



Linear versus bent bonding in metal-phosphinidene complexes: Theoretical studies of the electrophilic phosphinidene complexes $[(\text{Cp})(\text{CO})_2\text{M}\equiv\text{PMe}]^+$, $[(\text{Cp})(\text{CO})_3\text{M}=\text{PMe}]^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)

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ABSTRACT

Density functional theory calculations have been performed for the title phosphinidene complexes using the exchange correlation functionals BP86 and B3LYP. The optimized bond lengths and angles of the model compounds are in excellent agreement with experiment. The M–P bond lengths in linear phosphinidene complexes correspond to a Pauling bond order of ~ 3 . The bent geometries at phosphorus in the bent metal phosphinidene complexes are consistent with the presence of a trivalent phosphorus(III) center which is singly bonded to carbon and doubly bonded to transition metal. The analysis of the delocalized Kohn–Sham orbitals shows the polarization of the M–P σ bonding orbitals towards the phosphorus atom in the $\text{M}\equiv\text{PMe}$ bonds, while in the $\text{M}=\text{PMe}$ bond, the contributions of metal and phosphorus are almost the same. In the linear phosphinidene complexes the contributions of the covalent bonding ΔE_{orb} are more than the electrostatic interaction ΔE_{elstat} . The bent phosphinidene complexes have a lower degree of covalent bonding than the linear phosphinidene complexes. The major differences between the linear and bent phosphinidene complexes are found in the degree of π -bonding. The $\text{M}\equiv\text{PMe}$ bonds show a true M–P π bond and a deviated π bond due to slight bent M–P–C bond angles. The $\text{M}=\text{PMe}$ bonds show a true M–P π bond and a lone-pair on phosphorus.

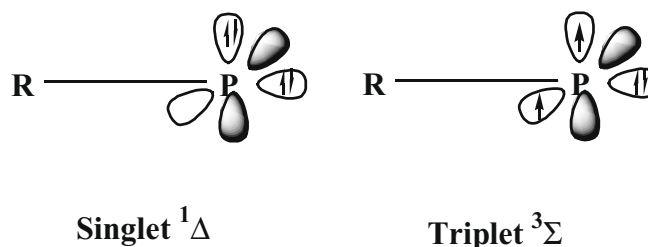
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1. Introduction

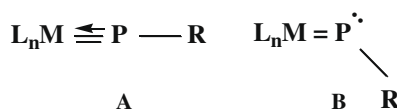
The coordination of the phosphinidene ligand to transition metals is currently the subject of intense research interest in both structural and interpretive inorganic chemistry [1–9]. Like metal carbene complexes, terminal metal phosphinidene complexes can be classified into electrophilic or nucleophilic categories on the basis of the reactivity of its phosphorous atom. The isolation of electrophilic phosphinidene complexes has proven to be more difficult [1]. However, extensive studies of transient electrophilic phosphinidene complexes have been carried out [5,10–17]. Since the investigation of the first examples of the stable terminal phosphinidene complexes by Lappert et al. [18–19], synthesis, structure, reactivity and bonding of several mononuclear phosphinidene complexes have been reported [20–58].

Phosphinidenes have either a singlet ground state with two lone pairs and an empty p-orbital on the phosphorus atom or a triplet state with one lone pair in sp-hybrid orbital and two

singly occupied p-orbitals. Phosphinidenes much prefer a triplet ground state [7a,7b]



There are two possible bonding modes in terminal phosphinidene complexes: the linear complexes of type (A) and bent complexes of type (B)



In valence bond terms, the phosphorus in linear phosphinidenes is sp hybridized. Lone-pair $p(\pi) \rightarrow \text{M}(d)$ donation is effective leading linear structure depicted in **A**. Structure **B** depicts an sp^2

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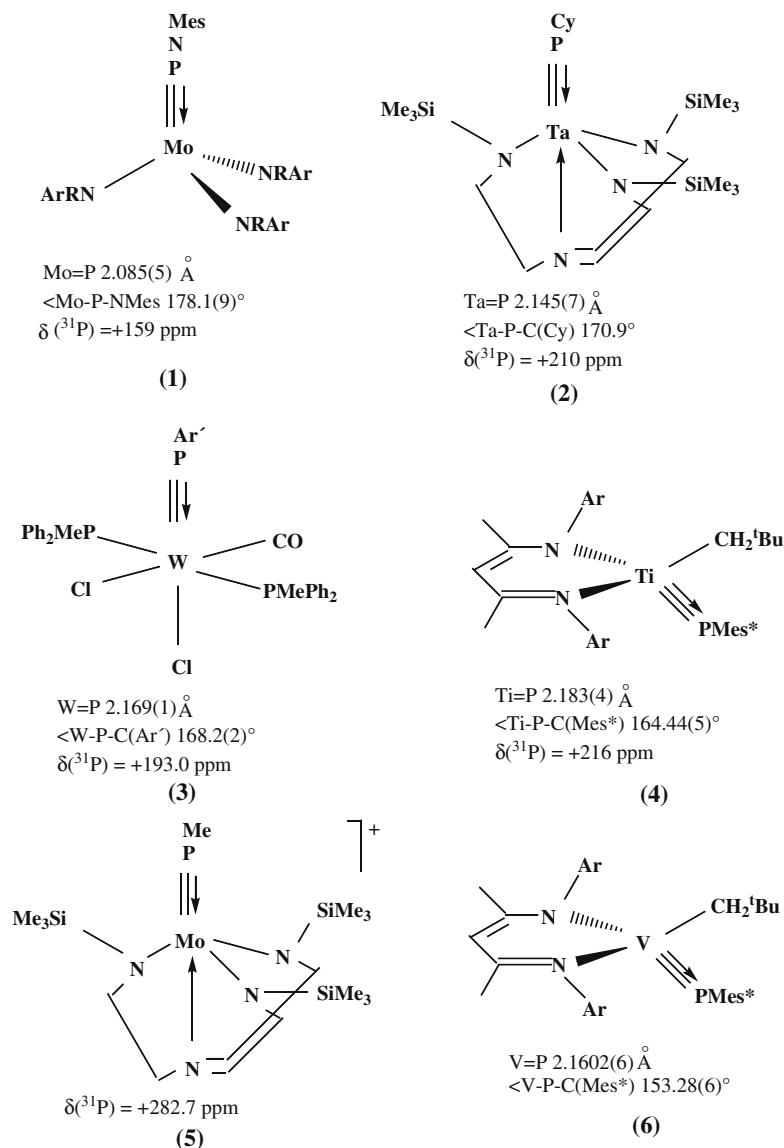


