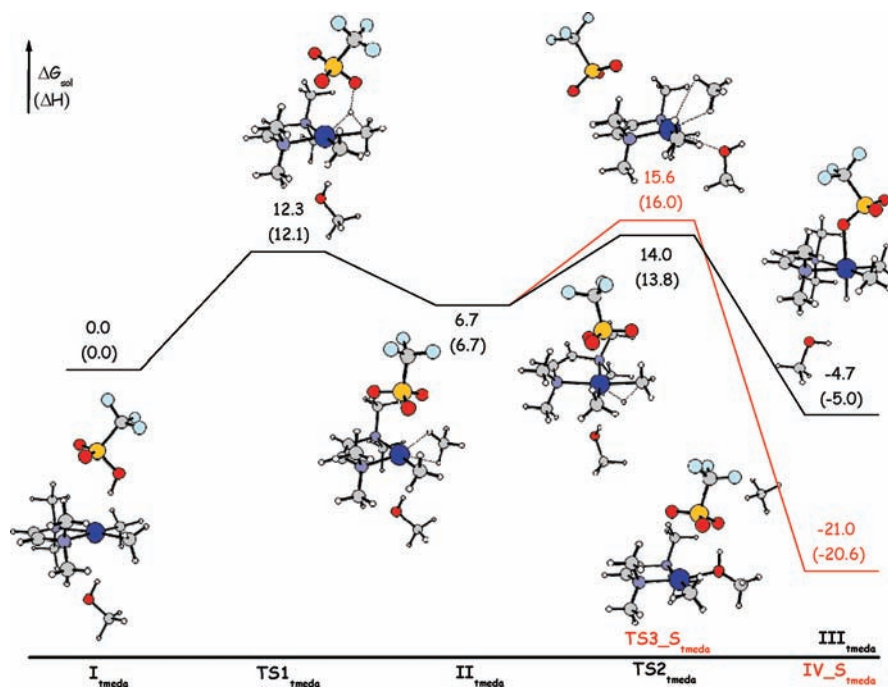


Figure 5. Calculated energy profile for the one-step protonolysis of the (tmeda)Pt(Me)₂ complex, in presence of triflic acid and in MeOH solvent. Both subsequent pathways for the formation of a six-coordinate complex (tmeda)Pt(Me)₂-(H)OTf and elimination of methane from the [(tmeda)Pt(CH₃)(CH₄)]⁺ σ -complex (in red) are shown. Relative free energies in MeOH (ΔG_{sol}) and gas-phase enthalpies (ΔH) are in kcal/mol.

the basis of the HOMO nature and the mechanism ($S_{\text{E}}2$) that the system is constrained to follow as a consequence of the inaccessibility of the sixth coordination by the sterically hindered solvent molecule.

Our calculations suggest that the spectator ligand characteristics that are directly connected with the σ -bond localized or d metal based nature of the HOMO are crucial in promoting the mechanism of Pt–C bond protonolysis of dimethylplatinum(II) complexes, but also steric effects are implicated to impose the mechanism by which the attack of the proton at metal–carbon bond occurs.

3.4. Formation of Five- and Six-Coordinate Pt(IV) Hydride Intermediates. Investigations of protonolysis of Pt(II) alkyl complexes and its reverse are all consistent with the proposal that when methane release occurs following a $S_{\text{E}}(\text{ox})$ mechanism, the reaction step sequence is as follows: initial protonation to generate a six-coordinate Pt(IV) hydride, dissociation of the solvent or anion of the acid to provide a five-coordinate species, and reductive coupling to give the σ -methane species.^{4b}

It is noteworthy that the five-coordinate Pt(IV) methyl hydrides postulated to be involved in such processes have never been observed and their existence has been inferred and only indirectly supported by a few literature reports on isolable, five-coordinate Pt(IV) alkyl complexes.²⁸ Moreover, in light of the results of the present investigation, theoretical characterization of five-coordinate Pt(IV)-H intermediates is the consequence of an inappropriate simulation of the reaction environment that is due to unavailability of a sixth ligand. In fact, the reactions to yield the five-coordinate products are always calculated to be uphill in energy, whatever the species is from which they are generated.^{10,24}

There is, instead, a good number of quite stable six-coordinate methyl Pt(IV) hydride complexes, which have been isolated and characterized. Although their detection does not provide

definitive evidence that protonation occurs at the metal center,^{6d} failure to detect such intermediates does not necessarily exclude their involvement, because of the difficulty in observing short-lived intermediates.

