J. Phys. Chem. A **2001,** *105,* 2031−2038

Interaction of Dichloromethane with Palladium Complexes: A Comparative Symmetry-Adapted Perturbation Theory, Supermolecule, and Self-Consistent Reaction Field Study

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Received: October 3, 2000

This paper reports 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 influence of the solvent is investigated by continuum self-consistent reaction field (SCRF) calculations and compared with discrete second-order Møller−Plesset (MP2) calculations. We present a theoretical analysis of the free energy of solvation in the continuum model in terms of the physical contributions (electrostatic, induction, dispersion, and exchange-repulsion) as defined by the symmetry-adapted perturbation theory (SAPT). It is shown that the free energy of solvation in the continuum model correctly accounts for the electrostatic energy and for that part of the induction term which describes the polarization of the solvent by the solute. These theoretical findings are in agreement with the numerical results from the discrete SAPT and continuum SCRF calculations. The global agreement between the SCRF dispersion contribution computed from empirical atom−atom type expressions and the SAPT results is rather good. By contrast, the SCRF exchange-repulsion term is strongly underestimated, which suggests that the parametrization of the SCRF empirical expression is not correct for the palladium compounds. Both the discrete MP2 and continuum SCRF models predict the same relative stabilization for the isomers of the palladium complexes in dichloromethane.

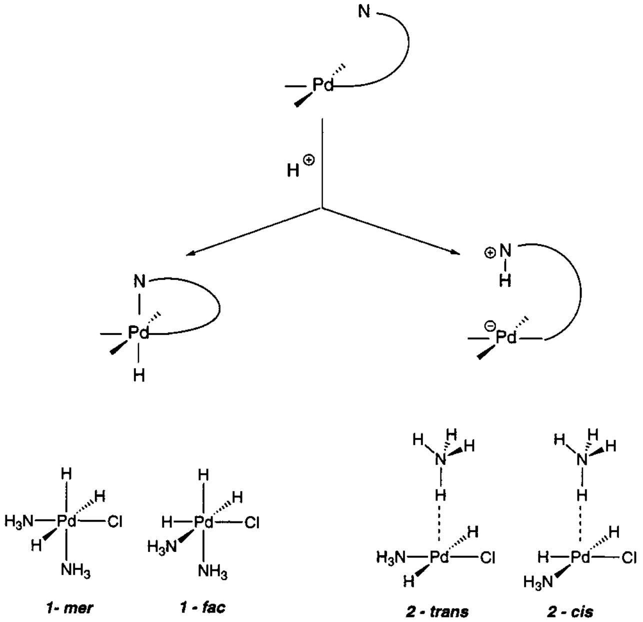
I. Introduction

As discussed in the previous paper,[1] only a few theoretical studies have considered the influence of the solvent in the realm of organometallic reactivity, in contrast with what is currently done in organic chemistry. Furthermore, the solvents that have been considered in most theoretical studies carried out so far on such systems seem to have either strong coordinative properties or a strong hydrogen bonding ability in addition to their intrinsic polarity;[2−6] see, however, ref 7. We have chosen, instead, to focus on the dielectric properties of the solvent and started recently a systematic study of some palladium hydride complexes in dichloromethane.[1,8,9] Palladium hydride complexes are key intermediates in many palladium-mediated or catalyzed reactions[10−13] that are very often carried out in dichloromethane. It is generally assumed that CH_2Cl_2 has weak hydrogen bonding or coordinative properties (note, however, that there have been a few cases in which such properties have been exemplified).[14−18] The systems we concentrated on are models of Pd(II) or Pt(II) complexes that can be protonated either on the metal or on the nitrogen atom; see Scheme 1.[12] We first considered the systems in the gas phase[19−22] and then started to look at the effect of the solvent on the neutral and zwitterionic forms.[1,8,9]

Two categories of methods can be used to study the solvent effect in such systems: one can either treat the full system (made of the solute and a few solvent molecules) as an ensemble of discrete particles or use a continuum model. Both possibilities have been explored. The results obtained with the discrete model are reported in ref 1. In particular, taking advantage of the complementary nature of the supermolecule and the perturbative treatments, we could examine the behavior of the interaction energy components according to the ligands and the forms of the palladium system. One should stress, however, that the size of the systems under study puts some limits on the accuracy of the results obtained within the discrete model. As far as the other alternative—the continuum model—is concerned, its performance for organometallic systems is quite unexplored. In the self-consistent reaction field (SCRF) treatment the solvent is represented by a polarizable continuum in which the palladium complex is immersed within a cavity. In a preliminary work, we proposed to use a cavity of adjustable dimensions.[9,23] The SCRF approach allows, in particular, to check the influence of

10.1021/jp003625s CCC: $20.00

SCHEME 1



the electrostatic type interactions (both short range and long range) on the relative stability of the different forms of the complexes.

The present paper is focused on an overall comparison of the discrete supermolecule model and the SCRF approach. We also briefly compare the systems of the Scheme 1 to their bis(methyl) analogues $\mathrm{Pd(H)(CH_3)_2Cl(NH_3)_2}$ and $\mathrm{[Pd(CH_3)_2Cl(NH_3)]^-(NH_4)^+}$. Numerical results are reported, together with a formal analysis of the energetical contributions considered. The paper will be organized as follows. We will first outline in section II the methods that have been used in our calculations. In particular, we will present an analysis of the free energy of solvation in the continuum model in terms of the physical contributions, as defined by the perturbation theory of intermolecular forces. Computational details are also given in this section, and the geometries used for either the SCRF calculations or within the discrete solvation model are recalled. Numerical results and discussion, focused on the comparison of the solvation energies from the continuum and discrete calculations, are presented in section III. Finally, concluding remarks are given in section IV.

