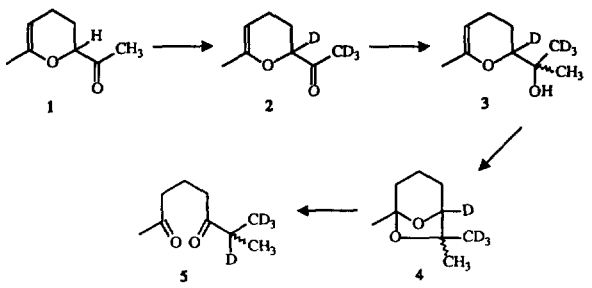
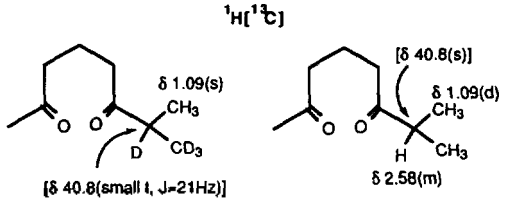


Scheme 3.



Scheme 4.

Now we wish to prove the mechanism for this novel skeletal transformation of bicyclic ketal to 1,5-diketone *via* deuterium labelling study.

If we have deuterium labelling at C-1 of bicyclic ketal, it will be easy to choose the correct mechanism between "a" and "b" as shown in Scheme 2. The deuterated diketone must result from path "a", whereas the protonated diketone must result from path "b".

To make deuterium labelled bicyclic ketal at C-1, MVK dimer **1** was deuterated with D_2O using NaOD as a catalyst (Scheme 3). We found that the less substituted site of the ketone (methyl group) is more reactive for deuterium exchange even in the thermodynamic conditions. So we deuterated all α and α′ protons to give compound **2** which was methylated with MeLi to carbinol **3** and cyclized to give expected deuterated bicyclic ketal **4**.

Finally, bicyclic ketal **4** was reacted with aluminium chloride-sodium iodide in methylene dichloride. The proton NMR spectrum indicated that deuterated diketone **5** was the only product; A multiplet at δ 2.58 of the methine proton disappeared and methyl group at δ 1.09 showed singlet. Also proton-decoupled carbon NMR spectrum showed that a singlet at δ 40.8 of the methine carbon turned to small triplet (J=21 Hz) (Scheme 4).

In conclusion, the mechanism for the transformation of bicyclic ketal to 1,5-diketone must be involved O(6)-C(5) bond cleavage followed by 1,2-hydride shift as shown in path "a" of Scheme 1.

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Spectral data for (**3**): ^{1}H-NMR (200 MHZ, $CDCl_3$) δ 4.44 (1H, m, CH=), 2.46 (1H, br s, OH), 2.09-1.75 (4H, m, CH_2 CH_2), 1.73 (3H, br s, CH_3C=), 1.21 (1H, s, CH_3) and 1.18 (2H, s, CH_3) indicates 1 : 2 ratio of diastereomer (threo : erythro); ^{13}C-NMR ($CDCl_3$) δ 151.2 (MeC=), 96.0 (CH=), 81.9 (small t, J=22 Hz, OCD), 26.2 and 24.5 (1 : 2 ratio of diastereomer for CH_3, small septet of CD_3 buried in this region), 22.5 (CH_2), 21.4 ($\underline{C}H_3C$=), 20.4 (CH_2).
Spectral data for (**4**): ^{1}H-NMR (200 MHZ, $CDCl_3$) δ 2.00-1.45 (6H, m, $CH_2CH_2CH_2$), 1.40 (3H, s, CH_3), 1.36 (2H, s, *endo*-CH_3); 1.26 (1H, s, *exo*-CH_3); ^{13}C-NMR ($CDCl_3$) δ 107.2 (s, OCO), 81.1 (small t, J=26 Hz, OCD), 80.8 (s, $O\underline{C}Me_2$), 34.2 (t, CH_2), 29.2 (q, CH_3), 24.2 (t, CH_2), 17.2 (t, CH_2), 25.8 and 20.9 (1 : 2 ratio of *exo* and *endo* CH_3, small septet for CD_3 also buried in the region).
Spectral data for (**5**): ^{1}H-NMR (200 MHZ, $CDCl_3$) δ 2.49 (2H, t, J=7 Hz, CH_2CO), 2.46 (2H, t, J=7 Hz, CH_2CO), 2.13 (3H, s, CH_3CO), 1.83 (2H, pent, J=7 Hz, CH_2), 1.09 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 214.2 (s, C=O), 208.4 (s, C=O), 42.6 (t, $\underline{C}H_2CO$), 40.8 (small t, J=21 Hz, $CDMe_2$), 39.0 (t, $\underline{C}H_2CO$), 29.8 (q, $\underline{C}H_3CO$), 18.2 (q, CH_3, CD_3, also buried as small multiplet in this region), 17.8 (t, CH_2).

