this class of compounds and that even at low temperatures fast intramolecular movements occur. This explains why the heterogeneous reduction is diffusion controlled even at high scan speeds and only minor molecular rearrangements are needed in solution with very small activation energy.

Acknowledgment. We thank P. P. J. Schlebos for the recording of the ^{31}P NMR spectra, A. A. Klaassens for the recording of the ESR spectra, Drs. J. W. A. van der Velden and J. J. Bour, and Professor J. J. Steggerda for their discussions and interest in this work, and H. Spijkerman and B. Smalbrugge for their valuable contributions to this research. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. $Au_9(PPh_3)_8(PF_6)_3$, 38999-04-1; $Au_9(PPh_3)_8PF_6$, 84623-16-5.

Cobalt Metallacycles. 11. On the Transformation of Bis(acetylene)cobalt to Cobaltacyclopentadiene[1]

Yasuo Wakatsuki,*[2a] Okio Nomura,[2a] Kazuo Kitaura,[2b] Keiji Morokuma,[2c] and Hiroshi Yamazaki[2a]

Contribution from The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351 Japan, and the Institute for Molecular Science, Myodaiji, Okazaki, 444 Japan.
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Abstract: Formation of η^5-cyclopentadienyl(triphenylphosphine)cobaltacyclopentadienes (**4**) by the reaction of acetylenes with (η^5-cyclopentadienyl)(triphenylphosphine)(acetylene)cobalt (**1**) has been investigated in detail. Kinetic studies indicate the intermediacy of (η^5-cyclopentadienyl)bis(acetylene)cobalt (**2**), which cyclizes to coordinatively unsaturated η^5-cyclopentadienylcobaltacyclopentadiene (**3**) by a spontaneous oxidative coupling reaction. Regioselectivity of the cyclization process is controlled by the steric factor of substituents rather than their electronic factor. The structures and bonding of intermediates **2** and **3** are studied with ab initio molecular orbital calculations. The transition state of the cyclization reaction is postulated to be a low-symmetry C_s conformation derived from an "upright" bis(acetylene)cobalt. This accounts for the observed regioselectivity that the acetylenic carbon bearing a bulky substituent becomes the α-carbon of the metallacycle.

Introduction

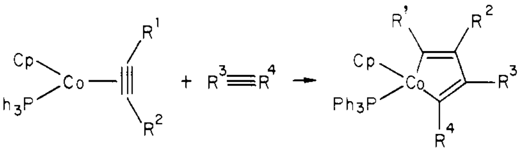
There has been much recent interest in metallacyclic compounds, especially those formed from unsaturated ligands such as olefins and acetylenes, principally in connection with the mechanism of transition-metal-catalyzed oligomerization reactions. While many experimental results have been accumulated, there has been little theoretical analysis of the reaction. A recent work by Stockis and Hoffmann deals with the reaction path of bis(olefin)tricarbonyliron to ferracyclopentane interconversion on the basis of extended Hückel molecular-orbital calculations.[3] More recently a closely related reaction, the degradation of nickelacyclopentane to ethylene, has also been analyzed by them.[4]

In the course of our investigation of the η^5-cyclopentadienylcobalt system, we have found that the reaction with acetylene to give cobaltacyclopentadiene is a very facile one. This property of $(\eta^5\text{-}C_5H_5)Co$ has been utilized by us and other workers for stoichiometric and catalytic preparation of a variety of cyclic organic compounds.[5]

In this paper we focus on the fundamental part of these reactions, i.e., the formation of the cobalt metallacycle from two molecules of acetylene, and elucidate its detailed mechanism with the aid of molecular orbital theory.

Results and Discussion

Reaction Route. Previously we reported that the reaction of η^5-cyclopentadienyl(triphenylphosphine)(acetylene)cobalt (**1**) with acetylene yielded cobaltacyclopentadiene complexes (**4**) with various substituents (eq 1).[6] To date over 20 compounds of **4**

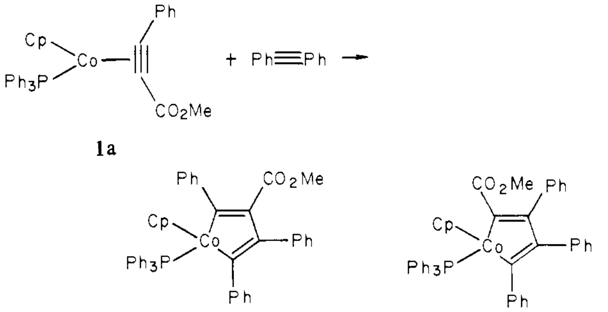


(1)

1 **4**

R^1, R^2 = Ph, CO_2Me, CN
R^3, R^4 = H, Me, Ph, CO_2Me, Fc
Cp = $\eta^5\text{-}C_5H_5$
Fc = ferrocenyl

have been prepared by this and similar reactions. For example, the reaction of methyl phenylpropiolate complex **1a** with excess diphenylacetylene gives two isomeric cobaltacyclopentadienes (**4a-1** and **4a-2**) in 5:1 ratio (eq 2).



1a **4a-1** **4a-2** (2)

The rate of reaction 2 at room temperature in CD_2Cl_2 was followed by NMR spectra with or without the addition of free

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(1) For part 10, see: Wakatsuki, Y.; Sakurai, T.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1982**, 1923.

(2) (a) The Institute of Physical and Chemical Research. (b) Present address: Osaka City University, Sumiyoshi-ku, Osaka 558. (c) Institute for Molecular Science.

