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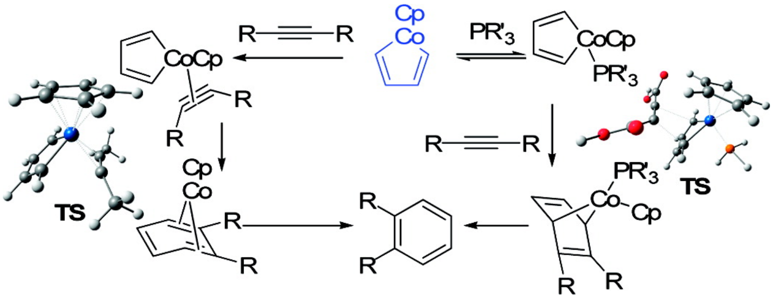

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Cobalt-Catalyzed Cyclotrimerization of Alkynes: The Answer to the Puzzle of Parallel Reaction Pathways

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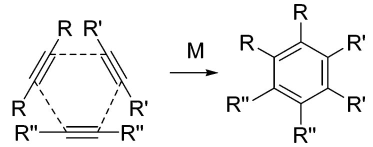
Abstract: To understand some experimental data at odds with the computed mechanism of the CpCo(L$_2$)-catalyzed [2 + 2 + 2] cyclotrimerization of ethyne, DFT computations were carried out following the fate of methyl- and hydroxycarbonyl-substituted alkynes to give the corresponding arenes. The key intermediate in all cases is a triplet cobaltacyclopentadiene obtained by oxidative coupling of the corresponding CpCo(bisalkyne) complex and subsequent spin change via a minimum energy crossing point (MECP). From that species, two different catalytic cycles lead to an arene product, depending on the nature of the alkyne and other ligands present: either alkyne ligation to furnish a cobaltacyclopentadiene(alkyne) intermediate or trapping by a σ-donor ligand to generate a coordinatively saturated cobaltacyclopentadiene(PR$_3$) complex. The former leads to the CpCo-complexed arene product via *intramolecular* cobalt-assisted [4 + 2] cycloaddition, whereas the latter may, in the case of a reactive dienophile (butynedioic acid), undergo direct *intermolecular* [4 + 2] cycloaddition to generate a cobaltanorbornene. The bridgehead cobalt atom is then reductively eliminated after another change in spin state from singlet to triplet. The necessary conditions for one or the other mechanistic pathway are elaborated.

Introduction

The transition-metal catalyzed [2 + 2 + 2] cycloaddition of alkynes is a very powerful method for the construction of arenes in a single operational step (Scheme 1). During the past three decades this reaction has been extensively investigated and the topic reviewed thoroughly.[1]

Scheme 1. Prototypical Metal-Catalyzed [2 + 2 + 2] Cocyclization of Alkynes



Cobalt complexes of type CpCoL$_2$ (L = CO, PR$_3$, alkenes) have been used extensively for mediating cocyclizations of alkynes, often with high levels of chemo-, regio-, and stereoselectivity. Although the mechanism of this reaction has been the subject of multiple experimental and computational studies, it is not as yet fully elucidated. After pioneering semiempirical[2] and *ab initio* efforts,[11] a more detailed DFT analysis was reported by Albright and co-workers in 1999.[3] This work was

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[†] Université Pierre et Marie Curie.

[‡] University of California at Berkeley.

[§] Lawrence Berkeley National Laboratory.

(1) For reviews, see: (a) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 1129−1162. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (c) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635−662. (d) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901−2915. (e) Malacria, M.; Aubert, C.; Renaud, J.-L. In *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*; Lautens, M., Trost, B. M., Eds.; Georg Thieme Verlag: Stuttgart, 2001; Vol. 1, pp 439−530. (f) Gevorgyan, V.; Radhakrishnan, U.; Takeda, A.; Rubina, M.; Rubin, M.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 2835−2841. (g) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 1699−1712. (h) Miljaniæ, O. Š.; Vollhardt, K. P. C. In *Carbon-Rich Compounds: From Molecules to Materials*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006; pp 140−197. (i) Kotha, S.; Brahmachar, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741−4767. (j) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307−2327. (k) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209−2217. (l) Agenet, N.; Buisine, O.; Slowinski, F.; Gandon, V.; Aubert, C.; Malacria, M. In *Organic Reactions, Vol. 68*; Overman, L. E., Ed.; John Wiley & Sons: New York, 2007.

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(6) 16-Electron d^8-CpML species are known to exhibit triplet ground states, whereas the corresponding 18-electron CpMLL′ complexes are usually singlets. See: (a) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487−1496. (b) Poli, R.; Smith, K. M. *Eur. J. Inorg. Chem.* **1999**, 877−879. (c) Su, M.-D.; Chu, S.-Y. *Chem.*−*Eur. J.* **1999**, *5*, 198−207. (d) Smith, K. M.; Poli, R.; Harvey, J. N. *Chem.*−*Eur. J.* **2001**, *7*, 1679−1690. (e) Carreón-Macedo, J.-L.; Harvey, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 5789−5797. (f) Petit, A.; Richard, P.; Cacelli, I.; Poli, R. *Chem.*−*Eur. J.* **2006**, *12*, 813−823 and pertinent references cited therein.

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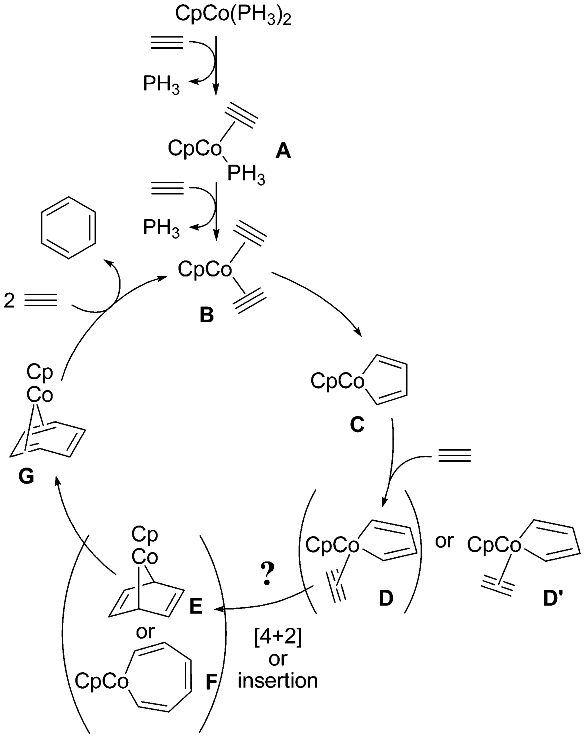
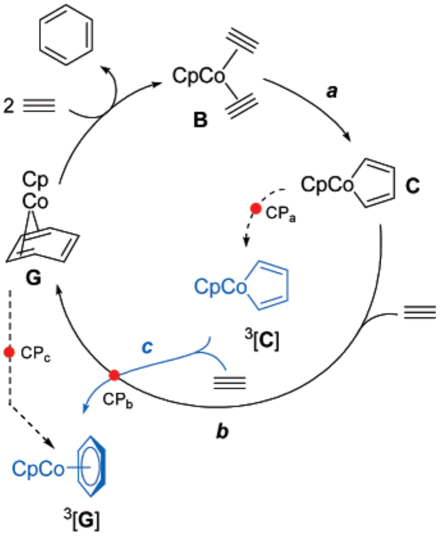
Scheme 2. Partial Closed-Shell DFT/B3LYP Mechanism



restricted to closed-shell species, featuring CpCo(PH$_3$)$_2$ as a model precatalyst and ethyne as a model reagent. To summarize, initially one and then two alkyne moieties displace sequentially two phosphines from the metal to form alkyne complexes **A** and then **B** (Scheme 2). Bisalkyne complex **B** undergoes spontaneous oxidative coupling to give the corresponding coordinatively unsaturated Cpcobaltacyclopentadiene **C**. How **C** and ethyne transform into the final intermediate CpCo(η^4-benzene) **G** could not be ascertained rigorously. According to earlier EHT calculations,[4] two coordinatively saturated Cpcobaltacyclopentadiene(ethyne) complexes had to be considered: In the more stable one, the coordinated ethyne lies parallel to the C$_\beta$−C$_\beta$ bond of the metallacycle (**D**); in the second, the coordinated alkyne is oriented roughly perpendicular to the C$_\beta$−C$_\beta$ bond (**D′**). At the DFT/B3LYP level, complex **D** could not be found on the potential energy surface because of the direct collapsing of the structure to **G**. Another potential intermediate, the 7-cobaltanorbornene **E**, which would arise from a formal intramolecular [4 + 2] cycloaddition of the coordinated alkyne to the terminal diene carbons of the metallacycle, could also not be located on the reaction coordinate. Complex **D′** was found, in addition to an energetically very close-lying transition state with similar geometry ($\Delta H^\ddagger = 0.5$ kcal/mol). Examination of the transition vector was inconsistent with an insertion mechanism that would give the Cpcobaltacyloheptatriene **F** but indicated a simple rotation of the coordinated ethyne on the collapse route to **G**.

