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Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950–2009)

DECARBONYLATION OF $P_2Co_2(CO)_6$, A BINUCLEAR COBALT CARBONYL DERIVATIVE OF DIPHOSPHORUS**

Guoliang LI,[a] Qian-Shu LI,[*a,b] Yaoming XIE,[c] R. Bruce KING*[a,c] and Henry F. SCHAEFER III[c]

[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] Department of Chemistry and Center for Computational Chemistry University of Georgia, Athens, Georgia 30602, USA

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The structures and relative energies of the $P_2Co_2(CO)_n$ (n = 6, 5, 4) derivatives are predicted by density functional theory to be very similar to those of the corresponding valence isoelectronic $H_2C_2Co_2(CO)_n$ and $As_2Co_2(CO)_n$ derivatives. Thus $P_2Co_2(CO)_6$ is predicted to have three carbonyls bonded to one cobalt atom and eclipsed relative to the three carbonyls on the other cobalt atom. The corresponding $P_2Co_2(CO)_6$ structure with a staggered rather than eclipsed arrangement of the $Co(CO)_3$ units is a transition state instead of a genuine minimum. For $P_2Co_2(CO)_5$ the structure in which an equatorial group is removed from the $P_2Co_2(CO)_6$ structure and a singly bridged $P_2Co_2(CO)_4(\mu\text{-}CO)$ structure are predicted to have essentially the same energies, within less than 2 kcal/mol. A higher energy (by 9 ± 2 kcal/mol) $P_2Co_2(CO)_5$ structure is derived from the $P_2Co_2(CO)_6$ structure by removal of an axial carbonyl group. Five structures were found for $P_2Co_2(CO)_4$ within ~5 kcal/mol of energy. The lowest energy of these (by ~1 kcal/mol) is the only such structure with a bridging carbonyl group. The other four $P_2Co_2(CO)_4$ structures, as well as two higher energy structures within ~20 kcal/mol of the global minimum, are derived from $P_2Co_2(CO)_6$ by removal of two carbonyl groups in various ways.

INTRODUCTION

In recent years the analogy between CH units and phosphorus atoms in organic structures has been recognized.[1] However, an important difference arises from the lone pair of electrons on phosphorus, as compared with the external hydrogen atom on an isovalent CH unit. This leads to significant chemical differences between isovalent P: and CH units in otherwise analogous molecules, since a phosphorus analogue to a non-basic CH derivative has significant basic properties arising from this lone pair. Also, acetylene HC≡CH is a stable molecule, whereas the isovalent diphosphorus, :P≡P:, is unstable with respect to dimerization to tetrahedral P_4. The same is even true for diarsenic, As_2, where the basicity of the external lone pairs is greatly reduced with respect to P_2. Thus only small amounts of the dimers E_2 (E = P, As) are present in phosphorus and arsenic vapors at elevated temperatures, as indicated by gas-phase Raman spectra.[2] For diphosphorus the equilibrium $P_4 \rightarrow,\leftarrow 2P_2$ becomes significant only at temperatures > 1100 K.[3] Robinson and coworkers have recently prepared a stable N-heterocyclic carbene complex of diphosphorus.[4]

Even though diphosphorus and diarsenic are unfavored as isolated molecules, they can be stabilized in transition metal complexes. Perhaps the earliest examples of such syntheses involve complexation of E_2 units (E = P, As) with the $Co_2(CO)_6$ moiety to give $E_2Co_2(CO)_6$ structures isovalent with the well-known[5] (alkyne)$Co_2(CO)_6$ derivatives. The arsenic compound $As_2Co_2(CO)_6$ was first synthesized by Foust, Foster, and Dahl[6] in 1969 by the reaction of $Co_2(CO)_8$ with excess $AsCl_3$. Structure determination by X-ray crystallography indicated an As_2Co_2 tetrahedrane structure closely related to the C_2Co_2 tetrahedrane structures of the (alkyne)$Co_2(CO)_6$ derivatives (Figure 1). Subsequent work by Vizi-Orosz, Pályi, and Markó[7,8] led to the synthesis of the much less viable phosphorus analogue $P_2Co_2(CO)_6$ as a low-yield product from the related reaction of $NaCo(CO)_4$ with PCl_3. The lower stability of $P_2Co_2(CO)_6$ relative to $As_2Co_2(CO)_6$ appears to be a consequence of the significantly higher basicity of the external phosphorus lone pairs relative to the external arsenic lone pairs.