On the basis of the outcomes of our computational analysis we can add a further piece to the puzzle. No five-coordinate hydridoplatinum(IV) intermediates have been intercepted both in presence of nucleophiles such as CH₃CN and MeOH solvents able to trap the five-coordinate intermediate to form the corresponding six-coordinate complexes, and in presence of species, such as the sterically hindered Et₂O solvent, unable to access the apical coordination site. In this latter case, moreover, the steric congestion prevents the six-coordinate intermediate formation and induces, as shown above, a change, from $S_{\text{E}}(\text{ox})$ to $S_{\text{E}}2$, of the preferred protonolysis mechanism. Another important piece of information concerns the formation of six-coordinate methylhydridoplatinum(IV) intermediates and involvement in the protonolysis process. Unmistakable evidence for their formation does not necessarily imply that the $S_{\text{E}}(\text{ox})$ mechanism is the preferred one. We have examined this hypothesis for the (tmeda)Pt(Me)₂ complex to reconcile experimental observation of a six-coordinate Pt(IV) intermediate^{4a} and theoretical results supporting a $S_{\text{E}}2$ mechanism that does not involve any intermediate prior to form the σ -methane complex. The possibility has been explored that a six-coordinate Pt(IV) hydride complex might be formed from the σ -complex by a hydrogen shift from the carbon atom of the methane molecule to the Pt ion together with coordination of the anion of the acid. The calculated PES for the one-step protonolysis of the (tmeda)Pt(Me)₂ complex, in presence of triflic acid and in MeOH solvent, and subsequent formation of a six-coordinate complex (tmeda)Pt(CH₃)₂-(H)OTf from the corresponding [(tmeda)Pt(CH₃)(CH₄)]⁺ σ -complex is sketched in Figure 5. Calculations give an activation energy barrier of 7.3 kcal/mol. Since the barrier for the elimination

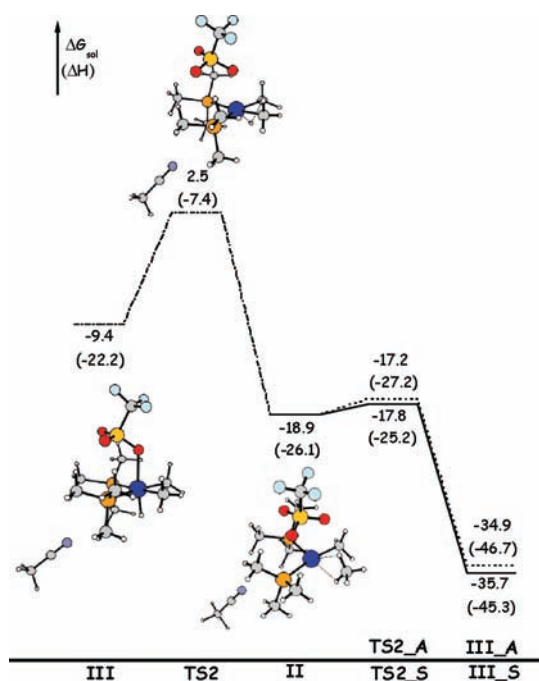


Figure 6. Comparison between the calculated energy profiles for the six-coordinate *cis*-[PtMe₂(PMe₃)₂]-(*H*)OTf complex formation (left) and methane loss (right) starting from the *cis*-[PtMe(PMe₃)₂(CH₄)]⁺ σ -complex in presence of the OTf⁻ anion and CH₃CN solvent. Relative free energies in CH₃CN (ΔG_{rel}) and enthalpies (ΔH) at 298 K are reported. Relative energies are in kcal/mol.

of CH₄, shown in the same Figure 5, is 8.9 kcal/mol experimental detection of deuterium scrambling between hydride and alkyl positions prior to methane elimination and subsequent generation of the full range of methane isotopomers is consistent with the computational results reported here.

To address the issue of whether the hydrogen migration from the methane molecule to the platinum center should compete with methane elimination, calculations have been performed to locate stationary points along the pathway leading to the six-coordinate intermediate by a hydrogen shift from the methane molecule of the σ -complex for the *cis*-[PtMe₂(PMe₃)₂] model complex. The calculated energy profile is depicted in Figure 6 compared with the corresponding alternative pathway that leads to methane loss. Expectedly, the energy barrier to methane loss is significantly lower than that for the six-coordinate complex formation. The protonation rate determining step is followed by rapid methane loss in agreement with the experimental findings that CH₃D has been the only deuterated methane isotopologue observed.

