Article

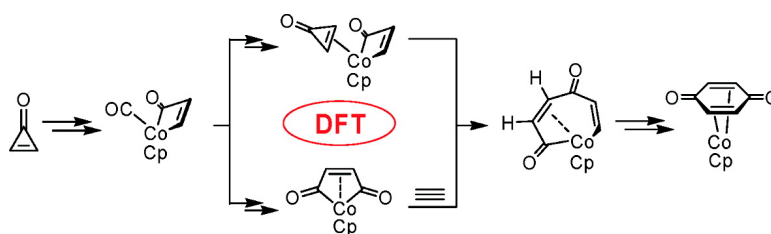# CpCo-Mediated Reactions of Cyclopropenones: A DFT Study

Daniel B. Werz, Gu#nter Klatt, Jevgenij A. Raskatov, Horst Ko#ppel, and Rolf Gleiter

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

CpCo-Mediated Reactions of Cyclopropenones: A DFT Study

Daniel B. Werz,[†,§] Günter Klatt,[‡] Jevgenij A. Raskatov,[†,ǁ] Horst Köppel,[‡] and
Rolf Gleiter*,[†]

*Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany, and Physikalisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany*

Quantum chemical calculations using density functional theory at the B3LYP/6-311G(d)/Wachters+f level have been carried out to model possible pathways for the reaction of $CpCo(CO)_2$ (**15**) with cyclopropenone to yield CpCo-capped *p*-benzoquinone complexes. For a number of intermediates, including all relevant 16-electron species, energies and geometries of the triplet electronic state were also obtained, which permitted us to locate four crossings of the singlet and triplet potential surfaces. It was found that first a metallacyclobutenone complex (**21**) is formed. Our calculations indicate a dissociative mechanism; the previously observed associative mechanism in ligand substitution reactions of **15** is shown to be a consequence of lower reaction temperatures. The addition of a second cyclopropenone unit to **21** reveals a higher energy path (path I) than does the addition of CO to **21**, followed by acetylene addition (path II). The latter path is favored, which has already been shown by labeling and trapping experiments. Despite favorable energetics, the paths involving the triplet surface have not been observed experimentally; we tentatively attribute this to the very short lifetime of the initially formed triplet.

Introduction

Examples of complexation between cyclic 6π electron systems and metal fragments are legion.[1] Much less is known about the reaction of cyclic 2π systems such as cyclopropenylium ions or cyclopropenones with metal fragments. It has been shown that the cyclopropenylium system may be bound to a metal center in an η^3,[2–6] η^2,[7] or η^1 fashion.[8] Besides these structural possibilities, the isomeric metallacyclobutadienyl structures have also been reported. For example, the reaction of triphenylcyclopropenylium tetrafluoroborate (**1**) with tetrakis-(triphenylphosphine)platinum (**2**) led to **3** (Scheme 1),[7] which can be described as an η^2-complexed cyclopropenylium ring with a long CC bond (1.58(2) Å)[7] or a metallacyclobutadienyl ring. A similar outcome is reported for the reaction of **1** with

Scheme 1
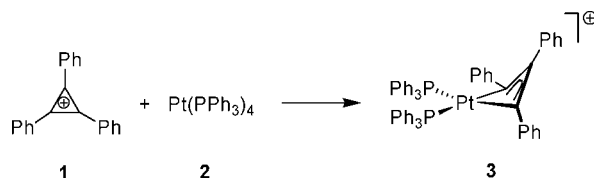
IrCl(CO)(PPh$_3$)$_2$[9] and of tri(*tert*-butyl)cyclopropenylium tetrafluoroborate with sodium (hexacarbonyl)vanadate.[10]

The opening up of a cyclopropenylium cation to a 4-membered metallacycle has been described by means of extended Hückel calculations.[11] The bond-breaking process of one CC bond of the cyclopropenylium ring starts with an η^2 interaction, which can be described approximately by a bonding interaction between the occupied metal b_2 orbital and the empty π_2^* orbital of the cyclopropenylium ligand (Scheme 2a). This interaction weakens the CC bond by populating the antibonding π_2^* orbital. By increasing the angle θ, the π_2^* and even more the corresponding σ^* orbital is stabilized. Finally, at larger angles θ and φ, the interaction between σ^* and b_2 is dominant, as shown in Scheme 2.

For cyclopropenone derivatives, a metal insertion into a CC bond was observed. The reaction of the cobalt complex **4** with diphenylcyclopropenone (**5**) afforded the cobaltacyclobutenone chelate complex **6** in 91% yield[12a] (Scheme 3). Analogously, the reaction of methylcyclopropenone (**7**) with bis(triphenylphos-

* Corresponding author. E-mail: rolf.gleiter@oci.uni-heidelberg.de.
† Organisch-Chemisches Institut der Universität Heidelberg.
‡ Physikalisch-Chemisches Institut der Universität Heidelberg.
§ Present address: Institut für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany.
ǁ Present address: Chemistry Research Laboratory, 12 Mansfield Road, Oxford OX1 3TA, U.K.

(1) (a) Elschenbroich, C. *Organometallchemie*, 5th ed.; Teubner: Wiesbaden, 2005. (b) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1995.
(2) Gowling, E. W.; Kettle, S. F. A. *Inorg. Chem.* **1964**, *3*, 604–605.
(3) (a) Rausch, M. D.; Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 4981–4982. (b) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1971**, *10*, 1504–1510. (c) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1971**, *10*, 2599–2604.
(4) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, 81–83.
(5) Olander, W. K.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 2139–2140.
(6) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687–1691.
(7) McClure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1973**, *54*, C59–C61.
(8) Gompper, R.; Bartmann, E.; Nöth, H. *Chem. Ber.* **1979**, *112*, 218–233.

