



Binuclear cyclopentadienylcobalt sulfur and phosphinidene complexes $\text{Cp}_2\text{Co}_2\text{E}_2$ (E = S, PX): Comparison with their Iron carbonyl analogues

Guoliang Li^a, Qian-Shu Li^{a,b,*}, Ioan Silaghi-Dumitrescu^{c,*}, R. Bruce King^{a,d,*}, Henry F. Schaefer III^d

^a Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, China

^b Institute of Chemical Physics, Beijing Institute of Technology, Beijing 100081, China

^c Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania

^d Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA

ARTICLE INFO

Article history:

Received 9 October 2009

Received in revised form 9 December 2009

Accepted 15 December 2009

Available online 23 December 2009

Keywords:

Cyclopentadienylcobalt derivatives

Sulfur

Phosphinidene

Density functional theory

Tetrahedrane structures

Butterfly structures

ABSTRACT

Density functional theory studies on a series of $\text{Cp}_2\text{Co}_2\text{E}_2$ derivatives (E = S and PX; X = H, Cl, OH, OMe, NH_2 , NMe_2) predict global minimum butterfly structures with one Co–Co bond for the “body” of the butterfly and four Co–E bonds at the edges of the “wings” of the butterfly. Tetrahedrane structures with both Co–Co and E–E bonds are higher in energy for $\text{Cp}_2\text{Co}_2\text{S}_2$ and $\text{Cp}_2\text{Co}_2(\text{PH})_2$ and are not found in the other systems. This differs from the corresponding $\text{Fe}_2(\text{CO})_6\text{S}_2$ and $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ derivatives where tetrahedrane structures are predicted to be the lowest energy structures for all cases except X = NR_2 and OH and such a tetrahedrane structure is found experimentally for $\text{Fe}_2(\text{CO})_6\text{S}_2$. The butterfly structures for the $\text{Cp}_2\text{Co}_2\text{E}_2$ derivatives are of two types. For $\text{Cp}_2\text{Co}_2(\text{PX})_2$ (X = H, OH, OMe, NH_2 , NMe_2) the lowest energy structures are unsymmetrical butterflies $\text{Cp}_2\text{Co}_2(\text{P})(\text{PX})_2$ with two X groups on one phosphorus atom and a lone pair on the other (naked) phosphorus atom. Related low-energy unsymmetrical butterfly $\text{Fe}_2(\text{CO})_6(\text{P})(\text{PX})_2$ structures, not observed in previous theoretical studies, are now found for the corresponding $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ derivatives. Symmetrical butterfly singlet diradical structures with one X group on each phosphorus atom in relative *cis* or *trans* positions are also found for the $\text{Cp}_2\text{Co}_2(\text{PX})_2$ derivatives and are the global minima for $\text{Cp}_2\text{Co}_2(\text{PCL})_2$ as well as $\text{Cp}_2\text{Co}_2\text{S}_2$. In all cases the *cis* structures are of lower energy than the corresponding *trans* structures. Rhombus structures having neither Co–Co nor E–E bonds are also found for all of the $\text{Cp}_2\text{Co}_2(\text{PX})_2$ derivatives but always at higher energies than the butterfly structures, ranging from 17 to 29 kcal/mol above the global minima.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The Fe_2S_2 tetrahedrane [1,2] $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ (Fig. 1: [M] = $\text{Fe}(\text{CO})_3$, E = S) is not only a very useful synthon in metal carbonyl chemistry [3] but also a model for the [FeFe]-only hydrogenase from *Clostridium pasteurianum* [4]. In addition the S–S bond in this Fe_2S_2 tetrahedrane undergoes rupture upon photolysis in a Nujol matrix to give an Fe–Fe butterfly diradical, characterized by comparison of its infrared $\nu(\text{CO})$ frequencies with those predicted by density functional theory [5]. Related chemistry is also known in which the sulfur atom in $\text{Fe}_2(\text{CO})_6\text{S}_2$ is replaced by a phosphinidene unit to give $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ derivatives. Thus the Fe_2P_2 tetrahedrane $\text{Fe}_2(\text{CO})_6(\text{P}^t\text{Bu})_2$ has been isolated as a stable molecule and struc-

* Corresponding authors. Address: Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA, and Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, China (R.B. King).

E-mail addresses: qqli@sclu.edu.cn (Q.-S. Li), rbking@chem.uga.edu (R. Bruce King).

¹ Prof. Ioan Silaghi-Dumitrescu passed away in Cluj-Napoca, Romania, on December 25, 2009.

turally characterized by X-ray crystallography [6]. In addition, a rare example of a stable isolable rhombus structure is $\text{Fe}_2(\text{CO})_6(\text{POC}_6\text{H}_2\text{-4-Me-2,6-}^t\text{Bu}_2)_2$ in which both the iron–iron and phosphorus–phosphorus distances are too long for direct bonding [7].