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*Corresponding authors: rbking@chem.uga.edu or qsli@scnu.edu.cn

** This paper is dedicated to the memory of our friend Professor Ioan Silaghi-Dumitrescu (1950–2009), in recognition of his contributions to diverse areas of inorganic and computational chemistry as well as his leadership in Roumanian science.

In recent years the photochemical decarbonylation of the alkyne derivatives $R_2C_2Co_2(CO)_6$ has been studied by Bitterwolf and coworkers in Nujol matrices at 90 K.[9] The infrared ν(CO) spectra in such low temperature matrices indicate the presence of two isomers of the $R_2C_2Co_2(CO)_5$ single decarbonylation product, in accord with subsequent theoretical studies.[10] Analogous experimental[9] and theoretical[11] results were also obtained in the analogous matrix photolysis of $As_2Co_2(CO)_6$. A question of interest is whether the higher basicity of the phosphorus atoms in $P_2Co_2(CO)_6$, relative to the weakly basic arsenic atoms in $As_2Co_2(CO)_6$ and the non-basic CH groups in $H_2C_2Co_2(CO)_6$, would lead to significant differences in their decarbonylation behavior. In order to explore this possibility we have carried out density functional theory studies on the $P_2Co_2(CO)_n$ (n = 6, 5, 4) derivatives. The present paper reports our results in this area.

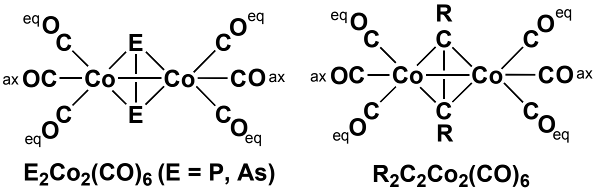


Fig. 1 – Analogy between the Co_2E_2 tetrahedrane structures of $E_2Co_2(CO)_6$ (E = P, As) and the Co_2C_2 tetrahedrane structures of $R_2C_2Co_2(CO)_6$, showing the axial and equatorial carbonyl groups.

THEORETICAL METHODS

Electron correlation effects were considered employing density functional theory (DFT) methods. Similar to our previous work on the $H_2C_2Co_2(CO)_n$ and $As_2Co_2(CO)_n$ systems,[10,11] two DFT methods were used herein. The first functional is designated B3LYP, which is an HF/DFT hybrid method combining Becke's three-parameter exchange functional (B3)[12] with the Lee-Yang-Parr generalized gradient correlation functional (LYP).[13] The second functional is BP86, which is a pure DFT method using Becke's 1988 exchange functional (B)[14] and Perdew's 1986 gradient correlation functional (P86).[15]

The basis sets used in this research were double-ζ plus polarization (DZP) sets. The DZP basis sets for C, O and P atoms begin with the Huzinaga-Dunning-Hay[16,17,18] contracted double-ζ Gaussian basis sets by adding a set of pure spherical harmonic d-like polarization functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$ and $\alpha_d(P) = 0.6$. The contraction schemes are C(9s5p1d/4s2p1d), O(9s5p1d/4s2p1d), and P(11s7p1d/6s4p1d). For Co, the DZP basis set, designated as (14s11p6d/10s8p3d), uses the Wachters' primitive set[19] augmented by two sets of p functions and one set of d functions and contracted following Hood *et al.*[20] For $P_2Co_2(CO)_6$, there are 324 contracted Gaussian functions with the present DZP basis set.

