J|A|C|S
ARTICLES

Cobalt-Mediated Cyclic and Linear 2:1 Cooligomerization of Alkynes with Alkenes: A DFT Study

Vincent Gandon,*,† Nicolas Agenet,† K. Peter C. Vollhardt,‡ Max Malacria,† and Corinne Aubert*,†

Contribution from the Université Pierre et Marie Curie-Paris 6, Laboratoire de Chimie Organique (UMR CNRS 7611), Institut de Chimie Moléculaire (FR 2769), case. 229, 4 place Jussieu, F-75252 Paris Cedex 05, France, and Center for New Directions in Organic Synthesis, Department of Chemistry, University of California at Berkeley, and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

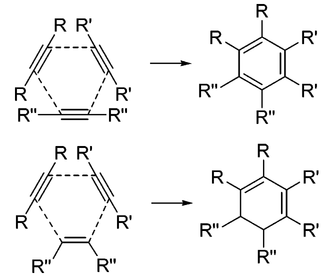
Received February 1, 2006; E-mail: gandon@ccr.jussieu.fr

Abstract: The mechanism of the cobalt-mediated [2 + 2 + 2] cycloaddition of two alkynes to one alkene to give CpCo-complexed 1,3-cyclohexadienes (cyclic oligomerization) has been studied by means of DFT computations. In contrast to the mechanism of alkyne cyclotrimerization, in which final alkyne inclusion into the common cobaltacyclopentadiene features a direct "collapse" pathway to the complexed arene, alkene incorporation proceeds via insertion into a Co−C σ-bond rather than inter- or intramolecular [4 + 2] cycloaddition. The resulting seven-membered metallacycle **7** is a key intermediate which leads to either CpCo-complexed cyclohexadiene **5** or hexatriene **13**. The latter transformation, particularly favorable for ethene, accounts, in part, for the linear oligomerization observed occasionally in these reactions. With aromatic double bonds, a C−H activation mechanism by the cobaltacyclopentadiene seems more advantageous in hexatriene product formation. Detailed investigations of high- and low-spin potential energy surfaces are presented. The reactivity of triplet cobalt species was found kinetically disfavored over that of their singlet counterparts. Moreover, it could not account for the formation of CpCo-complexed hexatrienes. However, triplet cobalt complexes cannot be ruled out since all unsaturated species appearing in this study were found to exhibit triplet ground states. Consequently, a reaction pathway that involves a mixing of both spin-state energy surfaces is also described (two-state reactivity). Support for such a pathway comes from the location of several low-lying minimum-energy crossing points (MECPs) of the two surfaces.

Introduction

The [2 + 2 + 2] cycloaddition of unsaturated moieties is a powerful method for the construction of three new bonds in a one-step process. For instance, the cycloaddition of three alkynes, or two alkynes and one alkene (cyclic 2:1 cooligomerization), is one of the most elegant methods for forming benzene or 1,3-cyclohexadiene derivatives (Scheme 1). Transition metal catalysts are often used for cycloadditions that would be otherwise very difficult or impossible.

Scheme 1. Prototypical [2 + 2 + 2] Cycloadditions



Cobalt complexes proved to be reagents of choice for mediating alkyne/alkene 2:1 cooligomerization in a highly chemo-, regio-, and stereoselective way.[1] In that respect, complexes of type $CpCoL_2$ (L = CO, PR_3, alkenes) have been used widely to produce selectively, e.g., nitrogen-containing heterocycles,[2] steroid derivatives,[3] terpenoids,[4] or borylated compounds.[5] Based on experimental results and in analogy to

---

† Laboratoire de Chimie Organique.

‡ Center for New Directions in Organic Synthesis.

(1) For general reviews of transition metal-mediated [2+2+2]cycloadditions of alkynes to alkenes, see: (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (b) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Hegedus, L., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, pp 741−770. (c) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741−4767. For reviews of corresponding cobalt-mediated reactions, see: (d) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−556. See also: (e) Eichberg, M. J.; Dorta, R. L.; Grotjahn, D. B.; Lamottke, K.; Schmidt, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **2001**, *123*, 9324−9337 and pertinent references therein.

(2) (a) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2091−2093. (b) Boese, R.; Van Sickle, A. P.; Vollhardt, K. P. C. *Synthesis* **1994**, 1374−1382. (c) Pelissier, H.; Rodriguez, J.; Vollhardt, K. P. C. *Chem.*−*Eur. J.* **1999**, *5*, 3549−3561. (d) Pérez, D.; Siesel, B. A.; Malaska, M. J.; Davis, E.; Vollhardt, K. P. C. *Synlett* **2000**, 306−310. (e) Eichberg, M. J.; Dorta, R. L.; Lamottke, K.; Vollhardt, K. P. C. *Org. Lett.* **2000**, *2*, 2479−2481.

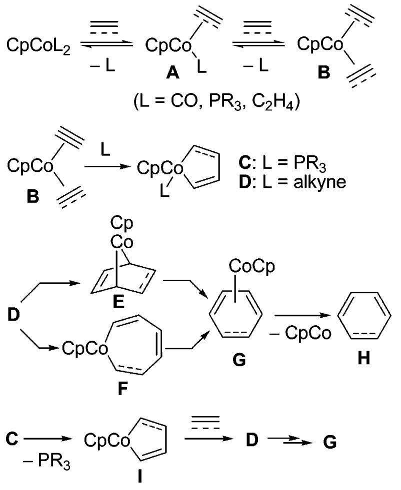
(3) Vollhardt, K. P. C. *Pure Appl. Chem.* **1985**, *57*, 1819−1826 and references therein.

(4) (a) Johnson, B. M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *113*, 381−382. (b) Germanas, J.; Aubert, C.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *113*, 4006−4008.

(5) Gandon, V.; Leboeuf, D.; Amslinger, S.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 7114−7118.

10.1021/ja060756j CCC: $33.50

Scheme 2. CpCo-Mediated [2 + 2 + 2] Cycloadditions to Benzene or 1,3-Cyclohexadiene



the transition-metal-mediated cyclotrimerization of alkynes for constructing benzenes,[1b,c,6] several mechanisms have been proposed for the assembly of 1,3-cyclohexadienes (Scheme 2). Initially, one and then two alkyne (alkene) moieties displace sequentially two ligands of the metal to form alkyne (alkene) complexes **A** and then **B**. The nature of these substitutions at $CpCoL_2$ (associative or dissociative) depends on the steric congestion around the metal and its electrophilicity. For instance, S_N2 mechanisms have been reported for $^{14}CO/CO$[7] and Ph_3P/CO exchange[8] in $CpCo(CO)_2$. From experimental data, it transpires that, in the case of the replacement of L in $CpCoL_2$ ($L = PR_3$, CO, alkenes) by η^2-ligands, such as alkenes or alkynes, S_N1 mechanisms prevail,[9] unless electron-withdrawing groups are present on the Cp ring.[9c] Alkyne (alkene) complexes of type **A** ($L = CO, PR_3$), as well as bisalkene complexes, have been isolated and structurally characterized.[6e] Bisalkyne and alkyne/alkene complexes **B** undergo spontaneous oxidative coupling to give the corresponding cobaltacyclopentadienes[10] or cobaltacyclopentenes.[11] Such compounds have been isolated as 18-electron phosphine- or alkyne-adducts of type **C** or **D**, and compelling confirmation of the intermediacy of cobaltacyclopentadiene(alkyne) complexes of type **D** in the formation of arenes has been provided by their thermal transformation into stable CpCo(η^4-arene) complexes of type **G**, followed by thermal CpCo dissociation to give the free arene **H**.[12] Phosphine-ligated cobaltacyclopentadienes and cobaltacyclopentenes of type **C** also lead to CpCo(η^4-cyclohexadiene) complexes by reaction with alkenes[13] or alkynes,[9a,10] respectively, thus rendering both species viable intermediates in the overall [2 + 2 + 2] process. Two types of reactions of alkenes (alkynes) with cobaltacycles have been suggested: either a Diels−Alder type reaction leading to bicyclic intermediate **E**[13] or an insertion of the coordinated alkene (alkyne) into a Co−C σ-bond giving a cobaltacycloheptadiene (-triene) **F**.[11] In both cases, a reductive elimination step furnishes the η^4-cyclohexadiene (-arene) CpCo complex **G**. Typically, whereas CpCo(η^4-cyclohexadiene) complexes are isolated as such, η^4-arene complexes undergo spontaneous displacement of CpCo to give the free arene **H**. Kinetic studies of McAlister, Bercaw, and Bergman revealed that the mechanism of the conversion of **C** into **H** is dependent critically on the nature of the alkyne.[14] With electron-rich ones, dissociation of the phosphine occurs to give coordinatively unsaturated cobaltacyclopentadiene **I**. It subsequently reacts with an alkyne to give **D**.

On the other hand, it has also been shown that trialkylphosphine-complexed cobaltacyclopentadienes react with electron-deficient alkynes without phosphine dissociation. Therefore, it was suggested that a direct reaction might occur between the uncomplexed alkyne and the metallacycle: a [4 + 2] cycloaddition of the electron-rich butadiene framework with the electron-poor dienophiles, an associative ligand substitution, or a direct insertion. It is worthy of note that from an experimental point of view such cases remain quite particular. In general, blocking the vacant site of cobalt by an excess of phosphine or CO inhibits significantly the rate of the cycloaddition.

Occasionally, C−H activation leading to open-chained hexatriene complexes has been observed. Such activations, sometimes dominant, were reported in cocyclizations of alkynes with the 2,3-double bonds in indole,[2b] pyrimidine,[2c] furan, and thiophene[15] but are not restricted to heteroaromatic compounds, since cyanoalkenes[11] and even ethene itself[16] furnish such products. Possible mechanistic rationales include a β-hydride/reductive elimination sequence from the cobaltacycloheptadiene intermediate **F**; direct electrophilic aromatic substitution by the intermediate cobaltacyclopentadiene; or oxidative addition to the C−H bond to give a (rare[17]) Co(V) species. The latter options were made plausible by early findings of Yamazaki and Wakatsuki, who reported that heating mixtures of PR_3-complexed cobaltacyclopentadienes of type **C** and benzene resulted in the addition of aryl−H across the butadiene framework of the metallacycle (Scheme 3).[18] The addition became predominant when the aryl group was forced to stay close to the metal center, such as in η^5-benzylcyclopentadienyl complexes. Similar conversions were recorded with pyrroles and thiophenes.[19] It

---

(6) 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.; 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.

