



Unsaturation in binuclear cyclopentadienylrhodium carbonyls: Comparison with their cobalt analogs

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ARTICLE INFO

Article history:

Received 16 November 2010

Received in revised form

3 February 2011

Accepted 7 February 2011

Keywords:

Cyclopentadienyl

Rhodium

Metal–metal bonding

Metal carbonyls

Density functional theory

ABSTRACT

The $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) derivatives have been examined by density functional theory using the BP86 and MPW1PW91 functionals. The known tricarbonyl $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ is predicted to have a singly bridged structure with a predicted Rh–Rh single bond distance of ~ 2.70 Å in close agreement with the experimental value of 2.68 Å, determined by X-ray crystallography. In contrast to the cobalt analog, no evidence for a triply bridged $\text{Cp}_2\text{Rh}_2(\mu\text{-CO})_3$ structure was found. The known dicarbonyl $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ is predicted to have a doubly bridged structure with a predicted Rh=Rh double bond distance of 2.58 Å in close agreement with the experimental Rh=Rh double bond distance of 2.564 Å, found by X-ray crystallography for the permethylated derivative $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Rh}_2(\mu\text{-CO})_2$. The monocarbonyl $\text{Cp}_2\text{Rh}_2(\text{CO})$ is predicted to have a four-electron donor bridging carbonyl group with a Rh–O distance of ~ 2.5 Å and a Rh=Rh double bond distance of ~ 2.54 Å. This differs from $\text{Cp}_2\text{Co}_2(\text{CO})$ which was previously predicted to have only a two-electron donor bridging carbonyl group with a long $\text{Co}\cdots\text{O}$ distance and a short $\text{Co}\equiv\text{Co}$ distance of ~ 2.0 Å suggesting a formal triple bond. For $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ doubly bridged *trans* and *cis* isomers were found within ~ 1.0 kcal/mol in energy with non-bonding Rh \cdots Rh distances of ~ 3.2 Å. However, these $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ isomers are predicted to be unstable with respect both to CO loss to give $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ and to fragmentation into two $\text{CpRh}(\text{CO})_2$ units.

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1. Introduction

Cyclopentadienylrhodium carbonyl chemistry (Fig. 1) dates back to 1961 with the synthesis of $\text{CpRh}(\text{CO})_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) by Fischer and Bittler [1] using the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with sodium cyclopentadienide in petroleum ether. The binuclear derivative $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu\text{-CO})$ was subsequently obtained from $\text{CpRh}(\text{CO})_2$ upon standing for several weeks at room temperature or upon photolysis [2]. Further photolysis of $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu\text{-CO})$ at low temperatures gives the unstable $\text{Cp}_2\text{Rh}_2(\mu\text{-CO})_2$ (Fig. 1) [3]. More stable derivatives are obtained using the pentamethylcyclopentadienyl ligand, starting from $(\eta^5\text{-Me}_5\text{C}_5)\text{Rh}(\text{CO})_2$ [4,5]. X-ray crystal structures indicate a Rh–Rh single bond distance [2] of 2.68 Å in $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu\text{-CO})$ and a significantly shorter Rh=Rh double bond distance [6] of 2.564 Å in $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Rh}_2(\mu\text{-CO})_2$. Higher nuclearity cyclopentadienylrhodium carbonyl clusters include two

isomers [7–10] of the triangular $\text{Cp}_3\text{Rh}_3(\text{CO})_3$ and the tetrahedral [10] $\text{Cp}_4\text{Rh}_4(\mu_3\text{-CO})_2$ (Fig. 1). These cyclopentadienylrhodium carbonyl derivatives are of particular interest since photolysis of cyclopentadienylrhodium carbonyl systems has been shown to activate alkane C–H bonds [11,12].

This paper describes a theoretical study on the binuclear $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ derivatives ($n = 4, 3, 2, 1$) using density functional (DFT) theory methods. The compounds $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ and $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ are known compounds as discussed above. The monocarbonyl $\text{Cp}_2\text{Rh}_2(\text{CO})$ is a possible intermediate in the formation of the tetrahedral cluster $\text{Cp}_4\text{Rh}_4(\mu_3\text{-CO})_2$ via its dimerization. The tetracarbonyl $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ was also included in this study as a possible dimer of the known $\text{CpRh}(\text{CO})_2$ as well as a possible intermediate in the known conversion of $\text{CpRh}(\text{CO})_2$ to $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ noted above. A similar theoretical study of the analogous cobalt complexes $\text{Cp}_2\text{Co}_2(\text{CO})_n$ ($n = 3, 2, 1$) was reported several years ago [13].

2. Theoretical methods

Density functional theory (DFT) appears to be a powerful and effective computational tool to study organotransition metal

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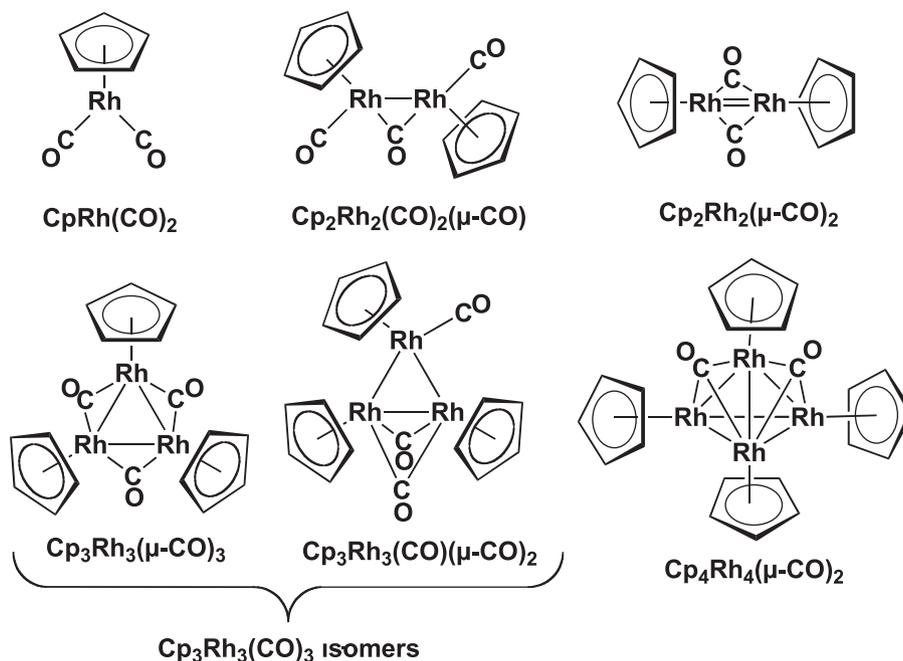


