

Selected Paper

Theoretical Study of the Formation of a Benzene Cobalt Complex from Cobaltacyclopentadiene and Acetylene

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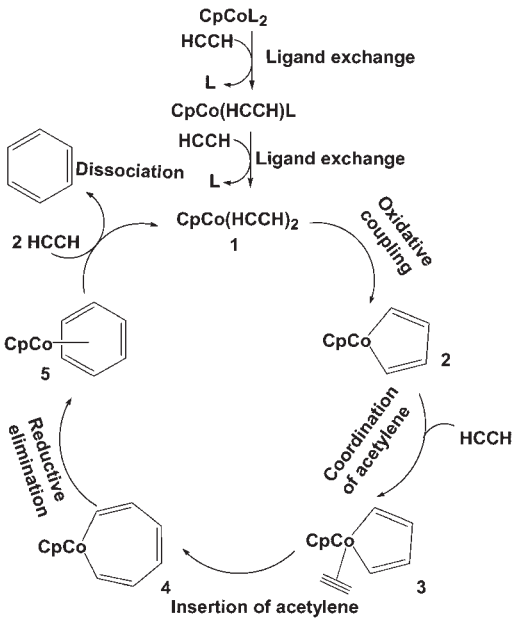
With the B3LYP theoretical method, the reaction of cobaltacyclopentadiene complex with acetylene in singlet and triplet states leading to benzene cobalt complex was studied in detail. In the most favorable path in the singlet state, an acetylene molecule attacks cobaltacyclopentadiene from the side, where the vacant d orbital extends over, so that [4 + 2] cycloaddition gives a η^4-benzene complex without any activation energy, called the collapse mechanism. The reaction in the triplet state passes through a single transition state with an activation barrier of 14.1 kcal/mol, leading to the η^6-benzene complex. The reactant of cobaltacyclopentadiene and the product of the benzene complex in the triplet state are more stable than those in the singlet state, whereas a substantial activation energy is required in the triplet state, suggesting that the spin may change during the reaction. Calculations of the crossing points between the singlet and triplet states showed that in the most favorable reaction path, the spin changes to the singlet state before passing through the triplet transition state, and that the collapse mechanism in the singlet state is followed. The energy required to lead to the crossing point for this spin change was calculated to be 7.0 kcal/mol, which is lower than the activation barrier.

The thermal trimerization of acetylene to benzene is a highly exothermic process, as confirmed in experimental (−142 kcal/mol) and theoretical (−145, −152 kcal/mol) studies.[1,2] However, this reaction is not feasible, because it requires a very high energy barrier of around 80 kcal/mol,[2,3] meaning that it apparently has no synthetic utility. On the other hand, a transition metal-catalyzed cyclization of alkynes is considered to be an alternate way for the synthesis of functionalized benzene derivatives.[4] The first such reaction was reported in the classic work by Reppe et al.,[5] in which the oligomerization of alkyne giving predominantly cyclooctatetraene and the cyclotrimerization of acetylene giving benzene in the presence of nickel catalyst were described.

Subsequent studies in this area have found that metallacyclopentadiene-based complexes are very important intermediates in the transition-metal-catalyzed oligomerization of alkynes,[4,6] especially in the synthesis of aromatic benzenoid systems and heterocyclic compounds. A wide variety of such catalysts with Co, Ru, Pd, Ni, Ti, Ir, Zr, and Rh atoms have been reported by experimentalists.[5–7] Among them, appropriately ligated $CpCoL_2$ type Co(I) systems (most commonly used L is olefins, CO, and PR_3) were found to be the most effective catalysts for a number of highly useful reactions, such as the synthesis of a variety of natural products, functionalized pyridines, and benzocyclobutenes.[7–11]

Several experimental mechanistic investigations on CpCo-catalyzed alkyne trimerization have led to the proposed mechanism in Scheme 1, which is described in a review written by Schore more than a decade ago.[11] In this mechanism, the formations of cobaltacyclopentadiene **2** and cobaltacycloheptatriene **4** intermediates were considered as key steps.



Scheme 1. Proposed mechanism by Schore.

In a recent review by Yamamoto et al., a mechanism similar to the Schore mechanism is discussed, in which the acetylene [4 + 2] cycloaddition to cobaltacyclopentadiene or acetylene insertion into the Co–C_α bond of cobaltacyclopentadiene takes place to finally give a benzene complex.[7a]

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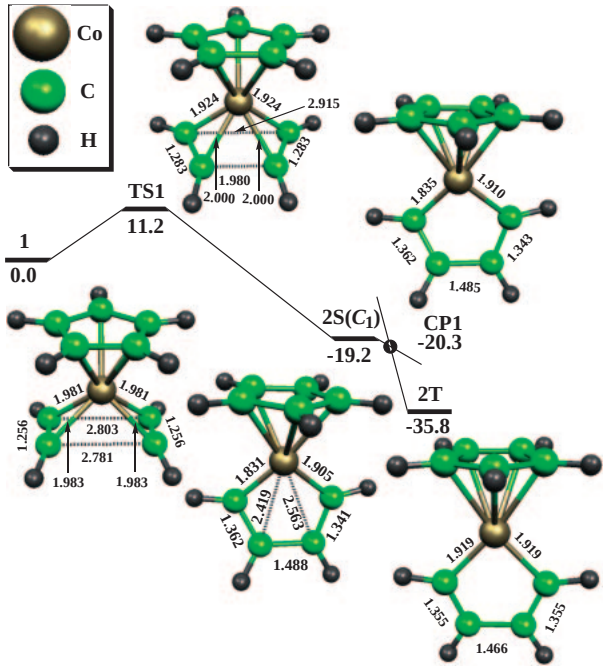
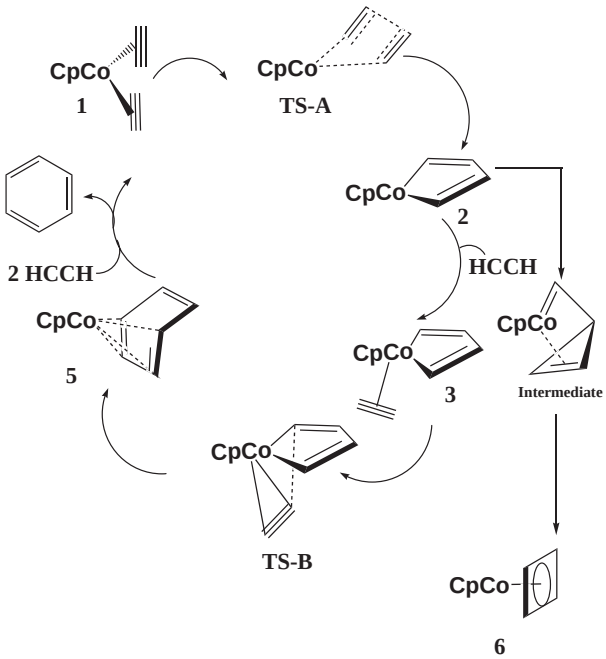


Fig. 1. Reaction profile for the oxidative coupling of acetylene ligands.[14] Energies are zero-point energy (ZPE) corrected and relative to **1** in kcal/mol. The energy of **2S** is that calculated by the approximately spin-projected UB3LYP method. All bond lengths are in Å.