(9) (a) Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 5523–5524. (b) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237–2242.
(10) Blunden, R. B.; Cloke, F. G. N.; Hitchcock, P. B.; Scott, P. *Organometallics* **1994**, *13*, 2917–2919.
(11) Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570–2575.
(12) (a) Foerstner, J.; Kakoschke, A.; Wartchow, R.; Butenschön, H. *Organometallics* **2000**, *19*, 2108–2113. (b) Visser, J. P.; Ramakers-Blom, J. E. *J. Organomet. Chem.* **1972**, *44*, C63–C65.
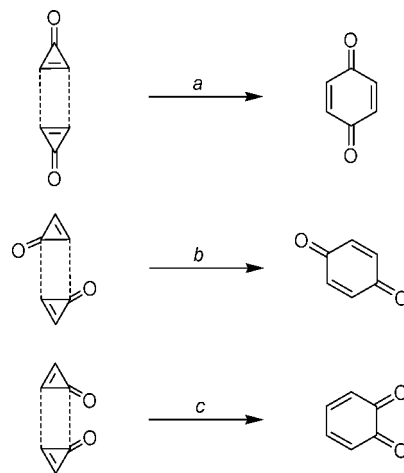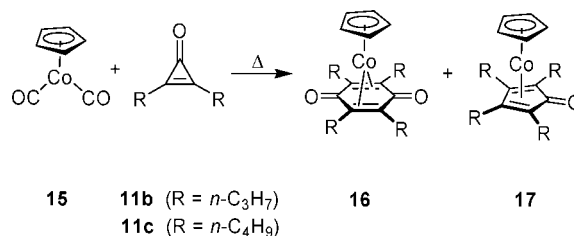
Scheme 2
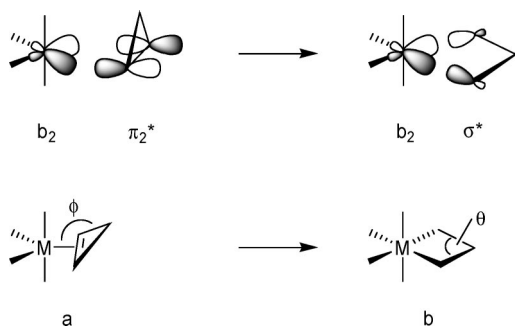
Scheme 3

Scheme 4

Scheme 5

15	**11b** (R = *n*-C$_3$H$_7$)	**16**	**17**
	11c (R = *n*-C$_4$H$_9$)		
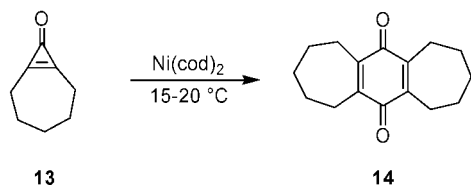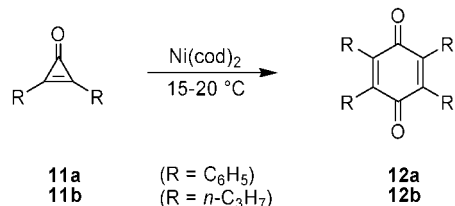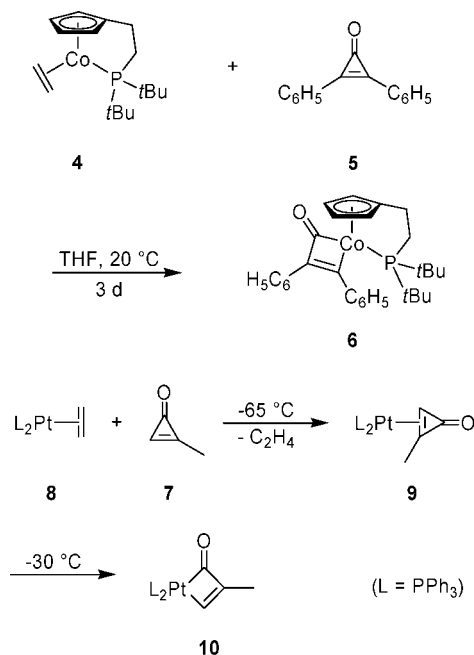
The reaction of cyclopropenone derivatives **11a** and **11b** in the presence of bis(1,5-cyclooctadiene)nickel did not lead to the formation of the expected η^2-complex.[15] At room temperature, this reaction afforded the corresponding *p*-benzoquinone derivatives **12a** and **12b**. Likewise, the reaction with a 2,3-bridged cyclopropenone **13** led to **14**. These observations suggest that the reaction proceeds via the formation of a nickelacyclobutenone rather than via metathesis of the double bonds. In Scheme 4, we have shown three possibilities for the dimerization process: *a*, *b*, and *c*. Path *a* can be eliminated, because the experiment with the bicyclic cyclopropenone **13** yields **14**. Path *c* is also very unlikely, as no *o*-quinone derivative was observed. Thus, path *b* remains.

Recent studies of reactions between CpCo(CO)$_2$ (**15**) and cyclopropenones are reminiscent of the reaction with Ni(cod)$_2$ and cyclopropenones, as shown in Scheme 3,[16] where the main product is the CpCo complex of the *p*-benzoquinone-derivative **16**.[16] As a side product one finds **17**, but no *o*-quinone complex is obtained (Scheme 5). These results suggest that a multistep mechanism via path b is likely. To clarify the reaction mechanism, we heated **15** with **11b**, bearing a ^{13}C label at the CO unit ([13]CO). It was found that 74% of the product **16** contained only 1 ^{13}C equiv, 12% contained zero, and 14% contained 2 equiv.[16] Furthermore, we heated **11c** and 4-octyne with **15** and obtained as the main product the CpCo-complexed 2,3-di(*n*-butyl)-5,6-di(*n*-propyl)-*p*-benzoquinone, and the CpCo-capped 2,3-di(*n*-butyl)-4,5-di(*n*-propyl)cyclopentadienone as the side product. To postulate a reasonable reaction mechanism of this multistep reaction, we carried out a DFT(B3LYP) study considering the reaction of 1 and 2 equiv of cyclopropenone with CpCo(CO)$_2$ (**15**).

phine)(ethylene)platinum (**8**) at −65 °C yielded the anticipated η^2-complex **9** (Scheme 3).[12b] At higher temperatures, the metallacyclobutenone derivative **10** was observed. Related reactions between various cyclopropenones and tetrakis(triphenylphosphine)platinum,[13] chlorotris(triphenylphosphine)-rhodium, and *trans*-chlorocarbonyl(triphenylphosphine)rhodium also showed a ring enlargement.[14]

(13) Wong, W.; Singer, S. J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672–673.
(14) Song, L.; Arif, A. M.; Stang, P. J. *Organometallics* **1990**, *9*, 2792–2797.

