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THEORETICAL STUDY OF P(III)=C-P(V) TYPE DIPHOSPHAPROPENES COORDINATED TO TRANSITION METALS

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ABSTRACT. DFT calculations at BP86/6-311G*(d,p) level of theory were performed RP(Cl)=C-P(=E)MeCl (R=H, Me or Ph and E=O, S) units, in order to realized a energetic and geometric analysis. The coordination modes of diphosphapropenic systems to transition metals were also investigated in the case of $W(CO)_5$, $PtCOCl_2$ and $PdCOCl_2$ organometallic fragment.

Keywords: *DFT calculations, diphosphapropene, coordination models*

INTRODUCTION

Heteropropene compounds of the X=C-X' type (X, X' being p-block elements) have been intensively studied in the last three decades due to the presence in the system of multiple reactive sites such as the X=C double bond or the X, X' atoms. On the other hand, heteropropenes (especially the ones bearing one or two halogen atoms) are precursors in the synthesis of unsaturated X=C=X' heteroallene compounds. The presence of one or multiple unsaturations in heteropropenic and heteroallenic systems created serious problems in the stabilization of these compounds. Two methods are currently known for solving this problem: the use of bulky groups to thermodynamically stabilize these compounds and the coordination to ML_n fragments that can increase the stability of the X=C=X' moiety by kinetic effects. The literature offers many information on stabilizing the heteropropenes and heteroallenes by connecting the bulky organic groups to the X=C=X' or X=C-X' moieties.

Multiple experimental studies were reported [1-10] regarding the synthesis pathways of this type of compounds and their physico-chemical characterization. Computational studies were performed in order to determine the factors leading to the stabilization of such systems [11-13]. Most of these studies refer to the stabilizing effect of different organic groups with different electronic and steric properties.

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Our group is particularly interested in the field of heterophosphaallenic and heterophosphapropenic compounds [14], their synthesis, physico-chemical characterization and computational studies. Regarding the theoretical investigation, *ab initio* calculations have previously been reported for heterophosphaallenes like RP=C=PR (R = H, F, Cl) [15, 16], HP=C=NH [16, 17] HP=C=O [18], RP=C=AsR or R_3P=C=AsR_3 [19, 20] or in cumullenic systems of the type RP=C=P(=O)R' [12, 13]. All these studies take into account the thermodynamic stabilizing effect induced by the groups attached to the X=C=X' fragment. No extensive computational studies that discuss the effects induced by the presence of one or more MLn organometalic fragments attached to the X, X' atoms or the X=C moiety were reported.

This work presents a theoretical study on the coordination ability of diphosphapropenic systems RP(Cl)=C-P(E)(Cl)Me (E = O, S) towards organometallic fragments ML_n ($W(CO)_5$, $PtCOCl_2$, $PdCOCl_2$). Several substituents (R= H, Me, Ph) were taken into account in order to asses a possible influence on the coordination. DFT calculations were carried out on the model compounds to determine the optimized geometries and energies. For the tungsten derivatives, a clear predilection towards coordination though the phosphorus atom involved in the P=C bond was evidenced. Calculations suggest that in the case of palladium or platinum, diphosphapropenes would act as bidentate ligands. The Wiberg bond orders for the M-E bond (E = the donor atom of the diphosphapropenic unit) were also calculated.

RESULTS AND DISCUSSIONS

All starting structures were built with Gaussview 4.1[21]; the geometries were optimized with Gaussian 09[22] package of programs at the DFT BP86/6-311++G(d,p) level of theory for the C, H, Cl, P, O and S atoms and using the LANL2TZ [23] basis set for the metallic atoms. Vibrational analyses were carried out in order to ensure that all structures represent true energy minima.

The most stable geometries as well as the coordination possibilities of diphosphapropenic systems of RP(Cl)=C-P(=E)MeCl (R= H, Me, Ph and E=O, S) to transition metal fragments such as $W(CO)_5$, $PdCOCl_2$ and $PtCOCl_2$ have been studied.

In each of the investigated phosphapropenic system, the geometry of the diphosphapropene system was optimized and the energy minima of the potential surface were used as starting structures for the modeling of the derivatives coordinated to the transition metal.