Fig. 1. Some known cyclopentadienylrhodium carbonyls.

chemistry [14–28]. In this connection two different DFT methods were used in the present study. The first DFT method is the BP86 method, which uses Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86) [29,30]. The second DFT method is a newer generation functional, MPW1PW91, which is a combination of the modified Perdew–Wang exchange functional with Perdew–Wang's 91 gradient–correlation functional [31]. This MPW1PW91 functional has been shown to be better than the first generation functionals for some heavy transition metal compounds [32,33]. The reliability of such density functional theory (DFT) methods is governed by the quality of the approximate exchange–correlation (XC) energy functional. When these two different DFT methods agree, confident predictions can be made. For most the compounds investigated in this work, both methods agree quite well. The only exception is the triplet–singlet splitting for $\text{Cp}_2\text{Rh}_2(\text{CO})_2$, which will be further discussed.

The Stuttgart/Dresden double- ζ basis set (SDD) with an effective core potential (ECP) [34,35] were used for the rhodium atoms. In this basis set 28 core electrons of the rhodium atoms are replaced by an effective core potential (ECP), and the valence basis set is contracted from (8s7p6d) primitive sets to (6s5p3d). The effective core approximation includes scalar relativistic contributions, which may become significant for the heavy transition metal atoms. For the C and O atoms, the all–electron DZP basis sets are used. They are Huzinaga–Dunning's contracted double- ζ contraction sets [36,37] plus a set of spherical harmonic d polarization functions with the orbital exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{O}) = 0.85$. The DZP basis sets for C and O atoms may be designated as (9s5p1d/4s2p1d). For the H atoms, a set of p polarization functions, $\alpha_p(\text{H}) = 0.75$, is added to the Huzinaga–Dunning DZ set. For $\text{Cp}_2\text{Rh}_2(\text{CO})_4$, there are 392 contracted Gaussian functions. All of the computations were carried out with the Gaussian 03 program [38] in which the tight option is set up for the geometry optimization. The symmetry for the molecules was maintained throughout the geometry optimization.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical

integration procedures used in the DFT computations. Thus all imaginary vibrational frequencies with a magnitude less than $100i \text{ cm}^{-1}$ are considered questionable, and are given less weight in the analysis [39,40]. Therefore, we do not always follow such low imaginary vibrational frequencies.

The geometries of all structures were fully optimized using the two DFT methods independently. The harmonic vibrational frequencies were obtained at the same levels. The corresponding infrared intensities were evaluated analytically. The infrared $\nu(\text{CO})$ frequencies of the $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ derivatives (Table 1), which are particularly useful for characterizing metal carbonyl derivatives, were obtained using the BP86 functional, which has been found to be more reliable for $\nu(\text{CO})$ frequencies than the B3LYP and MPW1PW91 functionals [17,41]. Unless otherwise indicated, the optimized $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ structures are genuine minima with no imaginary vibrational frequencies.

Table 1

Metal carbonyl $\nu(\text{CO})$ frequencies (in cm^{-1}) and their IR intensities (in km/mol , in parentheses) predicted by the BP86 method for the $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) structures.

Cp₂Rh₂(CO)₄	
4S-1 (C _i)	1773(711), 1786(0), 1989(1278), 1997(0)
4S-2 (C ₂)	1774(717), 1788(6), 1990(206), 2016(1242)
4T-3 (C ₂)	1816(817), 1842(3), 1948(290), 1978(1369)
4T-4 (C _{2h})	1817(815), 1843(0), 1930(1512), 1945(0)
4T-5 (C _s)	1894(623), 1919(706), 1976(620), 2019(319)
Cp₂Rh₂(CO)₃	
3S-1 (C ₂)	1832(497), 1963(1141), 1975(1)
3S-2 (C _s)	1838(835), 1866(1656), 1982(490)
3T-3 (C _i)	1808(896), 1836(11), 1972(876)
3T-4 (C _i)	1769(375), 1958(1393), 1970(22)
Cp₂Rh₂(CO)₂	
2S-1 (C ₂)	1792(998), 1830(0)
2T-2 (C _{2v})	1796(792), 1820(38)
2T-3 (C _i)	1787(859), 1827(0)
Cp₂Rh₂(CO)	
1S-1 (C _i)	1753(489)
1T-2 (C _i)	1916(1255)
1T-3 (C _i)	1701(384)