Chart 1. Selected linear metal phosphinidene complexes.

hybridized phosphorus leading to a $\text{M}=\text{P}$ double bond (1σ , 1π) and $\text{M}-\text{P}-\text{R}$ linkage with the lone-pair residing in a sp^2 orbital. The majority of structurally characterized phosphinidene complexes exhibit bent geometries with $\text{M}-\text{P}-\text{R}$ bond angles in the range 100–120°. Unlike imido complexes [59–61], few nearly linear phosphinidene complexes are known. Representative examples of linear and bent metal phosphinidene complexes are presented in Charts 1 and 2. In addition to shorter $\text{M}=\text{P}$ distances in linear phosphinidene complexes, the differences are also reflected in the much more shielded ^{31}P NMR chemical shift of the linear phosphinidene (Chart 1) as compared to the bent phosphinidene that generally show ^{31}P NMR shifts at lower field (Chart 2).

Theoretical studies of terminal bent phosphinidene complexes have been reported so far. Three studies are rather dated: (i) Mathy et al. [40] performed an Extended Hückel study as well as HF calculations on $[(\text{CO})_5\text{Cr}=\text{PH}]$ and $[(\text{CO})_4\text{Fe}=\text{PH}]$, (ii) Ko performed an Extended Hückel study on $[(\text{CO})_5\text{Cr}=\text{PH}]$ and $[(\text{CO})_3\text{Ni}=\text{PH}]$ [42], and (iii) Cowley et al. [43] investigated the bonding in $[(\text{CO})_5\text{Cr}=\text{PH}]$ using the RHF method. Nguyen and coworkers investigated the geometry and bonding in $[(\text{CO})_5\text{Cr}=\text{PR}]$ ($\text{R} = \text{H}, \text{CH}_3, \text{SiH}_3, \text{NH}_2, \text{PH}_2, \text{OH}, \text{SH}$) at CASSCF/CASPT2(12/12) as well as at DFT/B3LYP levels of theories [44–45].

Multiple $\text{M}=\text{P}$ bonding in $[(\text{CO})_5\text{M}=\text{PR}]$ has been studied with ADFs energy decomposition analysis (EDA) from which σ , π -separation is obtained using C_s symmetry [46,62]. The values of binding energy increase strongly on substituting π -electron donating groups on the phosphorus atom [46]. Ehlers, Baerends and Lamertsmas investigated the factors governing the philicity of the terminal bent phosphinidene complexes $\text{LnM}=\text{PH}$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W}, \text{Fe}, \text{Ru}, \text{Os}, \text{Co}, \text{Rh}, \text{Ir}$; $\text{L} = \text{CO}, \text{PH}_3, \text{Cp}$). The philicity is influenced by the type of spectator ligand L rather than for the nature of the transition metal M [62]. DFT calculations on model compounds $(\text{E}/\text{Z})-[(\text{Cp})(\text{L})\text{M}=\text{PH}]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$; $\text{L} = \text{CO}, \text{PH}_3$) [63] and on four coordinate vanadium(IV) phosphinidene complex $[(\text{Nacnac})\text{V}=\text{Pmes}(\text{CH}_2^t\text{Bu})]$ have been reported [64]. Recently, Mendiola and coworkers have synthesized titanium(IV) phosphinidene complexes $[(^t\text{Bu}\text{nacnac})\text{Ti}(\text{P}(\text{Trip}))(\text{R})]$ ($\text{R} = \text{CH}_2^t\text{Bu}, \text{CH}_3$) ($^t\text{Bu}\text{nacnac} = [\text{Ar}]\text{NC}(^t\text{Bu})\text{CHC}(^t\text{Bu})\text{N}[\text{Ar}]$, $[\text{Ar}] = 2,6-(\text{CHMe}_2)_2\text{C}_6\text{H}_3$, $\text{Trip} = 2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$) [58]. These titanium(IV) phosphinidene complexes possess the shortest $\text{Ti}=\text{P}$ bonds reported, have linear phosphinidene groups, and reveal significantly upfielded ^{31}P NMR chemical shifts. DFT studies of these titanium phosphinidene complexes suggest the terminal metal-phosphinidene linkage to be stabilized via a pseudo $\text{Ti}=\text{P}$ bond [58].