II. Methods of Calculations

A. Discrete Model: Supermolecule and SAPT Calculations. For the discrete model, both the supermolecule second-order Møller−Plesset theory (MP2) and the symmetry-adapted perturbation theory (SAPT) have been used. In the previous paper it was shown that we could restrict ourselves to the pair solute−solvent approximation, neglecting the pair solvent−solvent and nonadditive many−body interactions. The MP2 interaction energy, $E_{\mathrm{int}}^{\mathrm{MP2}}$, was thus given by the sum of the pair energies, $E_{\mathrm{int}}^{\mathrm{MP2}}(\mathrm{SB}_i)$, describing the interaction between the molecule of the solute (S) and the ith molecule of the solvent (B_i). The supermolecular energies were corrected for the basis set superposition error (BSSE) with the counterpoise method of Boys and Bernardi.[24]

Similarly, the SAPT interaction energy of the solute−solvent system, $E_{\mathrm{int}}^{\mathrm{SAPT}}$, is represented as the sum of the SAPT solute−solvent pair interaction energies, $E_{\mathrm{int}}^{\mathrm{SAPT}}$. The interaction energy for the pair SB_i was computed from the following expression,[25]

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

where the consecutive terms on the rhs of eq 1 denote the electrostatic, induction, dispersion, and exchange energies, respectively. The exchange contribution, dominated by the first-order exchange term, $E_{\mathrm{exch}}^{(1)}(\mathrm{SB}_i)$, which gives most of the total exchange energy, also accounts for second-order terms (exchange-induction, $E_{\mathrm{exch-ind}}^{(2)}(\mathrm{SB}_i)$, exchange-deformation, $E_{\mathrm{exch-def}}^{(2)}(\mathrm{SB}_i)$, and exchange-dispersion, $E_{\mathrm{exch-disp}}^{(2)}(\mathrm{SB}_i)$). For computational reasons, the intramonomer correlation effects on these terms[26−31] have been neglected. As commented in ref 1, this may affect the electrostatic and first-order exchange energies.

B. SCRF Calculations. In the SCRF formalism, as developed by Rivail and collaborators,[32−39] the solute−solvent system is modeled by a polarizable continuum (characterized by a dielectric constant ϵ) in which the solvent molecule is immersed within an ellipsoidal cavity.[34,35] The Hamiltonian describing the solute in the cavity is given by

$$H = H_0 + V^{\mathrm{SCRF}} \quad (2)$$

where H_0 is the Hamiltonian of the solute in the vacuum and the operator V^{SCRF} describes the interaction between the permanent multipole moments of the solute and the moments of the reaction field generated by the polarized solvent,

$$V_{\mathrm{SCRF}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} R_l^m M_l^m \quad (3)$$

Here M_l^m denotes the operator of the mth spherical component of the multipole moment of order l of the solute, and the reaction field moments are given by

$$R_l^m = \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} f_{ll'}^{mm'} \langle \Psi_{\mathrm{S}} | M_{l'}^{m'} | \Psi_{\mathrm{S}} \rangle \quad (4)$$

The numerical factors $f_{ll'}^{mm'}$ are the so-called reaction field factors, and depend on the dielectric constant ϵ of the solvent, and on the geometrical parameters of the ellipsoidal cavity. The wave function Ψ_{S} appearing in eq 4 is the solution of the Schrödinger equation with the Hamiltonian given by eq 2. Thus, in the SCRF theory one solves a nonlinear Schrödinger equation that describes the interactions of the solute molecule with a polarizable continuum representing the solvent. The free energy of solvation is given by the expectation value,

$$\Delta G = \frac{\left\langle \Psi_{\mathrm{S}} \middle| H_0 + \frac{1}{2} V^{\mathrm{SCRF}} \middle| \Psi_{\mathrm{S}} \right\rangle}{\langle \Psi_{\mathrm{S}} | \Psi_{\mathrm{S}} \rangle} - E_0 \quad (5)$$

where E_0 is the exact energy of the solute in the vacuum. One may note that the factor of half appearing in the expression for ΔG is a direct consequence of the fact that the solvent is assumed to be a linear dielectric.

In practice, the Schrödinger equation with the Hamiltonian of eq 2 is first solved within the self-consistent field approximation,[35] leading to the so-called SCRF free energy of solvation, ΔG^{SCRF}. If the correlation corrections are included, e.g., via the MP2 approach,[38,39] we get the MP2-SCRF free energy of solvation $\Delta G^{\mathrm{MP2-SCRF}}$.

It should be noted that the free energy of solvation as given by eq 5 does not account for the dispersion and repulsive contributions (cf. also section III.B; note also that $\Delta G^{\mathrm{MP2-SCRF}}$ includes the intramonomer correlation effects at the MP2 level but entirely neglects the intermonomer correlation, i.e., the dispersion). In principle, the dispersion term could be evaluated using the methodology of Rivail and collaborators.[36,37] Since we did not have access to the corresponding code, and since we also wanted to include the repulsive contribution (not implemented thus far in the group of Rivail), we decided to compute these two terms with the SCRF approach advocated by Tomasi and collaborators[40−43] (see, also, ref 44 for a review). Thus, the dispersion and repulsive contributions were obtained from empirical atom−atom type expressions[43] and averaged over the solvent distribution using the prescription of ref 43.