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(5) (a) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1973**, 280. (b) Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383. (c) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Ibid.* **1974**, 4549. (d) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (e) Hillard, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058. (f) Funk, R. L.; Vollhardt, K. P. C. *Ibid.* **1980**, *102*, 5245, 5253. (g) Stenberg, E. D.; Vollhardt, K. P. C. *Ibid.* **1980**, *102*, 4839.

(6) (a) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157. (b) Yasufuku, K.; Yamazaki, H. *Ibid.* **1977**, *127*, 197.

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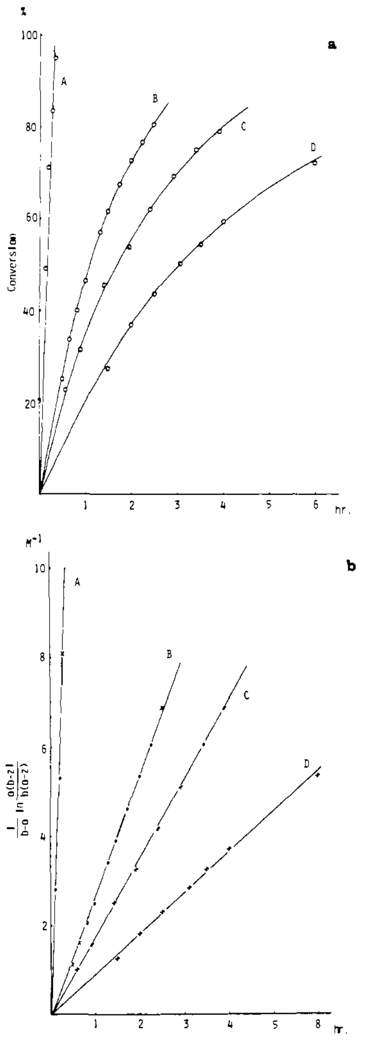
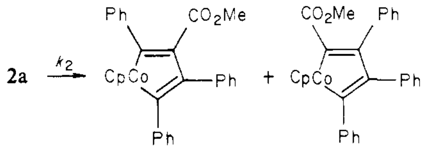


Figure 1. Effect of PPh_3 concentration on the rate of cobaltacyclopentadiene formation from **1a**, 0.5×10^{-1} M, and tolan, 2.6×10^{-1} M: (A) no PPh_3 added, (B) 0.8×10^{-1} M, (C) 1.3×10^{-1} M, (D) 2.6×10^{-1} M PPh_3.

triphenylphosphine. As the PPh_3/**1a** ratio was increased from 0 to 5.2, the apparent rate of reaction decreased markedly (Figure 1a). The influence of added triphenylphosphine for reaction 2 may be explained by the mechanism outlined in eq 3–6, which involves the bis(acetylene)cobalt intermediate **2**.

$$\mathbf{1a} + Ph_2C_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{2a}}{CpCo(Ph_2C_2)(PhC_2CO_2Me)} + PPh_3 \quad (3)$$



(4)

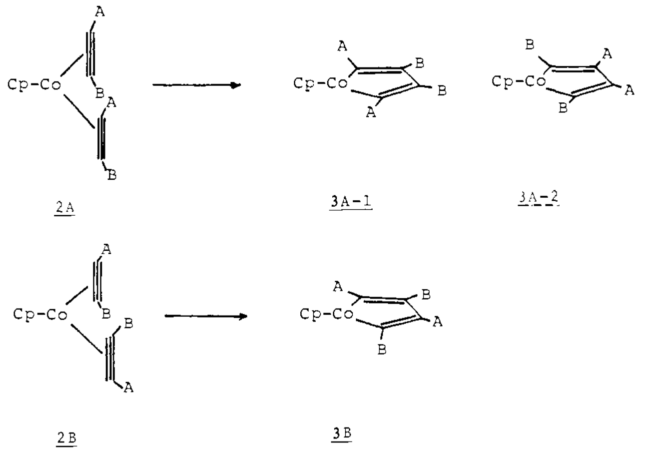
3a-1 3a-2

$$[\mathbf{3a\text{-}1}, \mathbf{3a\text{-}2}] \xrightarrow{PPh_3} \mathbf{4a\text{-}1} + \mathbf{4a\text{-}2} \quad (5)$$

$$\mathbf{2a} + PPh_3 \xrightarrow{k_3} \mathbf{4a\text{-}1} + \mathbf{4a\text{-}2} \quad (6)$$

It may be assumed that stationary state is retained for intermediates **2a** and **3a**. It is also assumed that the concentrations of these intermediates are much smaller than those of the reactants; i.e., concentrations of **1a**, diphenylacetylene, and triphenylphosphine during the reaction can be approximated as $a - z$, $b - z$, and c where a, b, and c are their initial concentrations and z is the concentration of the product **4a**.

Scheme I



One then gets the expression

$$d(\mathbf{4a})/dt = dz/dt = \frac{k_1(k_2 + k_3c)}{k_2 + k_3c + k_{-1}c}(a - z)(b - z)$$

or in an integrated form:

$$\frac{1}{(b - a)} \ln \frac{a(b - z)}{b(a - z)} = Kt \quad (7)$$

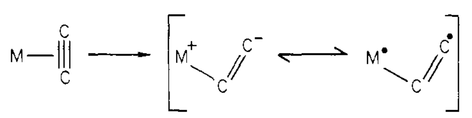
where

$$K = \frac{k_1(k_2 + k_3c)}{(k_2 + k_3c + k_{-1}c)}$$

Figure 1b shows the fit of data to eq 7 whose slopes gave the following values: $k_1 = 8.5 \times 10^{-3}$ M^{-1} s^{-1} (line A) and $K = 7.5 \times 10^{-4}$ (line B), 4.8×10^{-4} (line C), and 2.5×10^{-4} M^{-1} s^{-1} (line D). These k_1 and K values give $k_{-1}/k_2 = 1.3 \times 10^2$ M^{-1} and $k_3/k_2 = 1.0 \times 10^{-1}$ M^{-1}. The small k_3/k_2 value indicates that the bis(acetylene)cobalt **2** changes into coordinatively unsaturated metallocyclic intermediate **3**, which is then coordinated by phosphine to give the final product **4**. The direct formation of **4** from **2** and triphenylphosphine (eq 6) is a minor process and negligible under the phosphine concentrations employed here ($\sim$0.3 M), although it will become important in a extreme case where a large amount of phosphine is added.