(7) Wojcicki, A.; Basolo, F. *J. Inorg. Nucl. Chem.* **1961**, *17*, 77−83.

(8) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657−1663.

(9) (a) McDonnell Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445−456. (b) Janowicz, A. H.; Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1516−1518. (c) Wakatsuki, Y.; Yamazaki, H.; Sugawara, Y. *Organometallics* **1987**, *6*, 1191−1196.

(10) See, inter alia: Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907−1912.

(11) See, inter alia: Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123−1130.

(12) (a) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248. (b) Dosa, P. I.; Whitener, G. D.; Vollhardt, K. P. C. *Org. Lett.* **2002**, *4*, 2075−2078.

(13) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *139*, 169−177.

(14) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666−1668.

(15) Boese, R.; Harvey, D. F.; Malaska, M. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1994**, *116*, 11153−11154.

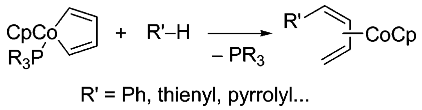
(16) Unpublished results.

(17) (a) Byrne, E. K.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 1282−1283. (b) Brookhart, M.; Grant, B. E.; Lenges, C. P.; Prosenc, M. H.; White, P. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1676−1679.

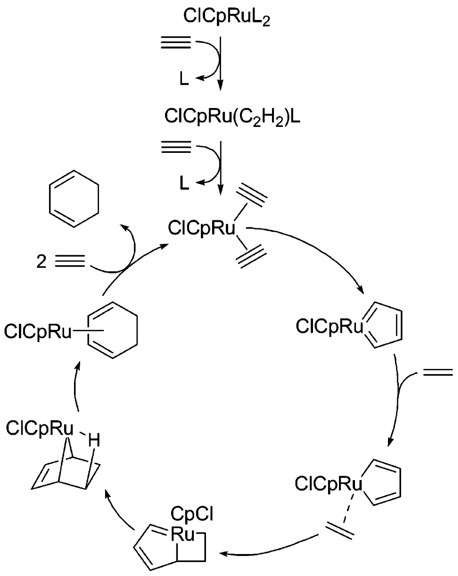
(18) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1978**, *149*, 377−384.

(19) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *149*, 385−393.

Scheme 3. Reaction of Cobaltacyclopentadiene with Aromatic C−H Bonds



Scheme 4. Mechanism of the CpRuCl-Catalyzed Cycloaddition of Two Acetylenes to Ethene

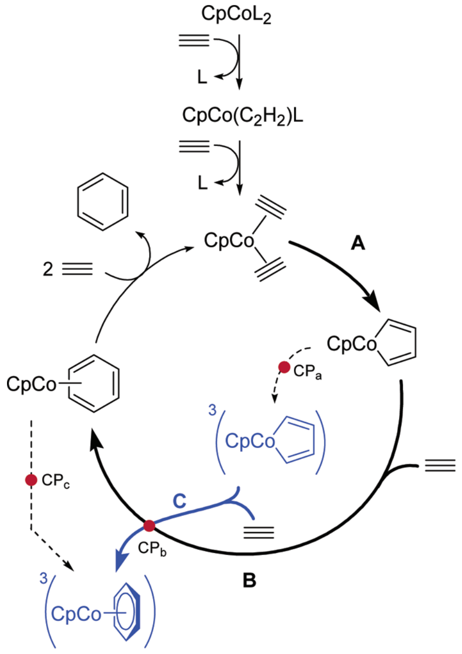


was postulated that, upon heating, dissociation of the phosphine from the metallacycle liberates a vacant site on cobalt with which C−H bonds may interact.

Even though a number of catalysts have been used to perform [2 + 2 + 2] cycloadditions of alkynes to alkenes, only the CpRuCl-catalyzed variant has been subject to a theoretical attempt at understanding the intimate mechanism of cyclohexadienes formation (Scheme 4).[20] This study showed that, first, a ruthenacyclopentatriene is formed by oxidative coupling of two alkyne ligands. Coordination of ethene then follows, giving the corresponding (η^2-C_2H_4)ruthenacyclopentadiene complex, which is subsequently converted into an unusual ruthenabicyclo[3.2.0]-heptadiene intermediate.[21] The latter then rearranges to a 7-ruthenanorbornene derivative displaying a $^{\beta}$H agostic interaction. Finally reductive elimination occurs to provide a Ru(η^4-cyclohexadiene) complex.

In the cobalt series, only the cyclotrimerization of alkynes has been scrutinized by theory. Pioneering studies were performed using semiempirical[22] or modest ab initio methods.[10] A complete analysis of $CpCoL_2$ catalysts (L = alkenes, CO, PR_3) was reported later by Albright and co-workers, who carried out computations at ab initio and DFT levels, restricted to closed-shell species.[23] Very recently, Koga and co-workers have enhanced this theoretical analysis by a scrutiny of singlet and triplet spin-state potential energy surfaces at the DFT/B3LYP level (Scheme 5).[24]

Scheme 5. Single- and Two-State Reactivity in the Cobalt-Catalyzed Acetylene Cyclotrimerization



On the singlet surface, it was shown that the most favorable reaction pathway proceeds via oxidative coupling of CpCo-$(C_2H_2)_2$ to a cobaltacyclopentadiene (path **A**) and subsequent barrierless addition of acetylene to give CpCo(η^4-benzene) (path **B**) (collapse mechanism). On the other hand, a barrier of 14.1 kcal/mol was computed for the addition of acetylene to triplet cobaltacyclopentadiene, leading to triplet CpCo(η^6-benzene) (path **C**). Although kinetically disfavored, this high-spin sequence connects the ground states of cobaltacyclopentadiene (singlet to triplet excitation energy: $\Delta E_{S-T} = -16.6$ kcal/mol) and CpCo(benzene) ($\Delta E_{S-T} = -13.4$ kcal/mol). Therefore, the occurrence of interspin crossings along the reaction coordinate was explicitly addressed. The discovery of several low-lying minimum energy crossing points (MECPs) between the singlet and the triplet spin-state potential energy surfaces led to the proposal of a nonadiabatic mechanism[25] (two-state reactivity). In it, singlet cobaltacyclopentadiene relaxes to the triplet ground state and then reacts with acetylene to give singlet CpCo(η^4-benzene) (path **A**, CP_a, CP_b, path **B**). A last spin change then occurs to give 20-electron CpCo(η^6-benzene) (CP_c). Interestingly, no favorable reaction path via cobaltacycloheptatriene of type **F** was found. If no insertion mechanism exists, another possibility would be the coordination of acetylene to Co, followed by intramolecular [4 + 2] cycloaddition between the alkyne and the external diene carbons of the metallacycle. This could not be established in the parent series, because of the collapsing of all potential intermediates. However, the presence of substituents on both the alkyne and the cobaltacyclopentadiene generates a barrier which allows the location of several isomeric minima of type **D** and their connections with **G** via intramolecular [4 + 2] cycloaddition transition states.[26]

---

(20) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721−11729.

(21) A related 1-iridabicyclo[3.2.0]hepta-1,3,6-triene has been characterized by X-ray diffraction study; see: Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 1610−1611.

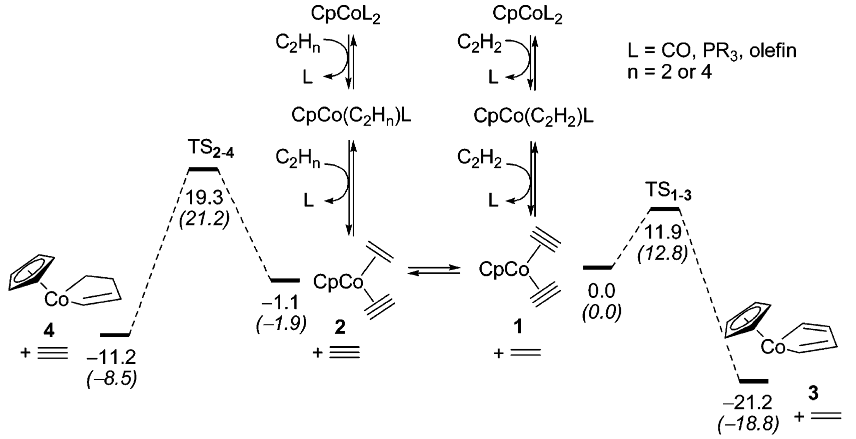
(22) (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952−2961. (b) Bianchini, C. et al. *Organometallics* **1994**, *13*, 2010−2023.

(23) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055−6067.

(24) (a) Dahy, A. A.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 781−791. (b) Dahy, A. A.; Suresh, C. H.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 792−803.

(25) (a) Yarkony, D. R. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed; World Scientific: Singapore, 1995; p 642. (b) Yarkony, D. R. *J. Phys. Chem.* **1996**, *100*, 18612−18628. (c) Schröder, D.; Shaik, S.; Schwartz, H. *Acc. Chem. Res.* **2000**, *33*, 139−145.

Scheme 6. Relative Energies (kcal/mol) for the Oxidative Couplings of **1** and **2**; Energies at the B3LYP/6-311+G(2d,2p) Level Are Indicated in Parentheses



The present work deals with the [2 + 2 + 2] cycloaddition of alkenes and alkynes to furnish cyclohexadienes and attempts to answer a number of questions: (*i*) does the mechanism proceed via cobaltacyclopentadienes or cobaltacyclopentenes?; (*ii*) does the conversion of these metallacycles with alkynes (alkenes) proceed via cycloaddition or insertion?; (*iii*) where does C−H activation come in energetically and what is its mechanism?; (*iv*) how does the reaction compare with the ruthenium series?. The stereochemistry of the reaction will not be discussed here but will be the object of a forthcoming paper.