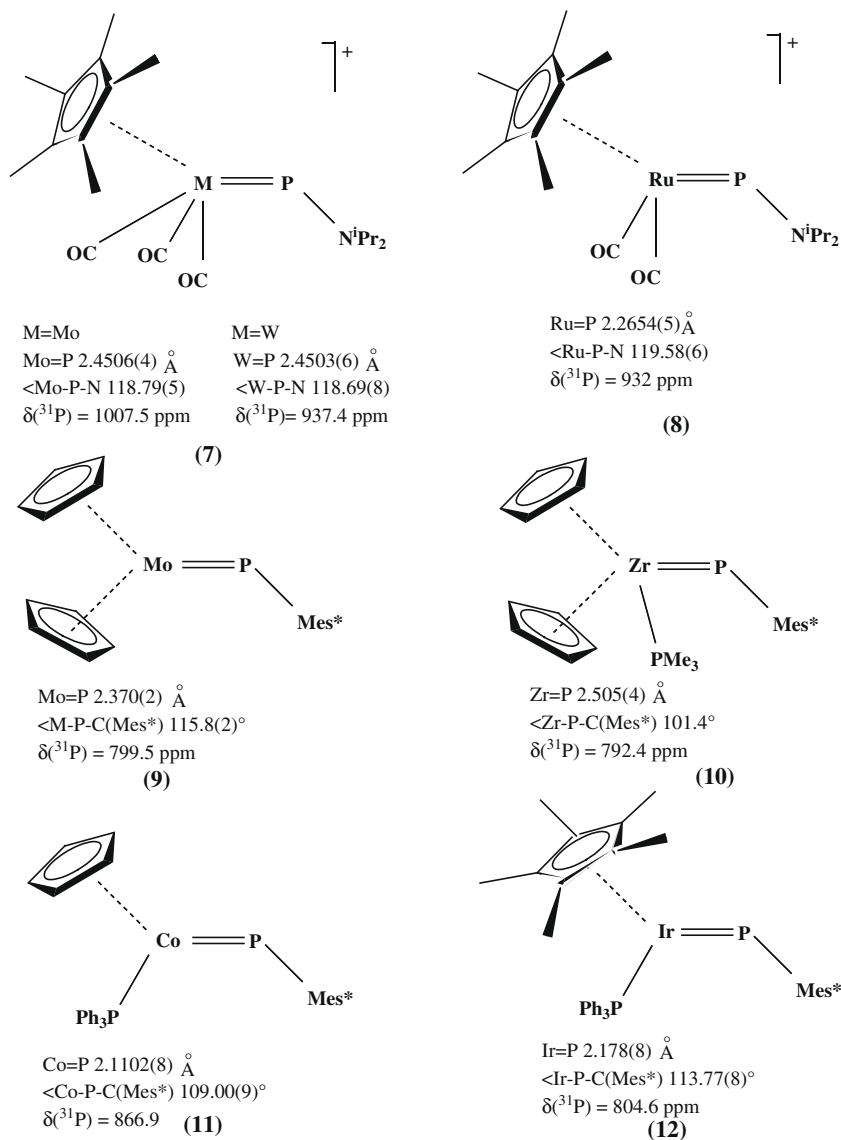


Chart 2. Selected bent metal phosphinidene complexes.

To the best of our knowledge the differences between the bonding situation of the linear $\text{M}\equiv\text{P-R}$ linkage (A) with bent $\text{M}=\text{P-R}$ linkage having lone pair on P (B) have never been studied before. We decided to investigate the bent versus linear chemical bonding in metal phosphinidene complexes with an energy decomposition analysis (EDA). In this paper, six electrophilic phosphinidene complexes $[(\text{Cp})(\text{CO})_2\text{M}\equiv\text{PMe}]^+$ (**Ia**, M = Cr; **Ib**, M = Mo, **Ic**, M = W) and $[(\text{Cp})(\text{CO})_3\text{M}=\text{PMe}]^+$ (**IIa**, M = Cr; **IIb**, M = Mo, **IIc**, M = W) have been investigated at the DFT level using B3LYP and BP86 functionals. The choice of the model compounds was made with the goal of comparing the differences between the bent and linear phosphinidene complexes. Simple electron-counting arguments suggest that the M–P–R bonding situation in **II** should be significantly different from the bonding situation in **I**. Compounds **II** displaying $\text{M}=\text{P}$ double bonds are 18-electron species. To keep the same electron-counting with a metal-phosphorus triple bond compounds **I** have one less CO ligand than complexes **II**. This simple picture of the M–(PR) bond will be deepened with the help of DFT calculations, allowing a comparative analysis of the geometries of the complexes and a quantitative analysis of the M–(PR) interaction. We report a comparative theoretical investigation of terminal bent

and terminal linear phosphinidene complexes. The main goal of the present study is to provide a quantitative differentiation between the linear $\text{M}\equiv\text{P-R}$ (A) and the bent $\text{M}=\text{P-R}$ (B) bonding modes.

2. Computational Methods

Calculations of all complexes have been performed using the hybrid B3LYP density functional method, which uses Becke's 3-parameter nonlocal exchange functional [65] mixed with the exact (Hartree-Fock) exchange functional and Lee-Yang-Parr's nonlocal correlation functional [66]. The geometries of the complexes $[(\text{Cp})(\text{CO})_2\text{M}\equiv\text{PMe}]^+$ and $[(\text{Cp})(\text{CO})_3\text{M}=\text{PMe}]^+$ (M = Cr, Mo, W) were optimized using C_s symmetry constraints with standard 6-311G(d) basis sets [67] for H, C, O and P atoms. For Cr, Mo and W quasi-relativistic effective core potentials (ECP) determined by Hay-Wadt have been used [68]. The valence basis sets for Cr, Mo and W have triple- ζ quality (10s10p5d1f/3s3p3d1f) which include $(n+1)p$ functions [69] which were augmented by an additional set of f orbitals with an exponent of 1.941 for Cr, 1.043 for Mo and

0.823 for W [70]. This basis set is denoted TZP. Frequency calculations were performed at B3LYP/TZP to determine whether the optimized geometries were minima on the potential energy surface. The electronic structures of the complexes were examined by NBO analysis [71]. The B3LYP/TZP calculations were carried out with the Gaussian98 program [72]. All MO pictures were made by using the MOLDEEN program [73].

