J. Phys. Chem. A **2001,** *105,* 2023−2030

Interaction of Dichloromethane with the Coordination Sphere of Palladium Complexes: Toward a First Solvation Shell Model

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Received: October 3, 2000

In this paper we report a theoretical study of the solvent effects on various isomers of the palladium $PdH_3Cl(NH_3)_2$/$[PdH_2Cl(NH_3)]^-(NH_4)^+$ complexes in dichloromethane. The solute−solvent interactions are investigated by discrete second-order Møller−Plesset (MP2) calculations and characterized in terms of the electrostatic, induction, dispersion, and exchange-repulsion contributions as defined by the symmetry-adapted perturbation theory (SAPT). The importance of various contributions to the solute−solvent interaction energy can be correlated with the chemical properties of the ligand to which the solvent molecule is attached. They are ligand dependent. However, the sum of these contributions (i.e., the total solvent−solute interaction for each ligand) is nearly isotropic around the solute. This allows us to propose a model for the first solvation shell composed of six solvent molecules. We checked that some changes in the geometry of the first solvation shell do not significantly alter the total interaction energy with the solute. The qualitative results are not significantly affected if the interaction energy is approximated by the sum of the solute−solvent pairs energies.

I. Introduction

Palladium hydride complexes are key intermediates in many palladium-mediated or catalyzed reactions.[1−4] Prototypical examples include the olefin insertion into the metal hydride bond of square planar Pd(II) complexes, H_2, or CH_4 reductive elimination from Pd(II) or Pd(IV) complexes. It is therefore not surprising that many theoretical investigations have been devoted to the study of the palladium hydride complexes and of their reactivity. However—and this is in contrast with what is currently done in the organic realm— in a few cases only has the influence of the solvent been considered. In the case of the olefin insertion reaction Matsubara et al.[5] have used a second ethylene molecule to model the coordinative properties of the cyclohexene solvent. One should also mention the extensive studies made by Siegbahn[6−8] and by Kragten et al.[9] on the Wacker reaction, where the solvent is either water[6−8] or acetic acid.[9] One theoretical study of the ruthenium-catalyzed hydrogen transfer between alcohols and ketones takes into account the effect of the solvent, which is the alcohol itself.[10] Thus, the investigations that had been carried out so far at the onset of our study had been restricted to solvent with either strong coordinative properties or strong hydrogen bonding ability. Such properties are not characteristic of dichloromethane, which, however, is a solvent commonly used in palladium chemistry.[11]

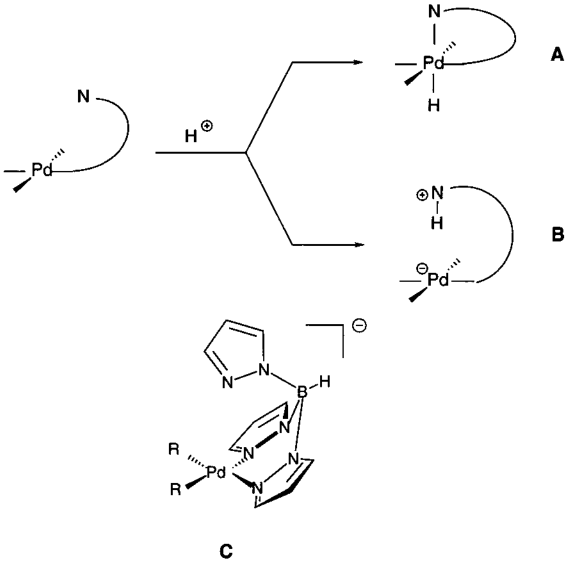

Figure 1. Possible sites of protonation for the Pd(II) complex with a pendant nitrogen arm.

We have over the years been interested[12−14] in studying from a theoretical point of view the ability of Pd(II) complexes with a pendant nitrogen arm to protonate either on the metal or on the nitrogen atom;[4] see Figure 1. Both forms, either the six-

10.1021/jp0036240 CCC: $20.00 © 2001 American Chemical Society
Published on Web 02/10/2001

coordinate Pd(IV) hydride complex, see A, or the zwitterionic $Pd(II)^-\cdots NH^+$ complex, see B, are, for instance, possible intermediates in the reduction of water to H_2 by diorganopalladium(II) complexes of tris(pyrazol-1-yl)borate complex, e.g., $[PdR_2\{(pz)_3BH\}]$,[4-13] $R_2 = (CH_3)_2$, $H_2C(CH_2)_2CH_2$, see C. N-Protonated Pd(II) and Pt(II) have been characterized either crystallographically or spectroscopically.[15] Examples of protonation of Pt(II) complexes to yield Pt(IV) hydride complexes have been documented,[4,13,16] but Pd(IV) hydrides appear to be more elusive.[17] It is clear that the relative stability of the *neutral* Pd(IV) hydride form A and the *zwitterionic* $Pd(II)^-\cdots NH^+$ form B should be influenced by the solvent, in particular via its dielectric properties.

We have therefore started a systematic study of the solvent effect on such palladium systems. In a preliminary investigation,[18] we examined the interaction of the 1-*mer* palladium hydride $PdH_3Cl(NH_3)_2$ with one dichloromethane molecule, the goal being to check the efficiency of a methodology based on the optimization of the geometries using the density functional methods (DFT) followed by a calculation of the interaction energy corrected for the basis-set superposition error by the second-order Møller–Plesset theory (MP2). Simultaneously, the influence of the solvent effect was studied for various isomers of the complex using the self-consistent reaction field (SCRF) method.[19] In particular, we proposed an adjustable ellipsoidal cavity, combined with a multipolar treatment, which turned out to be an efficient alternative to the cavities used so far in the methods based on the continuum model.