Computational Details

Most of the DFT computations were carried out using the B3LYP5 functional, which is based on the VWN formula 5 local spin-density approximation.[27] Some additional calculations were carried out using B3LYP, PW91, BPW91, and B3PW91 functionals. The relative energies and activation barriers were qualitatively in agreement with those obtained at the B3LYP5 level. All geometries of intermediates and transition states were optimized fully without symmetry constraints using the PC GAMESS 6.5 version[28] of the GAMESS (US) QC package.[29] The bulk of the computations was 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),[30] and the 6-31G(d,p) basis set[31] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coordinate calculations (IRC). The Gaussian 03 program package[32] was employed for natural population analysis (NPA),[33] giving charges and Wiberg indices (WIs),[34] and also for single-point B3LYP/6-311+G(2d,2p) calculations. The minimum energy crossing points (MECPs) were optimized using the code developed by Harvey and co-workers.[35] The vibrational analyses at these points were executed within the ($3N-7$)-dimensional hypersurface of the seam of crossing.[36] The Chemcraft program was used to draw the calculated structures.[37]

Results and Discussion

Synthetic applications of the title transformation typically have the alkyne, the alkene, and the CpCo source present simultaneously in solution.[38] Therefore, the chemoselectivity for a cobaltacyclopentadiene **3** or a cobaltacyclopentene **4** will depend on (Scheme 6) the following: (*i*) the kinetics of ligand substitution in CpCoL$_2$ to give the bisalkyne complex **1** or the alkyne/alkene complex **2**; (*ii*) the feasibility of interconversion between **1** and **2**; (*iii*) the relative activation energies of the oxidative coupling of **1** and **2**.

For (*i*) and (*ii*), we first envisaged S$_N$2 mechanisms. The present DFT method was calibrated on ^{14}CO/CO exchange in CpCo(CO)$_2$, for which an activation energy of 16.0 kcal/mol was measured experimentally.[7] Optimizations of the reactants and the transition state (η^3-Cp)Co(CO)$_3$ at the B3LYP5/LACVP-(d,p) level, followed by single-point calculations using the 6-311+G(2d,2p) basis set[39] for all atoms, gave an activation energy of 15.0 kcal/mol (15.7 kcal/mol after applying the B3LYP5 zero-point energy correction), in good agreement with the experimental value. However, extensive efforts failed to locate an associative transition state for substitution by acetylene and ethene. This is not surprising if one considers the experimental data (see Introduction). If the mechanism is actually dissociative, an approximation of the energy required for the substitution can be obtained by computing the binding energy of the substituent to be replaced. This was achieved by comparing the energy differences between CpCoLL′ and the component fragments L′ and CpCoL, the latter being optimized in their triplet ground states (Scheme 7).[40] CpCoL species have already been described with L = CO, PH$_3$, and C$_2$H$_4$ (see ref 40). Unrestricted calculations (UB3LYP5) also confirmed the triplet ground-state of CpCo(C$_2$H$_2$) ($\Delta E_{S-T} = -10.5$ kcal/mol).

---

(26) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. Manuscript in preparation.

(27) (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(28) Granovsky, A. A. http://classic.chem.msu.su/gran/gamess/index.html.

(29) Schmidt, M. et al. *J. Comput. Chem*. **1993**, *14*, 1347−1363.

(30) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.

(31) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (c) Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta* **1973**, *28*, 213−222. (d) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209−214. (e) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−168.

(32) Frisch et al. *Gaussian 03*, revision B.02; Gaussian, Inc.: Wallingford, CT, 2004.

(33) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 1736−1740. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066−4073. (d) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735−746. (e) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926. (f) Weinhold, F.; Carpenter, J. E. In *The Structure of Small Molecules and Ions*; Naaman, R., Zeev, V., Eds.; Plenum Press: New York, 1988; p 227. (g) Carpenter, J. E.; Weinhold, F. *THEOCHEM* **1988**, *169*, 41−62.

(34) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

(35) Harvey, J. N.; Aschi, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5555−5563.

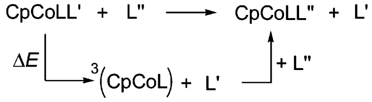
(36) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95−99.

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

(38) For a typical example, see, inter alia, ref 5 and pertinent references therein.

(39) The 6-311+G(2d,2p) basis set has two sets of polarization functions on all atoms, including two *f* sets on Co, also in addition to diffuse functions.

Scheme 7. B3LYP/6-311+G(2d,2p) Dissociation Energies (kcal/mol)



ΔE (kcal/mol)

L = L' = CO	27.5
L = L' = PH_3	6.8
L = L' = C_2H_4	3.8

L = C_2H_2;	L' = CO	16.3
	L' = PH_3	1.5
	L' = C_2H_4	1.9
L = C_2H_4;	L' = CO	21.5
	L' = PH_3	5.1
	L' = C_2H_2	5.8
L = PH_3;	L' = C_2H_2	9.7
	L' = C_2H_4	10.1

Geometrical parameters of this complex compared to other CpML species (M = Co, Rh, Ir; L = CO, PH_3, C_2H_4) are striking, which were all described as bent compounds in either spin states. Indeed, singlet and triplet $CpCo(C_2H_2)$ display a linear geometry with respect to the Cp centroid, cobalt, and the middle of the coordinated C−C triple bond. The LUMO of bent CpCoL consists mainly of an empty d orbital of Co. As predicted by Hofmann and Padmanabhan, a ligand with extra π-donor ability compared to CO, PH_3, or C_2H_4 could engage two additional electrons to fill this orbital, thus giving a linear geometry (see Supporting Information for details).[41]

The values displayed in Scheme 7 are qualitatively in good agreement with experimental facts.[42] For instance, $CpCo(CO)_2$ requires light and/or heat (>100 °C) to be active, whereas $CpCo(PPh_3)_2$ and $CpCo(C_2H_4)_2$ turn over already at room or lower temperatures. Accordingly, at the B3LYP/6-311+G (2d,2p) level, the energies required for the dissociations of CO are much higher than those of PH_3 and ethene.[43] For CO and PH_3, the second dissociation energies show a net preference for acetylene instead of ethene (CO: 16.3 vs 21.5 kcal/mol; PH_3: 1.5 vs 5.1 kcal/mol). Therefore one might infer that the formation of **1** will be faster than that of **2**, but they equilibrate fast relative to the next steps.

Concerning (*iii*), the transformation of **1** into **3** has been well documented experimentally,[10] and by theory.[23,24a,44] In agreement with others, we found that the oxidative coupling requires 11.9 kcal/mol of activation energy and is exothermic by 21.2 kcal/mol.[45] On the other hand, the cyclization of **2** to **4** was found kinetically much less facile, the energy of TS_{2-4} being 20.4 kcal/mol higher than that of **2** and acetylene, and also less exothermic than the transformation of **1** into **3** (−11.2 kcal/mol).[46] Overall these results support the intermediacy of a cobaltacyclopentadiene derived by coupling two acetylene units in the initial phase of the cocyclization of acetylene with ethene to give CpCocyclohexadiene.[47]

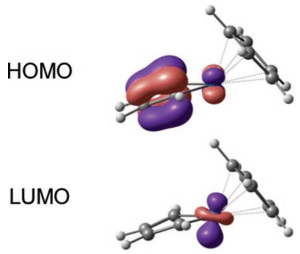


Figure 1. Frontier orbitals of **3**.

It is now well established that 18-electron cobalt species usually exhibit a singlet ground state, whereas their 16-electron relatives are more stable in the triplet state.[40] Changes in the spin state might occur along the reaction coordinates and thus affect the mechanism. Therefore, singlet and triplet state hypersurfaces of the transformations of metallacycles **3** and **4** were determined, as will be described in the following two sections. Subsequently, a proposal of a nonadiabatic mechanism involving spin-state changes will be presented.

Singlet State Pathway to 1,3-Cyclohexadiene. Cobaltacyclopentadiene **3** shows two different reactive sites: The cobalt center and the diene moiety.[24b] The largest component of the LUMO is an empty d orbital of cobalt, whereas the HOMO is centered mostly on the diene part of the metallacycle (Figure 1).

Consequently, if an alkyne or an alkene interacts with the HOMO, a standard bimolecular [4 + 2] cycloaddition is expected. With ethene, the activation energy associated with this symmetry-allowed reaction (10.8 kcal/mol, Scheme 8, pathway a) was found comparable to the value reported for acetylene (11.3 kcal/mol).[24b] Even though the calculations were performed without any symmetry constraints, complex **5** exhibits a mirror plane (Figure 2). The Co−C distance to the terminal diene carbons (2.04 Å) is longer than that to their internal neighbors (1.99 Å). Small variations in the bond lengths of the diene skeleton are observed (~1.43 Å each). These and all other geometrical parameters are in excellent agreement with reported values obtained from X-ray analyses.[5,48]

---

(40) Electron d^8 CpML species are known to exhibit triplet ground states, whereas the corresponding 18-electron CpMLL′ complexes usually have a singlet ground state; 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 therein.

(41) Hofmann, P.; Padmanabhan, M. *Organometallics* **1983**, *2*, 1273−1284.

(42) As an example, these calculated values show that the displacement of PPh_3 by ethene in $CpCo(PPh_3)_2$ is easier than the reverse reaction (6.8 vs 9.7 kcal/mol); see: Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3973−3974.

(43) The value of 27.5 kcal/mol for the first CO bond energy appears too low. An experimental value of 44 kcal/mol has been reported; see: Sztaray, B.; Szepes, L.; Baer, T. *J. Phys. Chem. A* **2003**, *107*, 9486−9490. In this case, the CCSD(T) level of theory gave better results than the DFT method; see ref 40e. The fast method used herein provides only qualitative comparisons.

