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Theoretical Study on the Transformation of Bis(acetylene)cobalt to Cobaltacyclopentadiene and the Regioselectivity in this Transformation

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The transformation of bis(acetylene)cobalt complex to cobaltacyclopentadiene complex was studied using a hybrid density functional theory method. B3LYP calculations showed that the reaction of an unsubstituted system, bis(η^2-acetylene)cobalt complex, on a singlet potential energy surface is an easy reaction with a small activation energy of 11.2 kcal/mol and an exothermicity of -19.2 kcal/mol. The low activation barrier was as expected for a symmetry-allowed reaction. Because the product of cobaltacyclopentadiene has a low-lying unoccupied orbital, the two Co–C_α bonds are different in distance due to the second-order Jahn–Teller effect, and the triplet cobaltacyclopentadiene is more stable than the singlet cobaltacyclopentadiene, different from the reactant and transition state. In addition, we performed calculations for the reactions of acetylenes substituted by methyl and/or methoxycarbonyl groups, in order to investigate the factors that control the regioselectivity observed in this type of reaction. The calculations for the mono- and disubstituted reactions showed that these substituents prefer α-carbon to β-carbon. We analyzed the origin of this regioselectivity based on the relative stability of the products, to find that it is closely related to the site preference in the substituted butadienes. This suggests that the site preference of substituents is an important factor of regioselectivity.

Organic compounds have been prepared thermally as well as catalytically. The high-energy barriers for the thermal formation of such compounds would give products other than the target compounds.[1] For instance, the energy barrier to the thermal formation of benzene by trimerization of acetylene is 80 kcal/mol, although it is a highly exothermic reaction.[2,3] Also, the thermal formation of pyridine derivatives from ketoxime is conducted at temperatures higher than 300 °C.[4] Accordingly, since the preparation of benzene and cyclooctatetraene from alkynes in the presence of nickel catalysts has been devised, transition-metal catalysts have been extensively used in the preparation of arenes.[5,6] These catalysts lower the energy barriers as well as give regio- and chemoselective products.

It was found that metallacyclopentadiene complexes are important intermediates in the preparation of arenes. For example, metallacyclopentadiene complexes have received considerable attention as important intermediates in the transition metal-catalyzed cyclotrimerization of alkynes. There have been many experimental studies on such complexes (metal = Ti, Zr, Ta, Fe, Ru, Co, Rh, Ir, Ni, Pd), because this intermediates react with other molecules, such as alkynes, nitriles, olefins, N=N, C=O, and C=N, to form heterocycles as well as benzene derivatives.[7–16] Also, they react with dihalonaphthalenes and dihalopyridines to form substituted anthracene, quinolines, and isoquinoline derivatives.[17] However, theoretical studies about metallacyclopentadiene have been few. For example, theoretical studies on the oxidative coupling of bis(acetylene)ruthenium to ruthenacyclopentatriene, which is an important intermediate for the preparation of arenes, and that for the reaction of $Cp_2Zr(C_6F_5C{\equiv}CC_6H_5)$ with $C_6F_5C{\equiv}CC_6H_5$ have been reported only recently.[18]

One of the important metallacyclopentadiene intermediates is the cobaltacyclopentadiene complex. It has been used extensively in the preparation of various organic compounds; they are reacted with nitriles, carbon disulfide, and methyl isothiocyanates to give pyridines, 1,2-dithiopyrones, and *N*-methylthiopyridone.[19] Also, they react with acetylenes, allenes, olefins, and nitrosobenzenes to give substituted benzenes, cyclohexadienes, and pyrroles.[20,21] Their reactions with sulfur and selenium give thiophenes and selenophenes, respectively.[20] The interaction of cobaltacyclopentadiene complexes with isocyanate gives pyridinone derivatives.[22] The cobaltacyclopentadiene ring is opened by the addition of Si–H, S–H, N–H, and C–H to the diene moiety. For example, the additions of triethylsilane, thiol, thioacetanilide, dimethyl thiourea, ethylene thiourea, pyrrole, and thiophene to cobaltacyclopentadiene complexes give diene complexes, or highly substituted butadiene derivatives.[23]

For the reaction of the acetylene cobalt complex with another acetylene molecule, giving cobaltacyclopentadiene, Wakatsuki and his co-workers proposed that the transformation of the bis(η^2-acetylene)cobalt complex to cobaltacyclopentadiene is the rate-determining step. Also, the substituted groups in cobaltacyclopentadiene define the regioselectivity in the product.[23] In another study, this transformation was analyzed experimentally in detail.[24] The kinetic study has indicated that the bis(η^2-acetylene)(η^5-cyclopentadienyl)cobalt intermediate **1** cyclizes to lead to coordinatively unsaturated (1,3-butadiene-1,4-diyl)(η^5-cyclopentadienyl)cobalt **2**. Also, it has been shown that the regioselectivity of the cyclization process is controlled by the steric factor of substituents, rather than the

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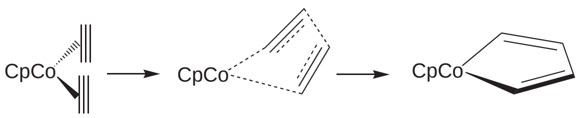


1 **TS1** **2**

Scheme 1. Oxidative coupling of bis(acetylene)cobalt, **1**, to cobaltacyclopentadiene, **2**.

electronic factor. There have been two major theoretical studies reported in the literature that discuss the transformation of bis(η^2-acetylene)cobalt complex **1** to cobaltacyclopentadiene complex **2**.[25,26] In the first study, conducted almost two decades ago by Wakatsuki et al.,[25] the structures of **1** and **2** were partially optimized by using the Hartree–Fock (HF) method and small basis sets under a C_s symmetry constraint. Further, for the **1** to **2** transformation, they postulated the transition state **TS1** to be as in Scheme 1. According to their calculations, this transformation was found to be endothermic by 14.0 kcal/mol.

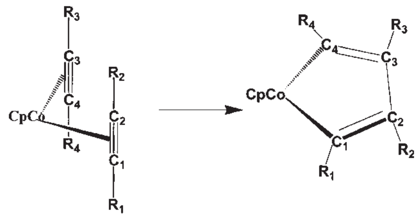
A more significant theoretical study in this area is the relatively recent work of Hardesty et al.,[26] in which they described the $CpCoL_2$-catalyzed formation of benzene from acetylene at the density functional theory (DFT) level. As compared to Wakatsuki et al., their study suggested an exothermicity of 13.1 kcal/mol for the transformation of **1** to **2**. Further, it was shown that this reaction requires an activation energy of 12.8 kcal/mol, indicating that it is very feasible. They ascribed the difference between their results and those by Wakatsuki et al. to the difference in the methods used for the calculations.