The present paper is focused on a systematic and detailed analysis of ab initio calculations based on a discrete solvation model. To study the interaction of the coordination sphere of model systems for A and B with CH_2Cl_2, both the supermolecule approach and the perturbation theory were used. A detailed analysis of the interaction of the CH_2Cl_2 solvent molecule with each component of the coordination sphere of A and B is done using the symmetry-adapted perturbation theory (SAPT). Beyond its interest to understand and compare the methods, this analysis is of importance for further possible theoretical developments (e.g., molecular dynamics simulations) in which the quality of the potential function (e.g., two-body vs three-body functions, including polarization effects or not, etc.) used to represent the potential energy surface needs to be assessed. In the next paper, an SCRF treatment of the same systems will be discussed and compared with the ab initio results.

The calculations have been carried out on the systems shown in Figure 2, as models of experimental systems bearing methyl (or alkyl) groups and amine type ligands. One might argue about the relevance of hydrides to mimic methyl or alkyl ligands. We are well aware of the fact that the interaction of an hydride with CH_2Cl_2 should be somewhat different from the interaction of CH_3 with CH_2Cl_2. However, as far as the relative stability of the forms A and B is concerned, test calculations[20,21] performed in the gas phase and in bulk CH_2Cl_2 (see next paper) did not show any significant difference between the systems of Figure 2 and their bis(methyl) analogues. This justifies our choice of the palladium hydrides as models for the present investigation. One should also mention that the Pd–H bonds of the *mer* and *fac* trihydride complexes 1-*mer* and 1-*fac*, and of *cis* and *trans* dihydride complexes 2-*cis* and 2-*trans*, are different in character, ranging from quite ionic to rather covalent. Thus, a thorough analysis of the interaction of CH_2Cl_2 with these various types of Pd–H bonds is also chemically relevant.

This paper will be organized as follows. We will first outline in section II the methods that have been used in our calculations. In section III the geometries used for the discrete solvation model are described. Numerical results and discussion are presented in section IV. Finally, concluding remarks are given in section V.

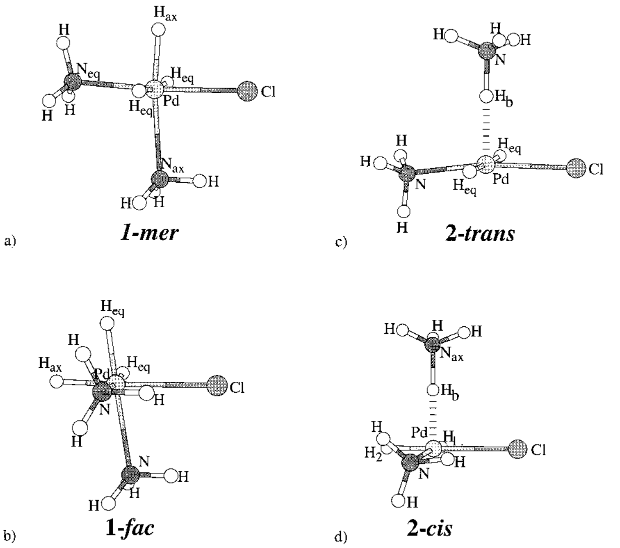

Figure 2. Geometries of the $PdH_3Cl(NH_3)_2$ complex corresponding to the (a) 1-*mer*, (b) 1- *fac*, (c) 2-*trans*, and (d) 2-*cis* forms.

II. Methods of Calculations

A. Supermolecule and SAPT Calculations. In the present work both the supermolecule second-order Møller–Plesset theory (MP2) and the symmetry-adapted perturbation theory (SAPT) have been used. If we restrict ourselves to pair solute–solvent interactions and, thus, neglect nonadditive many-body and solvent–solvent pair interactions, the MP2 interaction energy is given by the sum of the pair energies, $E_{\rm int}^{\rm MP2}({\rm SB}_i)$, describing the interaction between the molecule of the solute (S) and the *i*th molecule of the solvent (B_i),

$$E_{\rm int}^{\rm MP2} = \sum_{i=1}^{N} E_{\rm int}^{\rm MP2}({\rm SB_i}) \tag{1}$$

$$E_{\rm int}^{\rm MP2}({\rm SB}_i) = E_{{\rm SB}_i}^{\rm MP2} - E_{\rm S}^{\rm MP2} - E_{{\rm B}_i}^{\rm MP2} \tag{2}$$

where $E_{{\rm SB}_i}^{\rm MP2}$ denotes the total energy of the system composed of the solute molecule and the *i*th molecule of the solvent, while $E_{\rm S}^{\rm MP2}$ and $E_{{\rm SB}_i}^{\rm MP2}$ are the energies of the isolated solute molecule and the *i*th molecule of the solvent, respectively. The supermolecular energies were corrected for the basis set superposition error (BSSE) with the counterpoise method of Boys and Bernardi[22] by performing all the calculations in the full basis of the dimer SB_i.

In the SAPT calculations the interaction energy of the solute–solvent system is represented as

$$E_{\rm int}^{\rm SAPT} = \sum_{i=1}^{N} E_{\rm int}^{\rm SAPT}({\rm SB_i}) \tag{3}$$

where $E_{\rm int}^{\rm SAPT}({\rm SB}_i)$ denotes the SAPT interaction energy between the solute and the *i*th molecule of the solvent. The interaction energy for the pair SB_i, $E_{\rm int}^{\rm SAPT}({\rm SB}_i)$, was computed from the following expression,[23]

$$E_{\text{int}}^{\text{SAPT}}(\text{SB}_i) = E_{\text{elst}}^{(1)}(\text{SB}_i) + E_{\text{ind}}^{(2)}(\text{SB}_i) + E_{\text{disp}}^{(2)}(\text{SB}_i) + E_{\text{exch}}(\text{SB}_i) \quad (4)$$