C. Comparison of the SAPT and SCRF Approaches. In this section we will derive approximate relations between the SCRF and SAPT methods. Before we go on with the derivations, we would like to stress that these two methods are quite different. Indeed, the former describes the solvation energetics in terms of the free energy of solvation at a finite temperature T, while in the latter one considers the interaction energy between the molecule of the solute and all molecules of the solvent at $T = 0$ K. One should also note that in the SCRF theory the solvent is modeled by a polarizable continuum, so the Hamiltonian of eq 2 is semiempirical, although the actual mathematical form of V^{SCRF} can to some extent be justified on nonempirical grounds.[45−47] Thus, our comparison of the two methods will only be qualitative, and the agreement between the SCRF and SAPT results within, e.g., 30% will be considered as reasonable (see section III.B).

Since in the SCRF model one considers the interaction of the solute molecule with a polarizable continuum of the solvent, we will assume a mean-field[47] or Hartree−Fock[48] type separation of the wave function describing the system solute−solvent. Thus, the discrete equivalent of the Hamiltonian of eq 2 describing the solute in the electrostatic field of the polarized solvent should read

$$H = H_0 + \sum_{\mathrm{i}=1}^{N} \frac{\langle \Psi_{\mathrm{B}_i} | V_{\mathrm{SB}_i} \Psi_{\mathrm{B}_i} \rangle_{\mathrm{B}_i}}{\langle \Psi_{\mathrm{B}_i} | \Psi_{\mathrm{B}_i} \rangle_{\mathrm{B}_i}} \tag{6}$$

where V_{SB_i} denotes the intermolecular interaction operator between the electrons and nuclei of the solute molecule and the ith molecule of the solvent, and Ψ_{B_i} is the wave function of the ith molecule of the solvent including the induction effects to infinite order. I.e., this wave function fully accounts for the electrostatic polarization of the ith molecule of the solvent by the electrostatic field of the solute. The subscript B_i at $\langle ... \rangle_{\mathrm{B}_i}$ means that the integration is performed only over the coordinates of the electrons of B_i. Although there is no formal correspondence between the perturbation operator appearing on the rhs of eq 6 and the SCRF operator V^{SCRF} (see, for instance, refs 45−47 for a discussion of this point), their physical meaning is quite similar. Both operators describe the interaction of the permanent and induced moments on S and B_i. We will solve the Schröndinger equation with the Hamiltonian of eq 6 by perturbation theory and employ the resulting perturbation expansion for the wave function of the solute to derive a perturbation expansion of the free energy of solvation, eq 5. We will limit the perturbation expansion for the wave function of the solute to the first order in V_{SB_i}, so the expansion of ΔG will be exact to the second order.

To proceed further, first we note that the wave function of the ith solvent molecule including the polarization by the electrostatic field of the solute can be written as

$$\Psi_{\mathrm{B}_i} = \Psi_{\mathrm{B}_i}^{(0)} + \Psi_{\mathrm{B}_i}^{(1)}(\mathrm{B_i} \leftarrow \mathrm{S}) + ... \tag{7}$$

where $\Psi_{\mathrm{B}_i}^{(0)}$ is the wave function of the ith molecule of the solvent in the vacuum, and $\Psi_{\mathrm{B}_i}^{(1)}(\mathrm{B}_i \leftarrow \mathrm{S})$ denotes the first-order induction wave function describing the (first-order) polarization of the ith molecule of the solvent by the electrostatic field of the isolated solute.[49] Thus, the Hamiltonian of eq 6 can be rewritten as

$$H = H_0 + \sum_{i=1}^{N} (\zeta \langle \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{B}_i}^{(0)} \rangle_{\mathrm{B}_i} + 2\mathrm{Re}\,\zeta^2 \langle \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{B}_i}^{(1)}(\mathrm{B_i} \leftarrow \mathrm{S}) \rangle_{\mathrm{B}_i} + ...) \tag{8}$$

where the parameter ζ was introduced to order the perturbation expansion in V_{SB_i}, and its physical value is obviously 1. The perturbation expansion of the solute wave function satisfying the Schrödinger equation with the Hamiltonian (8) is given by

$$\Psi_{\mathrm{S}} = \Psi_{\mathrm{S}}^{(0)} + \sum_{i=1}^{N} \zeta \Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i) + ... \tag{9}$$

where $\Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i)$ denotes the induction wave function of the solute polarized (to the first order) by the electrostatic field of the isolated ith molecule of the solvent. We will impose the intermediate normalization condition on Ψ_{S}, i.e.

$$\langle \Psi_{\mathrm{S}} | \Psi_{\mathrm{S}}^{(0)} \rangle = 1 \tag{10}$$

Thus, the wave function $\Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i)$ is orthogonal to $\Psi_{\mathrm{S}}^{(0)}$. It follows directly from eqs 8 and 9 that the perturbation expansion of ΔG, eq 5, for $\zeta = 1$ reads

$$\Delta G = \sum_{i=1}^{N} \Big(\frac{1}{2} \langle \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} \rangle + \mathrm{Re} \langle \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(1)}(\mathrm{B}_i \leftarrow \mathrm{S}) \rangle + \mathrm{Re} \langle \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i) \Psi_{\mathrm{B}_i}^{(0)} \rangle + \langle \Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i) \Psi_{\mathrm{B}_i}^{(0)} | H_0 - E_0 | \Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i) \Psi_{\mathrm{B}_i}^{(0)} \rangle + ... \Big) \tag{11}$$