In these theoretical studies the transformation of bis(η^2-acetylene)cobalt complex to cobaltacyclopentadiene was without substituents on acetylene molecules. Therefore, in order to understand the variety of chemistry included in this type of reaction, and to obtain information useful for designing such reactions, we started a series of theoretical studies on the formation reactions of various metallacyclopentadienes from alkynes, and subsequent reactions giving cyclic organic compounds. Here, we report on the results of the reactions shown in Scheme 2, the transformation of bis(η^2-acetylene)cobalt complex **1** to cobaltacyclopentadiene complex **2** and that of mono- and disubstituted complexes.

In order to explore the profile of a potential energy surface for this transformation, we studied this transformation theoretically without a substituent on the acetylene molecules. To shed light on the factors controlling the regioselectivity, we introduced methyl and methoxycarbonyl substituents on the acetylene molecules as examples of electron-donating and electron-withdrawing substituents.

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.[27] 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.[28,29] For all of the atoms, the all electron split valence basis set 6-31G** is used, which contains polarization functions on heavy atoms and on hydrogen atoms.[30,31] 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[32] near the TS region, followed by geometry optimization of both reactants and products were performed for all reactions to confirm the connectivity of the TS. Unscaled vibrational frequencies were used to calculate a zero-point vibrational energy (ZPE) correction to the total energy. The referred energies are the ZPE-corrected energies at the B3LYP level, unless otherwise noted.



	Reaction	R_1	R_2	R_3	R_4
1	**1→TS1→2**	H	H	H	H
2a	**8a→TS5a→9a**	Me	H	H	H
2b	**8b→TS5b→9b**	H	Me	H	H
3a	**11a→TS6a→12a**	H	H	H	MeOCO
3b	**11b→TS6b→12b**	H	H	MeOCO	H
4a	**14a→TS7a→15a**	Me	H	H	Me
4b	**14b→TS7b→15b**	H	Me	H	Me
4c	**14c→TS7c→15c**	H	Me	Me	H
5a	**16a→TS8a→17a**	Me	H	H	MeOCO
5b	**16b→TS8b→17b**	H	Me	H	MeOCO
5c	**16c→TS8c→17c**	Me	H	MeOCO	H
5d	**16d→TS8d→17d**	H	Me	MeOCO	H

Scheme 2. Transformation of bis(acetylene)cobalt complexes to cobaltacyclopentadiene complexes.

The restricted Slater determinant wavefunction for the cobaltacyclopentadiene structure located by the restricted B3LYP method is not stable with respect to becoming an unrestricted wavefunction, because there is a low-lying triplet state. Therefore, we determined the structure of singlet cobaltacyclopentadiene by the unrestricted B3LYP (UB3LYP) method as well. Since the unrestricted wavefunction has a high-spin contaminant, we calculated the energy with an approximate spin-projection method by Yamaguchi et al.[33] We also determined the structure of an energy minimum crossing point between the singlet and triplet potential energy surfaces of cobaltacyclopentadiene with a constraint.[34] A vibrational analysis at this point was performed within the (3N-7)-dimensional hypersurface of the seam of crossing.[34]

For a comparison we performed single-point energy calculations for the B3LYP optimized structures of an unsubstituted reaction. The methods used were coupled cluster theory with single and double excitations with and without perturbative triple excitations (CCSD(T) and CCSD, respectively),[35,36] and B3PW91 and BPW91 functionals, where the nonlocal correlation functional of Lee, Yang, and Parr was replaced by the nonlocal correlation functional of Perdew and Wang; also, Becke's three-parameter hybrid-exchange functional was replaced by Becke's exchange functional.[37,38] The thus-obtained energies were corrected with the B3LYP zero-point vibrational energies. The MOLEKEL program was used to draw all of the structures shown in Figs. 1–10.[39]

Results and Discussion

Transformation of Bis(η^2-acetylene)cobalt to Cobaltacyclopentadiene. According to the Schore mechanism,[6] the simple ligand exchange reaction of the $CpCoL_2$ complex (where L = CO, PR_3, or olefin) with acetylene produces the active intermediate $CpCo(\eta^2\text{-}C_2H_2)_2$. Hardesty et al.[26] found in a theoretical study that, when $L = PH_3$, the conversion of $CpCo(PH_3)_2$ to $CpCo(\eta^2\text{-}C_2H_2)_2$ could take place with a net exothermicity of −11.3 kcal/mol, meaning that the thermodynamic driving force promotes the formation of an active catalyst. We started our geometry optimization from $CpCo(\eta^2\text{-}C_2H_2)_2$ **1**, known from several experimental evidences as an active intermediate in the cyclotrimerization path for the formation of benzene and pyridine.[6,40–45] The optimized geometry of the 18-electron d^8 system **1** is depicted in Fig. 1. The acetylene coordination to the metal elongates its CC bond length from 1.205 Å to 1.256 Å. **1** has a C_s symmetry and non-bonded C···C distances of 2.781 and 2.803 Å between two acetylene ligands (cf. Fig. 1). It is to be noted that the nearly free rotation of the Cp ring envisages equal distances to these C···C distances. However, according to the stationary geometry of **1** in Fig. 1, the two carbon atoms separated at the shorter distance of 2.781 Å are more preferable for oxidative coupling.

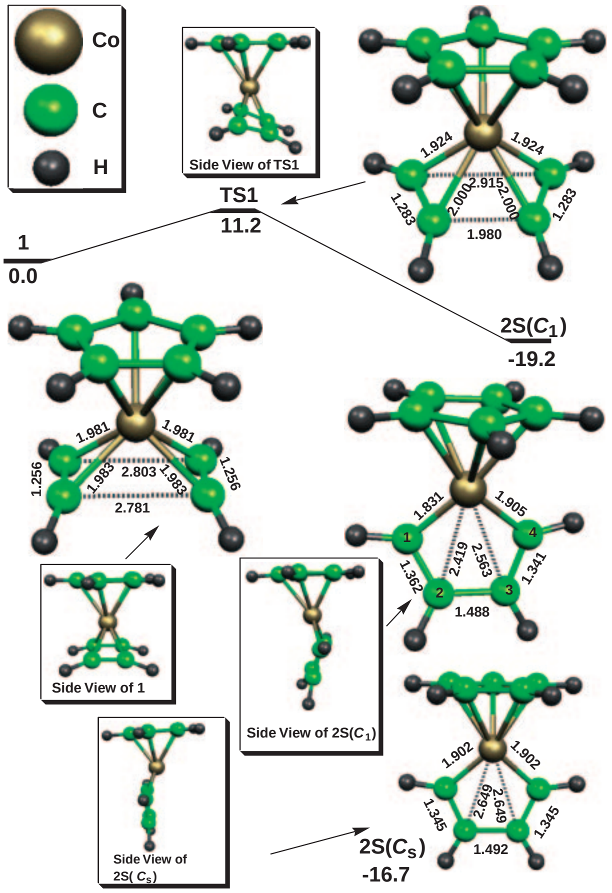


Fig. 1. Reaction profile for the oxidative coupling of acetylene ligands, reaction 1. Energies are zero-point energy (ZPE) corrected and relative to **1** in kcal/mol. The energy of **2S** is that calculated by the approximately spin-projected UB3LYP method. All the bond lengths are in Å.