where the consecutive terms on the rhs of eq 4 denote the electrostatic, induction, dispersion, and exchange energies, respectively. We recall to the reader that the electrostatic term describes the classical electrostatic (Coulomb) interactions of the charge distributions of the isolated monomers. At large distances it can be represented as a sum of the classical electrical interactions between the permanent multipole moments of the unperturbed monomers. The induction energy (sometimes also referred to as the polarization energy) results from the mutual polarization of the monomers by the static electric fields of the unperturbed partners. Asymptotically, at large distances, this effect is fully determined by the permanent multipole moments and static multipole polarizabilities of the isolated monomers. The dispersion interaction, in turn, is a pure intermolecular correlation effect. It may be viewed as a stabilizing energetic effect of the correlations of instantaneous multipole moments of the monomers. Finally, the repulsive exchange term represents the effect of the resonance tunneling of the electrons between the interacting systems. The exchange contribution can further be decomposed as follows,

$$E_{\text{exch}}(\text{SB}_i) = E_{\text{exch}}^{(1)}(\text{SB}_i) + E_{\text{exch-ind}}^{(2)}(\text{SB}_i) + E_{\text{exch-def}}^{(2)}(\text{SB}_i) + E_{\text{exch-disp}}^{(2)}(\text{SB}_i) \quad (5)$$

Here, $E_{\text{exch}}^{(1)}(\text{SB}_i)$ is the first-order exchange energy, while $E_{\text{exch-ind}}^{(2)}(\text{SB}_i)$, $E_{\text{exch-def}}^{(2)}(\text{SB}_i)$, and $E_{\text{exch-disp}}^{(2)}(\text{SB}_i)$ denote the exchange-induction, exchange-deformation, and exchange-dispersion terms. Although the exchange terms appearing on the rhs of eq 5 have also an appealing physical interpretation (see, for instance, ref 23), in this paper we will only present the global repulsive contribution given by E_{exch}. The contributions appearing on the rhs of eqs 4 and 5 have been computed with the complete neglect of the intramonomer correlation effects.[24−29] The exchange-deformation energy[30,31] was computed directly from the supermolecule Hartree−Fock interaction energy. The computational scheme for the solute−solvent interactions follows closely the decomposition of the supermolecule MP2 interaction energy advocated by Chalasinski, Szczesniak, and collaborators.[32] One may note here that for computational reasons, our ansatz for the SAPT interaction energy, eq 4, neglects the intramolecular correlation effects on the electrostatic and first-order exchange energies. The experience gained thus far[24−26] shows that these effects are rather important, so one can expect that the agreement between the MP2 and SAPT results will only be qualitative.

When more than two molecules are simultaneously interacting, the solute−solvent pair approximation proposed in eq 1 assumes that both the solvent−solvent pair interaction and the nonadditive many-body contributions can be neglected. To test the validity of such an assumption, MP2 calculations were performed for the solvent−solvent pairs, and the nonadditive contribution was computed at the Hartree−Fock level. This will be presented in section IV.B.2.

B. Computational Details. The basis sets employed in the present calculations were selected for their efficiency from comparisons with several all electron bases.[18] Pseudo-potential basis sets were used for the palladium[33] and chlorine[34] atoms. A polarization function was added on the chlorine atom. The valence shells were described in the following way: Pd (5/6/4) contracted to [3/3/2][33,35] and Cl (3/3) contracted to [2/2].[34] All electron bases were used for the hydrogen, carbon, and nitrogen atoms. The C and N atoms were described by a polarized split valence basis set (9/5/1) contracted to [3/2/1].[36] For the hydrogen atom we used a triple-ζ basis[37] including a diffuse function and supplemented with a polarization function: (6/1) contracted to [3/1]. The exponents of the polarization functions are $d(\text{Cl}) = 0.54$, $d(\text{C}) = 0.63$, $d(\text{N}) = 0.95$, and $p(\text{H}) = 0.80$.[38−40] In a previous work[18] we have shown that this basis set was sufficient to correctly describe the solute−solvent interaction with the supermolecule MP2 method. For palladium and chlorine we used pseudopotentials with 28 and 10 core electrons, respectively.

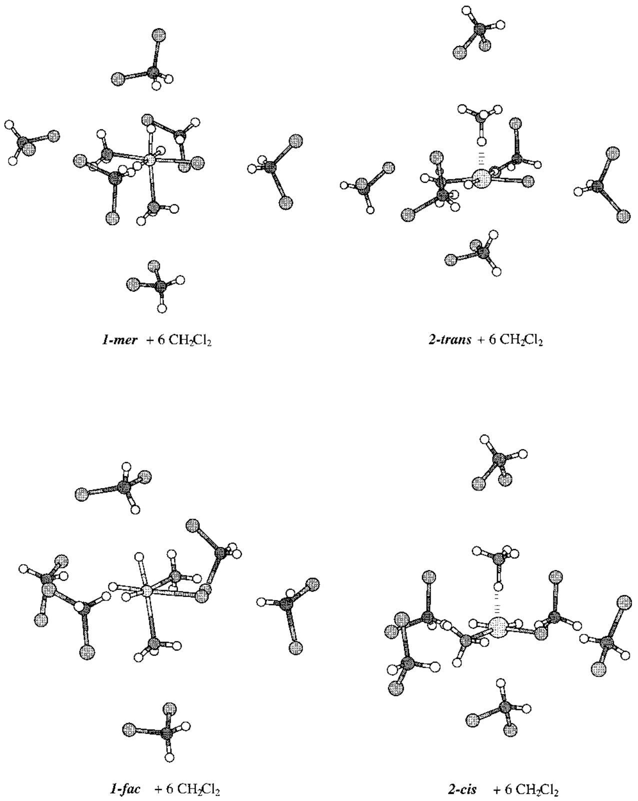
1-mer + 6 CH_2Cl_2
2-trans + 6 CH_2Cl_2
1-fac + 6 CH_2Cl_2
2-cis + 6 CH_2Cl_2

Figure 3. Location of the six dichloromethane molecules surrounding the $PdH_3Cl(NH_3)_2$ complex: 1-*mer*, 1-*fac*, 2-*trans*, and 2-*cis* forms.