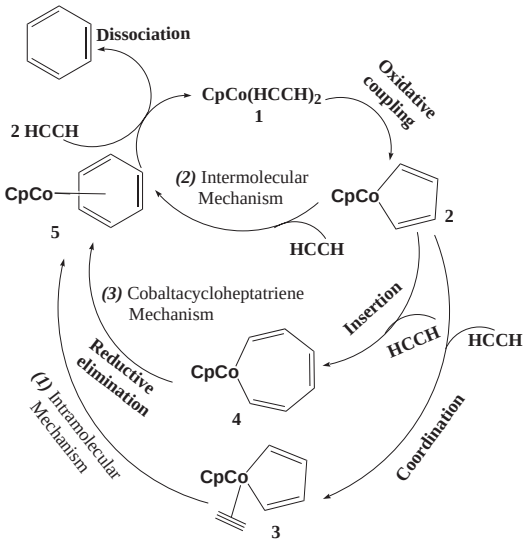
Scheme 2. Calculated mechanism by Hardesty et al.[13] **TS-A** and the intermediate between **2** and **6** were postulated by Wakatsuki et al. and Vollhardt et al., respectively.[13,15]

The oxidative coupling of **1** to give cobaltacyclopentadiene, **2**, has been theoretically discussed in detail.[12–14] First, Wakatsuki et al. studied this oxidative coupling with a partial geometry optimization technique at the Hartree–Fock (HF) level with small basis sets.[12] They found that this transformation is endothermic by 14.0 kcal/mol, and postulated the transition-state structure based on a symmetry argument that this is symmetry-allowed. Second, Hardesty et al. discussed the same transformation in detail based on the B3LYP method.[13] They found that this step is exothermic by −13.1 kcal/mol with an activation energy of 12.8 kcal/mol, a small activation energy expected for a symmetry-allowed reaction. More recently, we have studied the same transformation with the B3LYP method using a better basis set in more detail.[14] We found, as shown in Fig. 1, that the exothermicity for this step (19.2 kcal/mol) is larger than that obtained by Hardesty et al., while a similar activation energy of 11.2 kcal/mol was obtained. Different from the other theoretical studies, we found that cobaltacyclopentadiene in a closed-shell singlet state, **2S**, has C_1 symmetry with different Co–C_α bond distances due to the second-order Jahn–Teller effect. The ground state was found to be a triplet state. The optimized structure in the triplet state is **2T** in Fig. 1, which is C_s symmetric and 16.6 kcal/mol more stable than **2S**. The conversion of **2S** to **2T** is possible through the energy minimum crossing point between the singlet and triplet states, **CP1**, in Fig. 1. The calculations showed that **CP1** is close to **2S** in energy and structure, suggesting an easy conversion. In addition, we analyzed the origin of regioselectivity in the oxidative coupling to find that the site preference of substituents in the diene fragment is an important factor concerning the selectivity.[14]

Continuing a study of a **1** to **2** transformation, Hardesty et al. further studied the succeeding reaction steps in the singlet state for the trimerization of acetylene catalyzed by CpCo. They located the transition state **TS-B** for the formation of the η^4-benzene complex **5** from the acetylene-coordinated cobaltacyclopentadiene, **3** (cf. Scheme 2). The activation energy for this reaction was only 0.5 kcal/mol, because it is a symmetry-allowed intramolecular [4 + 2] cycloaddition, associated with a large thermodynamic driving force, releasing an energy of 81.4 kcal/mol. Hardesty et al. also discussed the possibility of the formation of a cyclobutadiene complex (**6**) via an intermediate precursor molecule (cf. Scheme 2), as suggested by Vollhardt et al.[15] Although **6** was 34.0 kcal/mol more stable than **2**, they did not find any role of **6** in the formation of **5**. As a result, they concluded that the reaction mechanism of benzene complex formation is an intramolecular [4 + 2] cycloaddition through **3**.

Meanwhile, they were unable to locate the cobaltacycloheptatriene intermediate **4** described by Schore,[11] and therefore have not performed calculations for the reaction path from **4** to **5**. Instead, they simply ruled out this possibility because it is symmetry-forbidden. Recent theoretical studies on the trimerization of acetylene in the presence of CpRuCl catalyst by Kirchner et al.[16] and Yamamoto et al.[17] showed that it adopts a path through ruthenacycloheptatetraene or an intramolecular [4 + 2] cycloaddition path, and that the first path is more favorable, suggesting that the reaction path through cobaltacycloheptatriene cannot be negligible. Also, the intermolecular mechanism has been untouched by Hardesty et al., although it is symmetry-allowed, as it was found previously.[18]

It is important to clarify the true nature of the Schore's mechanism, because it was not satisfactorily done in previous theoretical studies, as shown above. In addition, since the



Scheme 3. Investigated mechanisms in this study.

ground state of cobaltacyclopentadiene is in a triplet state,[14] we have to study the triplet reaction mechanism for the formation of a benzene cobalt complex from cobaltacyclopentadiene and acetylene. Also, we will discuss whether the conclusive mechanism is a single-state reactivity (adiabatic) or a two-state reactivity (non-adiabatic) mechanism. The former takes place via one potential-energy surface, while the latter takes place via more than one potential surface crossing at some points. One of the known examples for non-adiabatic reactions is dissociation of the CO ligand from $HCo(CO)_4$ catalysts.[19]

In the present work, we therefore performed a more detailed and quantitative work on this problem at a restricted and unrestricted density functional theory level using a better basis set. The possible mechanisms in Scheme 3, starting from complex **2**, according to the previous experimental and theoretical studies, are the target of the present investigation.[7a,11,13,20–23]

In the first path (intramolecular [4 + 2] cycloaddition) through the acetylene complex, **3**, cycloaddition between coordinating acetylene and cobaltacyclopentadiene takes place to lead to the benzene complex, **5**. In the second path (intermolecular [4 + 2] cycloaddition), no intermediate is passed during [4 + 2] cycloaddition. In the third path, acetylene insertion into the Co–C_α bond gives a cobaltacycloheptatriene intermediate, **4**, followed by a reductive elimination of benzene.

Computational Methods

All of the molecular geometries were optimized at the density functional theory (DFT) level using the B3LYP hybrid functional with the Gaussian 98 suite of programs.[24] The B3LYP method takes the electron correlation effects into account, since it consists of Becke's three-parameter hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr.[25,26] For all the atoms, the all-electron split valence basis set 6-31G** is used, which contains polarization functions on heavy atoms and on hydrogen atoms.[27,28] In other words, the B3LYP/6-31G** level of theory used in this work is a reasonable method for obtaining reliable geometries. Normal coordinate analysis has been performed for all stationary points to characterize the transition states (TSs) and equilibrium structures. Therefore, the energy minimum structures reported in this paper show positive eigenvalues of the Hessian matrix, whereas TSs have one negative eigenvalue. Intrinsic reaction coordinate (IRC) calculations[29] near the TS region, followed by geometry optimization of both reactants and products, were performed for all of the reactions to confirm the connectivity of the TS. Unscaled vibrational frequencies were used to calculate a zero-point energy (ZPE) correction to the total energy. Also, we determined the structures of the energy minimum crossing points between the singlet and triplet potential energy surfaces of the benzene complex with a constraint.[30] The vibrational analysis at this point was performed within the (3*N*-7)-dimensional hypersurface of the seam of crossing.[30]