(44) Veiros, L. F.; Dazinger, G.; Kirchner, K.; Calhorda, M. J.; Schmid, R. *Chem.*−*Eur. J.* **2004**, *10*, 5860−5870.

(45) (a) To date, neither an experimental structure of a mononuclear CpCo(bisalkyne) complex nor that of a 16-electron cobaltacyclopentadiene is available. (b) The geometry of **3** was significantly different from that calculated by Dahy and Koga (ref 24). Thus, the cobaltacycle was found to be nearly C_s-symmetric ($Co-C_\alpha = 1.914$ Å; $Co-C_{\alpha'} = 1.912$ Å). At the B3LYP/6-31G(d,p) level, Dahy and Koga obtained an asymmetric structure ($Co-C_\alpha = 1.905$ Å; $Co-C_{\alpha'} = 1.831$ Å), a finding attributed to a second-order Jahn−Teller effect. We have ascertained that these variations in geometry are not ascribable to the different basis set used, but to the hybrid functional, and that they do not alter significantly the relative energies. Jahn−Teller distortions can also be observed at the B3LYP5/LACVP(d,p) level on substituted cobaltacyclopentadienes. For a discussion, see Supporting Information.

(46) (a) The Co−C distances of coordinated ethene in **2** are slightly longer than those of coordinated acetylene (2.05 vs 1.99 Å). The Wiberg indices, which reflect bond strengths, show that ethene (WIs of $Co-C_{ethene} = 0.409$) binds slightly more weakly than acetylene (WIs of $Co-C_{acetylene} = 0.419$). Other structural parameters, such as the C−C distances in coordinated acetylene (1.25 Å) and ethene (1.40 Å), compare favorably with those in the only crystal structure of an alkyne/alkene cobalt complex available to date; see: Okuda, J.; Zimmermann, K. H.; Herdtweck, E. *Angew. Chem., Int. Ed., Engl.* **1991**, *30*, 430−431. (b) To date, no compound of **4** has been structurally characterized experimentally.

(47) One might expect steric and electronic effects to influence the manifold in Scheme 5. Thus, $CpCoPPh_3$ complexes of electron-poor alkynes incorporate two molecules of electron-poor alkenes to give, stoichiometrically or catalytically, appropriately substituted 1,3-hexadienes in a process that involves cobaltacyclopentene intermediates; see ref 11.

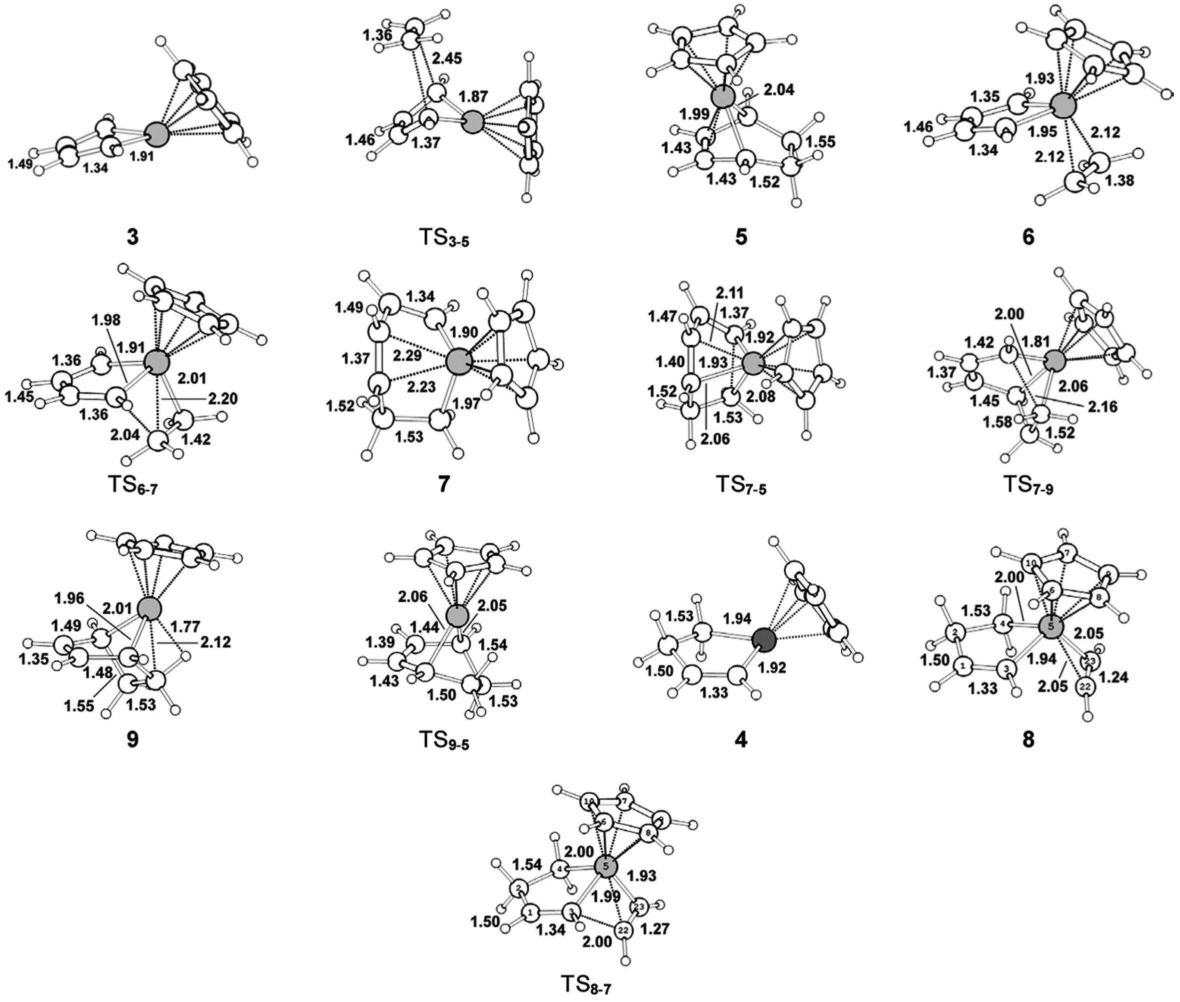
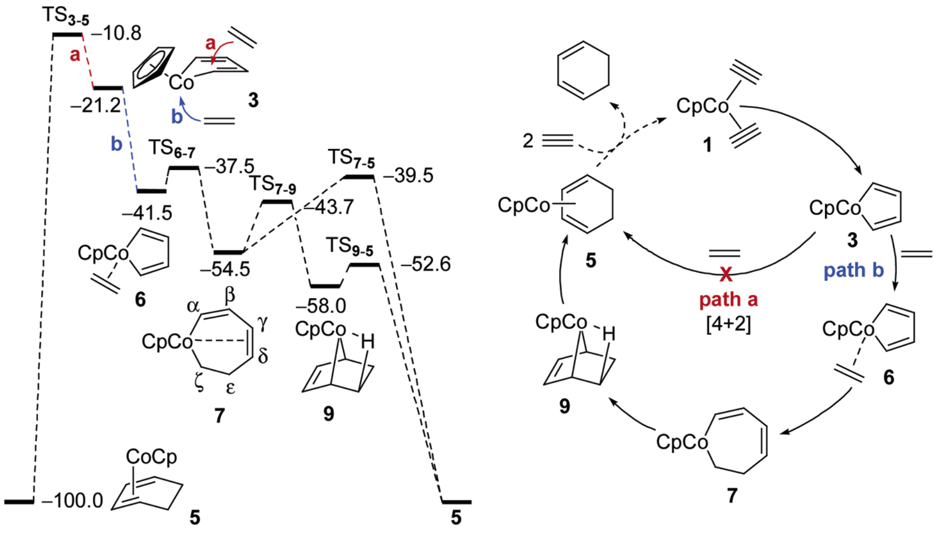


Figure 2. Structures of various cobalt species depicted in Scheme 8, with selected bond distances (Å).

Scheme 8. Singlet State Energy Profile for the Reaction of **3** with Ethene (kcal/mol) and Following Catalytic Cycle for the Cocyclization of Two Acetylenes with Ethene by CpCoL$_2$



The interaction of ethene with the LUMO of **3** proved much more favorable (pathway b). As shown by carrying out a set of constrained geometry optimizations at successively smaller distances between Co and the center of ethene, the addition of ethene was found barrierless. The addition of acetylene to cobaltacyclopentadiene was also described as a barrierless process but leading directly to CpCo(η^4-benzene) without intermediates.[24] However, in the case of ethene, cobaltacyclopentadiene(ethene) **6** was obtained as an intermediate with an exothermicity of 20.3 kcal/mol. The energetically equally

---

(48) Macomber, D. W.; Verma, A. G.; Rogers, R. D. *Organometallics* **1988**, *7*, 1241−1253 and references therein.

unobstructed addition of ethene or acetylene to **3** suggests that both should compete equally successfully in this step. This competition is indeed observed experimentally. Thus, cyclotrimerization of alkynes using CpCo(ethene)$_2$ leads frequently to ethene-derived cyclohexadiene side products.[49] In accordance with experimental data for phosphine or alkyne ligated cobaltacyclopentadienes, the metallacyclic part of **6** is essentially planar.[50] Ethene is weakly bound, as indicated by the relatively large Co$-$C$_{\text{ethene}}$ distances (2.12 Å each, WIs = 0.286, 0.304) and the moderately elongated ethene C$-$C bond (1.38 Å; compare with 1.33 Å in free ethene and 1.40 Å in **2**). The ethylenic C$-$C bond is rotated by ~23° relative to the C$_\beta-$C$_\beta$ bond of the metallacycle. In **6**, a Wiberg index of 0.129 was found between one of the carbons of ethene and the juxtaposed C$_\alpha$ of the metallacycle, suggesting some extent of early bonding. An insertion of coordinated ethene into a Co$-$C$_\alpha$ bond is thus presaged as the next step.[51] A transition state toward cobaltacycloheptadiene **7** was indeed located 4.0 kcal/mol above **6**. While the forming C$-$C bond distance shortens (from 2.56 Å to 2.04 Å; WI 0.478), the coordinated ethene is further rotated by 21°, virtually aligning it parallel to the Co$-$C$_\alpha$ bond. The resulting formation of **7** is exothermic by 13.0 kcal/mol. So as to stabilize the complex as a formal 18-electron species, this cobaltacycloheptadiene is strongly puckered, bringing the C$_\gamma-$C$_\delta$ double bond close to the metal center (Co$-$C$_\gamma$: 2.29 Å, WI 0.184; Co$-$C$_\delta$: 2.23 Å, WI 0.213).[52] Cobaltacyclopentene **4** can equally transform to **7**, after a barrierless complexation to acetylene rendering initially **8** (exothermic by 9.4 kcal/mol), followed by insertion requiring 6.4 kcal/mol. In **8**, acetylene binds slightly stronger than ethylene in **6**, as shown by the bond lengths and Wiberg indices (2.05 Å each, WIs = 0.314, 0.331). It is rotated so as to maximize the distance to the CH$_2-$Co fragment. Consequently, a regioselective insertion into the Csp$^2-$Co bond takes place.

