

Theoretical Study of the Acetylene Trimerization with CpCo

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Abstract: A theoretical investigation of the mechanism of the CpCoL₂ (L = CO, PR₃, olefin) catalyzed acetylene cyclotrimerization reaction has been carried out at the ab initio and density functional theory (DFT) levels. The mechanism begins with a stepwise pair of ligand substitution reactions in which precatalyst CpCo(PH₃)₂ (**1**) is converted, via CpCo(PH₃)(η^2 -C₂H₂) (**2**), to CpCo(η^2 -C₂H₂)₂ (**3**) with the liberation of 11.3 kcal/mol at the B3LYP level. Oxidative coupling of the alkyne ligands in **3** to give a cobaltacyclopentadiene complex (**4**) is exothermic by 13.1 kcal/mol and is predicted to occur in a facile manner ($\Delta H^\ddagger = 12.8$ kcal/mol). Reductive cyclization of the bidentate C₄H₄ ligand in **4** to generate CpCo(η^4 -cyclobutadiene) (**8**) is considerably exothermic ($\Delta H = -34.0$ kcal/mol). However, the least motion pathway that transforms **4** directly into **8** which conserves a mirror plane is found to be symmetry forbidden, implying the presence of a large barrier. Coordination of a third acetylene to **4** results in the formation of CpCo(C₄H₄)(η^2 -C₂H₂) (**5**). Energetically, this third acetylene is weakly bound (12.4 kcal/mol). This is attributed to the parallel orientation of the acetylenic C–C bond vector occupies with respect to the Co–Cp bond axis. Collapse of **5** to CpCo(η^4 -C₆H₆) (**7**) occurs in a kinetically very facile process ($\Delta H^\ddagger = 0.5$ kcal/mol) reflecting the extremely exothermic nature of this transformation ($\Delta H = -81.4$ kcal/mol). An alternate path converting **5** to **7** via the intermediacy of a cobaltacycloheptatriene complex (**6**) was found to be energetically prohibitive due to the symmetry-forbidden nature of the reductive elimination converting **6** to **7**. In addition, a stationary point corresponding to **6** on the B3LYP potential energy surface could not be located. Completion of the catalytic cycle is achieved via a stepwise ligand substitution process in which two acetylene molecules displace the arene in **7** to regenerate **3** with the release of 7.4 kcal/mol at the B3LYP level. Two alternative pathways leading to arene formation in which a phosphine intercepts **4** and remains attached to the Co atom throughout the arene construction process were found to be unlikely mechanistic candidates.

Introduction

The thermal cyclotrimerization of acetylene to benzene is an intriguing reaction. The transformation is remarkably exothermic, liberating an estimated 142 kcal/mol¹ as three acetylenic π -bonds are converted into carbon–carbon σ -bonds. The reaction possesses an enormous activation barrier, calculated to lie in the 60–80 kcal/mol regime,² contrary to the generalization of the Hammond postulate regarding highly exothermic reactions. Moreover, this is a symmetry-allowed reaction, and the presence of such a large barrier is unusual in the context of the Woodward–Hoffmann rules. Overcoming a barrier of such magnitude requires temperatures in excess of 400 °C, rendering the product distribution uncontrollable and the resulting mixture of aromatic hydrocarbons too complex to efficiently separate.³ Thus the reaction is synthetically useless, despite the numerous synthetic advantages it possesses.⁴ Reppe's disclosure⁵ that low-valent nickel complexes catalyze alkyne cyclooligomerization provided the key to unleashing the synthetic potential of the cyclotrimerization process. A wide array of transition metal

containing fragments were subsequently found to actively catalyze the reaction. The CpCo-based catalysts proved particularly efficient while tolerating the presence of varied functionality on the alkyne.⁶ As a result, the CpCoL₂ (L = CO, PR₃, olefin) catalyst family was singled out for intensive study culminating in the development of Vollhardt's benzocyclobutene synthesis⁷ and Bönnemann's pyridine synthesis,⁸ both of which have appeared as key steps in the total synthesis of numerous natural products.⁴ Concurrent mechanistic investigations led to the proposal of the mechanism shown in Scheme 1.⁹ As an 18-electron complex, CpCoL₂ (**1**), undergoes a pair of ligand-substitution reactions resulting in the formation of a bisacetylene complex **3**, the catalytically active species.

Oxidative coupling of the alkyne ligands in **3** generates the coordinatively unsaturated cobaltacyclopentadiene, **4**, which is readily capable of coordinating a third acetylene to give the acetylene-coordinated cobaltacycle **5**. Insertion of this coordinated alkyne into one of the Co–C σ -bonds forms cobaltacycloheptatriene **6**, which subsequently undergoes reductive elimination to the η^4 -benzene complex, **7**. Decomplexation of the arene and coordination of a pair of acetylene molecules

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catalyzed by CpCo centers using molecular orbital calculations at the extended Hückel, ab initio, and density functional theory (DFT) levels. We have chosen to model the CpCo(PPh₃)₂ system due to its use in a number of important mechanistic studies and because of the puzzling mechanistic alternatives this catalyst presents.

Computational Methods

The structures reported herein were initially optimized at the Hartree–Fock level, and single-point energy calculations were performed on the HF-optimized geometries at the MP2 and CISD levels with the Gaussian90¹⁷ and GAMESS¹⁸ program packages. The post-HF calculations utilized the frozen-core approximation, and the CISD energies were corrected for the effects of size-consistency by using the Davidson correction. Electron correlation effects were accounted for more fully by optimizing the geometries at the DFT level using Becke's three parameter hybrid exchange–correlation functional¹⁹ containing the nonlocal gradient correction of Lee, Yang, and Parr (Becke3LYP)²⁰ within the Gaussian92/DFT²¹ and Gaussian94²² program packages. Unless otherwise noted, the energies reported herein are at the B3LYP/B3LYP level and include corrections for zero-point vibrational energies and basis set superposition error. The BSSE correction was estimated for all species by performing counterpoise (CP) calculations. Coordinates and total energies for all the molecules reported in this paper are available upon request. The alkyl and aryl phosphine moieties present in the experimentally observed complexes were modeled as PH₃ to reduce the computational complexity of the calculations involving these ligands. All geometries were optimized under C_s symmetry unless otherwise specified and were confirmed as minima or transition structures by calculation of analytic vibrational frequencies. An all-electron basis set for Co was constructed from Huzinaga's (4333/43/4) primitive set²³ for Co by replacing the d, 4s, and augmented 4p functions by corresponding basis functions optimized for molecular environments^{24,25} to yield a basis of the form (4333/433/31). Standard 3-21G basis sets²⁶ were used for P, O, C, and all H atoms not contained within an η⁵-C₅H₅ group or PH₃; these remaining H atoms were described by the standard STO-3G basis set.²⁷ Atomic coordinates and energies are available from the authors by request.

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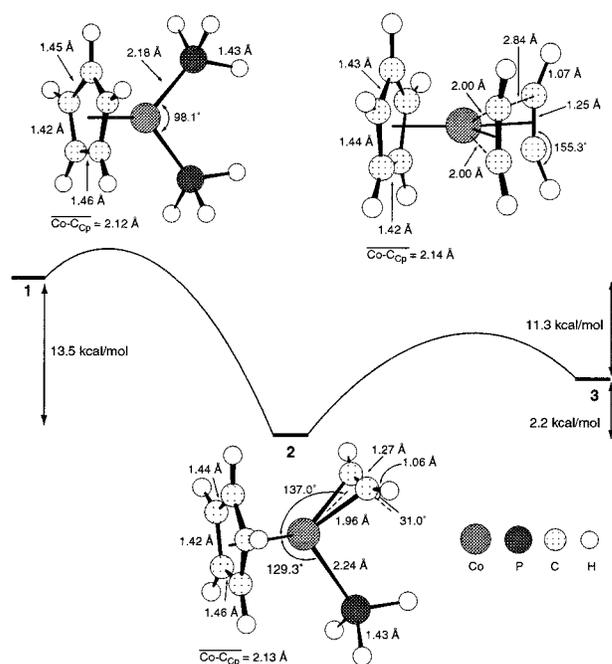


Figure 1. Optimized geometries and a thermodynamic profile of the conversion of CpCo(PH₃)₂ (**1**) to catalytically active CpCo(η²-C₂H₂)₂ (**3**) obtained at the B3LYP level.

For some time it has been known that the frontier orbitals of the cyclopentadienide anion and the imido dianion are topologically equivalent, providing a theoretical basis for the cyclopentadienyl-imido analogy of Schrock, Gibson, and co-workers.²⁸ Green's recent photoelectron spectroscopy results²⁹ confirming the validity of this analogy prompted us to investigate its utility in theoretical calculations, primarily as a method to reduce computational cost through reduction of the number of basis functions. To enhance the speed with which stationary points were located at all levels of theory, we chose to carry out two series of calculations; in the first series the η⁵-C₅H₅ ring was replaced by an HO⁻ ligand constrained to maintain a linear H–O–Co bond angle. Our selection of HO⁻ rather than NH₂⁻ was made specifically to exclude the introduction of charging effects absent within the catalytically active complexes. The second series of calculations adopted the relevant portions of the geometries of these HO-substituted complexes for the initial geometries of the Cp-substituted complexes providing an efficient method for the location of these stationary points.