The restricted Slater determinant wavefunctions for several transition states (**TS4**, **TS5**, and **TS6**) as well as cobaltacyclopentadiene **2** are not stable with respect to becoming unrestricted wavefunctions. In the case of **2**, single-point energy calculations by the approximately spin-projected, unrestricted B3LYP (UB3LYP) method at a restricted B3LYP (RB3LYP) structure were shown to give reliable results.[14] Therefore, we followed this procedure to calculate the energies of **TS4**, **TS5**, and **TS6** using the approximate spin-projection method by Yamaguchi et al.[31]

For a comparison, energy calculations using the B3PW91 and BPW91 levels, where the nonlocal correlation functional of Lee, Yang, and Parr is replaced by a nonlocal correlation functional of Perdew and Wang and Becke's three parameter hybrid exchange functional in the first is replaced by Becke's functional, which includes the Slater exchange along with corrections involving the gradient of the density, were performed for intermediates and transition states in the singlet state and cobaltacyclopentadiene and benzene complex in the triplet state.[32,33] In addition, energy calculations using the coupled cluster theory with the single and double substitutions (CCSD) were performed for the benzene complex in the singlet and triplet states.[34] The MOLEKEL program was used to draw all of the structures in Figs. 1–10.[35]

Results and Discussion

As stated in the introduction, the singlet and triplet states are accessible for **2**. Therefore, we separately present the results for the reactions from **2** in these two states.

1. Formation of a Benzene Co(I) Complex in the Singlet State. There are three possible reaction mechanisms for attacking an acetylene molecule to **2**, as suggested in Scheme 3. We first investigated these possibilities on a singlet potential energy surface.

1.1 Intramolecular [4 + 2] Cycloaddition: The LUMO of **2S** shown in Fig. 2 mainly consists of a vacant d orbital on the Co atom, and extends over an empty coordination site, called the front side. In the intramolecular [4 + 2] cycloaddition path, the most likely initial step toward the formation of a benzene complex is acetylene coordination from the front side by donating the π electrons to the LUMO. To investigate the possibility of acetylene coordination, we tried to determine the structure of the acetylene complex with (i) a parallel and (ii) a perpendicular orientation of acetylene with respect to the C_β–C_β bond of the pentagonal ring. However, the final geom-

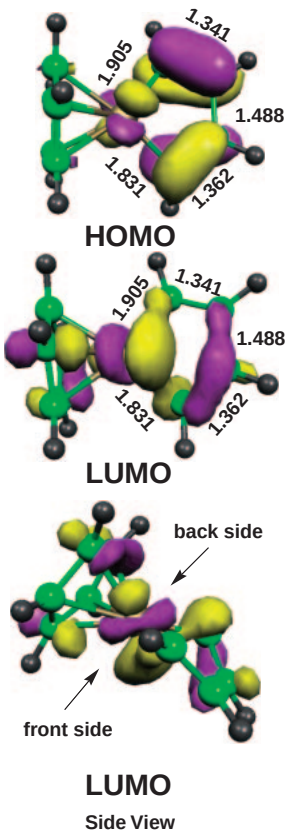


Fig. 2. The canonical molecular orbitals 45 (HOMO) and 46 (LUMO) for complex **2S**.

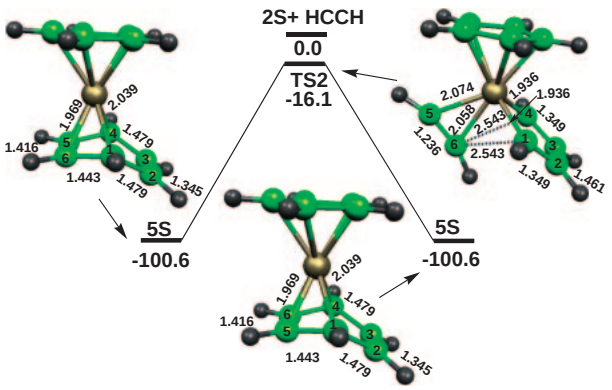


Fig. 3. Profile for the downhill [4 + 2] cycloaddition, a "collapse mechanism", of HCCH to **2S** to form η^4-benzene Co(I) complex **5S**. All energies are ZPE-corrected and relative to **2S** + HCCH in kcal/mol. All bond lengths are in Å.

etry that we obtained in the geometry determination was the η^4-benzene complex **5S** (Fig. 3) in both cases. A careful investigation of the intermediate structures during geometry optimizations showed that the formation of **5S** is [4 + 2] cycloaddition, as expected from the nodal properties of the HOMO and LUMO of **2S** in Fig. 2, and that the acetylene carbon atoms keep interactions with the Co atom as well as the diene moiety during benzene formation.

These results suggest that the reaction mechanism is downhill [4 + 2] cycloaddition, for which the transition state and the acetylene complex disappear, the former structure being more stable than the latter. In other words, the formation of **5S** can be considered as the result of a "collapse mechanism" involving **2S** and acetylene. As will be shown in 1.2, for the case of the intermolecular mechanism, there is a transition state without an interaction between the Co atom and acetylene, and a substantial activation energy of 11.3 kcal/mol was obtained, clearly demonstrating the role of the interaction between the Co atom and acetylene and that the front side of the $C_\alpha CoC_\alpha$ moiety is a very active reaction site. The importance of this interaction could account for the experimental facts that the added phosphine retards the rate of benzene formation.[23]

A transition state search starting from a structure with a perpendicular conformation gave us the transition state **TS2**, in which the acetylene molecule is only slightly deviated from free acetylene, as shown in Fig. 3. Therefore, the structure of **TS2** can be regarded as that of a perpendicular acetylene complex with a binding energy of 16.1 kcal/mol. Acetylene coordination in **TS2** raises the energy of LUMO to make the second-order Jahn–Teller distortion disappear. The reaction coordinate at **TS2** is the rotation of acetylene, and Fig. 3 shows that IRCs calculated starting from the **TS2** lead to **5S** as the reactant and product. This supports the above result that the reaction of **2S** with acetylene is downhill.

The path directly connecting **2S** + acetylene and **5S** could be the predominant path because it is downhill and a highly exothermic process liberating the energy of 100.6 kcal/mol. The high exothermicity of this reaction may be considered to be the main reason for the absence of the acetylene complex **3**. Further, previous studies[13,18] showed that the addition of acetylene to **2S** is a symmetry-allowed process, and therefore the spontaneous formation of **5S** is very much possible.

Hardesty et al. have obtained results supporting the intramolecular [4 + 2] cycloaddition mechanism through the acetylene complex **3** in Scheme 2.[13] According to our calculations, **3** does not exist, meaning that a transition state structure is more stable than the acetylene complex structure, and that the reaction path is changed from the intramolecular [4 + 2] cycloaddition mechanism to a collapse mechanism. Compared with our value of −100.6 kcal/mol, their calculations with a small basis set gave a smaller value of −81.4 kcal/mol for the exothermicity of the reaction. In the present study, the better basis set makes the reaction more exothermic, and consequently downhill.

The structure of **5S** is compared with that by the theoretical and related X-ray crystallography experimental studies in Table 1.[10d,13] Our results are in good agreement with the theoretical and experimental structures.