(15) Noyori, R.; Umeda, I.; Takaya, H. *Chem. Lett.* **1972**, 1189–1190.
(16) Schuster-Haberhauer, A.; Gleiter, R.; Körner, O.; Leskovar, A.; Werz, D. B.; Fischer, F. R.; Rominger, F. *Organometallics* **2008**, *27*, 1361–1366.

Computational Details

All calculations were carried out using the Gaussian 03[17] software package. Preoptimizations were performed at the B3LYP/ LANL2DZ level, and final geometry and energy optimizations were performed at the B3LYP/6-311G(d)/Wachters+f(Co) level of theory for all calculated singlet and triplet species.[18−21] This combination of basis set and level of theory has been used successfully in our previous studies of organometallic compounds.[22] For species with 16 valence electrons (**18**, **22**, and **29**), as well as additional species preceding or following them in the reaction sequence, we also calculated the triplet energies to find out whether a crossing between the singlet and the triplet energy surfaces[23−25] matters in our reactions. Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS) and zero for minima.[26] Transition states were obtained by either a combined scanning and transit-guided quasi-Newton (STQN) method, or a combination of the two STQN approaches LST[27] and QST3,[28] as implemented in Gaussian 03. All optimizations were performed without any constraints (C_1 symmetry). Gibbs free energies G_T were calculated at the appropriate temperature T (to properly compare with experiment) and for p = 1 atm, using the harmonic frequencies approximation. The latter is considered a sufficiently good approximation, given that the temperatures do not exceed 450 K (∼1 kcal/mol). Relative energies were compared taking into account the total number of molecules present. A natural population analysis (NPA)[29] and resulting Wiberg bond indices (WBI)[30] were used for a detailed study of the electronic structure and bonding in some cases. Instead of the distances, WBIs describe the bond strengths, allowing the limitation of looking only at bond lengths to be overcome. For four relevant crossings of our singlet and triplet energy surfaces, we calculated minimum energy crossing points (MECPs) using the code developed by Harvey and co-workers.[31]

Results and Discussion

The objective of this Article is to elucidate possible reaction paths of cyclopropenone reacting with CpCo(CO)$_2$ to yield CpCo-complexed *p*-benzoquinone, incorporating one or two CO units from cyclopropenone.

The reaction proceeds by heating the mixture to 150 °C in cyclooctane. Therefore, the possibility of the thermolysis of cyclopropenone into CO and ethyne has to be taken into account. Recent studies of the decarbonylation reaction of phenylcyclo-propenone by means of DFT calculations and transient spec-troscopy support a stepwise mechanism.[32] The calculations reveal an energy barrier of 32.2 kcal/mol, the fragments CO and phenylacetylene being 4.2 kcal/mol more stable than the starting material. In our study, the free energy difference ΔG_{423} between cyclopropenone and CO + ethyne was found to be 19.2 kcal/mol in favor of the fragments; we calculated activation barriers of 29.4 and 25.4 kcal/mol for the stepwise fragmentation of cyclopropenone. The presence of CO and ethyne in the reaction mixture is therefore very likely; the related compound diphenylcyclopropenone is known to gradually decarbonylate when heated to 160 °C.[33] In the first part (path I), we neglect any fragmentation of cyclopropenone. In the second part (path II), we take into account the presence of CO and ethyne during the reaction.

Formation of the Metallacyclobutenone Complex 21 (Path I). For the initial steps of the reaction of CpCo(CO)$_2$ (**15**) with cyclopropenone to yield **20** (Figure 1), two different reaction pathways can be envisioned: either a dissociative (a) or an associative (b) mechanism via **18** or **19**, respectively, as depicted in Figure 1. Since it is known that 16-electron CpCoL complexes frequently exist as triplet ground states,[25] we also investigated an alternative dissociative mechanism (c) involving **18** in its triplet electronic state, that is, ³**18**. These potential pathways are outlined as follows.

In mechanism (a), **15** loses CO by thermal dissociation to form the 16-electron compound ¹**18**, which subsequently adds cyclopropenone to form **20**. No barrier for the removal of CO from **15** exists.[23] For the bonding of cyclopropenone to **18**, no transition state was located, implying that this step lacks an energy barrier. Mechanism (b) is characterized by an initial addition of cyclopropenone to **15**, which yields the associative intermediate **19** via "ring slippage", that is, reorganization of the delocalized Cp ring into an allyl-ene structure, where the metal is bound only to the η³-allyl portion.[34a] This compound then loses CO to form **20**. Two low activation barriers separate **19** from its precursor and product. Mechanism (c) corresponds to (a), the difference being that here the intermediate ³**18** is

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D. Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Wallingford, CT, 2004.

(18) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785– 789. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200–206. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648– 5652.

(19) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

(20) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033–1036.

(21) (a) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976; Vol. 3, pp 1−28. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.

(22) (a) Volland, M. A.; Kudis, S.; Helmchen, G.; Hyla-Kryspin, I.; Rominger, F.; Gleiter, R. *Organometallics* **2001**, *20*, 227–230. (b) Gleiter, R.; Roers, R.; Rominger, F.; Nuber, B.; Hyla-Kryspin, I. *J. Organomet. Chem.* **2000**, *610*, 80–87. (c) Hyla-Kryspin, I.; Gleiter, R.; Rohmer, M. M.; Devemy, J.; Gunale, A.; Pritzkow, H.; Siebert, W. *Chem.-Eur. J.* **1997**, *3*, 294–299. (d) Schaefer, C.; Werz, D. B.; Staeb, T. H.; Gleiter, R.; Rominger, F. *Organometallics* **2005**, *24*, 2106–2113.

(23) Carréon-Macedo, J.-L.; Harvey, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 5789–5797.

(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) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860–8871.

(26) Because of Cp rotation, very small imaginary frequencies were found for the complexes **15**, **24**, and **29**, but a series of calculations for one complex showed a negligible energetic dependence of the complex on the imaginary frequency according to this rotation (see Supporting Information).

(27) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225– 232.

(28) Peng, C.; Schlegel, H. B. *Isr. J. Chem* **1993**, *33*, 449–454.

(29) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41–62.

(30) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083–1096.

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

(32) Poloukhtine, A.; Popik, V. V. *J. Phys. Chem. A* **2006**, *110*, 1749– 1757.