Extended Hückel calculations³⁰ were performed by using the modified Wolfsberg–Helmholtz formula.³¹ The H_{ii} and orbital exponents were taken from the literature.³²

Results and Discussion

Catalyst Formation. We begin with the optimized geometry of precatalyst **1**, which is shown in Figure 1. The important geometric parameters of this species are the Co–P bond lengths of 2.18 Å, the P–Co–P bond angle of 98.1°, and the average Co–C_{cp} bond length of 2.12 Å. Despite numerous reports in the literature, CpCo(PPh₃)₂ has never been crystallographically characterized, preventing a direct comparison of the theoretical geometry of **1** with an experimental benchmark. Nevertheless,

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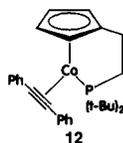
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the 2.18 Å Co–P and 2.12 Å Co–C bond distances in **1** compare favorably to the corresponding values in a number of related Co complexes bearing Cp and phosphine ligands.³³ Substitution of the phosphine ligands in **1** with alkynes can occur by either of two mechanisms. The most likely path is an associative mechanism in which coordination of acetylene is accompanied by slippage of the η^5 -Cp ring to an η^3 -coordination mode to give $(\eta^3\text{-Cp})\text{Co}(\text{PR}_3)_2(\text{C}_2\text{H}_2)$ as an intermediate. Subsequent phosphine dissociation and Cp ring slippage back to an η^5 -coordination mode generates $(\eta^5\text{-Cp})\text{Co}(\text{PR}_3)(\text{C}_2\text{H}_2)$, **2**, a diphenylacetylene analogue of which has been isolated and shown to activate cyclotrimerization in the presence of additional alkyne.^{10,34} An alternative path proposed by Bergman and co-workers^{35a} for the case of $\text{CpCo}(\text{PPh}_3)_2$ involves dissociation of a phosphine ligand to give $\text{CpCo}(\text{PPh}_3)$, an intermediate 16e⁻ monophosphine complex that was shown by extended Hückel calculations to exhibit a bent geometry, largely retaining the structure of the bisphosphine precursor.^{35b} Subsequent occupation of the vacant coordination site in this species by an alkyne molecule generates **2**. Examination of the structure of **2** in Figure 1 reveals the presence of a moderately bound acetylene ligand. The 1.27 Å acetylenic C–C bond is elongated by 0.09 Å relative to free acetylene, which agrees with the implied acetylenic bond order of $\text{CpCo}(\text{PPh}_3)(\text{C}_2\text{Ph}_2)$ obtained from infrared spectroscopy. At 1818 cm⁻¹ the acetylenic stretch of this species lies approximately halfway between 1700 cm⁻¹ where strongly bound alkyne ligands typically appear and 1900 cm⁻¹ where very weakly bound alkynes are usually found.¹¹ The remaining phosphine in **2** lies 2.24 Å from the Co atom, which is 0.06 Å longer than the Co–P bond lengths in **1**. We attribute this difference to the stronger π -acceptor character of the alkyne, which reduces the strength of the Co–P bond. Recently, Butenschön and co-workers³⁶ isolated and structurally characterized $\{\eta^5\text{-}\eta^1\text{-}[2\text{-}(\text{di-}t\text{-butylphosphanyl-P})\text{ethyl}]\text{cyclopentadienyl}\}\{\eta^2\text{-diphenylethyne}\}\text{cobalt(I)}$, **12**, by X-ray crystallographic analysis, providing a structural benchmark to compare with our optimized geometry of **2**. Table S1 in the Supporting Informa-

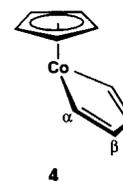


tion lists the relevant data and shows that the theoretical geometry parallels that of **12** to a remarkable degree. The only appreciable difference occurs in the tilt angle adopted by the phosphine ligand with respect to the Cp ring where the experimental structure possesses an angle $\sim 8^\circ$ smaller than the corresponding value in the theoretical geometry of **2**. We attribute this characteristic to the influence of the two-carbon bridge connecting the Cp ring to the phosphorus atom.

Substitution of the remaining phosphine in **2** for an acetylene molecule results in the formation of bisacetylene adduct **3**, which has been proposed as an intermediate along the acetylene

cyclotrimerization pathway on a number of occasions.^{10,34,37a,38} The B3LYP-optimized geometry of **3** is also shown in Figure 1. The acetylene ligands are found to exhibit the characteristics of moderately bound alkynes with Co–C_{acetylene} bond lengths of 2.00 Å, elongated acetylenic C–C bonds measuring 1.25 Å, and complements to the C–C–H bond angles of $\sim 25^\circ$. The slight weakening of the metal–alkyne bond upon going from **2** to **3** is probably reflective of the increased π -acceptor character of an alkyne relative to a phosphine. A previous theoretical investigation of the structure of **3** carried out at the HF level³⁹ found comparable Co–C bond lengths of 2.05 Å. However, little elongation of the acetylenic C–C bonds to 1.215 Å and complements to the C–C–H bond angles of only 12.5° pointed to an underrepresented back-bonding contribution to the Co–alkyne bonds typical of metal–olefin interactions modeled at this uncorrelated level of theory.^{39,40} Due to the fact that no bisalkyne complexes have ever been isolated from this reaction, no experimental structure is available to directly compare with our calculated structure. The relative energies of complexes **1–3** are also shown in Figure 1; the initial substitution of acetylene for phosphine is moderately exothermic, releasing 13.5 kcal/mol. Replacement of the remaining phosphine is slightly endothermic, requiring 2.2 kcal/mol resulting in a net exothermicity of 11.3 kcal/mol for the overall conversion of **1** to **3**. Thus, a significant thermodynamic driving force promotes the formation of active catalyst.

Formation of the Cobaltacyclopentadiene. Oxidative coupling of the acetylene ligands in **3** results in the formation of cobaltacyclopentadiene **4** a coordinatively unsaturated, 16-electron species which has been proposed as an intermediate in



the catalytic cycle by a number of authors.^{10,34,37a,41} Metallacyclopentadiene rings containing d⁶ or d⁸ metal centers such as **4** are well-known to exhibit π -bond localization despite the presence of lone pairs on the metal that could contribute to the formation of an aromatic sextet. Using extended Hückel calculations, Thorn and Hoffmann⁴² found that the required interaction of a filled metal d-orbital with the in-phase combination of olefinic π^* -orbitals suffered from ineffective overlap, preventing electronic delocalization. Furthermore, a two-orbital/four-electron interaction arising from the overlap of a filled metal d-orbital with the out-of-phase combination of olefin π^* -orbitals reinforced the trend toward π -localization within the metallacycle. The optimized geometry of **4**, shown in Figure 2, reveals the operation of these factors. Extensive π -localization is found along the C _{α} –C _{β} bonds of the metallacycle; at 1.34 Å, these bonds are only 0.02 Å longer than that found in

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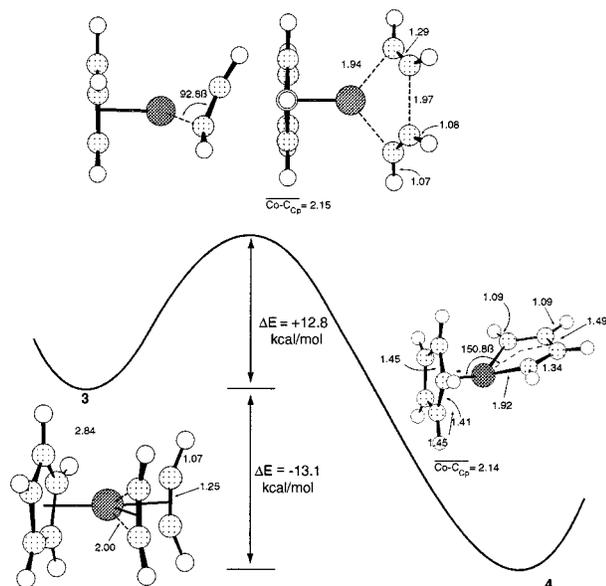


Figure 2. A reaction coordinate diagram of the oxidative coupling of the alkyne ligands in **3** to give **4** calculated at the B3LYP level.