The CpCo unit (Cp = $\eta^5\text{-C}_5\text{H}_5$) is isoelectronic and isolobal with the $\text{Fe}(\text{CO})_3$ unit that is a fundamental building block for the above compounds. However, the Cp ring in a CpCo unit is a weaker π -acceptor than the three carbonyl groups in an $\text{Fe}(\text{CO})_3$ unit. Therefore, the cobalt atom in a CpCo unit is electron richer than the iron atom in an $\text{Fe}(\text{CO})_3$ unit. This greater electron density in a CpCo unit might be expected to lead to significant differences in the relative stabilities of the tetrahedrane, butterfly diradical, and planar rhombus isomers for $\text{Cp}_2\text{Co}_2\text{E}_2$ derivatives (Fig. 1: [M] = CpCo) relative to $\text{Fe}_2(\text{CO})_6\text{E}_2$ derivatives with the same E units (E = S or PX).

The research discussed in this paper explores the possibilities when the $\text{Fe}(\text{CO})_3$ units are replaced by CpCo units in these $[\text{M}]_2\text{E}_2$ systems (Fig. 1). Reported relevant experimental work with the CpCo derivatives is much more limited than with the corresponding $\text{Fe}(\text{CO})_3$ derivatives. The first example of a $\text{Cp}_2\text{Co}_2\text{E}_2$ derivative to be synthesized is the Co–Co-butterfly $\text{Cp}_2\text{Co}_2(\text{SMe})_2$ from the reaction of $\text{CpCo}(\text{CO})_2$ and dimethyldisulfide [8]. This

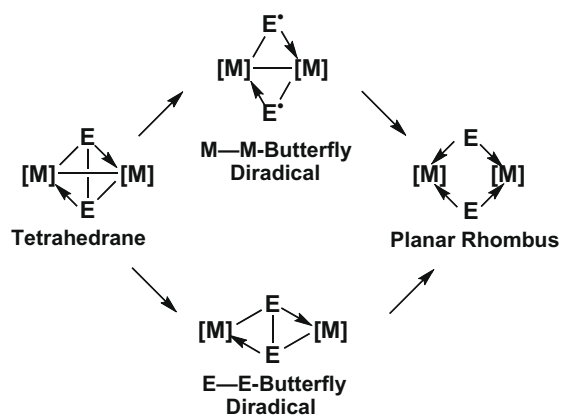


Fig. 1. The four fundamental types of structures for $[M]_2E_2$ complexes ($[M] = Fe(CO)_3$ or $CpCo$; $E = S, PX$; $X = Me, ^tBu, NH_2, NMe_2, N^iPr_2, OH, OMe, Cl$).

complex has apparently not been structurally characterized by X-ray diffraction. However, the related Co–Co-butterflies $Cp_2Co_2(PMe_2)_2$ (Ref. [9]) and $Cp_2Co_2(SCMe_3)_2$ (Ref. [10]) have been characterized structurally.

2. Theoretical methods

Electron correlation effects were considered using density functional theory (DFT) methods. Two DFT methods were used in this study. The first functional, designated B3LYP, is an HF/DFT hybrid method using Becke's three-parameter functional (B3) [11] and the Lee–Yang–Parr generalized gradient correlation functional (LYP) [12]. The BP86 functional is a pure DFT method combining Becke's 1988 exchange functional (B) [13] with Perdew's 1986 gradient correlation functional (P86) [14].

All-electron 6–311G(d) basis sets were used herein. The 6–311G specifies the standard split-valence triple- ζ 6–311G basis set for the C, N and O atoms, the triple- ζ 311G basis set for the H atom, the McLean–Chandler (12s9p/6s5p) basis set for the P, S and Cl atoms [15,16], and the Wachters–Hay all electron basis set [17,18], using the scaling factors of Raghavachari and Trucks [19], for the Co atoms. The 6–311G basis sets were augmented with one set of d-type polarization functions for C, N, O, P, S and Cl and one set of f-type polarization functions for Co. For $Cp_2Co_2S_2$ and $Cp_2Co_2(PNMe_2)_2$ complexes, there are 354 and 498 contracted Gaussian functions, respectively, with the present 6–311G(d) basis set.

The optimized geometries for the $Cp_2Co_2S_2$ and $Cp_2Co_2(PX)_2$ ($X = H, Cl, OH, OMe, NH_2$ or NMe_2) structures and their relative energies were determined by B3LYP and BP86 methods. The phosphorus substituents (X) were chosen to provide examples of both electron withdrawing (e.g., $X = Cl$) and electron-releasing ($X = NH_2$ and NMe_2) substituents.

All of the calculations were initially carried out on the singlet potential energy surfaces (PESs). Both the B3LYP and BP86 methods gave exactly the same energy ordering of the singlet $Cp_2Co_2S_2$ structures (i.e. **Co-but** and **Tet**, *vide infra* for the geometries) and the singlet $Cp_2Co_2(PX)_2$ structures (i.e. **Co-but-u**, **Co-but-c**, **Co-but-t**, **Tet** and **Rhomb**), although the energy values are somewhat different. Based on the optimized singlet geometries, further calculations were performed on the triplet PESs. For the $Cp_2Co_2S_2$ system, both B3LYP and BP86 methods predicted that the optimized triplet structures have higher energies than the corresponding singlet structures, with the **Tet** structure of $Cp_2Co_2S_2$ at B3LYP level being the only exception, in which the triplet state is energetically lower than the corresponding singlet state by 7.6 kcal/mol and converges to an **S-but** structure.