(33) Breslow, R.; Eicher, T.; Krebs, A.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1320–1325.
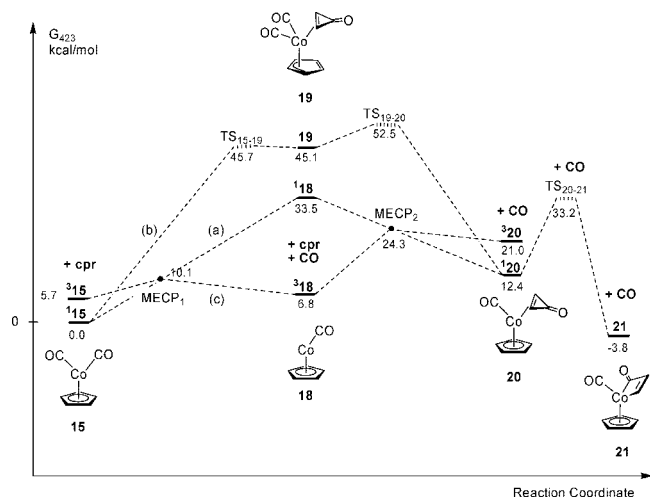
Figure 1. Free energy profile G_{423} (for a reaction temperature of 423 K) for the formation of metallacycle **21**. Part (a) shows a dissociative, (b) an associative, and (c) a dissociative pathway involving the triplet surface. All energies are given in kcal/mol, relative to CpCo(CO)$_2$ (**^{1}15**), and include the free energy of separate cyclopropenone (**cpr**) and CO where indicated.

located on the triplet energy surface. Two crossing points of the singlet and triplet surfaces are therefore involved, which are in the following labeled MECP$_1$ and MECP$_2$ and strongly resemble their preceding or following triplet state (i.e., **^{3}15** or **^{3}20**, respectively) in terms of both geometry and energy. We would like to point out that **^{1}18** and **^{3}18** represent true minima of the potential energy surface; they appear to be transition states in Figure 1 because the full reactive system includes the molecules CO and cyclopropenone at infinite distance.

As compared to a free cyclopropenone moiety (C=C bond length of 1.35 Å), the coordinated double bond in **20** becomes significantly longer (1.47 Å), which is due to the population of its π^* fragment orbital. The single bonds are also weakened by populating the σ^* orbitals. Therefore, the next step, a ring enlargement leading to the cobaltacyclobutanone **21**, can readily occur (Figure 1), in a manner similar to that proposed for the cyclopropenylium ion.[11] The metallacycle **21** is already located lower in energy than the starting materials, which is consistent with the release of ring strain through the enlargement of the three-membered cycle to the four-membered metallacycle. Selective bond distances for the conversion of **19**−**21** are given in Figure 2.

Our free energy calculations show that the associative intermediate **19** is disfavored by about 12 kcal/mol in comparison to the alternative 16-electron compound **^{1}18** formed by CO dissociation from **15** (45.1 versus 33.5 kcal/mol). On the other hand, a number of kinetic studies on various derivatives of CpCo(CO)$_2$[34] and CpRh(CO)$_2$[35] appear to demonstrate unequivocally that ligand substitution reactions for these complexes follow an associative mechanism. Previous theoretical investigations of such compounds were also based on this assumption.[36]

To clarify the situation, we carried out an additional study of one of the substitution reactions previously examined by
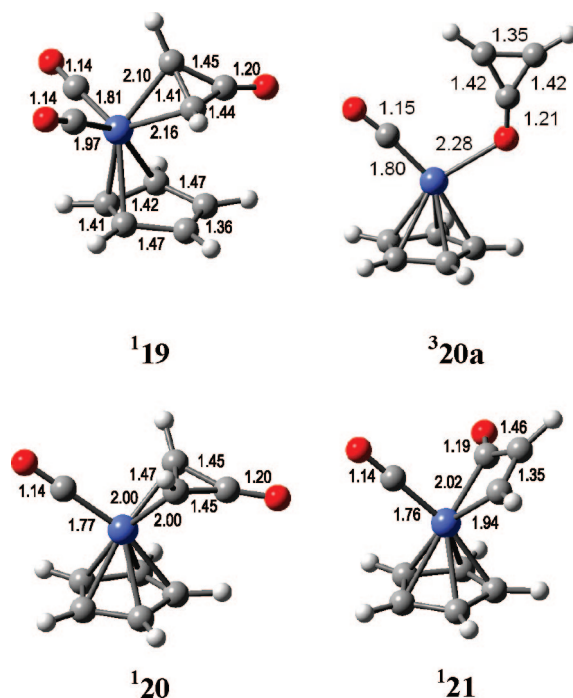

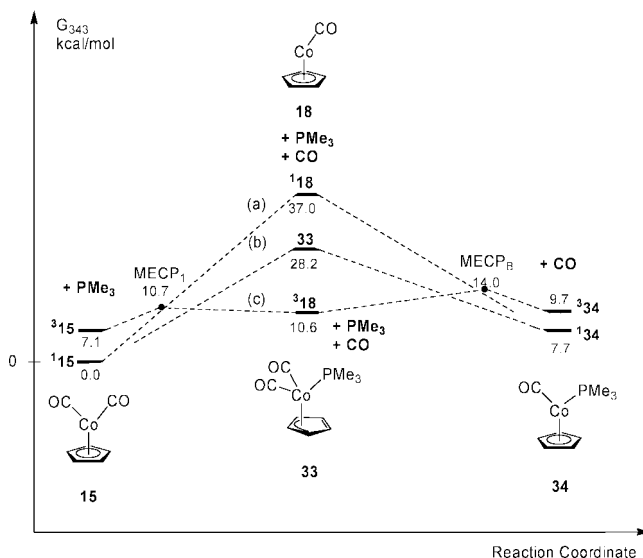**Figure 2.** Relevant distances [Å] in the optimized geometries **19**−**21**.

Figure 3. Free energy profile G_{343} (for a reaction temperature of 343 K) for the formation of complex **34**. Pathways (a), (b), (c) are defined as for Figure 1. All energies are given in kcal/mol, relative to **^{1}15**, and include the energy of separate PMe$_3$ or CO where indicated.