Calculations of the model complexes have also been performed at the nonlocal DFT level of theory using the exchange functional of Becke [74] and the correlation functional of Perdew [75] (BP86). Scalar relativistic effects have been considered using the ZORA formalism [76]. Uncontracted Slater-type orbitals (STOs) using triple-basis sets augmented by two sets of polarization functions were employed for the SCF calculations [77]. The $(1s)^2$ core electrons of the carbon and oxygen, $(1s2s2p)^{10}$ core electrons of chromium and phosphorus, $(1s2s2p3s3p3d)^{28}$ core electrons of molybdenum and $(1s2s2p3s3p3d4s4p4d)^{46}$ core electrons of tungsten were treated by the frozen-core approximation [78]. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to present the coulomb and exchange potentials accurately in each SCF cycle [79]. The latter calculations were performed utilizing the program package ADF-2004.01 [80].

The binding interactions in the complexes $[(Cp)(CO)_2M \equiv PMe]^+$, $[(Cp)(CO)_3M \equiv PMe]^+$ ($M = Cr, Mo, W$) between the metal fragments (triplet state) and phosphinidene PMe fragments (triplet state) have been analyzed with C_s symmetry using the energy decomposition scheme of ADF which is based on the methods of Morokuma [81] and Ziegler and Rauk [82]. The bond energy ΔE between fragments can be decomposed as:

$$\Delta E = \Delta E_{int} + \Delta E_{prep} \quad (1)$$

Here, ΔE_{prep} is the energy required to promote the structures of the free fragments from their equilibrium structure in the electronic ground state to the geometry and electronic state which they take up in the molecule:

$$\Delta E_{prep} = E_{total} \text{ (distorted fragments)} - E_{total} \text{ (fragments in the equilibrium structure)} \quad (2)$$

ΔE_{int} in equation 1 is the instantaneous interaction energy between the two fragments in the molecule. It can be decomposed into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{pauli} + \Delta E_{orb} \quad (3)$$

ΔE_{elstat} describes the classical Coulomb interaction between the fragments which is attractive in most cases. The term ΔE_{pauli} , which is called exchange repulsion or Pauli repulsion, takes into account the destabilizing two-orbital three- or four-electron interactions between occupied orbitals of both fragments. ΔE_{pauli} is calculated by enforcing the Kohn-Sham determinant of the molecule, which results from superimposing both fragments, to obey the Pauli principle through antisymmetrization and renormalization. The last term ΔE_{orb} in equation 3 gives the stabilizing orbital interactions between occupied and virtual orbitals of the two fragments. ΔE_{orb} can be further partitioned into contributions by the orbitals that belong to different irreducible representations of the point group of the system. It has been suggested that the covalent and electrostatic character of a bond is given by the ratio $\Delta E_{elstat}/\Delta E_{orb}$ [83–85].