For the $Cp_2Co_2(PX)_2$ ($X = H, Cl, OH, OMe, NH_2$ or NMe_2) derivatives, the situation is somewhat complicated. With the B3LYP method, most of the triplet $Cp_2Co_2(PX)_2$ structures have lower energies than the corresponding singlet structures by about 1–20 kcal/mol except for the triplet **Co-but-u** structure of $Cp_2Co_2(PX)_2$ for $X = H, Cl, OH, OMe, NH_2, NMe_2$ and the triplet **Co-but-c** structure for $X = H, Cl$. However, the BP86 method predicts that most of the optimized triplet $Cp_2Co_2(PX)_2$ states are less stable than the corresponding singlet states, with the **Rhomb** structures of $Cp_2Co_2(PH)_2$ and $Cp_2Co_2(PhCl)_2$ being exceptions. On the other hand, the BP86 method predicts that all of the optimized triplet $Cp_2Co_2(PX)_2$ structures lie energetically higher than the corresponding singlet global minima by at least 12 kcal/mol. Based on our experience on related organometallic systems [20,21], the BP86 functional should be more reliable for the systems involved herein, so only the BP86 results are shown in this paper and the optimized triplet isomers are not considered further.

All of the optimizations were carried out using the GAUSSIAN 03 program [22] in which the fine grid (75, 302) is the default for evaluating integrals numerically and the tight (10^{-8} hartree) designation is the default for the SCF convergence. Symmetry constraints were used for the initial optimizations. Then the normal modes of any imaginary vibrational frequencies were followed with removal of the initial symmetry constraints. The final geometries are depicted in Figs. 2–4, whereas Tables 1 and 2 list their electronic states, relative energies and most important bond distances. All of the final structures listed in Tables 1 and 2 are genuine minima with no imaginary vibrational frequencies.

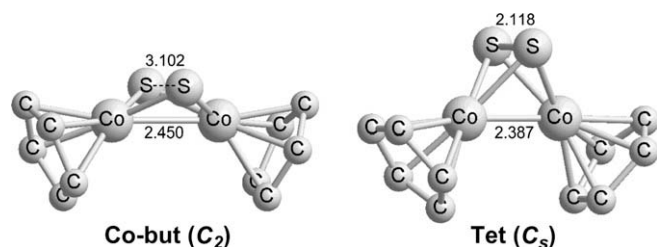


Fig. 2. Optimized structures for $Cp_2Co_2S_2$ determined by the BP86 method. All structures are confirmed to be (local) minima and all bond distances are given in angstroms.

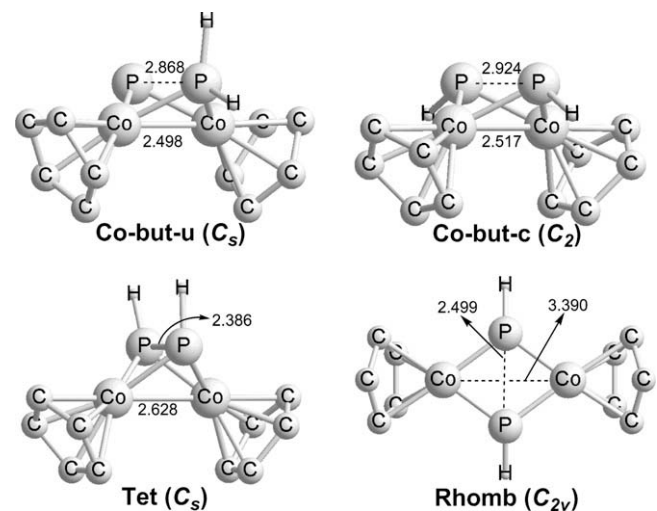


Fig. 3. Optimized structures of $Cp_2Co_2(PH)_2$ determined by the BP86 method.

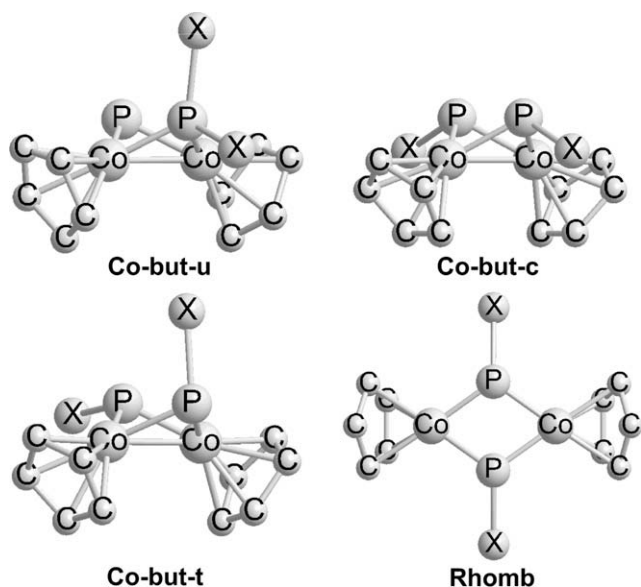


Fig. 4. The structures of $\text{Cp}_2\text{Co}_2(\text{PX})_2$ ($\text{X} = \text{Cl}, \text{OH}, \text{OMe}, \text{NH}_2$ or NMe_2).