The optimized geometries for the MePCl=C-P(Me)ClE (E=O, S) systems are presented in Figure 1. The considered ligands present several possibilities of coordinating to transition metals: through the λ^3P atom, the P=C moiety or one of the O or S atoms, as depicted in Figure 2. The coordination modes taken into account for this study represent the most common behavior towards transition metals of phosphapropenes functionalized with group 16 elements as monodentate ligands.

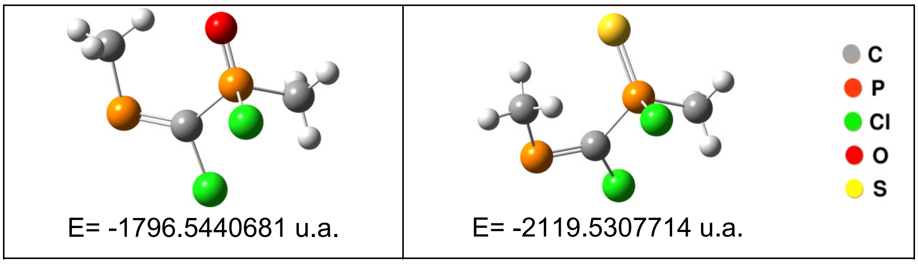


Figure 1. Optimized structures for MePCl=C-P(=E)ClMe, E=O (a), S (b)

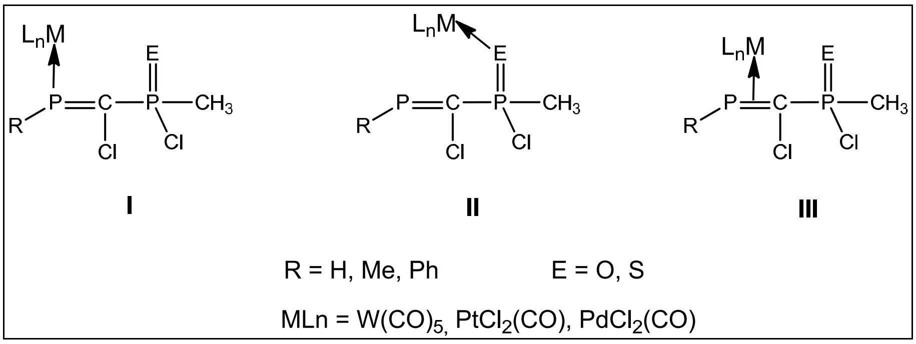


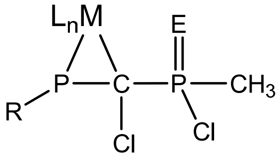
Figure 2. Considered types of PCP(E) systems coordination to organometallic fragments.

Tungsten coordination compounds

The optimization of the three tungsten complexes with diphosphapropenic ligands, corresponding to the considered coordination modes, was followed by a vibrational analysis to ensure that the structures represent true minima. The calculated geometrical parameters are presented in Table 1, along with the relative energies compared to the coordination isomer with the lowest energy of the series.

The metal-diphosphapropenic bond lengths are estimated between 2.372 Å and 2.623 Å for PCPS systems, and 2.269 Å -2.471 Å for the PCPO systems.

The coordination of a sulfur-containing ligand to a metal atom generally leads to an increase in the length of the P=C double bond by up to 0.1 Å. The most dramatic shift was observed (as expected) in type III coordination, together with the lowering of P=C bond order. For instance for MeP=C(Cl)-P(=S)MeCl→$W(CO)_5$ coordination isomers, the calculated Wiberg [24] bond order estimated through the NBO [25] analysis, decreases from 1.66 for the free ligand to 1.52 for the P-coordinated isomer and 1.12 for type III complexes, losing entirely the double bond character. The NBO analysis suggests in this case a type IIIb structure (see Scheme 1), and not a direct electron donation from the P=C bond to the metal atom. This can be credited to the different electronegativity of the atoms involved in the double bond, allowing an uneven distribution of the electronic charge. A coordination through the sulfur atom does not affect in a significant manner the P=C bond, with an estimated Wiberg bond order of 1.65.