Scheme 3. Single- and Two-State Reactivity in the Cobalt-Catalyzed Cyclotrimerization of Ethyne (Two-State Mechanism: **B** → **C** → ^{3}[**C**] → **G** → ^{3}[**G**])



Using a larger basis set, Koga and co-workers explored singlet and triplet spin state potential energy surfaces at the DFT/B3LYP level (Scheme 3).[5] This work took explicit account of the fact that 18-electron cobalt species (i.e., **A**, **B**, **G**) exist usually as singlet ground states, whereas their 16-electron congeners (i.e., **C**, **E**, **F**) prefer to be triplets.[6] Thus, changes in spin state along the reaction coordinate can be part of a mechanism. Even though labeled as “spin-forbidden”, there are a number of fast reactions of triplet cobalt species that end in singlet products.[7] Although there is no appropriate computational method for calculating adiabatic spin-coupled potential energy surfaces of cobalt complexes, semiquantitative information can be gleaned from a determination of the enthalpy for accessing a crossing point at which the two spin states differ minimally in structure and energy (MECP). While finding such a point is not sufficient for an evaluation of the probability of surface hopping taking place,[8] it presents enthalpic data that can be used to explain the outcome of kinetic studies.[6a,e] Therefore, the transformations of bisalkyne complex **B** were followed along both singlet and triplet hypersurfaces, and a nonadiabatic mechanism[9] involving spin state changes was proposed (Scheme 3).

When limited to closed-shell species, the most favorable reaction pathway proceeds via oxidative coupling of **B** to **C** (path ***a***) and subsequent barrier-less addition of ethyne to give CpCo(η^4-benzene) (**G** via path ***b***, collapse mechanism). Thus, no intermediate of type **D** or **D′** (see Scheme 2) could be optimized. In the triplet state, a barrier of 14.1 kcal/mol was calculated for the addition of ethyne to Cpcobaltacyclopentadiene (^{3}[**C**]). This reaction leads to CpCo(η^6-benzene) ^{3}[**G**] via path ***c***. While kinetically disadvantaged, this high-spin sequence connects the ground states of Cpcobaltacyclopentadiene (singlet to triplet excitation energy: $\Delta E_{\mathrm{S-T}} = -16.6$ kcal/mol) and CpCo(benzene) ($\Delta E_{\mathrm{S-T}} = -13.4$ kcal/mol). The identification of several low-lying MECPs between the singlet and the triplet potential energy surfaces led to the formulation of a nonadiabatic

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[8] For a discussion on transition probabilities in surface-hopping and two-state reactivity, see: Mercero, J. M.; Matxain, J. M.; Lopez, X.; York, D. M.; Largo, A.; Eriksson, L. A.; Ugalde, J. M. *Int. J. Mass. Spectrom.* **2005**, *240*, 37−99.

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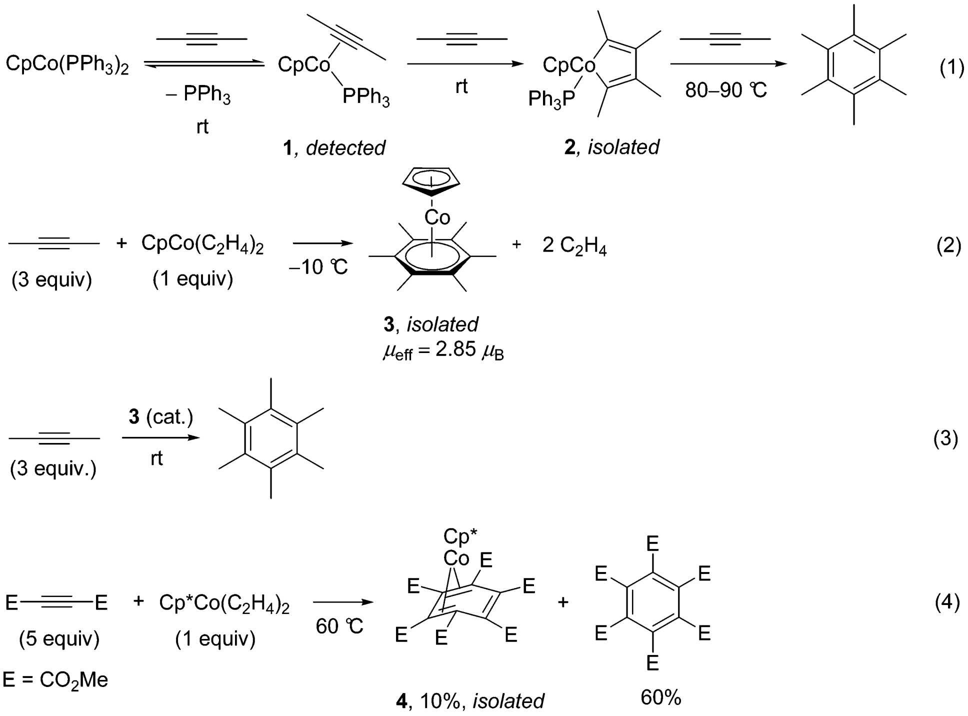
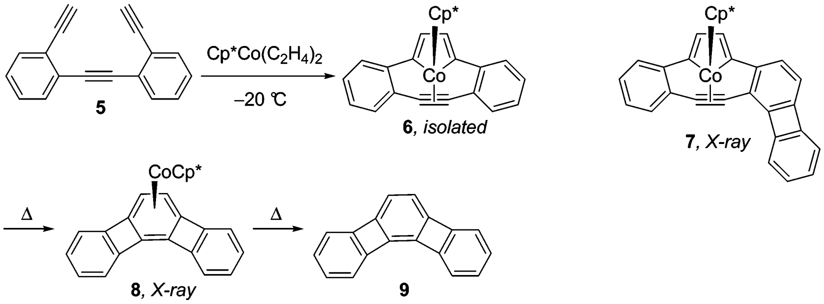
Scheme 4. Experimental Results of the Cyclotrimerization of 2-Butyne and DMAD



Scheme 5. Isolated Intermediates during the Stepwise Cycloisomerization of Triyne **5**



mechanism (two-state reactivity). Here, singlet Cpcobaltacyclopentadiene relaxes to the triplet and then reacts with ethyne to give singlet CpCo(η^4-benzene) (path ***a***, CP_a, path ***c***, CP_b, path ***b***). A last spin change occurs (CP_c) to give 20-electron CpCo-(η^6-benzene). Overall, the catalytic cycle comprises five intermediates (**B** → **C** → ^{3}[**C**] → **G** → ^{3}[**G**]). One notes that a cobaltacycloheptatriene of type **F** (see Scheme 2), exemplifying the possibility of an insertion mechanism, could not be computed. The alternative, the coordination of ethyne to Co, followed by intramolecular [4 + 2] cycloaddition, could also not be ascertained in the parent series, because of the collapsing of all potential intermediates.

Aspects of the two preceding DFT analyses are in consonance with experiment. For instance, when $CpCo(PPh_3)_2$ was treated with 2-butyne at room temperature, the monoalkyne complex **1** was detected in the mixture, and the cobaltacyclopentadiene-(phosphine) complex **2** was eventually isolated [Scheme 4, eq 1].[10,11] At higher temperatures (80−90 °C), **2** transformed with 2-butyne to hexamethylbenzene. The reaction of 2-butyne with $CpCo(C_2H_4)_2$ gave the paramagnetic 20-electron sandwich complex **3** at −10 °C (eq 2).[12] The magnetic moment of this product agrees with the presence of two unpaired electrons (triplet state). Interestingly, this complex catalyzed the cyclotrimerization of 2-butyne at room temperature (eq 3) and is consequently considered as another viable intermediate of the catalytic cycle. Diamagnetic η^4-arene complexes have also been isolated. For instance, the reaction of (η^5-Me_5C_5)$Co(C_2H_4)_2$ with 5 equiv of dimethyl butynedioate (DMAD) provided hexamethyl benzenehexacarboxylate in 60% yield, accompanied by 10% of Cp*Co(η^4-($(MeO_2C)_6C_6$) **4** (eq 4).[13]

On the other hand, two experimental observations are at odds with the computations (Schemes 5 and 6). The first is the isolation of derivatives of the "collapsing" species **D**, namely **6** (and analogues) in the reaction of triyne **5** with various CpCo species (Scheme 5).[14] These are the only examples of metallacyclopentadiene(alkyne) species, the structural details of one of which (complex **7**) were determined by X-ray diffraction.[15] On simple warming, they converted to Cp*Co(η^4-arene) complexes of type **8**, and further heating in the presence of external ligands resulted in liberation of free arene **9**. This set of results

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[12] Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716−717; *Angew. Chem. Suppl.* **1983**, 1005−1016.