As already underlined (see Figure 1), the estimated energy barrier for methane release from the [(N–N)Pt(Me)(CH₄)]⁺ σ -complex is about 3 kcal/mol higher with respect to the energy barrier for the formation of a six-coordinate Pt(IV)-hydride complex. Extensive H/D scrambling between hydride and methyl sites has been observed when the (N–N)Pt(Me)₂ has been treated with DOTf in polar solvent. The estimation of a difference of about 3 kcal/mol is compatible with the experimental observations.

For all the considered complexes calculations have been carried out to ascertain whether five-coordinate species might be generated. Hydrogen transfer is always subordinated to the coordination of the sixth ligand.

Summarizing the results of this last part of our computational work we can conclude that, even when the protonolysis reaction is likely to occur by a S_E2 mechanism because of ancillary ligands' donating ability, steric congestion, and environmental conditions in terms of nucleophilicity of solvent and counteranion, six-coordinate hydrido-intermediates can be formed by a hydrogen transfer to the metal center from the σ -complex methane molecule. Nevertheless, for platinum(II) complexes containing soft electron-rich ligands the energetics of methane release are definitely more favorable, whereas for complexes containing hard poor-donor spectator ligands, methane loss and scrambling proceeds at comparable rates.

4. CONCLUSIONS

The calculations reported in this study address the points raised in the Introduction. First, the outcomes of our computational analysis show that although a one-step protonolysis pathway is characteristic for complexes containing P-based ligands, for complexes containing N-based and, in general, hard poor-donor ligands a common behavior cannot be indicated. Therefore, which the most likely mechanism is cannot be predicted on the basis of the spectator ligands' donating properties. Second, the involvement of a five-coordinate platinum(IV) hydrido intermediate in the multistep S_E(ox) mechanism is not supported by computational results. Proton transfer to the metal center invariably occurs concomitantly to coordination of a sixth ligand. It is worth underlining that formation and detection of six-coordinate hydrido-intermediates should not be considered an unmistakable evidence that a S_E(ox) mechanism is operative since they can be also generated by a hydrogen migration from carbon atom of the σ -complex methane molecule formed by S_E2 attack. Third, the methane elimination from the formed σ -complexes occurs by an associative mechanism in all the examined cases. Both solvent and anion of the acid can assist the methane displacement. Finally, it has been shown that the electronic structure and donor ability of the spectator ligands of dimethylplatinum(II) complexes is directly connected to the nature of the HOMO. For all the examined systems the relative accessibility of d metal based or σ -bond localized HOMO in turn is the main factor in determining the preferred protonation site. Solvent nucleophilicity influences only the rate of the reaction when the S_E(ox) mechanism is operative. On the contrary, solvent steric hindrance can even induce a change of the mechanism that appears to be the preferred one on the basis of the HOMO characteristics. The sign of the partial charges induced on the polarized Pt and C atoms, instead, is not a criterion always suitable to explain the preference for one of the two protonolysis mechanisms.

■ ASSOCIATED CONTENT

S Supporting Information. Complete list of authors for ref 14. Fully optimized structures and selected geometric parameters of all the stationary points intercepted along the pathways for the protonolysis of both (N–N)PtMe₂ and *cis*-[PtMe₂(PMe₃)₂] complexes; HOMO plots for all the complexes discussed in section 3.3; Cartesian coordinates of all optimized stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Fax: +39-0984-492044. E-mail: siciliae@unical.it.