Regioselectivity. Having established that the key step of cobaltacyclopentadiene formation is spontaneous cyclization of bis(acetylene)cobalt, we now consider if unsymmetric acetylenes react regioselectively.

Otsuka and Nakamura have interpreted the regioselectivity of reaction 1 in terms of a different degree of ionic character in thermally activated η^1-acetylene intermediates.[7]



On the basis of a theoretical analysis Stockis and Hoffmann have proposed that in the coupling reaction of bis(olefin) or bis(acetylene) complexes the controlling orbital is the HOMO of the complex, the ligand part of which is dominated by π^*.[3] Regioselectivity, therefore, originates from polarity in the π^* orbital of an unsymmetrical olefin or acetylene; i.e., the carbon with the electron-withdrawing substituent is transformed into the α-carbon of the metallacycle while the carbon with the electron-donating substituent is transformed into the β-carbon of the metallacycle.

The pathway for the coupling reaction of two asymmetric acetylenes on our $(\eta^5\text{-}C_5H_5)Co$ system is illustrated in Scheme

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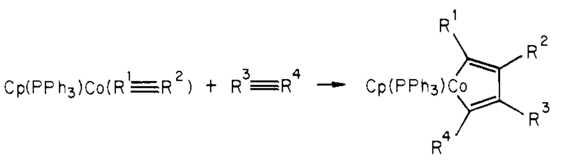
(7) Otsuka, S.; Nakamura, A.; *Adv. Organomet. Chem.* **1976**, *14*, 245.

Table I. Isomers of Cobaltacyclopentadienes



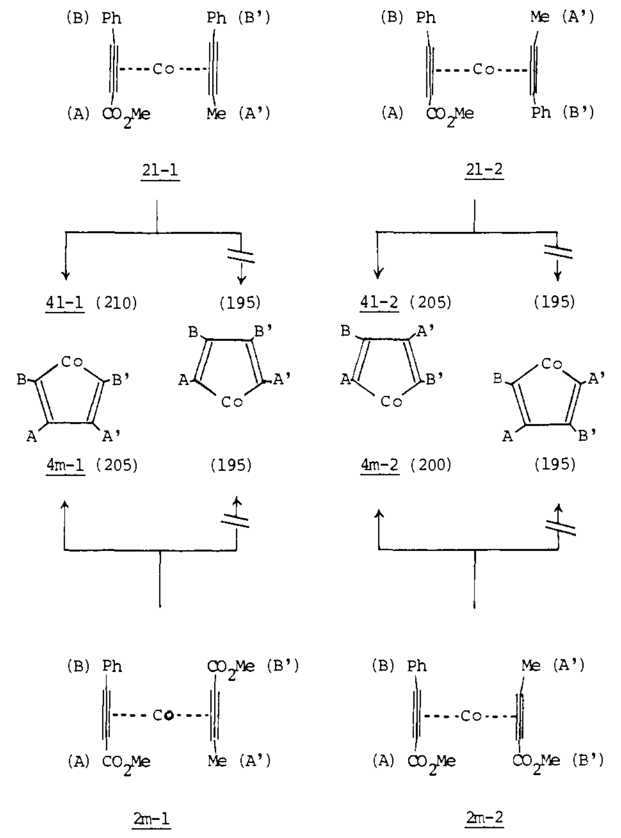
	R^1	R^2	R^3	R^4	yield, %
4b	Ph	Ph	H	Ph	85
4c	Ph	Ph	H	*p*-MeC_6H_4	55
4d	Ph	Ph	Me	Ph	67
4e	Ph	Ph	H	CO_2Me	64
4f	Ph	Ph	Me	CO_2Me	68
4g	CO_2Me	CO_2Me	Ph	Fc	60
4h·1	Ph	Ph	CO_2Me	Ph	82
4h-2	Ph	Ph	Ph	CO_2Me	13
4i	Ph	Me	Me	Ph	54
4j-1	Ph	CO_2Me	Ph	CO_2Me	40
4j-2	Ph	CO_2Me	CO_2Me	Ph	22
4k-1	CO_2Me	Me	CO_2Me	Me	50
4k-2	CO_2Me	Me	Me	CO_2Me	9
4l-1	Ph	CO_2Me	Me	Ph	48
4l-2	CO_2Me	Ph	Me	Ph	24
4m-1	Ph	CO_2Me	Me	CO_2Me	39
4m-2	CO_2Me	Ph	Me	CO_2Me	19
4n-1	CO_2Me	Ph	Ph	Fc[a]	25
4n-2	Ph	CO_2Me	Ph	Fc	24

[a] Fc = ferrocenyl.