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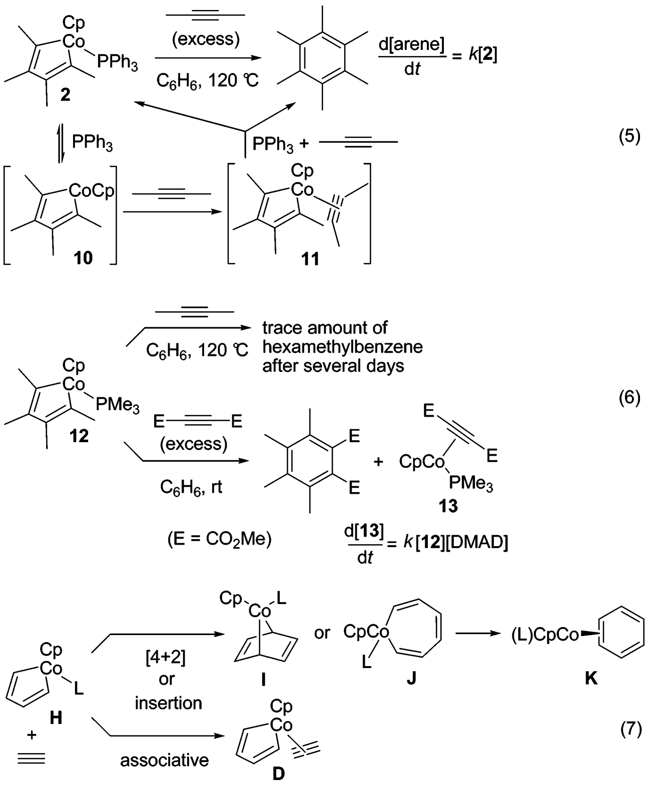
Scheme 6. Kinetics of the Reactions of Cobaltacyclopentadiene(phosphine) Complexes with Alkynes (eqs 5−6) and Plausible Mechanistic Interpretations (eq 7)



clearly indicates that cobaltacyclopentadiene(alkyne) complexes do not necessarily collapse but can be minima along the potential energy surface. While the emergent cyclobutadienoid strain in the phenylene product **8** undoubtedly plays a dominant role in the stabilization of **6**, the question is raised as to what is the minimal alteration required to obviate collapse.

The second discrepancy between theory and experiment is embedded in a kinetic study by McAlister, Bercaw, and Bergman. It revealed that the reaction pathway for the transformation of species of type **2** is dependent critically on the nature of the alkyne (Scheme 6).[16] Thus, for the conversion of 2-butyne into hexamethylbenzene, catalyzed by **2**, eq 5 pertains. Specifically, the reaction is retarded by PPh_3, indicating the necessity of phosphine dissociation. At low phosphine levels, the rate of formation of arene is independent of the concentration of 2-butyne. As a consequence, the proposed catalytic cycle features rate determining competition between phosphine and 2-butyne for the coordinatively unsaturated cobaltacyclopentadiene **10**. Hence, the formation of hexamethylbenzene becomes limited by the rate of dissociation of PPh_3 from **2**, and the kinetics point to the viability of **11** as a species. Moreover, a critical change occurs when 2-butyne is replaced by DMAD, namely direct attack on trialkylphosphine-complexed cobaltacyclopentadienes such as **12** without phosphine dissociation (eq 6). For example, complex **12** and DMAD are converted at room temperature to dimethyl 3,4,5,6-tetramethylphthalate and the monoacetylene complex **13**. With the alkyne in excess, the pseudo-first-order rates fit the expression depicted in eq 6. Direct reaction of the alkyne might occur by [4 + 2] cycloaddition of the electron rich butadiene framework with the electron poor dienophile to provide **I**, or by direct insertion to **J**, or by associative ligand substitution, as pictured in eq 7.[17] None of these options were viable pathways in the computed mechanism of the conversion of the parent ethyne to benzene.

Table 1. Energies (kcal/mol) Relative To ^{3}[**C**] and the Alkyne for the Species Depicted in Scheme 7

	C	CP1	CP2	D^a	TS$_{D-G}$	G	CP3	^{3}[G]
$R^1 = R^2 = H$	16.1	17.4	6.5	*b*	-	−84.5	−83.9	−103.0
$R^1 = H$, $R^2 = CO_2H$			7.2	*b*	-	−86.5	−84.6	−101.8
$R^1 = H$, $R^2 = Me$			7.4	−3.7	−2.5	−75.4	−74.7	−93.6
$R^1 = R^2 = Me$	16.2	16.2	11.0	1.2	2.4	−68.1	−67.4	−83.2
$R^1 = CO_2H$, $R^2 = Me$	13.0	13.9	4.5	−5.5	−1.5	−69.5	−67.0	−75.8

[a] Optimization of these species in the triplet state results in ejection of the coordinated alkynes. [b]Collapse occurs directly to **G**.

As a sequel to our previous computational study dealing with cobalt-mediated cyclic and linear 2:1 cooligomerization of alkynes with alkenes,[18] we describe herein a two-state mechanism for the CpCo-catalyzed [2 + 2 + 2] cyclotrimerization of substituted alkynes that includes all putative intermediates. In addition, the mechanistic puzzle posed by results of McAlister et al. was solved by establishing the feasibility of direct Diels−Alder cycloaddition pathways on exposure of cobaltacyclopentadienes to DMAD.

Computational Methods

All geometries of intermediates and transition states were optimized fully without symmetry constraints using the Gaussian 03 program.[19] The DFT computations were carried out using the B3LYP functional as implemented in Gaussian. The computations were done using the LACVP(d,p) basis set: The cobalt atom was described by a double-ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ),[20] and the 6-31G(d,p) basis set[21] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPEs). The connectivity between stationary points was established by intrinsic reaction coordinate calculations (IRCs). Single-point calculations were carried out at the B3LYP/6-311+G(2d,2p) level, and the energies given are uncorrected.[22] Unless stated otherwise, the energies discussed throughout the manuscript are those obtained after single-point calculations. Taking the zero-point corrections into account proved inconsequential with respect to the conclusions reached. The PCM approach for accounting solvent effects (single points with benzene as solvent) was occasionally applied, but no significant changes of the relative energies were observed (see Supporting Information). The minimum energy crossing points (MECPs) were optimized using the code developed by Harvey and co-workers.[23a] The vibrational analyses at these points were executed within the (3*N*-7)-dimensional hypersurface

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(16) (a) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666−1668. (b) McAlister, D. R. Ph.D. Thesis, California Institute of Technology, 1978.

(17) The reaction of saturated Cpcobaltacyclopentadiene(PH_3) complexes with ethyne to give CpCo(PH_3)-complexed benzene via intermolecular Diels−Alder cycloaddition was partly investigated by theory (see ref 3). However, the formation of the intermediate 7-Cpcobaltanorbornene(PH_3) complex **I** could not be computed in the parent series, due to the collapsing of this structure into (PH_3)CpCo(h^2-benzene) **K**.

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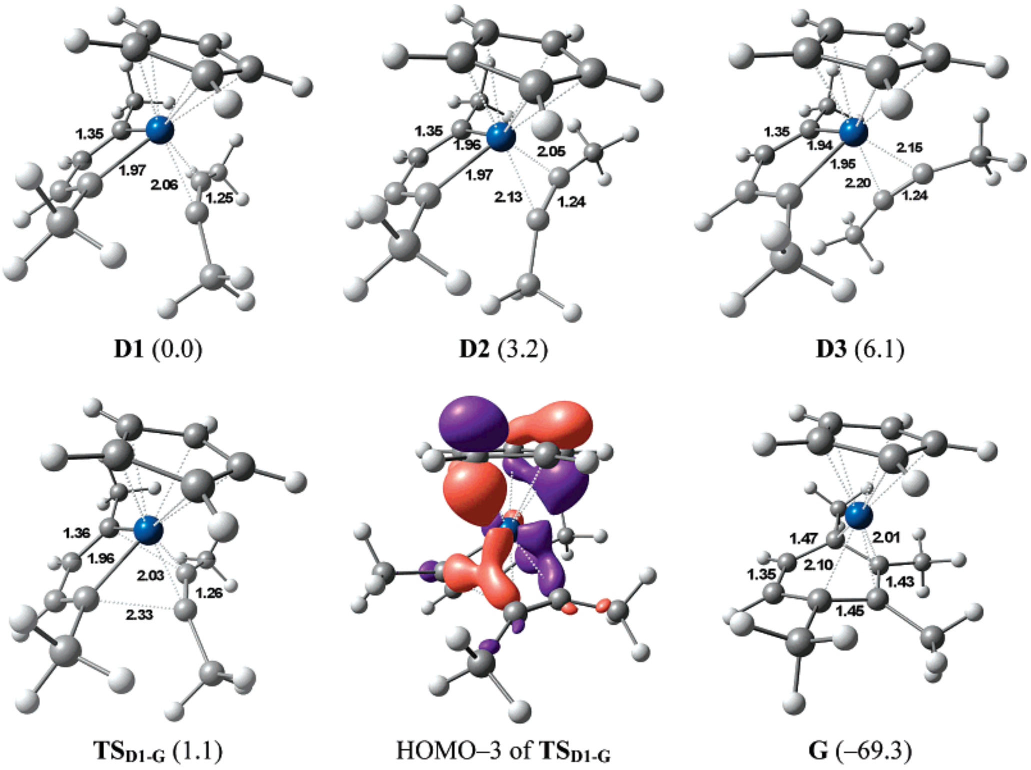
(22) The computational method used herein was calibrated in our previous study (see ref 18).

(23) (a) Harvey, J. N.; Aschi, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5555−5563. (b) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95−99.