We assumed here that the operator V^{SCRF} in eq 5 is replaced by $H - H_0$, H being defined by eq 8. Furthermore, we can assume that the wave functions appearing in eq 11 are real (which is always the case for the interactions of closed-shell systems). Then, the last two terms of eq 11 cancel, since by virtue of the perturbation equation for $\Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i)$,

$$(H_0 - E_0) \Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i) = (\langle \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} \rangle - \langle \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i}\, \Psi_{\mathrm{B}_i}^{(0)} \rangle_{\mathrm{B}_i}) \Psi_{\mathrm{S}}^{(0)} \tag{12}$$

and of the orthogonality of $\Psi_{\mathrm{S}}^{(1)}(\mathrm{S} \leftarrow \mathrm{B}_i)$ to $\Psi_{\mathrm{S}}^{(0)}$, their sum gives zero. Thus, the expression for ΔG becomes

$$\Delta G = \sum_{i=1}^{N} \Big(\frac{1}{2} \langle \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} \rangle + \langle \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(0)} | V_{\mathrm{SB}_i} \Psi_{\mathrm{S}}^{(0)}\, \Psi_{\mathrm{B}_i}^{(1)}(\mathrm{B}_i \leftarrow \mathrm{S}) \rangle + ... \Big) \tag{13}$$

Using the fact that

$$E^{(1)}_{\mathrm{elst}}(\mathrm{SB}_i) = \langle \Psi^{(0)}_{\mathrm{S}}\,\Psi^{(0)}_{\mathrm{B}_i} | V_{\mathrm{SB}_i} \Psi^{(0)}_{\mathrm{S}}\,\Psi^{(0)}_{\mathrm{B}_i} \rangle \tag{14}$$

and

$$E^{(2)}_{\mathrm{ind}}(\mathrm{B}_i \leftarrow \mathrm{S}) = \langle \Psi^{(0)}_{\mathrm{S}}\,\Psi^{(0)}_{\mathrm{B}_i} | V_{\mathrm{SB}_i} \Psi^{(0)}_{\mathrm{S}}\,\Psi^{(1)}_{\mathrm{B}_i}(\mathrm{B}_i \leftarrow \mathrm{S}) \rangle \tag{15}$$

we find that ΔG is given by

$$\Delta G = \sum_{i=1}^{N} \left(\frac{1}{2} E^{(1)}_{\mathrm{elst}}(\mathrm{SB}_i) + E^{(2)}_{\mathrm{ind}}(\mathrm{B}_i \leftarrow \mathrm{S}) + ... \right) \tag{16}$$

where $E^{(2)}_{\mathrm{ind}}(\mathrm{B}_i \leftarrow \mathrm{S})$ is the part of the induction energy $E^{(2)}_{\mathrm{ind}}(\mathrm{SB}_i)$ that describes the polarization of the solvent, i.e., the interaction between the permanent moments of the solute with the moments induced on the solvent by the electrostatic field of the solute. Equation 16 is the main result of this section. It shows that the SCRF theory correctly accounts for the electrostatic and major induction effects. One may note, however, that the SCRF treatment neglects the induction energy corresponding to the interaction of the permanent moments of the solvent with the moments induced on the solute by the electrostatic field of the solvent, $E^{(2)}_{\mathrm{ind}}(\mathrm{S} \leftarrow \mathrm{B}_i)$. For strongly polar solvents this term may be very important. When the SAPT and SCRF results are compared, care should be taken of the fact that in the SAPT approach eq 16 is evaluated at $T = 0$ K, while the SCRF calculations are done at a finite T. To get one-to-one correspondence between the two sets of calculations, the SAPT results should be Boltzmann averaged over all configurations of the solvent molecules.[47,50] In the comparisons reported in section III.B we will assume that the statistical average does not fundamentally change the SAPT results. It is worth noting that eq 16 can efficiently be evaluated within the multipole approximation[51,52] for a large number of the solvent molecules, and for a sufficient number of configurations to perform the Boltzmann average. This approach would present an ab initio alternative to the semiempirical SCRF-type calculations.

We wish to end this section by noting that in the SCRF calculations one first computes half of the expectation value of V^{SCRF} with the wave function of the isolated solute, next the ΔG term, and also half of the expectation value of V^{SCRF} with the exact wave function of the solute Ψ_{S}. The term $\langle \Psi^{(0)}_{\mathrm{S}} | V^{\mathrm{SCRF}} \Psi^{(0)}_{\mathrm{S}} \rangle$ is often referred to as the electrostatic term, while $\langle \Psi_{\mathrm{S}} | V^{\mathrm{SCRF}} \Psi_{\mathrm{S}} \rangle$ is believed to represent both the electrostatics and the induction. In view of the analysis reported above, we see that these two statements are not fully correct.

D. Computational Details. *1. Basis Sets.* The basis sets employed in the present calculations were described in ref 1. They were selected for their efficiency from comparisons with several all electron bases.[8] We recall their main characteristics, the details being already given in ref 1. Pseudopotential basis sets are used for the palladium and chlorine atoms (28 and 10 core electrons, respectively), all electron basis sets for the other atoms (C, N, H). All these bases are contracted according to a split valence scheme, one extra diffuse valence function being added for H. These basis sets are supplemented with a polarization function on each atom except for palladium.

2. Discrete and SCRF Calculations. The details of the discrete calculations are given in ref 1. The geometry optimizations and the supermolecular calculations of the interaction energies were done with the Gaussian-94 package.[53] SAPT calculations of the solute−solvent interaction energies were made with the programs SAPT.[54]

Most of the SCRF calculations of the present study are based on the formalism developed by Rivail and collaborators,[32−39] as described in section II.B. The expansion (3) was truncated at $l = 6$. The dielectric constant of dichloromethane at $T = 298$ K is $\epsilon = 9.1$.[55] In a previous work[9] we proposed the ellipsoidal cavity used in the present study. It is derived from the original model of Rinaldi et al.[56,57] The center of the cavity is located at the center of inertia of the van der Waals spheres of the atoms of the solute, and the axes of this ellipsoid are obtained from the inertial tensor of the van der Waals solid of the solute. In the original model of Rinaldi et al., the volume of the cavity is equal to the van der Waals volume of the solute. As our experience shows for the present systems,[9] this volume is too small, implying that such an isotropic transformation is not satisfactory. We thus proposed a corrected cavity obtained by applying an anisotropic transformation to the original cavity, as described in details in ref 9. The computer code for the SCRF calculations with the cavity described above was linked with the Gaussian-94 package.[53] Part of this code for the calculations with the ordinary ellipsoidal cavity was previously implemented in this link by Rinaldi et al.[58] The code performing the optimization of the new ellipsoidal cavity, referred to as cavity IIc in ref 9, was written in our laboratory.[9] As shown in ref 9, this cavity allows fast calculations.