Figure 1 also depicts the transition state **TS1** for the oxidative coupling of **1** and the resulting product, cobaltacyclopentadiene **2**, labeled by **2S**(C_1), along with the ZPE-corrected energy profile of the reaction. Since a 16 electron Co(III) complex **2** is coordinatively unsaturated, its triplet state could be low in energy. Accordingly, we determined the equilibrium structures of **2** in the singlet and triplet states, which are called **2S**(C_1) and **2T**, respectively.

The structural parameters of the pentagonal cobaltacyclopentadiene fragment of **2S**(C_1) is slightly different from the theoretical structure by Hardesty et al. as well as the X-ray structure of $CpCo(C_4H_4)(PPh_3)$, shown in Table 1.[26,46] As compared to their C_s symmetric structure of the cobaltacyclopentadiene fragment, the present calculation gave a C_1 symmetric structure with significantly different Co–C bond distances. In fact, the structure optimization of **2S** under the C_s symmetry constraint gave **2S**(C_s) in Fig. 1 with one imaginary frequency for the mutual rotation of the Cp ring and the cobaltacyclopentadiene fragment; therefore, it is the transition state for the isomerization between two enantiomeric **2S**(C_1)s. **2S**(C_s) is 2.5 kcal/mol less stable than **2S**(C_1).

The canonical molecular orbitals presented in Fig. 2 for **2S**(C_s) and **2S**(C_1) illustrate the reason for the deformation of the cobaltacyclopentadiene structure, which is nothing but a second-order Jahn–Teller distortion. The HOMO of a″ symmetry in **2S**(C_s) is made from the highest occupied π orbital on the butadiene framework and the d orbital of the Co atom, whereas the LUMO, which is mainly the empty Co d orbital,

Table 1. Theoretical and Experimental Structures (Bond Lengths and Bond Angles) of Cobaltacyclopentadiene Complex **2S**

Variables[a),b)]	Theoretical (this study)	Theoretical[c)]	Experimental[d),e)]
$Co\text{–}C_{C_p}$	2.017–2.143	2.14	2.144(6)
$C_{C_p}\text{–}C_{C_p}$	1.411–1.434	1.43	1.409(8)
$C_{C_p}\text{–}C_{C_p}\text{–}C_{C_p}$	108.0	108.0	
$Co\text{–}C_1$, $Co\text{–}C_4$	1.831, 1.905	1.92	1.945(3)
$C_1\text{–}C_2$, $C_4\text{–}C_3$	1.362, 1.341	1.34	1.344(10)
$C_2\text{–}C_3$	1.488	1.49	1.447(10)
$C_1\text{–}Co\text{–}C_4$	90.5	85.5	83.2(3)
$Co\text{–}C_1\text{–}C_2$	97.4	111.4	
$Co\text{–}C_4\text{–}C_3$	102.9	111.4	
$C_1\text{–}C_2\text{–}C_3$	118.3	114.5	
$C_4\text{–}C_3\text{–}C_2$	112.0	114.5	
$Co\text{–}C_1\text{–}H_1$	129.2	124.3	
$Co\text{–}C_4\text{–}H_4$	130.1	124.3	

a) Bond distances in angstroms and bond angles in degrees. b) Average values obtained for experimental data. c) Theoretical data from reference 26. d) X-ray data obtained from reference 46. e) Values in parentheses refer to errors in X-ray data.

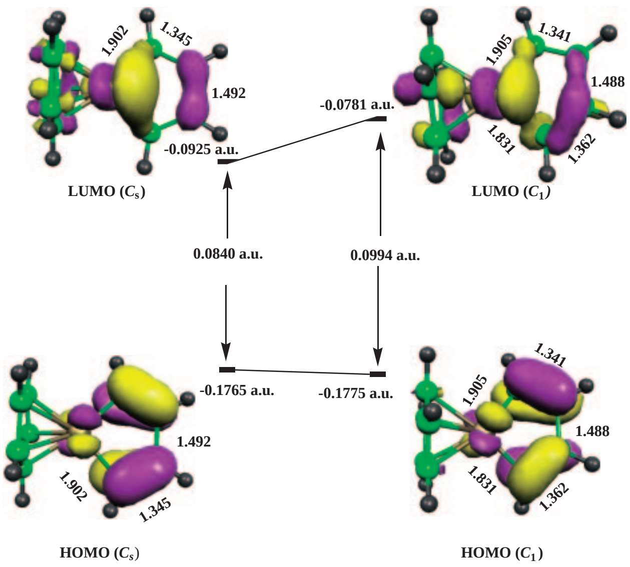
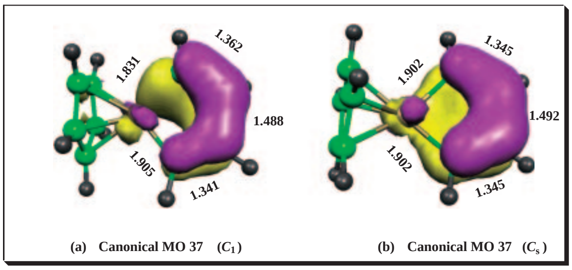
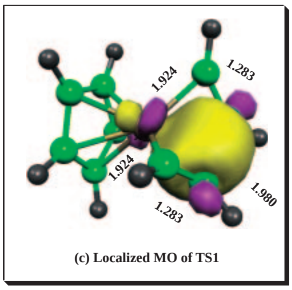


Fig. 2. The energy gaps between the HOMOs and LUMOs for complex **2S** in the C_s and C_1 symmetries.



(a) Canonical MO 37 (C_1) (b) Canonical MO 37 (C_s)



(c) Localized MO of TS1

Fig. 3. The canonical molecular orbitals 37 for complex **2S** in (a) C_1 and (b) C_s symmetries, respectively. (c) One of the localized molecular orbitals for **TS1**.

is of a′ symmetry. Because of the small energy gap between them, the distortion from the C_s symmetry mixes the HOMO and LUMO, resulting in stabilization. As shown in Fig. 2, this mixing leads to an increase of the antibonding interaction between the Co–C_4 atom in the HOMO, and therefore the longer Co–C_4 bond than the Co–C_1 bond. As we can see from Figs. 3a and 3b, this distortion forms a selective bonding interaction between the Co and C_1 atoms in the lower-lying occupied π orbital as well.