Rerek and Basolo, the substitution of CO by PMe$_3$ in Cp*Co(CO)$_2$.[34a] For reasons of computational feasibility, we used the unsubstituted cyclopentadienyl ligand in our calculations. To properly compare with experiment, we used the same less elevated temperature (343 K) as these authors. The free energies for all three pathways discussed above are presented in Figure 3. It is seen that here the associative intermediate **33** is about 9 kcal/mol lower in free energy than its dissociative singlet counterpart **^{1}18** (28.2 versus 37.0 kcal/mol), in agreement with the experimental findings. The conversion of **15** + PMe$_3$ to the monosubstituted product **34** is slightly endergonic, indicating that the reaction is driven to completion by the release of CO from the reaction mixture. The reason for the reordering

(34) (a) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372–376. (b) Moreno, C.; Macazaga, M. J.; Delgado, S. *Organometallics* **1991**, *10*, 1124–1130.

(35) (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908–5912. (c) Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041–2044.

(36) (a) Bühl, M. *Organometallics* **1997**, *16*, 261–267. (b) Fan, H.-J.; Hall, M. B. *Organometallics* **2001**, *20*, 5724–5730.

of pathways (a) and (b) can be found in the different reaction temperatures; while Rerek and Basolo conducted their kinetic study at 70 °C, our cyclopropenone dimerization was carried out at 150 °C. This results in a relative lowering of the dissociative pathway due to the increase of the entropic contribution to *G* at this elevated temperature. Our calculated activation parameters $\Delta H^{\ddagger} = +18.4$ kcal/mol and $\Delta S^{\ddagger} = -28.8$ cal/(mol K) compare well to the values for the substitution reaction with the P(OEt)$_3$ ligand (+18.2 kcal/mol and −26.7 cal/(mol K), respectively).[34a] We did not try to locate the transition states involving **33**, because we expect the associated activation barriers to be similar to those for intermediate **19** and therefore without consequence for the relative order of pathways (a) and (b).

Looking at Figures 1 and 3, one notices that the lowest energy pathway is actually represented by mechanism (c) in both instances and involves intermediate **³18** in the form of a crossing to/from the triplet surface via MECP₁ and (in the latter case) MECP_B, which again resemble the neighboring triplet structures **³15** and **³34**. However, this pathway is experimentally not observed. Conventional wisdom holds that the formation of **³18** is "spin-forbidden", because the total electronic spin is thought to be conserved in the course of chemical reactions. On the other hand, numerous examples have come to light in which the principle of spin conservation is violated.[23] Spin−orbit coupling is believed to be the driving force behind a change in multiplicity, which is the reason why such cases usually involve transition metal compounds, for which the effect should be particularly important.

We noted that MECP₁ closely resembles **³15** in terms of both structure and ZPE-corrected potential energy (12.5 versus 11.5 kcal/mol). If we start from **¹15** and surface hopping initially occurs, we can assume the resulting triplet to oscillate in the potential minimum around the equilibrium structure of **³15**, passing through the crossing seam once in each vibrational period. The vibration best approximating the reaction coordinate is the asymmetric Co−C stretch with a wavenumber of 383 cm⁻¹, which corresponds to a vibrational period of 8.7 ps. Surface hopping at the MECP is mediated by the spin−orbit coupling matrix element. If we assume it to be similar to that in ³Fe(CO)₅, resulting in surface hopping only once out of 20 seam crossing events,[23] we should expect **³15** to return to the singlet surface in about 170 ps. This is considerably shorter than the time needed for thermal excitation of **³15** to **³18**, that is, collisional loss of CO. In terms of ZPE-corrected potential energy, complex **³18** is 13 kcal/mol above **³15**, which is over 10 times a molecule's average kinetic energy at $T = 150$ °C (1.3 kcal/mol). It follows that well over 10 collisions would on average be required for thermal CO loss. Because the mean time between collisions in our system is about 50 ps, the formation of **³18** should require in excess of 500 ps, about 3 times more than the approximate time required for a return to the singlet surface. The reason why pathway (c) is not seen experimentally, despite its favorable energetics, is therefore not the fact that the formation of **³15** is in any way "spin-forbidden" or "spin-blocked", but rather the rapid return of the initially formed triplet to the singlet surface, which is much faster than the time needed to continue on the triplet surface via collisional excitation.

Formation of the CpCo Cyclopropenone Metallacyclobutenone Complex 24. Three pathways can again be envisioned for the formation of complex **24** (Figure 4): (a) The first is dissociation of the remaining carbonyl, thus forming intermediate **22**, and subsequent addition of cyclopropenone to the vacant site, leading to **24**. This route would proceed via the 16e metal
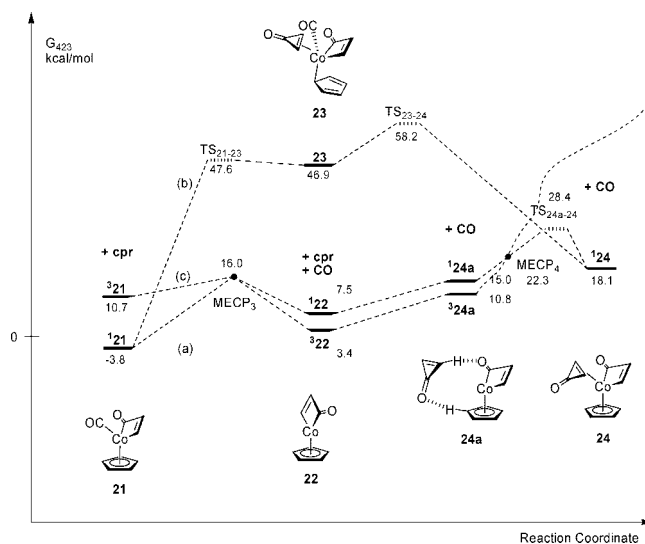

Figure 4. Free energy profile G_{423} (for a reaction temperature of 423 K) for the formation of metallacycle **24**. Pathways (a), (b), (c) are defined as for Figure 1. All energies are given in kcal/mol and include the free energy of separate cyclopropenone (**cpr**) and CO where indicated. For reasons of comparability with Figure 1, the free energy of **¹21** + **cpr** has been set to −3.8 kcal/mol.

complex **22**. (b) The second is additional bonding of another cyclopropenone unit to the metal center by shifting the hapticity of the Cp ligand, leading to **23**, and subsequent loss of CO. Only 18e intermediates would be formed in this reaction path. (c) The third is dissociation of the remaining carbonyl leading to the 16e complex in its triplet state, that is, **³22**, and subsequent addition of cyclopropenone.