The Mechanism for Cyclooligomerization of Acetylene: The Structures of $CpCo(C_4H_4)$ and $CpCo(\eta^2\text{-}C_2H_2)_2$ as Intermediates

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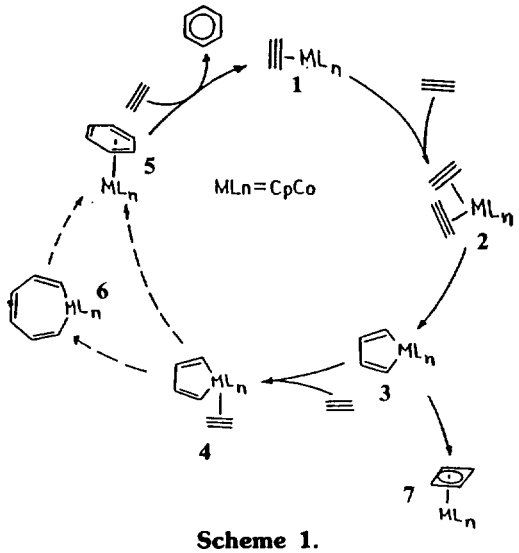
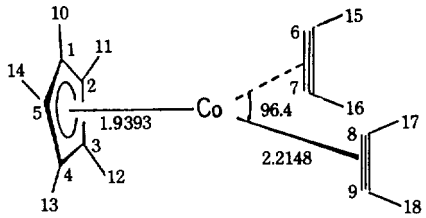
A reaction of long-standing interest to the organometallic chemistry has been the trimerization of acetylene to give benzene *via* a number of transition metal catalysts. Despite its commercial and academic importance, there has been no prior theoretical work and several important issues are not yet resolved.

The basic mechanism[1-3] is outlined in Scheme 1. An acetylene-ML_n adduct, **1**, adds a second acetylene ligand to give



Scheme 1.

Table 1. The Optimized Geometry for Bis(Acetylene)Cobalt Complex



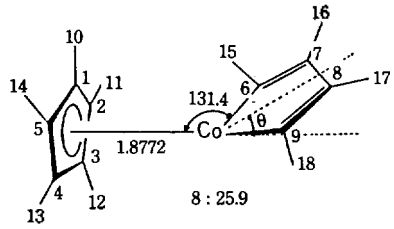
Bond lengths (Å)		Angles (deg.)		Total energies (a.u.)
C(1)-C(2)	1.4145	C(2)-C(1)-C(5)	107.5	−1723.7885 (HF level)
C(2)-C(3)	1.4177	C(1)-C(2)-C(3)	108.4	−1724.8142 (MP2 level)
C(3)-C(4)	1.4133	C(2)-C(3)-C(4)	107.8	
Co-C(6)	2.2833	C(2)-C(1)-H(10)	126.2	
C(6)-C(7)	1.1996	C(1)-C(2)-H(11)	125.9	
C(1)-H(10)	1.0787	C(2)-C(3)-H(12)	125.9	
C(2)-H(11)	1.0790	C(7)-C(6)-H(15)	172.3	
C(3)-H(12)	1.0787	C(6)-C(7)-H(16)	172.3	
C(6)-H(15)	1.0518			
C(7)-H(16)	1.0518			

2 which then cyclizes to 3 and picks up a third acetylene to yield 4. The metalacyclopentadiene 3 (under some conditions) can undergo an irreversible reductive cyclization to 7. This, of course, kills the catalytic cycle.