3. Results

3.1. $\text{Cp}_2\text{Co}_2\text{S}_2$

Four initial structures were optimized for $\text{Cp}_2\text{Co}_2\text{S}_2$, namely those with tetrahedron, Co-butterfly, S-butterfly, and rhombus central Co_2S_2 units. However, only two genuine minima were obtained (Fig. 2). The Co-butterfly structure (**Co-but**) is the global minimum for $\text{Cp}_2\text{Co}_2\text{S}_2$. It is characterized by a 2.450 Å Co–Co bonding distance and a 3.102 Å S··S nonbonding distance. This Co–Co distance is very close to the Co–Co distances of 2.47 Å found by X-ray diffraction [10] for the related Co_2S_2 butterfly structure $\text{Cp}_2\text{Co}_2(\text{SCMe}_3)_2$. The four Co–S bond lengths are 2.129 Å, 2.136 Å, 2.129 Å, and 2.136 Å, respectively. The other $\text{Cp}_2\text{Co}_2\text{S}_2$ structure is the tetrahedrane (**Tet**) at 15.4 kcal/mol above the **Co-but** structure of $\text{Cp}_2\text{Co}_2\text{S}_2$. This structure has both a Co–Co bond (2.387 Å) and an S–S bond (2.118 Å). The Co–Co bond in the **Tet** structure of $\text{Cp}_2\text{Co}_2\text{S}_2$ is ~ 0.1 Å shorter than the Co–Co bond in the corresponding **Co-but** structure. Attempts to optimize S-butterfly or rhombus structures of $\text{Cp}_2\text{Co}_2\text{S}_2$ converged to the **Co-but** structure.

3.2. $\text{Cp}_2\text{Co}_2(\text{PX})_2$ ($\text{X} = \text{H}, \text{Cl}, \text{OH}, \text{OMe}, \text{NH}_2$, and NMe_2)

Four structures (Fig. 3 and Table 2) were found for $\text{Cp}_2\text{Co}_2(\text{PH})_2$, namely unsymmetrical and cis-symmetrical Co-butterfly structures (**Co-but-u** and **Co-but-c**), a tetrahedrane structure (**Tet**), and a rhombus structure (**Rhomb**). The lowest energy $\text{Cp}_2\text{Co}_2(\text{PH})_2$ structure is the unsymmetrical Co-butterfly structure **Co-but-u**, with a direct Co–Co bond of 2.498 Å, but the phosphorus atoms outside of direct bonding distance (2.868 Å). In **Co-but-u**, both hydrogen atoms are bonded to the same phosphorus atom and the other phosphorus atom is bonded only to cobalt atoms. The cis-symmetrical Co-butterfly structure of $\text{Cp}_2\text{Co}_2(\text{PH})_2$, namely

Co-but-c, lies 9.1 kcal/mol energetically above **Co-but-u**, although it also has a bonding Co–Co distance (2.517 Å) and nonbonding P··P distance (2.924 Å). Both tetrahedrane (**Tet**) and rhombus (**Rhomb**) structures are also found for $\text{Cp}_2\text{Co}_2(\text{PH})_2$ but at more than 20 kcal/mol above the **Co-but-u** global minimum. No P-butterfly structure was found for $\text{Cp}_2\text{Co}_2(\text{PH})_2$.

Structures with Co-butterfly and rhombus central Co_2P_2 units were found for $\text{Cp}_2\text{Co}_2(\text{PCl})_2$ (Fig. 4). The two types of Co-butterfly structures (**Co-but-u** and **Co-but-c**) and the rhombus structure (**Rhomb**) found for $\text{Cp}_2\text{Co}_2(\text{PH})_2$ were also found for $\text{Cp}_2\text{Co}_2(\text{PCl})_2$. However, the global minimum for $\text{Cp}_2\text{Co}_2(\text{PCl})_2$ is the cis-symmetrical butterfly structure **Co-but-c**, rather than the unsymmetrical butterfly structure **Co-but-u** found for $\text{Cp}_2\text{Co}_2(\text{PH})_2$. Next in energy at only 1.6 kcal/mol above the global minimum **Co-but-c** is the unsymmetrical butterfly **Co-but-u** with the two chlorine substituents bonded to the same phosphorus atom. A trans-symmetrical butterfly structure **Co-but-t** was also found for $\text{Cp}_2\text{Co}_2(\text{PCl})_2$ at 10.4 kcal/mol above the **Co-but-c** global minimum. The trans-symmetrical **Co-but-t** butterfly structure can be derived from a tetrahedron structure by breaking the P–P bond. The highest energy of the four $\text{Cp}_2\text{Co}_2(\text{PCl})_2$ structures is the rhombus **Rhomb** at 16.7 kcal/mol above the **Co-but-c** global minimum. Neither tetrahedrane nor P-butterfly structures were found for $\text{Cp}_2\text{Co}_2(\text{PCl})_2$.