I. The bis(acetylene)cobalt intermediate will take either conformation **2A** or **2B**. From the antiparallel orientation **2B**, a distinct product, **3B**, is formed, whereas two linkages, **3A-1** and **3A-2**, are possible in the case of **2A**. Table I lists cobaltacyclopentadienes (**4**) from unsymmetric acetylenes, the preparation and isolated yield of which we have already reported.[6] We reexamined the isomer ratio by NMR spectra without separating the isomers to obtain more accurate values. Complexes **4b** to **4g** in Table I show that only one of the two possible metallocycles is formed. Although both of the possible structures are obtained in the case of **4h**, one of them is predominant.[8] When the coordinated acetylene and the attacking one are of the same kind as in **4i–k**, exactly the case shown in Scheme I, the products indicate that only one of the two possible linkages from **2A** type bis(acetylene)cobalt occurs. Unexpectedly **3B**-type "cross" cyclization is not observed in **4i**. In the case of **4l–n**, where the acetylene added was different than the one present in the acetylene complex, only two of four possible metallacycles are obtained.

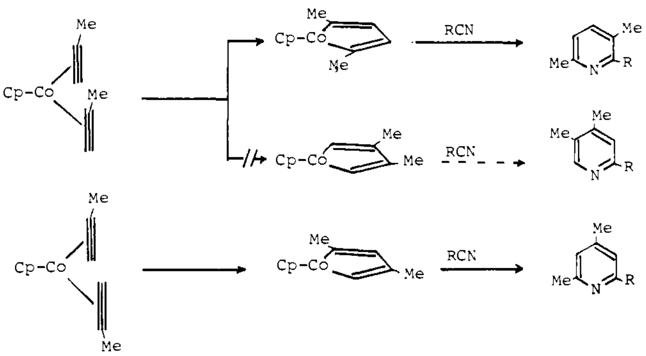
All the results in Table I suggest a regioselective nature of the reaction. But it is difficult to explain some of these results by the electronic effect suggested by Otsuka or Hoffmann. The electronic effect here appears to be a minor factor. In a typical example, addition of methyl propiolate or methyl methylpropiolate to the diphenylacetylene complex gives **4e** and **4f**, in which the strongly electron-withdrawing carbomethoxy group occupies the α-position, in accord with the prediction by Stockis and Hoffmann. Addition of methyl phenylpropiolate to the same acetylene complex, however, gives predominantly **4h-1** in which the less electron-withdrawing phenyl group rather than the carbomethoxy group occupies the α-position of the metallacycle. Likewise, formation of **4g**, **4j-2**, **4n-1**, and **4n-2**, as well as predominance of **4l-1** and **4m-1** and **4l-2** and **4m-2** does not meet the presumption based on polarity of the π^* MO.[9] In contrast, all the experimental results in Table I are compatible with the rule that the cobalt atom of bis(acetylene) intermediate tends to form σ bonds with the acetylenic carbons bearing bulky substituents.[10] Let us consider the most complicated examples, **4l–n**, where two different acetylenes with unsymmetrical substituents are involved. For simplicity we mark the smaller substituent as A and the bulkier one as B for one acetylene, A′ and B′ for the other acetylene. The correlations of the bis(acetylene)cobalt intermediates, **2l** and **2m** with cobaltacyclopentadiene derived therefrom, **4l** and **4m**, are illustrated in Scheme II.

Scheme II[a]



[a] Values in parentheses indicate the sum of the cone angle values of two α substituents.[10]

Scheme III



The "parallel" orientation of the bis(acetylene) intermediates **2l-1** and **2m-1** results in **4l-1** and **4m-1** in which bulky substituents B and B′ occupy the α-positions of the metallacycle. In the case of the "antiparallel" orientation, **2l-2** and **2m-2**, the situation is more complicated. To predict which pair of the substituents, i.e., (A B′) or (A′ B), occupies the α-positions, the total of bulkiness, e.g., cone angle, appears to be useful. The pair (A B′) is preferred for the α positions because the sum of cone angles of A and B′ is greater than that of A′ and B, as indicated in Scheme II.[10] In

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(8) Isomers **4h-1** and **4h-2** are the same complexes as **4a-1** and **4a-2**, respectively. Their isomer ratios are nearly the same in spite of the different reaction route in different reaction media, providing evidence for the common intermediate **2a**.

(9) σ values: Fc, −0.15; Me, −0.07; Ph, 0.22; CO_2Me, 0.40: (a) Nesmeyanov, A. N.; Perevalova, E. G.; Gubin, S. P.; Grandberg, K. I.; Kozlovskii, A. G. *Tetrahedron Lett.* **1966**, 2381. (b) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

(10) Cone angles: H, 75; Me, 90; COMe, 100; Ph, 105: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. Our CPK model study showed the cone angle of CO_2Me is comparable to that of the COMe group and Fc is much larger than Ph.