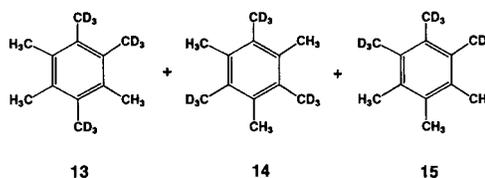
ethylene.⁴³ The $C_{\beta}-C_{\beta'}$ bond length of 1.49 Å falls into the range expected for a C–C σ -bond between two sp^2 -hybridized carbon atoms; indeed, it nearly matches the length of the internal C–C bond in butadiene.⁴³ At 1.92 Å the Co–C bonds fall at the short end of the range expected for late transition metal–carbon σ -bonds.^{33c,44} The cobaltacycle adopts a bent conformation with respect to the Cp ligand, tilting off of the axis defined by the Co atom and the centroid of the Cp ring by 29.2°. Furthermore, the metallacycle exhibits an appreciable envelope fold angle of $\sim 15^\circ$ placing the Co atom ~ 0.3 Å below the mean plane defined by the carbon atoms of the metallacycle. A previous theoretical investigation of **4** carried out at the HF level by Morokuma and co-workers³⁹ found Co–C bonds to be 1.93 Å and a cobaltacycle conformation in which the mean plane of the metallacycle lies off the Co–Cp axis by 24°. These features compare favorably with the values we obtained. Table S2 in the Supporting Information compares the important parameters of the optimized geometry of **4** shown in Figure 2 with the corresponding values found in the X-ray crystal structure of the triphenylphosphine-complexed analogue of **4** isolated by Yamazaki and Wakatsuki.⁴⁴ Our calculated geometry closely parallels that of the experimental structure.

Energetically the conversion of **3** to **4** is exothermic by 13.1 kcal/mol at the B3LYP level. This result is somewhat surprising given that **3** is a coordinatively saturated, 18-electron complex and **4** is an unsaturated, 16-electron species. Examination of the bonding changes that occur during this transformation reveal, however, that such an energetic ordering is possible. One can estimate that two Co–acetylene π -interactions worth approximately 30 kcal/mol each and two C–C π -bonds worth ~ 53 kcal/mol apiece^{45a} are given up for a pair of Co–C σ -bonds of ~ 50 kcal/mol each^{45b} and a C–C σ -bond worth ~ 92 kcal/mol. Therefore, ΔH_{rxn} is estimated to be ~ -27 kcal/mol. While this

value is numerically larger than our calculated value, it highlights the dominant factor responsible for the exothermic nature of the reaction, namely, the formation of a new C–C σ -bond. The finding that **4** is more stable than **3** contradicts the earlier HF results of Morokuma and co-workers,³⁹ who carried out partial geometry optimizations and found the bisacetylene complex to lie 14.0 kcal/mol lower in energy than the cobaltacyclopentadiene. Examination of our own calculations at the HF level provides a more appropriate comparison to Morokuma's calculations. The absence of correlation in these calculations is most noticeable in the geometry of **3** where the acetylene ligands are found to bind much more weakly to the metal atom (Co–C bond lengths of 2.28 Å) than in the DFT-optimized geometry, whereas the geometry of **4** remains largely unchanged relative to the DFT-optimized structure. Despite the significantly altered structure of **3**, we find the conversion of **3** to **4** still to be exothermic by 27.1 kcal/mol at the HF//HF level. Inclusion of electron correlation at the MP2//HF level lowers the magnitude of the thermodynamic driving force to 19 kcal/mol, placing it more in line with the result obtained at the density functional level.

The oxidative coupling of the alkyne ligands in **3** to give **4** is a symmetry-allowed reaction when C_s symmetry is preserved. Location of the transition state for this reaction revealed a moderate activation barrier of 12.8 kcal/mol implying a transition state structure quite geometrically dissimilar from the reactant. This is confirmed by the transition state structure shown in Figure 2. Particularly noteworthy are the Co–C $_{\alpha}$ bonds measuring 1.96 Å, which are essentially fully formed, and the $C_{\beta}-C_{\beta'}$ distance of 1.97 Å, a value considerably shorter than the corresponding 2.84 Å distance found in **3**. Loss of any remaining C–C triple bond character within the former alkyne ligands of **3** has largely been achieved resulting in elongated C $_{\alpha}-C_{\beta}$ bonds of 1.29 Å. Interestingly this significant reorganization of σ - and π -bonding within the forming metallacycle is not accompanied by appreciable flattening of the newly forming metallacycle.

The η^4 -Cyclobutadiene Intermediate. Two reaction pathways leading to coordinatively saturated species are available to **4**, association of an additional donor ligand, such as acetylene (vide infra), and reductive elimination of the chelating butadienoid ligand to generate an η^4 -cyclobutadiene complex, **8**. The transformation of phosphine adducts of **4** to cyclobutadiene complexes has been observed on at least two occasions,^{10,11} suggesting that **8** may serve as an intermediate along the acetylene cyclotrimerization pathway despite the more generally held belief that the extraordinary stability of an η^4 -cyclobutadiene complex serves to deactivate cyclotrimerization catalysts.^{46a,47} In a classic investigation Whitesides and Ehmman⁴⁸ examined the cyclotrimerization of 2-butyne-*1,1,1*-*d*₃ using a number of main group and transition metal catalysts, including low-valent Co complexes. Noting that only two η^4 -cyclobutadiene complexes could arise during the course of the reaction, they proposed that if these species served as intermediates leading to arene formation, the high local symmetry of the C₄R₄ ligands could give isomers **13**, **14**, and **15** as aromatic products whereas only compounds **13** and **14** could arise from



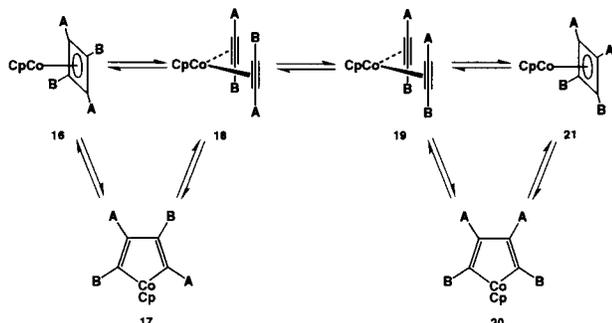
the three possible metallacyclopentadiene intermediates. Sub-

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(44) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1984**, *272*, 251.

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Scheme 3



sequent characterization of the product mixtures obtained from the reactions catalyzed by low-valent Co complexes showed no presence of **15**. This has been taken as strong evidence arguing against the intermediacy of η^4 -cyclobutadiene complexes and supports the contention that **8** is an inert byproduct of catalyst deactivation brought about by the thermodynamic stability of the metal–cyclobutadiene bond.

Recent experiments, however, suggest that the η^4 -cyclobutadiene ligand may be more reactive than previously thought. Gleiter and Kratz⁴⁹ have reported that tricyclic η^4 -cyclobutadiene complexes, obtained from the intramolecular cyclodimerization of 1,6-cyclododecadiyne or 1,7-cyclododecadiyne, readily convert to aromatic ring systems in the presence of alkynes or nitriles. The substitution patterns found in the resulting arenes required the metathesis of an alkyne linkage originally present within the cyclic diynes, prompting these authors to propose a mechanism in which the key step is the interconversion of one regioisomeric cobaltacyclopentadiene into another, less sterically strained, regioisomer via an intermediate η^4 -cyclobutadiene complex. More recent experiments by Vollhardt and co-workers⁵⁰ suggest that these reactions occur via dinuclear species.

Similar issues concerning the reactivity of η^4 -cyclobutadiene complexes were examined by Vollhardt and co-workers in a series of experiments aimed at evaluating the role of these species in the mechanism of CpCo-catalyzed alkyne metathesis reactions.⁵¹ Gas- and solution-phase pyrolyses of disubstituted cyclobutadiene complexes resulted in the interconversion of regioisomers **16** and **21** (Scheme 3); the results of a number of sophisticated labeling experiments prompted these authors to propose a mechanism for this isomerization in which an η^4 -cyclobutadiene complex undergoes a retro-[2 + 2] cycloaddition giving a bisacetylene complex. Following alkyne rotation, ring closure via a forward [2 + 2] process generates the isomeric cyclobutadiene complex formally establishing an equilibrium between the **16/21** pair and revealing yet another reaction path available to **8**. The activation energy measured for this interconversion in solution was quite large at 51.7 kcal/mol.^{51b,c}

With this experimental backdrop we chose to theoretically ascertain the role of **8** in the acetylene cyclotrimerization

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(51) (a) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 409. (b) Ville, G.; Vollhardt, K. P. C.; Winter, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 5267. (c) Ville, G.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177.