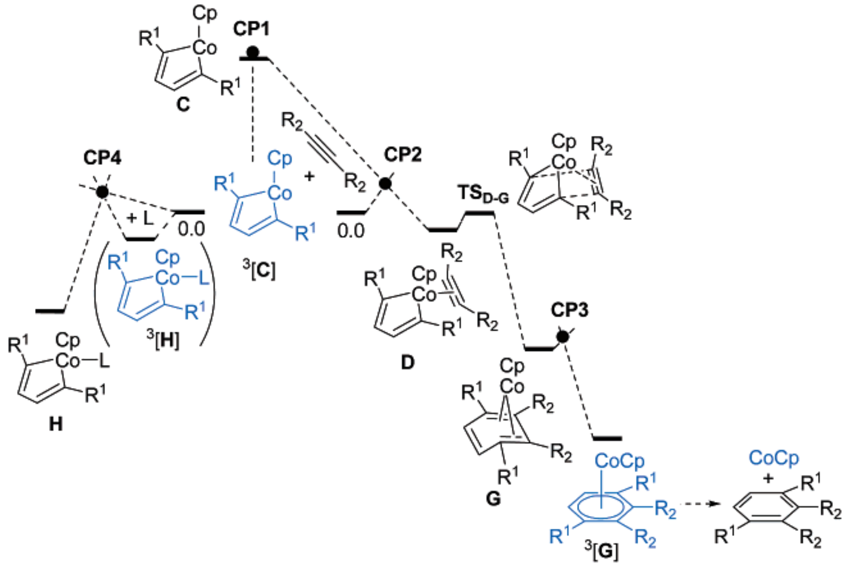


D1 (0.0) **D2** (3.2) **D3** (6.1)

TS$_{D1-G}$ (1.1) HOMO–3 of **TS$_{D1-G}$** **G** (–69.3)

Figure 1. Structures and selected bond distances (Å) for the various coordination modes of 2-butyne to Cpcobalta-2,5-dimethylcyclopentadiene and the subsequent formation of the CpCo(η^4-arene) complex **G**; energies (kcal/mol) are given relative to **D1**.

Scheme 7. Energy Profile for the Two-State Transformation of Cobaltacyclopentadienes into Benzenes (Triplet Species Are Depicted in Blue)



of the seam of crossing.[23b] The Chemcraft program was used to draw the calculated structures.[24]

Results and Discussion

The formation of bisalkyne complexes of type **B** and their subsequent transformation into cobaltacyclopentadienes of type **C** were previously studied by DFT computations. To summarize, the ligands in CpCoL$_2$ (L = CO, PR$_3$, olefin) are successively replaced by ethyne via S$_N$1 mechanisms.[18] Energies of activation of 11−13 kcal/mol were reported for the subsequent oxidative coupling leading to **C**.[3,5a,18,25] Relaxation to the triplet ground state of this coordinatively unsaturated species is facilitated by the presence of a minimum energy crossing point of the singlet and triplet surfaces located at 0.1[18] or −1.1[5a] kcal relative to the singlet complex, depending on the MECP location technique and level of theory used. The same features were observed in the formation of the three cobaltacyclopentadienes **C** under investigation in this work (R^1 = H, Me, CO$_2$H, Scheme 7). The triplet species ^{3}[**C**] are more stable by 13.0−16.2 kcal/mol, and

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(24) http://www.chemcraftprog.com.

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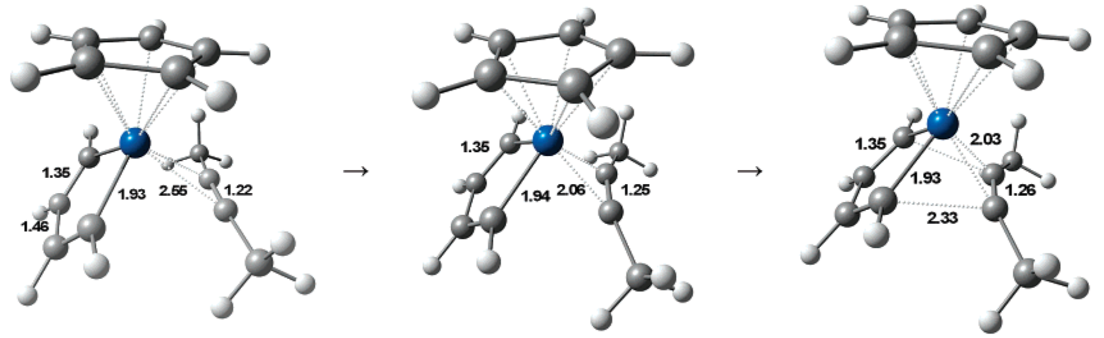
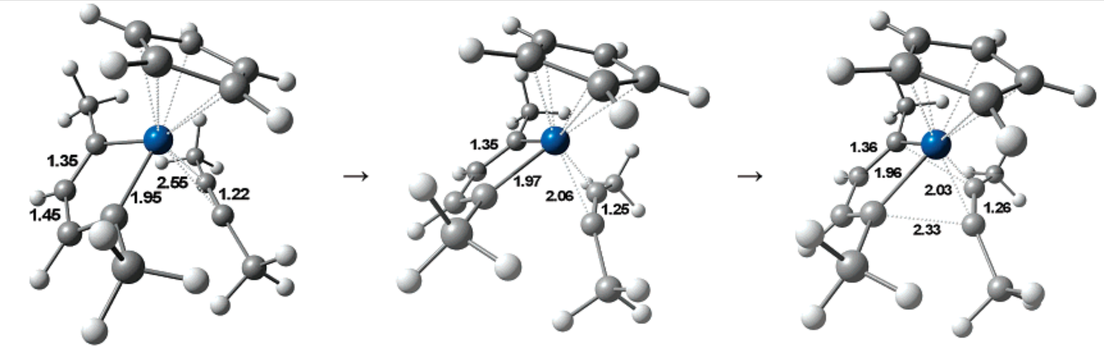
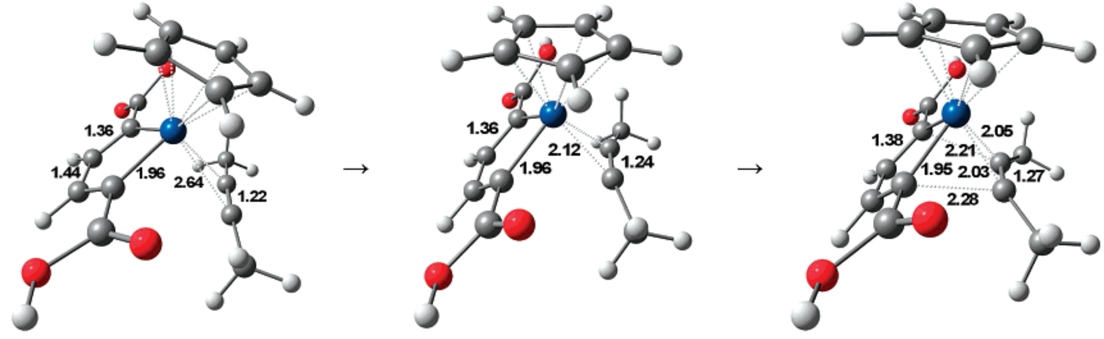


CP2 (R^1 = H, R^2 = Me) **D** (R^1 = H, R^2 = Me) $\mathbf{TS_{D\text{-}G}}$ (R^1 = H, R^2 = Me)



CP2 (R^1 = Me, R^2 = Me) **D** (R^1 = Me, R^2 = Me) $\mathbf{TS_{D\text{-}G}}$ (R^1 = Me, R^2 = Me)



CP2 (R^1 = CO_2H, R^2 = Me) **D** (R^1 = CO_2H, R^2 = Me) $\mathbf{TS_{D\text{-}G}}$ (R^1 = CO_2H, R^2 = Me)

Figure 2. Structures and selected bond distances (Å) for the various species **CP2**, **D**, and $\mathbf{TS_{D-G}}$ depicted in Scheme 7 and Table 1.

the crossing points (**CP1**) are only 0−1.3 kcal/mol more energetic (Table 1). Therefore, it is reasonable to believe that the change in the spin state will occur readily.

While in the computed cyclotrimerization of ethyne, **D** collapses directly to **G**, we hoped to render the former computationally viable by adding substituents that would stabilize it kinetically. Methyl groups were successively added, first to the coordinated alkyne and then also at the α-carbon atoms of the metallacycle, until the structure was constrained to convergence. The minimum required to achieve this goal was simply two methyl groups on the alkyne (Table 1).