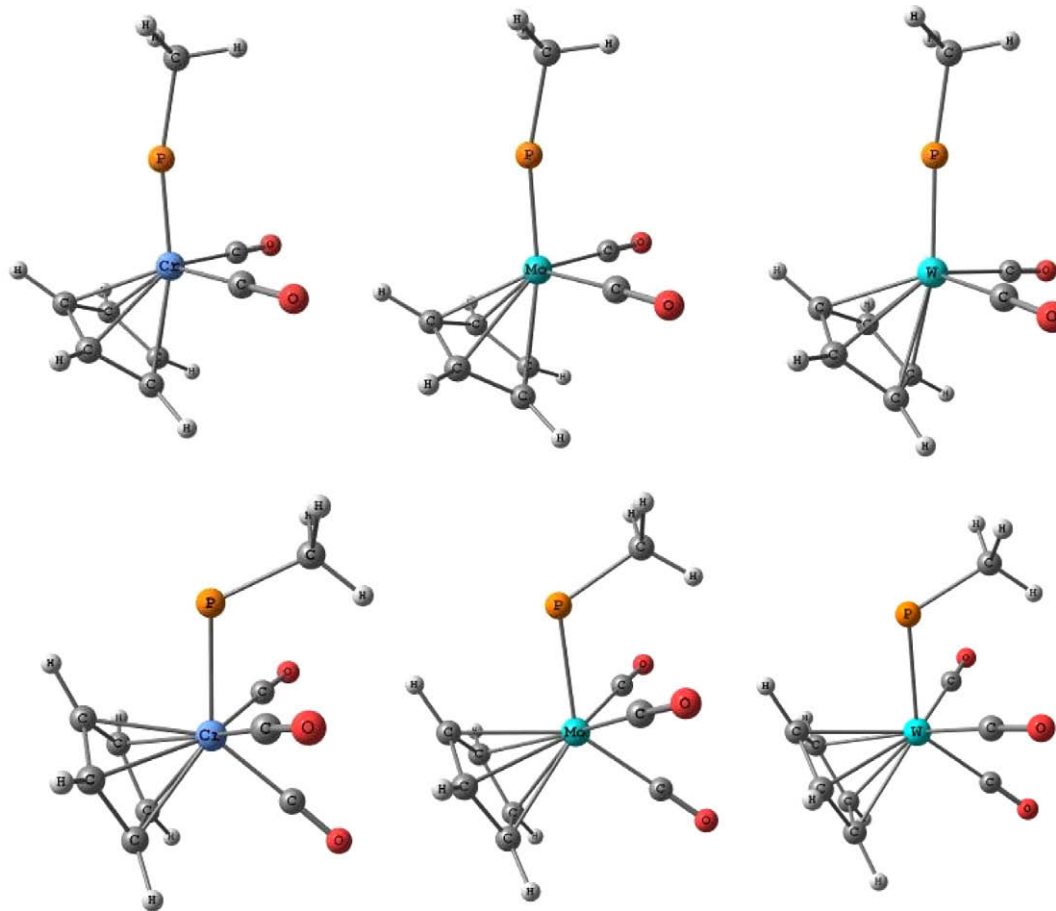


Fig. 1. Optimized geometries of linear (Ia–Ic) and bent (IIa–IIc) phosphinidene complexes. The important bond lengths and angles are given in Table 1.

Table 1
Selected optimized geometrical parameters for linear [(Cp)(CO)₂M≡PMe]⁺ and bent [(Cp)(CO)₃M≡PMe]⁺ (M = Cr, Mo, W) phosphinidene complexes.^a

	[(Cp)(CO) ₂ M≡PMe] ⁺					
	M = Cr (Ia)		M = Mo (Ib)		M = W (Ic)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
<i>Bond lengths</i>						
M–P	2.008	2.022	2.149	2.159	2.150	2.164
P–C	1.818	1.819	1.821	1.823	1.820	1.822
M–CO	1.891	1.867	2.026	2.002	2.013	2.002
C–O	1.136	1.151	1.367	1.151	1.139	1.152
M–C(Cp) ^b	2.225	2.218	2.382	2.366	2.370	2.365
<i>Bond angles</i>						
M–P–C	165.2		164.5		172.1	
P–M–CO	93.7		92.1		93.9	
C(O)–M–C(O)	90.5		90.1		90.6	
	[(Cp)(CO) ₃ M≡PMe] ⁺					
	M = Cr (IIa)		M = Mo (IIb)		M = W (IIc)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
<i>Bond lengths</i>						
M–P	2.276	2.276	2.405	2.390	2.412	2.401
P–C	1.832	1.828	1.834	1.829	1.835	1.830
M–CO ^c	1.886	1.872	2.032	2.013	2.019	2.014
	(1.905)	(1.879)	(2.072)	(2.037)	(2.054)	(2.039)
M–C(Cp) ^b	2.249	2.246	2.402	2.395	2.393	2.394
C–O ^c	1.140	1.155	1.140	1.153	1.142	1.155
	(1.134)	(1.148)	(1.132)	(1.146)	(1.135)	(1.148)
<i>Bond angles</i>						
M–P–C	113.7	115.4	114.3	117.1	114.2	116.4
P–M–CO ^c	75.6	74.6	76.6	75.2	76.7	75.9
	(131.8)	(129.7)	(135.2)	(132.4)	(133.9)	(132.4)
C(O)–M–C(O)	113.6	112.3	105.9	105.2	105.8	105.4

^a Distances are in (Å) and angles are in (°).

^b Average value.

^c The values in parentheses refer to the trans CO ligand.

3. Results and Discussion

3.1. Geometries of Phosphinidene Complexes [(Cp)(CO)₂M≡PMe]⁺ (**Ia**, M = Cr; **Ib**, M = Mo; **Ic**, M = W) and [(Cp)(CO)₃M≡PMe]⁺ (**IIa**, M = Cr; **IIb**, M = Mo; **IIc**, M = W)

The optimized geometries of the linear phosphinidene complexes **Ia–Ic** and bent phosphinidene complexes **IIa–IIc** are shown in Fig. 1. The most important optimized bond lengths and angles at B3LYP and BP86 are presented in Table 1.

There are no structural data for [(Cp)(CO)₂Cr≡PR]⁺ type of phosphinidene complexes. The structural data for the [(^tBu₃acnac)Ti≡P(Trip)(R)] (R = CH₂^tBu, Ti–P = 2.157(2) Å; R = CH₃, Ti–P = 2.1644(7) Å) [58], [(ArRN)₃Mo≡PNMe] [27] (Mo–P = 2.085(5) Å) and [(PMePh₂)Cl₂(CO)W≡PAf] [23] (W–P = 2.169(1) Å) were reported. On going from chromium to tungsten, we found a steady increase of the M–P bond lengths from 2.008 Å (**Ia**), 2.149 Å (**Ib**), 2.150 Å (**Ic**). The optimized distances for Mo–P and W–P bonds are in close agreement with the experimental values. The M–P distances are significantly shorter than those expected for single bond based on covalent radii predictions (Cr–P = 2.34 Å, Mo–P = 2.46 Å, W–P = 2.47 Å) [86]. Using the relationship between bond order and bond length suggested by Pauling [87], we find the calculated M–P distances (Cr–P = 2.00 Å, Mo–P = 2.12 Å, W–P = 2.13 Å). It is interesting to note that the optimized M–P distances correspond to a Pauling bond order of ~ 3. The P–C optimized bond lengths 1.818 Å in **Ia**, 1.821 Å in **Ib** and 1.820 Å in **Ic** are as expected for a single bond based on covalent radii predictions (P–C = 1.83 Å). The M–P–C bond angles in **Ia–Ic** deviate slightly from linearity.