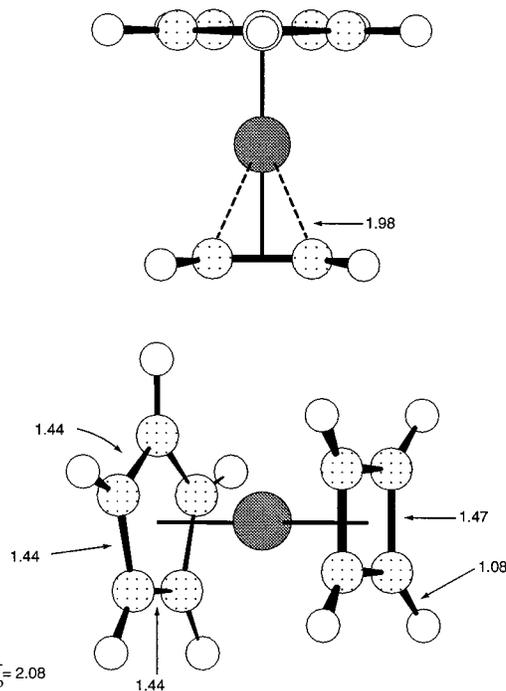


Figure 3. The B3LYP-optimized geometry of CpCo(η^4 -cyclobutadiene) (**8**).

reaction. Since the fragmentation of η^4 -cyclobutadiene complexes can result in the formation of either bisalkyne (**3**) or metallacyclopentadiene (**4**) species, by microscopic reversibility these same compounds become the most likely precursors to cyclobutadiene complexes and serve as simultaneous points of departure for our investigation. A number of years ago Mango and Schachtschneider⁵² predicted the symmetry-forbidden nature of [2 + 2] cycloadditions of acetylenes occurring on bare metal atoms. Since that time their conclusion has generally been assumed to include [2 + 2] processes on ML_n fragments as well, despite the absence of any general theoretical treatment confirming the validity of this assumption. The large kinetic barriers to cyclobutadiene isomerization measured by Vollhardt suggested to us that the presence of an η^5 -cyclopentadienyl ligand at Co has no effect upon the symmetry-forbidden nature of metal-mediated [2 + 2] cycloadditions. We confirmed our suspicions by constructing a Walsh diagram for the conversion of bisacetylene complex **3** to η^4 -cyclobutadiene complex **8**. As anticipated, a HOMO/LUMO crossing occurs. As a result of this finding, we focused our attention upon the reductive elimination converting cobaltacyclopentadiene **4** to **8**.

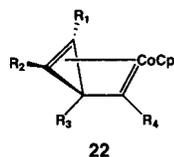
Optimization of **8** at the B3LYP level resulted in the structure shown in Figure 3. The cyclobutadiene ligand is strongly bound and exhibits Co–C_{cbd} bond lengths of 1.98 Å. All four C–C bonds within the cyclobutadiene ligand possess an identical bond length of 1.47 Å highlighting the expected back-bonding contribution to the Co–cyclobutadiene interaction; a secondary effect of this interaction is observed in the bending of the hydrogen atoms of the cyclobutadiene ligand out of the plane of the C₄ ring and away from the metal atom by 7.1°. Overall this geometry compares quite favorably with X-ray crystal structures of isolated CpCo(η^4 -C₄R₄) complexes particularly with respect to the ligated cyclobutadiene moieties.^{31c,53} An alternative conformation of **8** in which the cyclobutadiene ligand is rotated by $\sim 45^\circ$ relative to the CpCo fragment, placing one

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(53) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1976**, *113*, 157.

carbon atom of the C_4H_4 ligand opposite the symmetry unique carbon atom of the Cp ring, was also investigated. EHT calculations revealed these conformers to be energetically equivalent, and subsequent calculations at the HF//HF level confirmed this fact, reflecting the presence of equivalent binding interactions between cobalt and the cyclobutadiene ligand in both conformations. As a result, the structure shown in Figure 3 was arbitrarily chosen to represent **8**.

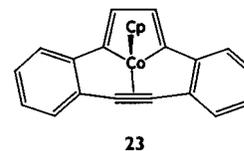
A Walsh diagram for the reductive cyclization responsible for the transformation of **4** to **8** was constructed at the EHT level and is shown in Figure S1 in the Supporting Information. The net result is a HOMO/LUMO crossing rendering this transformation symmetry forbidden. Interestingly this is not the case for the $Re(CO)_4^+$ system where the bisacetylene complex rearranges to the metallacyclopentadiene at room temperature.⁵⁴ In the present molecule, however, as a result of the symmetry-forbidden nature of the **4** to **8** conversion, a substantial kinetic barrier is expected. In addition, once the η^4 -cyclobutadiene complex is formed, we believe the kinetic barrier it must overcome to regenerate **4** becomes prohibitively high. This belief is based upon our calculations which reveal that **8** lies 34.0 kcal/mol lower in energy than **4**. Overall this result supports the hypothesis that **8** arises from the deactivation of active catalyst via a thermodynamic trap created by the formation of an additional carbon-carbon σ -bond. We do not wish to imply that C_s symmetry must be conserved for this process. A number of reaction pathways leading through asymmetric transition states could be envisioned that would convert **4** to **8**. One example is Vollhardt's proposal of the cyclopropenyl carbene complex **22** shown below as a possible precursor leading to



8.^{51c} This species could arise via a rearrangement of **4** analogous to that responsible for the scrambling of substituents in furans, thiophenes, and pyrroles.⁵⁵ Further support of this hypothesis comes from recent studies by Hughes and co-workers⁵⁶ who have demonstrated that 3-vinylcyclopropenes readily rearrange to $Cp^*Rh(\eta^4-C_4R_4)$ complexes in the presence of $[RhCl(C_2H_4)_2]_2$ and Cp^*Li .

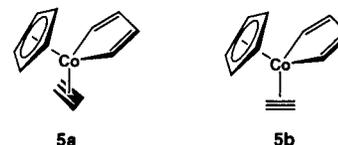
The Reaction of the Third Acetylene. An alternative way for **4** to achieve saturation is to coordinate a third acetylene molecule. The resulting cobaltacyclopentadiene complex, **5**, has been proposed as an intermediate leading to arene formation on a number of occasions.^{10,13,37a,38,57} Early in the development of the mechanism shown in Scheme 1, the most significant evidence arguing for the intermediacy of **5** was the observation that blocking the empty coordination site in **4** with an ancillary ligand slowed the rate of arene formation, implying that the third acetylene coordinated to the Co atom prior to arene construction.¹² Recently, Vollhardt and co-workers¹³ supplied more concrete evidence for the appearance of **5** in the catalytic cycle with their isolation of **23** from the intramolecular

cyclotrimerization of bis(2-ethynylphenyl)ethyne with CpCo-



$(C_2H_4)_2$, providing the first experimentally isolated example of this structural motif in CpCo chemistry.

Coordination of the third acetylene to **4** can occur to give either of two conformations as shown below. In **5a** the acetylenic C-C bond lies perpendicular to the $Co-X_{Cp}$ axis whereas in



5b the acetylene is oriented parallel with the $Co-X_{Cp}$ axis. Schilling, Hoffmann, and Lichtenberger⁵⁸ examined the conformational preferences of coordinated olefins and alkynes in d^6 $CpM(CO)_2$ complexes at the EHT level. Their results indicated a distinct energetic preference for **5a** over **5b** resulting primarily from a stronger back-bonding contribution to the metal-acetylene bond in the perpendicular orientation. A secondary effect reinforcing the preference for **5a** was attributed to a diminished two-orbital/four-electron π -interaction between a filled, nonbonding metal orbital and the acetylenic π -orbital normal to the metal-acetylene bond axis in **5a** relative to that in **5b**. Vollhardt's recently reported **23** adopted conformation **5a**,¹³ although it is geometrically constrained to adopt such a conformation.

Optimization of the geometry of **5a** was achieved at the HF level, but the resulting structure exhibited an extraordinarily weakly bound alkyne. The $Co-C_{acetylene}$ bond lengths were 2.50 Å, between 0.50 and 0.60 Å too long for a normal Co -acetylene bond. Additional support for this view included the essentially unperturbed acetylenic C-C bond, measuring 1.19 Å, and an effectively linear acetylenic C-C-H bond angle (176.2°). The weak nature of this interaction was confirmed when it was found that **5a** was only 0.3 kcal/mol more stable than **4** and free acetylene leading us to conclude that **5a** is modeled as a van der Waals complex at this level of theory. Given our experience with loosely coordinated alkynes in the HF-optimized geometry of **3** and the well-known problem HF calculations have in modeling metal-olefin interactions in general,⁴⁰ we carried out a partial optimization of the HF-optimized geometry of **5a** at the MP2 level. In this calculation the acetylenic $Co-C$ and $C-C$ bond lengths as well as the acetylenic $C-C-H$ bond angles were the only geometric parameters allowed to vary. The results were quite striking. The acetylene moved closer to the metal atom by 0.70 Å generating $Co-C$ bond lengths of 1.80 Å. Furthermore, a considerable back-bonding interaction appeared resulting in elongation of the $C-C$ bond to 1.38 Å and reduction of the acetylenic $C-C-H$ bond angles to 138.2° . Together these results suggest that the HF method grossly underestimated the back-bonding contribution to the Co -acetylene bond. Subsequent efforts to locate the stationary point corresponding to **5a** at the B3LYP level resulted in collapse of the structure to an η^4 -benzene complex, **7**. We attribute this inability to locate **5a** on the density functional potential energy surface to the presence of a very small barrier for the rearrangement converting **5** to **7**. As will be shown (vide infra), the conversion of **5b** to **7** is