The four-methyl case is illustrated in Figure 1. Depending on the orientation of the coordinated alkyne, three structures were found as minima. In complex **D1**, which displays quasi C_s symmetry, 2-butyne is aligned almost parallel to the $C_\beta-C_\beta$ bond of the metallacycle (1.1°). In **D2**, less stable than **D1** by 3.2 kcal/mol, the acetylenic C−C bond is rotated by 28.3° relative to $C_\beta-C_\beta$. Last, in complex **D3**, 2-butyne is aligned almost perpendicularly. This complex is less stable than **D1** by 6.1 kcal/mol (82.7°).[26] Compound **D1** could be connected to the corresponding CpCo(η^4-arene) complex **G** via C_s-symmetrical $\mathbf{TS_{D1-G}}$, lying only 1.2 kcal/mol above **D1**.[27] The main difference in geometry between **D1** and the transition state is the distance between the coordinated acetylenic carbons and the α-carbons which is reduced by 0.2 Å (**D1**: 2.53 Å; $\mathbf{TS_{D1-G}}$: 2.33 Å). Canonical MO 60 (HOMO-3) shows the expected interaction for the metal-assisted [$4\pi_s + 2\pi_s$] cycloaddition.[28] This finding corroborates clearly complexes of the

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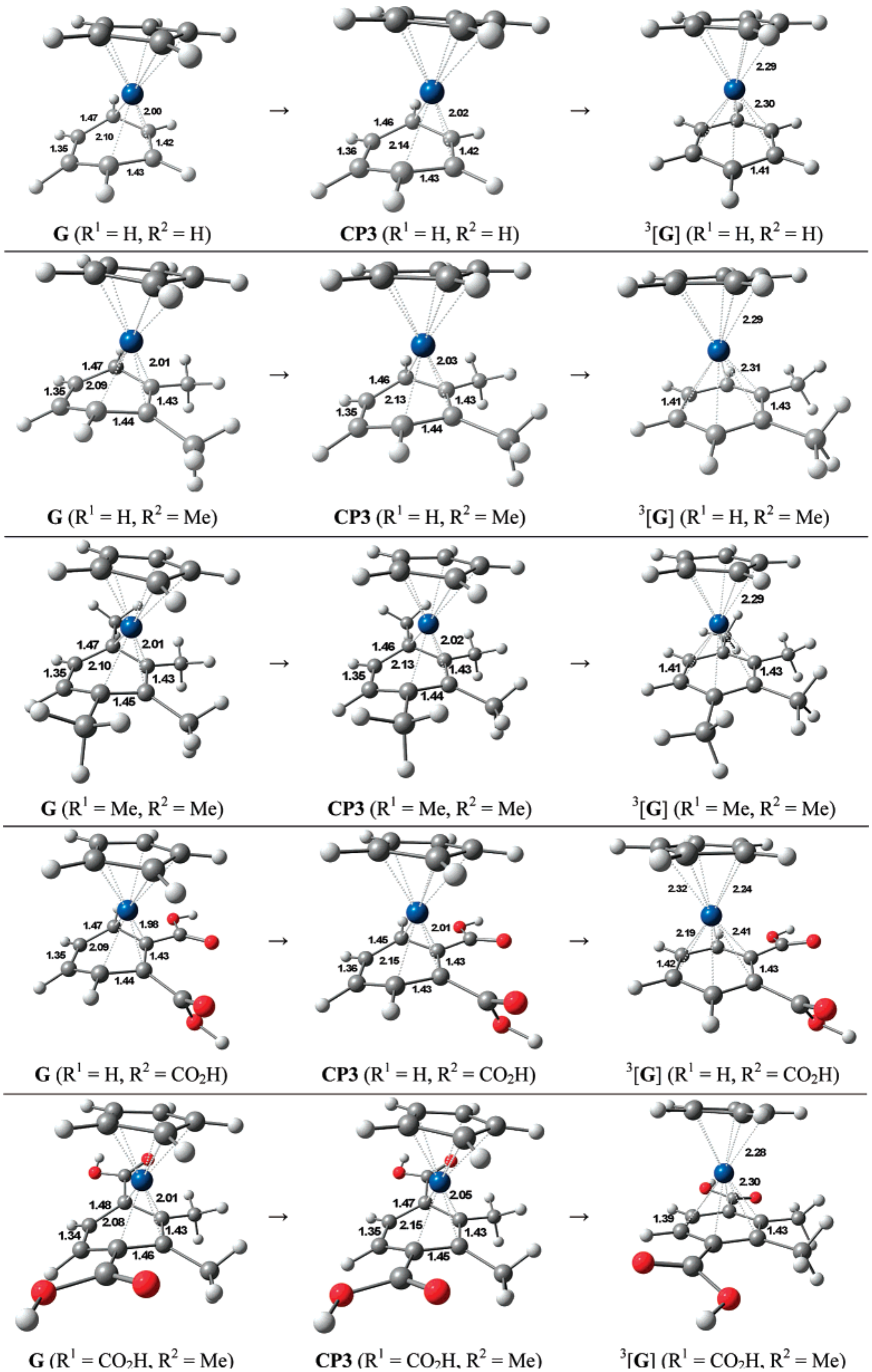
[26] With two methyl groups instead of four, **D2** does not exist on the potential energy surface. **D3** is less stable than **D1** by 10.7 kcal/mol.

[27] The corresponding enthalpy of activation with just two methyl groups is also 1.2 kcal/mol.

[28] In the parent series, Albright and coworkers could locate a complex similar to **D3** only and found a transition state to **G** (see ref 3 and Introduction). Because **D3** and **D2** are less stable than **D1** and also less stable than $\mathbf{TS_{D1-G}}$ itself, we did not try to compute transition states to **G** from these complexes.



G (R^1 = H, R^2 = H) **CP3** (R^1 = H, R^2 = H) ^{3}[**G**] (R^1 = H, R^2 = H)

G (R^1 = H, R^2 = Me) **CP3** (R^1 = H, R^2 = Me) ^{3}[**G**] (R^1 = H, R^2 = Me)

G (R^1 = Me, R^2 = Me) **CP3** (R^1 = Me, R^2 = Me) ^{3}[**G**] (R^1 = Me, R^2 = Me)

G (R^1 = H, R^2 = CO_2H) **CP3** (R^1 = H, R^2 = CO_2H) ^{3}[**G**] (R^1 = H, R^2 = CO_2H)

G (R^1 = CO_2H, R^2 = Me) **CP3** (R^1 = CO_2H, R^2 = Me) ^{3}[**G**] (R^1 = CO_2H, R^2 = Me)

Figure 3. Structures and selected bond distances (Å) for the various species **G**, **CP3**, and ^{3}[**G**] depicted in Table 1.

type **6** and **11** as kinetically relevant intermediates in the mechanism of the CpCo-catalyzed alkyne cyclotrimerization.[29]

Having found species ^{3}[**C**] and **D**, we next sought a proper crossing point (**CP2**) to connect them (Scheme 7, right side, and Figure 2).[30] Energies for these transformations are depicted

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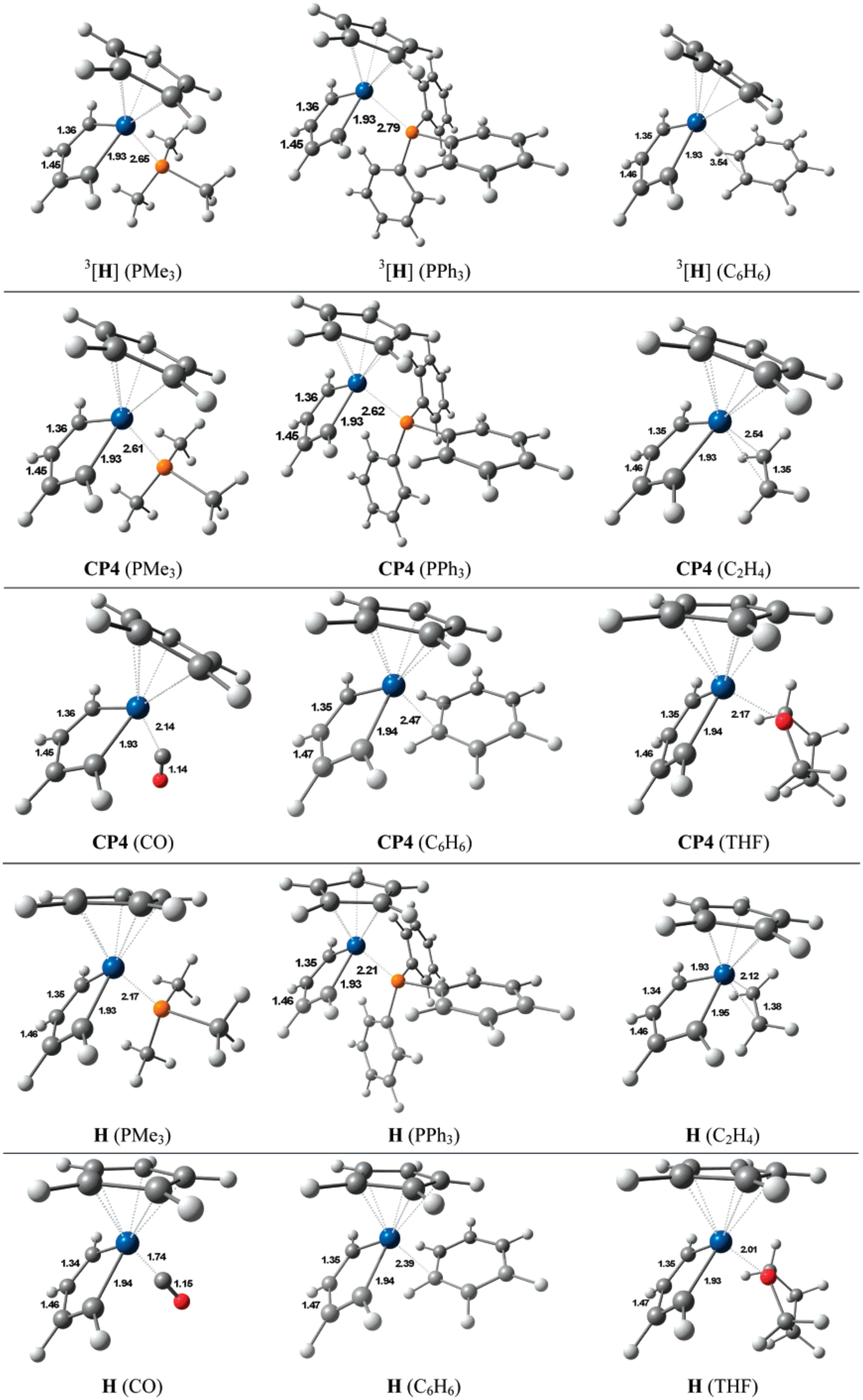
(29) It is worthy of note that unsubstituted or monosubstituted alkynes (ethyne, propyne) were not the only groups that lead to collapse. With two hydroxycarbonyl groups (butynedioic acid), no structure of type **D** could be obtained.