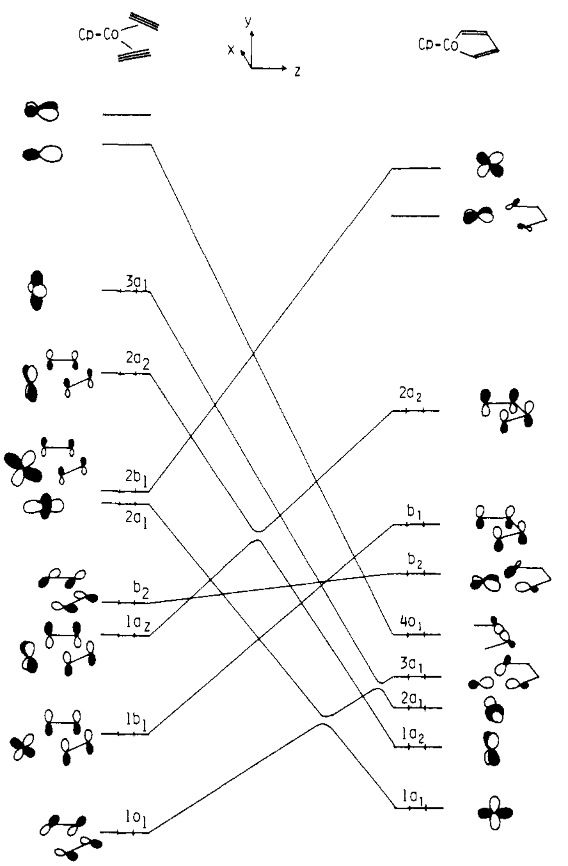

Figure 2. Schematic correlation diagram for the transformation of coplanar bis(acetylene)cobalt (left) into prependicular cobaltacyclopentadiene (right). C_{2v} symmetry is assumed.

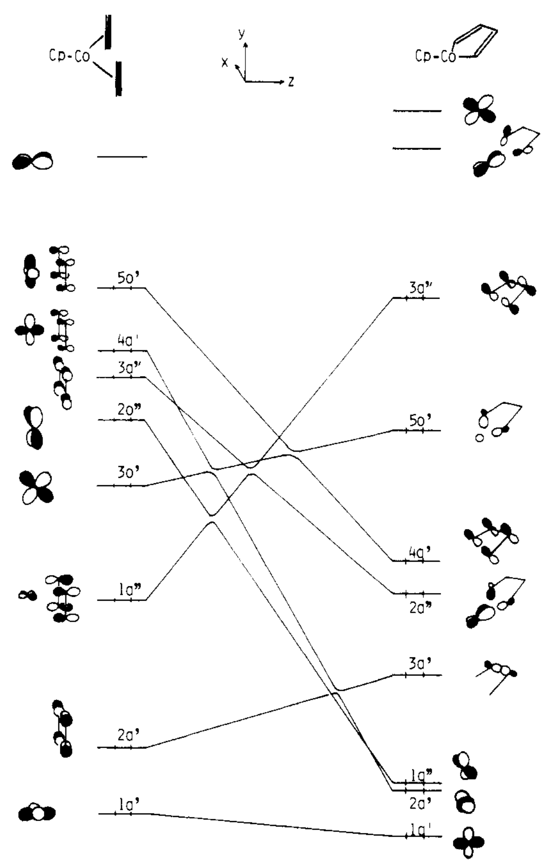

Figure 3. A schematic correlation diagram forr the transformation of upright bis(acetylene)cobalt (left) into tilted cobaltacyclopentadiene (right). C_s symmetry is assumed.

simpler cases, **4b–k**, the validity of the above rule can easily be confirmed.

This rule also controls the regioselectivity of catalytic reactions. In "CpCo" catalyzed co-cyclotrimerization of alkylacetylenes with nitriles, the reaction route has been well established to involve the attack of acetylene on (acetylene)cobalt to form a cobaltacyclopentadiene intermediate.[11] The fact that the product of this reaction is a mixture of 2,3,6- and 2,4,6-substituted pyridine but not the 2,4,5-substituted isomer[12] indicates a strong preference of 2,5-dialkyl metallacycle over 3,4-dialkyl metallacycle, as illustrated in Scheme III.

Theoretical Analysis. In order to obtain a mechanistic picture of the cyclization process, we carried out molecular orbital calculations on bis(acetylene)cobalt (**2**) and cobaltacyclopentadiene (**3**) intermediates. The calculations were based on the ab initio SCF-MO method, and throughout the model calculations unsubstituted acetylene was used.

For bis(acetylene)cobalt, two conformations may be considered, "upright" acetylene (**2**) and "coplanar" acetylene (**2′**) (see Scheme IV). The schematic correlation diagrams for their oxidative cyclization process, based on calculated MO levels of the reactant and the product, are compared in Figures 2 and 3. The cyclization of the "coplanar" coordination (**2′**) in a least-motion process (C_{2v} symmetry) is thermally forbidden (Figure 2). The basic reason is that the symmetry of the filled metal orbital to be oxidized (d_{yz}, $2b_1$) is not matched by the symmetry of the C–C bond ($4a_1$) that is newly formed as the result of oxidative cyclization. In this connection, a similar cyclization process with lower symmetry, C_s (the plane of symmetry is yz), is allowed since both the metal orbital to be oxidized and the orbial of the new C–C bond are of a′ symmetry. The other C_s cyclization process, starting from the "upright" form and leading to the tilted metallocycle, is also allowed, as illustrated schematically in Figure 3.

The optimized structures and the relative energies of bis(acetylene)cobalt and cobaltacyclopentadiene are illustrated in Figure 4. There is no experimental structure that can be directly compared with the calculated geometry of **2**, but the calculated cobalt–acetylene distance of 2.05 Å is longer than the experimental values for metal–olefin distance in known first-row d^8 transition-metal–monoolefin complexes (in $(CO)_4$Fe(fumaric acid)[13] and $(CO)_4$Fe(acrylonitrile)[14] the Fe–olefin bond length is 1.97 Å). This longer distance in our bis(acetylene) complex may be real and due to repulsion between the two acetylenes. When the metal–acetylene distance was shortened to 1.90 Å with other factors fixed, the total energy increased by ca. 11 kcal/mol (Table II). As shown in Table II for the bis(acetylene) fragment, about one-half of this destabilization is caused by repulsive interaction between the two acetylene molecules, which are separated by 2.84 Å from each other in this unstable geometry (the van der Waals radius of acetylenic carbon is 1.60 Å).

