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A THEORETICAL STUDY FOR QUANTUM CHEMICAL CALCULATIONS OF TUNGSTEN TETRACARBONYL COMPLEXES WITH TETRYLONE LIGANDS $E(PH_3)_2$ (E = C − Pb): A QUEST FOR UNDERSTANDING

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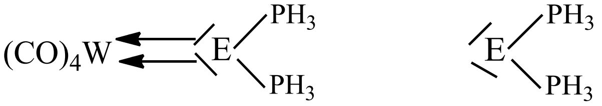
Abstract

Quantum chemical calculations at the BP86 level with various basis sets (SVP, TZVPP) have been carried out for transition metal complexes of carbodiphosphorane analogues (called tetrylones) $E(PH_3)_2$ with E = C, Si, Ge, Sn, Pb. The nature of the $[W(CO)_4\text{-}E(PH_3)_2]$ (**W4-EP$_2$**) bonds was analyzed with charge method. The equilibrium structures of the tetrylone complexes $W(CO)_4\text{-}E(PH_3)_2$ exhibit an interesting trend which possess for E = C, Si a trigonal bipyramidal coordination at tungsten where the tetrylone ligand occupies an equatorial position. The heavier homologues with E = Ge, Sn, Pb exhibit a square pyramidal coordination at tungsten where the tetrylone ligand is at a basal position while one phenyl group is found *trans* to the apical CO group which yields a hexacoordinated tungsten complex. The calculated equilibrium structures of the complexes $[(CO)_4W\text{-}\{E(PH_3)_2\}]$ show that only the carbone ligand $C(PH_3)_2$ is bonded head-on to the metal fragment in the adduct **W4-CP$_2$** which the bending angle, α, is 180.0° and the heavier homologues **W4-SiP$_2$** to **W4-PbP$_2$** have side-on bonded ligands $E(PH_3)_2$ which the bending angle, α become more acute. The theoretically predicted bond dissociation energies (BDEs) of **W4-EP$_2$** system slightly increase from **W4-GeP$_2$** (D_e = 46.1 kcal/mol) to **W4-PbP$_2$** (D_e = 48.5 kcal/mol). The strange trend has been observed for the slighter homologues with E = C, Si which exhibits the largest value BDE 54.1 kcal/mol for **W4-CP$_2$** and 50.1 kcal/mol for **W4-SiP$_2$**. Analysis of the bonding situation shows that the W-E bonds have a significant contribution from $(CO)_4W \leftarrow E(PH_3)_2$ π-donation. This is because the energy levels of the π-type donor orbitals of **W4-CP$_2$ – W4-SnP$_2$** are higher lying than the σ-type donor orbitals except for **W4-PbP$_2$** where the σ donor HOMO is higher in energy than the π-type donor HOMO-2. All complexes $[W(CO)_4\text{-}E(PH_3)_2]$ are suitable targets for synthesis which would open up completely new perspectives for experimental researchers.

Keywords. Tetrylone; natural bond orbital (NBO); bond dissociation energy; bonding analysis; donor-acceptor interactions; Wiberg bond indies (WBI).

