Articles

CpCo-Mediated Reactions of Cyclopropenones: Access to CpCo-Capped Benzoquinone Complexes

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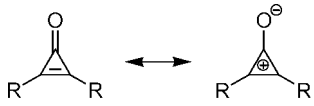
The reaction of di(*n*-propyl)cyclopropenone (**7**), di(*n*-butyl)cyclopropenone (**16**), and bicyclo[12.1.0]pentadeca-1(14)-en-7-yn-15-one (**21**) with $CpCo(CO)_2$ and CpCo(cod) yielded CpCo-complexed benzoquinone and cyclopentadienone derivatives. When **16** was reacted with $CpCo(CO)_2$ and a 10-fold surplus of 4-octyne, a mixture of CpCo-capped benzoquinone **25** and cyclopentadienone **26** was isolated. The reaction of cyclopropenone **16** containing a ^{13}C-labeled CO group with $CpCo(CO)_2$ yielded a CpCo-capped tetrakis(*n*-butyl)-*p*-benzoquinone with one ^{13}C nucleus per molecule as the main product. The mechanism of the formation of *p*-benzoquinone is discussed on the basis of the results of trapping and labeling experiments.

Introduction

Cyclopropenones are highly strained and polar molecules that can best be described by the two valence formulas **1a** and **1b**.[1] From this description we anticipate that these components react with transition metals either at the C═C double bond or at the oxygen center. This is indeed the case. In 1967 it was reported that Co(II) salts afforded complexes with two or six cyclopropenone ligands bound via the oxygen centers of the CO group.[2]

Chart 1

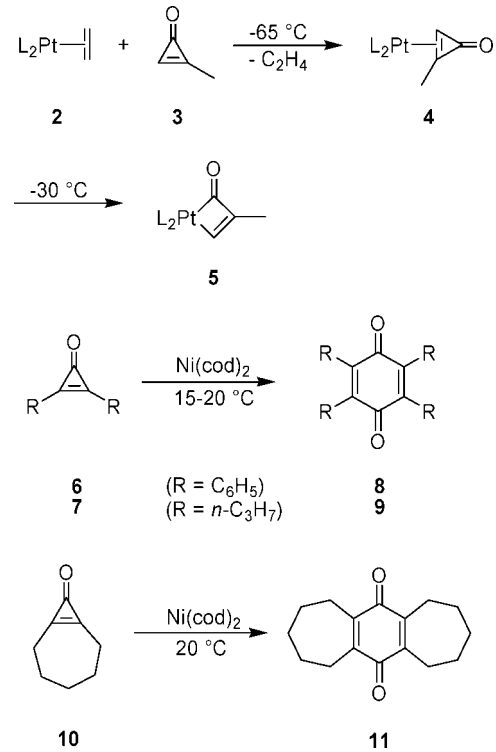


1a **1b**

In 1972 there were two reports[3,4] that described either a complexation of the C═C double bond or a breaking of a C−C bond, as shown in Scheme 1.

The reaction of **6** and **7** with $Ni(cod)_2$ was conducted in a 7:1 ratio.[4] A key reaction for understanding the reaction mechanism of the Ni-catalyzed process was the reaction of the bicyclic cyclopropenone **10**, which afforded the dimer **11**

Scheme 1



(Scheme 1). This outcome was rationalized by assuming a nickel cyclobutenone analogous to **5**.

With Rh(I) complexes the cyclopropenones **6** and **7** yielded 1-rhodacyclopentene-2,5-diones **12** and **13**, respectively (Scheme 2), and decarbonylation led to acetylenes.[5] The insertion of a Fischer carbene complex into the C−C bond of diphenylcyclopropene was also reported.[6] More recently cyclopropenone-

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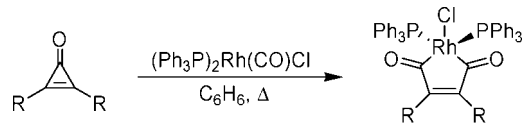
Scheme 2



6 (R = C_6H_5) **12**
7 (R = *n*-C_3H_7) **13**

acetals[7,8] as well as cyclopropenones[9] were used to synthesize cyclopentadienone derivatives in a metal catalyzed [3+2] cycloaddition reaction with alkynes.