IIIb

Scheme 1.

The calculated P-C single bond lengths range between 1.820 Å and 1.882 Å, in good agreement with reported experimental data [2]. The presence of various atoms on the P(V) atom does not have a strong influence on the bond lengths of the considered compounds.

Figure 3 represents the optimized geometries of the complexes resulted by the coordination of PhP=C(Cl)-P(=O)MeCl to the $W(CO)_5$ organometallic fragment. When the coordination takes place through the P atom or the double bond, the ligand adopts a *cis* configuration, relative to the P=C bond, allowing for a less sterically hindered derivative. If the donor atom is the oxygen, the coordination can occur in a *trans* configuration as well. The geometry around the tungsten atom is that of distorted octahedron.

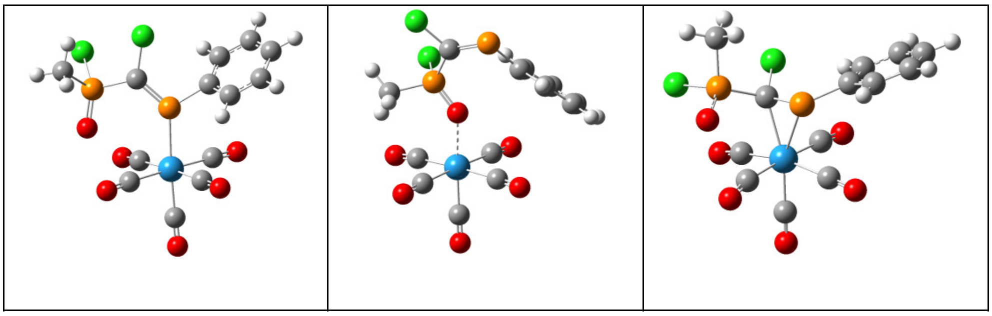


Figure 3. Calculated geometries of $PhP=C(Cl)-P(=O)MeCl \rightarrow W(CO)_5$

Based on the relative energies presented in Table 1 (as compared to the energy minima of the series of isomers) a general preference for the coordination of the phosphapropenic system to the tungsten atom through the double bonded phosphorus atom is evidenced. There are no noticeable differences in energy between complexes of this type and the ones having a type III coordination, but in all cases the coordination through oxygen and sulfur atoms are disfavored - with an energy higher by more than 10 kcal/mol when compared to their isomers. The only observed exception was for HPCPS systems, where the least favored structure is the one with the coordination of the metal fragment through the double bond.

Table 1. Calculated relative energies and geometric parameters of PCP(E)$\rightarrow$W(CO)$_5$ structures.

	R	**E rel (kcal/mol)**	**M-lig***	**λ^3P -C (Å)**	**λ^5P -C(Å)**	**E= λ^5P(Å)**
PCPO	H			1.699	1.845	1.498
PCPO_W-P	H	0	2.451	1.697	1.843	1.496
PCPO_W-O	H	10.35	2.269	1.702	1.832	1.515
PCPO_W-leg	H	1.06	2.338	1.813	1.847	1.501
PCPO	Me			1.703	1.834	1.500
PCPO_W-P	Me	0	2.463	1.705	1.827	1.501
PCPO_W-O	Me	14	2.292	1.704	1.818	1.519
PCPO_W-leg	Me	7.15	2.323	1.809	1.844	1.502
PCPO	Ph			1.691	1.826	1.483
PCPO_W-P	Ph	0	2.471	1.712	1.820	1.500
PCPO_W-O	Ph	12.25	2.285	1.710	1.817	1.516
PCPO_W-leg	Ph	5.41	2.35	1.815	1.852	1.501
PCPS	H			1.699	1.861	1.946
PCPS_W-P	H	0	2.458	1.709	1.827	1.946
PCPS_W-S	H	6.14	2.623	1.701	1.844	2.000
PCPS_W-leg	H	10.85	2.372	1.794	1.869	1.943
PCPS	Me			1.704	1.844	1.950
PCPS_W-P	Me	0	2.465	1.704	1.838	1.952
PCPS_W-S	Me	14.34	2.617	1.707	1.848	2.003
PCPS_W-leg	Me	9.89	2.393	1.796	1.882	1.950
PCPS	Ph			1.705	1.850	1.946
PCPS_W-P	Ph	0	2.485	1.709	1.842	1.947
PCPS_W-S	Ph	6.36	2.616	1.712	1.834	2.003
PCPS_W-leg	Ph	4.91	2.393	1.802	1.882	1.948

* for systems in which the coordination occurs through the double bond, this value corresponds to the distance between the transition metal and an imaginary point situated at the middle of P-C distance.