The same four structures found for $\text{Cp}_2\text{Co}_2(\text{PCl})_2$, namely **Co-but-u**, **Co-but-c**, **Co-but-t** and **Rhomb**, were also found for $\text{Cp}_2\text{Co}_2(\text{POH})_2$, $\text{Cp}_2\text{Co}_2(\text{POMe})_2$, $\text{Cp}_2\text{Co}_2(\text{PNH}_2)_2$, and $\text{Cp}_2\text{Co}_2(\text{PNMe}_2)_2$. In all four of these cases the unsymmetrical butterfly structure **Co-but-u** was the global minimum, similar to $\text{Cp}_2\text{Co}_2(\text{PH})_2$. The bonding Co–Co distance is nearly the same in $\text{Cp}_2\text{Co}_2(\text{POH})_2$ (2.539 Å), $\text{Cp}_2\text{Co}_2(\text{POMe})_2$ (2.534 Å), and $\text{Cp}_2\text{Co}_2(\text{PNH}_2)_2$ (2.529 Å) but somewhat longer in $\text{Cp}_2\text{Co}_2(\text{PNMe}_2)_2$ (2.553 Å). This is also the case for the nonbonding P··P distance. For comparison the experimental Co–Co distance in the Co-butterfly $\text{Cp}_2\text{Co}_2(\text{PMe}_2)_2$, determined by X-ray diffraction [9], is reported to be 2.542 Å. The cis-symmetrical butterfly **Co-but-c** lies in energy below the corresponding trans structure **Co-but-t** for $\text{Cp}_2\text{Co}_2(\text{POH})_2$, $\text{Cp}_2\text{Co}_2(\text{POMe})_2$, and $\text{Cp}_2\text{Co}_2(\text{PNH}_2)_2$. However, for $\text{Cp}_2\text{Co}_2(\text{PNMe}_2)_2$ the relative energies are reversed, so that the cis-symmetrical butterfly **Co-but-c** lies 1.6 kcal/mol above the corresponding trans structure **Co-but-t**. This reversal of relative energies is probably a consequence of the larger size of the NMe_2 group relative to the NH_2 group. The **Rhomb** structure is the highest energy of the four structures for all four $\text{Cp}_2\text{Co}_2(\text{PX})_2$ ($\text{X} = \text{OH}, \text{OMe}, \text{NH}_2$, or NMe_2) derivatives, just as for $\text{X} = \text{H}$ or Cl . No tetrahedrane or P–P-butterfly structures were found for $\text{Cp}_2\text{Co}_2(\text{POH})_2$, $\text{Cp}_2\text{Co}_2(\text{POMe})_2$, $\text{Cp}_2\text{Co}_2(\text{PNH}_2)_2$, or $\text{Cp}_2\text{Co}_2(\text{PNMe}_2)_2$.

3.3. Unsymmetrical Fe–Fe-butterfly structures of the $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ ($\text{X} = \text{H}, \text{Cl}, \text{OH}, \text{OMe}, \text{NH}_2$ or NMe_2) analogues

The energetically low-lying unsymmetrical Co–Co-butterfly structures **Co-but-u** of $\text{Cp}_2\text{Co}_2(\text{PX})_2$ suggest the existence of similar structures for their $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ analogues, even though such structures were not found in the previous theoretical study [23]. Table 3 and Fig. 5 give the optimized results for the unsymmetrical Fe–Fe-butterfly structures (**Fe-but-u**) of the $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ compounds. For comparison, the symmetrical Fe–Fe-butterfly

Table 1
The $\text{Cp}_2\text{Co}_2\text{S}_2$ structures at the BP86/6–311G(d) level of theory.

Structure	State (sym)	Rel energy ^a (kcal/mol)	Co–Co (Å)	S–S (Å)	Co–S (Å)
Co-but	¹ A (C_2)	0.0	2.450	3.102	2.129, 2.136
Tet	¹ A (C_s)	15.4	2.387	2.118	2.199, 2.200

^a Based on the total electronic energies without zero point energy corrections. The total energy of the **Co-but** structure is -3949.66873 a.u.

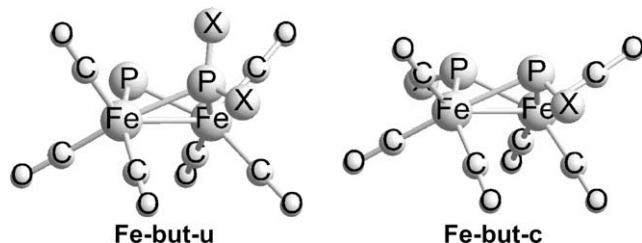
Table 2The singlet structures of the $\text{Cp}_2\text{Co}_2(\text{PX})_2$ ($X = \text{H, Cl, OH, OMe, NH}_2$ or NMe_2) complexes at the BP86/6–311G(d) level of theory.