(30) In all cases discussed herein, the transformation of ^{3}[**C**] and the alkyne into ^{3}[**G**] (via transition states rather than crossing points) requires activation energies approximately twice as large as the enthalpy required to reach **CP2**.



^{3}[**H**] (PMe_3) ^{3}[**H**] (PPh_3) ^{3}[**H**] (C_6H_6)

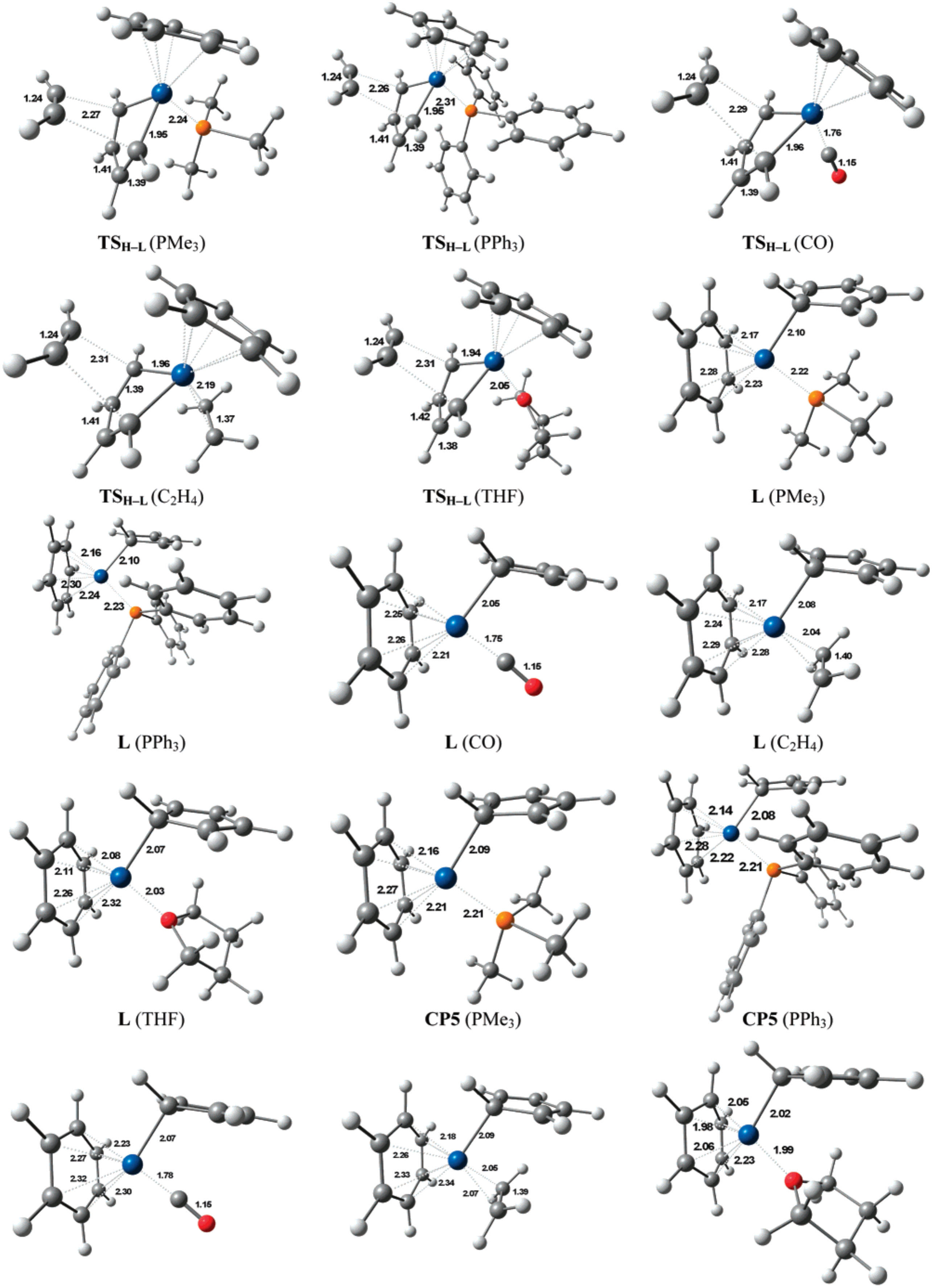
CP4 (PMe_3) **CP4** (PPh_3) **CP4** (C_2H_4)

CP4 (CO) **CP4** (C_6H_6) **CP4** (THF)

H (PMe_3) **H** (PPh_3) **H** (C_2H_4)

H (CO) **H** (C_6H_6) **H** (THF)

Figure 4. Structures and selected bond distances (Å) for the various species ^{3}[**H**], **CP4**, and **H** depicted in Table 2.



TS$_{\mathbf{H-L}}$ (PMe$_3$) **TS$_{\mathbf{H-L}}$** (PPh$_3$) **TS$_{\mathbf{H-L}}$** (CO)

TS$_{\mathbf{H-L}}$ (C$_2$H$_4$) **TS$_{\mathbf{H-L}}$** (THF) **L** (PMe$_3$)

L (PPh$_3$) **L** (CO) **L** (C$_2$H$_4$)

L (THF) **CP5** (PMe$_3$) **CP5** (PPh$_3$)

CP5 (CO) **CP5** (C$_2$H$_4$) **CP5** (THF)

Figure 5. Structures and selected bond distances (Å) for the various species depicted in Table 3.

Table 2. Energies (kcal/mol) Relative To ^{3}[**C**] and L for the Species Depicted in Scheme 7

L	^{3}[**H**]	**CP4**	**H**
PH_3	−1.2	−1.7	−18.4
PMe_3	−5.0	−5.7	−24.7
PPh_3	−0.6	−0.6	−14.9
C_2H_4	*a*	5.9	−5.3
CO	*a*	−1.7	−26.7
C_6H_6	−0.01	11.6	11.3
THF	−0.9	2.3	−1.5

[a] L is ejected during optimization.

Table 3. Energies (kcal/mol) Relative to **H** and Ethyne for the Species Depicted in Scheme 8

L	TS_{H-L}	**L**	**CP5**	**M**
PH_3	35.0	−59.5	−59.5	−90.6
PMe_3	37.1	−54.3	−54.4	−90.6
PPh_3	38.2	−56.4	−56.4	−96.4
CO	32.8	−63.9	−62.0	−95.2
C_2H_4	33.1	−68.7	−68.0	−108.3
THF	28.6	−62.7	−59.0	−96.8

Scheme 8. Energy Profile for the Two-State Transformation of Cobaltacyclopentadienes(L) and Ethyne to Benzene Featuring Diels−Alder Cycloadditions (Triplet Species Are Depicted in Blue)

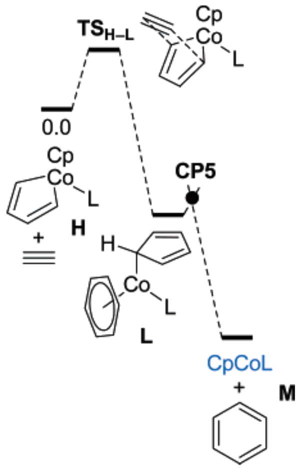


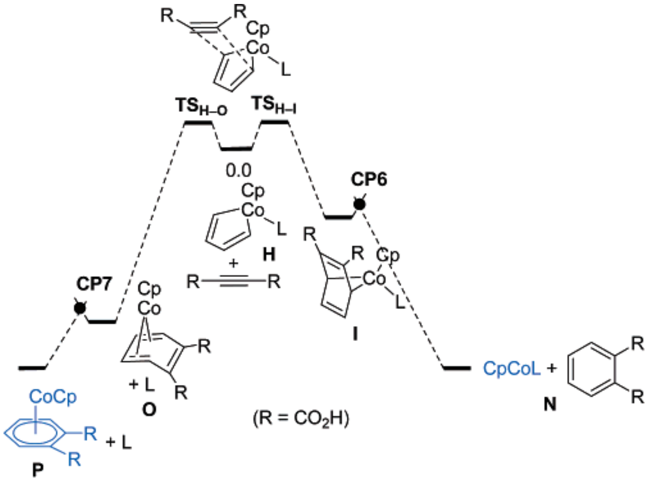
Table 4. Energies (kcal/mol) Relative to **H** and Butynedioic Acid for the Species Depicted in Scheme 9

L	TS_{H-I}	**I**	**CP6**	**N**
PH_3	17.9	−34.2	−33.1	−90.9
PMe_3	18.0	−29.8	−29.2	−90.8
CO	17.1	−36.5	*a*	−95.5

L	TS_{H-O}	**O**	**CP7**	**P**
PPh_3	17.7	−74.9	−73.5	−86.7
C_2H_4	16.2	−84.5	−83.1	−96.3
THF	11.7	−88.4	−87.0	−100.2

[a] Calculation of this CP failed.