We have investigated several elementary steps in this cyclooligomerization mechanism for η^5-cyclopentadienylcobalt (CpCo) as an organometal catalyst. CpCo has also been utilized by other workers for stoichiometric and catalytic preparation of a variety of cyclic organic compounds.[4]

In this study we focus on the formation of bis(acetylene) cobalt complex by the reaction of two acetylenes with CpCo (1→2) and the transformation of bis(acetylene)cobalt into cobaltacyclopentadiene by an oxidative coupling reaction (2→3 cyclization step). For this purpose, the structures of the bis (acetylene)cobalt and cobaltacyclopentadiene intermediates are studied with *ab initio* molecular orbital calculations.[5]

Table 2. The Optimized Geometry for Cobaltacyclopentadiene Complex



Bond lengths (Å)		Angles (deg.)		Total energies (a.u.)
C(1)-C(2)	1.4186	C(2)-C(1)-C(5)	107.7	−1723.8316 (HF level)
C(2)-C(3)	1.4111	C(1)-C(2)-C(3)	108.3	−1724.8445 (MP2 level)
C(3)-C(4)	1.4262	C(2)-C(3)-C(4)	107.8	
Co-C(6)	1.9443	C(2)-C(1)-H(10)	126.1	
C(6)-C(7)	1.3282	C(1)-C(2)-H(11)	125.7	
C(7)-C(8)	1.4870	C(2)-C(3)-H(12)	126.1	
C(1)-H(10)	1.0779	Co-C(6)-C(7)	112.3	
C(2)-H(11)	1.0792	C(6)-C(7)-C(8)	115.3	
C(3)-H(12)	1.0793	C(6)-Co-C(9)	84.8	
C(6)-H(15)	1.0780	Co-C(6)-H(15)	125.2	
C(7)-H(16)	1.0763	C(7)-C(6)-H(15)	122.5	
		C(6)-C(7)-C(16)	124.2	
		C(8)-C(7)-H(16)	120.5	

First, the more stable conformation in the two possible conformations (where the acetylenes were upright or coplanar with respect to the Cp-Co axis) of the bis(acetylene)cobalt complex was the upright form. The optimized geometry[6] of the upright bis(acetylene)cobalt complex is shown in Table 1, together with the total energies. There is no experimental structure that can be directly compared with the calculated geometry of upright bis(acetylene)cobalt but the calculated cobalt-acetylene distance of 2.21 Å is longer than the experimental value for metal-olefin distance in known first-row d^8 transition-monoolefin complexes.[7,8] This is a frequent problem in geometry optimizations of olefin-metal complexes at the Hartree-Fock (HF) level.

The most stable conformation of cobaltacyclopentadiene that can be obtained in the 2→3 cyclization step was calculated to be a tilted geometry. The optimized geometry[6] of the tilted cobaltacyclopentadiene complex is shown in Table 2, together with the total energies. At the HF level 3 is computed to be 27.1 Kcal/mol more stable than 2. The difference decreases to 19.0 Kcal/mol at the MP2 level. This result is somewhat unexpected in that 2 is a saturated 18 electron complex, whereas, 3 is an unsaturated 16 electron species. A very qualitative thermodynamic rationale for this result can be constructed on the basis of experimentally determined bond dissociation energies for related transition metal complexes.[9] In the transformation of 2 to 3, two Co-acetylene bonds and two C-C π bonds are broken which are worth ~60 and 105 Kcal/mol, respectively. On the other hand, two Co-C σ bonds and a C-C σ bond are formed which results in an energy gain of ~100 and 92 Kcal/mol, respectively. This yields a net exothermic process of 27 Kcal/mol which is fortuitously close to the HF and MP2 values. This estimate takes into account that there is little difference in the M-