The coplanar bis(acetylene)cobalt was optimized only for the C_2H_2–Co–C_2H_2 angle, and the other factors were taken from the most stable geometry of the upright conformation. The free bis(acetylene) fragment with the coplanar conformation is ca. 5 kcal/mol higher in energy than the upright bis(acetylene) fragment, presumably due to steric repulsion. The energy difference is enhanced to 42 kcal/mol upon coordination to CpCo, most probably due to the additional steric repulsion between the Cp group and acetylene molecules in the coplanar orientation as well as the effective back-donation in the upright form. The full optimization for the coplanar structure would reduce the energy difference to a certain extent but would not upset the trend. Thus we suppose that the large destabilization by the conformational change, upright (**2**) → copolanar (**2′**), would exclude a reaction pathway that includes **2′** and related coplanar forms.

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[11] Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1278.

[12] Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26.

[13] Pedone, C.; Sirigu, A. *Inorg. Chem.* **1968**, *7*, 2614.

[14] Luxmoore, A. R.; Truter, M. P. *Acta Crystallogr.* **1962**, *15*, 1117.

Table II. Calculated Relative Energies for the Bis(acetylene)cobalt 2,2′, Bis(acetylene) Fragment, and the Cobaltacyclopentadiene 3,3′[a]

form	*l*(M-CC), Å	*l*(C-C), Å	CC-M-CC, deg	CCH bend, deg	rel energy, kcal/mol
2 upright	2.05	1.215	96.5	12.8	0.0[b]
	(1.90)	(1.215)	(96.5)	(12.8)	+10.7
2′ coplanar	(2.05)	(1.215)	109.6	(12.8)	+42.4

form	*l*(Or[c]-CC), Å	*l*(C-C), Å	CC-Or[c]-CC, deg	CCH bend, deg	rel energy, kcal/mol
2 × (C_2H_2)		(1.215)		(12.8)	−4.4
upright					
(C_2H_2)$_2$	(2.05)	(1.215)	(96.5)	(12.8)	0.0[d]
(C_2H_2)$_2$	(1.90)	(1.215)	(96.5)	(12.8)	+5.2
coplanar					
(C_2H_2)$_2$	(2.05)	(1.215)	(109.6)	(12.8)	+4.6

form	Cp-diene dihedral angle ϕ, deg	*l*(M-C), Å	θ(M-Cα-H), deg	rel energy, kcal/mol	
3	66	1.93_4	126	0.0[e]	0.0[f]
3′	(90)	(1.93_4)	(126)	+3.8	+4.9[f]

[a] Assumed geometrical parameters in parentheses. [b] Total energy = −370.8644 hartrees. [c] Origin of the coordinate: In complexes, the Co atom is placed at the origin. [d] Total energy = −151.68044 hartrees. [e] Total energy = −370.84198 hartrees. [f] Calculated with set B.

The geometry of cobaltacyclopentadiene **3** was partially optimized in the calculation. The butadiene skelton of the metallocycle was fixed at the experimental structure of the closely related but coordinatively saturated Co complex.[15] The geometry was optimized for the metal–C_α bond length (*l*), the bond angle of $CoC_\alpha H_\alpha$ (θ), and the angle between the Cp and the metallacycle planes (ϕ). The optimized *l* and θ were 1.93_4 Å and 126°, in reasonable agreement with the experimental values, 1.99 Å and 127°.[15] The geometrical parameter of particular interest is the dihedral angle (ϕ) between the two planes in the molecule. The most stable conformation was calculated to be a "tilted" geometry with the angle ϕ of 66° (**3** in Scheme IV). The total energies of this geometry and the "perpendicular" geometry (angle 90° with all other parameters assumed to be unchanged, **3′** in Scheme IV) were further calculated by using a double-ζ basis set (set B) to obtain more reliable values. The small energy difference between the two geometries thus calculated, 5 kcal/mol (Table II), suggests easy flipping of the metallacycle, and this is in accord with our previous postulation that a cyclopentadienylcobaltacycloheptene flips at room temperature.[16]

Ville, Vollhardt, and Winter have reported evidence that the cyclobutadiene unit coordinated to CpCo reversibly retrocyclizes in a severe condition (540–650 °C), forming a bis(acetylene)cobalt intermediate.[17] Using an enantiomerically enriched complex, they have proved that the retrocyclization of ligating cyclobutadiene proceeds directly, and if cobaltacyclopentadiene is involved in the course of retrocyclization process, the metallacycle has to be configurationally stable. The configurational lability of **3** calculated here supports their conclusion that metallacycle **3** or **3′** is not an intermediate in their reaction.

The present calculation using the basis set A and partially optimized structures suggests that the transformation of **2** to **3** is an endothermic reaction (ΔE = 14 kcal/mol, Figure 4).

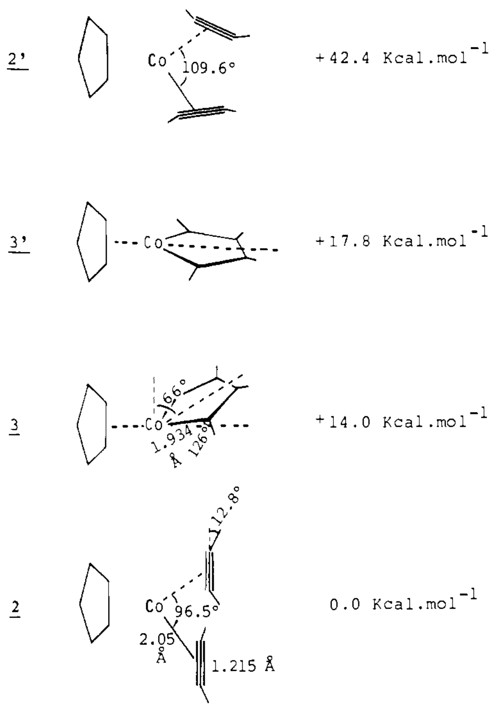

Figure 4. Calculated geometries for the bis(acetylene)cobalt **2,2′** and the cobaltacyclopentadiene **3,3′**.