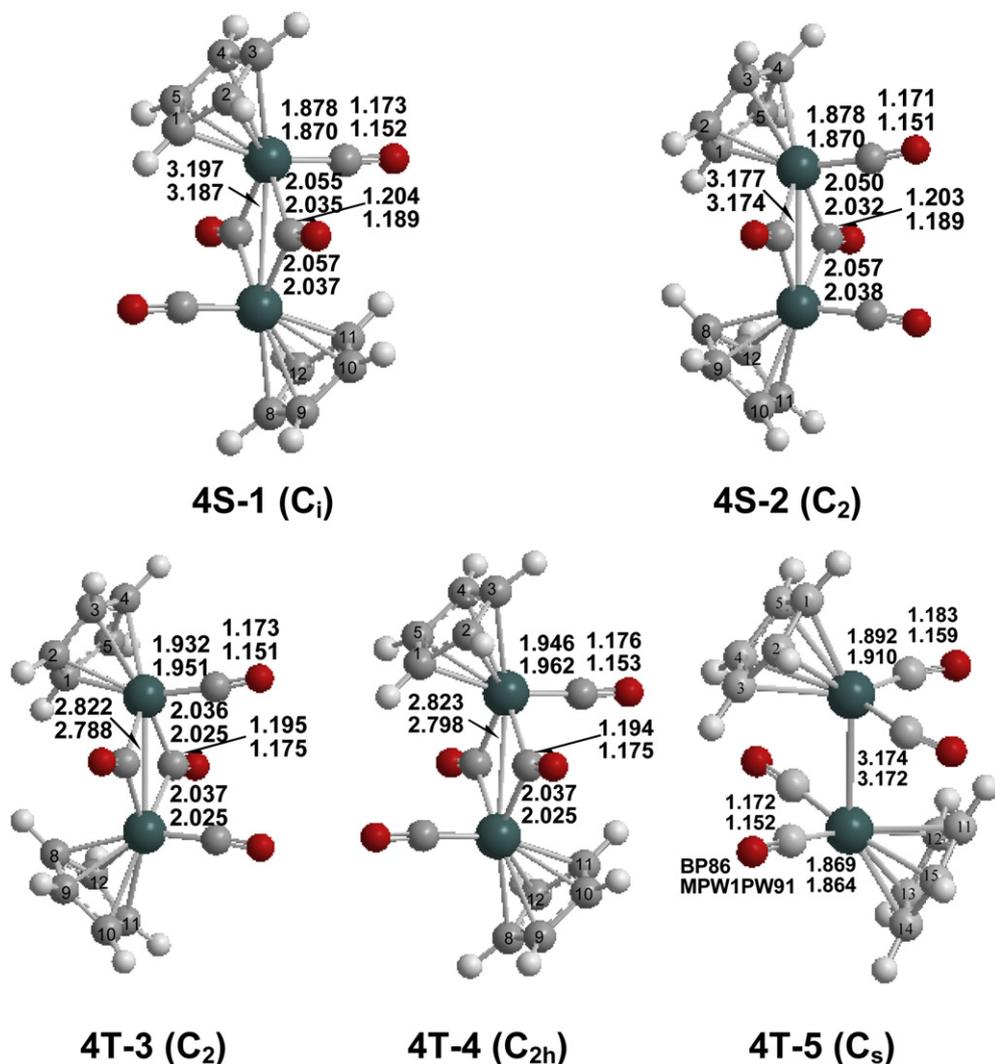


Fig. 2. The five optimized structures for $\text{Cp}_2\text{Rh}_2(\text{CO})_4$.

3. Results

3.1. $\text{Cp}_2\text{Rh}_2(\text{CO})_4$

Five structures were found for $\text{Cp}_2\text{Rh}_2(\text{CO})_4$, namely two singlet structures and three triplet structures (Fig. 2 and Table 2 and S1). The C_i doubly bridged *trans* structure **4S-1** is the global minimum with all real vibrational frequencies. The C_2 doubly bridged *cis* structure **4S-2** is predicted to be a local minimum lying only 0.6–0.7 kcal/mol above this global minimum. The Rh···Rh distance in **4S-1** is 3.197 Å (BP86) or 3.187 Å (MPW1PW91), which is slightly longer than that in **4S-2** (3.177 Å by BP86, 3.174 Å by MPW1PW91). These relatively long Rh···Rh distances suggest the lack of

a rhodium–rhodium bond. The rhodium atoms in a binuclear $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ derivative have the favored 18-electron configurations in the absence of a rhodium–rhodium bond.

The triplet C_2 doubly bridged $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ structure **4T-3** lies at the high energy of 18.8 kcal/mol (BP86) or 16.3 kcal/mol (MPW1PW91) above **4S-1**. The triplet C_{2h} doubly bridged $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ structure **4T-4** lies at a higher energy, namely 19.5 kcal/mol (BP86) or 16.3 kcal/mol (MPW1PW91) above **4S-1**. The Rh–Rh bond lengths in both **4T-3** and the **4T-4** are very similar, namely 2.822 Å (BP86) or 2.788 Å (MPW1PW91) in **4T-3** and 2.823 Å (BP86) or 2.798 Å (MPW1PW91) in **4T-4**. The third triplet C_s $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ structure **4T-5** lies at the relatively high energy of 24.5 kcal/mol (BP86) or 16.3 kcal/mol (MPW1PW91) above **4S-1**.

Table 2
Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), and numbers of imaginary vibrational frequencies (Nimg) for the $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ structures.

		4S-1 (C_i)	4S-2 (C_2)	4T-3 (C_2)	4T-4 (C_{2h})	4T-5 (C_s)
BP86	E	−1062.00891	−1062.00790	−1061.97866	−1061.97789	−1061.96999
	ΔE	0.0	0.6	18.8	19.5	24.5
	Nimg	0	0	0	1(10i)	0
MPW1PW91	Rh–Rh	3.197	3.177	2.822	2.823	3.174
	E	−1061.61246	−1061.61139	−1061.58689	−1061.58610	−1061.58673
	ΔE	0.0	0.7	16.3	16.3	16.3
	Nimg	0	0	0	0	0
	Rh–Rh	3.187	3.174	2.788	2.798	3.172

The Rh–Rh bonds in **4T-5**, namely 3.174 Å (BP86) or 3.172 Å (MPW1PW91), are very similar to that in **4S-2**.