Scheme 9. Energy Profile (kcal/mol) for the Two-State Transformation of Cobaltacyclopentadienes(L) and Butynedioic Acid to Benzenes Featuring Diels−Alder Cycloadditions (Triplet Species Are Depicted in Blue)



in Table 1. For the parent system ($R^1 = R^2 = H$), a crossing point between the reaction coordinates of ^{3}[**C**] with ethyne and those of **C** with ethyne is available 6.5 kcal/mol above the triplet.[31] When the singlet reaction coordinates are dovetailed, they lead directly to **G**, lying 84.5 kcal/mol below ^{3}[**C**] and the alkyne. A second crossing point, **CP3**, is readily available on route to ^{3}[**G**] ($\Delta E_{\mathbf{G-CP3}} = 0.6$ kcal/mol). The geometrical parameters of **CP3** are indeed very similar to those of **G** (Figure 3). This transformation is exothermic by 19.1 kcal/mol.[32] Dissociation of ^{3}[**G**] would finally furnish the arene and generate ground state triplet CpCo.[33,34] Comparable results were obtained by substituting the coordinated alkyne by hydroxycarbonyl groups ($R^1 = H$, $R^2 = CO_2H$). With $R^1 = H$ and $R^2 = Me$, **CP2** is now located 7.4 kcal/mol above ^{3}[**C**] and 2-butyne, but as stated above, the singlet reaction coordinates halt at **D** ($\Delta E = -3.7$ kcal/mol), which subsequently transforms into **G** ($\Delta E^\ddagger = 1.2$ kcal/mol; $\Delta E = -71.0$ kcal/mol). In this case, **CP3** is found 0.7 kcal/mol above **G**. With four methyl groups in the system ($R^1 = R^2 = Me$), the reaction of ^{3}[**C**] with 2-butyne meets a seam of crossing 11.0 kcal/mol above the reactants. The transformation of ^{3}[**C**] into **D** is moderately endothermic by 1.2 kcal/mol. **G** is then obtained as described in Figure 1 ($\Delta E^\ddagger = 1.2$ kcal/mol; $\Delta E = -69.3$ kcal/mol). The final transformation into ^{3}[**G**] is exothermic by 15.8 kcal/mol and may proceed through **CP3** ($\Delta E = 0.7$ kcal/mol). The replacement of the methyls on the metallacycle by hydroxycarbonyl groups ($R^1 = CO_2H$ and $R^2 = Me$) also allows the location of a complex of type **D** and of a transition state leading to **G**. **CP2** is now located only 4.5 kcal/mol above ^{3}[**C**] and the alkyne, and **CP3** is found 2.5 kcal/mol above **G**. The transformation of **D** into **G** is still straightforward ($\Delta E^\ddagger = 4.0$ kcal/mol).

To summarize the above, based on the location of new intermediates, the comprehensive catalytic cycle for the formation of arenes from alkynes now includes six minima: **B** → **C** → ^{3}[**C**] → **D** → **G** → ^{3}[**G**]. *For the first time, transition states for the key step of arene formation in the Co-catalyzed [2 + 2 + 2] cyclotrimerization of alkynes have been described. They correspond to metal-assisted concerted [4 + 2] cycloadditions.*

According to the kinetic studies summarized in Scheme 6, there is a competition between PPh_3 and 2-butyne for the 16-electron cobaltacyclopentadiene. Because the reaction of PPh_3 is faster, its dissociation from the complex becomes the rate-determining step. Following this lead, we next investigated the

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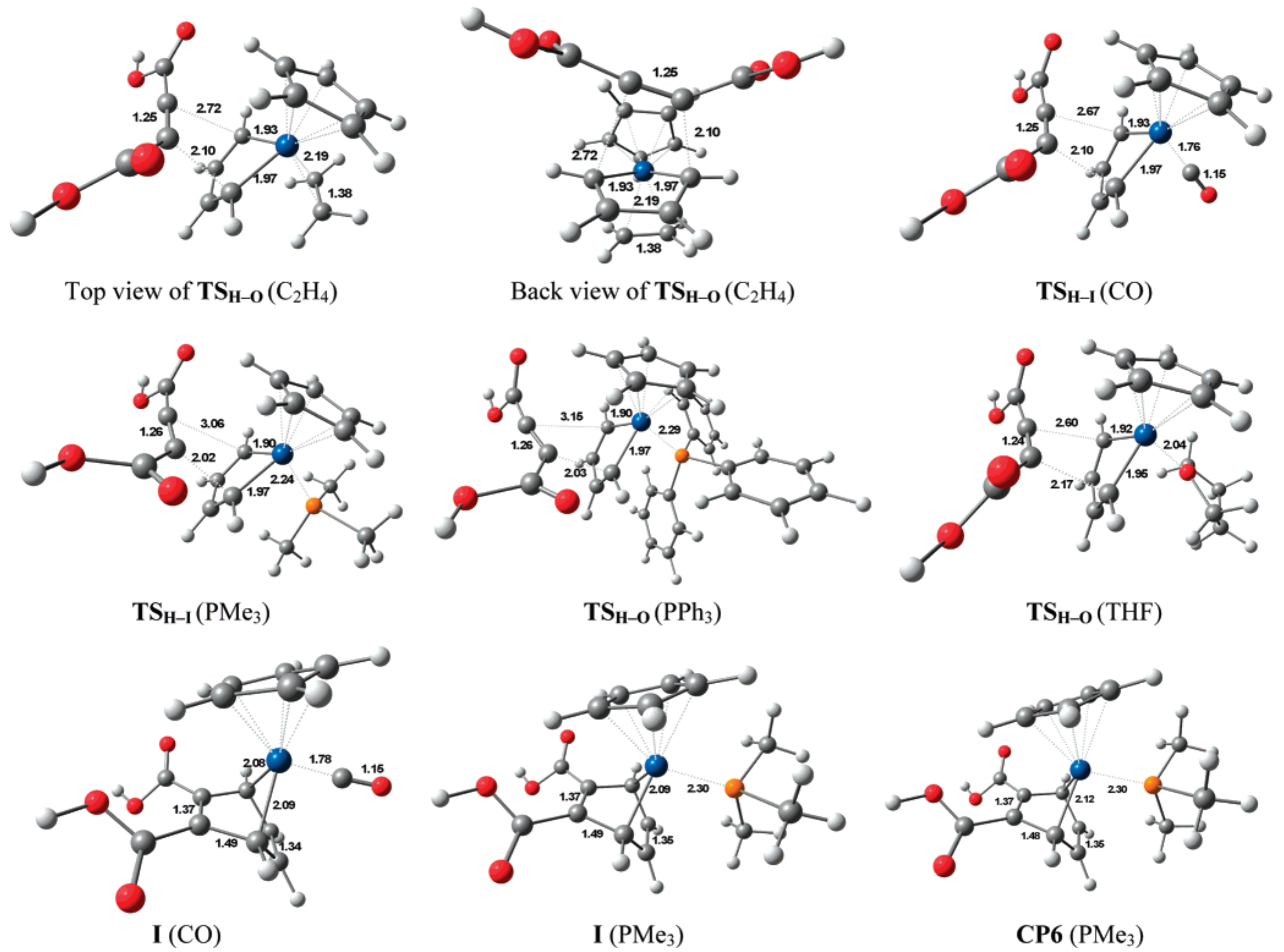
(31) At the B3LYP/6-31G(d,p) level for all atoms including cobalt and using a different method for locating MECP (Koga, N.; Morokuma, K. *Chem. Phys. Lett.* **1985**, *119*, 371), Koga et al. computed a value of 5.8 kcal/mol for the same transformation; see ref 5b.

(32) The values obtained are similar to those reported previously; see ref 5b.

(33) Singlet to triplet excitation energy: $\Delta E_{S-T} = -38.0$ kcal/mol; quintet to triplet excitation energy: $\Delta E_{Q-T} = -29.3$ kcal/mol.

(34) An energetically reasonable transition state for the displacement of CpCo by incoming acetylene could not be found. Therefore, we believe that the last step of the mechanism is dissociative rather than associative.