Table III. Muliken Populations for the Cobaltacyclopentadiene with Different Metal–Carbon Distances[a]

Co–C_α, Å	cobalt 3d	4s	4p	charge
1.934	7.597	0.767	0.483	+0.153
2.200	7.798	0.666	0.608	−0.072

Co–C_α, Å	C_α π	C_α σ	C_α charge	C_β π	C_β σ	C_β charge	2(C_α + C_β) π	2(C_α + C_β) σ
1.934	0.925	3.208	−0.125	0.923	3.129	−0.044	3.696	12.674
2.200	0.960	3.057	−0.009	0.957	3.094	−0.044	3.834	12.302

[a] These results were obtained with the minimal basis set (set A) and with the geometries: bond angle $CoC_\alpha H_\alpha$ = 126°; angle between Cp and metalloring = 66°.

Another point of interest is the extent of electron delocalization in the metallacycle. Based on the fragment population analysis ($Cp(PH_3)Co^{2+}$ and $C_4H_4^{2-}$) of an extended Hückel calculation, Thorn and Hoffmann have suggested a very small electron delocalization involving the C_4H_4 π-type orbitals.[18] A measure of delocalization in the metal-bonded π system would be the π-charge flow between the metal and C_4H_4 unit. For this purpose, total and orbital populations for the "tilted" metallacycle at two different Co–C_α bond lengths (*l*) are compared in Table III. We see first that the atomic population for the most stable geometry ($l = 1.93_4$ Å) is consistent with the designation of widely accepted metal–carbon σ bond, M(δ+)–C(δ−). At the M–C_α distance of 2.20 Å, however, the polarity of M–C is reversed, indicating that the distance is too far to form a reasonable bond. The charge flow from the metal to C_α is observed as the bond length is shortened. The atomic charge on Co in Table III suggests ca. 0.23 electron moves from Co to the C_4H_4 unit as the M–C_α bond decreased from 2.20 to 1.934 Å. This is, as indicated by the valence orbital populations of C_α and C_β, brought about mainly by charge flow through the σ bond, while through the π bond ca. 0.14 electron moves reversely from the C_4H_4 unit to Co. On this basis one may conclude that the charge flow through the Co–C_α π bond in cobaltacyclopentadiene is small but should not be neglected.

Conclusions

The present molecular orbital calculation on bis(acetylene)cobalt **2** and cobaltacyclopentadiene **3** gives a qualitative picture

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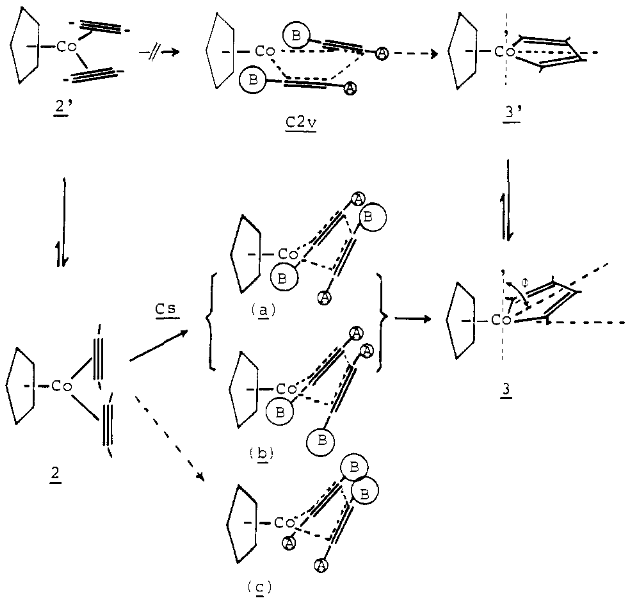
Scheme IV



of the **2** to **3** transformation, which is summarized in Scheme IV.

Assuming concerted reaction paths, one can imagine two transition states, C_{2v}, derived from the coplanar conformation **2′**, and C_s, derived from the upright conformation **2**. On the basis of the following reasons, we conclude that the C_s transition starting from **2** is operating in the reaction. (i) The transformation of **2′** to **3′** in a least-motion process is thermally forbidden. (ii) Coplanar bis(acetylene)cobalt **2′** is found to be substantially less stable than the upright conformer **2**. Presumably **2′** has a smaller back-donative stabilization and a larger steric repulsion. When substituted acetylene is used in the reaction, the steric repulsion between Cp and the bulky acetylenic substituents will further destabilize **2′**. (iii) The tilted geometry of the metallacycle **3** is calculated to be more stable than the perpendicular geometry (**3′**). (iv) The experimental observation that the acetylenic carbon having a bulky substituent becomes the α-carbon of the metallocycle is in accord with the C_s transition state derived from **2**. When the two acetylene molecules are not antiparallel, the system has two choices, C_s-b and C_s-c. Path C_s-b must be preferred to C_s-c because the bulkier substituents, B's, are directed to the most vacant site as shown in Scheme IV. Thus the transition state suffers only a small steric repulsion between the two less bulky substituents, A's. On the contrary, the path where the less bulky substituents, A's, become the α-carbons as in C_s-c is unfavorable because of a large steric repulsion between two bulky B's at the β-positions.