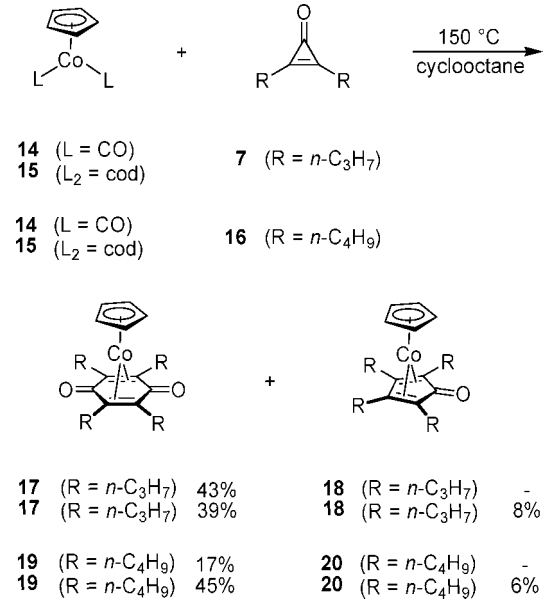
In the course of our investigations of cyclopropenones[10] and cyclopropenonophanes[11] we were interested in the reaction of these species with (η^5-cyclopentadienyl)cobalt complexes. In this article we report the results of these investigations.

Results

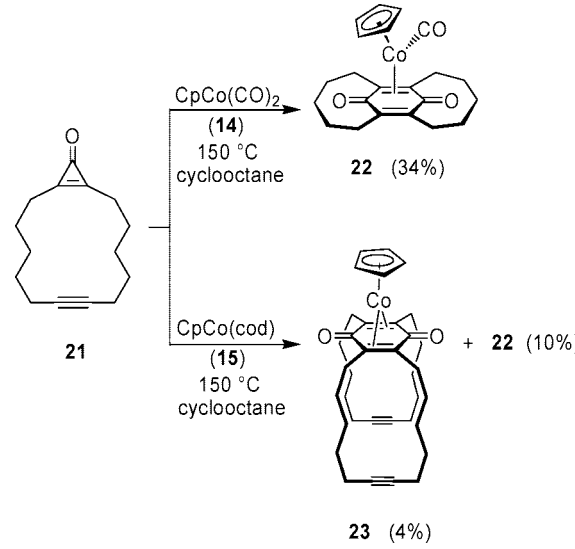
Reaction of di(*n*-propyl)cyclopropenone (**7**)[12] and di(*n*-butyl)cyclopropenone (**16**) with $CpCo(CO)_2$ (**14**) yielded as main product the *p*-benzoquinone complexes **17** and **19**, respectively. As minor products we could isolate the CpCo-capped cyclopentadienone derivatives **18** and **20**, respectively (Scheme 3). Similar results were obtained by using CpCo(cod) (**15**) as reagent. By applying $FeCl_3$ as oxidant we were able to remove the CpCo cap from **17** to obtain tetra(*n*-propyl)-*p*-benzoquinone.

The structural assignment of **17**−**20** is based on their spectroscopic data. The NMR data show C_{2v} symmetry for **17** and **19** and C_s symmetry for **18** and **20** in solution. The fact that the carbonyl frequencies in **17** and **19** are split is in line with other CpCo complexes of *p*-benzoquinone derivatives.[13] In the cases of **18** and **20** we could compare the spectral data of identical systems that were prepared by heating the corresponding alkyne (4-octyne, 5-decyne) with $CpCo(CO)_2$.[14] Additionally to our spectroscopic investigations we were able to grow single crystals of **17** and **19**, which allowed a detailed investigation of their molecular structures. These data reveal that the *p*-benzoquinone ring adopts a boat-shaped structure. The CO groups are bent away by 20° from the plane spanned by the four remaining sp^2 carbon atoms in **17** and **19**. The structural parameters found are very close to those reported for the CpCo complex with duroquinone.[15] Also for **18** we were able to study the structure in the solid state. The obtained