From cobaltacycloheptadiene **7**, two routes may lead to **5**. A transition state corresponding to the direct reductive elimination of CpCo was found 15.0 kcal/mol above **7** (TS$_{\mathbf{7-5}}$). On the other hand, a more favorable route to **5** was computed: complex **7** could be connected to bicyclic intermediate **9** through a lower-lying transition state (activation energy of 10.8 kcal/mol). The motion leading to TS$_{\mathbf{7-9}}$ is quite similar to the one leading to TS$_{\mathbf{7-5}}$, with C$_\alpha$ approaching C$_\zeta$ (2.16 Å, WI 0.461) and a narrowing of the Co$-$C$_\delta$ distance (2.00 Å, WI 0.561). However, the interaction between Co and C$_\gamma$ is lost (2.77 Å, WI 0.068), and the Co$-$C$_\alpha$ bond distance is reduced, gaining some double bond character (1.81 Å, WI 0.711). As a result, 7-cobaltanorbornene **9**, which displays a $^{\beta}$H agostic interaction (1.77 Å) and a moderately perturbed C$-$C double bond (1.35 Å), is obtained. In the Ru-catalyzed cocyclization of ethene with acetylene, the same kind of intermediate originated from the ruthenabicyclo[3.2.0]heptatriene.[20] From this complex, only 5.4 kcal/mol are required for breaking the agostic interaction and transforming the di-σ-cobaltacyclopentene moiety into a CpCo(η^4-butadiene) framework. This rearrangement is greatly exothermic by 42.0 kcal/mol. The completion of the catalytic cycle requires the displacement of the cyclohexadiene by two acetylenes to regenerate **1**. This process is exothermic by only 0.7 kcal/mol, which may be part of the rationale why this reaction is catalytic only under specific conditions.[53] On the whole (Scheme 8), the singlet state mechanism resembles that of the CpRuCl-catalyzed cocyclization of two acetylene molecules with ethene[8] (Scheme 4), yet without cyclic carbene intermediates.

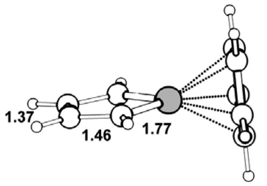


Figure 3. Selected bond distances in **10** (Å).

Singlet State Pathway to Hexatriene. Yamamoto and coworkers showed that the Ru(II)-catalyzed addition of 1,6-diynes to strained bicycloalkenes may give rise to tandem cyclopropanation as a result of the carbenoid behavior of the ruthenacyclopentatriene intermediate.[54] In the case of the cobalt-mediated cocyclizations, no such products have been reported so far. Accordingly, we found that C_s-symmetric cobaltacyclopentatriene **10** is 9.5 kcal/mol less stable than cobaltacyclopentadiene **3**. Extensive delocalization in the ruthenium series formally makes ruthenacyclopentatrienes coordinatively saturated 18-electron species and thus energetically more favorable than ruthenacyclopentadienes. In **10**, the C$_4$Co cycle is essentially planar and perpendicular to the Cp plane (Figure 3). The short distance between Co and C$_\alpha$ of 1.77 Å and the high WI of 1.181 are indicative of strong double bond character. However, the C$_\alpha-$C$_\beta$ (1.46 Å, WI 1.188) and C$_\beta-$C$_\beta$ (1.37 Å, WI 1.620) bonds show little if any delocalization.

Rather than cyclopropanes, CpCo-complexed hexatrienes have been reported on several occasions as unexpected products of the cobalt-mediated reaction of two alkynes with an alkene (see Introduction). Among the different mechanisms that could account for the formation of these compounds, one could be related to the well-documented C$-$H activation of olefins and aromatic compounds by d^8 CpML fragments (M = Co,[55] Rh,[56] Ir[40d,57]) that would be followed by sequential alkyne insertion. We were not able to establish such a pathway by calculations.

---

(49) (a) Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, *221*, C25$-$C27. (b) Kölle, U.; Fuss, B. *Chem. Ber.* **1986**, *119*, 116$-$128.

(50) To the best of our knowledge, only two structurally characterized mononuclear metallacyclopentadiene(alkene) complexes have been reported, both in the iridium series: (a) O'Connor, J. M.; Closson, A.; Gantzel, P. *J. Am. Chem. Soc.* **2002**, *124*, 2434$-$2435. (b) Martín, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406$-$5417.

(51) Kinetic studies of Bercaw, Bergman, and co-workers revealed that arene formation from a cobaltacyclopentadiene(PMe$_3$) complex and DMAD occurs without phosphine dissociation (see Introduction and ref 14). Likewise, a direct reaction between ethene and **6** was envisaged. No TS corresponding to a direct insertion of ethene into a Co$-$C bound in **6** or to an associative substitution of the coordinated alkene could be located. Instead, a TS corresponding to an intermolecular [4 + 2] cycloaddition was obtained. This pathway was found kinetically difficult, the TS being 30.2 kcal/mol above the reactants. It leads to 18-electron (ethene)(7-cobaltanorbornene), favorable by 25.2 kcal/mol. Dissociation of coordinated ethene is then required for obtaining CpCo(η^4-cyclohexadiene).

(52) In the case of the CpRuCl-catalyzed [2 + 2 + 2] cycloaddition of two alkynes to one alkene, ruthenacyclopentadiene(C$_2$H$_4$) was not converted into a ruthenacycloheptadiene but into an unusual ruthenabicyclo[3.2.0]-heptatriene; see Introduction and ref 20.

(53) Although this reaction usually requires stoichiometric amounts of CpCo, several examples of catalytic reactions have been reported; see: (a) Malacria, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1984**, *49*, 5010$-$5012. (b) Duñach, E.; Halterman, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1664$-$1671. (c) Cammack, J. K.; Jalisatgi, S.; Matzger, A. J.; Negrón, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1996**, *61*, 4798$-$4800.

(54) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143$-$12160.

(55) See, inter alia: (a) Klang, J. A.; Collum, D. B. *Organometallics* **1988**, *7*, 1532$-$1537. (b) Wadepohl, H.; Borchert, T.; Pritzkow, H. *Chem. Ber./Recl* **1997**, *130*, 593$-$603. (c) Lenges, C. P.; White, P. S.; Marshall, W. J.; Brookhart, M. *Organometallics* **2000**, *19*, 1247$-$1254. (d) O'Connor, J. M.; Bunker, K. D. *J. Organomet. Chem.* **2003**, *671*, 1$-$7.

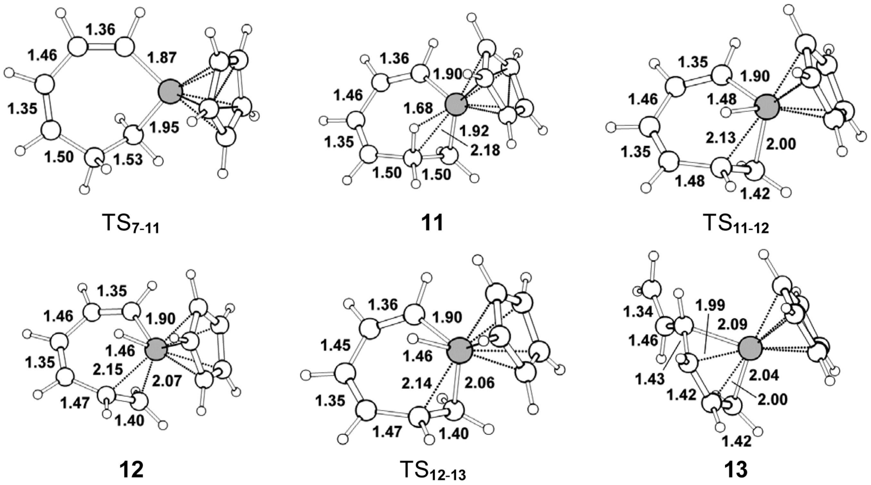
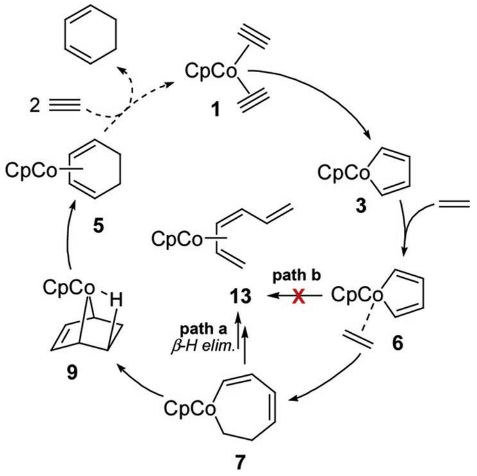


Figure 4. Structures of various cobalt species depicted in Scheme 10, with selected bond distances (Å).