3.2. $Cp_2Rh_2(CO)_3$

Two singlet and two triplet structures were found for $Cp_2Rh_2(CO)_3$ (Fig. 3 and Table 3 and S2). The C_2 singly bridged structure **3S-1** is the global minimum. The C_s doubly bridged singlet structure **3S-2** lies 6.2 kcal/mol (BP86) or 9.1 kcal/mol (MPW1PW91) in energy above **3S-1** with two imaginary vibrational frequencies (Table 4). Following the corresponding normal mode leads to **3S-1**. The Rh–Rh distances of 2.719 Å (BP86) or 2.691 Å (MPW1PW91) in **3S-1** and 2.718 Å (BP86) or 2.706 Å (MPW1PW91) in **3S-2** are consistent with the formal single bonds needed to give each rhodium atom the favored 18-electron configuration. X-ray crystallography [2] indicates that the known $Cp_2Rh_2(CO)_3$ has structure **3S-1** with an Rh–Rh distance of 2.68 Å in accord with our theoretical predictions.

The C_1 doubly bridged triplet $Cp_2Rh_2(CO)_3$ structure **3T-3** lies 28.2 kcal/mol (BP86) or 30.6 kcal/mol (MPW1PW91) above **3S-1** (Fig. 3 and Table 3). The Rh–Rh distance in this triplet structure is 2.722 Å (BP86) or 2.717 Å (MPW1PW91), which is slightly longer than that in **3S-1**. The C_1 singly bridged triplet $Cp_2Rh_2(CO)_3$ structure **3T-4** lies 33.3 kcal/mol (BP86) or 33.9 kcal/mol (MPW1PW91) in energy above **3S-1**. The Rh–Rh distance is 3.045 Å (BP86) or 3.021 Å (MPW1PW91) in **3T-4**, which is significantly longer than

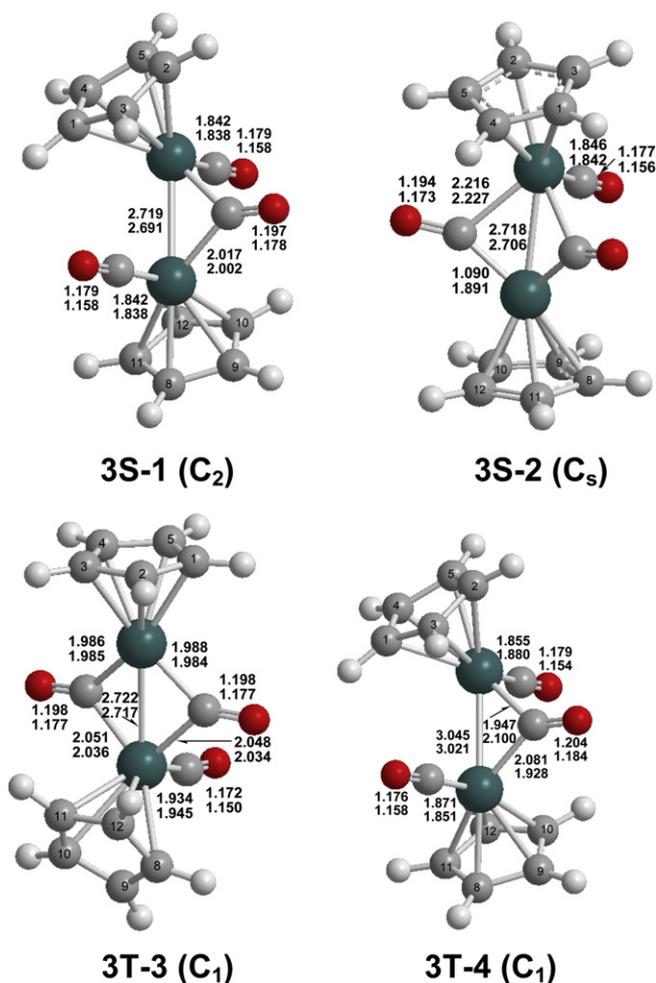


Fig. 3. Four optimized structures for $Cp_2Rh_2(CO)_3$.

Table 3

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), and numbers of imaginary vibrational frequencies (Nimg) for the $Cp_2Rh_2(CO)_3$ structures.

		3S-1 (C_2)	3S-2 (C_s)	3T-3 (C_1)	3T-4 (C_1)
BP86	E	−948.66990	−948.65995	−948.62498	−948.61668
	ΔE	0.0	6.2	28.2	33.3
	Nimg	0	2(28i,22i)	0	0
	Rh–Rh	2.719	2.718	2.722	3.045
MPW1PW91	E	−948.32094	−948.30644	−948.27213	−948.26737
	ΔE	0.0	9.1	30.6	33.9
	Nimg	0	2(86i,15i)	0	0
	Rh–Rh	2.691	2.706	2.717	3.021

that in **3S-1**. This may be the effect of two bridging carbonyl groups in **3T-3** but only one bridging carbonyl group in **3T-4**.