Thorn and Hoffmann suggested that in the five-coordinated d^6 complex, a second-order Jahn–Teller distortion could lead to unequal C–M bond distances.[47] This is the case of **2S**(C_1), and the distortion takes place on the Co–C_4 and Co–C_1 σ-bonds. Also, the above discussion is supported by the C_s symmetric structure of $CpCo(C_4H_4)(PR_3)$ without a low-lying empty d orbital, which was verified both experimentally and theoretically (Fig. 4b).[46] The optimized structure of **2T** is also of C_s symmetry, as shown in Fig. 4a. This is because the orbital corresponding to the LUMO of **2S**s is singly occupied in **2T**.

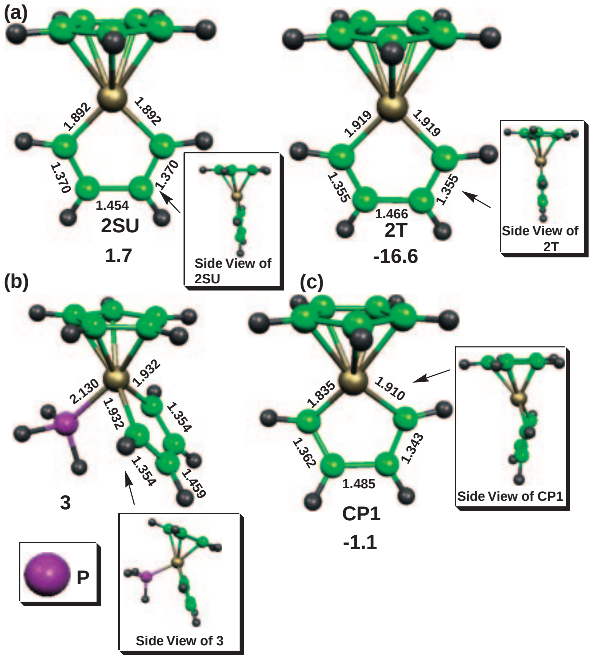


Fig. 4. (a) Optimized structures of cobaltacyclopentadiene, **2SU** and **2T**. Their ZPE-corrected energies are relative to **2S** in kcal/mol. (b) Optimized structure of $CpCo(C_4H_4)(PH_3)$ complex, **3**. (c) Optimized structure of **CP1** between **2S** and **2T** and its energy relative to **2S** in kcal/mol. All the bond lengths are in Å.

From a theoretical point of view, it should be noted that a single-determinant wavefunction with restricted orbitals for **2S**(C_1) as well as **2S**(C_s) is unstable. A calculation at the structure of **2S**(C_1) showed that there is a more stable unrestricted solution with an $\langle S^2 \rangle$ value of 0.4789. Approximately spin-projected unrestricted B3LYP energy is 1.9 kcal/mol lower than the restricted B3LYP energy. Geometry optimization using the unrestricted B3LYP method gives **2SU** in Fig. 4a with an $\langle S^2 \rangle$ value of 1.0919; the structure of **2SU** is similar to that of **2T**. These results showed that the unrestricted singlet-determinant wavefunction for **2SU** is a 1:1 mixture of singlet and triplet wavefunctions, and the structure is determined by the triplet contaminant. Note that, though **2SU** is 7.8 kcal/mol more stable than **2S**(C_1), approximate spin-projection makes **2SU** 1.7 kcal/mol less stable than **2S**(C_1).[33] CCSD single point energy calculations support this result; **2S**(C_1) is 13.0 kcal/mol more stable at the CCSD level.[36] Accordingly, **2S**(C_1) is the singlet structure of cobaltacyclopentadiene and approximately spin-projected UB3LYP method improves its energy. From now on, **2S** refers the structure of **2S**(C_1).

B3LYP calculations showed that, compared with **2S**, **2T** is more stable by 16.6 kcal/mol, and therefore the ground state of cobaltacyclopentadiene is a triplet state. This result seems to be inconsistent with the experimental results,[25] which show a singlet spin state of the product. Presumably, in the experimentally observed species a different molecule, such as acetylene, solvent, and phosphine molecules coordinates to **2S** to stabilize a singlet state, like in CpCo(C_4H_4)(PH_3), **3**, in Fig. 4b. As we show elsewhere,[48] **2S** is very reactive, and it is unlikely that **2S** exists alone under the experimental condition.

Spin changes are considered to be common in transition-metal chemistry.[49] For instance, the CO addition to triplet TpCo(CO) yields the singlet TpCo$(CO)_2$.[50] Since the two up spins in **2T** localize on the Co atom, a spin change is expected to take place easily. The spin change from one spin state to the other would take place through an energy minimum point on the crossing seam between two potential energy surfaces. The structure of an energy minimum crossing point (**CP1**) near **2S** is shown in Fig. 4c. The structure and potential energy of **CP1** are close to those of **2S** and the structure change from **CP1** to **2T** is downhill on the triplet potential energy surface. Consequently, once **2S** is formed, the conversion of **2S** to **2T** is expected to be quite easy. This means that the reaction is controlled by the step to **2S** through **TS1** on the singlet potential energy surface.

Interestingly, the coordinatively unsaturated **2S** is 19.2 kcal/mol more stable than the coordinatively saturated **1**. The reasons for such a behavior are well explained in the work of Hardesty et al.[26] as the formation of three strong C–C σ bonds in **2** at the expense of relatively weaker Co–acetylene π interactions in **1**. The energetics of the reaction is qualitatively in agreement with that obtained by Hardesty et al. with a small basis set. For instance, as compared to the 11.2 kcal/mol obtained for the energy barrier of the reaction in the present case, their work reported a value of 12.8 kcal/mol. However, the exothermicity of the reaction is affected more because the present value of −19.2 kcal/mol is 6.1 kcal/mol higher than their value.[26] Note that with their method, the C_s symmetric structure of **2** was obtained, and that they were not aware of the triplet state.

The activation energy of 11.2 kcal/mol for the present reaction is low, as expected for a symmetry-allowed reaction. To investigate other factors that would lower the activation barrier, we also performed a localized molecular orbital (LMO) analysis at the **TS1** structure. An important finding is the orbital interaction depicted in Fig. 3c. The electron delocalization from an occupied d orbital to a bonding combination of π^* orbitals of two acetylene molecules is known to play a crucial role in such an oxidative coupling.[51,52] The LMO shown in Fig. 3c is considered to represent this electron delocalization.