1.2 Intermolecular [4 + 2] Cycloaddition: We successfully determined the transition state **TS2a** for a reaction toward the η^4-benzene Co(I) complex **5S** without passing any intermediate, as shown in Fig. 4, while this possibility was not taken into account by Hardesty et al. The transition state **TS2a** with C1···C6 and C4···C5 distances of 2.479 Å is a transition state for attacking acetylene from the back side with the small lobe of the LUMO. **TS2a** has C_s symmetry. Starting from **TS2a**, two σ-bonds are formed simultaneously, a synchronous [4 + 2] cycloaddition. The activation energy of 11.3 kcal/mol

Table 1. Geometric Parameters for Selected Bonds in $CpCo(\eta^4\text{-}C_6H_6)$, **5S** in Å

Bond/Å	Theoretical (This study)	Theoretical[a)]	Experimental[b),c)]
Co–C_α	1.969	2.00	1.973(7)
Co–C_β	2.040	2.07	2.081(7)
C_α–$C_{\alpha'}$	1.416	1.42	1.431(9)
C_α–C_β	1.443	1.44	1.430(9)
C_β–C_γ	1.479	1.48	1.523(9)
C_γ–$C_{\gamma'}$	1.345	1.35	1.330(9)

a) Theoretical data are taken from reference 13. b) X-ray data are taken from reference 10d. c) Numbers in parentheses refer to the error in X-ray data.

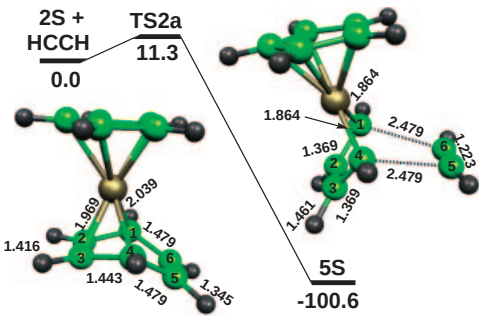


Fig. 4. Profile for the intermolecular [4 + 2] cycloaddition of HCCH to **2S** to form η^4-benzene Co(I) complex **5S**. All energies are ZPE-corrected and relative to **2S** + HCCH in kcal/mol. All bond lengths are in Å.

for this path is small, consistent with the finding that this reaction is symmetry-allowed.[18] It is, however, obviously less favorable than the collapse mechanism discussed in 1.1.

In **TS2a**, the distance between the Co atom and the acetylene carbon atoms is 3.456 Å, meaning that there is no interaction between them. Compared with the collapse mechanism just discussed in 1.1, one can notice that the interaction favors [4 + 2] cycloaddition in the collapse mechanism.

1.3 Mechanism via Cobaltacycloheptatriene: We obtained the two structures of cobaltacycloheptatriene, **4aS** and **4bS**, shown in Fig. 5. They are of C_s symmetry. In **4aS** the C_γ–C_γ bond of 1.383 Å is longer than the two C_α–C_β bonds of 1.339 Å, and one can observe the puckered geometry, suggesting that the C_γ–C_γ bond donates the π electrons to the Co atom. Therefore, **4aS** is described as an 18-electron system with the Co(III) atom. There is another cobaltacycloheptatriene, **4bS**, which has a planar structure. This is more stable than **4aS** by 13.7 kcal/mol. Through the formally vacant d orbital of the Co atom, the six π electrons of the cobaltacycloheptatriene ring in **4bS** can constitute an aromatic ring. The high stability of **4bS** compared to **4aS** may be ascribed to these delocalized π-electrons. As a matter of fact, the five CC bond distances in the seven-membered ring have almost the same bond lengths, and the Co–C_α bond distances of 1.823 Å are shorter than those of 1.886 Å in **4aS**. The nucleus-independent chemical-shift calculated at the center of seven-membered ring of **4bS** is −12.85, indicating the aromaticity of **4bS** compared with the value of −9.84 for benzene.

The α carbon atoms in **4aS**, (C1 and C6 in Fig. 5) separated

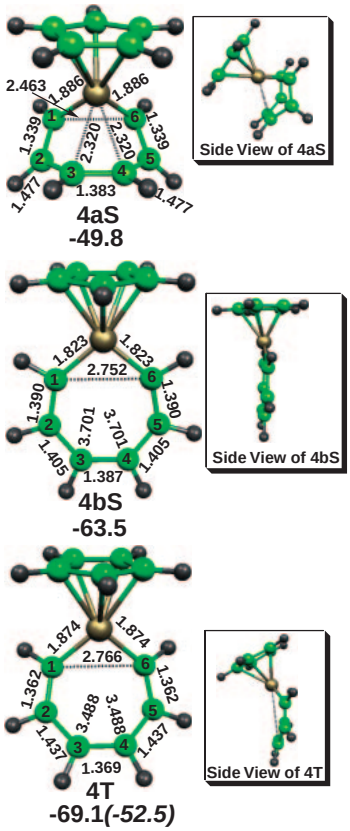


Fig. 5. Optimized structures for cobaltacycloheptatriene intermediates **4aS** and **4bS** in the singlet state and cobaltacycloheptatriene intermediate **4T** in the triplet state. All energies are ZPE-corrected and relative to **2S** + HCCH in kcal/mol. The energy in parenthesis for **4T** is ZPE-corrected and relative to **2T** + HCCH in kcal/mol. All bond lengths are in Å.

at a distance of 2.463 Å, are nicely placed for C–C bond formation through reductive elimination. The profile of this reductive elimination is shown in Fig. 6. The transition state for such a process is located as C_s symmetric **TS4**, which is 0.1 kcal/mol less stable than **4aS** at the restricted B3LYP level. However, **TS4** is more stable with the approximately spin-projected UB3LYP method, as shown in Fig. 6. The reaction coordinate at **TS4** is of a′ symmetry and corresponds to C1–C6 bond stretching. As a result, the C1–C6 distance in **TS4** is reduced to 2.342 Å, as compared to 2.463 Å in **4aS**. The calculations showed that the IRC from **TS4** leads to **TS5** as the product. The reaction coordinate at **TS5** is the rotation of the benzene ring, and it is of a″ symmetry to break the symmetry of the molecule. The IRC calculations from **TS5** in both direction lead to **5S**. This indicates that there is a bifurcation point of the reaction path between **TS4** and **TS5**.[36] In other words, the IRC is a ridge on the potential energy surface after the bifurcation point is passed. **TS5** can be regarded as the η^2-benzene complex with a longer coordinating C1–C6 bond and the localized C2–C3 and C4–C5 double bonds.