3.3. $Cp_2Rh_2(CO)_2$

Three doubly bridged structures were found for $Cp_2Rh_2(CO)_2$, namely one singlet and two triplets (Fig. 4 and Table 4 and S3). The C_2 singlet structure **2S-1** is the global minimum. The C_{2v} triplet $Cp_2Rh_2(CO)_2$ structure **2T-2** lies at a significantly higher energy, namely 21.3 kcal/mol (BP86) or 17.4 kcal/mol (MPW1PW91) above **2S-1**. The Rh=Rh bonds in both the singlet **2S-1** and the triplet **2T-2** are very similar, namely 2.595 Å (BP86) or 2.574 Å (MPW1PW91) for **2S-1** and 2.591 Å (BP86) or 2.584 Å (MPW1PW91) for **2T-2**. This predicted Rh=Rh distance for **2S-1** is close to the experimental value of 2.564 Å, found by X-ray crystallography [6] for the permethylated derivative $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Rh}_2(\mu\text{-CO})_2$. These distances correspond to formal double bonds thereby giving the rhodium atoms in both $Cp_2Rh_2(CO)_2$ structures the favored 18-electron configuration. In the singlet **2S-1** this Rh=Rh formal double bond is of the $\sigma + \pi$ type with a singlet two-electron π bond component in addition to the two-electron σ component. However, in the triplet **2T-2** this Rh=Rh formal double bond is of the $\sigma + {}^2_2\pi$ type with the two unpaired electrons of the triplet in two orthogonal π “half-bonds” similar to the O=O double bond in the normal (triplet) dioxygen. A similar $\sigma + {}^2_2\pi$ Fe=Fe double bond is found in the cyclopentadienyliron derivative $Cp_2Fe_2(\mu\text{-CO})_3$, which is stable enough for isolation and structure determination by X-ray crystallography [42–44].

Another triplet C_1 structure **2T-3** for $Cp_2Rh_2(CO)_2$ lies 22.6 kcal/mol (BP86) or 17.6 kcal/mol (MPW1PW91) above **2S-1**. In **2T-3** the Rh–Rh distance is 2.647 Å (BP86) or 2.651 Å (MPW1PW91), which is slightly longer than that in **2S-1**.

3.4. $Cp_2Rh_2(CO)$

One singlet and two triplet structures were found for $Cp_2Rh_2(CO)$ (Fig. 5 and Table 5 and S4). The global minimum is a C_1

Table 4

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), and numbers of imaginary vibrational frequencies (Nimg) for the $Cp_2Rh_2(CO)_2$ structures.

		2S-1 (C_2)	2T-2 (C_{2v})	2T-3 (C_1)
BP86	E	−835.29724	−835.26322	−835.26124
	ΔE	0.0	21.3	22.6
	Nimg	0	0	0
	Rh–Rh	2.595	2.591	2.647
MPW1PW91	E	−834.97583	−834.94813	−834.94735
	ΔE	0.0	17.4	17.6
	Nimg	0	1(9i)	0
	Rh–Rh	2.574	2.584	2.651

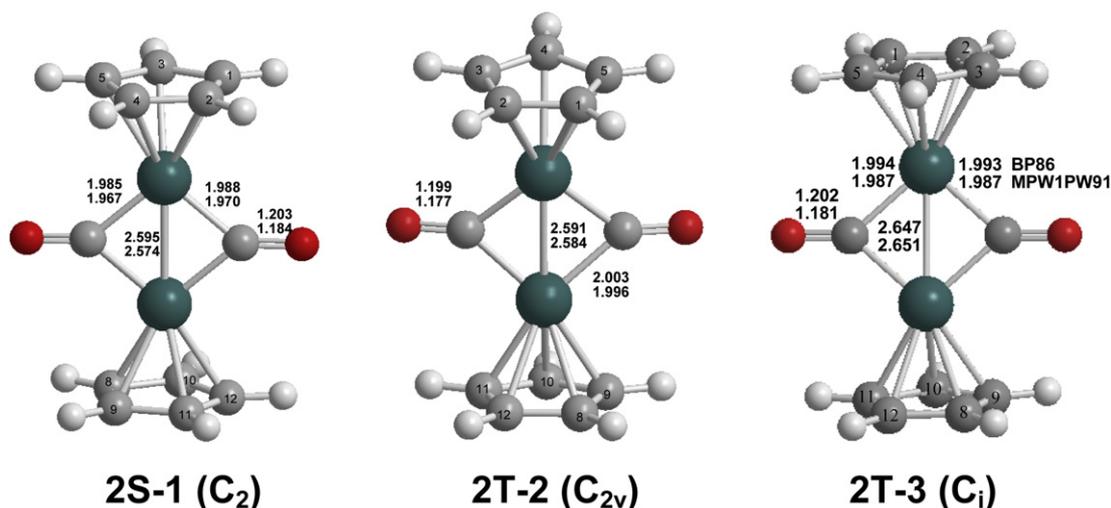


Fig. 4. The three optimized structures for $\text{Cp}_2\text{Rh}_2(\text{CO})_2$.

singly bridged structure **1S-1**. The bridging carbonyl in **1S-1** is a four-electron donor, which donates two σ electrons to one Rh atom and two π electrons to the other Rh atom. This four-electron donor bridging carbonyl group is characterized by a short Rh–O distance of 2.547 Å (BP86) or 2.485 Å (MPW1PW91) and a very low $\nu(\text{CO})$ frequency of 1753 cm^{-1} (Table 1). The Rh=Rh distance of 2.559 Å (BP86) or 2.522 Å (MPW1PW91) can be interpreted as the formal double bond required to give both rhodium atoms in **1S-1** the favored 18-electron configuration in a $\text{Cp}_2\text{Rh}_2(\text{CO})$ structure with a four-electron donor bridging carbonyl group.