The geometry optimizations and the supermolecular calculations of the interaction energies have been done with the Gaussian-94 package.[41] SAPT calculations of the solute−solvent interaction energies were made with the programs SAPT.[42]

III. Geometries and the Discrete Solvation Model

The geometries considered in this work have been obtained at the DFT/B3LYP level.[43,44] Our previous work showed that this level is adequate for both palladium systems of type A and B,[18,21] and for their adduct with solvent molecules as well.[18] It should also be adequate for further comparison of geometries optimized via the continuum model and via the discrete solvation models. The geometries considered in the present paper are summarized in Figure 2, Figure 3, and Table 1. Full details can be found in ref 21 and are available on request. Note that the geometry optimizations for the 1-*mer* and 1-*fac* systems were performed without any constraints.[19] On the other hand some constraints were introduced for the zwitterionic forms B to closely mimic the experimental structures.[4] For the 2-*trans* form the C_s symmetry was imposed, the Pd, H_b, and N_{ax} atoms were

TABLE 1: Pd···Ligand Distances for the Four Forms of the Palladium Complex in the G_0, G_{1-1}, G_{6-6}, and $G_{SCI-PCM}$ Geometries (Definitions in Section III)[a]

		G_0 vacuum	G_{1-1} $1{*}CH_2Cl_2$	G_{6-6} $6{*}CH_2Cl_2$	$G_{SCI-PCM}$ continuum
1-*mer*	$Pd\cdots H_{ax}$	1.50	1.49	1.50	1.51
	$Pd\cdots H_{eq}$	1.65	1.65	1.69	1.65
	$Pd\cdots Cl$	2.34	2.35	2.36	2.37
	$Pd\cdots N_{ax}$	2.13	2.13	2.11	2.10
	$Pd\cdots N_{eq}$	2.30	2.30	2.27	2.27
1-*fac*	$Pd\cdots H_{ax}$	1.53	1.53	1.52	1.53
	$Pd\cdots H_{eq}$	1.51	1.51	1.51	1.52
	$Pd\cdots Cl$	2.50	2.51	2.52	2.52
	$Pd\cdots N$	2.28	2.28	2.25	2.26
2-*trans*	$Pd\cdots H_{eq}$	1.66	1.65	1.69	1.66
	$Pd\cdots Cl$	2.33	2.34	2.35	2.39
	$Pd\cdots N_{ax}H_4$	2.95	2.97	3.00	3.11
	$N_{ax}\cdots H$	1.16	1.14	1.11	1.07
	$Pd\cdots N_{eq}H_3$	2.14	2.14	2.12	2.11
2-*cis*	$Pd\cdots H_1$	1.53	1.53	1.54	1.54
	$Pd\cdots H_2$	1.56	1.56	1.55	1.55
	$Pd\cdots Cl$	2.47	2.49	2.48	2.52
	$Pd\cdots N_{ax}H_4$	2.96	2.97	3.00	3.12
	$N\cdots H$	1.20	1.16	1.12	1.08
	$Pd\cdots N_{eq}H_3$	2.29	2.28	2.25	2.26

[a] For the G_{1-1} structures, only the ligand near the interacting dichloromethane molecule is reported, the change with respect to the G_0 structures being negligible for the other ones.

constrained to be aligned, and the $\angle(ClPdN_{ax})$ angle was kept fixed at 90°. Similar constraints were imposed for the 2-*cis* form with the Pd, H_b, and N_{ax} atoms kept aligned, and the angles $\angle(ClPdN_{ax})$, $\angle(H_1PdN_{ax})$, and $\angle(H_2PdN_{ax})$ fixed at 90°. The geometries optimized in the vacuum (for the solute as well as for the solvent molecules) will be denoted hereafter by G_0.

For the discrete solvation model several levels of discretization have been used. In the first one,[18] we considered the interaction of one CH_2Cl_2 molecule with the complex, via each ligand (and via the palladium atom for the zwitterionic forms) successively. The optimum geometries of the adduct were obtained under the additional constraint of the alignment of the carbon atom of CH_2Cl_2 with the metal-to-ligand bond. This resulted in four sets of six geometries, hereafter denoted as G_{1-1}, in which the first subscript holds for the solute, and the second one for the solvent. They are sketched in Figure 3a−d. The most important geometrical parameters are summarized in Table 1.

In the next level of discretization, a supermolecule made of the solute and six CH_2Cl_2 solvent molecules has been optimized. As will be seen in section IV.B.2, it was necessary to keep the constraint of the Pd−ligand−C alignment. In addition, the internal geometries of the CH_2Cl_2 molecules were frozen at their G_0 optimized values in the vacuum. Pilot calculations carried out on some representative examples[45] showed that the latter constraint had no significant effect on both the geometry of the solute and the intermolecular distance between the solute and the CH_2Cl_2 molecules. We shall denote such optimized structures as G_{6-6}, the solute being surrounded by six solvent molecules. Compared to the G_{1-1} structures, the largest change in the geometry of the G_{6-6} structures is found for the $Pd\cdots NH_4^+$ bond of the zwitterionic forms.

To study some geometrical effects, combinations of the above geometries were also considered in the rest of this study. For instance, the palladium system can be frozen in the vacuum geometry G_0 and the solvent molecules in their position and geometry corresponding to G_{1-1} or in the position that they have in the G_{6-6} model. Such combinations will be referred to as G_{0-1} or G_{0-6}, respectively.