The profile in Fig. 6 shows that the direct reaction from **4aS** to **5S** needs the symmetry lowering during the reaction. This is because the reaction is symmetry-forbidden, as pointed out by Hardesty et al.[13] As a matter of fact, in the present calcula-

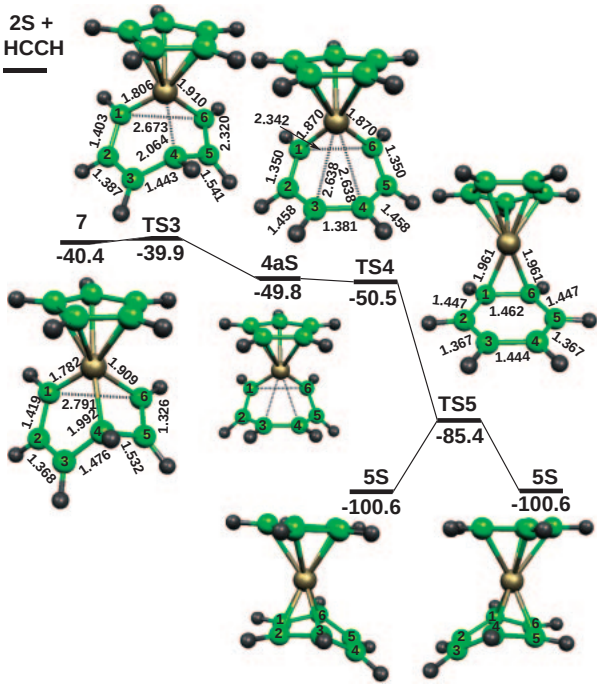


Fig. 6. Profile for the possible formation of η^4-benzene Co(I) complex **5S** via cobaltacycloheptatriene intermediate **4aS**. All energies are ZPE-corrected and relative to **2S** + HCCH in kcal/mol. All bond lengths are in Å.

tions, **4aS** as well as **TS4** and **TS5** has thirty two a′ and twenty a″ occupied orbitals, whereas **5S** has thirty three a′ and nineteen a″ occupied orbitals. This made Hardesty et al. exclude the possibility of the reaction through cobaltacycloheptatriene. However, there is an alternate, favorable path through **TS5**, as shown in Fig. 6. Note that, since there is a bifurcation point between **TS4** and **TS5**, **TS5** is not necessary passed.[37]

We did not find any reaction path of **4bS** to **5S**. This is presumably because aromatic stabilization in **4bS** would be lost during such a reaction.

The profile in Fig. 6 shows that, once cobaltacycloheptatriene **4aS** is formed, it changes to the benzene complex **5S** without any barrier. Thus, we next investigated the reaction path leading to **4aS**. Our calculations for locating the transition state for the reaction of **2S** + acetylene to **4aS** gave **TS3**, in which the reaction coordinate is mainly Co–C4 bond stretching, and **TS3** is the transition state between **4aS** and metallabicycle **7**, as shown in Fig. 6.

7 is cobaltabicyclo[3.2.0]heptatriene as shown in Chart 1. Therefore, **7** is an 18-electron species. The Co–C1 and C2–C3 bonds of the pentagonal ring in **7** are shorter than those of **2S**, suggesting their larger double-bond character. The four-membered ring of **7** imposes much strain in the system, and

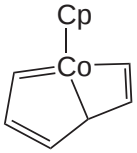


Chart 1.

therefore a rupture of the Co–C4 bond can easily occur. This is indeed true because **4aS** is easily formed from **7** through **TS3** by acquiring a small activation energy of 0.5 kcal/mol.

In the cases of a CpRuCl complex studied by Kirchner et al.[16] and Yamamoto et al.,[17] the transition state between a ruthenabicycle similar to **7** and a ruthenacyclopentadiene acetylene complex was located. Accordingly, although there was no acetylene complex in the present case, we tried to find the reaction path from **2S** + acetylene to **7**. We started geometry determinations of the transition state from various structures, but could not find any transition state. To obtain information on the potential-energy surface, we started equilibrium structure optimization from the structure determined by fixing the C4–C5 distance to be 2.282 Å and the Co–C4–C5 and C4–C5–C6 angles and Co–C4–C5–C6 dihedral angle to be those in **7**. The thus-obtained structure is that of **7**. When the initial structure was similarly determined by fixing the C4–C5 distance to be 2.532 Å, we obtained **5S**. The second result is consistent with the collapse mechanism discussed in the previous subsection. Also, no transition state was found directly connecting **7** and **5S**.

These results in addition to those shown in 1.1 indicate that there is a wide valley from **2S** + acetylene to **5S** on the potential energy surface, and that a narrow well for **7** is on the wall of that valley. When the acetylene molecule approaches **2S**, the bottom of the valley is followed so that **5S** is exclusively reached. Consequently, we concluded that there is no favorable reaction path for the Schore mechanism via the cobaltacycloheptatriene intermediate. A comparison with the reaction of the CpRuCl complex through the ruthenacyclopentadiene acetylene complex[16,17] suggests that, if an acetylene complex exists, a reaction path toward **7** might exist. However, in the present case, there is no acetylene complex and the [4 + 2] cycloaddition is very easy.

Single-point energy calculations for the intermediates and transition states in the singlet state were performed at the BPW91 and B3PW91 levels with the same basis set to verify the present B3LYP results. The results are given in Table 2 together with those for oxidative coupling.[14] Though the relative energies and activation barriers are qualitatively in agreement with those obtained by the B3LYP method, it should be noted that the results at the BPW91 level are significantly different from those at the B3LYP level, as well as at the B3PW91 level. It is obvious that the Hartree–Fock exchange absent in the BPW91 functional plays an important role.

In a summary of section 1, we have found that the reaction of cobaltacyclopentadiene with an acetylene molecule adopts the downhill [4 + 2] cycloaddition mechanism (collapse mechanism). The intermolecular [4 + 2] cycloaddition requires a substantial activation energy, whereas in the case of a reaction through cobaltacycloheptatriene there is no reaction path giving an important metallabicycle intermediate **7**.

2. Formation of Benzene Co(I) Complex in the Triplet State. 2.1 η^6-Benzene Co(I) Complex: The optimized structure of the triplet benzene Co(I) complex is η^6-benzene Co(I) complex **5T**, shown in Fig. 7. **5T** is more stable than **2S** + acetylene and **2T** + acetylene by 114.0 and 97.4 kcal/mol, respectively. This high stability is ascribed to the formation of two new σ-bonds between the carbons of acetylene and

Table 2. Relative Energies of Equilibrium Structures and Transition States for Oxidative Coupling of **1** and the Reaction of **2S** with Acetylene in kcal/mol

	B3LYP	BPW91	B3PW91
Oxidative coupling of **1**			
1	0.0	0.0	0.0
TS1	11.2	6.2	9.4
2S	−19.2	−17.0	−18.0
2T	−35.7	−21.4	−34.1
Reaction of **2S** with acetylene			
2S + acetylene	0.0	0.0	0.0
TS2	−16.1	−21.4	−20.9
TS2a	11.3	5.0	7.8
7	−40.4	−51.7	−47.6
TS3	−39.9	−47.0	−46.3
4aS	−49.8	−53.3	−55.3
TS4	−49.7	−50.4	−55.2
TS5	−82.7	−82.1	−90.3
5S	−100.6	−98.4	−112.2
5T	−114.0	−104.9	−123.4

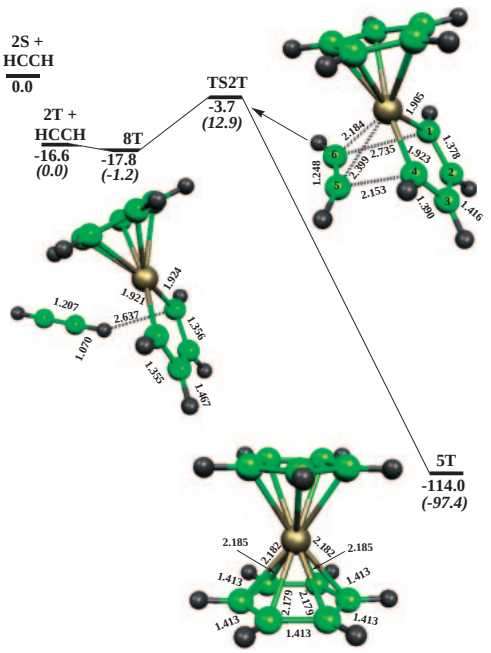


Fig. 7. Profile for the reaction of cobaltacyclopentadiene **2T** with HCCH to form η^6-benzene Co(I) complex **5T**. All energies are ZPE-corrected and relative to **2S** + HCCH in kcal/mol. The energies in parentheses are ZPE-corrected and relative to **2T** + HCCH in kcal/mol. All bond lengths are in Å.