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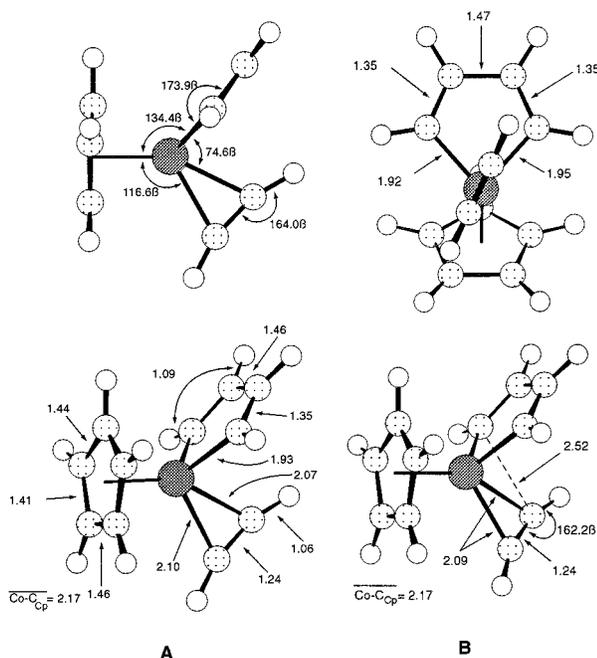
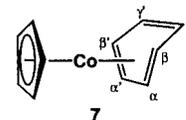


Figure 4. The B3LYP-optimized geometry of acetylene-coordinated cobaltacyclopentadiene (**5**) (left) and the structure of the transition state leading to CpCo(η^4 -C₆H₆) (**7**) (right).

obstructed by an extraordinarily small barrier that arises from the requirement that the acetylene ligand in **5b** rotate into an orientation resembling that in **5a**. We believe the only reason **5a** was located at the HF/HF level was because of the aforementioned absence of appreciable bonding between the Co atom and the incoming acetylene. This prompted us to search for a structure corresponding to **5b** at this level of theory. Fortunately, the small barrier to conversion of **5b** to **7** was large enough to enable us to locate **5b** at the B3LYP level. The resulting geometry, shown in Figure 4A, displays a Co–acetylene interaction significantly greater than that found in the HF-optimized geometry of **5a**. However, at 2.10–2.07 Å the Co–C_{acetylene} bonds lie at the long end of the expected binding range for a metal–alkyne interaction, perhaps reflecting the less favorable orbital interactions occurring in this rotamer as noted by Hoffmann and co-workers.⁵⁸ Indeed compared to the Co–acetylene interactions we obtained in **2** and **3**, this interaction appears quite weak. Energetically, **5b** lies 12.4 kcal/mol lower in energy than **4** and free acetylene at the B3LYP level. The correspondingly smaller degree of back-bonding that accompanies such an interaction is seen in the 1.24 Å acetylenic C–C bond length and the 164.0° C–C–H bond angle found in the alkynyl ligand. Comparison of the optimized geometry of **5b** with that of **4** reveals that coordination of this third acetylene scarcely perturbs the cobaltacyclopentadiene framework. The short–long–short sequence of C–C bond lengths within the metallacycle is present as expected, although the long C_β–C_{β'} bond in **5b** is approximately 0.03 Å longer than that found in **4**. In addition the Co–C_α and C_α–C_β bonds are both elongated by about 0.01 Å compared to the corresponding distances in **4**. We attribute these differences to the considerable steric crowding at the Co atom that arises from the parallel orientation the acetylene adopts with respect to the Co–X_{Cp} axis. In an effort to reduce these interactions, the metallacycle tilts off of the Co–X_{Cp} axis by 45.6° in **5b**, an increase of just under 16° compared to the same measurement in **4**. Furthermore, the cobaltacycle inverts its envelope fold placing the C_β atoms on the same side of the metallacycle as the Cp ligand. Table

S3 in the Supporting Information compares our B3LYP-optimized geometry of **5b** with the theoretically calculated geometry of **23** reported by Vollhardt.¹³ As the table shows, our geometry for **5b** closely parallels that calculated for **23** despite the different conformations the acetylene adopts with respect to the Co–X_{Cp} axis.

The final intermediate appearing in the catalytic cycle of Scheme 1 is CpCo(η^4 -C₆H₆), **7**. Although the exact mechanism for the formation of **7** is unknown, three pathways are logical



candidates. Schore's mechanism⁹ envisions the insertion of the coordinated alkyne ligand of **5** into a Co–C_α σ -bond of the cobaltacyclopentadiene ring to generate cobaltacycloheptatriene **6**, a frequently proposed intermediate.^{12,37a,38} Subsequent reductive elimination of the bidentate C₆H₆ ligand in **6** then generates **7**. The likelihood of this pathway suffers from two drawbacks. First is the fact that we were unable to locate a stationary point corresponding to **6** at the B3LYP level. This result was a bit surprising given that such a point was located on the HF potential energy surface. The second major problem with this transformation is that the reductive elimination carrying **6** to **7** is symmetry forbidden. Thus, even if **6** had been located at the density functional level, this reaction path is expected to be kinetically difficult. Additionally, given the greater stability of **7** relative to **6**, any reaction path bypassing **6** and progressing directly to **7** will possess a larger thermodynamic driving force and would thus be expected to occur more rapidly than a reaction passing through **6**. In the second path, free acetylene is proposed to undergo an intermolecular [4 + 2] cycloaddition with the cobaltacycle's π -system in **4**. Bianchini and co-workers⁵⁹ found this reaction path to be symmetry allowed in the case of an isolobal iridacyclopentadiene complex. While we cannot arbitrarily rule out the possibility of this direct coupling mode for the CpCo system, we believe the 12.4 kcal/mol stabilization afforded by prior complexation of the alkyne to **4** is strong enough to funnel the reaction through acetylene-coordinated cobaltacycle **5**. Furthermore, as we noted earlier, the intermediacy of **5** is inferred from the observation¹² that blocking the vacant coordination site in **4** with an ancillary ligand reduces the rate of arene formation, implying that coordination of the third acetylene to **4** occurs prior to final arene construction. The third pathway then envisions **7** as arising from an intramolecular [4 + 2] cycloaddition between the coordinated alkyne and the cobaltacycle π -system in **5**. The pathway responsible for this conversion requires the acetylene ligand in **5** to rotate by 90° about its bond axis with Co while simultaneously bending back toward the cobaltacyclopentadiene moiety. The asymmetric transition state structure we located is shown in Figure 4B. The most noticeable change from **5b** is the rotation of the acetylene ligand by $\sim 25^\circ$ virtually aligning the acetylenic carbon–carbon bond parallel to one Co–C_α bond of the metallacycle. The rotation does not perturb the strength of the Co–acetylene bond as indicated by the 2.09 Å Co–C and the 1.24 Å acetylenic C–C bond lengths, both of which are unchanged from their

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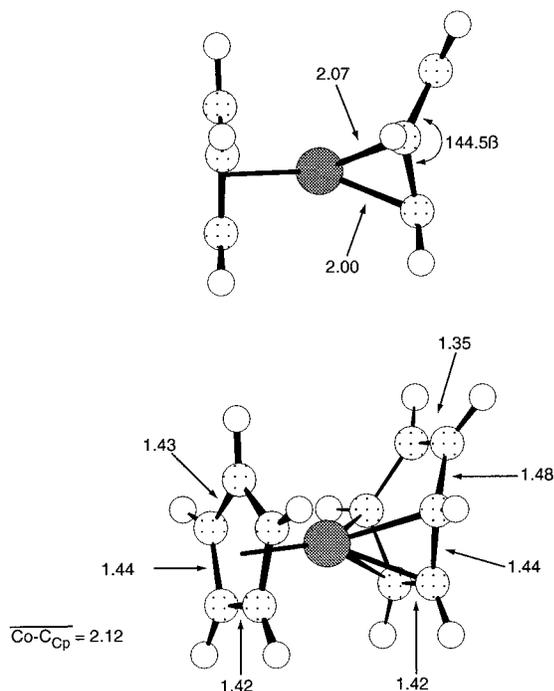
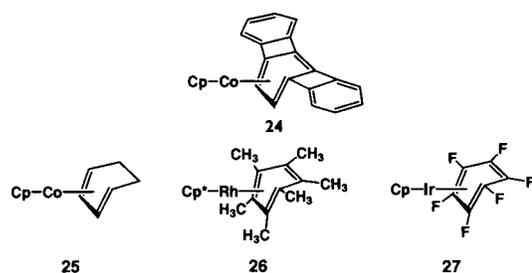


Figure 5. The B3LYP-optimized geometry of CpCo(η^4 -C₆H₆) (7).

values in **5b**. The Co–C_α bond lying parallel to the acetylene ligand is elongated by 0.03 Å indicating a slight loss of bonding character between these two atoms. Coupled with the long 2.52 Å C_α–C_{acetylene} bond distance, this indicates that the transition state structure occurs quite early along the reaction coordinate leading to **7**. Energetically this transition structure lies a mere 0.5 kcal/mol higher in energy than **5b**. An alternative interpretation is to view the combination of alkyne alignment and Co–C_α bond elongation as characteristics of a transition state leading to metallacycloheptatriene, **6**. However, examination of the transition vector shows no component consistent with insertion into the Co–C_α bond of the cobaltacycle. Instead the components of the vibrational motion associated with the transition state vector indicate almost pure rotation of the acetylene about the Co–acetylene bond axis. Additionally, the extraordinarily small magnitude of the kinetic barrier leading from **5** is not consistent with the considerably larger activation energies measured in migratory insertion reactions of acetylenes⁶⁰ and olefins⁶¹ into metal–carbon σ -bonds. We attribute the origin of this small kinetic barrier to the large thermodynamic driving force associated with the conversion of **5b** to **7**. At the B3LYP level the release of resonance stabilization energy upon arene formation combines with the construction of two new carbon–carbon σ -bonds to release 81.4 kcal/mol.