Our calculations of the prospective intermediates and transition states revealed that the intermediate **¹22** involved in pathway (a) has a considerably lower free energy than the associative intermediate **23** formed via pathway (b) (7.5 versus 46.9 kcal/mol). For the CO dissociation from **21** to form **22** no transition state was located, implying that this step lacks an energy barrier. Comparing **³22** with **¹22**, it is seen that the triplet intermediate is again more stable. However, the difference is now only 4.1 kcal/mol, as opposed to 26.7 kcal/mol in the first example (Figure 1). We elucidated the geometric and electronic structures of both intermediates and observed that in the Cp-capped cobaltacyclobutenone **¹22**, the four-membered ring is rather distorted from a planar geometry (see Figure 5). The NBO analysis of **¹22** revealed a WBI of 0.20 between the C-2 and Co atom, which is contrasted by a much lower value of 0.04 in **³22** (for definition, see Figure 5). This shows that the simplified view of **¹22** as a 16e species may only be valid to a limited extent, if at all. By the same token, the four-membered ring is tilted strongly, and the WBI of the formal double bond is only 1.58, as compared to a value of 1.74 in the associative intermediate **23**. The open-shell species **³22**, on the other hand, is characterized by a planar four-membered ring, because the triplet structure is more stable as a 16e species. This observation leads us to conclude that, while 16e CpCoL complexes often prefer to be triplets, the reverse statement also applies. Thus, the possibility of an association of the double bond of the metallacyclobutenone **¹22** (cf., Figure 5) to afford a quasi 18e species leads to a drastic reduction of the singlet−triplet energy difference as compared to **18**. Two orthogonal projections of **¹22**, along with other intermediates leading from **21** to **24**, are shown in Figure 5.
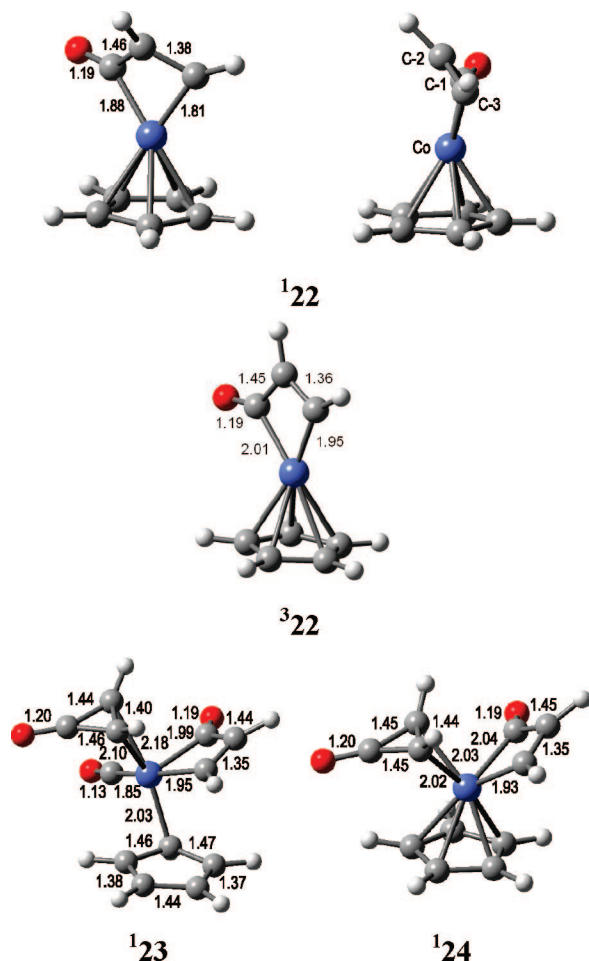
Figure 5. Relevant distances [Å] in the optimized geometries for going from **22** (two views) to **24**.

Complexes **^{1}22** and **^{3}22** may add cyclopropenone to yield **^{1}24a** and **^{3}24a**. The character of **24a** as a local minimum on the reaction path was established by a scan of the potential energy surface in which the distance of cyclopropenone from **24** was increased in a stepwise fashion to obtain **22** and free cyclopropenone. The connectivity of **24a** and **24** via TS$_{24a-24}$ was confirmed by IRC calculations. Again, the energy gap between singlet and triplet is quite small (2 kcal/mol in favor of the triplet), because in **^{1}24a** the metallacyclobutenone ring, which is planar for the 16e triplet, will distort from planarity to enable association of the double bond to the metal center and afford a quasi 18e species. In **24a**, the cyclopropenone is attached via two hydrogen-like bonds to the Cp and metallacyclobutenone moieties, respectively. In the following step, **^{1}24a** is converted to **^{1}24** (in which the cyclopropenone fragment is η^2-bound to the metal center) via transition state TS$_{24a-24}$ at 28.4 kcal/mol, whereas we were unable to locate a species corresponding to **^{3}24**. With a starting geometry of **^{1}24**, our triplet geometry optimization converged to **^{3}24a**, leading us to conclude that no distinct local minimum corresponding to **^{3}24** appears to exist on the B3LYP triplet potential energy surface. Again, the triplet species is thus found to adopt a 16e configuration. Compound **24** still shows a higher free energy (18 kcal/mol) than the starting materials.