Scheme 9. Formation of CpCo(η^4-hexatriene) **13**

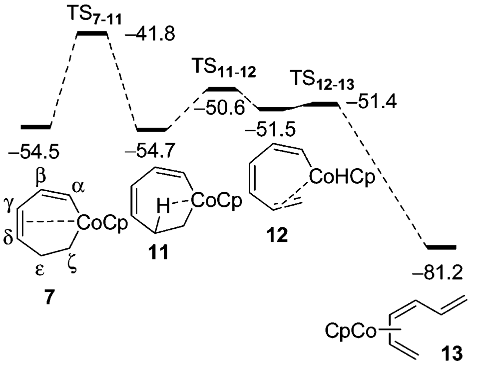


On the basis of the fast formation of **1** and then **3** and of the known ability of complexes of type **3** to promote C−H activation of aromatic double bonds (see Introduction),[18,19] we envisaged several other mechanisms involving cobaltacycles as precursors to CpCo(hexatrienes) (Scheme 9, path a and path b)

A first possible way could be a β-hydride elimination from cobaltacycloheptadiene **7** (Scheme 10).[58] Conformational analysis allowed us to locate cobaltacycloheptadiene **11**, which is marginally more stable than **7** by 0.2 kcal/mol. Complex **11** is stabilized by a $^{\beta}$H agostic interaction instead of a double bond (Figure 4). The activation energy for the conversion of **7** into **11** is 12.7 kcal/mol.

An activation barrier of 4.1 kcal/mol was computed for the endothermic transformation ($\Delta E = 3.2$ kcal/mol) of **11** into cobalt−hydride complex **12**, in which the terminal double bond is loosely coordinated to cobalt (Co−C$_\epsilon$ = 2.15 Å, WI = 0.284; Co−C$_\zeta$ = 2.07 Å, WI = 0.347). The reductive elimination giving CpCo(η^4-hexatriene) **13** was found straightforward kinetically (activation energy 0.08 kcal/mol) and appreciably exothermic ($\Delta E = -30.2$ kcal/mol). Structural features of the coordinated butadiene framework of **13** and those of compound **5** are very much alike, the Co−C distances to the terminal diene carbons (2.04 and 2.09 Å) being slightly larger than those to the internal carbon atoms (1.99 and 2.00 Å). Bond distances of the diene skeleton are also very close (1.42−1.43 Å).[59]

Scheme 10. Energy Profile (kcal/mol) for the Formation of CpCo(η^4-hexatriene) **13** from Cobaltacycloheptadiene **7** via β-Hydride Elimination (Path a of Scheme 9)



Alternative hydrogen transfers were also envisioned, i.e., stepwise or concerted C−H bond metathesis type mechanisms (Scheme 11). Investigation of the former allowed us to locate a transition state connecting intermediates **6** and **12**. The energetic requirement of 30.0 kcal/mol is prohibitively high compared to the direct insertion of ethene, for which only 4.0 kcal/mol were calculated (Scheme 8).

Complex **6** could also be connected to the dienylcobalt species **14** via transition state TS$_{\mathbf{6-14}}$, located 19.8 kcal/mol above **14** ($\Delta E = 7.7$ kcal/mol). It shows one imaginary frequency of 990 cm^{-1} corresponding to the movement of the hydrogen. The relatively short Co−C and Co−H bonds in TS$_{\mathbf{6-14}}$ (Figure 5), the quite long breaking and forming C−H bonds, as well as the C···H···C angle of 165°, indicate that this transformation may not be a σ-bond metathesis but what was referred to as "*oxidative hydrogen migration*" by Goddard and co-workers.[60] However, a direct proton transfer cannot be ruled out at this

---

(56) See, inter alia: (a) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151−160. (b) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685−7695 and references therein. (c) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140−146. (e) Cunningham, J. L.; Duckett, S. B. *J. Chem. Soc., Dalton Trans.* **2005**, 744−759 and references therein.

(57) (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581−4582. (b) Comstock, M. C.; Shapley, J. R. *Organometallics* **1997**, *16*, 4816−4823.

(58) A direct C$_\epsilon$C$_\alpha$ H transfer could not be achieved.

(59) For X-ray structures of CpCo(η^4-butadiene) complexes, see: (a) Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. *Organometallics* **1987**, *6*, 848−853. (b) O'Connor, J. M.; Chen, M.-C.; Frohn, M. *Organometallics* **1997**, *16*, 5589−5591.

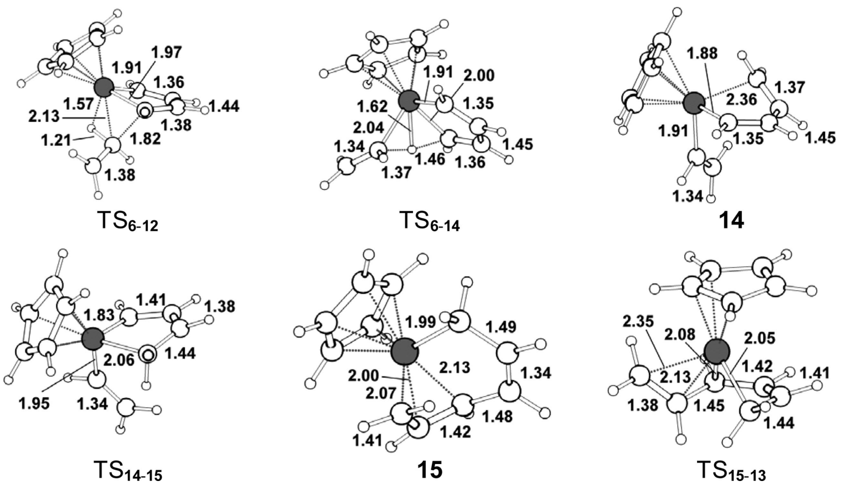
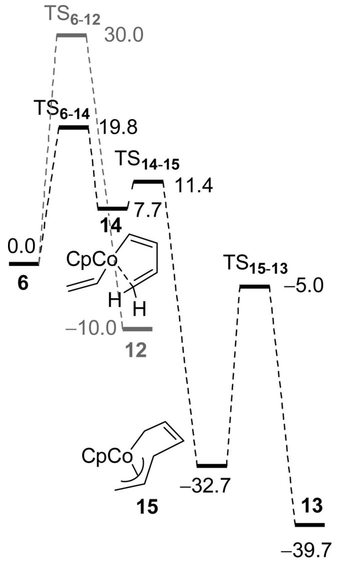


Figure 5. Structures of various cobalt species depicted in Scheme 11, with selected bond distances (Å).

Scheme 11. Energy Profile (kcal/mol) for the Formation of CpCo(η^4-hexatriene) **13** from Cobaltacyclopentadiene(ethene) **6** (Path b of Scheme 9)



time. Intermediate **14** displays a short distance between the terminal diene carbon and cobalt (2.36 Å). The terminal double bond is quite long (1.37 Å), while the C−H bonds are normal. It suggests that the π-orbital of the terminal C−C double bond interacts with the unoccupied d orbital of cobalt. This species converts to the σ,π-allylhexadiene complex **15** ($\Delta E = -25.0$ kcal/mol). This migration materializes through the carbenic transition state $\mathrm{TS}_{\mathbf{14-15}}$, evidenced by the development of a short (1.83 Å) Co−C double bond. Reductive elimination to the final complex **13** requires 27.7 kcal/mol to reach η^3-Cp $\mathrm{TS}_{\mathbf{15-13}}$ and is exothermic by 7.0 kcal/mol. The quite high activation energy associated with this transformation finds a parallel in the C−H activation of ethene by iridacyclopentadienes, which yields σ,π-allylhexadiene complexes that can be characterized at room temperature.[61] Thermal isomerization of these species into Ir-complexed hexatriene is possible at 70 °C.[61a]

Although the mechanism described in Scheme 11 seems unreasonable for ethene when compared to the insertion/$^{\beta}$H-elimination sequence, the related stationary points were also calculated for thiophene,[62] furan, and benzene.[63] Experimentally, the first two show both [2 + 2 + 2] cycloaddition products (presumably by insertion) and C−H activation.[15,19] Benzene, which undergoes only C−H activation,[18] was first chosen as a model study (Scheme 12).

Benzene interacts with cobaltacyclopentadiene **3** to give **16** in which benzene coordinates cobalt by a π orbital (Co−C = 2.39 Å, Figure 6).[64] This adduct is more stable than the reactants by only 4.6 kcal/mol. Contrary to the behavior of ethene, the transformation of complex **16** into the dienylcobalt species **17** is exothermic ($\Delta E = -5.6$ kcal/mol) and requires only 7.3 kcal/mol. This species converts to the σ,π-allylphenylbutadiene complex **18** ($\Delta E = -24.4$ kcal/mol). The uncomplexed butadiene framework in **18** shows slight bond alternation (1.38−1.42−1.37 Å). Reductive elimination to the final complex **19** requires 19.9 kcal/mol and is exothermic by 22.1 kcal/mol. Comparatively, insertion of a C−C double bond of benzene into a Co−C bond of cobaltacyclopentadiene **3** requires 14.8 kcal/mol, thus making the C−H activation the preferred pathway.

Several adducts of **3** with thiophene or furan are possible, but only the most stable stereoisomers have been taken into account in the following discussion (see Supporting Information for details). With thiophene, η^1-coordination by sulfur proved slightly more favorable than η^2-coordination to a double bond ($\Delta E = -23.2$ kcal/mol vs -20.3 kcal/mol). Activation of the C^2−H bond of thiophene required 8.7 kcal/mol, and that of the C^3−H bond was found to be quite similar, with an activation energy of 9.1 kcal/mol. On the other hand, insertion of a C−C double bond of thiophene into a Co−C bond required 10.1 kcal/mol. With furan, η^2 coordination of **3** to a double bond was slightly better than (η^1-O)-coordination ($\Delta E = -10.8$ kcal/mol vs -9.3 kcal/mol). Activation of the C^2−H bond of furan required 8.7 kcal/mol, the same value as that computed for thiophene and that of the C^3−H bond 9.7 kcal/mol. Insertion of the double bond of furan into the Co−C bond was found

---

(60) Oxgaard, J.; Muller, R. P.; Goddard, W. A., III; Periana, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 352−363.