1. INTRODUCTION

The recent revival of carbodiphosphorane (CDP) chemistry [1, 2] and the interpretation of $C(PR_3)_2$ as divalent carbon(0) compounds (carbones), in which the carbon atom retains two lone electron pairs, and is bonded to two σ-donor ligands L→C←L [2, 3] opened the door to a new field of chemistry. The first example for which this bonding mode was proposed is the carbodiphosphorane $C(PPh_3)_2$, which was synthesized in 1961 [4], and structurally characterized by X-ray analysis in 1978 [5]. From this, the name "carbones" was coined for compounds CL_2, which are composed of two donor-acceptor bonds L→C through a bare carbon atom in the ^1D excited singlet state. Recent theoretical studies suggested that the bonding situation in carbodiphosphoranes $C(PR_3)_2$ is not limited to carbon as a central atom, but that it can be extended to heavier group-14 homologues, $E(PPh_3)_2$ [6], and other tetrylones EL_2 species with E = Si, Ge, Sn, and Pb [7]. It was suggested that the isolated trisilaallene and trigermaallene compounds [8], which contain a strongly bent [E]=E=[E] moiety where [E] is a five-membered cyclic silylene or germylene, are better described as divalent E(0) complexes [E]→E←[E]. Very little is known about tetrylones EL_2 as free molecules or as ligands in complexes where EL_2 may serve as two- or four-electron donors. The structures and bonding situation in $[(CO)_5W\text{-}\{E(PPh_3)_2\}]$ was recently investigated by Nguyen and Frenking [9]. The finding suggested that the ligands $E(PPh_3)_2$ possess two lone-pairs orbitals at atom E which makes them potential four-electron donors motivated us to investigate the structures and bonding situation of [$W(CO)_4$-$E(PH_3)_2$] with E = C–Pb (Scheme 1) which possess less bulky phosphane than $E(PPh_3)_2$ [9]. Complexes of $W(CO)_4$ with carbodiphosphorane analogues $E(PH_3)_2$ may provide, for the first time, an extension of the bonding concept in carbodiphosphorane $C(PH_3)_2$ (**1C**). Furthermore, it has been known that the complex prepared from $W(CO)_4$ has an important role in catalytically enhanced dehydrogenation [10]. It has been pointed that transition metal complexes of carbodiphosphorane analogues were calculated in many literatures [1-5]. We also found a well displacement of one PPh_3 by L^3 (L^3 = 1,3-bis(diphenylphosphino)propane on $[Au(PPh_3)_2]$+ was studied with transition path sampling calculations with Car-Parrinello molecular dynamics simulations as described in the recent past [11]. To inherit the useful results from the studies (1-7, 11), our investigation on [$W(CO)_4$-$E(PH_3)_2$] complexes mainly focuses on the theoretical calculations for predicting the structure and bonding. We want to emphasize that all complexes are suitable targets for synthesis which would open up completely new perspectives for the future experimental studies. This make us decided to choose [$W(CO)_4$-$E(PH_3)_2$] (**W4-EP$_2$**) complexes to study in order to see whether the interesting bonding situation between $W(CO)_4$ and carbodiphosphorane-analogues, which is revealed by the bonding analysis has any unusual bonding mode to their chemical behavior. This paper provides detailed information on the structures and bonding situation of complexes. To the best of our knowledge, the present work is the first detailed study of the structures and bonding situation of the complexes **W4-EP$_2$** and would set the stage for experimental researchers. We optimized the geometries and energies of the parent compounds and the fragments $E(PH_3)_2$ (**EP$_2$**), and $W(CO)_4$. We also investigated the bonding situation in **W4-EP$_2$** – **W4-PbP$_2$** with natural bond orbital analysis.