As before, we assume that pathway (c) via MECP$_3$ and MECP$_4$ is not accessible due to kinetic reasons and that pathway (a) with a free energy maximum of 28.4 kcal/mol is therefore preferred. Our calculations reveal that MECP$_3$ is again quite close in energy and geometry to the preceding triplet species
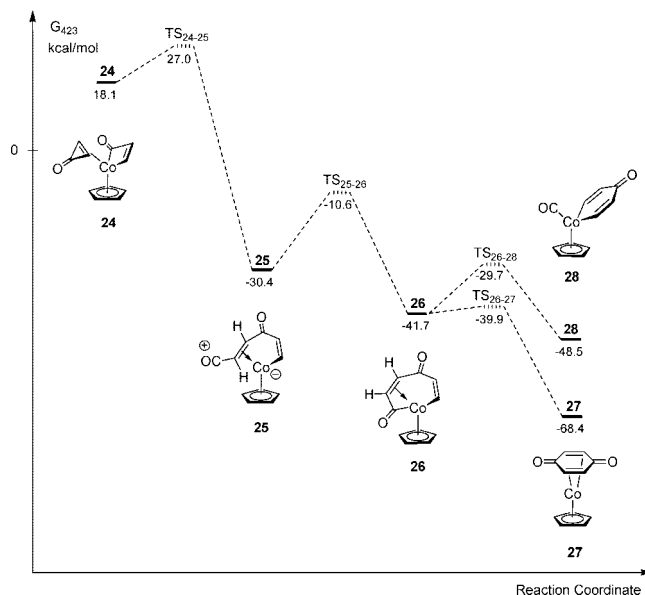

Figure 6. Free energy profile G$_{423}$ (for a reaction temperature of 423 K) for the conversion of metallacycle **24** into the final *p*-benzoquinone complex **27**. All energies are given in kcal/mol, relative to **^{1}15**.

^{3}21. Surprisingly, the B3LYP results predict an opening of the metallacyclobutenone ring for this open-shell complex. The population analysis identifies it as a biradical, because the Mulliken atomic spin density on the C of the carbonyl is as high as 0.6; the remaining spin is localized on the Co (1.1) and O (0.3) atoms. This finding can be interpreted in terms of the aforementioned preference of a 16e environment by the triplet complexes. MECP$_3$ has a higher free energy than do any of the connected singlet and triplet species **21** and **23**, despite the fact that no transition states could be located between them. This is indicative of an entropic barrier to dissociation, similar to that obtained for the case of olefin elimination from transition metal hydrides.[37] MECP$_4$ resembles **24a** in terms of energy and structure, but here the differences are found to be larger than for the preceding three MECPs.

Conversion of the Metallacycle 24 into the Benzoquinone Complex 27. For complex **24**, our calculations predict a ring opening of the three-membered ring to **25**. The activation barrier of this process is relatively low (8.9 kcal/mol), and the formation of **25** itself is associated with a release of energy (49 kcal/mol), which is due to the complete opening of the ring system. This results in the formation of a structure containing a vinylogous CO system complexed by Co at the CC π-bond (Figure 6). The coordinated formal double bond in **25** is *trans*-substituted, whereas for benzoquinone formation a *cis* configuration is required. The rotation to form complex **26** with a *cis* configuration of the double bond has an activation barrier of 19.8 kcal/mol. While still significant, this barrier is lower than the torsional barrier for an olefin such as ethylene because of a reduced double bond character that is reflected in an elongation of the C=C bond (r_{CC} = 1.48 Å, as compared to 1.33 Å in ethylene and 1.54 Å in ethane). The subsequent reductive elimination to close the *p*-benzoquinone framework via TS$_{26-27}$ has a small activation barrier and is again associated with an energy gain (27 kcal/mol). Overall, the CpCo-mediated reaction of the two cyclopropenone moieties to form the CpCo-capped *p*-benzo-

(37) Döhring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. *Organometallics* **2001**, *20*, 2234–2245.
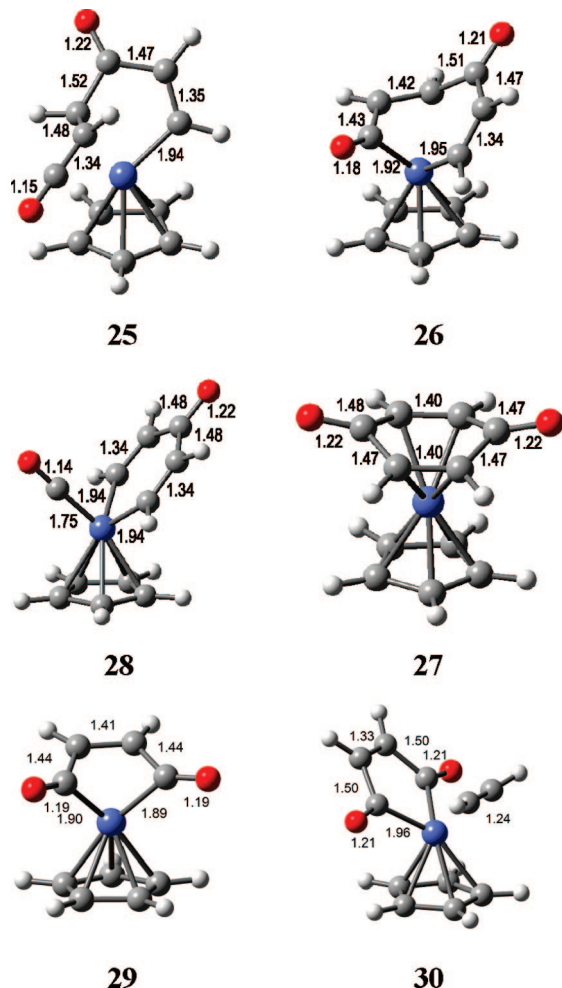
Figure 7. Relevant distances [Å] in the optimized geometries for going from **25** to **27** and **28**, respectively. Furthermore, the optimized structures of **29** and **30** are depicted.
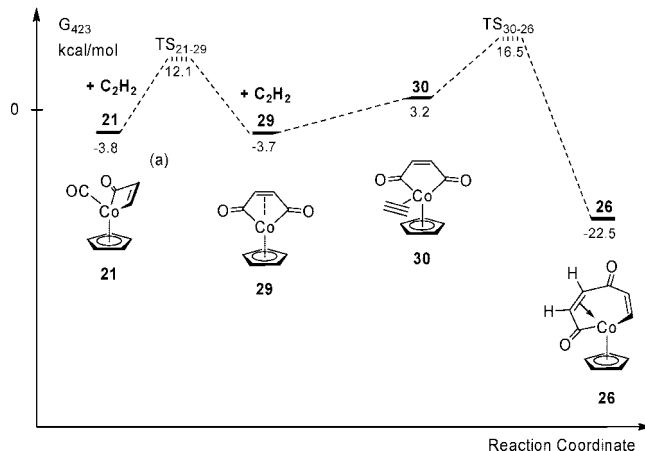