Another possible path of cobaltacyclopentadiene formation is the reaction of an acetylene cobalt phosphine complex, CpCo(PH_3)(η^2-C_2H_2), with another acetylene molecule. The reaction expected in the first step is a replacement of the phosphine with an acetylene molecule, giving **1**. The succeeding reaction is that shown in Fig. 1. We tried to locate the transition state for the exchange of a phosphine ligand with an acetylene molecule. However as shown in Fig. 5, the transition state we could find was for acetylene coordination accompanied by a change from η^5-Cp to η^1-Cp, giving a bis(acetylene)-cobalt phosphine complex, (η^1-Cp)Co(PH_3)(η^2-C_2H_2)$_2$, **5**. Although phosphine dissociation is possible from **5**, we excluded the possibility of this reaction path, because the transformation of **4** to **5** (the first step) requires a high activation energy of 33.3 kcal/mol.

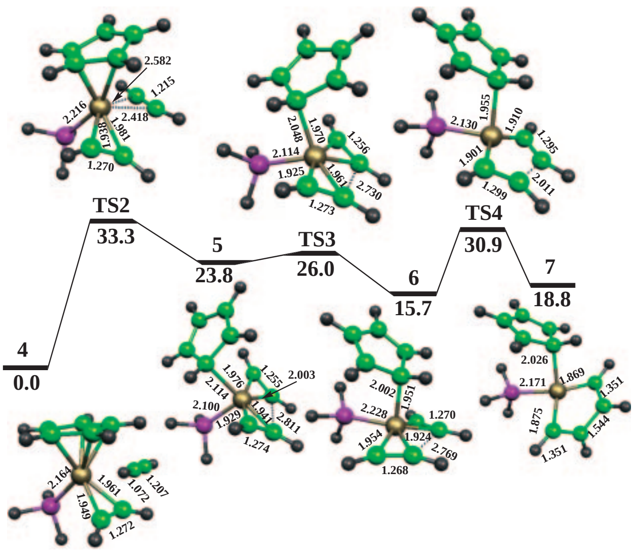


Fig. 5. Profile for the reaction of CpCo(PH_3)(η^2-C_2H_2) complex with acetylene to form cobaltacyclopentadiene complex. All energies are ZPE-corrected and relative to **4** in kcal/mol. All the bond lengths are in Å.

Also, for a comparison, single-point energy calculations for **1**, **2S**, **TS1**, and **2T** were carried out using B3PW91 and BPW91 functionals as well as the CCSD(T) method.[35,37,38] In the DFT calculations of **2S**, an unrestricted method with approximate spin projection was used. The energies of **TS1**, **2S**, and **2T** relative to **1** at those levels are qualitatively in good agreement with those at the B3LYP level (6.2, −17.0, and −21.4 kcal/mol at the BPW91 level, 9.4, −18.0, and −34.1 kcal/mol at the B3PW91 level, and 10.3, −15.9, and −26.7 kcal/mol at the CCSD(T) level, compared to 11.2 and −19.2, and −35.7 kcal/mol at the B3LYP level.

In summary, the oxidative coupling of two acetylene molecules in the Co complex takes place from CpCo(η^2-C_2H_2)$_2$ with a small activation energy, as expected of a symmetry-allowed reaction. The product is cobaltacyclopentadiene with the low symmetric structure because of the second-order Jahn–Teller effect. The ground state of the product is not a singlet state, but a triplet state. Changing the spin state is also an easy process.

Monosubstituted Reaction. In order to elucidate the factors controlling the regioselectivity observed in cyclization reactions, we first performed theoretical calculations for the oxidative coupling reactions of acetylene–propyne and acetylene–methyl propiolate complexes. It is generally considered that the regioselectivity in cyclization reactions giving benzene and pyridine derivatives is realized in the coupling reactions. The methyl group in propyne and the methoxycarbonyl group in methylpropiolate were selected as examples of electron-donating and electron-withdrawing substituents, respectively. One of R_1, R_2, R_3, and R_4 in Scheme 2 is a methyl or methoxycarbonyl group, and the others are hydrogen atoms. The optimized structures for the reactants and transition states as well

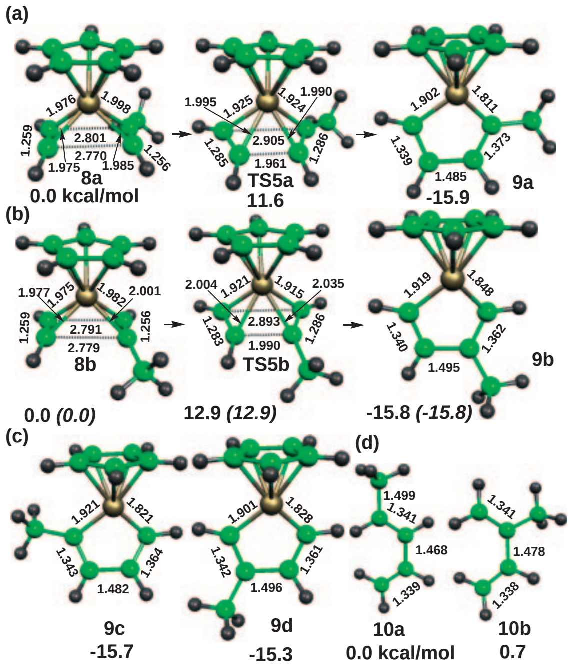


Fig. 6. Reaction profile for the oxidative coupling of acetylene–propyne ligands, reactions (a) 2a and (b) 2b with the ZPE-corrected energies relative to **8a** in kcal/mol. Energies in parentheses for reaction 2b are relative to **8b**. (c) Optimized structures of **9c** and **9d** and their relative ZPE-corrected energies in kcal/mol. (d) Optimized structures of two isomers of methylbutadiene, **10a** and **10b** and their relative ZPE-corrected energies in kcal/mol. All the bond lengths are in Å.

as the products in the singlet state are shown in Figs. 6 and 7.

Since the step in the triplet state after the formation of cobaltacyclopentadiene is easy, a comparison of the activation energies as well as the energies of the reactions in the singlet state is expected to give information on the regioselectivity. Therefore, in this and the following sections the results for only the singlet state are shown, and the energies of the substituted cobaltacyclopentadiene complexes were those by the restricted B3LYP method, because approximate spin-projection affected the energy only slightly in the case of **2**. The Co–C_1 and Co–C_4 bonds in substituted cobaltacyclopentadienes are considered to be shorter and longer Co–C bonds, respectively.

We can have four isomers of methyl-substituted cobaltacyclopentadiene, **9a**–**d**, shown in Figs. 6a–c, because the two Co–C bonds are different in distance. **9a** with the methyl group on C_1 is the most stable, and **9b** with that group on C_2 is the second. These results show that the methyl substituent in the product prefers the carbon atoms on the side of the shorter Co–C bond and, in addition, it prefers an α-carbon atom to a β-carbon atom.