The DFT-optimized geometry of **7** is shown in Figure 5. As in the case of the η^4 -cyclobutadiene complex, there are two rotational orientations that the benzene ligand in **7** may adopt with respect to the Cp ring under C_s symmetry. In Figure 5 the uncoordinated olefinic bond of the C₆H₆ ring lies opposite the symmetry unique carbon atom of the Cp ligand, whereas rotation of the coordinated arene by 180° places this olefin in an alternative conformation in which it eclipses the edge of the Cp ring opposite the symmetry unique carbon atom. The geometries of both members of this rotameric pair were

optimized at the HF level and were found to be energetically equivalent. For convenience the conformation shown in Figure 5 was arbitrarily chosen to represent the geometry of **7**. Inspection of the structure shown in the figure reveals the presence of a folded aromatic ring bound to the metal. This common geometric distortion is the result of the complex preventing the attainment of a 20 valence-electron count at the metal by bending one olefinic bond of the ring away from the metal. The arene is found to be strongly bound to the Co atom with Co–C_{α/α'} and Co–C_{β/β'} bonds measuring 2.00 and 2.07 Å, respectively. As expected, a considerable degree of π -localization is observed within the ring. Most notable in this regard is the C_γ–C_{γ'} bond length of 1.35 Å, a value merely 0.03 Å longer than a typical olefinic carbon–carbon bond. Furthermore, the coordinated butadiene portion of the ring (C_β–C_α–C_α–C_β) exhibits a long–short–long alternating sequence of carbon–carbon bond lengths, reflecting the presence of a considerable back-bonding contribution to the Co–arene interaction. Table S4 in the Supporting Information summarizes these parameters and compares them with the corresponding values observed in **24**, the first structurally characterized CpCo(η^4 -arene) complex¹³



to appear in the literature, and three other structurally analogous complexes, **25**,⁶³ **26**,⁶² and **27**,⁶⁶ that up until the recent isolation of **24** were the best structural benchmarks available to compare with our optimized geometry of **7**. As shown in the table, the general structural trends found in these experimentally observed structures are reproduced in the optimized geometry of **7**. The only appreciable differences arise in the magnitudes of the metal–carbon bond lengths. The Co–C bonds appearing in **7** compare quite favorably with the corresponding bond lengths in **24** and **25**, whereas, the M–C bonds appearing in **26** and **27** are considerably longer than the corresponding bonds in **7** due to the considerably larger covalent radii of the second- and third-row transition metals in **26** and **27**. An indication of the relative strength of the Co–arene bond is given by the magnitude of the arene fold angle Θ . The fold angle of 35.5° in **7** is approximately 10° smaller than the corresponding angles in **25**, **26**, and **27**, although it is quite comparable to the 32.3° arene bend found in **24**. We attribute the larger angles in **26** and **27** to the stronger binding interactions that occur between second- and third-row transition metals with organic ligands.⁶ The larger angle found in **25** we attribute to the absence of a π -bond along the C_γ–C_{γ'} bond, which prevents π -overlap along the C_β–C_γ bonds from flattening the ring to any degree.

Completion of the catalytic cycle in Scheme 1 requires the displacement of the arene ligand in **7** by a pair of alkyne ligands. Thermodynamically, the primary barrier to overcome in this process is the Co–arene binding energy that our calculations estimate to be 18.5 kcal/mol. Such a large value agrees with the strength of this interaction we inferred from the calculated

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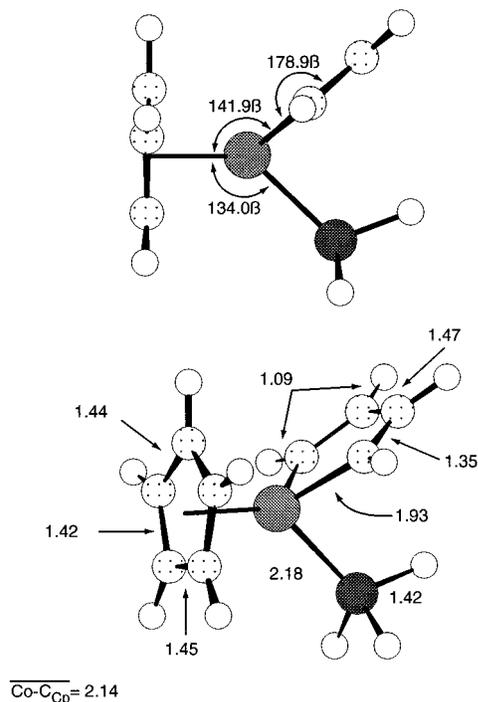


Figure 6. The B3LYP-optimized geometry of $\text{CpCo}(\text{C}_4\text{H}_4)(\text{PH}_3)$ (**9**).

geometry of **7**. However, it seems excessively large with respect to the loss of arene required of a catalytic system. Analogous calculations at the HF level revealed a considerably smaller binding energy of 4.1 kcal/mol, which was reflected in the HF-optimized geometry of **7**. We believe these values represent two extremes with the true value lying somewhere in between. Interestingly, evaluation of the energetic consequences of the displacement reaction reveals that at the B3LYP level the reaction of **7** with two acetylenes to give **3** and benzene is exothermic by 7.4 kcal/mol despite the large metal–arene binding energy. At the uncorrelated HF level the same reaction sequence is endothermic by 3.3 kcal/mol. Most importantly, these reaction enthalpies argue that regardless of where the true Co–arene binding energy lies, arene displacement is thermodynamically accessible.

The Possibility of Phosphine Adducts. The catalytic cycle shown in Scheme 1 is generally thought to be operative in all CpCo-catalyzed cyclotrimerization reactions regardless of the nature of the labile ligands present in the catalyst precursor (CO, C_2H_4 , etc.). However, the use of $\text{CpCo}(\text{PR}_3)_2$ as a precatalyst introduces free phosphine into the reaction mixture during the conversion of **1** to **3**. The strong σ -donating nature of phosphine allows it to compete effectively with alkyne for the vacant coordination site in **4** despite its low concentration relative to alkyne. Successful coordination of a phosphine to **4** generates **9**, the optimized structure of which is shown in Figure 6. Inspection of the resultant geometry reveals that phosphine coordination does little to perturb the structure of the cobaltacycle. The expected short–long–short alternating sequence of carbon–carbon bonds is present within the metallacycle, although the bond lengths in **9** are 0.01–0.02 Å longer than the corresponding values in **4**. The only appreciable geometric differences between **9** and **4** are the result of steric interactions arising between the phosphine and the metallacycle in **9**. This manifests itself primarily as a reduction of $\sim 9^\circ$ in the angle at which the cobaltacycle lies off of the $\text{Co}-\text{X}_{\text{Cp}}$ axis relative to the corresponding angle in **4**. Additionally, the presence of the phosphine removes the preference of the metallacycle to adopt

an envelope folded conformation. Table S5 in the Supporting Information compares our theoretical geometry of **9** to the crystallographically characterized structure of the isolated species containing a triphenylphosphine ligand.⁴⁴ The theoretical and experimental geometries compare quite favorably to one another despite the difference in the steric bulk of PH_3 and PPh_3 . Coordination of PH_3 to **4** is calculated to be exothermic by 31.5 kcal/mol, reflecting a strong Co–P bond. Comparison of this value to the binding energy of the coordinated alkyne in **5** reveals that phosphine coordination is thermodynamically favored over alkyne coordination by 19.1 kcal/mol. Our calculated binding energy for the phosphine in **9** can be compared with experimental data⁴¹ which report a 31.6 kcal/mol activation energy for the dissociation of PPh_3 from $\text{CpCo}(\text{C}_4\text{Ph}_4)(\text{PPh}_3)$. For a simple donor/acceptor interaction such as the addition of phosphine to **4** to form **9**, a small barrier height is expected. Estimating this barrier to be no more than 3 to 5 kcal/mol and adding our calculated binding energy for the phosphine in **9** gives a kinetic barrier of 35–37 kcal/mol, in reasonable agreement with the experimental result considering the steric and electronic differences between PPh_3 and PH_3 .