C bond dissociation energies across the first transition metal row.[9] The value of 50 Kcal/mol for the Co-C σ bonds in **3** is absolutely critical. This value is derived from $PhMn(CO)_5$ where the C atom is sp^2 hybridized as it is in **3**. For a M-C σ bond where the C atom is sp^3 hybridized (*e.g.*, $CH_3Mn(CO)_5$) the bond dissociation energy drops typically to 40-45 Kcal/mol.[9] Thus, cyclization of bis(ethylene)CoCp to a cobaltacyclopentane would be expected to be endothermic by 22 to 12 Kcal/mol (the C-C bond energy is 88 Kcal/mol). As noted before, a bis(acetylene)CoCp complex is unknown, whereas, phosphine adducts of the cobaltacyclopentadiene have been isolated. On the other hand, bis(ethylene)CoCp, in fact, does exist.[9] Our finding that **2** is 19 Kcal/mol less stable than **3** has an important implication on the catalytic cycle is Scheme 1. We suspect that a direct conversion of **1** (or a weakly coordinated benzene complex of **1**) to **3** occurs without the intermediacy of **2**.

The fully optimized cobaltacyclopentadiene complex at the HF level suggests that the structure tilts by 25.9 degrees, and takes a form which facilitates coordination of the third acetylene molecule in the catalytic cyclotrimerization of a acetylene. What is surprising is that optimization of **4** at the HF level yields only a van-der-Waals type of complex between the cobaltacyclopentadiene and acetylene. Consequently, at the present time we suspect that the acetylene either directly reacts in a Diels-Alder fashion with **3** to yield **5** or that acetylene insertion into the Co-C bond proceeds from **3** directly to **6** without the intermediacy of **4**. These details, as well as, model computations at more highly correlated levels will be reported in the future.

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Solvent Effects on the Optical Rotation of Some Amino Acid Derivatives

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The measurement of the optical rotation of optically active compounds at a single wavelength is widely used for the determination of the absolute configuration and the optical purity.[1-3] However, it is well known that the degree and/or sign of the rotation is sometimes dependent on concentration, solvent and temperature.[3] For example, L-tartaric acid is dextrorotatory in water, but is levorotatory in ethanol-benzene (1 : 1).[4] Another example is (R)-2-benzyloxy-1-octanol that is levorotatory in chloroform, but is dextrorotatory in methanol.[5] In this case C-1 methyl ether derivative is dextrorotatory in both solvents. This reversal in the sign of optical rotation has been ascribed to the conformational change caused by hydrogen bonding.[5] In chloroform, intramolecular hydrogen bonding leads to a OH/OR gauche conformation, whereas in electron pair donor (EPD) solvent[6] such as methanol the intramolecular hydrogen bond is broken by the intermolecular hydrogen bonding with the solvent, resulting in a predominance of different conformer (presumably anti conformer). Similar phenomenon is observed in (S)-5-hydroxy-1,7-diphenyl-3-heptanone, which is dextrorotatory in chloroform and levorotatory in methanol.[7]

We like to report another example of solvent effect on optical rotation observed in the case of some amino acid derivatives[8]

When the optical rotation of *N*-benzyloxycarbonyl-L-aspartic acid α-methyl ester (**1**)[9] was measured in chloroform and methanol, the rotation was dextrorotatory in chloroform but levorotatory in methanol. Similar reverse in sign of the rotation was observed in other amino acids such as methyl ester **4** of **1**, glutamic acid derivatives **2**, **3**[10] and serine derivative **7**,[11] as shown in Table 1. In the case of L-phenylalanine methyl ester **5**[12] the sign reversal was not observed. Instead, the rotation was nearly zero in methanol.

This reversal of sign or the change of magnitude can be explained by the similar reasoning given above in the case