For the sake of comparison, the geometry of the palladium system was also optimized using the SCI-PCM continuum model (self-consistent isodensity-polarized continuum model).[46] When comparing the geometries optimized in solution via the SCI-PCM calculations ($G_{SCI-PCM}$) or the discrete model (G_{1-1} and G_{6-6}) to those optimized in the discrete model vacuum (G_0), we find similar features. However, the changes are generally more pronounced in the SCI-PCM geometries. It is clear from Table 1 that the largest difference is found for the $Pd\cdots NH_4^+$ moiety of the two zwitterionic forms. The discrete G_{1-1} and G_{6-6} geometries do not account for the large magnitude of the Pd···N lengthening upon solvation obtained for the zwitterionic form through the SCI−PCM calculations; see Table 1. The SCI−PCM geometries result in a greater charge separation and a larger enhacement of the zwitterionic character: in the 2-trans form the Pd···N distance is increased by 0.16 Å, from 2.95 Å, in the vacuum to 3.11 Å, in the continuum (0.05 Å in the G_{6-6} model). Concomitantly the $N\cdots H_{ax}$ bond is shortened by 0.09 Å, from 1.16 to 1.07 Å (0.05 Å in the G_{6-6} model). This corresponds to a greater cationic character of NH_4^+, whose charge increases from +0.89e (G_0) to +0.93e (G_{6-6}) and +0.95e ($G_{SCI-PCM}$). Similar features are found for the 2-*cis* form; see Table 1. The larger enhancement of the zwitterionic character in the SCI-PCM geometry may, however, result from some artifacts which will be discussed in a subsequent paper.[47]

IV. Numerical Results and Discussion

A. Interaction of a Dichloromethane Molecule with the Coordination Sphere. The results of the supermolecule and SAPT calculations allow a detailed analysis of the interaction energy of one solvent molecule with the palladium complex via each ligand in terms of various energetic contributions. Such calculations were done for all ligands of the four forms of the palladium complex. While the hexacoordination of the neutral form prevents a direct interaction with the palladium atom, which is completely surrounded by the ligands, the structure of the zwitterionic complexes (a square-planar moiety capped by an NH_4^+ ion) allows a direct interaction between a solvent molecule and the palladium atom. Six positions of the solvent molecule are thus considered for the four forms. The results obtained for the geometries G_{1-1} are reported in Table 2 (note that, for symmetry reasons, results for equivalent ligands are not duplicated). SAPT components are given together with the MP2 interaction energy. We also give the sum of the main SAPT terms, though this sum does not represent the total interaction.

It is interesting to examine the interaction energy from two viewpoints: either the interaction of a solvent molecule via the different ligands belonging to the same form of the complex or the interaction of a solvent molecule via a given ligand belonging to different forms of the complex. For the sake of language convenience, the “interaction of a solvent molecule with the palladium complex via a ligand” will be referred to as “interaction of a solvent molecule with a ligand”.

1. Ligand−Solvent Interactions for the Same Form of the Complex. For the 1-*mer* palladium hydride the largest attractive contribution is the electrostatic energy $E^{(1)}_{elst}$ for all ligands, due to the large dipole moment of this form of the complex. The dispersion energy $E^{(2)}_{disp}$ is generally more important than the induction term $E^{(2)}_{ind}$ (except for the H_{eq} ligand). Note that the two components of the induction energy (solvent polarized by the solute and solute polarized by the solvent) may be strongly different, as seen by comparing the total induction energy and the $S \rightarrow B_i$ terms in Table 2. The exchange term (mainly due

TABLE 2: Components of the Interaction Energy (in kcal mol^{-1}) for the Dichloromethane Interacting with Various Ligands of the Four Forms of the Palladium Complex (G_{1-1} structures)

		$E_{\mathrm{elst}}^{(1)}$	$E_{\mathrm{ind}}^{(2)}$	$E_{\mathrm{disp}}^{(2)}$	E_{exch}	$E_{\mathrm{int}}^{\mathrm{SAPT}}(\mathrm{SB_i})$	$E_{\mathrm{int}}^{\mathrm{MP2}}$
1-*mer*	H_{ax}	−4.76	−1.95 (−0.99)[a]	−2.76	4.66 (3.71)[b]	−4.81[c]	−4.22
	H_{eq}	−7.01	−3.41 (−2.82)	−3.09	8.33 (6.50)	−5.18	−4.34
	Cl	−4.32	−1.01 (−0.65	−1.51	2.69 (2.23)	−4.15	−2.95
	$N_{eq}H_3$	−3.15	−0.83 (−0.17)	−1.32	2.45 (1.94)	−2.85	−2.01
	$N_{ax}H_3$	−2.75	−0.77 (−0.26)	−1.43	2.51 (2.02)	−2.44	−2.39
	total	−29.00	−11.39 (−7.71)	−13.21	28.98 (22.89)	−29.80	−20.26
1-*fac*	H_{ax}	−1.72	−0.69 (−0.55)	−1.50	2.05 (1.70)	−1.86	−1.73
	H_{eq}	−1.83	−0.63 (−0.46)	−1.61	1.78 (1.45)	−2.29	−2.03
	Cl	−5.41	−1.52 (−0.95)	−1.67	3.68 (3.30)	−4.92	−3.79
	$N_{eq}H_3$	−2.71	−0.80 (−0.27)	−1.44	2.56 (2.05)	−2.39	−2.01
	total	−16.21	−5.06 (−2.94)	−9.27	14.42 (12.00)	−20.80	−13.60
2-*trans*	H	−10.04	−5.05 (−4.03	−3.29	11.25 (8.80)	−7.13	−5.43
	Cl	−6.58	−1.81 (−1.08)	−1.78	4.23 (3.38)	−5.94	−4.28
	Pd	−5.65	−2.41 (−1.16)	−3.58	5.28 (4.13)	−6.36	−5.44
	NH_3	−2.74	−0.71 (−0.18)	−1.26	2.25 (1.81)	−2.46	−2.07
	NH_4^+	−5.24	−1.66 (−0.17)	−1.42	3.34 (2.49)	−4.98	−3.81
	total	−40.29	−16.70 (−10.64)	−14.62	37.60 (29.40)	−41.14	−26.45
2-*cis*	H_1	−5.33	−2.05 (−1.47)	−2.11	4.84 (4.05)	−4.65	−3.27
	H_2	−5.67	−2.33 (−1.84)	−2.24	5.76 (4.74)	−4.48	−3.16
	Cl	−6.90	−2.11 (−1.30)	−1.89	4.98 (4.38)	−5.92	−4.52
	Pd	−6.62	−2.73 (−1.63)	−3.43	6.76 (5.17)	−6.02	−4.74
	NH_3	−2.54	−0.79 (−0.33)	−1.47	2.55 (2.03)	−2.25	−1.84
	NH_4^+	−4.83	−1.53 (−0.20)	−1.40	3.18 (2.41)	−4.58	−3.47
	total	−31.89	−11.54 (−6.76)	−12.52	28.07 (22.78)	−27.88	−20.99