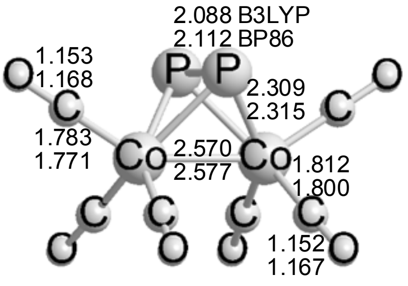
All of the computations were carried out with the Gaussian 03 program.[21] Possible structures of $P_2Co_2(CO)_n$ (n = 6, 5, 4) were fully optimized using the methods mentioned above. Harmonic vibrational frequencies were computed at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The default integration grid (75, 302) of Gaussian 03 was used for evaluating integrals numerically, and the tight (10^{-8} hartree) designation was employed for self-consistent field (SCF) convergence. The optimized geometries from the B3LYP/DZP and BP86/DZP computations are reported in Figures 2 and 3 with all bond distances given in angstroms, while Table 1 lists their electronic states and energies, and Table 2 shows their ν(CO) frequencies.

RESULTS AND DISCUSSION

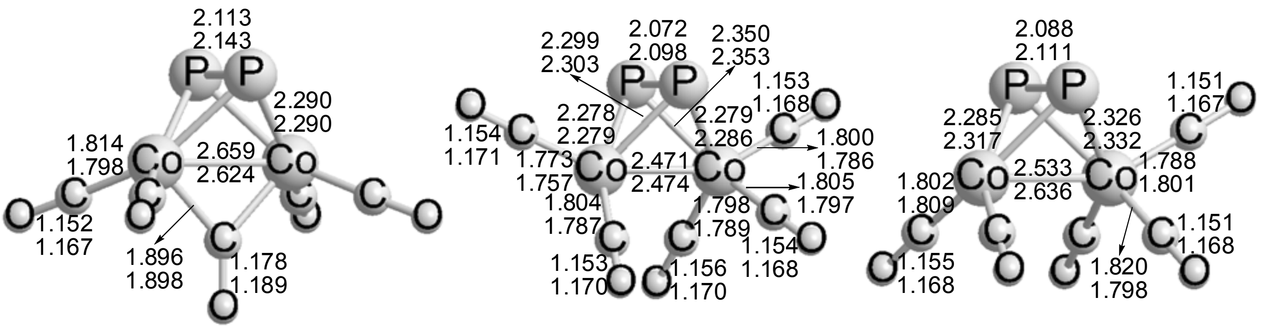
1. $P_2Co_2(CO)_6$

Similar to $H_2C_2Co_2(CO)_6$ and $As_2Co_2(CO)_6$, two $P_2Co_2(CO)_6$ structures are investigated here, namely the structures with the three carbonyls on one cobalt atom being in either eclipsed (C_{2v} symmetry) or staggered positions (C_s symmetry) relative to the three carbonyls on the other cobalt atom. The eclipsed C_{2v} structure **6-1S** (Figure 2) is predicted to be a genuine minimum, consistent with the experimental crystal structure.[7,8] In structure **6-1S**, the two axial carbonyls (CO_{ax}) are approximately *trans* to the Co-Co "bent" bond, while the remaining four equatorial carbonyls (CO_{eq}) are approximately coplanar with the two bridging phosphorus atoms. This provides a distorted octahedral arrangement of six bonds about each cobalt atom. The staggered C_s structure is a transition state with a small imaginary vibrational frequency of 41*i* cm^{-1} (B3LYP) or 31*i* cm^{-1} (BP86). The normal mode corresponding to the imaginary frequency is related to the inner rotation around the Co-Co bond. Following the corresponding normal mode leads to the eclipsed $P_2Co_2(CO)_6$ structure **6-1S**.