the α-carbons of the cobaltacyclopentadiene ring in **2T** and that of the stable, planar benzene molecule on the Co atom (vide infra). All of the bond lengths in the benzene ring are equal to 1.413 Å, and the six Co–$C_{benzene}$ distances are 2.179–2.185 Å, indicating that **5T** has a sandwich geometry of (η^5-C_5H_5)Co(η^6-C_6H_6). These Co–$C_{benzene}$ distances are longer than those in **5S**, indicating that the coordination of the benzene ligand in **5T** is weaker than that in **5S**. Similarly, the coordination of the Cp ligand with bond lengths of 2.254–2.255 Å is weaker than that in **5S**. While **5S** is an 18-electron η^4-benzene complex, the η^6-benzene complex **5T** is a 20-electron complex. The orbitals singly occupied by the two extra electrons in **5T**, shown in Fig. 8, are antibonding between the Co atom and the benzene and Cp ligands. This explains the weaker coordination of these ligands. These orbitals also show that the singly occupied e_1 orbitals of triplet CpCo interact with the doubly occupied e_{1g} orbitals of benzene, which keeping the six CC bond distances in benzene almost the same.

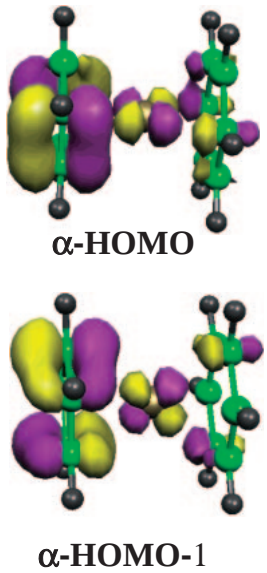


Fig. 8. The α-spin canonical molecular orbitals HOMO and HOMO–1 in η^6-benzene Co(I) complex **5T**.

The results given in Figs. 6 and 7 show that the triplet η^6-benzene complex **5T** is 13.4 kcal/mol more stable than the singlet η^4-benzene complex **5S**. The single-point energy calculations for these complexes at the BPW91 and B3PW91 levels (Table 2) and the CCSD level showed that **5S** is less stable than **5T** by 6.5, 11.2, and 10.8 kcal/mol, respectively, supporting the result by the B3LYP calculations.

In order to analyze the origin of the stability of **5T**, we decomposed the CpCo–benzene binding energy into the deformation energies of the fragments and the interaction energy between the deformed fragments. Here, it is considered that the CpCo and benzene fragments are first deformed, and then the deformed fragments interact with each other. We used here the potential energies, because the ZPE correction cannot be calculated for the deformed fragments. The results are given in Table 3.

In **5S** the Co atom has a formally vacant d orbital to which a donation from benzene occurs. To facilitate this donation, the benzene fragment is greatly deformed. Accordingly, though this deformation of benzene requires a large energy of 45.8 kcal/mol, the resultant interaction (−124.6 kcal/mol) is strong. Compared with this, the interaction in **5T** is weaker, because all of the d orbitals of the Co atom are singly or doubly occupied, and the benzene molecule is deformed only slightly. As a result, the binding energy in **5S** is 23.4 kcal/mol larger than that in **5T**. However, this is not enough to make **5S** more stable, because for CpCo the singlet state is 35.6 kcal/mol less stable than the triplet state.

Table 3. The Energy Components of CpCo–Benzene Binding Energy in **5S** and **5T** in kcal/mol

	5S	5T
Deformation energy	51.6	14.3
CpCo	5.8	13.2
Benzene	45.8	1.1
Interaction energy	−124.6	−64.0
Binding energy[a)]	73.0	49.7

a) The negative of the sum of the deformation energy and the interaction energy.

2.2 Triplet State Mechanism: In this subsection, we discuss the reaction in the triplet state connecting cobaltacyclopentadiene **2T** and the η^6-benzene Co(I) complex **5T**. Because **2T** and **5T** are the ground states for the reactant and the product, respectively, the triplet state path for the formation of **5T** from **2T** and acetylene was investigated. The optimized structures of the reactant complex **8T** and the transition state **TS2T** with the ZPE-corrected energy profile for the reaction are shown in Fig. 7.

In this path, the acetylene molecule approaches **2T** to form the reactant complex **8T**, in which acetylene weakly interacts with **2T** with a small binding energy of 1.2 kcal/mol. Therefore, the structure of acetylene as well as that of complex **2T** are affected only little.

8T is transformed to **5T** through the transition state **TS2T**. This reaction requires a substantial activation energy of 14.1 kcal/mol, different from the downhill reaction in the singlet state. The reaction coordinate at **TS2T** is C4–C5 stretching. This results in reducing the distance of this newly formed bond to 2.153 Å in **TS2T**. Also, the Co···C6 distance of 2.184 Å suggests the interaction between the acetylene and the Co atom. These interactions between the acetylene molecule and cobaltacyclopentadiene elongate the Co–C4 bond, which is 0.018 Å longer than the Co–C1 bond, and the acetylene CC bond (1.248 Å).

The difference of 0.482 Å between the two newly formed C–C bond distances suggests that the reaction mechanism is not [4 + 2] cycloaddition. The IRC calculation showed that the structure change during the course of the reaction from **TS2T** to **5T** is similar to that found in the reaction from **7** to **TS5** in the singlet state; namely, the reaction passes through the structure in a way similar to **7** first, and then the Co–C4 bond is broken, followed by the formation of a new C1–C6 bond. This indicates that this reaction is a combined reaction of acetylene insertion into the Co–C_α bond and reductive elimination. There is no formally vacant d orbitals in **8T** as well as **2T**, prohibiting a strong symmetric interaction between acetylene and the $C_\alpha CoC_\alpha$ moiety.

We did not find in the triplet state any equilibrium structure similar to **7** in the singlet state. Geometry optimization in the triplet state starting from the singlet state structure of **7** led to **5T**. At the early stage of this geometry optimization, the Co–C4 bond is broken so as to lead to a structure similar to the cobaltacycloheptatriene complex, and in the later stage a new bond is formed between the α-carbons (C1 and C6) in cobaltacycloheptatriene ring to result in **5T**. This means that there is no bicycle structure in the triplet state, consistent with the structure changes during the course of the reaction from **TS2T** to **5T**.

In the triplet-state reaction, cobaltacycloheptatriene is not an equilibrium structure, but a structure passed through during the reaction from **8T** to **5T**. This cobaltacycloheptatriene structure might correspond to **4aS** on the reaction path from **7** to **5S**. Since there are two equilibrium structures of cobaltacycloheptatriene in the singlet state, as shown in 1.3, we try to locate the structure of a triplet cobaltacycloheptatriene similar to **4bS**. The thus-obtained structure is **4T**, which is shown in Fig. 5 along with its relative energy. Similar to the case of **4bS**, no reaction path for the formation of η^6-benzene Co(I) complex **5T** through **4T** was found.