Since the energy differences among **9**s are very small, we tried to locate the four transition states for the oxidative coupling, each of which would lead to one of **9**s. However, we obtained only two transition states, **TS5a** and **TS5b** shown in Figs. 6a and 6b. As shown in Fig. 1, **TS1** is symmetric, indicating that the deformation due to the second-order Jahn–Teller effect occurs after passing through the transition state; therefore there should be only two transition states for the monosubstituted system. The IRC calculations demonstrated that the reaction paths from **TS5a** and **TS5b** lead to **9a** and **9b**, which are more stable isomers of **9**s, indicating that there are no reaction paths giving less stable isomers of **9**s. The reactants, **8a** and **8b**, are also shown in Figs. 6a and 6b. The reaction of **8a** to **9a** through **TS5a** and that of **8b** to **9b** through **TS5b** are reactions 2a and 2b, respectively, in Scheme 2.

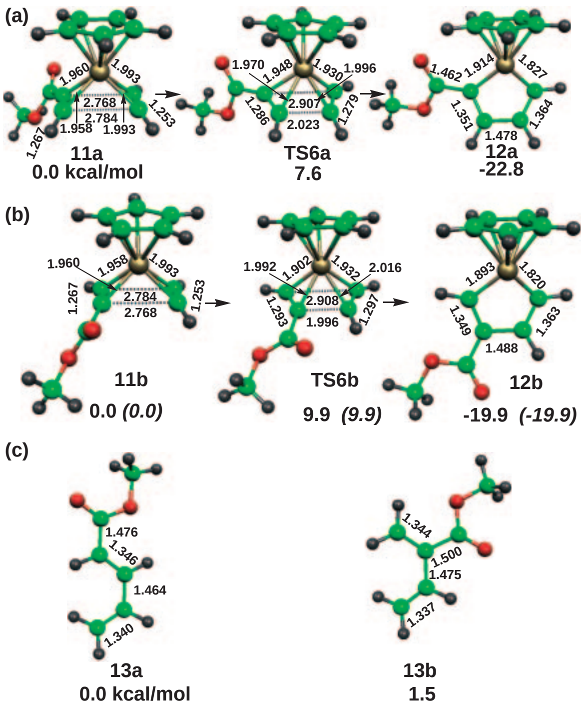
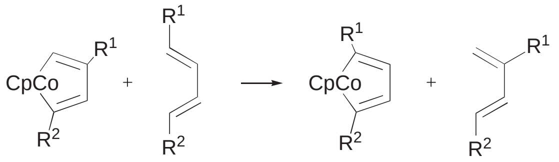


Fig. 7. Reaction profile for the oxidative coupling of acetylene–methylpropiolate ligands, reactions (a) 3a and (b) 3b with the ZPE-corrected energies relative to **11a** in kcal/mol. Energies in parentheses for reaction 3b are relative to **11b**. (c) Optimized structures of the two isomers of methoxycarbonylbutadiene, **13a** and **13b** and their relative energies in kcal/mol. All the bond lengths are in Å.

Because **8a** and **8b** differ only in the positions of the methyl substituent, they have almost the same energy. Accordingly, reaction 2a, leading to a more stable **9a**, is slightly more exothermic than reaction 2b. The energy barrier of 11.6 kcal/mol for reaction 2a is lower than that of 12.9 kcal/mol for reaction 2b, as expected of a more exothermic reaction. As a corollary of the Hammond principle,[53] it follows that a factor stabilizing a product would stabilize the transition state. This is true in both the present and later cases. The above results show that the methyl group prefers C_1 to C_2 both kinetically and thermodynamically.

It is known that an electron-donating group on the α-carbon atom destabilizes the M–C bond, with which the present results seem to be in disagreement.[52] In addition, **9a** is more crowded because of the steric interaction between the methyl group and the Cp ligand. These discrepancies come from the fact that the methyl group prefers the terminal carbon in the diene skeleton, as shown in Fig. 6d, in which 1,3-pentadiene with the terminal methyl group is 0.7 kcal/mol more stable than 2-methyl-1,3-butadiene with the central methyl group.

Table 2. The Energies of Reaction



C1 **B1** **C2** **B2**

R^1	R^2	**C1**	**B1**	**C2**	**B2**	$\Delta E^{a),b)}$	E(**C1**)–E(**C2**)[a)]	E(**B2**)–E(**B1**)[a)]
Me	H	**9b**	**10a**	**9a**	**10b**	0.6	0.1	0.7
MeOCO	H	**12b**	**13a**	**12a**	**13b**	−1.4	2.9	1.5
Me	Me	**15b**	**18a**	**15a**	**18b**	0.3	0.3	0.6
Me	MeOCO	**17b**	**19a**	**17a**	**19b**	0.5	0.8	1.3
MeOCO	Me	**17c**	**19a**	**17a**	**19c**	−0.9	2.9	2.0

a) in kcal/mol. b) $\Delta E = \{E(\mathbf{B2})–E(\mathbf{B1})\} - \{E(\mathbf{C1})–E(\mathbf{C2})\}$.

Compared with this value, the energy difference of 0.1 kcal/mol between **9a** and **9b** as well as that of 0.4 kcal/mol between **9c** and **9d** (Fig. 6c) is much smaller, demonstrating that the electron-releasing methyl group on the α-carbon atoms (C_1 and C_4) in fact destabilizes the cobaltacyclopentadiene to decrease the energy difference. This becomes clearer by calculating the energy of the reaction in the first row of Table 2, which represents the difference in the substituent effect between **9a** and **9b** (E(**C1**)–E(**C2**)) relative to that between **10a** and **10b** (E(**B2**)–E(**B1**)). Table 2 shows that this reaction is 0.6 kcal/mol endothermic, indicating that the methyl group on the α-carbon atom destabilizes the cobaltacyclopentadiene by 0.6 kcal/mol, compared with that in the hydrocarbons, presumably by destabilizing a negatively charged α-carbon atom. However, in the methyl-substituted butadiene the methyl group prefers the terminal position by 0.7 kcal/mol, resulting in the α-carbon preference.

The Co–C_1 bond in **9a** is shorter than that in **9b**. Presumably, this is due to the stronger π conjugation between the Co atom and the C_1–C_2 π-bond; the C_1–C_2 bond of **9a** (1.373 Å) is longer than that in **9b** (1.362 Å). This difference may make a contribution to the larger stability of **9a**. Such a difference in the bond lengths will be seen in the following cases as well.