The calculation of the dispersion and repulsive contributions to the free energy of solvation were obtained using the Gaussian-98 code,[59] from empirical atom−atom expressions averaged over the solvent distribution according to Floris et al.[43]

Since no gradient technique was implemented in our code, additional SCRF calculations for optimizing geometries in the continuum were performed with the PCM method using the self-consistent isodensity surface (SCI-PCM code).[40,41,60,61] We checked, with pointwise calculations, that both codes lead to similar geometrical parameters.[9] The SCI-PCM optimized geometries were reported in ref 1.

3. Geometries. Our previous studies[8] have shown that the DFT/B3LYP[62,63] level is adequate for optimizing the geometries. Four sets of geometrical parameters (G_0, G_{1-1}, G_{6-6}, and $G_{\mathrm{SCI-PCM}}$) have been considered in the present work. They were described in detail in ref 1. Their main characteristics are as follows:

−The G_0 geometries refer to the separated systems optimized in the vacuum (we have thus four G_0 geometries corresponding to the two neutral and the two zwitterionic forms of the solute, and one G_0 geometry for the solvent molecule).

−The G_{1-1} geometries correspond to a geometry optimization performed for each solute−solvent pair, one solvent molecule being in interaction with each form of the solute via one of its ligands (and the palladium atom in the case of the zwitterionic forms). Thus, six G_{1-1} geometries are considered for each form of the solute.

−The G_{6-6} geometries correspond to the solute surrounded by six solvent molecules (we have thus four G_{6-6} geometries, one for each form of the solute).

−The four $G_{\mathrm{SCI-PCM}}$ geometries result from a geometry optimization of the four forms of the solute embedded in the continuum and treated in the SCI-PCM method.

III. Numerical Results and Discussion

Since it was shown in the previous paper[1] that the use of the different sets of geometries (G_0, G_{1-1}, G_{6-6}) lead to close results, we can refer to any of these discrete models without affecting the conclusions.

TABLE 1: Comparison of the Components and Global Solvation Energies (in kcal mol^{-1}) for the Four Forms of the Palladium Complex Calculated by the Discrete and Continuum Methods

	1-*mer*	2-*trans*	1-*fac*	2-*cis*
ΔG^{SCRF}	−16.8	−33.2	−11.1	−22.8
$\Delta G^{\mathrm{SAPT}\,a}$	−22.2	−30.8	−11.0	−22.7
$E_{\mathrm{int}}^{\mathrm{HF}}$	−13.1	−21.6	−7.7	−17.0
ΔG^{disp}	−11.7	−11.8	−11.6	−11.7
$E_{\mathrm{disp}}^{(2)}$	−13.2	−14.6	−9.3	−12.5
ΔG^{exch}	1.4	1.4	1.4	1.4
E_{exch}	29.0	37.6	14.4	28.1
$\Delta \mathrm{G}^{\mathrm{MP2-SCRF}\,b}$	−15.6	−28.3	−10.3	−19.0
	(−14.8)	(−28.0)	(−10.6)	(−21.0)
$\Delta \mathrm{G}^{\mathrm{MP2-SCRF}} + \Delta G^{\mathrm{disp}} + \Delta G^{\mathrm{exch}}$	−25.9	−38.7	−20.5	−29.4
$E_{\mathrm{int}}^{\mathrm{MP2}}$	−20.3	−26.5	−13.6	−21.0

[a] Computed from eq 16. [b] Computed with an ellipsoidal cavity as described in the computational section. The SCI−PCM values are given in parentheses.

A. Validity of the Discrete First Solvation Shell Model. To assess the effect of the second and higher solvation shells we carried out calculations that couple, at the SCF level, the discrete and the continuum models in the following way. For the system made of the complex and six solvent molecules (G_{6-6} geometry), we first subtract the SCRF energy of the six solvent molecules and the energy of the complex in the vacuum from the SCRF energy of the full system. The same cavity was used for the full system and the subsystem made of the six solvent molecules. The comparison with the Hartree−Fock results for the solute and the six solvent molecules in the vacuum yields an estimate of the energy correction due to the second and higher shells neglected in our discrete model. In this way, the screening due to the first solvation shell is also taken into account. The energy correction amounts to −1.2, −1.1, +0.7, and −0.6 kcal mol^{-1} for the four forms, respectively. These values are very small and suggest that the interaction energy of the solvent with the solvation shells is correctly accounted for by our model based on the six solvent molecules in the first solvation sphere.

B. Comparison of the Discrete and Continuum Solvation Models. In this section, SCRF calculations are performed on the 1-*mer*, 1-*fac*, 2-*cis*, and 2-*trans* forms of the solute. SCRF calculations were performed with the G_0 and G_6 geometries of the solute. Both geometries give nearly identical values of ΔG^{SCRF} for the neutral forms, and the G_6 geometries are slightly more stabilized than the G_0 ones (by about 2.5 kcal mol^{-1}) for the zwitterionic forms. Since the qualitative analysis will not be altered by these differences, we report here the SCRF results obtained with the G_0 geometries only.