Top view of **TS$_{H-O}$** (C$_2$H$_4$) Back view of **TS$_{H-O}$** (C$_2$H$_4$) **TS$_{H-I}$** (CO)

TS$_{H-I}$ (PMe$_3$) **TS$_{H-O}$** (PPh$_3$) **TS$_{H-O}$** (THF)

I (CO) **I** (PMe$_3$) **CP6** (PMe$_3$)

Figure 6. Structures and selected bond distances (Å) for the various species depicted in Table 4.

reaction of ^{3}[**C**] with phosphines (Scheme 7, left side). A set of constrained geometry optimizations at decreasing distances between Co and P revealed a barrierless addition of phosphines. The formation of ^{3}[**H**] is moderately exothermic by 0.6−5.0 kcal/mol (Table 2, Figure 4). These 18-electron complexes are more stable as singlets by 14.3−19.7 kcal/mol. We found points (**CP4**) allowing intersystem crossing that are close in energy to ^{3}[**H**] (−0.5−0.0 kcal/mol). We also examined other potential ligands, such as typical solvents used in the cyclotrimerization (C_6H_6, THF) or ligands arising from CpCoL$_2$ precatalyst dissociation (L = CO, C_2H_4). In the triplet state, CO and C_2H_4 do not bind to the metallacycle. For these species, **CP4** exists but corresponds to a “reaction” crossing point directly connecting {^{3}[**C**] + L} and **H**, rather than a “relaxation”. With C_2H_4, **CP4** is located 5.9 kcal/mol above the reactants, whereas, with CO, it is found 1.7 kcal/mol below them. In addition, the formation of **H** is moderately exothermic with C_2H_4 ($\Delta E = -5.3$ kcal/mol) compared to CO ($\Delta E = -26.7$ kcal/mol). The complexation of C_6H_6 or THF to ^{3}[**C**] is poorly exothermic (−0.01 and −0.9 kcal/mol, respectively). Whereas the crossing point to **H** is quite accessible with THF ($\Delta E^3_{[\mathbf{H}]-\mathbf{CP4}} = 3.2$ kcal/mol), that with C_6H_6 is found 11.6 kcal/mol above ^{3}[**H**]. Besides, C_6H_6 is the only ligand for which **CP4** is higher in energy than **CP2** (6.5 kcal/mol above ^{3}[**C**], see Table 1). Thus, unlike the others, it should not compete with the alkyne for complexation of ^{3}[**C**]. *Providing that the probabilities for surface hopping are comparable, this set of results shows that, pursuant to the kinetic experiments exposed above, the key intermediate cobaltacycopentadienes may follow a different path from the axiomatic direct reaction with a new alkyne unit.*

Continuing along the lines of the McAlister, Bercaw, and Bergman study, we next investigated direct reactions between complexes of type **H** and alkynes. As in the previous computational studies,[3,5b] we could not model a direct insertion of the alkyne into a Co−C σ-bond or an η^1- or η^3-Cp transition state corresponding to the associative substitution of the phosphine by the alkyne. On the other hand, the Diels−Alder addition of ethyne to complexes **H** could be computed, but the associated energies of activation seem prohibitively high (Scheme 8). Synchronous transition states leading to (η^6-benzene)(η^1-Cp)-CoL complexes of type **L** were located 29−38 kcal/mol above **H** (Table 3, Figure 5).[35] The dissociations of these complexes into benzene and triplet CpCoL are facilitated by the presence of nearby crossing points (**CP5**, ΔE 0.0−3.7 kcal/mol).[36]

In contrast, with butynedioic acid, asynchronous [4 + 2] transition states for the concerted cycloaddition were found

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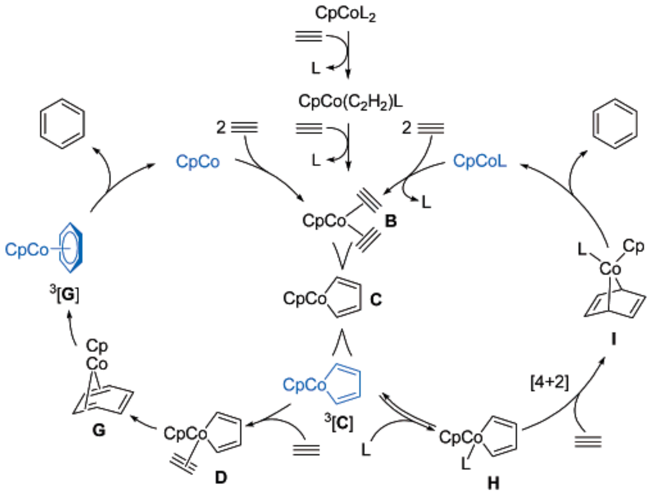
(35) The alkyne must enter from the same side as the Cp. Repeated attempts at computing [4 + 2] transition states with the alkyne entering on the phosphine side failed.

(36) Transition states connecting **L** to CpCoL(η^2-benzene) complexes were found, but the corresponding enthalpies of activation are much higher than those required to reach **CP5**. For instance, with PH$_3$, PMe$_3$, and PPh$_3$: $\Delta H^{\ddagger}_{298} = 10.2$, 11.2, 12.6 kcal/mol and $\Delta H_{298} = -18.9$, −18.0, −14.5 kcal/mol, respectively.

Scheme 10. Two-State Mechanisms for the Cobalt-Catalyzed Ethyne Cyclotrimerization to Benzene (Triplet Species Are Depicted in Blue)



(Scheme 9). The C_s symmetry was enforced to obtain the corresponding synchronous transition states, but it failed to give stationary points.[37] In addition, a polar stepwise mechanism could not be found, perhaps not surprisingly, as it would generate an unfavorable positive charge α to the metal.[38] As expected (Table 4, Figure 6), the energies of activation are much lower than those found with ethyne (16−18 vs 29−38 kcal/mol). Depending on the ligand, the [4 + 2] transition states connect the species **H** and the alkyne to either 7-cobaltanorbornenes of type **I** or CpCo(η^4-arene) complexes (system **O**). Thus, strong donor molecules (PH_3, PMe_3, and CO) remain on cobalt to give **I**, whereas the less coordinating ones (PPh_3, C_2H_4, THF) are ejected. The formation of species of type **I** is exothermic by 30−37 kcal/mol, and that of **O**, by 75−88 kcal/mol. In both cases, there is a close-lying crossing point to triplet species (0.7−1.4 kcal/mol above).[39] From **I**, **CP6** leads to CpCoL and the free arene ($\Delta E_{\mathbf{I-N}} \approx -60$ kcal/mol), and from **O**, **CP7** leads to the (η^6-benzene)CpCo complex **P** ($\Delta E_{\mathbf{O-P}} \approx -12$ kcal/mol).

This set of results appears fully consistent with the experimental facts: If one compares the relative energies of **CP4** and **CP2** (Tables 1 and 2), the formation of phosphine complexes of type **H** seems to be easier than the formation of ethyne or butynedioic complexes of type **D**. Whereas the dissociation of PPh_3 can be estimated to cost 14.9 kcal/mol, that of PMe_3 requires as much as 24.7 kcal/mol. With PMe_3 on the cobaltacyclopentadiene and ethyne, either dissociation of the phosphine (24.7 kcal/mol) or Diels−Alder reaction of ethyne ($\Delta E^\ddagger = 37.1$ kcal/mol) requires very high energies. Thus, a very slow reaction is anticipated between 2-butyne and the PMe_3-complexed cobaltacyclopentadiene **12** (Scheme 6). On the other hand, the Diels−Alder reaction with butynedioic acid is expected to occur readily ($\Delta E^\ddagger = 18.0$ kcal/mol). With PPh_3 on the cobaltacyclopentadiene, the dissociation of the phosphine is much faster than the Diels−Alder reaction with ethyne (14.9 vs 38.2 kcal/mol). The mechanistic pathway depicted in Scheme 7 is thus likely to operate.[40]

Conclusion

In this study, parallel mechanisms for the [2 + 2 + 2] cyclotrimerization of alkynes have been investigated (Scheme 10). In both a bisalkyne complex (**C**) undergoes oxidative coupling to a cobaltacyclopentadiene (**B**), which spontaneously relaxes to the triplet ground state (^{3}[**C**]). The trapping of that species to give 18-electron complex **H** is faster with σ-donor ligands (PR_3, CO, THF) than with π-donors (alkyne, alkene, arene). Therefore, for reactions in strong σ-donor solvents or employing $CpCo(PR_3)_2$ or $CpCo(CO)_2$, the species **H** is a likely relay point. Subsequently, strongly dienophilic alkynes add to **H** by intermolecular [4 + 2] cycloaddition to furnish cobaltanorbornadiene **I**. A change in the spin state results in the formation of the free arene and CpCoL. In the absence of strong σ-donors and electron poor alkynes, another catalytic cycle takes over: ^{3}[**C**] reacts with the alkyne to give **D**, which subsequently transforms into the CpCo(η^4-arene) complex **G** via intramolecular metal-assisted [4 + 2] cycloaddition. A spin change transforms **G** into the 20-electron sandwich complex ^{3}[**G**], whose dissociation provides the free arene and CpCo. It is worthy of note that the two coordinatively unsaturated intermediates **E** and **F** (Scheme 2), frequently invoked in the literature, are not part of any of the computed mechanistic pathways. One might anticipate that, using sterically hindered groups, intermediates of type **D** or **I** could become isolable and give further credit to this study.

Acknowledgment. This work was supported by CNRS, MRES, DGA, and the NSF (CHE 0451241). M.M. is a member of the Institut Universitaire de France. We are grateful for the use of the computing facilities of CRIHAN, Plan Interrégional du Bassin Parisien (project 2006-013), and the Centre de Calcul Recherche et Enseignement (CCRE) of the Université Pierre et Marie Curie-Paris 6. We are indebted to Professor R. G. Bergman for supplying a copy of ref 16b.

Supporting Information Available: Coordinates and energies of computed structures; complete refs 2b and 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) For instance, with the PH_3-complexed cobaltacyclopentadiene, the optimized geometry shows two imaginary frequencies at −341 and −69 cm^{-1}, the latter corresponding to the symmetry break.

(38) For a related DFT study of the cycloaddition of 1,3-butadienes with dimethyl butynedioate, see: Domingo, L. R.; Arnó, M.; Contreras, R.; Pérez, P. *J. Phys. Chem. A* **2002**, *106*, 952−961.

(39) Extensive efforts were made in order to find a transition state connecting species of type **I** to any type of CpCo(arene) complex, but without success.

(40) The investigation of the reaction of **2** with DMAD was not possible due to rapid reaction of the diester with liberated phosphine; see ref 16b.