In Figs. 7a and 7b the results for the monosubstituted methoxycarbonyl cobaltacyclopentadiene are shown. Different from the reaction with propyne, there are only two isomers of the products, methoxycarbonyl substituted cobaltacyclopentadiene, **12a** and **12b**. Furthermore, the substituents in **12a** and **12b** are on the carbon atoms in the side with the longer Co–C_α bond (the Co–C_4 bond). As shown in Fig. 2, the HOMO of the cobaltacyclopentadiene has larger lobes on the C_3 and C_4 atoms. The methoxycarbonyl group, which can conjugate with the π framework of the cobaltacyclopentadiene, should locate on the C_3 and C_4 atoms, different from the methyl group.

From the results shown in Figs. 7a and 7b, one can know that the methoxycarbonyl group prefers C_4 to C_3, because the energy barrier of 7.6 kcal/mol for reaction 3a is lower, and reaction 3a is more exothermic. Again, the more exothermic reaction has a smaller activation energy, suggesting that the energy of the reaction explains the regioselectivity of this reaction.[53] Thus, we next discuss the stability of the products. **12a** in reaction 3a is more stable than **12b** in reaction 3b by 2.9 kcal/mol. This trend is in agreement with that in substituted butadiene, as shown in Fig. 7c; methyl 2,4-pentadienoate with a terminal substituent, **13a**, is 1.5 kcal/mol more stable than methyl 2-methylene-3-butaenoate, **13b**, in which the methoxycarbonyl group is on the central carbon. Furthermore, as shown in Table 2, the electron-withdrawing methoxycarbonyl group on the α-carbon atom stabilizes the cobaltacyclopentadiene by 1.4 kcal/mol, presumably by stabilizing the negatively charged α-carbon atom, so that the regioselectivity is enhanced compared with the site preference in the substituted butadienes.

It is observed from a comparison among the results shown in Figs. 1, 6, and 7 that the electron-releasing methyl group decreases the exothermicity of the reaction, while the electron-withdrawing methoxycarbonyl has an opposite result. Consequently, the activation barrier for the methyl substituted system increases, and that for the methyoxycarbonyl group decreases. While the electron-donating group makes the reaction kinetically and thermodynamically less favorable, the electron-withdrawing group produces opposite results.

Disubstituted Reaction. Based on these results for the monosubstituted reactions, in order to obtain deeper insight into the substituent effects on the regioselectivity, we performed theoretical calculations for the reactions of bis(η^2-propyne) and propyne–methylpropiolate complexes. The optimized geometries of the reactants and transition states (TSs) as well as the products for these reactions are shown in Figs. 8 and 9, and the energies for the reactions are summarized in Table 3.

For the reactions of bis(η^2-propyne)cobalt complex in Fig. 8, although **14a** with $R_1 = $ Me and $R_4 = $ Me is not the most stable reactant, the activation energy for the reaction from **14a** (reaction 4a) is the smallest and, in addition, it is the most exothermic reaction among the reactions of bis(η^2-propyne) complex, indicating that reaction 4a is the most favorable. While the energy profiles of the reactions are in accord with a corollary from the Hammond postulate,[53] the activation energy for reaction 4c with $R_2 = $ Me and $R_3 = $ Me is much larger than the others. Apparently, the steric repulsion between the two methyl groups at **TS7c** for this reaction makes the activation energy larger. As a matter of fact, the distance between methyl carbons is 3.025 Å at **TS7c**, while that of

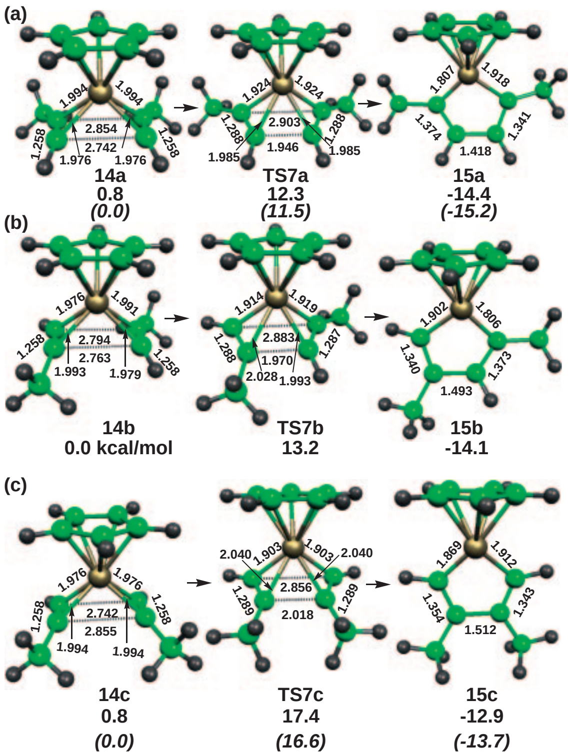


Fig. 8. Reaction profile for the oxidative coupling of bis(propyne) ligands, for reactions (a) 4a, (b) 4b, and (c) 4c with the ZPE-corrected energies relative to **14b** in kcal/mol. Energies in parentheses for reactions 4a and 4c are relative to **14a** and **14b**, respectively, in kcal/mol. All bond lengths are in Å.

Table 3. The Energies for All the Reactants, TSs, and Products for Reactions 1, 2, 3, 4, and 5 Relative to the Most Stable Reactant for Each Reaction in kcal/mol

Reaction	Reactant	TS	Product
1	0.0	11.2	−19.2
2a	0.0	11.6	−15.9
2b	0.0 *(0.0)*	12.9 *(12.9)*	−15.8 *(−15.8)*
3a	0.0	7.6	−22.8
3b	0.0 *(0.0)*	9.9 *(9.9)*	−19.9 *(−19.9)*
4a	0.8 *(0.0)*	12.3 *(11.5)*	−14.4 *(−15.2)*
4b	0.0	13.2	−14.1
4c	0.8 *(0.0)*	17.4 *(16.6)*	−12.9 *(−13.7)*
5a	0.0	7.7	−21.3
5b	0.3 *(0.0)*	9.7 *(9.4)*	−20.5 *(−20.8)*
5c	0.3 *(0.0)*	10.9 *(10.6)*	−18.4 *(−18.7)*
5d	0.0 *(0.0)*	13.7 *(13.7)*	−17.3 *(−17.3)*

Energies in parentheses are relative to each reactant.

product **15c** (3.075 Å) is larger. The steric interaction between the two methyl groups affects the distance between C_2 and C_3. As shown in Fig. 8, the C_2–C_3 distances in **TS7c** and **15c** as well as **14c** are larger than those for reactions 4a and 4b.