There are three possible reaction paths accessible to **9** depending upon the nature of the coordinated phosphine. When the phosphine is sterically bulky (i.e. PPh_3) **9** is known to actively catalyze alkyne cyclotrimerization, presumably reentering the catalytic cycle in Scheme 1 via initial, rate-limiting dissociation of phosphine to regenerate **4**.^{12,64} When the coordinated phosphine in **9** is sterically compact (i.e. PMe_2Et), the phosphine binds to Co in an irreversible fashion inhibiting catalytic activity.^{12,57} Finally, a unique example was uncovered by McAlister, Bercaw, and Bergman,¹² who noted the formation of 1,2-dicarbomethoxy-3,4,5,6-tetramethylbenzene from the stoichiometric reaction of dimethylacetylenedicarboxylate (DMAD) with $\text{CpCo}(\text{C}_4(\text{CH}_3)_4)(\text{PMe}_3)$, **18**. While the formation of this product was not in and of itself surprising, their observation of two experimental rate laws for the reaction of $\text{CpCo}(\text{C}_4\text{Me}_4)\text{PR}_3$ with 2-butyne was unprecedented. When $\text{R} = \text{Ph}$ and no additional phosphine was added to the reaction mixture, a rate law zeroth order in 2-butyne was observed, consistent with a mechanism in which the catalyst undergoes initial rate-limiting phosphine dissociation followed by acetylene coordination and subsequent benzene formation according to the pathway in Scheme 1. Furthermore, when $\text{R} = \text{Me}$ or Et under the same reaction conditions no reaction was observed; even after several days at 120 °C very little hexamethylbenzene was found, confirming as we have already noted that sterically compact phosphines bind strongly enough to cobalt to inhibit cyclotrimerization. However, reaction of these same trimethyl- or triethylphosphine-substituted catalysts with dimethylacetylenedicarboxylate (DMAD) proceeded smoothly at room temperature under a second-order experimental rate law that was first order in catalyst and first order in DMAD, implying an associative reaction mechanism that they suggested as passing through a 7-cobaltanorbomadiene intermediate in lieu of acetylene coordination at the metal with Cp-ring slippage.

Before we investigate this reaction pathway in detail, we turn our attention to the calculated geometry of the intermediate η^2 -benzene complex **11** that is ultimately formed via this mechanism, which is shown in Figure 7. The interaction between the bound arene and the $\text{CpCo}(\text{PH}_3)$ moiety resembles that of a strongly bound olefin, with a coordinated C–C bond that is 0.06 Å longer than that found in benzene. The hydrogen atoms

(64) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123.

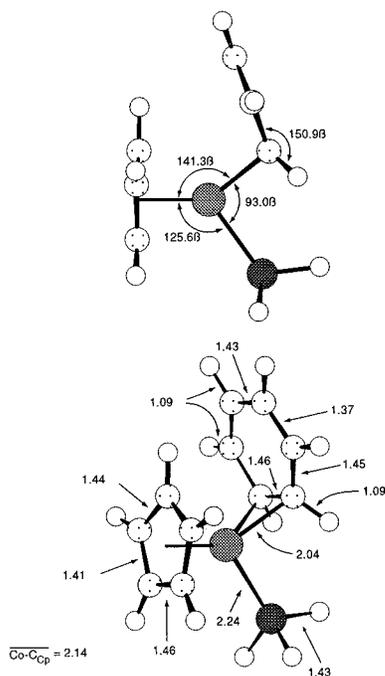
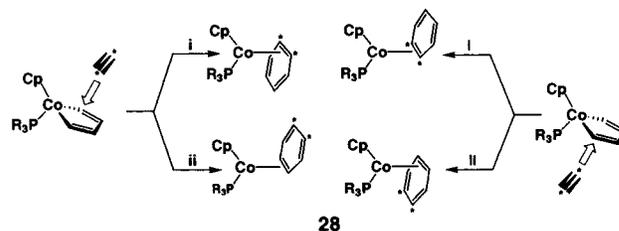


Figure 7. The B3LYP-optimized geometry of CpCo(η^2 -C₆H₆)(PH₃) (**10**).

bound to the coordinated carbon atoms are bent back away from the metal center by nearly 30° indicating the presence of a considerable back-bonding contribution to the Co–arene interaction. Given the degree to which this single C–C linkage is perturbed by the presence of the CpCoL fragment, it is no surprise to find a localized dienyl π -system within the uncoordinated portion of the arene ligand. Our optimized geometry of **11** is compared to the X-ray crystal structures of CpRh(PMe₃)(η^2 -C₆F₆)⁶⁵ and CpIr(η^2 -C₂H₄)(η^2 -C₆F₆)⁶⁶ in Table S6 of the Supporting Information. All three complexes possess tightly bound aromatic rings as indicated by relatively short M–C _{α} bond lengths of 2.00–2.10 Å, although the values for the Rh and Ir complexes imply much stronger coordination, as expected, than the value for Co. This strong η^2 -coordination perturbs the geometry of the arene ring in all three structures in the same manner by elongating the coordinated C–C bond, localizing π -density along the C _{β} –C _{γ} bond of the ring, and bending the substituents bound to the coordinated olefinic moiety away from the metal center. Considering the significantly different electronic and steric forces operating in these three complexes, the degree of structural homology is exceptional.

Two related associative cycloaddition mechanisms ending in the formation of CpCo(η^2 -C₆H₆)(PR₃), **11**, can account for the kinetics results of McAlister, Bercaw, and Bergman as shown in Scheme 2. The most direct pathway requires the approach of an uncoordinated acetylene toward the C _{α} atoms of the cobaltacyclopentadiene ring along a trajectory resembling the Diels–Alder reaction. Furthermore, as carbon–carbon bond formation occurs between the acetylene and the metallacycle, the CpCoL moiety simultaneously migrates toward either the remaining π -bond of the incoming acetylene (i) or toward the newly forming π -bond along what had been the C _{β} –C _{β'} linkage of the cobaltacycle (ii). This generates either of two rotamers of **11**. Given that the acetylene can initiate cycloaddition from either face of the cobaltacycle in **9**, a total of four modes of

addition are open to this reaction as seen below in **28**. As might be expected of a reaction in which an aromatic ring is formed,



the reaction between **9** and an acetylene to produce **11** is highly exothermic, releasing 62.6 kcal/mol of energy at the B3LYP level. While the presence of such a large thermodynamic driving force argues persuasively for the formation of **11**, we believe that there is a prohibitively large activation barrier associated with this reaction. A Walsh diagram was constructed for each of the four direct reaction pathways leading to **11**. In all cases a HOMO–LUMO crossing occurred along the reaction coordinate. This is shown in Figure S2 for the case in which acetylene approaches the face of the cobaltacycle syn to the phosphine with the CpCo(PH₃) moiety migrating toward the remaining π -bond of the alkyne. Thus, we do not believe that a least motion cycloaddition reaction can occur.

The second mechanism leading to **11** that is shown in Scheme 2 breaks the concerted process described above into two distinct steps. The first step is a Diels–Alder cycloaddition of an acetylene to the cobaltacyclopentadiene leading to the formation of the 7-cobaltanorbornadiene complex **10**. Subsequent reductive elimination and migration to an η^2 -coordination position generates **11**. While **10** has been proposed as a viable intermediate in the literature for some time,^{12,37a} the only experimental evidence supporting the formation of this species is the kinetics result of McAlister, Bercaw, and Bergman. Repeated attempts at optimizing the structure of **10** ended in failure. Two electronic states were probed as potential ground states; in both cases geometric optimization of the structure resulted in collapse to **11** at the B3LYP level. Analogous attempts to locate **10** on the Hartree–Fock potential energy surface resulted in either collapse of the structure to **11** or retrocycloaddition to **9** and uncoordinated acetylene. Thus, we are compelled to conclude that kinetic barriers tend to prevent the direct reaction of **9** with most alkynes.

This conclusion appears to contradict the aforementioned kinetics results of McAlister, Bercaw, and Bergman.¹² The instability associated with **10** can be explained by a simple molecular orbital argument. An interaction diagram is shown in Figure 8 in which the frontier MO's of **10** are generated by interacting the two highest occupied MO's (1a' and 1a'') and LUMO (2a') of a CpCoPR₃ fragment,^{35b} shown on the right, with the two highest occupied MO's (1 π_s and 1 π_a) and LUMO (2 π_s) of a 1,4-cyclohexadienyl diradical, shown on the left. Examination of the cyclohexadienyl MO's reveal them to be derived from the pair of filled e_{1g} orbitals (1 π_s and 1 π_a) and one member of the empty e_{2u} set (2 π_s) in benzene via deformation of the arene ring toward a boat-type conformation. Binding of the metal fragment to this ligand occurs via a pair of σ -interactions and a single π -type interaction. The first σ -bond arises from a strong interaction between 1 π_a of the cyclohexadienyl ligand and 1a'' of the metal fragment giving rise to the 1 π_a + 1a'' bonding combination and its antibonding counterpart, labeled 1 π_a – 1a'' in the figure. The second σ -interaction results from the in-phase combination of the 2 π_s ligand-based MO with the 2a' metal-centered fragment orbital to generate 2 π_s + 2a'.