X	Structure	State (sym)	Rel energy ^a (kcal/mol)	Co–Co (Å)	P–P (Å)	Co–P (Å)
H	Co-but-u	¹ A' (C _s)	0.0	2.498	2.868	2.096, 2.131
	Co-but-c	¹ A (C ₂)	9.1	2.517	2.924	2.151, 2.159
	Tet	¹ A' (C _s)	20.9	2.628	2.383	2.048, 2.240
	Rhomb	¹ A ₁ (C _{2v})	29.0	3.390	2.499	2.106
Cl	Co-but-u	¹ A' (C _s)	1.6	2.556	2.729	2.069, 2.099
	Co-but-c	¹ A ₁ (C _{2v})	0.0	2.532	2.745	2.120
	Co-but-t	¹ A' (C _s)	10.4	2.561	2.859	2.033, 2.203
	Rhomb	¹ A ₁ (C _{2v})	16.7	3.405	2.397	2.086
OH	Co-but-u	¹ A (C ₁)	0.0	2.539	2.770	2.072, 2.074, 2.095, 2.102
	Co-but-c	¹ A (C ₁)	11.4	2.504	2.801	2.071, 2.082, 2.164, 2.167
	Co-but-t	¹ A (C ₁)	18.3	2.535	2.805	2.017, 2.024, 2.202, 2.205
	Rhomb	¹ A (C ₂)	22.5	3.401	2.404	2.084, 2.087
OMe	Co-but-u	¹ A (C ₁)	0.0	2.534	2.748	2.080, 2.081, 2.097, 2.100
	Co-but-c	¹ A (C ₁)	10.8	2.507	2.795	2.070, 2.085, 2.171, 2.172
	Co-but-t	¹ A (C ₁)	17.0	2.536	2.803	2.021, 2.028, 2.207, 2.208
	Rhomb	¹ A (C ₂)	22.1	3.414	2.407	2.080, 2.100
NH ₂	Co-but-u	¹ A (C ₁)	0.0	2.529	2.814	2.097, 2.907, 2.907, 2.099
	Co-but-c	¹ A (C ₁)	13.9	2.521	2.839	2.064, 2.068, 2.197, 2.214
	Co-but-t	¹ A (C ₁)	17.2	2.529	2.907	2.036, 2.037, 2.216, 2.236
	Rhomb	¹ A ₁ (C _{2v})	20.0	3.401	2.447	2.098
NMe ₂	Co-but-u	¹ A (C ₁)	0.0	2.553	2.842	2.094, 2.098, 2.099, 2.132
	Co-but-c	¹ A (C ₁)	13.7	2.556	2.816	2.057, 2.063, 2.218, 2.224
	Co-but-t	¹ A (C ₁)	12.1	2.539	2.856	2.027, 2.048, 2.200, 2.264
	Rhomb	¹ A ₁ (C _{2v})	19.4	3.380	2.413	2.107

^a Based on the total electronic energies without zero point energy corrections. The total energies of the **Co-but-u** isomer are –3837.13726, –4756.50719, –3987.67286, –4066.29001, –3947.91553 and –4105.15771 a.u. for $\text{Cp}_2\text{Co}_2(\text{PH})_2$, $\text{Cp}_2\text{Co}_2(\text{PCI})_2$, $\text{Cp}_2\text{Co}_2(\text{POH})_2$, $\text{Cp}_2\text{Co}_2(\text{OMe})_2$, $\text{Cp}_2\text{Co}_2(\text{NH}_2)_2$ and $\text{Cp}_2\text{Co}_2(\text{NMe}_2)_2$, respectively.

Table 3The singlet unsymmetrical (**Fe-but-u**) and symmetrical (**Fe-but-c**) structures of the $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ ($X = \text{H, Cl, OH, OMe, NH}_2$ or NMe_2) complexes at the BP86/6–311G(d) level of theory.

X	Structure	State (sym)	Total energy (a.u.)	Relative energy (kcal/mol)
H	Fe-but-u	¹ A' (C _s)	–3892.16857	0.0
	Fe-but-c	¹ A' (C _s)	–3892.15971	5.6
Cl	Fe-but-u	¹ A' (C _s)	–4811.52369	0.5
	Fe-but-c	¹ A' (C _s)	–4811.52456	0.0
OH	Fe-but-u	¹ A (C ₁)	–4042.70442	0.0
	Fe-but-c	¹ A (C ₁)	–4042.68881	9.8
OMe	Fe-but-u	¹ A (C ₁)	–4121.32278	0.0
	Fe-but-c	¹ A (C ₁)	–4121.30852	8.9
NH ₂	Fe-but-u	¹ A (C ₁)	–4002.96140	0.0
	Fe-but-c	¹ A (C ₁)	–4002.94349	11.2
NMe ₂	Fe-but-u	¹ A (C ₁)	–4160.21086	0.0
	Fe-but-c	¹ A (C ₁)	–4160.18588	15.7

**Fig. 5.** The unsymmetrical (**Fe-but-u**) and symmetrical (**Fe-but-c**) Fe–Fe–butterfly structures of the $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ ($X = \text{H, Cl, OH, OMe, NH}_2$ or NMe_2) compounds.

structures (**Fe-but-c**) of the $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ compounds are also shown. Similar to their $\text{Cp}_2\text{Co}_2(\text{PX})_2$ analogues, the unsymmetrical **Fe-but-u** structures of $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ are more stable than the corresponding **Fe-but-c** structures by 5.6, 9.8, 9.0, 11.2 and 15.7 kcal/mol for $X = \text{H, OH, OMe, NH}_2$ and NMe_2 , respectively, at

the BP86/6–311G(d) level of theory. For $\text{Fe}_2(\text{CO})_6(\text{PCI})_2$, the unsymmetrical **Fe-but-u** structure lies energetically above the corresponding **Fe-but-c** structure. However, the energy difference (0.5 kcal/mol by BP86) is very small.