Platinum complexes

For the platinum complexes, the metallic fragment considered for the study is $PtCOCl_2$, starting from the optimized geometry of the ligand and a surrounding close to the ideal plan-squared geometry of the metallic atom. The calculated geometrical parameters are presented in Table 2, along with the relative energies, compared to the coordination isomer with the lowest energy of the series.

The metal-phosphapropenic system bond lengths calculated at the BP86/6-311G*(d,p)//LANLTZ level of theory range from 2.100 to 2.342 Å for PCPO derivatives and 2.330 Å and 2.412 Å for the PCPS systems. The P=C double bond length in the coordinative systems increases in general, disregarding the type of coordination. It is worth noticing that the single P-C bond (ranging from 1.811 Å to 1.905 Å, in good agreement with experimental data) is influenced by the type of coordination; in the cases in which the coordination occurs through the group 16 element, the λ^5P –C distance is shortened by around 0.2 Å.

Table 2. Calculated relative energies and geometrical parameters of PCP(E) systems coordinated to $PtCOCl_2$.

	R	E rel (kcal/mol)	M-lig*	λ^3P -C (Å)	λ^5P –C (Å)	E= λ^5P (Å)
PCPO	H			1.699	1.845	1.498
PCPO_Pt-P	H	0.39	2.331	1.689	1.851	1.498
PCPO_Pt-O	H	0.00	2.100	1.700	1.828	1.528
PCPO_Pt-leg	H	10.94	2.188	1.791	1.885	1.497
PCPO	Me			1.703	1.834	1.500
PCPO_Pt-P	Me	0.00	2.333	1.687	1.847	1.496
PCPO_Pt-O	Me	3.42	2.104	1.704	1.813	1.532
PCPO_Pt-leg	Me	11.98	2.173	1.807	1.872	1.498
PCPO	Ph			1.691	1.826	1.483
PCPO_Pt-P	Ph	0.00	2.342	1.694	1.835	1.497
PCPO_Pt-O	Ph	3.92	2.103	1.711	1.811	1.528
PCPO_Pt-leg	Ph	14.91	2.216	1.800	1.899	1.493
PCPS	H			1.699	1.861	1.946
PCPS_Pt-P	H	1.68	2.333	1.689	1.866	1.945
PCPS_Pt-S	H	0.00	2.334	1.690	1.866	1.946
PCPS_Pt-leg	H	13.45	2.233	1.784	1.905	1.945
PCPS	Me			1.704	1.844	1.950
PCPS_Pt-P	Me	0.00	2.332	1.688	1.851	1.946
PCPS_Pt-S	Me	0.33	2.412	1.704	1.827	2.028
PCPS_Pt-leg	Me	15.70	2.186	1.805	1.881	1.946
PCPS	Ph			1.705	1.850	1.946
PCPS_Pt-P	Ph	0.00	2.342	1.697	1.866	1.939
PCPS_Pt-S	Ph	1.26	2.392	1.710	1.853	2.036
PCPS_Pt-leg	Ph	13.37	2.222	1.829	1.898	1.940

Figure 4 represents the BP86 optimized geometries of platinum complexes and HP=C(Cl)-P(=S)MeCl through the phosphorus or sulfur atoms. In the second case it can be noted that the optimization converges to a geometry in which the phosphapropenic system tends to behave as a bidentate ligand, the λ^3P-Pt distance being 2.68 Å.