(65) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429.

(66) Bell, T. W.; Helliwell, M.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911.

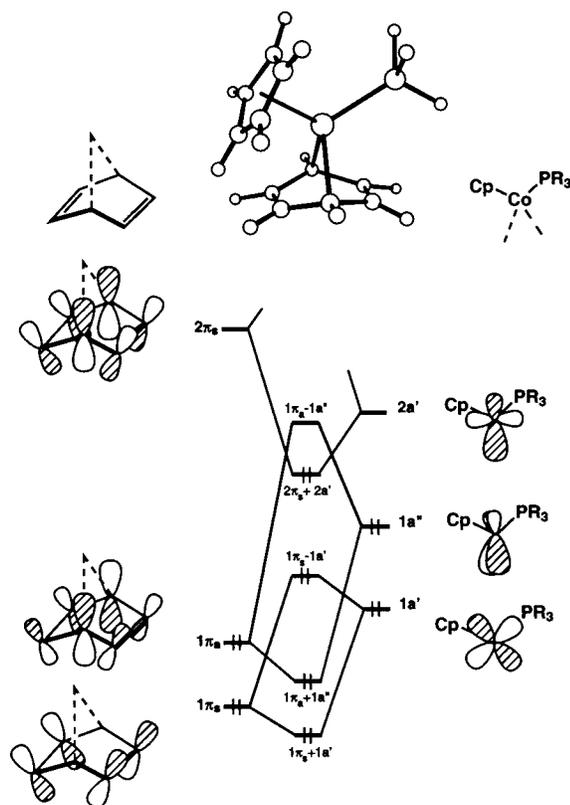


Figure 8. An orbital interaction diagram of the frontier MO's of a $\text{CpCo}(\text{PR}_3)$ fragment with a 1,4-cyclohexadienyl diradical.

The corresponding antibonding MO lies high in energy and is not shown. The π -type interaction arises between the filled $1\pi_s$ orbital of the cyclohexadienyl ligand and the filled $1a'$ MO of the CpCo fragment giving rise to a destabilizing two-orbital/four-electron interaction. The critical element to notice in the figure is the small HOMO–LUMO gap that arises between $2\pi_s + 2a'$ and $1\pi_a - 1a''$. It is the different occupations of these two MO's which leads to the two-electron configurations previously mentioned. Substitution of strong electron-withdrawing groups (e.g., carbomethoxy) onto the cyclohexadienyl fragment generates an electronegativity perturbation of the ligand-based orbitals forcing them down in energy with respect to the metal-centered fragment orbitals.⁴⁷ The $1\pi_s$ and $2\pi_s$ MO's fall further in energy than the $1\pi_a$ MO as a result of the greater localization of electron density at the substituent sites in $1\pi_s$ and the larger coefficients appearing at the substitution sites in $2\pi_s$ relative to the corresponding coefficients in $1\pi_a$. As a result the $2\pi_s + 2a'$ HOMO of **10** drops further in energy than the $1\pi_a - 1a''$ LUMO, widening the HOMO–LUMO gap. Furthermore, the stabilization of the ligand-based $1\pi_s$ orbital relative to the metal-centered $1a'$ MO reduces the magnitude of the two-orbital/four-electron interaction between these fragment MO's resulting in a net electronic stabilization of the complex. While we believe that these factors will combine to stabilize the 7-cobaltanorbadiene species (**10**) allowing its existence as an intermediate, it is not clear that the carbomethoxy groups in DMAD are electron withdrawing enough to explain the associative mechanism observed by Bergman and co-workers.¹² Other scenarios⁵⁰ such as a rate-determining step for the substitution of DMAD for PMe_3 either directly or via an η^5 to η^3 associative mechanism are also consistent with the kinetic results and are in accord with our theoretical studies. We encourage further work to resolve this issue.

The free phosphine present in solution when $\text{CpCo}(\text{PR}_3)_2$ is used as a precatalyst could play one additional role in the acetylene cyclotrimerization mechanism. We noted that for the active catalyst, **3**, to be regenerated following the formation of **7**, the η^4 -coordinated arene ring must be displaced by a pair of acetylenes. We did not theoretically examine the mechanism for this reaction as we assumed that the relatively weak binding energy of an acetylene would favor a stepwise process in which **7** underwent ring-slippage to an electronically unsaturated $\text{CpCo}(\eta^2\text{-C}_6\text{H}_6)$ species followed by coordination of alkyne, release of arene, and alkyne coordination. Given the greater Co–phosphine bond energy, it would be reasonable to assume that a concerted process in which free phosphine coordinates to Co forcing the slippage of the arene in **7** to an η^2 -binding mode occurs to give **11**. Although thermodynamically favorable (exothermic by 2.4 kcal/mol), this reaction path is symmetry forbidden when C_s symmetry is retained, as confirmed from a Walsh diagram constructed at the EHT level. Unless a lower symmetry pathway is accessible this reaction must also occur in a stepwise fashion.

Conclusions

The cyclotrimerization of alkynes in the presence of CpCoL_2 ($L = \text{CO}, \text{PR}_3, \text{C}_2\text{H}_4$) catalysts begins once the catalyst precursor is converted to $\text{CpCo}(\eta^2\text{C}_2\text{H}_2)_2$ via a pair of ligand-substitution reactions. Oxidative coupling of the acetylene ligands in this complex is thermodynamically favorable ($\Delta H = -13.1$ kcal/mol) and occurs in a facile manner ($\Delta H^\ddagger = 12.8$ kcal/mol) to generate the cobaltacyclopentadiene complex **4**. Subsequent coordination of a third alkyne ligand to this species liberates an additional 12.4 kcal/mol of energy. Contrary to the generally accepted mechanism, the final carbon–carbon bond forming step in the construction of the arene occurs via an intramolecular, metal-mediated [4 + 2] cycloaddition of the cobaltacycle with the coordinated alkyne to generate the η^4 -benzene complex **7**. This transformation occurs with a very small barrier ($\Delta H^\ddagger = 0.5$ kcal/mol), reflecting the extraordinarily large thermodynamic driving force ($\Delta H = -81.4$ kcal/mol) associated with the formation of two C–C σ -bonds and an aromatic π -system. Completion of the catalytic cycle occurs upon displacement of benzene in **7** by a pair of acetylene molecules to regenerate $\text{CpCo}(\eta^2\text{C}_2\text{H}_2)_2$ with concomitant release of an additional 7.4 kcal/mol of energy. While this mechanistic pathway strongly parallels the generally accepted mechanism for transition metal catalyzed acetylene cyclotrimerization (Scheme 1), it does differ in some important respects. First, the final step in the construction of the arene does not appear to be a reductive elimination from a cobaltacycloheptatriene complex. Our unsuccessful efforts to locate a stationary point corresponding to the structure of **6** on the DFT potential energy surface cannot allow us to arbitrarily preclude the intermediacy of **6**; however, at the Hartree–Fock level we did locate an optimized structure corresponding to **6**, and we find that the reductive elimination leading to **7** is symmetry forbidden. Furthermore, given the fact that **7** is more stable than **6**, it follows on thermodynamic grounds alone that the direct rearrangement of **5** to **7** will have a lower activation energy than the reductive elimination giving **7** from **6**. Second, the results of our investigation reveal that η^4 -cyclobutadiene complexes, **8**, isolated from acetylene cyclotrimerization reaction mixtures do not form via a reductive elimination of the chelating butadienoid portion of cobaltacyclopentadiene **4**. The conversion of **4** to **8** is symmetry forbidden making this transformation kinetically inaccessible. Coupled with the results of Mango and Schachtschneider, who showed

that simple [2 + 2] cycloadditions of acetylenes bound to metal atoms were symmetry forbidden, this result necessitates the operation of a more complicated mechanism leading to the formation of **8**. Finally, the presence of free phosphine in the reaction mixture, resulting from the displacement of phosphine in CpCo(PR₃)₂ by acetylene, does not significantly alter the reaction path leading to benzene formation. While phosphine does effectively compete with acetylene for the empty coordination site in **4**, there appears to be no reaction path in which CpCo(PR₃) promotes cyclotrimerization. We examined two potential pathways resulting in benzene formation in the presence of this moiety. In the first case the direct conversion of **9** to η^2 -benzene complex **11** was found to be symmetry forbidden, and in the second case, in which **9** is converted to **11** via the intermediacy of **10**, no stationary point corresponding to **10** could be located.

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Supporting Information Available: Tables comparing geometric details for the computed structures of **2**, **4**, **5a**, **7**, **9**, and **11** along with Walsh diagrams for the conversion of **4** to **8** and **9** to **11** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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