1. Physical Origins of the Solvation Energy in the SCRF Theory. As shown in section II.C the free solvation energy in the SCRF model mainly accounts for the electrostatic term and for the induction contribution due to the polarization of the solvent by the solute, cf. eq 16. In more sophisticated approaches it can be supplemented with the dispersion and exchange-repulsion terms. Since all the contributions mentioned above were computed by SAPT (G_{1-1} model),[1] we can check the correctness of the SCRF treatment of the electrostatic/induction forces, as well as of the dispersion and repulsive contributions.

We start the discussion with the electrostatic and induction effects. It follows from eq 16 that the free solvation energy in the SCRF theory computed at the Hartree−Fock level, ΔG^{SCRF}, can directly be compared with the sum of the electrostatic and induction components from the SAPT calculations. The SAPT and SCRF results are reported in Table 1. An inspection of this table shows that the agreement between the results of the discrete and continuum calculations is good. Indeed, the two sets of the results agree within 0.1 kcal mol^{-1} for the 1-*fac* and 2-*cis* forms; i.e., the agreement is within 1−2%. Given the fact that the discrete solvation model is limited to six solvent molecules, and that the geometry of the solute is not exactly the same in both calculations, one should say that the observed agreement is to some extent fortuitous. For the two other forms, the 1-*mer* and the 2-*trans* forms, the agreement is also good, although for the 1-*mer* form the discrepancy reaches 24%. Let us also mention that the level of agreement between the SCRF and SAPT results supports the correctness of the (partly heuristic) theoretical analysis of the SCRF free solvation energy presented in section II.C. For a further comparison of the corresponding neutral and zwitterionic forms, we must note, however, that the discrepancies on the 1-*mer* and 2-*trans* ones are cumulative, due to their opposite sign.

As a last comment on this part of the work, we want to stress that only the polarization of the solvent by the solute is considered, according to the development of section II.C. This must be underlined since it is often believed that both the induction of the solvent by the solute and that of the solute by the solvent are included through the self-consistent process of the SCRF treatment. It was shown[1] that these two contributions may be seriously different. However, as can be seen from the corresponding values quoted in ref 1, the use of half of the total SAPT induction energy would not modify our qualitative conclusions.

Usually, the dispersion and exchange-repulsion contributions to the free energy of solvation are not considered in the SCRF treatment. As mentioned in section II.D, our code for the SCRF calculations with an anisotropic ellipsoidal cavity was interfaced with the Gaussian-94 code, which did not allow us to account for such terms. Some indicative values could be obtained, however, using a cavity built on an ensemble of interlocking spheres and empirical atom−atom expressions averaged over the solvent distribution according to Floris et al.[43] (see section II.B) as implemented in the Gaussian-98 release.[59] The corresponding values are reported in Table 1.

The results presented in Table 1 show that the SCRF dispersion contribution is in agreement with the SAPT results, whichever the form of the complex is considered. Indeed, the differences between the two sets of the results are not larger than 25%. Interestingly, the SAPT dispersion term varies more along the series 1-*mer*, 2-*trans*, 1-*fac*, 2-*cis* than the corresponding SCRF one. This suggests that the parametrization of the atom−atom SCRF expression for the dispersion energy could be slightly improved.

More delicate is the SCRF description of the exchange-repulsion energy. An inspection of Table 1 shows that the SCRF results are off by a factor of 10−20 depending on the form of the complex considered. This shows that the parametrization of the SCRF exchange-repulsion energy is completely unrealistic for our organometallic complexes.

2. Solvation Energies: Comparison of the Discrete and Continuum Results. An important goal of our study was to examine the ability of various theoretical approaches to describe the solvent effects in organometallic chemistry. In the previous paper,[1] we reported a detailed analysis of the physical contributions governing the intermolecular forces in the system composed of the palladium complex surrounded by the solvent molecules. In the previous section of the present paper, we analyzed the applicability of the continuum model to describe the solvent effects by comparison of its physical ingredients, such as the sum of the electrostatic and induction contributions,

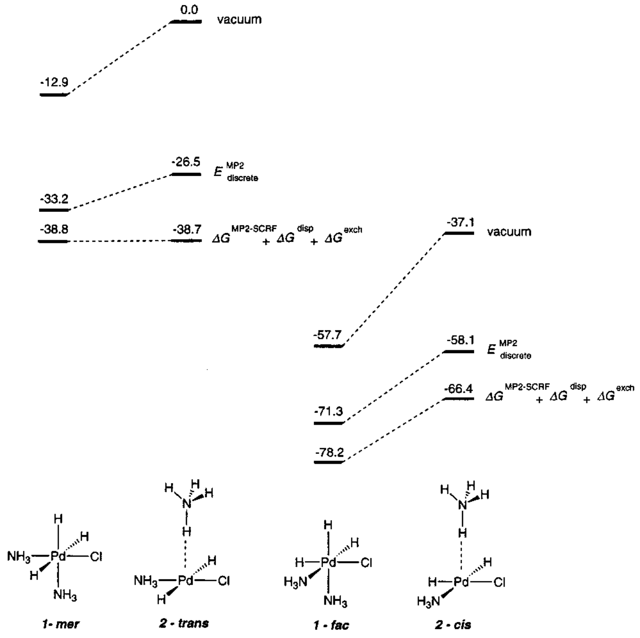


Figure 1. Relative stabilization energies for the four forms of the $PdH_3Cl(NH_3)_2$ complex in the CH_2Cl_2 solvent calculated by the discrete supermolecule and continuum SCRF methods at the MP2 level. The zero of energy corresponds to the 2-*trans* form in the vacuum.

or the dispersion and exchange-repulsion terms, with the results of SAPT calculations. It is also of interest to compare the ability of the continuum and discrete models to account for the variation of the solvation energies among the four forms. We want to reiterate here that in the discrete model we consider the solvation energy at $T = 0$ K, while in the continuum model we compute the free energy of solvation at $T = 298$ K. These two quantities are different. Besides the difference of the temperatures, the free energy of solvation takes into account the entropy effect neglected in the discrete model. Note that the effects of the solvent reorganization[64] were not considered in the present comparisons. Thus, a disagreement between the two sets of the results does not necessarily need to be related to some limitations of the computational methods.