It remains to be answered whether intermediate **2** prefers a parallel or antiparallel orientation for a given substituted acetylene.

The present study and the Stockis and Hoffmann results reveal two controlling factors, steric and electronic, for the regioselectivity of the oxidative coupling reaction. When the substituents are bulky, the steric factor controls the selectivity. This factor, as we found, can override the electronic factor when they compete and gives a trend that is the reverse of that predicted by the electronic factor.

Experimental Section

Acetylenes were commercial grade and used without further purification. Acetylene complexes of cobalt were prepared according to the previously reported method.[6]

Kinetics. The kinetic study on the formation of **4a-1** and **4a-2** was conducted at 27.0 °C in CD_2Cl_2 solutions. A mixture of **1a** (11.0 mg, 0.02 mmol), triphenylphosphine (four runs, 0.0, 1.55, 2.60, 5.20 in molar ratio to **1a**) and diphenylacetylene (18.4 mg, 0.103 mmol) was placed in an NMR tube and dissolved in CD_2Cl_2 (0.4 mL) under an atmosphere of argon. The reaction was monitored by peak intensities of sharp CO_2Me resonances of **1a** (δ 3.06), **4a** (δ 2.52), and **4b** (δ 2.29).

Measurements of Isomer Ratio in 4. In a typical experiment, a mixture of **1a** (60 mg, 0.11 mmol) and triphenylphosphine (29 mg, 0.11 mmol) was dissolved in benzene (10 mL) under an atmosphere of argon, and phenylpropyne (0.1 mL) was added. The solution was stirred overnight and chromatographed on alumina (Sumitomo KCG-30, 1.5 × 5 cm) to remove a small amount of decomposed materials. Free triphenylphosphine was eluted with benzene/hexane (1:1), and then all the fractions eluted with CH_2Cl_2 were collected. On removal of the solvent under reduced pressure, the residue crystallized; it was then weighed and subjected to NMR measurement. Besides the expected peaks of **4l-1** and **4l-2**, very small peaks due to 1-carbomethoxy-2,4,5-triphenyl-3,6-dimethylbenzene and **4g** were detected.

Details of Calculations. All the ab initio calculations were performed on the HITAC-M200H computer at the Institute for Molecular Science by using the program package IMSPACK.

In Hartree–Fock calculations the [Ar] core of Co was replaced with an effective core potential (ECP). 4s and 4p orbitals of Co were three-term GTO's evaluated by Topiol et al. for the electronic configurations $(4s)^2(3d)^7$ and $(4p)^1(3d)^8$, respectively.[19] To represent 3d-valence orbitals, five-term GTO's of Hay[20] were contracted to [2d]. The standard STO-3G set built in GAUSSIAN 70 was used for C and H. This basis set (set A), thus, is a minimal basis set except for double-ζ (DZ) functions for the 3d orbitals. All the calculations on bis(acetylene)cobalt and geometry optimization of the metallacycle were carried out with this basis set. Since the energy difference between the most stable geometry of the "tilted" and the "perpendicular" metallacycle was small, it was further calculated with a DZ basis set (set B) in which Topiol's (3s,3p) primitive set of Co contracted to [2s,2p], and a 4-31G set of C and H was used. The difference of results between the two basis sets was small.

Throughout the calculations the CpCo fragment was held rigid, with Cp–Co distance of 1.8 Å and C–C and C–H distances of 1.43 and 0.98 Å. The C and H atoms of Cp were placed in a plane. Geometrical optimization of **2** was carried out with fixed acetylenic C–H bond length of 1.06 Å. Its CCH bend-back is away from the metal. In the geometrical optimization of **3** the framework of C_1–C_4 of the metallacycle ($C_1C_2 = C_3C_4 = 1.33$ Å, $C_2C_3 = 1.45$ Å, $C_1C_2C_3 = C_2C_3C_4 = 116.2°$) and C–H distances (1.08 Å) were also held fixed. The metal, C, and H atoms of the metallacycle were placed in a plane.

Registry No. 1a, 53469-97-9; **1** ($R^1 = R^2 =$ Ph), 12172-41-7; **1** ($R^1 = R^2 = CO_2Me$), 50277-79-7; **1** ($R^1 =$ Ph; $R^2 =$ Me), 84802-72-2; **1** ($R^1 = CO_2Me$; $R^2 =$ Me), 72159-88-7; **2**/**2′**, 81628-35-5; **3**/**3′**, 84802-73-3; **4a-1**, 55410-82-7; **4a-2**, 55410-92-9; **4b**, 55522-56-0; **4c**, 42516-59-6; **4d**, 55410-85-0; **4e**, 55410-84-9; **4f**, 55410-83-8; **4g**, 62842-91-5; **4i**, 55410-91-8; **4j-1**, 42442-00-2; **4j-2**, 42442-01-3; **4k-1**, 55410-90-7; **4k-2**, 55410-89-4; **4l-1**, 74658-46-1; **4l-2**, 84802-71-1; **4m-1**, 55410-87-2; **4m-2**, 55410-86-1; **4n-1**, 62842-89-1; **4n-2**, 62842-90-4; ethynylbenzene, 536-74-3; 1-ethynyl-4-methylbenzene, 766-97-2; 1-propynylbenzene, 673-32-5; methyl 2-propynoate, 922-67-8; methyl 2-butynoate, 23326-27-4; phenylethynylferrocene, 1292-14-4; methyl 3-phenyl-2-propynoate, 4891-38-7.

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