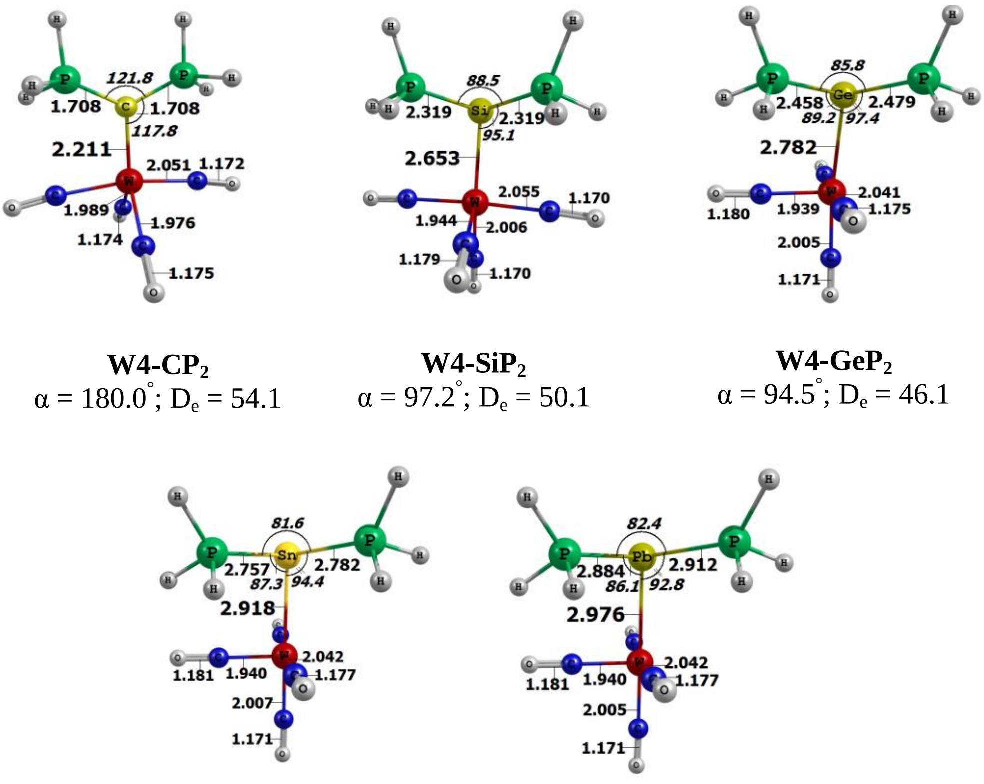
Scheme 1: Compounds investigated in this study: **W4-EP$_2$** and fragments **EP$_2$** (E = C – Pb)

2. COMPUTATIONAL METHODS

Geometry optimizations of the molecules in this thesis have been carried out without symmetry constraints using the Gaussian03 [12] optimizer together with Turbo mole 6.0.1 [13] energies and gradients at the BP86 [14] /def2-SVP [15] level of theory (denoted BP86/SVP). For the heavier group-13 atoms In, Tl, and for W, small-core quasi-relativistic effective core potentials (ECPs) were used [16]. The RI approximation was used for all structure optimizations by using the appropriate auxiliary basis sets. The convergence criterion for the SCF energy was set to 10^{-8} a.u and the modified integration grid "m4" was used. For the structure optimizations the standard criteria of Gaussian were used. The stationary points on the potential energy surface (PES) obtained on this level of theory which is denoted as BP86/def2-SVP was characterized by inspection of the analytically calculated Hessian. All structures presented in this chapter turned out to be minima on the potential energy surface (PES). Single point calculations with the same functional but the larger def2-TZVPP [17] basis set and the small core ECPs for In, Tl and W atoms were carried out with Gaussian03 [12] on the structures derived on BP86/SVP level of theory. The level of theory BP86/def2-TZVPP//BP86/def2-SVP used for the calculation of the bond dissociation energies, Wiberg bond orders and natural charges, and further used for plotting molecular orbitals and orbital energies which was analyzed by the natural bond orbital (NBO) [18] method available in Gaussian 03.

3. RESULTS AND DISCUSSION

Structures and energies: Figs. 1 and 2 show the optimized geometries and bond dissociation energies D_e of the parent compounds **W4-CP$_2$** – **W4-PbP$_2$** and the geometries of the free ligands **CP$_2$** – **PbP$_2$** at the BP86/SVP level together with the most important bond lengths and angles. There is an interesting shape in the structures of the complexes **W4-EP$_2$** when E becomes heavier. The two lightest species **W4-CP$_2$** and **W4-SiP$_2$** have a trigonal bipyramidal coordination mode where the ligands **CP$_2$** and **SiP$_2$** occupy an equatorial position. In contrast, the heavier species **W4-GeP$_2$**, **W4-SnP$_2$**, and **W4-PbP$_2$** possess a square pyramidal structure where the ligands **GeP$_2$**, **SnP$_2$**, and **PbP$_2$** occupy a basal position. However, the apparently vacant position that is *trans* to the apical CO group appears to be occupied by one less bulky PH_3 group of the ligand. Thus, complexes **W4-GeP$_2$ – W4-PbP$_2$** may also be considered as hexacoordinated complexes where one phenyl substituent is bonded to tungsten. This leads to an asymmetry in the ligand geometries of the latter complexes where one PH_3 group is tilted toward the metal which has a shorter E-P bond and a more acute W-E-P angle than the other PH_3.



