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Solvent Influences on the Structure, Thermochemical Parameters, and Electronic Properties in a Carbyne Complex Catalyst: $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$

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Abstract

In this study, the carbyne complex, $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$, structural, themochemical and electronic properties were studied in solution and gas phases. For this investigation, the chosen solvents were five solvents (methanol, acetone, ethanol, DMSO, nitromethane) with various polarities. The influence of solvent polarity on the thermodynamic, structural, solvation energy parameters and frontier orbital energies of the complex were carried out. This study is helpful opportunity for more understanding the osmium carbyne complexes chemistry, particularly in the area of catalytic and reactivity properties of osmium carbyne complexes.

Keywords: *Carbyne complex, Frontier orbitals, Solvent influence, Thermodynamic parameters.*

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Introduction

The alkylidyne complexes chemistry is a rigorously studied area within organometallic science by the first transition metal carbyne complex rigorously in 1973 [1]. The synthesis, reactivity, structure and properties of theses complexes motivated many researches in the organometallics area [2-6]. They have contributions in diverse catalytic transformations [7-11]. By reacting carbonyl metalates, there are silicon analogues of the alkylidyne complexes [12], compounds series featuring metal–germanium, metal–lead or metal–tin triple bonds have been achived [13, 14].

In osmium carbyne complexes, many transition metals, such as osmium, can create stable osmium–carbon triple bonds. Roper et al. reported the first osmium carbyne complexes synthesis [15]. Especially in recent years, the osmium carbyne complexes chemistry has superior considerably, while it has not been extended as much as that of groups 5–7 metals. Different complexes of osmium carbyne have been synthesized from a synthetic routes range. Moreover, osmium carbyne complexes chemical reactivities have been studied. The osmium carbyne complexes chemistry has been reported generally in articles regarding metal carbyne complexes [16, 17] and in reviews dealing particularly with group 8 carbyne complexes [18, 19]. Solvent influence is one of the chemistry elementary matters, and causes considerable modifications in the molecular behavior as the interactions between solvent and solute [20-22]. Techniques for considering solvent influences in quantum mechanical electronic structure calculations have been provided. In this study, we evaluate the $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex structure in the various solvent and gas phases and show the influence of these solvents on the thermochemical, electronic and structural parameters.

Experimental

With the Gaussian 09 suite program, all calculations were performed [23] applying the method of Modified Perdew-Wang Exchange and Correlation (mpw1pw91) [24]. Using the standard 6-311G(d,p) basis set, calculations of systems include the main group elements (C, H, P, and Cl) were calculated [25-28]. The standard Def2-TZVPPD basis set [29] for Os element was applied and Os described by effective core potential (ECP) of Wadt and Hay pseudo-potential considering the Def2-TZVPPD basis set [30]. Frequency calculations were employed to confirm the acceptable nature of the stationary points. For the solvation effects study, all structures were reoptimized in solution by a self-consistent reaction field (SCRF) approach, in particular using the polarizable continuum model (PCM) [31].

Results and discussion

Energies of solvation

Figure 1 shows the structure of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex. The energies of stabilization by solvents (solvation energy, E_{solv}) were calculated (Table 1).

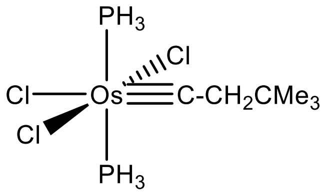

Figure 1. The structure of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex.

Table 1. Absolute energy (Hartree), solvation energies (kcal/mol) values of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex.

	ε	E	E_{solv}	μ
Gas	-	-2393.2095	-	
Acetone	20.49	-2393.2377	-17.70	11.45
EtOH	24.85	-2393.2382	-18.00	11.54
MeOH	32.61	-2393.2388	-18.35	11.65
$MeNO_2$	36.56	-2393.2390	-18.48	11.69
DMSO	46.83	-2393.2393	-18.70	11.75