The optimized bond distances for **6-1S** are shown in Figure 2. The Co–Co bond length in **6-1S** is 2.570 Å (B3LYP) or 2.577 Å (BP86), which is longer than that in $H_2C_2Co_2(CO)_6$ by ~0.08 Å but shorter than that in $As_2Co_2(CO)_6$ by ~0.04 Å. This can be ascribed to the smaller covalent radius of carbon and the larger covalent radius of arsenic relative to that of phosphorus. The Co–Co distance in **6-1S** suggests the formal single bond necessary to give both cobalt atoms the favored 18-electron configuration. The P-P bond length in **6-1S** is 2.088 Å (B3LYP) or 2.112 Å (BP86), which is ~0.1 Å shorter than the P–P single bond length found in P_4 (2.21 Å).[22] This P-P distance is ~0.24 Å shorter than the corresponding As-As distance in $As_2Co_2(CO)_6$, while the P-Co distances in $P_2Co_2(CO)_6$ **(6-1S)** are ~0.11 Å shorter than the analogous Co-As distances in As $_2Co_2(CO)_6$. These bond length changes agree well with the difference in the covalent radii for phosphorus (1.10 Å) and arsenic (1.22 Å).[23] Both B3LYP and BP86 methods suggest that the four equivalent Co-CO_{eq} bonds are longer than the two Co-CO_{ax} bonds by ~0.03 Å. For the terminal C-O bonds, the two unique C-O distances agree within 0.001 Å. For comparison, the corresponding experimental bond distances in the mono-substituted triphenylphosphine derivative[7,8] $Co_2(CO)_5[P(C_6H_5)_3](\mu_2\text{-}P_2)$ are Co–Co = 2.574 Å, P–P = 2.019 Å, Co-CO_{ax} = 1.75 Å, Co-CO_{eq} = 1.66 to 1.76 Å, C-O = 1.14 to 1.20 Å, Co-P = 2.243 to 2.286 Å, respectively. Our computational bond lengths agree well with the corresponding experimental distances.


2.088 B3LYP
2.112 BP86
1.153
1.168
2.309
2.315
1.783
1.771
2.570
2.577
1.812
1.800
1.152
1.167
P
P
Co
Co
C
O

6-1S (C_{2v})


2.113
2.143
2.290
2.290
1.814
1.798
2.659
2.624
1.152
1.167
1.896
1.898
1.178
1.189
2.299
2.303
2.072
2.098
2.350
2.353
1.153
1.168
2.278
2.279
2.279
2.286
1.800
1.786
1.154
1.171
1.773
1.757
2.471
2.474
1.805
1.797
1.798
1.789
1.804
1.787
1.154
1.168
1.153
1.170
1.156
1.170
2.088
2.111
2.285
2.317
2.326
2.332
1.151
1.167
1.802
1.809
2.533
2.636
1.788
1.801
1.151
1.168
1.155
1.168
1.820
1.798
P
Co
C
O

5-1S (C_{2v}) **5-2S (C_1)** **5-3S (C_s)**

Fig. 2 – Optimized structures for $P_2Co_2(CO)_n$ (n = 6, 5). In Figures 2 and 3 the upper bond distances were predicted by the B3LYP method and the lower bond distances were computed with the BP86 method. All structures are confirmed to be genuine (local) minima by the absence of significant imaginary vibrational frequencies.

Table 1

Total energies (E_{tot}, in Hartrees), relative energies (ΔE, in kcal/mol), and critical bond distances (in Å) for the optimized structures of $P_2Co_2(CO)_n$ (n = 6, 5, 4) complexes

		B3LYP/DZP					BP86/DZP				
n	Structure	State (Sym.)	$-E_{tot}$	ΔE	Co-Co	P-P	State (Sym.)	$-E_{tot}$	ΔE	Co-Co	P-P
6	**6-1S**	$^1A_1$ (C_{2v})	4128.60502	0.0	2.570	2.088	$^1A_1$ (C_{2v})	4129.17864	0.0	2.577	2.112
5	**5-1S**	$^1A_1$ (C_{2v})	4015.21772	0.0	2.659	2.113	$^1A_1$ (C_{2v})	4015.78562	0.0	2.624	2.143
	5-2S	^1A (C_1)	4015.21868	–0.6	2.471	2.072	^1A (C_1)	4015.78360	1.3	2.474	2.098
	5-3S	$^1A'$ (C_s)	4015.20550	7.7	2.533	2.088	$^1A'$ (C_s)	4015.76858	10.7	2.636	2.111
4	**4-1S**	^1A (C_1)	3901.82966	0.0	2.620	2.097	^1A (C_1)	3902.38804	0.0	2.575	2.123
	4-2S	^1A (C_2)	3901.82916	0.3	2.420	2.070	^1A (C_2)	3902.38628	1.1	2.417	2.093
	4-3S	$^1A'$ (C_s)	3901.82820	0.9	2.460	2.085	$^1A'$ (C_s)	3902.38532	1.7	2.479	2.115
	4-4S	$^1A'$ (C_s)	3901.82825	0.9	2.425	2.097	$^1A'$ (C_s)	3902.38197	3.8	2.439	2.122
	4-5S	^1A (C_1)	3901.82555	2.6	2.397	2.068	^1A (C_1)	3902.37956	5.3	2.422	2.102
	4-6S	^1A (C_1)	3901.81662	8.2	2.425	2.068	^1A (C_1)	3902.36814	12.5	2.452	2.099
	4-7S	$^1A_1$ (C_{2v})	3901.80837	13.4	2.466	2.077	$^1A_1$ (C_{2v})	3902.35815	18.8	2.521	2.115