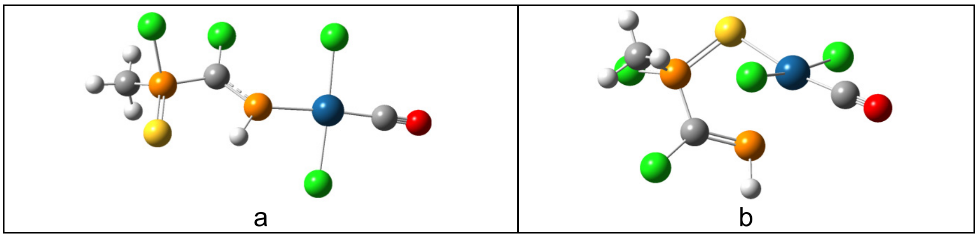


Figure 4. Optimized geometries of P=C(Cl)-P(=S)MeCl→PtCl$_2$CO

For the systems with H as substituent on the phosphorus atom, the lowest calculated energies are for the isomers with the diphosphapropenic unit coordinated through the E atom (E=O, S), with no significant energy differences between them and type II isomers. The structures in which the coordination of the metallic fragment occurs through the P=C double bond are the least favored in this case, with relative energies higher by more than 10 Kcal/mol.

The same behavior was noted for alkyl and aryl substituted derivatives, so that based on our theoretical result one can expect these systems to coordinate through either P(III) or E atoms. However, if the reaction takes place under the proper conditions (e.g., an appropriate stoichiometric ratio or irradiation) P=C-P(=E) diphosphapropenic derivatives can behave as bidentate ligands towards platinum.

Paladium complexes

Similar to the above mentioned complexes, geometric parameters and relative energies of some palladium complexes were calculated, using model molecules in which the diphosphapropenic systems coordinate to a PdCl$_2$(CO) organometallic fragment. The computed P=C bond lengths range from 1.699 and 1.891 Å, denoting a lowering of the double bond character. The P-C single bond lengths range between 1.814 and 1.8876 Å. Figure 5 presents the optimized geometries of MeP=C(Cl)-P(=S)MeCl→PdCl$_2$(CO) complexes for the first two types of investigated coordination modes.

All three investigated coordination modes lead to palladium complexes with similar energies; thus, the BP86 method cannot estimate a certain preference for coordination to the transition metal. The only exception was noted for HPCPO and PhPCPO, where the coordination through the double bond is clearly energetically disfavored (by 11.29 kcal/mol and 10.90 kcal/mol).

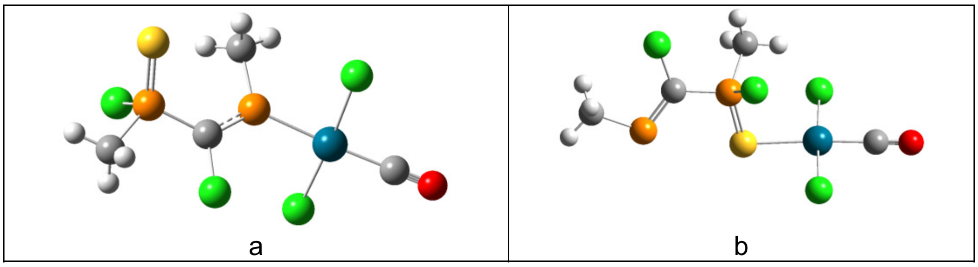


Figure 5. Optimized geometries of MeP=C(Cl)-P(=S)MeCl→$PdCl_2CO$

Bond orders

The Wiberg bond orders for the M-E bond corresponding to the first and second coordination modes considered were evaluated through NBO analysis. The calculated values are presented in Table 4.

The highest bond order was noted for tungsten derivatives for all considered substituents on the λ^3P atom. As reflected by the relative energies, the coordination to the tungsten atom will more preferably take place through the double bonded phosphorus atom for P=C-P=O systems. The W-E bond order is of about 0.3 for E=O and much higher for E=S, indicating higher preference to coordination of the sulfur atom to the metal, accordingly to the HSAB theory.