The optimized Cr–P distance (2.276 Å) in **IIa** is similar to the optimized Cr≡P bond length (2.271 Å) in [(CO)₅Cr≡PH] [46]. The

structure of molybdenum and tungsten phosphinidene complexes [(Cp)(CO)₃M≡PMe]⁺ (M = Mo, W) closely resemble those found by X-ray diffraction for [(Cp*)(CO)₃M≡PNⁱPr₂]⁺ (Cp* = C₅Me₅) [12,13]. The M–P distances 2.276 Å (**IIa**), 2.405 Å (**IIb**) and 2.412 Å (**IIc**) are shorter than those expected for single bond based on covalent radii predictions (Cr–P = 2.34 Å, Mo–P = 2.46 Å, W–P = 2.47 Å) [86]. The bent geometries at phosphorus (M–P–C bond angles: 113.7° in **IIa**, 114.3° in **IIb** and 114.2° in **IIc**) in these complexes are consistent with the presence of a trivalent phosphorus(III) center which is singly bonded to carbon and doubly bonded to transition metal. The optimized P–C distances 1.832 Å in **IIa**, 1.834 Å in **IIb** and 1.835 Å in **IIc** are longer than those found in linear phosphinidene complexes **Ia–Ic**.

3.2. Bonding Analysis of M≡PR and M=PR Bonds

We begin the analysis of the bonding situation in the linear **Ia–Ic** and bent **IIa–IIc** phosphinidene complexes with a discussion of bond orders and atomic charges. Table 2 gives the Wiberg bond indices (WBI) [88] and the results of the natural bond orbital (NBO) analysis.

Table 2 shows that the WBI values of the M≡P bonds in the linear phosphinidene complexes **Ia–Ic** are significantly higher (1.84–1.95) than the WBI values of the M=P bonds in the bent phosphinidene complexes **IIa–IIc** (0.89–1.05). The calculated NBO charge distributions indicate that the metal and the methyl group in both linear and bent phosphinidene complexes **Ia–Ic** and **IIa–IIc** carry a negative charge, while the phosphorus atoms are positively charged, in agreement with its electrophilic character. On going from chromium to tungsten in complexes **Ia–Ic** and **IIa–IIc**, the

Table 2

Wiberg bond indices (WBI) and results of the NBO analysis in linear [(Cp)(CO)₂M≡PMe]⁺ and bent [(Cp)(CO)₃M=PMe]⁺ (M = Cr, Mo, W) phosphinidene complexes.

	[(Cp)(CO) ₂ M≡PMe] ⁺			[(Cp)(CO) ₃ M=PMe] ⁺		
	M = Cr (Ia)	M = Mo (Ib)	M = W (Ic)	M = Cr (IIa)	M = Mo (IIb)	M = W (IIc)
WBI						
M–P	1.84	1.85	1.95	0.89	1.03	1.05
P–C	1.02	1.02	1.03	1.01	1.01	1.00
M–C(CO) ^a	0.81	0.88	0.94	0.81 (0.74)	0.88 (0.77)	0.95 (0.83)
C–O ^a	2.22	2.22	2.19	2.18 (2.24)	2.19 (2.25)	2.15 (2.23)
M–C(Cp) ^b	0.25	0.24	0.25	0.25	0.23	0.24
NBO charges						
M	–0.71	–0.39	–0.15	–0.98	–0.51	–0.27
P	0.92	0.82	0.75	0.93	0.81	0.77
Me	–0.12	–0.11	–0.15	–0.20	–0.20	–0.19
Cp	0.31	0.20	0.11	0.32	0.18	0.13
CO ^a	0.30	0.24	0.19	0.28 (0.37)	0.21 (0.30)	0.15 (0.26)
NBO bond analysis						
M–P σ-bond						
Occupation	1.932	1.937	1.949	1.725	1.776	1.796
%M	31.34	30.95	30.80	55.02	50.98	49.32
%s	29.08	35.53	35.62	21.46	18.85	18.68
%p	0.03	0.02	0.03	0.01	0.08	0.18
%d	70.88	64.45	64.30	78.53	81.05	81.31
P						
%s	58.70	60.55	59.34	13.88	13.14	14.77
%p	41.30	39.44	40.65	85.84	86.51	84.87
%d	0.00	0.01	0.01	0.28	0.35	0.36
M–P π-bond						
Occupation	1.886	1.883	1.878	1.678	1.684	1.630
%M	57.95	57.02	54.06	83.28	79.15	77.24
%p	0.01	0.01	0.01	0.00	0.02	0.03
%d	99.99	99.98	99.97	100.00	99.97	99.96
P						
%p	99.83	99.73	99.73	99.33	99.35	99.32
%d	0.17	0.27	0.27	0.67	0.65	0.68
M–P π-bond^c						
Occupation	1.795	1.697	1.840	Lone pair on P		1.934
%M	62.07	57.80	58.76	1.959	1.937	
%s	16.48	22.53	6.40			
%p	0.01	0.11	0.04			
%d	83.51	77.36	93.55			
P						
%s	6.02	1.71	2.63	71.22	71.70	69.82
%p	93.72	97.92	97.00	28.74	28.25	30.13
%d	0.26	0.37	0.37	0.04	0.05	0.05

^a The values in parentheses refer to the trans CO ligand.

^b Average value.

^c Not true π bond. Deviation from π bond due to slightly bent M–P–C(Me) bond angles.

negative charge on metal decreases sharply and the positive charge on the phosphorus also decreases but less.

A more definitive picture of M≡E bonding is obtained through NBO analysis of the delocalized Kohn-Sham orbitals. The characteristics of the M≡PMe and M=PMe bonding orbitals are listed in Table 2. In the M≡PMe bonds, the M–P σ bonding orbitals are always polarized towards the phosphorus atom while in the M=PMe bond, the contributions of metal and phosphorus are almost the same. The occupation for M=PMe σ bonding orbitals are relatively smaller. The M≡PMe bonds show a true M–P π bond and a deviated π bond due to slight bent M–P–C bond angles. The M–P π bonds show a small polarization towards the metal. The M=PMe bonds show a true M–P π bond and a lone-pair on phosphorus.