2. $P_2Co_2(CO)_5$

The three structures **5-1S**, **5-2S** and **5-3S** found for $P_2Co_2(CO)_5$ (Figure 2 and Table 1) have no imaginary vibrational frequencies, indicating that they all are genuine minima. These $P_2Co_2(CO)_5$ structures **5-1S**, **5-2S** and **5-3S** are similar to their $As_2Co_2(CO)_5$ analogues,[11] even in the matter of their relative energies. Furthermore, the analogous $P_2Co_2(CO)_5$ and $As_2Co_2(CO)_5$ structures differ only moderately in their geometrical parameters, such as bond lengths and bond angles. Structure **5-1S**, a C_{2v} symmetry mono-carbonyl-bridged $Co_2(CO)_4(\mu\text{-}CO)P_2$ structure, has the lowest energy at the BP86/DZP level. However, the B3LYP/DZP method predicts **5-2S** to lie lower in energy by 0.6 kcal/mol. The predicted Co–Co distance of 2.659 Å (B3LYP) or 2.624 Å (BP86) in **5-1S** is 0.05 to 0.09 Å longer than that in **6-1S** and thus also corresponds to a formal single bond. The P−P bond distance in **5-1S** is predicted to be 2.113 Å (B3LYP) or 2.143 Å (BP86), the longest in all of the $P_2Co_2(CO)_n$ structures found herein. As expected, the Co-CO bond distance to the bridging carbonyl group in **5-1S**, namely 1.896 Å (B3LYP) or 1.898 Å (BP86), is significantly longer than the two unique Co-CO bonds of 1.817 Å (B3LYP) or 1.798 Å (BP86) to the terminal carbonyl groups.

Removing an equatorial carbonyl group from the $P_2Co_2(CO)_6$ structure **6-1S** gives the $P_2Co_2(CO)_5$ structure **5-2S**. Structure **5-2S** is the lowest energy such isomer using the B3LYP/DZP method. However, the BP86/DZP method predicts **5-2S** to lie 1.3 kcal/mol higher than structure **5-1S**. The small energy difference of less than 2 kcal/mol between structures **5-1S** and **5-2S** indicates that these two structures can be considered to be essentially degenerate. The Co=Co bond in **5-2S** is ~0.1 Å shorter than the Co–Co bond in **6-1S**, suggesting a (long) formal double bond in **5-2S**.

The final $P_2Co_2(CO)_5$ structure **5-3S** can be derived from the $P_2Co_2(CO)_6$ structure **6-1S** by removal of an axial carbonyl group. Structure **5-3S** lies 7.7 kcal/mol (B3LYP) or 10.7 kcal/mol (BP86) above **5-1S**. The Co–Co distance in **5-3S** of 2.533 Å (B3LYP) or 2.636 Å (BP86) may also be regarded as a formal single bond giving the $Co(CO)_3$ cobalt the favored 18-electron configuration, but the $Co(CO)_2$ cobalt only a 16-electron configuration. The P-P and Co_{right}-CO bonds in **5-3S** are similar to those in **6-1S** because of their similar chemical environments.