For platinum and palladium, the lower differences between Pt-P and Pt-E bond orders suggest the possibility of coordination through both atoms, especially for the sulfur derivatives. These findings confirm reported experimental data [10] as well as the analysis of the electronic energies presented above, according to which diphosphapropenic derivatives can act as bidentate ligands in presence of transition metals.

Table 3. Calculated relative energies and geometrical parameters for PCP(E) systems coordinated to $PdCOCl_2$

	R	E rel (kcal/mol)	M-lig*	λ^3P -C (Å)	λ^5P –C (Å)	E= λ^5P (Å)
PCPO	H			1.699	1.845	1.498
PCPO_Pd-P	H	0.36	2.324	1.689	1.850	1.498
PCPO_Pd-O	H	0	2.097	1.700	1.830	1.525
PCPO_Pd-leg	H	11.29	2.254	1.769	1.885	1.498
PCPO	Me			1.703	1.834	1.500
PCPO_Pd-P	Me	0	2.317	1.686	1.842	1.498
PCPO_Pd-O	Me	4.33	2.107	1.704	1.815	1.528
PCPO_Pd-leg	Me	2.89	2.173	1.885	1.856	1.496
PCPO	Ph			1.691	1.826	1.483
PCPO_Pd-P	Ph	0	2.328	1.693	1.846	1.500

	R	E rel (kcal/mol)	M-lig*	λ^3P -C (Å)	λ^5P –C (Å)	E= λ^5P (Å)
PCPO_Pd-O	Ph	3.39	2.108	1.710	1.814	1.526
PCPO_Pd-leg	Ph	10.90	2.485	1.786	1.873	1.495
PCPS	H			1.699	1.861	1.946
PCPS_Pd-P	H	2.18	2.327	1.689	1.862	1.947
PCPS_Pd-S	H	0.00	2.414	1.701	1.827	2.027
PCPS_Pd-leg	H	4.48	2.971	1.691	1.866	1.938
PCPS	Me			1.704	1.844	1.950
PCPS_Pd-P	Me	0.94	2.327	1.691	1.853	1.946
PCPS_Pd-S	Me	0.00	2.424	1.702	1.831	2.009
PCPS_Pd-leg	Me	1.64	2.629	1.888	1.873	1.950
PCPS	Ph			1.705	1.850	1.946
PCPS_Pd-P	Ph	0	2.327	1.693	1.851	1.948
PCPS_Pd-S	Ph	1.36	2.406	1.710	1.840	2.024
PCPS_Pd-leg	Ph	0.8	2.497	1.891	1.876	1.939

Table 4. Wiberg bond orders for M-E (E= O, S) bond.

		PCPO		**PCPS**	
M	**R**	**M-P**	**M-O**	**M-P**	**M-S**
W	H	0.93	0.39	0.94	0.63
W	Me	0.92	0.38	0.91	0.64
W	Ph	0.91	0.39	0.88	0.66
Pt	H	0.72	0.34	0.72	0.65
Pt	Me	0.70	0.35	0.71	0.62
Pt	Ph	0.70	0.35	0.70	0.64
Pd	H	0.64	0.31	0.63	0.5
Pd	Me	0.63	0.31	0.63	0.53
Pd	Ph	0.63	0.31	0.63	0.56

CONCLUSIONS

Calculations performed at the BP86/6-311G*(d,p) level of theory allowed the energetic and geometric analysis of possible coordination modes of diphosphapropenic systems to transition metals. Several RP(Cl)=C-P(=E)MeCl (R=H, Me or Ph and E=O, S) were investigated and their coordination to organometallic fragments of $W(CO)_5$, $PtCOCl_2$ and $PdCOCl_2$ type were evaluated.

Theoretical calculations reveal a general preference for coordination of diphosphapropenic systems to tungsten through the double bonded phosphorus atom.

The coordination to platinum occurs through either the double bonded phosphorus atom or the E atom (E=S, O) of the diphosphapropenic system, without any apparent energetic preference. The least favorable coordination is through the double bond.

For the palladium complexes, no preference for either coordination mode was evidenced, when varying the diphosphapropenic system or the substituents on the phosphorus atom. An exception was observed for systems with R=H, Ph and E=O, for which the coordination is through the P=C moiety.

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