The triplet $\text{Cp}_2\text{Rh}_2(\text{CO})$ structures (Fig. 5 and Table 5) are predicted to lie at higher energies than the singlet structure **1S-1** although the singlet–triplet separations for $\text{Cp}_2\text{Rh}_2(\text{CO})$ are predicted to be smaller than those for the more carbonyl rich species $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ ($n = 3, 2$). Thus structure **1T-2** lies 8.5 kcal/mol (BP86) or 1.6 kcal/mol (MPW1PW91) above **1S-1**. Similarly structure **1T-3** lies 15.2 kcal/mol (BP86) or 5.9 kcal/mol (MPW1PW91) above **1S-1**. Thus the two functionals MPW1PW91 and BP86 appear to predict

different triplet–singlet splittings for $\text{Cp}_2\text{Rh}_2(\text{CO})$. This is not surprising, since Reiher and coworkers [45] found in 2001 that the BP86 method always favors the low-spin state in a series of the first-row transition–metal complexes. In the $\text{Cp}_2\text{Rh}_2(\text{CO})$ structure **1T-2** the carbonyl group is a terminal carbonyl group, one Cp ring bridges both metal atoms, and the other Cp ring is bonded only to a single metal atom. The Rh=Rh distance of 2.569 Å (BP86) or 2.580 Å (MPW1PW91) in the triplet structure **1T-2** is very similar to that in the singlet structure **1S-1** and can likewise be interpreted as a formal double bond. This gives each rhodium atom in **1T-2** a 17-electron configuration for a binuclear triplet. In the triplet $\text{Cp}_2\text{Rh}_2(\text{CO})$ structure **1T-3** the carbonyl group is a four-electron donor bridging η^2 - μ -CO group as indicated by a short Rh–O distance of 2.383 Å (BP86) or 2.370 Å (MPW1PW91) and a very low $\nu(\text{CO})$ frequency of 1701 cm^{-1} (Table 1). The Rh–Rh distance of 2.729 Å (BP86) or 2.725 Å (MPW1PW91) is consistent with the formal single bond required to give each rhodium atom the 17 electron configuration for a binuclear triplet.

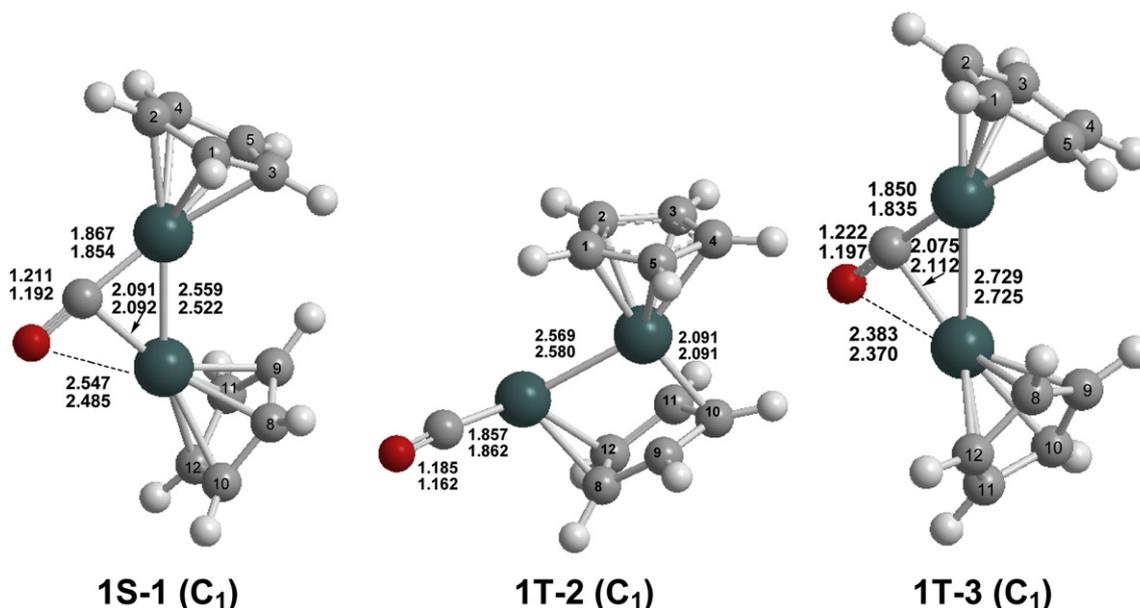


Fig. 5. The three optimized $\text{Cp}_2\text{Rh}_2(\text{CO})$ structures.

Table 5

Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the $\text{Cp}_2\text{Rh}_2(\text{CO})$ structures.

		1S-1 (C_1)	1T-2 (C_1)	1T-3 (C_1)
BP86	E	-721.84988	-721.83632	-721.82568
	ΔE	0.0	8.5	15.2
	Nimg	0	0	0
	Rh–Rh	2.559	2.569	2.729
MPW1PW91	E	-721.56426	-721.56172	-721.55486
	ΔE	0.0	1.6	5.9
	Nimg	0	0	0
	Rh–Rh	2.522	2.580	2.725

3.5. NBO analysis

Table 6 lists the Mulliken's populations and natural charges for the rhodium atoms as well as the Wiberg bond indices obtained by NBO analysis [46] for the rhodium atoms in the lowest energy $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) structures. The natural charges appear to be affected both by the number of carbonyl groups and the presence or absence of formal Rh–Rh bonding and typically fall in the range +0.10 to 0.22. An exception is the more positive formal charge of ~ 0.3 for the rhodium atom within bonding distance of the carbonyl oxygen of the $\eta^2\text{-}\mu\text{-CO}$ group. The $\text{Rh}^{\delta+} - \text{O}^{\delta-}$ polarization of this rhodium–oxygen bonding appears to be responsible for this higher positive natural charge.

The Wiberg bond index (WBI) for the formal Rh–Rh single bond in the lowest energy $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ structure **3S-1** is ~ 0.25 (Table 5) which is in a typical range for metal–metal single bonds [47]. The WBI of the formal Rh=Rh double bond in the $\text{Cp}_2\text{Rh}_2(\eta^2\text{-}\mu\text{-CO})$ structure **1S-1** is approximately twice this value at ~ 0.6 . However, the WBI of ~ 0.35 for the formal Rh=Rh double bond in the lowest energy $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ structure **2S-1** is significantly lower than that of the Rh=Rh double bond in **1S-1**. However, the two bridging carbonyl groups in **2S-1** can lower the effective Rh–Rh bond order by three-center bonding as suggested by Ponc and collaborators [48] for species such as $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$. The WBI of ~ 0.13 in the $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ structure **4S-1** indicates some residual rhodium–rhodium interaction in this species in the absence of formal metal–metal bonding. This weak interaction necessarily must involve the bridging carbonyl groups.