(61) (a) Bianchini, C.; Caulton, K. G.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1995**, *14*, 933−943. (b) Álvarez et al. *J. Am. Chem. Soc.* **2003**, *125*, 1478−1479.

(62) For C−H activation of thiophene, see: (a) Sargent, A.; Titus, E. P. *Organometallics* **1998**, *17*, 65−77. (b) Angelici, R. J. *Organometallics* **2001**, *20*, 1259−1275.

(63) For a comparative study in the rhodium series, see, inter alia: Lewis, J. C.; Wu, J.; Bergman, R. G.; Ellman, J. A. *Organometallics* **2005**, *24*, 5737−5746.

(64) For related examples of nonagostic η^1-benzene complexes, see: (a) Biswas, B.; Sugimoto, M.; Sakaki, S. *Organometallics* **2000**, *19*, 3895−3908. (b) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114−16126.

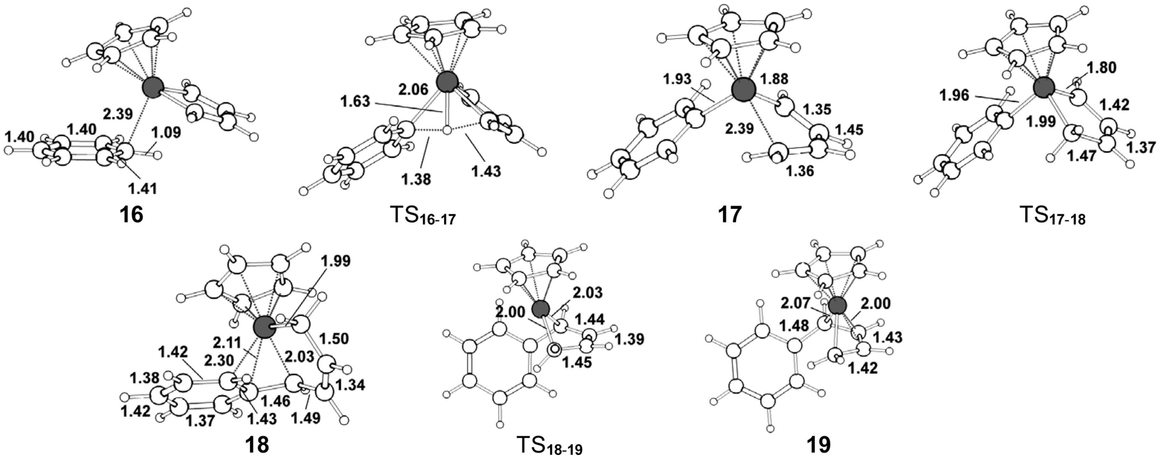
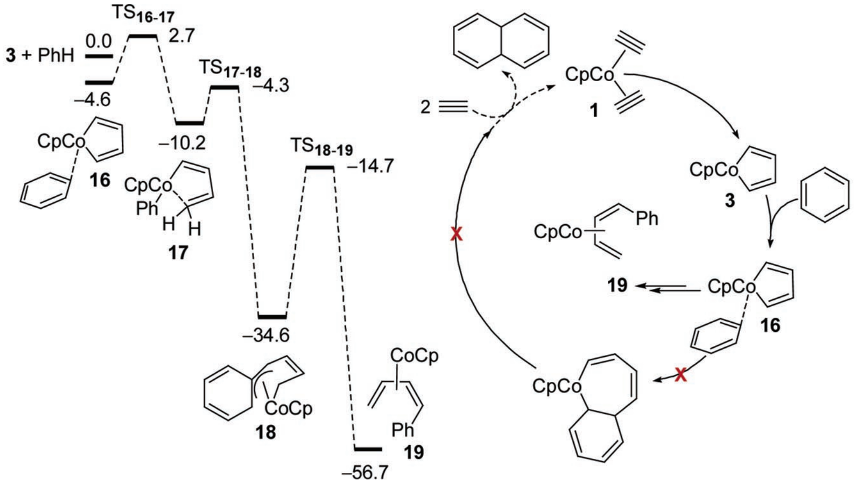


Figure 6. Structures of various cobalt species depicted in Scheme 12, with selected bond distances (Å).

Scheme 12. Energy Profile for the Reaction of Cobaltacyclopentadiene **3** with Benzene (kcal/mol)



energetically easier than the corresponding process for thiophene (6.7 kcal/mol). It seems clear from these values that insertion and C−H activation are competitive in the cases of thiophene and furan, as observed experimentally. Finally, the possibility that benzene, thiophene, and furan generate dienyl(hetero)arenes by the insertion/$^{\beta}$H-elimination sequence was probed. In all cases, attempts to optimize the structures of fused intermediates of type **11** failed, the initial geometries collapsing to internal double-bond stabilized cobaltacycloheptadienes of type **7**.

To summarize, we believe that the [2 + 2 + 2] and dienyl products in these cases arise via two different mechanisms starting from cobaltacyclopentadienes **6**. In the case of benzene, the [2 + 2 + 2] pathway is not competitive. On the other hand, the formation of hexatrienes by coupling two alkynes with a normal alkene occurs via an insertion/$^{\beta}$H-elimination sequence, rather than direct vinyl-H activation. What remained to be examined was the possible role of high-spin species in these transformations. As mentioned above, 16-electron cobalt complexes exhibit usually triplet ground states, which may give rise to reactivity that differs from that of their singlet analogues.

Triplet State Pathway to 1,3-Cyclohexadiene. As reported previously by others,[24] we, too, found that cobaltacyclopentadiene **3** has a triplet ground state ($\Delta E_{\mathrm{S-T}} = -18.8$ kcal/mol), is C_s symmetric, and exhibits an essentially planar metallacyclic moiety.[24] Similarly, we found that cobaltacyclopentene **4** also displays a triplet ground state ($\Delta E_{\mathrm{S-T}} = -13.8$ kcal/mol). The reaction path from triplet **3** to CpCo(η^6-benzene) emerges as a combination of acetylene insertion into a Co−C$_\alpha$ bond and reductive elimination. We failed to reproduce such a pathway with ethene. The only route to triplet CpCo(cyclohexadiene) that could be ascertained was the intermolecular [4 + 2] cycloaddition between ethene and the diene moiety of the metallacycle (Scheme 13). From triplet **4**, a reaction path to the final product could not be found.

TS$_{\mathbf{3-20}}$, which displays a mirror plane (Figure 7), was computed 16.7 kcal/mol above the reactants. IRC run from this transition state pointed toward a 7-cobaltanorbornene, which was found 24.3 kcal/mol below the reactants after full optimization. Frequency calculations gave one imaginary frequency, and the vibrational motion associated with the transition state vector indicated the loss of C_s symmetry from that stationary point (TS$_{\mathbf{20-20}}$). IRCs led to the enantiomeric forms of CpCo(η^2-cyclohexadiene) **20**, 58.2 kcal/mol below the reactants. Conformational analysis of **20** revealed the existence of isomer **21**, relatively stabilized by 2.0 kcal/mol. The connection between **20** and **21** requires a small activation energy of 0.8 kcal/mol. Complex **21** resembles closely the previously described triplet CpCo(η^2-C_2H_4) species.[40b] In particular, the angle defined by the Cp centroid, the cobalt atom, and the center of the coordinated double bond is 149.8°, comparable to the corresponding parameter in triplet CpCo(η^2-C_2H_4) (149.1°). C_s-Symmetric TS$_{\mathbf{21-21}}$, which connects the two enantiomeric forms of **21**, lies 3.9 kcal/mol above them. Complex **21** is slightly less stable than **5**, by less than 0.5 kcal/mol.

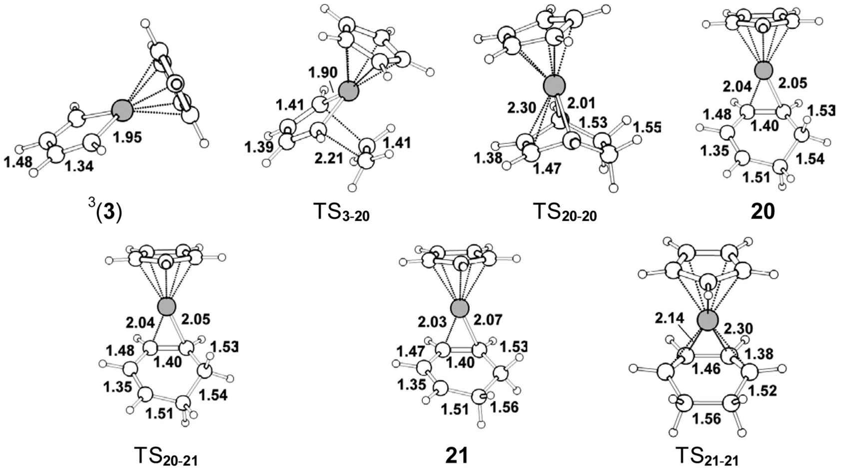
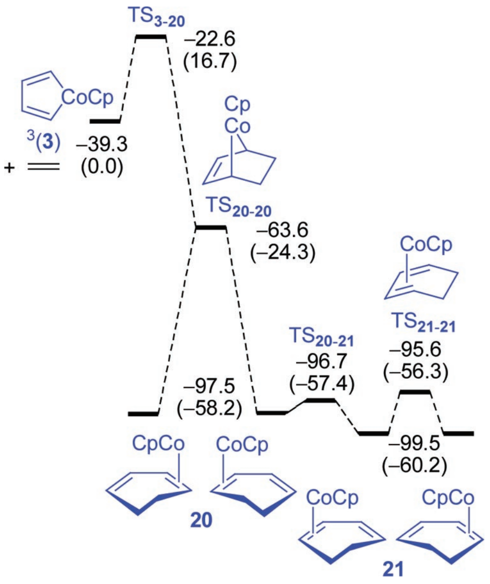


Figure 7. Structures of various cobalt species depicted in Scheme 13, with selected bond distances (Å).