4. Discussion

For the iron carbonyl compounds, the tetrahedranes with both Fe–Fe and E–E bonds (Fig. 1) are the lowest energy structures $\text{Fe}_2(\text{CO})_6\text{S}_2$ and $\text{Fe}_2(\text{CO})_6(\text{PX})_2$ ($X = \text{Me, } ^i\text{Bu, H, Cl}$) [5]. However, Fe–butterfly and rhombus structures are the lowest energy structures for the amino derivatives $\text{Fe}_2(\text{CO})_6(\text{PNR}_2)_2$ ($R = \text{H, Me, } ^i\text{Pr}$) where resonance structures involving P=N double bonding weaken the P–P bond (Fig. 6). These observations suggest that tetrahedrane structures for M_2E_2 systems are destabilized by negative charge on the metal atoms leading indirectly to weaker E···E interactions.

Cyclopentadienyl rings are poorer π -acceptors than three carbonyl groups for removal of electron density from transition metals. Therefore, the negative charge remaining on the metal atoms in $\text{Cp}_2\text{Co}_2\text{E}_2$ derivatives is higher than that on the analogous $\text{Fe}_2(\text{CO})_6\text{E}_2$ derivatives. This is consistent with the observation in this research that tetrahedrane structures are never the lowest energy structures for $\text{Cp}_2\text{Co}_2\text{E}_2$ derivatives. In fact $\text{Cp}_2\text{Co}_2\text{S}_2$ and $\text{Cp}_2\text{Co}_2(\text{PH})_2$ are the only $\text{Cp}_2\text{Co}_2\text{E}_2$ derivatives for which tetrahedrane structures were found, albeit at higher energies than various Co–butterfly structures.

The isolobal $\text{Fe}(\text{CO})_3$ and CpCo units require four electrons from the external ligands to give the metals the favored 18-electron configurations. It is impossible to draw valence bond structures for the symmetrical butterflies giving each metal atom the required four electrons without having single electrons left on each phosphorus atom (Fig. 7). If these electrons are paired, then the symmetrical butterfly structures are singlet diradicals similar to the singlet diradicals isolated by Bertrand and coworkers [24] as well as closely related (RPCR')₂ and (RNGeR')₂ species [25,26]. However, single electrons on the phosphorus atoms are avoided in the

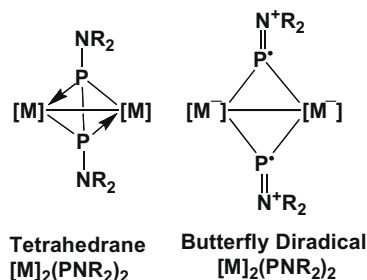


Fig. 6. Weakening the P–P bond by partial P=N double bonding to R_2N groups ($[M] = Fe(CO)_3$ or $CpCo$).

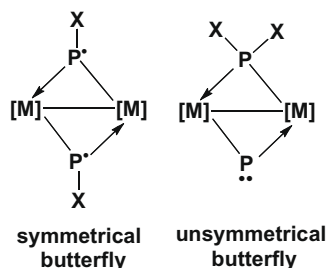


Fig. 7. Valence bond structures for the symmetrical and unsymmetrical butterfly structures for $[M]_2(PX)_2$ derivatives ($[M] = Fe(CO)_3$ and $CpCo$).

unsymmetrical butterfly structures having both X groups bonded to one phosphorus atom, with two-center two-electron bonds and the “naked” phosphorus atom having a lone pair (Fig. 7). The occurrence of unsymmetrical butterfly **Co-but-u** structures rather than the symmetrical butterfly **Co-but-c** and **Co-but-t** structures (Figs. 3 and 4) as the global minima for all of the $Cp_2Co_2(PX)_2$ ($X \neq Cl$) derivatives may relate to the avoidance of single electrons on phosphorus atoms. Analogous unsymmetrical butterfly structures $Fe_2(CO)_6(P)(PX_2)$ have now also been found for the iron carbonyl analogues at energies comparable to those of the symmetrical butterfly structures $Fe_2(CO)_6(PX)_2$ reported in the previous study [23].

5. Conclusions

Density functional theory studies on a series of $Cp_2Co_2E_2$ derivatives ($E = S$ and PX ; $X = H, Cl, OH, OMe, NH_2, NMe_2$) predict butterfly structures with one Co–Co bond for the “body” of the butterfly and four Co–E bonds at the edges of the “wings” of the butterfly. Tetrahedrane structures with both Co–Co and E–E bonds are higher in energy for $Cp_2Co_2S_2$ and $Cp_2Co_2(PH)_2$ and are not found in the other systems. This differs from the corresponding $Fe_2(CO)_6S_2$ and $Fe_2(CO)_6(PX)_2$ derivatives where tetrahedrane structures are predicted to be the lowest energy structures for all cases except $X = NR_2$ and OH . Furthermore, such tetrahedrane structures are found experimentally for $Fe_2(CO)_6S_2$ (Ref. [2]) and $Fe_2(CO)_6(PBu^t)_2$ (Ref. [6]).