The lone-pair occupies the orbital having approximately 70% s-character. The M–P π bond in **IIa–IIc** shows a strong polarization towards the metal. The hybridization of the M–P σ bonds at the phosphorus atom has a ca. 40% p-character in **Ia–Ic**, while a large p-character which is always > 80% of the total AO contribution, has been found in **IIa–IIc**.

Besides the charge decomposition analysis using the NBO method we also carried out an energy decomposition analysis of the metal-phosphorus bonds in linear **Ia–Ic** and bent **IIa–IIc** phosphinidene complexes. The results are given in Table 3.

Table 3 shows bond dissociation energy for linear M≡PMe and bent M=PMe bonds. From periodic trends the chromium complexes are expected to have the weakest M≡PMe and M=PMe bonds. However, as is seen in Table 3, even the Cr≡PMe bond (85.1 kcal/mol) and Cr=PMe bond (63.8 kcal/mol) are predicted to be quite strong. The tabulated results for W reveal the expected periodic trend in bond strength due to d-orbital extent: the W≡PMe and W=PMe bonds are slightly stronger than corresponding Mo≡PMe and Mo=PMe bonds. On going from linear phosphinidene to bent phosphinidene complexes, we note a steady decrease in bond dissociation energy. The magnitude of the dissociation energy decreases in the order W > Mo > Cr as coordinating metal.

The calculated data given in Table 3 show that the total interaction energies of the linear phosphinidene complexes **Ia–Ic** are more attractive than those in the bent phosphinidene complexes **IIa–IIc**. The differences are between 23.1 kcal/mol (**IIc–Ic**) and 9.1 kcal/mol (**IIa–Ia**). In the linear phosphinidene complexes **Ia–Ic**, the contributions of the covalent bonding ΔE_{orb} are more than the electrostatic interaction ΔE_{elstat} ; that is, the [M] – PR bonding in **Ia–Ic** has greater degree of covalent bonding (62 – 64%). The bent phosphinidene complexes **IIa–IIc** have a lower degree of covalent bonding (53 – 55%) than the linear phosphinidene complexes **Ia–Ic**. The covalent bonding in linear phosphinidene complexes **Ia–Ic** has a high degree of π character. We want to emphasize that the calculated energy contribution ΔE_{π} in the complexes **Ia–Ic** and **IIa–IIc** gives only the out of plane (π_{\perp}) component of the total [M] – PR π interaction. This is because the complexes **Ia–Ic** and **IIa–IIc** have only C_s symmetry and thus the orbitals can only have a'(σ) and a''(π) symmetry. Thus, the energy contributions of the a'(σ) orbitals in phosphinidene complexes **Ia–Ic** come from [M] – PR σ- and π- interactions. The major differences between the linear and bent phosphinidene complexes are found for the degree of π-bonding. The covalent bonding in the bent phosphinidene complexes **IIa–IIc** has lower degree of π character, because there is no in-plane [M] – PR π bonding in these complexes. It is interesting to note that in molybdenum and tungsten complexes, the a''(π) contributions in bent phosphinidene complexes **IIb–IIc** are weaker than the out-of-plane π contributions in the linear phosphinidene complexes **Ib–Ic**. This can be explained with the longer M–P bond lengths in the bent complexes than in the linear complexes. While the π bonding contributions in **IIa–IIc** are weaker than those in **Ia–Ic**, the σ bonding contributions in the bent complexes are stronger than those in linear complexes. We note that on going from chromium to tungsten, the interaction energy increases in both sets of complexes. Further, the tungsten complexes possess both the highest orbital interactions, ΔE_{orb} and the highest electrostatic interactions, ΔE_{elstat} .

To visualize the differences in M–P bonding between linear and bent phosphinidene complexes, envelope plots of some relevant orbitals of the tungsten complexes [(Cp)(CO)₂W≡PMe]⁺ **Ic** and [(Cp)(CO)₃W=PMe]⁺ **IIc** are given in Fig. 2.

Fig. 2a (HOMO-9) gives a pictorial description of the W–P σ bonding in **Ic**, Fig. 2b (HOMO-2) shows a deviated π orbital due to slight bending of W–P–C bond angle which has a'(σ) symmetry while Fig. 2c (HOMO-3) shows a true W–P π orbital, which has

Table 3
Energy decomposition analysis^a of linear [(Cp)(CO)₂M=PMe]⁺, and bent [(Cp)(CO)₃M=PMe]⁺ metal phosphinidene complexes at BP86/TZ2P.

	[(Cp)(CO) ₂ M=PMe] ⁺			[(Cp)(CO) ₃ M=PMe] ⁺		
	M = Cr (Ia)	M = Mo (Ib)	M = W (Ic)	M = Cr (IIa)	M = Mo (IIb)	M = W (IIc)
ΔE_{int}	-86.5	-99.5	-112.3	-77.4	-84.9	-89.2
ΔE_{Pauli}	141.7	154.0	165.2	196.9	185.1	202.4
ΔE_{elstat}	-81.6	-95.0	-106.4	-124.6	-121.8	-137.3
$\Delta E_{\text{orb}}^{\text{b}}$	-146.6	-158.5	-171.1	-149.7	-148.2	-154.3
	(64.2%)	(62.5%)	(61.7%)	(54.6%)	(54.9%)	(52.9%)
$\Delta E_{\sigma}(\text{a}')$	-98.3	-105.2	-114.4	-94.6	-95.0	-100.8
$\Delta E_{\pi}(\text{a}'')$ ^c	-48.3	-53.3	-56.7	-55.1	-53.2	-53.5
	(32.9%)	(33.6%)	(33.1%)	(36.8%)	(35.9%)	(34.7%)
ΔE_{prep}	1.4	1.9	3.0	13.6	12.3	13.4
$\Delta E(-D_e)$	-85.1	-97.6	-109.3	-63.8	-72.6	-75.8

^a Energy contributions in kcal/mol.