Figure 8. Free energy profile G_{423} (for a reaction temperature of 423 K) for the reaction of **21** to **26** via **29**. All energies are given in kcal/mol, relative to ^{1}**15**, and include the free energy of separate acetylene where indicated.
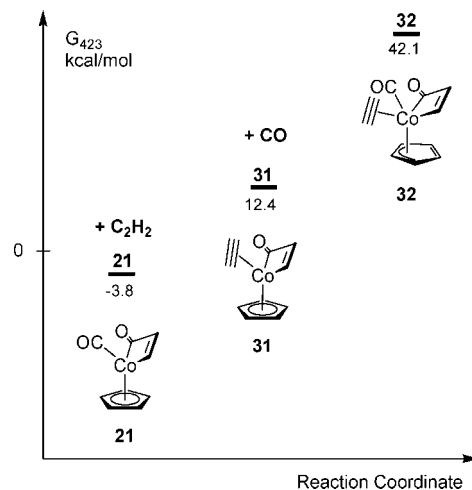

Figure 9. Comparison of the calculated free energies G_{423} for **21**, **31**, and **32** (at a temperature of 423 K). All energies are given in kcal/mol, relative to ^{1}**15**, and include the free energy of separate acetylene and CO where indicated.

quinone is a highly exergonic process (68 kcal/mol). Reaction of **26** can also lead to the formation of the cobaltacyclohexa-dienone system **28**, which serves as a precursor for the formation of cyclopentadienone complexes. The lower yields of the CpCo-stabilized cyclopentadienone complexes (cf., **17**) may be accounted for by the energy difference between the transition states TS$_{26-28}$ and TS$_{26-27}$ (10.2 kcal/mol). In Figure 7, we list the most relevant bond distances calculated for the products **25−28**.

Our suggestion that a metallacyclohexa-2,5-dien-4-one species is formed as an intermediate in the pathway to a CpCo-stabilized cyclopentadienone is supported by other findings: A congener of **28** was discussed as an intermediate in the hydrogenation of alkynes with Os$_3$(CO)$_{10}$(μ-H)$_2$ using *para*-hydrogen as a probe.[38] Also, clusters with a metallacyclohexa-2,5-dien-4-one fragment are reported in the literature.[39]

Alternative Reaction Path (Path II). The experiments performed with ^{13}C-labeled cyclopropenone revealed that to a major extent only one labeled carbon atom was present in the *p*-benzoquinone complex **27**.[16] Thus, a modification of reaction path I is necessary, insofar as only one labeled cyclopropenone

(38) Gobetto, R.; Milone, L.; Reineri, F.; Salassa, L.; Viale, A. *Organometallics* **2002**, *21*, 1919–1924.

(39) (a) Davidson, J. L.; Green, M.; Stone, F. G.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2044–2053. (b) Amoroso, A. J.; Clarke, L. P.; Davies, J. E.; Lewis, J.; Powell, H. R.; Raithby, P. R.; Shields, G. P. *J. Organomet. Chem.* **2001**, *635*, 119–131.

is incorporated, whereas the second equivalent can be replaced by CO and ethyne.

The starting point of our alternative route is complex **21**, which consists of a cobaltacyclobutenone with both a Cp and a CO ligand. The insertion of one CO unit into the cobaltacy-clobutenone ring, adjacent to the CC double bonds, leads to the intermediate **29**. For this step, an activation barrier of 15.9 kcal/mol (Figure 8) from **21** was calculated. The intermediate **29**, formally a 16e species, is intramolecularly stabilized by the coordination of the CC double bond to the cobalt center, as indicated in the figure. The coordination of the olefinic double bond in the metallacyclopent-3-ene-2,5-dione ring of **29** stabilizes the singlet state over its triplet state by 34.1 kcal/mol. Intermediate **29** is not predicted to be more stable than **21**, despite an expected strain release by enlarging the four-membered ring of **21**. The internally coordinated double bond in **29** can be displaced by the CC triple bond of ethyne, leading to intermediate **30**. The latter species was found to be 6.9 kcal/mol less stable than **29**. The insertion of the side-on coordinated ethyne into the five-membered ring of **30** requires an activation energy of 13.3 kcal/mol and affords complex **26** (cf., Figure 6). As discussed in the previous paragraph, compound **26** can rearrange to either **27** or **28**.

A third possibility is the replacement of the CO ligand in **21** by ethyne to yield **31** or the addition of ethyne to **21** to yield **32** (Figure 9). From the latter species, the insertion of a CO molecule or a second molecule of ethyne can occur, leading to **29** or **28**, respectively. Because **32** is 45.9 kcal/mol higher in free energy than **21** + C_2H_2 and 30.0 kcal/mol higher than the transition state TS_{21-29} + C_2H_2, we refrained from pursuing this path further.

Conclusion

We have compared the energetics of two reaction pathways, whereby 2 equiv of cyclopropenone and 1 equiv of $CpCo(CO)_2$ react to yield 1 equiv of CpCo-capped *p*-benzoquinone. In the first pathway, both cyclopropenone units were successively complexed by $CpCo(CO)_2$, followed by a metal-induced ring opening. To generate the metallacyclobutenone complex **21**, an activation energy of 33.5 kcal/mol is required. The addition of a second equivalent of cyclopropenone to this intermediate is accompanied by processes that demand an activation energy of 28 kcal/mol. A second reaction pathway that requires a significantly lower activation energy of merely 16.5 kcal/mol from **21** to **26** was found. It starts by an expansion of the metallacyclobutenone ring in **21** by one CO unit, followed by an alkyne insertion. The second cyclopropenone unit is therefore added as CO + C_2H_2. This opens up the possibility of substituting these two building blocks, as we found out by carrying out the reaction with ^{13}C-labeled cyclopropenone and by adding different alkynes. Both cases were verified[16] and confirmed the proposed mechanism. During our computations, we took special note of crossings of the singlet and triplet surface. Despite favorable energetics in same instances, the paths involving the triplet surface could be excluded by theoretical means due to the very short lifetime of the initially formed triplet species.

Our calculations also show a way of lowering the activation energy and even carrying out the reaction catalytically. This might be achieved by using an organometallic species that reacts with cyclopropenone to a congener of **21** at a much lower energy than $CpCo(CO)_2$. Candidates are likely to be found in group VIIIc.

Supporting Information Available: Gaussian archive entries of all calculated compounds, transition states, and minimum energy crossing points (MECPs) of the singlet and triplet potential surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800685T