3. $P_2Co_2(CO)_4$

Figure 3 reports the seven optimized structures for $P_2Co_2(CO)_4$, designated **4-1S**, **4-2S**, **4-3S**, **4-4S**, **4-5S**, **4-6S**, and **4-7S** according to their BP86/DZP energies (Table 1). These seven structures are genuine minima with all real vibrational frequencies. All of the $P_2Co_2(CO)_4$ structures have similar stereochemistry to their $As_2Co_2(CO)_4$ analogues.[11] Structures **4-1S** to **4-7S** are related to the $P_2Co_2(CO)_5$ structures **5-1S** to **5-3S** by removing one carbonyl from the latter. Thus, removing one CO_{eq} group from **5-1S** gives **4-1S**;

removing one CO_{eq} group from **5-2S** gives **4-2S** (C_2 symmetry), **4-3S** (C_s symmetry), or **4-4S** (C_s symmetry); and removing one CO_{eq} or CO_{ax} group from **5-3S** gives **4-5S** (C_1 symmetry), **4-6S** (C_1 symmetry), or **4-7S** (C_{2v} symmetry).

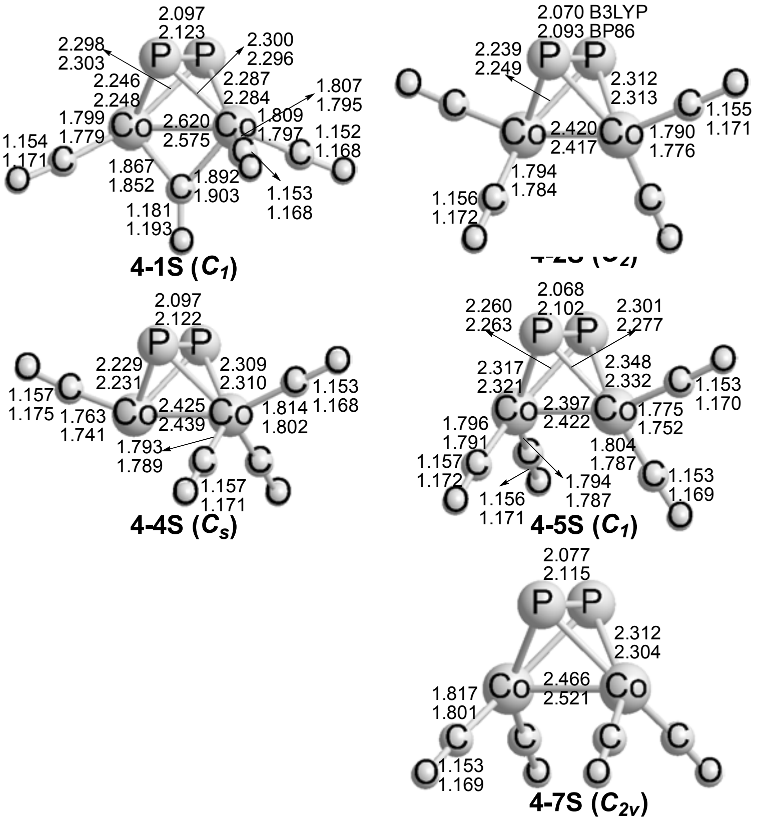

2.097 2.123
2.298 2.303
2.300 2.296
2.246 2.248
2.287 2.284
1.807 1.795
1.799 1.779
2.620 2.575
1.809 1.797
1.152 1.168
1.154 1.171
1.867 1.852
1.892 1.903
1.153 1.168
1.181 1.193
4-1S (C_1)
2.070 B3LYP 2.093 BP86
2.239 2.249
2.312 2.313
1.155 1.171
2.420 2.417
1.790 1.776
1.794 1.784
1.156 1.172
2.085 2.115
2.217 2.224
2.305 2.297
1.154 1.170
2.460 2.479
1.792 1.777
1.798 1.786
1.155 1.171
4-3S (C_s)
2.097 2.122
2.229 2.231
2.309 2.310
1.157 1.175
1.763 1.741
2.425 2.439
1.814 1.802
1.153 1.168
1.793 1.789
1.157 1.171
4-4S (C_s)
2.068 2.102
2.260 2.263
2.301 2.277
2.317 2.321
2.348 2.332
1.153 1.170
2.397 2.422
1.775 1.752
1.796 1.791
1.804 1.787
1.157 1.172
1.794 1.787
1.156 1.171
1.153 1.169
4-5S (C_1)
2.068 2.099
2.285 2.289
2.329 2.325
1.152 1.167
2.251 2.243
2.353 2.343
2.425 2.452
1.804 1.782
1.788 1.768
1.809 1.803
1.803 1.795
1.153 1.167
1.155 1.169
1.157 1.176
4-6S (C_1)
2.077 2.115
2.312 2.304
1.817 1.801
2.466 2.521
1.153 1.169
4-7S (C_{2v})