3.6. Dissociation energies

Table 7 summarizes the energies for successive carbonyl loss from the binuclear rhodium carbonyl derivatives $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$; Cp = $\eta^5\text{C}_5\text{H}_5$) considering the lowest energy structures. The carbonyl dissociation energy from $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ (**4S-1**) to give $\text{Cp}_2\text{Rh}_2(\text{CO})_3 + \text{CO}$ is very low at 6.0 kcal/mol (BP86) or -3.8 kcal/mol (MPW1PW91) suggesting that $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ is unstable with respect

to carbonyl loss. The energy for formation of the Rh–Rh bond in **3S-1** is undoubtedly a driving force for this reaction. The carbonyl dissociation energy of $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ to give $\text{Cp}_2\text{Rh}_2(\text{CO})_2 + \text{CO}$ is significantly higher at 26.3 kcal/mol (BP86) or 29.3 kcal/mol (MPW1PW91). This is in a typical range for stable metal carbonyl derivatives as indicated by the experimental carbonyl dissociation energies [49] for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively. The carbonyl dissociation energy of $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ to give $\text{Cp}_2\text{Rh}_2(\text{CO}) + \text{CO}$ is considerably higher at 72.2 kcal/mol (BP86) or 70.0 kcal/mol (MPW1PW91).

The disproportionation reactions $\text{Cp}_2\text{Rh}_2(\text{CO})_n \rightarrow \text{Cp}_2\text{Rh}_2(\text{CO})_{n+1} + \text{Cp}_2\text{Rh}_2(\text{CO})_{n-1}$ ($n = 3, 2$) are shown to be endothermic (Table 6) at 20.4 kcal/mol (BP86) or 33.1 kcal/mol (MPW1PW91) for $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ (**3S-1**) and 45.9 kcal/mol (BP86) or 40.7 kcal/mol (MPW1PW91) for $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ (**2S-1**). This is consistent with the fact that both $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ and $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ are stable compounds.

The energies for dissociation of the lowest energy $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ structures into mononuclear fragments were also investigated (Table 6). The dissociations of the stable compounds $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ (**3S-1**) and $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ (**2S-1**) are shown to be highly endothermic requiring >40 kcal/mol. However, the dissociation of $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ (**4S-1**) into two $\text{CpRh}(\text{CO})_2$ is exothermic at -8.3 kcal/mol (BP86) or -18.2 kcal/mol (MPW1PW91). This is consistent with the stability of the 18-electron complex $\text{CpRh}(\text{CO})_2$ and the requirement of a metal–metal bond for a stable binuclear carbonyl derivative of this type.

4. Discussion

Our previous studies on the cobalt derivative $\text{Cp}_2\text{Co}_2(\text{CO})_3$ suggest the existence of both singly and triply bridged structures even though only the singly bridged structure is known experimentally. For the analogous $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ the singly bridged structure **3S-1** (Fig. 2) is the lowest energy structure in accord with experiment. We were unable to optimize a triply bridged $\text{Cp}_2\text{Rh}_2(\mu\text{-CO})_3$ structure using either the BP86 or MPW1PW91 methods. Doubly bridged higher energy singlet and triplet $\text{Cp}_2\text{Rh}(\text{CO})(\mu\text{-CO})_2$ structures were also found (**3S-1** and **3T-3** in Fig. 2) without any cobalt analogues in the previous work. The tendency of the heavier transition metal carbonyls to favor structures with fewer bridging carbonyl groups is also noted in the series $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}$ [50,51], Ru [52], Os [53,54]) and $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co}$ [55], Rh [56], Ir [57]).

The dicarbonyls $\text{Cp}_2\text{M}_2(\text{CO})_2$ ($\text{M} = \text{Co}, \text{Rh}$) are shown to have analogous doubly bridged structures with $\text{M}=\text{M}$ distances shorter than those in the tricarbonyls $\text{Cp}_2\text{M}_2(\text{CO})_3$ indicative of the formal metal–metal double bonds required to give the metal atoms the favored 18-electron configuration (Fig. 3). For the monocarbonyls $\text{Cp}_2\text{M}_2(\text{CO})$ there is a significant difference between the lowest energy structures for cobalt and rhodium. The cobalt derivative $\text{Cp}_2\text{Co}_2(\mu\text{-CO})$ has a normal two-electron donor bridging carbonyl group with a predicted $\nu(\text{CO})$ frequency of 1870 cm^{-1} by the BP86

Table 6

Mulliken's population and natural charge for the rhodium atoms in the lowest energy $(\text{C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) structures.

		Mulliken's populations of the Rh atoms	Natural charges on the Rh atoms	Wiberg bond index for the Rh–Rh bond
$\text{Cp}_2\text{Rh}_2(\text{CO})_4$ 4S-1 (C_1)	MPW1PW91	0.054, 0.054	0.172, 0.172	0.14
	BP86	0.132, 0.132	0.147, 0.147	0.12
$\text{Cp}_2\text{Rh}_2(\text{CO})_3$ 3S-1 (C_2)	MPW1PW91	0.077, 0.077	0.138, 0.138	0.26
	BP86	0.123, 0.123	0.109, 0.109	0.25
$\text{Cp}_2\text{Rh}_2(\text{CO})_2$ 2S-1 (C_2)	MPW1PW91	0.104, 0.104	0.219, 0.219	0.35
	BP86	0.167, 0.167	0.216, 0.216	0.35
$\text{Cp}_2\text{Rh}_2(\text{CO})$ 1S-1 (C_1)	MPW1PW91	0.458, -0.255	0.149, 0.296	0.59
	BP86	0.511, -0.197	0.148, 0.322	0.60

Table 7
Energies and the relative free energies (kcal/mol) for carbonyl dissociation and disproportionation of $\text{Cp}_2\text{Rh}_2(\text{CO})_n$ derivatives after zero-point vibrational energy (ZPVE) corrections.