The solvation energy of the four forms can be analyzed from Table 1. At the Hartree–Fock level both the discrete (see E^{HF}_{int}) and continuum (see ΔG^{SCRF}) models predict the zwitterionic forms to be more stabilized by the solvent than the corresponding neutral ones. Furthermore, the 1-*mer* and 2-*trans* forms are more solvated than the 1-*fac* and 2-*cis* forms, respectively. This can be traced to a greater ionic character of the Pd–H bonds in the 1-*mer* and 2-*trans* forms. One can also note that the SCRF treatment leads to a stronger stabilization of the complex by the solvent when compared to the discrete model. This feature can be related, to some extent, to the incorrect description of the exchange-repulsion contribution.

Same conclusions are obtained at the MP2 level. Thus, both (SCRF and discrete) treatments give a similar description of the solvation of the four forms.

3. Relative Stability of the Solvated Forms: Comparison of the Discrete and Continuum Results. The previous section reported a comparison of the solvation energy of the four forms. To understand the role of the solvent in reactivity, we have also to consider, in fact, the relative stabilities of the four forms, in the vacuum and in solution. This is graphically done in Figure 1, the values of the solvated forms being computed either within the discrete model, $E^{MP2}_{discrete}$, or as MP2 free solvation energies, $\Delta G^{MP2-SCRF} + \Delta G^{disp} + \Delta G^{exch}$. On this figure, the origin of the energy scale corresponds to the energy of the 2-*trans* form in the vacuum, which is the highest. It is convenient to put all these data on the same figure. However, it must be emphasized that, as in the previous comparison of the solvation energies, we only compare the relative stabilities of the four forms in each model, not the values of $E^{MP2}_{discrete}$ and of the MP2 free solvation energy obtained for the same form.

At this stage a comment about electron correlation is appropriate. As discussed in refs 21–23, the inclusion of electronic correlation is crucial for a correct description of the relative energies of the four forms in the vacuum. The zwitterionic 2-*cis* form is less stable than the corresponding neutral 1-*fac* form, both at the Hartree–Fock and MP2 levels (by 5.3 and 20.6 kcal mol^{-1}, respectively). The situation is different for the two other forms: the 2-*trans* form is more stable than the 1-*mer* at the Hartree–Fock level (by 11.4 kcal mol^{-1}), while the opposite is true at the MP2 level (by 12.9 kcal mol^{-1}). We shall therefore only discuss the MP2 results.

In the discrete model the relative stability of the four solvated forms follows the trend observed for the vacuum, the energy differences between the zwitterionic and the corresponding neutral forms being only decreased (6.7 and 13.2 kcal mol^{-1} instead of 12.9 and 20.6 kcal mol^{-1}). From this discrete model, we can thus expect that the solvent will not deeply modify the gas-phase reaction pattern.

In the SCRF case, the solvated 1-*mer* and 2-*trans* forms have nearly the same energy. Some SCRF calculations performed for other geometries of the solute (G_6, SCI–PCM geometry) give even the solvated 2-*trans* form slightly more stable than the 1-*mer* one. In contrast, at both levels, the 1-*fac* structure is definitively more stable than the 2-*cis* one. Here too, however, there is a net decrease in the energy difference on going from the discrete to the continuum level. Thus, although both the discrete and the continuum models predict, globally, similar trends for the stabilization of various forms of the complex in the solvent, some finer energetic details may be quite different. In particular, one cannot conclude, from the SCRF model, wether or not the reactivity in solvent will follow the gas-phase reaction pattern.

It is interesting to note, as far as the entropy effect is concerned, that the results of the discrete MP2 and continuum SCRF calculations do agree. One may expect that this effect should be about the same for the solvation process of the two neutral and the two zwitterionic forms. An inspection of Figure 1 shows that this is indeed the case. The differences between the relative energies of the solvated 1-*mer* and 1-*fac* forms are about the same in the discrete and the continuum models (≈38 and 39 kcal mol^{-1}, respectively). The same is true for the 2-*trans* and 2-*cis* forms, the energetic differences being about 32 and 28 kcal mol^{-1} at the discrete MP2 and SCRF levels of the theory, respectively. Thus, as long as the comparison is concerned with either the neutral or the zwitterionic forms only, both methods correctly predict the relative stabilities of the various isomers in the solvent. As already recalled, the results of the discrete calculations are correct for $T = 0$ K, while the continuum calculations are valid at $T = 298$ K.

4. Qualitative Importance of the Exchange-Repulsion Contribution. We showed in Table 1 and section III.B.1 that the main discrepancies between the discrete model and the SCRF calculations arise for the exchange repulsive contributions. In the discrete model, the exchange terms are significantly larger for the zwitterionic than for the neutral forms. In the SCRF model, they are either neglected or evaluated from semiempirical expressions that give nearly the same value for the four forms.

It is clear from Figure 1 that larger repulsive contributions for the zwitterionic forms in the SCRF model would destabilize them, leading to results that parallel more those obtained in the discrete model. A reliable description of the exchange terms is thus needed to ensure a correct relative stabilities of the solvated forms. Our results should motivate further research in this direction.