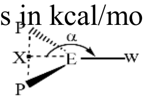
W4-CP$_2$
α = 180.0°; D_e = 54.1

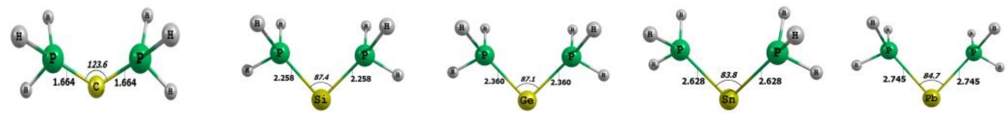
W4-SiP$_2$
α = 97.2°; D_e = 50.1

W4-GeP$_2$
α = 94.5°; D_e = 46.1

W4-SnP$_2$
α = 91.1°; D_e = 47.6

W4-PbP$_2$
α = 89.3°; D_e = 48.5

Figure 1: Optimized geometries of the complexes **W4-EP$_2$** at the BP86/def2-SVP level. Bond lengths are given in Å; angles in degrees. Calculated metal-ligand bond dissociation energies, D_e at the BP86/def2-TZVPP//BP86/def2-SVP level for the $(CO)_4$W-**EP$_2$** bonds in kcal/mol. The bending angle, α, is the angle W-E-X where X is the midpoint between the P-P distance: 



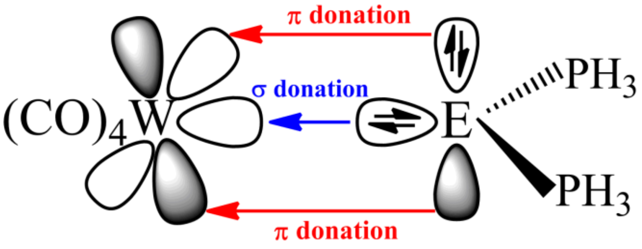
CP$_2$ **SiP$_2$** **GeP$_2$** **SnP$_2$** **PbP$_2$**

Figure 2: Optimized geometries of the fragment **EP$_2$** at the BP86/def2-SVP level.
Bond lengths are given in Å; angles in degrees

Fig. 2 shows also the optimized geometries of the free ligands $E(PH_3)_2$. It becomes obvious that the E-P bonds of the ligands become longer in the complexes **W4-EP$_2$** (Fig. 1) compared with the E-P bonds in the free ligands (Fig. 2). The W-E distances of **W4-EP$_2$** supports the suggestion that the heavier systems are pseudo haxacoordinated complexes. The W-E bonds of **W4-CP$_2$** (2.211 Å) and **W4-SiP$_2$**

(2.653 Å) are shorter than in the heavier complexes which **W4-GeP$_2$** exhibits 2.782 Å for the W-Ge bond length and increase from **W4-GeP$_2$** to **W4-PbP$_2$** (2.976 Å). Note that the W-E bonds of **W4-SnP$_2$** (2.918 Å) and **W4-PbP$_2$** (2.976 Å) have nearly the same distances. Fig. 1 shows that one CO group is tilted from the trigonal bipyramidal coordination mode toward a square pyramidal structure. The calculated equilibrium structures of the complexes $[(CO)_4W\text{-}\{E(PH_3)_2\}]$ show that only the carbon ligand $C(PH_3)_2$ is bonded head-on to the metal fragment in the adduct **W4-CP$_2$** which the bending angle, α, is 180.0° and the heavier homologues **W4-SiP$_2$** to **W4-PbP$_2$** have side-on bonded ligands $E(PH_3)_2$ which the bending angle, α become more acute. The theoretically predicted bond dissociation energies (BDEs) of **W4-EP$_2$** system slightly increase from **W4-GeP$_2$** (D_e = 46.1 kcal/mol) to **W4-PbP$_2$** (D_e = 48.5 kcal/mol). The strange trend has been observed for the slighter homologues with E = C, Si which exhibits the largest value BDE 54.1 kcal/mol for **W4-CP$_2$** and 50.1 kcal/mol for **W4-SiP$_2$**.