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REFERENCES

- (1) (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471–2526. (b) Labinger, J. A. *J. Mol. Catal. A: Chem.* **2004**, *220*, 27–35. (c) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507–514. (d) Bergman, R. G. *Nature* **2007**, *446*, 391–393.
- (2) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154–162. (b) *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990. (c) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley & Sons: New York, 1989. (d) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000.
- (3) (a) Garnett, J. L.; Hodges, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 4546–4547. (b) Gol'dshleger, N. F.; Shteinman, A. A.; Shilov, A. E.; Eskova, V. V. *Zh. Fiz. Khim.* **1972**, *46*, 1353–1354. (c) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174–2175.
- (4) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961–5976. (b) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259–320.
- (5) (a) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004–3005. (b) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horvath, I. T.; Eller, K. *Organometallics* **1993**, *12*, 895–905. (c) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1994**, *13*, 755–756. (d) Hutson, A. C.; Lin, M.; Basicckes, N.; Sen, A. *J. Organomet. Chem.* **1995**, *504*, 69–74.
- (6) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371–9372. (b) Wik, B. J.; Ivanovic-Burmazovic, I.; Tilset, M.; Eldik, R. V. *Inorg. Chem.* **2006**, *45*, 3613–3621. (c) Romeo, R.; Plutino, M. R.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 5909–5916. (d) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116–12117. (e) Parmene, J.; Ivanovic-Burmazovic, I.; Tilset, M.; Eldik, R. V. *Inorg. Chem.* **2009**, *48*, 9092–9103. (f) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966–4968.
- (7) Romeo, R.; D'Amico, G. *Organometallics* **2006**, *25*, 3435–3446.
- (8) (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Riedel: Dordrecht, The Netherlands, 1984. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848–849. (d) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115–6128. (e) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609–622. (f) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209–1217. (g) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745–8746. (h) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946–1955. (i) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684–5689. (j) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845–2847. (k) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13–C14.
- (9) (a) Belluco, U.; Giustiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494–6500. (b) Belluco, U.; Croatto, U.; Uguagliati, P.; Pietropaolo, R. *Inorg. Chem.* **1967**, *6*, 718–721. (c) Romeo, R.; Minniti, D.; Lanza, S. *J. Organomet. Chem.* **1979**, *165*, C36–C38. (d) Uguagliati, P.; Michelin, R. A.; Belluco, U.; Ros, R. *J. Organomet. Chem.* **1979**, *169*, 115–122. (e) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813–2818. (f) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim. Acta* **1985**, *100*, 107–113. (g) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U. *Inorg. Chim. Acta* **1986**, *112*, L15–L16. (h) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565–587.
- (10) Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B.-L. *Organometallics* **2010**, *29*, 4354–4359.
- (11) Li, J. L.; Geng, C. Y.; Huang, X. R.; Zhang, X.; Sun, C. C. *Organometallics* **2007**, *26*, 2203–2210.
- (12) (a) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Chem. Soc. Chem. Commun.* **1990**, 1367–1369. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916–9924. (c) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484–5493.
- (13) (a) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156–4164. (b) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1997**, *265*, 117–125. (c) Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 563–570.
- (14) Frisch, M. J.; et al. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.
- (15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (17) (a) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355–1364, and references therein. (b) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177–6186. (c) Ozimiński, W. P.; Garnuszek, P.; Bednarek, E.; Dobrowolski, J. *Cz. Inorg. Chim. Acta* **2007**, *360*, 1902–1914. (d) Karhánek, D.; Kačer, P.; Kuzma, M.; Šplíchalová, J.; Červený, L. *J. Mol. Model.* **2007**, *13*, 1009–1016.
- (18) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161–4163.
- (19) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161.
- (20) (a) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.* **1988**, *169*, 41–62. (b) Carpenter, J. E.; Weinhold, F. *The Structure of Small Molecules and Ions*; Plenum: New York, 1988.
- (21) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.
- (22) McQuarrie, D. A.; Simon, J. D. *Molecular thermodynamics*; University Science Books: Sausalito, CA, 1999.
- (23) Cooper, J.; Ziegler, T. *Inorg. Chem.* **2002**, *41*, 6614–6622.
- (24) Tobisch, S. *Chem.—Eur. J.* **2005**, *11*, 3113–3126.
- (25) (a) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831–10845. (b) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125. (c) Billups, W. E.; Chang, S.-C.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 2039–2041.
- (26) Ong, C. M.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2003**, *81*, 1196–1205.
- (27) (a) Jawad, J. K.; Puddephatt, R. J.; Stalder, M. A. *Inorg. Chem.* **1982**, *21*, 332–337. (b) Puddephatt, R. J.; Johnstone, R. A. W.; Behan, J. *J. Chem. Soc., Chem. Commun.* **1978**, 444–445. (c) Yang, D. S.; Bancroft, M. G.; Dignard-Bailey, L.; Puddephatt, R. J.; Tse Yang, J. S. *Inorg. Chem.* **1990**, *29*, 2487–2495.
- (28) (a) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724–12725. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423–6424. (c) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804–6805. (d) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286–15287. (e) Karshtedt, D.; McBee, J. L.; Bell, A. T.; Tilley, T. D. *Organometallics* **2006**, *25*, 1801–1811. (f) Kloek, S. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 3460–3461. (g) Khaskin, E.; Zavalij, P. Y.; Vedernikov, A. N. *Angew. Chem., Int. Ed.* **2007**, *46*, 6309–6312.