The butterfly structures for the $Cp_2Co_2E_2$ derivatives are found to be of two types. For $Cp_2Co_2(PX)_2$ ($X = H, OH, OMe, NH_2, NMe_2$) the lowest energy structures are unsymmetrical butterflies, $Cp_2Co_2(P)(PX_2)$, with two X groups on one phosphorus atom and a lone pair on the other (naked) phosphorus atom. Related low-energy unsymmetrical butterfly $Fe_2(CO)_6(P)(PX_2)$ structures, not observed in previous theoretical studies [23], have now been found

for the corresponding $Fe_2(CO)_6(PX)_2$ derivatives. Symmetrical butterfly singlet diradical structures with one X group on each phosphorus atom in relative *cis* or *trans* positions are also found for the $Cp_2Co_2(PX)_2$ derivatives and are the global minima for $Cp_2Co_2(PCI)_2$ as well as $Cp_2Co_2S_2$. In all cases the *cis* structures are of lower energy than the corresponding *trans* structures except for $Cp_2Co_2(PNMe_2)_2$. Rhombus structures having neither Co–Co nor E–E bonds are also found for all of the $Cp_2Co_2(PX)_2$ derivatives but always at higher energies than the butterfly structures, ranging from 17 to 29 kcal/mol above the global minima.

Acknowledgments

We are indebted to the National Natural Science Foundation (20873045 and 20973066) of China, as well as the U. S. National Science Foundation (Grants CHE-0749868 and CHE-0716718) for support of this research. Part of this work was undertaken with financial support from the CMMCCC 130/2007 program, Romania.

Appendix A. Supplementary data

Tables S1 to S7: The vibrational frequencies for the isomers of $Cp_2Co_2E_2$ ($E = S, PH, PCI, POH, POME, PNH_2$ or $PNMe_2$) at the B3LYP/6–311G(d) and BP86/6–311G(d) levels; Table S8 to S14: The Cartesian coordinates of the optimized $Cp_2Co_2E_2$ ($E = S, PH, PCI, POH, POME, PNH_2$ or $PNMe_2$) isomers at the B3LYP/6–311G(d) and BP86/6–311G(d) levels; complete GAUSSIAN 03 reference (Ref. [22]) Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.12.014.

References

- [1] W. Hieber, J.Z. Gruber, Z. anorg. allg. Chem. 296 (1958) 91.
- [2] (a) C.H. Wei, L.F. Dahl, Inorg. Chem. 4 (1965) 1; (b) K.L. Eremenko, H. Berke, A.A.H. van der Zeijden, B.I. Kolobkov, V.M. Novotorstev, J. Organometal. Chem. 471 (1994) 123.
- [3] R.B. King, T.E. Bitterwolf, Coord. Chem. Rev. 206–207 (2000) 563.
- [4] J.W. Peters, W.N. Lanzilotta, B.J. Lemon, L.C. Seefeldt, Science 282 (1998) 1853.
- [5] I. Silaghi-Dumitrescu, T.E. Bitterwolf, R.B. King, J. Am. Chem. Soc. 128 (2006) 5342.
- [6] L. De, D. Wolters, H. Vahrenkamp, Z. Naturforsch. 41b (1986) 283.
- [7] K.M. Flynn, R.A. Bartlett, M.M. Olmstead, and P.P. Power, Organometallics, 5 (1986) 813.
- [8] R.B. King, P.M. Treichel, F.G.A. Stone, J. Am. Chem. Soc. 83 (1961) 3600.
- [9] H. Werner, W. Hofmann, R. Zolk, L.F. Dahl, J. Kocal, A. Kühn, J. Organometal. Chem. 289 (1985) 173.
- [10] A. Shaver, S. Morris, R. Turrin, V.W. Day, Inorg. Chem. 29 (1990) 3622.
- [11] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [12] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [13] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [14] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
- [15] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639.
- [16] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
- [17] A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033.
- [18] P.J. Hay, J. Chem. Phys. 66 (1977) 4377.
- [19] K. Raghavachari, G.W. Trucks, J. Chem. Phys. 91 (1989) 1062.
- [20] H.Y. Wang, Y. Xie, R.B. King, H.F. Schaefer, J. Am. Chem. Soc. 127 (2005) 11646.
- [21] H.Y. Wang, Y. Xie, R.B. King, H.F. Schaefer, J. Am. Chem. Soc. 128 (2006) 11376.
- [22] M.J. Frisch, et al., GAUSSIAN 03, Revision D 01; Gaussian, Inc., Wallingford CT, 2004 (see Supporting Information for details).
- [23] I. Silaghi-Dumitrescu, T.E. Bitterwolf, R.B. King, J. Am. Chem. Soc. 130 (2008) 901.
- [24] (a) D. Scheschkewitz, H. Amii, H. Gornitzka, W.W. Schoeller, D. Bourissou, G. Bertrand, Science 295 (2002) 1880; (b) D. Scheschkewitz, H. Amii, H. Gornitzka, W.W. Schoeller, D. Bourissou, G. Bertrand, Angew. Chem., Int. Ed. 43 (2004) 585; (c) H. Amii, L. Vranicar, H. Gornitzka, D. Bourissou, G. Bertrand, J. Am. Chem. Soc. 126 (2004) 1344; (d) M.-J. Cheng, C.-N. Hu, Mol. Phys. 101 (2003) 1319.
- [25] M. Sebastian, M. Nieger, D. Szieberth, L. Nyulászi, E. Niecke, Angew. Chem., Int. Ed. 43 (2004) 637.
- [26] C. Cui, M. Brynda, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 126 (2004) 6510.