^b The values in parentheses are the percentage contribution to the total attractive interactions reflecting the covalent character of the bond.

^c The values in parentheses are the percentage of π -contribution to the total orbital interaction ΔE_{orb} .

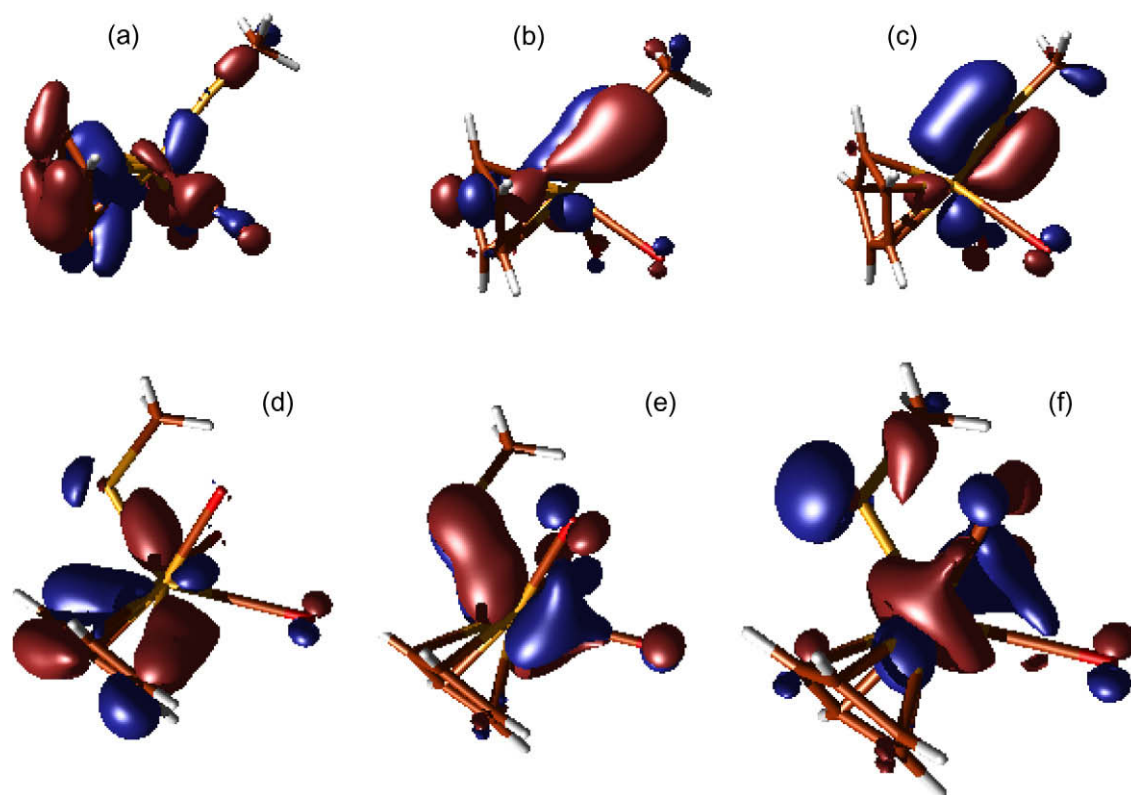


Fig. 2. Plot of some relevant orbital of the tungsten complexes [(Cp)(CO)₂W=PMe]⁺ **Ic** (a–c) and [(Cp)(CO)₃W=PMe]⁺ **IIc** (d–f).

π symmetry in the complex **Ic**. Fig. 2d (HOMO-5) shows W–P σ bonding and Fig. 2e (HOMO-3) represents a true W–P π orbital in **IIc**. Fig. 2f (HOMO) is mainly the lone pair orbital at P in **IIc**. It becomes clear that the linear bonding has a large contribution from π bonding orbitals.

4. Conclusion

We have presented the theoretical study where the bonding situations in linear and bent phosphinidene complexes are compared with each other. The relative bond strengths can be arranged in the following order: Cr < Mo < W. The WBI values of the M=P bonds in the linear phosphinidene complexes are significantly higher than

the WBI values of the M=P bonds in the bent phosphinidene complexes. In the M=P bonds, the M–P σ bonding orbitals are always polarized towards the phosphorus atom while in the M=PMe bonds, the contributions of metal and phosphorus are almost the same. The M=PMe bonds show a true M–P π bond and a deviated π bond due to slight bent M–P–C bond angles. The M–P π bonds show a small polarization towards the metal. The M=PMe bonds show a true M–P π bond and a lone-pair on phosphorus. The lone-pair occupies the orbital having approximately 70% s-character. The M–P π bond in **IIa–IIc** shows a strong polarization towards the metal. In the linear phosphinidene complexes the contributions of the covalent bonding ΔE_{orb} are more than the electrostatic interaction ΔE_{elstat} . The bent phosphinidene complexes have a lower degree of covalent bonding (53–55%) than the

linear phosphinidene complexes (62 – 64%). The major differences between the linear and bent phosphinidene complexes are found in the degree of π -bonding.

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