Natural bond orbital analysis: The bonding situation in the complexes **W4-CP$_2$** – **W4-PbP$_2$** was analyzed using NBO method. Table 1 gives the results of the NBO calculations for **W4-CP$_2$** – **W4-PbP$_2$** and for the free ligands **CP$_2$** – **PbP$_2$**. The calculated partial charges show that the $W(CO)_4$ fragment in the complexes carries always a negative charge which increases from **W4-CP$_2$** (-0.43 e) to **W4-PbP$_2$** (-0.82 e) except for the smaller values of **W4-SiP$_2$** (-0.27 e) compared with the carbon complex **W4-CP$_2$**. We realize that the amount of charge donation to the $W(CO)_4$ fragment is nearly the same as the donation to the $W(CO)_5$ moiety in the complexes that carry the same and even more bulky phosphine which was calculated in the recent past [9]. The Wiberg bond order for the W-C bond in **W4-CP$_2$** is slightly smaller (0.67) than that in heavier homologues where the values are almost constant between 0.70 for **W4-GeP$_2$** and 0.79 for **W4-SiP$_2$**. Note that the bond order for the E-P bond becomes significantly smaller in the complexes **W4-CP$_2$** – **W4-PbP$_2$** compared with the free ligands **CP$_2$** – **PbP$_2$**. We continuously comment on the atomic partial charges of the donor atoms E and the acceptor atom W in the complexes **W4-EP$_2$**. The tungsten atom always carries a large negative charge between -0.97 e (E = C) and -1.28 e (E = Si). The carbon donor atom in **W4-CP$_2$** has a negative charge of -1.30 e, while the heavier atoms have a positive charge between 0.12 e (E = Si) and 0.47 e (E = Pb).

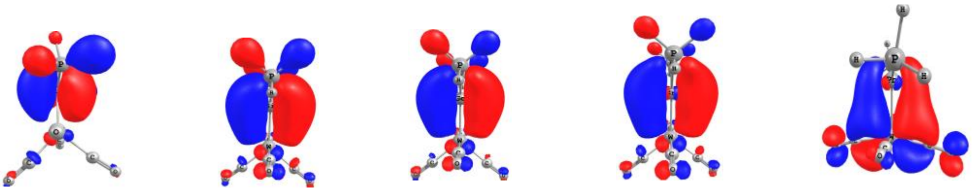


Scheme 2: Possible schematic representation of the bonding situation $(CO)_4W{\leftarrow}$**EP$_2$** donor-acceptor interactions

Table 1: NBO results with Wiberg bond indices (WBI) and natural population analysis (NPA) at the BP86/def2-TZVPP// BP86/def2-SVP level for complexes **W4-CP$_2$** – **W4-PbP$_2$** and fragments. The partial charges, q, are given in electrons [e]

Molecule	Bond	WBI	$q[W(CO)_4]$	Atom	q(NPA)
W4-CP$_2$	W – C	0.67	-0.43	W	-0.97
	$C – P_1$	1.18		C	-1.30
	$C – P_2$	1.18		P	0.82
CP$_2$	$C – P_1$	1.40		C	-1.32
	$C – P_2$	1.40		P	0.78
W4-SiP$_2$	W – Si	0.79	-0.27	W	-1.28
	$Si – P_1$	0.83		Si	0.12
	$Si – P_2$	0.83		P	0.15
SiP$_2$	$Si – P_1$	1.00		Si	-0.23
	$Si – P_2$	1.00		P	0.08

W4-GeP$_2$	W – Ge	0.70	-0.68	W	-1.20
	Ge – P$_1$	0.72		Ge	0.13
	Ge – P$_2$	0.75		P	0.13
GeP$_2$	Ge – P$_1$	0.94		Ge	-0.23
	Ge – P$_2$	0.94		P	0.07
W4-SnP$_2$	W – Sn	0.74	-0.79	W	-1.25
	Sn – P$_1$	0.55		Sn	0.40
	Sn – P$_2$	0.52		P	0.04
SnP$_2$	Sn – P$_1$	0.77		Sn	-0.12
	Sn – P$_2$	0.77		P	0.00
W4-PbP$_2$	W – Pb	0.74	-0.82	W	-1.24
	Pb – P$_1$	0.48		Pb	0.47
	Pb – P$_2$	0.44		P	0.02
PbP$_2$	Pb – P$_1$	0.69		Pb	-0.11
	Pb – P$_2$	0.69		P	-0.01