4T is more stable than **4aS** and **4bS** by 19.3 and 5.6 kcal/mol, respectively. A comparison among these three structures showed that, while **4aS** is puckered and **4bS** is planar, **4T** is in between, as can be seen in the Co–C_γ distances of 2.230, 3.701, and 3.488 Å in **4aS**, **4bS**, and **4T**, respectively. In the Co–C_α bond distances of 1.823, 1.874, and 1.886 Å in **4bS**, **4T**, and **4aS**, respectively, one can find the order with **4T** being between **4aS** and **4bS**. The spin population on the Co atom in **4T** is +1.94, indicating that there is no formal vacant d orbital in **4T**. Therefore, conjugation including the Co atom is impossible, resulting in the larger bond alternation compared with **4bS**.

As shown for cobaltacyclopentadiene **2**, in which the triplet state is 16.6 kcal/mol more stable than the singlet state, the ground state of coordinatively unsaturated Co complexes could be in a triplet state. Another example is the case of $CpCo(CH_3)_2$, in which the triplet state is 20.0 kcal/mol more stable than the singlet state. Similarly, **4T** is more stable than **4aS** by 19.3 kcal/mol. The smaller difference in energy between **4T** and **4bS** is ascribed to the aromaticity in the latter.

3. Two-State Reactivity Mechanism (Non-adiabatic Mechanism). As shown in the previous chapters, singlet-state collapse [4 + 2] cycloaddition has no activation barrier, while the triplet state reaction requires an activation energy of 14.1 kcal/mol. Based on only these results, one may conclude that the former reaction is more favorable. However, the reactant **2S** + HCCH and the product **5S** are less stable than the corresponding triplet analogues. In previous studies on such cases, it was considered that there are two possible mechanisms: (i) In one case the spin state is conserved during the course of a reaction, such as a singlet or triplet-state mechanism here; this is called the single-state reactivity (SSR) mechanism. (ii) In the other case the spin changes during the course of the reaction, to follow the most favorable path. The second case is known as the two-state reactivity (TSR) mechanism, spin crossing mechanism, or non-adiabatic mechanism. Some examples are known for the second case, especially for unsaturated 3d and 4d transition metal complexes,[38] although the examples of 4d transition metals are fewer. Spin change is considered to take place through a minimum energy crossing point between two spin states.[34,39] This crossing point can be regarded as being a transition state in the two-state reactivity (non-adiabatic) mechanism. Searching for such crossing points between singlet and triplet states leads to three crossing points, **CP1** in Fig. 1 and **CP2** and **CP3** in Fig. 9.

Geometry optimizations from these points on the singlet and

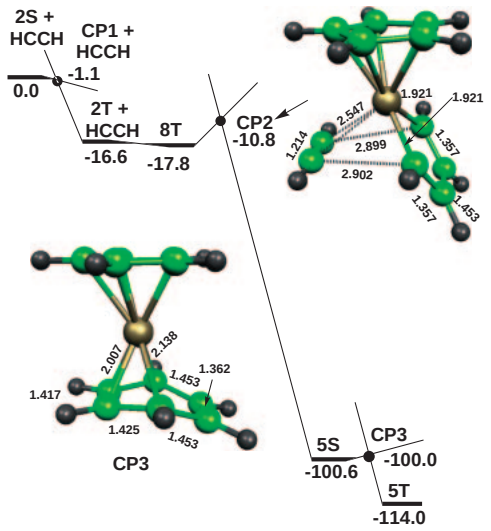


Fig. 9. ZPE-corrected energy profile for two-state reactivity mechanism with optimized structures for the crossing points **CP2** and **CP3**. All energies are relative to **2S** + HCCH in kcal/mol. All bond lengths are in Å.

triplet potential energy surfaces showed what reactions may take place through these crossing points. Such calculations for **CP1** showed that the rearrangement of **2S** to **2T** may take place through **CP1**. While **CP1** is very close to **2S** in potential energy and structure, the ZPE-correction makes **CP1** more stable than **2S** by 1.1 kcal/mol, as shown in Fig. 1.

The reaction from **8T** leads to **CP2**, which is 7.0 kcal/mol less stable than **8T**. Because **CP2** is 7.1 kcal/mol more stable than **TS2T**, the reaction through **CP2** would be easier than that through **TS2T**. After passing through **CP2**, the singlet benzene complex **5S** is given. **CP2** has a C_s symmetric structure, suggesting that it is at the bottom of a wide valley on the singlet potential-energy surface. Therefore, once the spin changes from the triplet state to the singlet state, [4 + 2] cycloaddition takes place spontaneously.

The third crossing point **CP3** connects **5S** in the singlet state and **5T** in the triplet state. Therefore, the structure of **CP3** is between those of **5S** and **5T**. In **CP3** the benzene ring is less folded and its four carbon atoms are more weakly coordinated to the Co atom compared to those in **5S**. A comparison of the CC bond lengths of the benzene ring in **CP3** and **5S** shows that the π-electrons in **CP3** are more delocalized than those in **5S**. **CP3** is closer in structure to **5S** than **5T**, and thus it is only 0.6 kcal/mol less stable than **5S**, indicating that the reaction of **5S** to **5T** through **CP3** is easy.

CP2 and **CP3** serve here as two transition states for changing from one spin state to the other. Therefore, the most favorable reaction path is the two-state reactivity (non-adiabatic) mechanism, and it can be considered as follows: **1** → **TS1** → **2S** → **CP1** → **2T**, and then **2T** + acetylene → **8T** → **CP2** → **5S** → **CP3** → **5T** as shown in Fig. 9. The important point to favor this mechanism is that **CP2** is much more stable than **TS2T**, resulting in an easier formation of **5T** through this mechanism than that through the triplet-state mechanism.

4. The Role of η^4-Cyclobutadiene in Cyclotrimerization of Acetylene. It is speculated that the cyclobutadiene metal complex may serve as an intermediate in the cyclotrimerization of alkynes.[40] This point of view mainly arose after Yamazaki and co-workers obtained the cyclobutadiene complex by heating cobaltacyclopentadiene over its melting point.[41] Although contrasting views on this topic were discussed in the literature, including an experimental study by Vollhardt et al., as well as a theoretical study by Hardesty et al.,[13,42–46] no specific role of η^4-cyclobutadiene was found in the metal-catalyzed cyclotrimerization of acetylene. Vollhardt et al. proposed that the transformation of cobaltacyclopentadiene **2S** to η^4-cyclobutadiene cobalt complex **6** does not take place directly, but firstly **2S** rearranges to the cyclopropenyl carbene cobalt complex shown in Scheme 2, which finally gives **6**. Hardesty et al. found the transformation of **2S** to **6** is symmetry-forbidden based on extended Hückel theory calculations, and that **6** is 34.0 kcal/mol more stable than **2S**, meaning that the activation energy needed for the transformation of **6** to **2S** is very large.[13] However, the transition state that connects **2S** and **6** was not located in their study and the role of Vollhardt intermediate remains to be elucidated. In this paper, we consider in detail the transformation of **2S** to **6** to obtain more and clearer information about this transformation. The optimized structures for the **TS6** as well as **6** are shown in Fig. 10 along with their relative energies.

We determined the structure of complex **6** without any constraint to obtain a structure with all C–C distances being 1.455 Å. The structure of **6** was very similar to the X-ray structure as well as that optimized by Hardesty et al., as shown in Table 4.[13,46]

In **TS6**, the bond distance for the newly formed CC bond is 2.377 Å, while the distance between these carbon atoms in **2S** is 2.654 Å, indicating a partial formation of the C–C bond.