In a solvent, these values are relative energy of the title compound compared to that in the gas phase. As we can be observed, the solvation energies are dependent on the dielectric constant size of solvents, and these values would decrease with the increase of solvents dielectric constants. Therefore, the $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex stability increases in more polar solvents. Therefore $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex would have more stability in polar solvent instead of in the gas phase. The correlation between dielectric constants and E_{solv} is a follows:

$$E_{solv} = -0.0375\,\varepsilon - 17.032; \qquad R^2 = 0.9451$$

Dipole moments

The dipole moments of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex in different solvents and gas phase were shown in Table 1. As can be seen in Table 1, in solution phase these values increase. In the solution phase, dipole moments increase with increasing of solvent polarity. In addition, these values reveal a good relationship with dielectric constants values:

$$\mu = 0.0112\,\varepsilon + 11.255; \qquad R^2 = 1$$

Geometrical parameters

$OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex selected geometrical parameters are given in Table 2. These values indicate that Os-C distance decrease in solution instead of that in the gas phase. However, Os-P, Os-Cl distances increase in solution instead of those in the gas phase. These values illustrate minor dependency on the solvent dielectric constant size. These values have minor dependency on the size of the dielectric constant of solvents.

Table 2. Selected structural parameters (bond distances in Å) of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex.

	Os-C	**Os-P**	**Os-Cl$_{cis}$**	**Os-Cl$_{trans}$**
Gas	1.7225	2.3708	2.4060	2.4689
Acetone	1.7196	2.3891	2.4153	2.5142
EtOH	1.7196	2.3893	2.4079	2.5154
MeOH	1.7195	2.3896	2.4080	2.5167
$MeNO_2$	1.7195	2.3897	2.4081	2.5172
DMSO	1.7195	2.3899	2.4150	2.5181

Molecular orbital analysis

The frontier orbitals energies, and HOMO–LUMO energy gaps of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex in different solvents and gas phase are given in Table 3.

Inclusion of solvation effects leads also the molecular orbital energies changes (Table 3). In solution, frontier orbitals would be stabilized, regarding the relevant values in vacuum.

As well, HOMO-LUMO gap of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex in solution phase are more compared to those in gas phase.

Table 3. Frontier orbital energies (a.u), HOMO-LUMO gap (**ΔE** , eV), of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex.

	E(HOMO)	**E(LUMO)**	**ΔE**
Gas	-0.241	-0.070	4.663
Acetone	-0.253	-0.072	4.930
EtOH	-0.253	-0.072	4.935
MeOH	-0.253	-0.072	4.940
$MeNO_2$	-0.253	-0.072	4.942
DMSO	-0.253	-0.072	4.945

Thermodynamic parameters:

Absolute enthalpy and free energy values of studied carbyne complex can be seen in Table 4. The solvation enthalpy and free energy values are computed via the following equation:

$\Delta X_{solvation} = X_{solv} - X_{gas}$; X=G, H

Table 4 shows that the ΔG_{solv} and ΔH_{solv} of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex amount decrease with increasing the dielectric constant. A good relationship was observed between ΔH_{solv} and ΔG_{solv} dielectric constant values:

$$\Delta G_{solv} = -0.0442\,\varepsilon - 17.302; \qquad R^2 = 0.949$$

$$\Delta H_{solv} = -0.0388\,\varepsilon - 17.089; \qquad R^2 = 0.9454$$

Table 4. Thermochemical parameters of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex (in $Cal.Mol^{-1}.K^{-1}$).

	G(Hartree)	H(Hartree)	S(Hartree)	G_{solv}(kcal/mol)	H_{solv} (kcal/mol)	S_{solv} ($Cal.Mol^{-1}.K^{-1}$)
Gas	-2393.044	-2392.972	150.926	-	-	-
Acetone	-2393.073	-2393.000	151.986	-18.09	-17.77	1.06
EtOH	-2393.073	-2393.001	152.090	-18.44	-18.09	1.16
MeOH	-2393.074	-2393.001	152.274	-18.85	-18.45	1.35
$MeNO_2$	-2393.074	-2393.002	152.337	-19.00	-18.58	1.41
DMSO	-2393.074	-2393.002	152.459	-19.27	-18.81	1.53

Conclusion

An investigation of the solvent influence on the properties and structure of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex presented in this paper, and indicated that solvation energies values show the increasing of $OsCl_3(\equiv CCH_2CMe_3)(PH_3)_2$ complex stability in more polar solvents. Inclusion of solvation influences leads to the frontier orbital stabilizing. By the increasing of the dielectric constant, the ΔG_{solv} and ΔH_{solv} values of the complex decreased.

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