The neglect or a poor description of the exchange terms may also have consequences on other properties, in particular the geometry. In ref 1, we reported the main geometric parameters obtained for the four forms taken in their geometry G_0, G_{1-1}, G_{6-6}, and $G_{SCI-PCM}$. We noted that the stretching of the Pd$\cdots NH_4^+$ bond of the zwitterionic forms is much larger in the $G_{SCI-PCM}$ than in the discrete cases. This can be understood as an effect of the neglect of the exchange contribution: since the solute−solvent attraction is not compensated by the repulsive contribution, the two NH_4^+ and $[PdH_3(NH_3)Cl]^-$ ionic parts are too much attracted by the solvent, thus leading to an increase of the Pd$\cdots$N distance.

IV. 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, as well as by the continuum SCRF calculations. Our conclusions can be summarized as follows:

1. A perturbation theory analysis of the free solvation energy, as defined by the continuum SCRF model, shows that this energy correctly accounts for the electrostatic and major induction contributions. It neglects, however, the induction term that describes the polarization of the solute by the solvent. Comparison of the numerical results from both SAPT and SCRF calculations fully supports these theoretical findings.

2. The SCRF dispersion contribution computed from empirical atom−atom type expressions agrees with the dispersion energy from SAPT calculations, although its anisotropy is somewhat less pronounced.

3. The SCRF exchange-repulsion term is strongly underestimated, compared to the exchange term from SAPT calculations. This suggests that the parametrization of the SCRF empirical expression is not correct for the palladium compounds.

4. Both the discrete MP2 and continuum SCRF models predict the same relative stabilization by dichloromethane: the zwitterionic forms are more stabilized than the neutral corresponding ones; within the same class of compounds the 1-*mer* and 2-*trans* forms are more stabilized than the 1-*fac* and 2-*cis* ones, respectively.

5. As long as either the neutral or the zwitterionic forms are compared together, some energetic differences between the results of the discrete and continuum calculations can be explained by the entropy effects, neglected in the discrete model.

6. The relative stability of the solvated forms differs somewhat between the discrete and the SCRF model: the neglect of the exchange terms in the SCRF model lead to larger solvation effects compared to the discrete model, especially for the trans zwitterionic isomer. In this case, this might lead to a different stability pattern in a vacuum and in solution.

One may of course worry about the ability of the $PdH_3Cl(NH_3)_2/[PdH_2Cl(NH_3)]^-(NH_4)^+$ systems used in the present study to model real complexes with methyl (or alkyl) groups. To check this point, a few calculations were carried out on the bis(methyl) analogues of these systems, viz. $Pd(H)(CH_3)_2Cl(NH_3)_2$ and $[Pd(CH_3)_2Cl(NH_3)]^-(NH_4)^+$; see Scheme 2, both in a vacuum and in solution (using the SCI-PCM method and the G_0 geometry). The corresponding results are summarized in Table 2. It is clear from this Table that the results for the 3-*mer*/4-*trans* and 3-*fac*/4-*cis* pairs of systems closely mimic those for the 1-*mer*/2-*trans* and 1-*fac*/2-*cis* pairs, respectively. This is not only true for the solvation energies but also for the relative energies (both in a vacuum and in solution). Thus, the above conclusions should also hold for the bis methyl analogues.

SCHEME 2

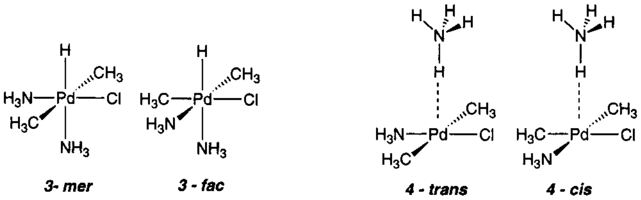


TABLE 2: Solvation and MP2 Relative Energies (ΔE, in a Vacuum and in Solution) for the Hydride and Methyl Systems[a]

	solvation energy	ΔE (vacuum)	ΔE (solution)^b
2-*trans*	−28.0	0.0	0.0
1-*mer*	−14.8	−12.9	+ 0.3
2-*cis*	−21.0	−37.1	−30.1
1-*fac*	−10.6	−57.7 (−20.6)^c	−40.3 (−10.2)^c
4-*trans*	−24.0	0.0	0.0
3-*mer*	−12.2	−15.5	−3.7
4-*cis*	−18.1	−28.4	−22.5
3-*fac*	−9.9	−48.3 (−19.9)^d	−34.2 (−11.7)^d

[a] For each type of systems the energy zero corresponds to the isomer with highest energy, i.e., the 2-*trans* and 4-*trans* isomers, respectively. [b] Using the SCI−PCM method and the G_0 geometry. [c] Relative energy with respect to the 2-*cis* isomer. [d] Relative energy with respect to the 4-*cis* isomer.

One should finally discuss, in connection with the SCRF model, other factors that may come into play. We have already mentioned that the neglect of the polarization of the solute by the solvent is not an important factor here but may be more critical for strongly polar solvents. Another case where this factor might come into play deals with systems bearing polarizable ligands. The model ligands used here, i.e., NH_3 and Cl, have low polarizability, and the corresponding induction term is relatively small. Ligands such as triphenylphosphine, pyridine, or heavier halogens (bromine or iodine) would probably behave differently. One may expect, for instance, that the polarization of the solute by the solvent would shift somewhat the energy balance between the neutral metal hydride and its zwitterionic hydride toward the zwitterionic isomer. Such effects certainly warrant further theoretical studies.

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 no. 7137). R.M. is grateful to the French Government and the University Louis Pasteur for a PAST position in Strasbourg.

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