Scheme 13. Energy Profile (kcal/mol) for the Reaction of Triplet Cobaltacyclopentadiene with Ethene



Energetically, the triplet state mechanism is disfavored compared to the singlet one. It should be noted that, experimentally, numerous singlet CpCo(η^4-cyclohexadiene) complexes have been reported but none in the triplet ground state. Moreover, we were unable to establish any connectivity between these triplet species and the hexatrienes discussed above. However, considering the triplet nature of the computed 16-electron intermediates, reaction modes involving states of different multiplicities were investigated.

Two-State Reactivity. Despite their so-called “spin-forbidden” nature, several fast reactions of triplet cobalt species giving singlet products have been uncovered.[65] Although no appropriate computational method is available for investigating adiabatic spin-coupled potential energy surfaces of the cobalt complexes described here, semiquantitative information can be provided by computing the required enthalpy for reaching a crossing point in which the two spin states have similar geometries and energies (MECP). Although the location of a crossing point is a necessary but not sufficient feature to evaluate the probability of surface hopping taking place,[66] it provides more enthalpic arguments which could be used to rationalize kinetic studies.[40a,e] Koga and co-workers reported the existence of a crossing point between singlet and triplet cobaltacyclopentadiene, in the vicinity of the singlet minimum.[24] Accordingly, we have found **CP$_1$** lying just 0.1 kcal/mol above singlet **3** (Scheme 14), both of them exhibiting near identical geometrical features.[67] Spin−orbit induced crossing is therefore very likely to occur. Even though the addition of ethene to singlet **3** has no activation energy, the lifetime of this complex should be extremely short before it relaxes to the triplet state. For the addition of ethene to ^{3}(**3**), a crossing point close in geometry and energy to the triplet system was found (Figure 8). **CP$_2$**, in which the metallacycle and ethene are mostly unperturbed compared to the component fragments, lies only 1.8 kcal/mol above the triplet system. Consequently, relaxing to singlet **6** should be straightforward. The crossing point for the addition of acetylene to **3** was reported 7.0 kcal/mol above the triplet system,[24b] which implies chemoselectivity in favor of ethene, at odds with experimental observations. With the present methodology,[35] this value was lowered to 1.6 kcal/mol. Since there is almost no difference in the ease by which ethene and acetylene reach an MECP when reacting with cobaltacyclopentadiene **3**, the expectations with respect to the relative competitive ability of these two reagents to attack triplet **3** remain unchanged from those of singlet **3**. It is noteworthy that cobaltacyclopentene **4** can also readily relax to the triplet state through an MECP that is just 0.9 kcal/mol more stable. The reaction of ^{3}(**4**) with acetylene to give ^{1}(**7**) benefits from a similarly accessible MECP lying 2.0 kcal/mol above the reactants.

UB3LYP5 optimizations starting from the singlet geometries of **7** and its agostic isomer **11** lead to the same triplet minimum in which no extra stabilization by a C−C double bond or a $^{\beta}$H agostic interaction remains. Species ^{3}(**7**) was obtained as the ground state (**7**/^{3}(**7**): $\Delta E_{\mathrm{S-T}} = -9.8$ kcal/mol; **11**/^{3}(**7**): $\Delta E_{\mathrm{S-T}} = -9.6$ kcal/mol). Complexes **7** and **11** should cross over readily to the triplet surface leading to ^{3}(**7**), since low-lying crossing

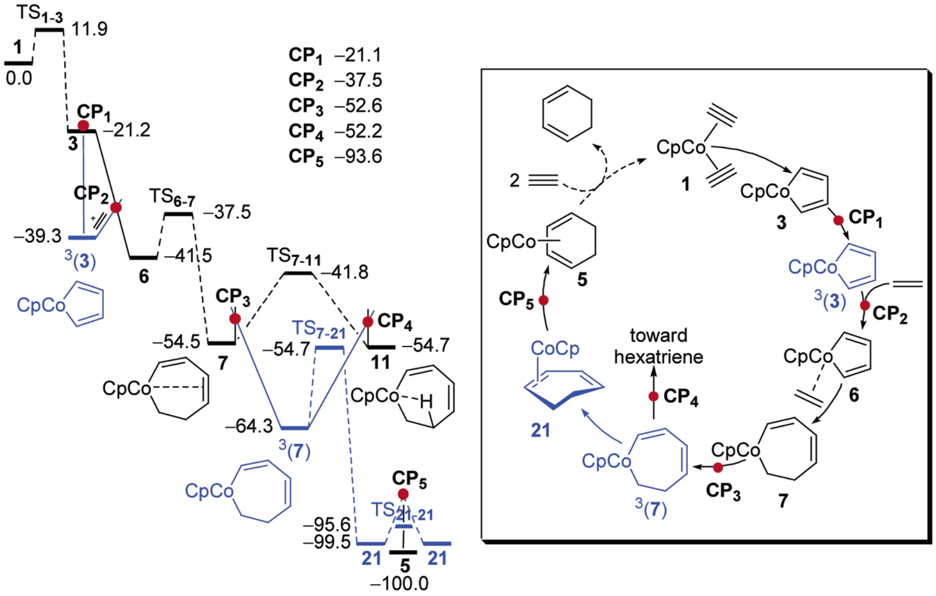
---

(65) (a) Wasserman, E. P.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1988**, *110*, 6076−6084. (b) Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 11745−11748.

(66) 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. Spectrosc.* **2005**, *240*, 37−99.

(67) Koga and co-workers found the crossing to lie 1.1 kcal/mol below the singlet minimum. This difference can be attributed to the different MECP-location techniques used. Koga employed a constrained geometry optimization procedure, whereas the optimization of the MECPs for the present study was made without geometry restriction.

Scheme 14. Two-State Reactivity Mechanism[a]



[a] Triplet Species and Pathways Appear in Blue. Relative Energies Are in kcal/mol

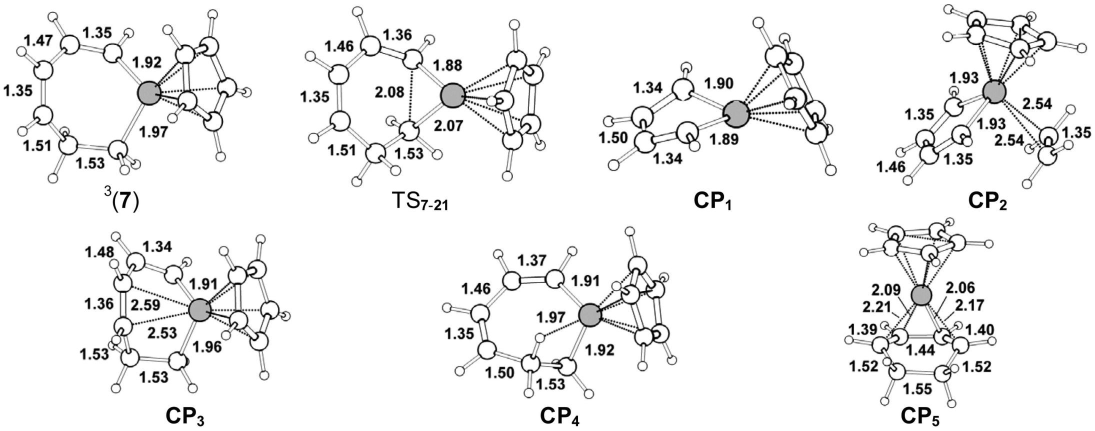


Figure 8. Structures of various cobalt species depicted in Scheme 14, with selected bond distances (Å).

points of similar geometry are located in their vicinity. **CP**$_3$ and **CP**$_4$ lie 1.9 and 2.5 kcal/mol above singlets **7** and **11**, respectively. In **CP**$_3$, the Co−C$_\gamma$ and Co−C$_\delta$ bonds are elongated by 0.3 Å relative to singlet **7**, and, in **CP**$_4$, the Co−$^\beta$H bond is similarly lengthened by 0.3 Å compared to singlet **11**. A reductive elimination transition state leading to CpCo-(η^2-cyclohexadiene) **21** was found 9.6 kcal/mol above ^{3}(**7**). The last crossing point, **CP**$_5$, lies 6.3 kcal/mol above **21**. The geometry of **CP**$_5$ shows η^4-coordination of cobalt to the cyclohexadiene ligand. The structural parameters of this crossing point are in fact very close to those of TS$_{21-21}$ from which **CP**$_5$ is separated by only 2.0 kcal/mol. On the whole, the two-state reactivity appears very feasible. Five spin changes are required, but all crossing points are readily accessible.

Conclusion

The major outcome of this study is that, in contrast to the mechanism of alkyne cyclotrimerization, in which final alkyne inclusion into the common cobaltacyclopentadiene features a direct “collapse” pathway to the complexed arene, alkene incorporation proceeds via insertion into a Co−C σ-bond, rather than inter- or intramolecular [4 + 2] cycloaddition. The resulting seven-membered metallacycle **7** is a key intermediate, which leads to CpCo-complexed cyclohexadiene via spin change to the triplet ground state, reductive elimination to triplet CpCo-complexed cyclohexadiene **21**, and finally another spin change to the singlet state giving **5**. Several pathways were investigated to take CpCo-complexed hexatrienes of type **13** into consideration. With benzene, thiophene, and furan a mechanism involving direct vinyl C−H activation was found. On the other hand, the obtainment of **13** from ethene is more likely to occur via an insertion/$^\beta$H-elimination sequence.

Acknowledgment. Financial support by CNRS, IUF, DGA, and the NSF (CHE-0451241) are gratefully acknowledged. The Center for New Directions in Organic Synthesis is supported by Bristol-Myers Squibb as a Sponsoring Member and Novartis as a Supporting Member. V.G. is thankful to Dr. Alex A. Granovsky and to Prof. Luís F. Veiros for useful discussions and also to Dr. Jeremy N. Harvey, who provided the MECP optimization program.

Supporting Information Available: Remarks pertaining to Jahn−Teller effects in cobaltacyclopentadienes. Selected optimized geometric parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

JA060756J