Fig. 3 – Seven optimized $P_2Co_2(CO)_4$ structures.

The $P_2Co_2(CO)_4$ structure **4-1S** with a single bridging carbonyl group (Figure 3 and Table 1) is the global minimum of $P_2Co_2(CO)_4$. Structures **4-2S**, **4-3S** and **4-4S** are almost isoenergetic to **4-1S**, with their B3LYP (BP86) relative energies lying only 0.3 (1.1), 0.9 (1.7), and 0.9 (3.8) kcal/mol, respectively, above that of **4-1S**. The $P_2Co_2(CO)_4$ structures **4-5S**, **4-6S** and **4-7S** lie above **4-1S** by 2.6 (5.3), 8.2 (12.5), and 13.4 (18.8) kcal/mol, respectively, at the B3LYP (BP86) level. All of the cobalt-cobalt bond distances in **4-1S** to **4-7S** are shorter than those in the corresponding **5-1S** to **5-3S** structures, reflecting the increasing unsaturation in the $P_2Co_2(CO)_4$ structures. Moreover, most of the Co-CO_{eq} bond distances in the $P_2Co_2(CO)_4$ structures are shorter than those in corresponding $P_2Co_2(CO)_5$ structures.

4. Vibrational Frequencies

Table 2 summarizes our theoretical ν(CO) frequencies for the compounds discussed in this paper using the BP86 method, which has been shown to provide better agreement with experimental data without the need for scaling factors.[24,25] The genuine terminal ν(CO) frequencies are seen to fall in the range 1970 to 2069 cm^{-1}, similar to other metal carbonyl derivatives. The ν(CO) frequencies for bridging carbonyl groups are significantly lower than those for terminal carbonyl groups as is generally found for metal carbonyl derivatives. Thus the bridging carbonyl frequencies (BP86) in **5-1S** and **4-1S** are 1865 cm^{-1} and 1839 cm^{-1}, respectively.

The predicted ν(CO) frequencies for the lowest energy $P_2Co_2(CO)_6$ structure **6-1S** are seen to be in close agreement with the experimental values (Table 2).[7] Thus the five predicted infrared active ν(CO) frequencies for **6-1S** of 1999, 2015, 2019, 2039, and 2067 cm^{-1} correspond to the experimental ν(CO) frequencies at 2029, 2042, 2046, 2066, and 2101 cm^{-1}. The experimental ν(CO) frequencies for $P_2Co_2(CO)_6$ are consistently an average 29 cm^{-1} higher than the theoretical ν(CO) frequencies.

Table 2

The ν(CO) frequencies (in cm^{-1}) and infrared intensities (in km/mol, given in parentheses) of the $P_2Co_2(CO)_n$ complexes. Experimental data are also given for comparison. Bridging carbonyl ν(CO) frequencies are in **bold** type