[a] Contribution due to $E_{\mathrm{ind}}^{(2)}$ ($S \rightarrow B_i$) given in parentheses. [b] First-order exchange contribution in parentheses. [c] Only the main SAPT terms are considered; see eq 4.

to the first-order contribution; see values in parentheses) cancels to a large extent the electrostatic contribution. It thus appears from these overall comparisons that the interaction energy between a solvent molecule and various ligands results from a balance of different attractive and repulsive contributions and cannot be easily guessed a priori. In particular, the present analysis shows that the preferred site for the solute−solvent interaction cannot be correctly predicted by looking at the electrostatic term alone, as it is done in the electrostatic model of Buckingham and collaborators.[48] While the values obtained for the components are clearly ligand dependent, the largest ones occurring with the equatorial H ligand, the MP2 level interaction is not too strongly ligand dependent. At the MP2 level, the strongest interaction is with the H ligands, then with the chlorine atom, and finally the NH_3 groups (which form a dative bond with the palladium atom).

For the other neutral form of the complex, the 1-*fac* form, the interaction energy does not result from a similar cancellation of the attractive and repulsive contributions. Though largely quenched by the exchange term, the electrostatic contribution governs the relative strengths, the induction term matching this tendency. At the MP2 level, the strongest interaction arises for the chlorine atom, while for the H and NH_3 ligands it is smaller and nearly of the same strength. This is not too surprising since the Pd− H bonds are more covalent in the 1-*fac* form than in the 1-*mer* form, inducing an enhancement of the ionic character of the *trans* Pd−Cl bond in the 1-*fac* form.[20,21] Similar trends are found when comparing the 2-*cis* and 2-*trans* forms, though less pronounced.

The ionic character of the whole complex in the 2-*trans* form induces significant changes in the net atomic charges of all ligands and of the palladium atom with respect to the neutral 1-*mer* form, except for NH_3 due to the dative character of the Pd−NH_3 bond. A general strengthening of the attractive interactions is observed. Although the electrostatic contribution is strongly ligand dependent, it does not govern the relative strength of the interaction. In particular, the hydride ligands are not more favored than the Pd atom, due to a large exchange-repulsion term. Note that the large values of the induction term for the hydride ligands are mainly due to the polarization of the solvent by the solute. The total MP2 interaction energies are much less ligand dependent than the individual components. They are all rather similar, except that involving the NH_3 group, which is less favored.

Although the anisotropy of the interaction at the MP2 level is rather similar for the two zwitterionic forms, the contributions governing these interactions are much more isotropic for the 2-*cis* than for the 2-*trans* zwitterionic form. This is especially true for the electrostatic and induction terms. Indeed, these terms are nearly isotropic if one excepts the NH_3 group. The same trend is also found for the MP2 interaction energies.

Thus, the analysis of the interaction of a solvent molecule with various ligands and the palladium atom (for the zwitterionic forms) shows that none of them is strongly favored or disfavored, whatever the form of the complex considered. The solvent molecules have the possibility to surround the solute in a rather isotropic way. This gives some hope that average treatments of the solvation may be used.

2. Ligand−Solvent Interactions for the Same Ligand in Various Forms of the Complex. Before discussing the global solvation energies of the four forms of the palladium complex, it is worthwhile to consider the interaction of a solvent molecule with each ligand (or with the palladium atom) in different forms of the complex.

We already mentioned the behavior of the NH_3 group, which forms a dative bond with the palladium atom. The interaction energies through this group are all close, independent of the form of the complex considered. The palladium atom or the NH_4^+ group of the two zwitterionic forms also shows a similar ability of the two zwitterionic forms to interact with a dichloromethane molecule.