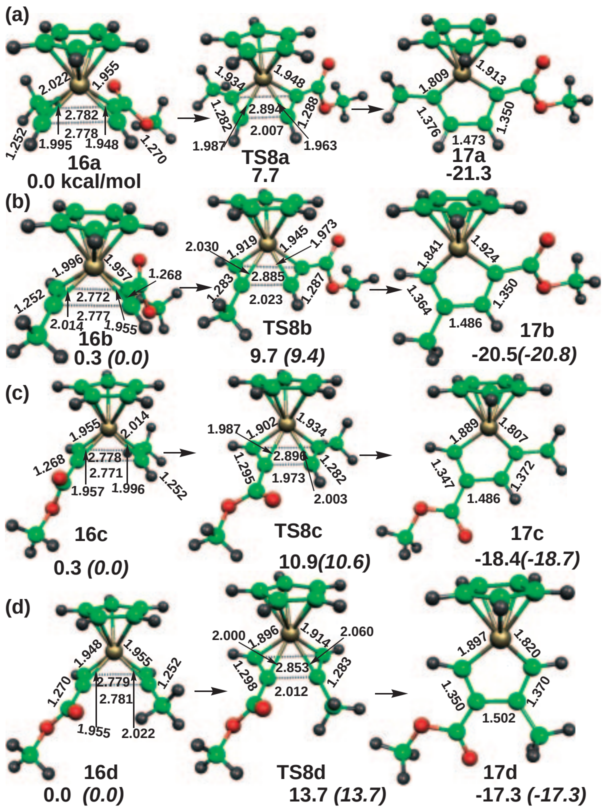
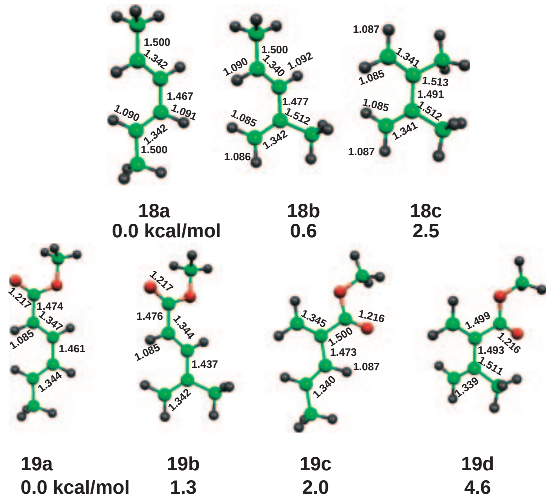


Fig. 9. Reaction profile for the oxidative coupling of propyne–methylpropiolate ligands, reactions (a) 5a, (b) 5b, (c) 5c, and (d) 5d with the ZPE-corrected energies relative to **16a** in kcal/mol. Energies in parentheses for reactions 5b, 5c, and 5d are relative to **16b**, **16c**, and **16d**, respectively, in kcal/mol. All bond lengths are in Å.

The results for reactions 5 of propyne–methylpropionate are shown in Fig. 9. Although eight isomers of the products are possible, there are only four of them, **17a–d** in Fig. 9. The site preference of the methoxycarbonyl group is $C_4 > C_3$, as shown in Fig. 7, and that of the methyl group is $C_1 > C_2$. The structures and relative energies of **17a–d** are those expected from these results. The most stable isomer is **17a** with R_1 = Me and R_4 = MeOCO, and the least stable is **17d** with R_2 = Me and R_3 = MeOCO. We also located the transition states for the reactions giving **17a–d** (Fig. 9). The activation energy for the most exothermic reaction 5a with R_1 = Me and R_4 = MeOCO is the smallest. Therefore, this reaction is the most favorable kinetically as well as thermodynamically.

The structures of isomers of disubstituted butadienes are shown in Fig. 10. In both cases of dimethyl substitution and methoxycarbonyl and methyl substitutions, the substituents prefer the terminal carbon atoms of butadiene. This is as expected from the trends in the cases of monosubstituted butadienes. Similar to the previous cases, the results summarized in Table 2 show that the site preference in substituted butadiene is an important factor for controlling the regioselectivity, and that the effect of the methoxycarbonyl group stabilizing the system is comparable.

In the previous section, a comparison of the energies of the reactions among reactions 1, 2a, and 3a shows that the methyl group makes the reaction less exothermic, while the methoxycarbonyl group makes it more exothermic. Changes in going from reactions 2a and 3a to reactions 4a and 5a are consistent with such effects. It is also to be noted that the more exother-



18a 0.0 kcal/mol **18b** 0.6 **18c** 2.5

19a 0.0 kcal/mol **19b** 1.3 **19c** 2.0 **19d** 4.6

Fig. 10. Optimized structures of the isomers of dimethylbutadiene, **18a–c**, and methoxycarbonyl methylbutadiene, **19a–d** and their relative energies in kcal/mol. All bond lengths are in Å.

mic is the reaction, the lower is the activation energy, in accord with the corollary from the Hammond postulate.[53] Consequently, the easiest reaction among the disubstituted reactions in Table 3 is reaction 5a.

The results mentioned above show that the site preference of the substituents is obviously a factor to be taken into account when considering the regioselectivity, and that it would make the oxidative coupling reactions giving uncrowded mono- and disubstituted cobaltacyclopentadienes regioselective. The regioselectivity of the coupling reactions of disubstituted acetylenes yielding tetrasubstituted cobaltacyclopentadienes has been studied experimentally.[25] The experimental results have shown the complicated nature of the regioselectivity. For instance, in some reactions the methoxycarbonyl group is at the α-carbon, and in others it is at the β-carbon. This suggests that in highly substituted cases there is an interaction between substituents, such as steric and electrostatic interactions, that would change the regioselectivity. Such an interaction would be larger at the TS, as shown for **TS7c**. Accordingly, an analysis of interactions at TSs is necessary for highly substituted systems. Calculations along these lines are now in progress, and the results will be published elsewhere.

Conclusion

The transformation of bis(η^2-acetylene)cobalt to cobaltacyclopentadiene by oxidative coupling was studied with the DFT method. A small activation energy of 11.2 kcal/mol was obtained, because this is a symmetry-allowed reaction. The reaction is also exothermic by -19.2 kcal/mol. These results show that the reaction should be easy. The triplet state of cobaltacyclopentadiene is the ground state, which is more stable than a singlet state by 16.6 kcal/mol. The calculations of the minimum energy crossing point between the singlet and triplet potential energy surfaces suggested that the spin change from the singlet state to the triplet state is easy.

The calculations for the mono- and disubstituted systems have shown that the transformation to mono- and disubstituted cobaltacyclopentadiene is regioselective with an α-carbon preference of the substituents. The α-carbon preference was found to be in the order MeOCO > Me, which can be explained by the site preference in the butadiene framework. In the cases of uncrowded reactions, this would explain the regioselectivity. A further analysis showed that the methoxycarbonyl group stabilizes the products, and that the methyl group destabilizes the products compared to the unsubstituted reaction. The more exothermic is the reaction, the lower is the activation energy, in agreement with the expectation from the Hammond principle.

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