n	Structure	BP86/DZP
6	**6-1S**	1998 (0), 1999 (15), 2015 (745), 2019 (1197), 2039 (1552), 2069 (257)
	Expt[7]	2029 (mw), 2042 (s), 2046 (s), 2066 (vs), 2101 (m)
5	**5-1S**	**1865 (279)**, 2002 (0), 2006 (1417), 2020 (1663), 2053 (288)
	5-2S	1984 (269), 1993 (614), 2006 (666), 2021 (1677), 2053 (320)
	5-3S	1978 (393), 1999 (291), 2016 (926), 2021 (1338), 2063 (423)
4	**4-1S**	**1839 (309)**, 1996 (1136), 2000 (1114), 2038 (524)
	4-2S	1972 (473), 1984 (796), 2003 (1935), 2031 (178)
	4-3S	1972 (7), 1990 (1071), 2006 (2004), 2037 (247)
	4-4S	1984 (1124), 1987 (701), 1999 (831), 2039 (487)
	4-5S	1977 (568), 1986 (436), 2004 (1508), 2039 (520)
	4-6S	1970 (631), 1996 (705), 2010 (944), 2050 (528)
	4-7S	1980 (0), 1997 (1370), 1998 (855), 2045 (594)

5. Carbonyl Dissociation Energies

Table 3 reports bond dissociation energies for the loss of one carbonyl group from $P_2Co_2(CO)_n$ (n = 6, 5), using the global minima found in this work. The predicted dissociation energy of $P_2Co_2(CO)_6$ to $P_2Co_2(CO)_5$ + CO is 36.8 kcal/mol (B3LYP) or 41.3 kcal/mol (BP86). Similarly, the predicted dissociation energy of $P_2Co_2(CO)_5$ to $P_2Co_2(CO)_4$ + CO is is 37.3 kcal/mol (B3LYP) or 44.2 kcal/mol (BP86). These CO dissociation energies are comparable to the experimental[26] CO dissociation energies of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for the known simple mononuclear metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.

Table 3

Dissociation energies (kcal/mol) for the successive removal of carbonyl groups from the $Co_2(CO)_nP_2$ derivatives, based on the lowest energy structures

Process	B3LYP/DZP	BP86/DZP
$Co_2(CO)_6P_2$ (**6-1S**) → $Co_2(CO)_5P_2$ (**5-1S**) + CO	36.8	41.3
$Co_2(CO)_5P_2$ (**5-1S**) → $Co_2(CO)_4P_2$ (**4-1S**) + CO	37.3	44.2

CONCLUSION

This theoretical study shows that the higher basicity of phosphorus relative to arsenic has very little effect on the preferred structures for the $P_2Co_2(CO)_n$ (n = 6, 5, 4) derivatives relative to the corresponding $As_2Co_2(CO)_n$ derivatives. Thus $P_2Co_2(CO)_6$ is predicted to have the three carbonyls on one cobalt atom eclipsed relative to the three carbonyls on the other cobalt atom. The corresponding $P_2Co_2(CO)_6$ structure with a staggered rather than eclipsed arrangement of the $Co(CO)_3$ units is a transition state rather than a genuine minimum. For $P_2Co_2(CO)_5$ the structures in which (a) an equatorial group is removed from the $P_2Co_2(CO)_6$ structure; and (b) a singly bridged $P_2Co_2(CO)_4(\mu\text{-}CO)$ structure are predicted to have essentially the same energies, within less than 2 kcal/mol. A higher energy $P_2Co_2(CO)_5$ structure (by 9 ± 2 kcal/mol) is derived from the $P_2Co_2(CO)_6$ structure by removal of an axial carbonyl group. Five structures were found for $P_2Co_2(CO)_4$ within an energetic range of ~5 kcal/mol. The lowest energy of these $P_2Co_2(CO)_4$ strucures (by ~1 kcal/mol) is the only such structure with a bridging carbonyl group. The other four $P_2Co_2(CO)_4$ structures, as well as two higher energy structures within ~20 kcal/mol of the global minimum, are derived from $P_2Co_2(CO)_6$ by removal of two carbonyl groups in various ways.

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Supporting Information (see you on http://web.icf.ro/rrch/)

Table S1: The vibrational frequencies (in cm^{-1}) and infrared intensities (in km/mol, given in parentheses) of the $P_2Co_2(CO)_n$ (n = 6, 5, 4) complexes at the B3LYP/DZP and BP86/DZP levels; Table S2: The Cartesian coordinates of the

optimized $P_2Co_2(CO)_n$ (n = 6, 5, 4) structures at the B3LYP/DZP and BP86/DZP levels; Complete Gaussian 03 reference (reference 21).

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