	Energies (ΔE)		Free energies (ΔG)	
	BP86	MPW1PW91	BP86	MPW1PW91
$\text{Cp}_2\text{Rh}_2(\text{CO})_4(\mathbf{4S-1}) \rightarrow \text{Cp}_2\text{Rh}_2(\text{CO})_3(\mathbf{3S-1}) + \text{CO}$	6.0	-3.8	-3.2	-12.9
$\text{Cp}_2\text{Rh}_2(\text{CO})_3(\mathbf{3S-1}) \rightarrow \text{Cp}_2\text{Rh}_2(\text{CO})_2(\mathbf{2S-1}) + \text{CO}$	26.3	29.3	16.4	19.1
$\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mathbf{2S-1}) \rightarrow \text{Cp}_2\text{Rh}_2(\text{CO})(\mathbf{1S-1}) + \text{CO}$	72.2	70.0	60.6	58.5
$2\text{Cp}_2\text{Rh}_2(\text{CO})_3(\mathbf{3S-1}) \rightarrow \text{Cp}_2\text{Rh}_2(\text{CO})_4(\mathbf{4S-1}) + \text{Cp}_2\text{Rh}_2(\text{CO})_2(\mathbf{2S-1})$	20.4	33.1	19.7	32.0
$2\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mathbf{2S-1}) \rightarrow \text{Cp}_2\text{Rh}_2(\text{CO})_3(\mathbf{3S-1}) + \text{Cp}_2\text{Rh}_2(\text{CO})(\mathbf{1S-1})$	45.9	40.7	44.2	39.3
$\text{Cp}_2\text{Rh}_2(\text{CO})_4(\mathbf{4S-1}) \rightarrow 2\text{CpRh}(\text{CO})_2$	-8.3	-18.2	-18.9	-33.8
$\text{Cp}_2\text{Rh}_2(\text{CO})_3(\mathbf{3S-1}) \rightarrow \text{CpRh}(\text{CO})_2 + \text{CpRh}(\text{CO})$	45.7	42.0	32.9	26.6
$\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mathbf{2S-1}) \rightarrow 2\text{CpRh}(\text{CO})$	79.5	69.5	65.0	55.0

method. The very short $\text{Co}\equiv\text{Co}$ distance of ~ 2.0 Å in $\text{Cp}_2\text{Co}_2(\mu\text{-CO})$ suggests the formal triple bond required to give both cobalt atoms the favored 18-electron configuration. However, the lowest energy structure of the rhodium derivative $\text{Cp}_2\text{Rh}_2(\text{CO})$, namely **1S-1** has a four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ group as indicated by a short Rh–O distance of ~ 2.38 Å (Fig. 5) and a much lower predicted $\nu(\text{CO})$ frequency of 1753 cm^{-1} by BP86. The Rh–Rh distance of ~ 2.54 Å in $\text{Cp}_2\text{Rh}_2(\eta^2\text{-}\mu\text{-CO})$ (**1S-1**) is much longer than the $\text{Co}\equiv\text{Co}$ distance in $\text{Cp}_2\text{Co}_2(\mu\text{-CO})$, even after allowing for the larger size of rhodium relative to cobalt. This is consistent with the fact that in $\text{Cp}_2\text{Rh}_2(\eta^2\text{-}\mu\text{-CO})$ (**1S-1**) with a four-electron donor bridging carbonyl group, only a formal double bond rather than a formal triple bond is required to give both rhodium atoms the favored 18-electron configuration.

The tetracarbonyl $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ was also investigated in order to investigate the prospects of synthesizing a stable binuclear derivative without direct rhodium–rhodium bonding. Furthermore, $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ was originally claimed to be formed upon exposure of $\text{CpRh}(\text{CO})_2$ to air in a paper published in 1961 [58], almost immediately after the original report [1] of $\text{CpRh}(\text{CO})_2$ that same year. At that early date metal–metal bonding in binuclear metal carbonyls was still very poorly understood since the first example of an unambiguous direct metal–metal bond in a binuclear metal carbonyl characterized by an X-ray structure determination, i. e., the Re–Re bond in $\text{Re}_2(\text{CO})_{10}$, was only reported only four years earlier in 1957 [59]. This purported $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ was later shown [60] to be the $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu\text{-CO})$ discussed elsewhere in this paper. We find *trans* and *cis* doubly bridged structures for $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ with C_i and C_2 point group symmetries, respectively (Fig. 2) lying within 1 kcal/mol of each other (Table 2). The predicted Rh...Rh distances of ~ 3.2 Å in these structures are ~ 0.5 Å longer than any of the Rh–Rh single bond distances in $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ and thus can indicate the lack of formal metal–metal bonding in the $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ structures. The following observations predict $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ to be thermodynamically disfavored:

- (1) The essentially thermoneutral dissociation of a carbonyl group from $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ to give $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ (Table 7).
- (2) The exothermic fragmentation of $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ into two $\text{CpRh}(\text{CO})_2$ fragments by 8.3 kcal/mol (BP86) or -18.2 kcal/mol (MPW1PW91).

For these reasons it is not surprising that the binuclear decomposition product of $\text{CpRh}(\text{CO})_2$ is $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ rather than $\text{Cp}_2\text{Rh}_2(\text{CO})_4$ [60].

Acknowledgment

This work was supported by the U. S. National Science Foundation (Grant CHE-0716718).

Appendix. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.02.006.

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