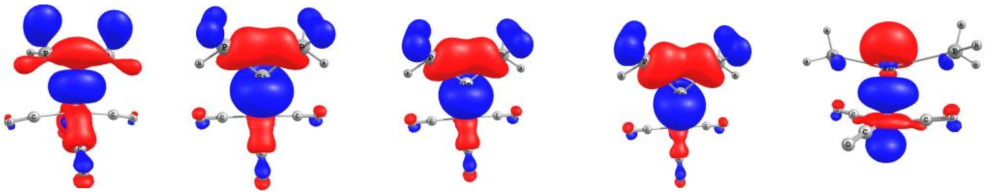
W4-CP$_2$ (π) HOMO-3 (-6.531 eV)

W4-SiP$_2$ (π) HOMO-2 (-5.252 eV)

W4-GeP$_2$ (π) HOMO-1 (-5.143 eV)

W4-SnP$_2$ (π) HOMO (-4.762 eV)

W4-PbP$_2$ (π) HOMO-2 (-5.361 eV)



W4-CP$_2$ (σ) HOMO-4 (-7.973 eV)

W4-SiP$_2$ (σ) HOMO-4 (-7.946 eV)

W4-GeP$_2$ (σ) HOMO-4 (-8.245 eV)

W4-SnP$_2$ (σ) HOMO-4 (-8.245 eV)

W4-PbP$_2$ (σ) HOMO (-4.898 eV)

Figure 3: Molecular orbitals and orbital energies of σ-type and π-type MOs from **W4-CP$_2$** to **W4-PbP$_2$** at the BP86/TZVPP level. Orbital energies are given in eV

4. CONCLUSION

The nature of the [W(CO)$_4$-E(PH$_3$)$_2$] (**W4-EP$_2$**) bonds was analyzed with charge method. The equilibrium structures of the tetrylone complexes W(CO)$_4$-E(PH$_3$)$_2$ exhibit an interesting trend which possess for E = C, Si a trigonal bipyramidal coordination at tungsten where the tetrylone ligand occupies an equatorial position. The heavier homologues with E = Ge, Sn, Pb exhibit a square pyramidal coordination at tungsten where the tetrylone ligand is at a basal position while one phenyl group is found *trans* to the apical CO group which yields a hexacoordinated tungsten complex. The calculated equilibrium structures of the complexes [(CO)$_4$W-{E(PH$_3$)$_2$}] show that only the carbone ligand C(PH$_3$)$_2$ is bonded head-on to the metal fragment in the adduct **W4-CP$_2$** and the heavier homologues **W4-SiP$_2$** to **W4-PbP$_2$** have side-on bonded ligands E(PH$_3$)$_2$. The theoretically predicted bond dissociation energies (BDEs) of **W4-EP$_2$** system slightly increase from **W4-GeP$_2$** (D_e = 46.1 kcal/mol) to **W4-PbP$_2$** (D_e = 48.5 kcal/mol). The strange trend has been observed for the slighter homologues with E = C, Si which exhibits the largest value BDE 54.1 kcal/mol for **W4-CP$_2$** and 50.1 kcal/mol for **W4-SiP$_2$**. Analysis of the bonding situation shows that the W-E bonds have a significant contribution from (CO)$_4$W←E(PH$_3$)$_2$ π-donation. This is because the energy levels of the π-type donor orbitals of **W4-CP$_2$** – **W4-SnP$_2$** are higher lying than the σ-type donor orbitals except for **W4-PbP$_2$** the σ donor is higher in energy than the π-type donor. All complexes W(CO)$_4$-E(PH$_3$)$_2$ are suitable targets for synthesis.

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