The interaction of a solvent molecule via the chlorine atom ligand is more sensitive to the form of the complex considered. The behavior of the MP2 interaction energies follows that of the electrostatic and induction contributions. It also roughly

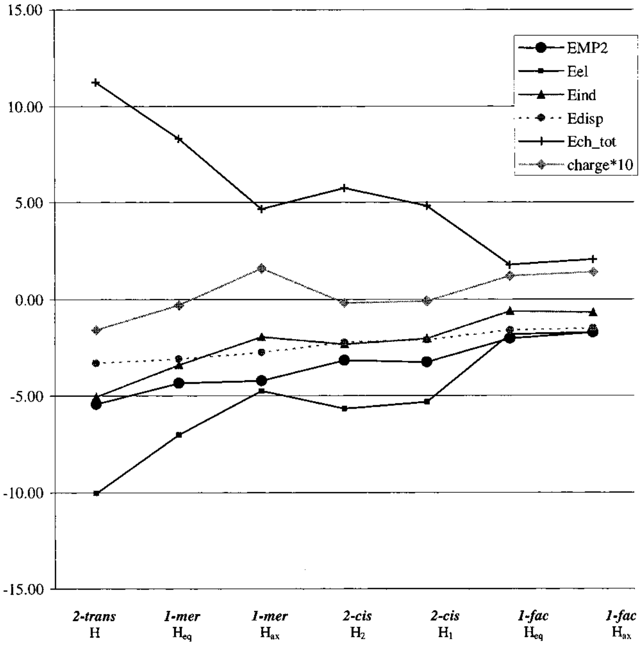

Figure 4. Correlation between the nature of the various H ligands and the attractive and repulsive contributions to the interaction energy.

follows that of the atomic net charges on the chlorine atom of the four forms.

The interactions of the solvent through the H ligands are highly sensitive to the form of the complex. This is illustrated in Figure 4, which shows the correlation between the nature of the H atoms (acidic, basic, neutral) and the strength of the intermolecular interactions. As expected, the interaction is stronger for the zwitterionic forms than for the *corresponding* neutral ones, i.e., 2-*trans* vs 1-*mer* and 2-*cis* vs 1-*fac* (see the MP2 interaction energies). This rule, of course, does not hold when we compare neutral and zwitterionic forms that are not related. The interaction energy components are much more sensitive to the structure of the complex than the MP2 interaction energy itself. The MP2 interaction energy is similar for all H atoms of the same form and increases (in absolute value) by about 1 kcal mol^{-1} in the following order 1-*fac*, 2-*cis*, 1-*mer*, 2-*trans*. By contrast, the electrostatic component differentiates the H atoms of a given 2-*cis* or 1-*mer* form: see, for instance, the equatorial and axial H atoms of the 1-*mer* form. While the MP2 interaction energy regularly increases (in absolute value) with the form of the complex considered in the series *fac* < *cis* < *mer* < *trans*, the behavior of the electrostatic component is more complicated (compare, for instance, the 1-*mer* and 2-*cis* forms). The effect of the electrostatic contribution, which strictly follows the net atomic charge on the H atoms (as does also the induction term), is smoothed by the exchange term. One should also point out that although the H atoms of the 1-*mer* form are not different from an interaction energy point of view at the MP2 level, they do lead to different relative orientations of the dichloromethane molecule; see Figure 3a.

B. First Solvation Shell. No information is available about the first solvation shell of such complexes. Ideally, one should optimize the structure of the systems composed of the solute and a large number of solvent molecules, such that the first solvation shell can be saturated. Unfortunately, this was not possible, either with the quantum chemistry methods because of the size of such systems or by simulation techniques (for instance Monte Carlo or molecular dynamics treatments) because of the lack of suitable parameters for analytical potential formulas. A model may be tentatively proposed for the first solvation shell taking into account the following three points:

—How many solvent molecules are needed to fill up the first solvation shell?

—Can the interaction energy be approximated by the sum of the solute—solvent pair interaction energies? This point is of special interest for a further comparison with an SCRF treatment and to get parameters for analytical formulas.

—How sensitive is the intermolecular interaction energy to the structure of the first solvation shell?

1. Number of Solvent Molecules in the First Solvation Shell. As shown in section IV.A.1, the solvent molecules can surround the solute in a nearly isotropic way. We can thus reasonably assume that the interaction of the solvent with the coordination sphere of the complex is correctly described by six molecules of dichloromethane interacting simultaneously with the ligands (and the palladium atom in the case of the zwitterionic forms). Moreover, as will be discussed in the subsequent paper,[47] an SCRF treatment including the six solvent molecules in the cavity shows that such a model of the first solvation shell accounts for most of the total interaction energy. This gives some confidence in its validity. Although one cannot totally exclude the possibility of some other structures close in energy, eventually involving a few more solvent molecules, the present structure appears to represent reasonably well the first solvation shell.

2. Validity of the Solute—Solvent Pair Approximation. The values reported in Table 2 correspond to the geometries G_{1-1} optimized separately for each solute—solvent pair. For each form of the solute, the last line (total) gives the sum of the interaction energy components over all the ligands and the palladium atom.

When six solvent molecules are interacting simultaneously with the solute, and assuming no change in the geometry, the total interaction energy must also account for the solvent—solvent pair interactions and the nonadditive contributions.

MP2 calculations on the total system are presently not feasible. However, the solvent—solvent pair interactions were computed at the MP2 level. The four forms of the complex being strongly polar, we can assume in the first approximation that the nonadditive interaction in the solvated system is mostly obtained at the Hartree—Fock level.[49,50] The nonadditive contributions were thus computed at this level only. For both solvent—solvent and nonadditive interactions, the same geometrical model was used. Since the geometry of the solute was optimized separately for each solute—solvent pair in the G_{1-1} geometry, it could not be employed for the total system. We thus built a model G_{0-1} that couples the geometry of the solute in the vacuum, G_0, and the G_1 geometry of the set of solvent molecules (intramolecular parameters, intermolecular distances and relative orientations of the solute—solvent molecules).