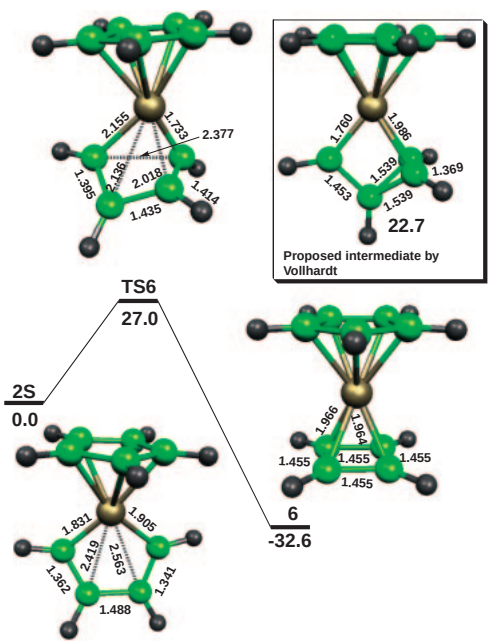


Fig. 10. Profile for transformation of cobaltacyclopentadiene complex **2S** to cyclobutadiene complex **6**. All energies are ZPE-corrected and relative to **2S** in kcal/mol. The optimized geometry inside the rectangle is the intermediate proposed by Vollhardt et al. All bond lengths are in Å.

Table 4. Theoretical and Experimental Structures of CpCo-(η^4-C_4H_4), **6**

Variables[a)]	Theoretical (This study)	Theoretical[b)]	Experimental[c),d)]
Co–C_{cb}	1.969	1.98	1.966(3)
Co–C_{cb}	1.966	1.98	1.965(2)
Co–C_{cb}	1.964	1.98	1.962(3)
Co–C_{cb}	1.966	1.98	1.965(2)
Co–C_{Cp}	2.039	2.08	2.027(3)
Co–C_{Cp}	2.044	2.08	2.037(2)
Co–C_{Cp}	2.052	2.08	2.037(2)
Co–C_{Cp}	2.060	2.08	2.045(2)
Co–C_{Cp}	2.065	2.08	2.045(2)
C_{cb}–C_{cb}–C_{cb}	90.0		
C_{cb}–C_{cb}–C_{cb}	90.0		
C_{cb}–C_{cb}	1.455	1.47	1.434(2), 1.440(2)
C_{Cp}–C_{Cp}	1.426–1.429	1.44	1.393(3), 1.384(3)
C_{cb}–H	1.08	1.08	0.94(2), 0.96(3), 0.99(3)

a) Bond lengths in Å and bond angles in degrees. C_{cb} and C_{Cp} are the carbon atoms in cyclobutadiene and cyclopentadienyl ligands, respectively. b) Theoretical data from reference 13. c) X-ray data obtained from reference 46. d) Numbers in parentheses refer to errors in X-ray data.

More important is the larger deformation of **TS6** from the C_s symmetric structure compared with **2S**. In **TS6** two of four carbons in the cobaltacyclopentadiene fragment coordinate more strongly to the Co atom with bond lengths of 1.733 and 2.018 Å than the other two carbons with Co–C bond lengths of 2.136 and 2.155 Å. This resulted in the longer bond length (1.414 Å) between the strongly coordinated carbons than that (1.395 Å) between the weakly coordinated carbons. As mentioned before, this reaction is symmetry-forbidden, and therefore the reaction requires passing through the symmetry-broken transition state structure.

While this conversion of **2S** to **6** requires a large activation energy of 27.0 kcal/mol, it is 32.6 kcal/mol exothermic. This large exothermicity comes from the formation of a new strong C–C σ-bond, and makes the activation barrier to the reverse reaction very high. Thus, the large activation barrier of 59.6 kcal/mol prohibits the transformation of **6** to **2S**. Therefore, the η^4-cyclobutadiene cobalt complex **6** is too stable to serve as an intermediate in this cyclotrimerization. The same conclusion was obtained by Hardesty et al. previously. Although we did not investigate the reaction path through the intermediate proposed by Vollhardt et al., it was calculated to be 22.7 kcal/mol less stable than **2S** (cf. Fig. 10 for the geometry), and TSs for the reaction mechanism through this intermediate would be very high in energy. Accordingly, this intermediate could not play a role.

Conclusion

Using restricted and unrestricted DFT/B3LYP methods with the 6-31G** basis set, the reaction of cobaltacyclopentadiene with an acetylene molecule leading to a benzene complex was studied. The ground state of cobaltacyclopentadiene is not a singlet state, but a triple state. The triplet structure, **2T**, is 16.6 kcal/mol more stable than the singlet structure **2S**. **2S** has a vacant d orbital that can interact strongly with the π orbital of acetylene, whereas the diene fragment of **2S** could conduct symmetry-allowed [4 + 2] cycloaddition with the acetylene molecule. These two electronic factors make the $C_\alpha CoC_\alpha$ moiety in **2S** very reactive to acetylene.

Because of the high reactivity of **2S**, when the acetylene molecule attacks **2S** from the side of large lobe of LUMO, the [4 + 2] cycloaddition requires no activation energy, a mechanism called a collapse mechanism. Consequently, this reaction is very possible. In addition to the favorable orbital interaction of a symmetry-allowed reaction, the large exothermicity of the formation of the η^4-benzene complex ($\Delta E = -100.6$ kcal/mol) makes the reaction downhill. Other possible reactions in the singlet state were investigated. In the first reaction in which the acetylene molecule attacks **2S** from the backside of the LUMO, there is a transition state with an activation energy of 11.3 kcal/mol, and therefore this reaction is less favorable than the collapse mechanism. A second possible reaction passes through cobaltacycloheptatriene intermediate, as suggested by Schore. Our calculations showed that there is no reaction path from **2S** + acetylene to **5S** through cobaltacycloheptatriene.

The reaction of **2T** with the acetylene molecule in the triplet state passes through a single transition state **TS2T** with a large activation energy of 14.1 kcal/mol relative to the acetylene complex **8T**, leading to 20-electron (η^5-C_5H_5)Co(η^6-C_6H_6), **5T**. During the reaction through **TS2T**, acetylene inserts into the Co–C_α bond, the Co–C_α bond breaks, and finally the benzene molecule reductively eliminates to give **5T**.

Similar to **2T**, **5T** is the ground-state structure of the benzene complex. Taking into account the result that the reaction in the singlet state is downhill, the spin would change during the course of the reaction to facilitate the reaction. Calculations of the energy minimum crossing points between the singlet and triplet states showed that there are energy minimum crossing points, (**CP2** and **CP3** as well as **CP1**), and that the spin could change there. Combining the results in a previous paper,[14] the most favorable reaction path for the trimerization of acetylene in the coordination sphere of CpCo is **1** (singlet) → **TS1** (singlet) → **2S** (singlet) → **CP1** → **2T** (triplet), and then **2T** (triplet) + acetylene → **8T** (triplet) → **CP2** → **5S** (singlet) → **CP3** → **5T** (triplet). **CP2** is 7.1 kcal/mol more stable than **TS2T**, favoring the two-state reactivity (non-adiabatic) mechanism.

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