The total nonadditive contribution was obtained by subtracting the monomers energies and all the pair contributions from the total Hartree—Fock energy of the system composed of the solute and six solvent molecules. It amounts to +0.90, −0.40, +0.21, and +0.02 kcal mol^{-1} for the 1-*mer*, 1-*fac*, 2-*trans*, and 2-*cis* forms, respectively. Thus, when comparing two forms, the error introduced by the neglect of the nonadditive part is, at the most, 1.3 kcal mol^{-1}. Given the order of magnitude of the total interaction energy for the four forms, such an error will not affect the qualitative results. The total nonadditive HF three-body solute—solvent—solvent contribution was also computed from the fifteen sets generated in the four cases. It amounts to −0.10, −0.25, −0.07, and −0.11 kcal mol^{-1}, respectively. The first-order and induction parts are rather similar, eventually of opposite sign. In the configurations considered, the solvent molecules are located near a given ligand (or near the palladium atom). Such constraints are unfavorable for trimers of the solvent molecules with small intermolecular distances. The solvent–solvent–solvent three-body contribution, which could be significant in favorable geometries (found for instance in the condensed phase), is expected to be much smaller than the solute–solvent–solvent one in the present case. The three-body terms do not appear dominant in the nonaddtive contribution for the configurations studied.

Slightly larger are the solvent–solvent pair contributions. They are repulsive and amount to 0.73, 0.53, 0.88, and 1.25 kcal mol^{-1}, respectively, for the four forms at the MP2 level. Note that their HF values are larger (2.19, 1.36, 1.53, and 2.04), showing the importance of the correlation contribution. The largest error involved at the MP2 level in a comparison of two *corresponding* forms is 0.72 kcal mol^{-1}. Thus, the solvent–solvent interactions do not significantly affect the relative stabilization of the four forms by the solvent.

It is worth mentionning that the solvent–solvent interaction energy for the optimal geometry of the solvent dimer is about −2.2 kcal mol^{-1} at the MP2 level. This is the order of magnitude of the interaction energy of one solvent molecule with some ligands of the solute. This implies that a competition between some solute–solvent and solvent–solvent interactions may exist. In particular, in a cluster composed of the solute and a limited number of solvent molecules, it would not be surprising that the second solvation shell is partly filled before the first one is completed. Indeed, this turns out to be the case with six solvent molecules. A DFT optimization of the geometry of a system involving the solute and six solvent molecules led to some clustering of the solvent molecules. Geometrical constraints must therefore be imposed to keep the first solvation shell chemically significant.

It thus appears that the interaction energy may be approximated by the sum of the solute–solvent pair interactions without significantly affecting the qualitative interpretation of the results. This is an important feature for further comparison with other methods.

3. Effect of the Geometry of the First Solvation Shell. The discussion of the discrete supermolecule/SAPT results reported in the previous sections was based on the geometries G_{1-1} or G_{0-1}. We checked that this choice of the geometries does not introduce artifacts leading to erroneous conclusions. For this purpose additional Hartree–Fock calculations were performed on the total system in the geometries G_{6-6} described in section III. The binding energies take into account the deformation energies, i.e., the energies needed to deform the monomers from their optimal equilibrium geometries to their geometries in the complex. The deformation energy was also taken into account in the case of the MP2 values reported in Table 2 (G_{1-1} geometries). For the sake of more comparisons, Hartree–Fock calculations were also performed on the total system in the geometries G_{0-1}, and G_{0-6}. The binding energies obtained for the G_{1-1}, G_{6-6}, G_{0-1}, and G_{0-6} geometries differ by at the most 1.6, 1.2, 2.6, and 1.4 kcal mol^{-1} for the 1-*mer*, 1-*fac*, 2-*trans* and 2-*cis* forms, respectively. Clearly, the effect of the geometry changes is small and will not affect our conclusions.

The values given in Table 2 and above show that the stabilization energy is significantly different for the four forms. As expected, the zwitterionic forms are more stabilized than the neutral ones. Also, the 1-*mer* and 2-*trans* forms are more stabilized than the 1-*fac* and 2-*cis* ones, respectively. A detailed analysis of the solvation effects on these forms will be presented in the subsequent paper,[47] together with the comparison with the SCRF treatment.

V. Conclusions

In this paper we reported a theoretical study of the solvent effects on various isomers of the palladium hydride complex $PdH_3Cl(NH_3)_2$ in dichloromethane. The influence of the solvent was investigated by the discrete second-order Møller–Plesset and SAPT calculations. The results of this paper can be summarized as follows:

1. For all isomers the interaction energy between a solvent molecule and the various ligands results from a balance of different attractive and repulsive contributions. The largest attractive contribution is given by the electrostatic term, followed by the induction and dispersion components. These attractive terms are canceled by a large exchange-repulsion contribution.
2. As a consequence, the electrostatic contribution does not systematically govern the relative magnitude of the interaction between a solvent molecule and the ligands (or the palladium atom) of the solute.
3. The importance of various contributions to the solute–solvent interaction energy can be correlated with the chemical properties of the ligand to which the solvent molecule is attached. In particular, the interaction is very sensitive to the degree of covalency of the Pd–H bond.
4. For each form of the solute, the interaction of a solvent molecule with the ligands (or the palladium atom) is rather isotropic, though the individual contributions may be strongly anisotropic. This allows to propose a structure for the first solvation shell made of six solvent molecules surrounding the solute.
5. The total interaction energy may be approximated by the sum of the solute–solvent pair interaction energies without significantly affecting the qualitative interpretation of the results.

Acknowledgment. The calculations were performed in Strasbourg (on our laboratory workstations and at the Centre Universitaire Régional de Ressources Informatiques CURRI)) and at the Centre IDRIS (Projects 970306 and 980306) of the CNRS (Centre National de la Recherche Scientifique, Orsay, France). The CNRS and the University Louis Pasteur of Strasbourg are acknowledged for providing computer facilities. We also thank Dr. Lilyane Padel and Mrs. Sylvie Fersing for their help and technical assistance. The travel expenses of E.K. and R.M. were supported by the French Ministère des Affaires Etrangères and by the Polish Scientific Research Council KBN (Projet concerté de coopération scientifique et technique entre la France et la Pologne, project n*o*. 7137). R.M. is grateful to the French Government and the University Louis Pasteur for a PAST position in Strasbourg.

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