Scheme 3



Scheme 4



structural data were close to those obtained for other CpCo-capped cyclopentadienones.[16]

When we used bicyclo[12.1.0]pentadeca-1(14)-en-7-yn-15-one (**21**)[11] as starting material and heated it with $CpCo(CO)_2$, we isolated the doubly bridged *p*-benzoquinone derivative **22**. In the case of CpCo(cod) as complexing agent instead of $CpCo(CO)_2$ we obtained **22** and the "dimer" **23**, both in low yields (Scheme 4).

The structural assignments of **22** and **23** are based on their spectroscopic properties. It is found that the NMR data of **22** show in solution only C_s symmetry and that in the mass spectrum (FAB+) one CO group is easily lost. For **23** the spectroscopic properties are similar to those found for **17** and **19**. The final proof of the structures of **22** and **23** was given by X-ray investigations on single crystals. In Figure 1 we show two different views of the molecular structure of **22**. It is seen that the *p*-benzoquinone ring adopts a boat conformation. Due

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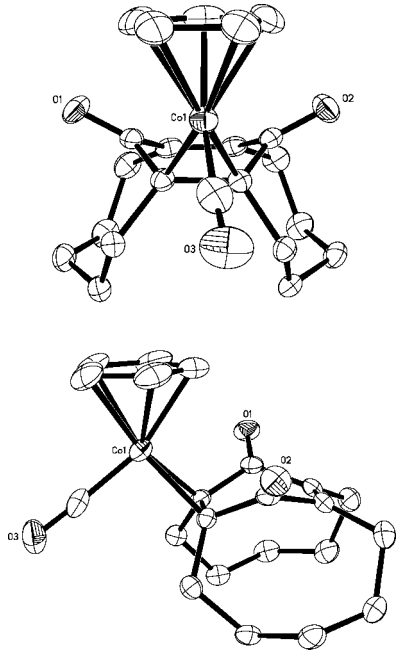


Figure 1. Two views of the molecular structure of **22**. At the top the view goes perpendicular to the C═C double bonds of the quinone ring; at the bottom the view goes parallel to the C═C double bonds. The hydrogen atoms are omitted for the sake of clarity.

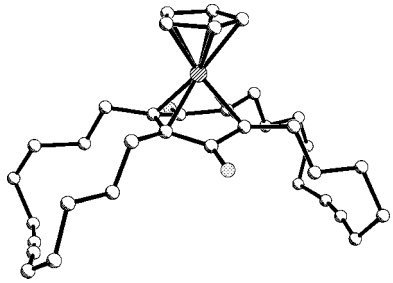


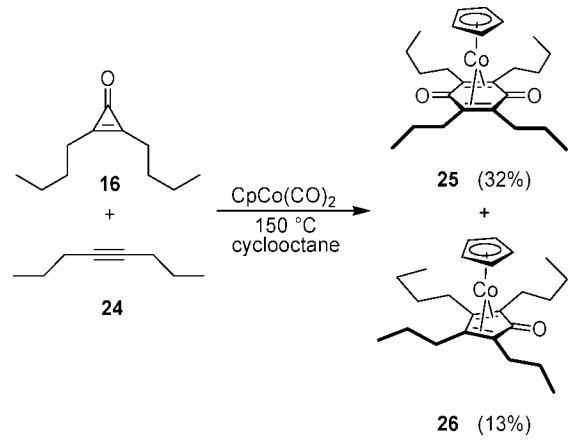
Figure 2. Molecular structure of **23**. Only one of the two molecules in the unit cell is shown. The hydrogen atoms are omitted for the sake of clarity.

to the short pentamethylene bridges, the CO groups point away from the bridges toward the metal by about 37° (top of Figure 1). At the bottom part of Figure 1 it is seen that the CpCo(CO) fragment is bound to one double bond only in such a way that C_s symmetry of **22** is maintained.

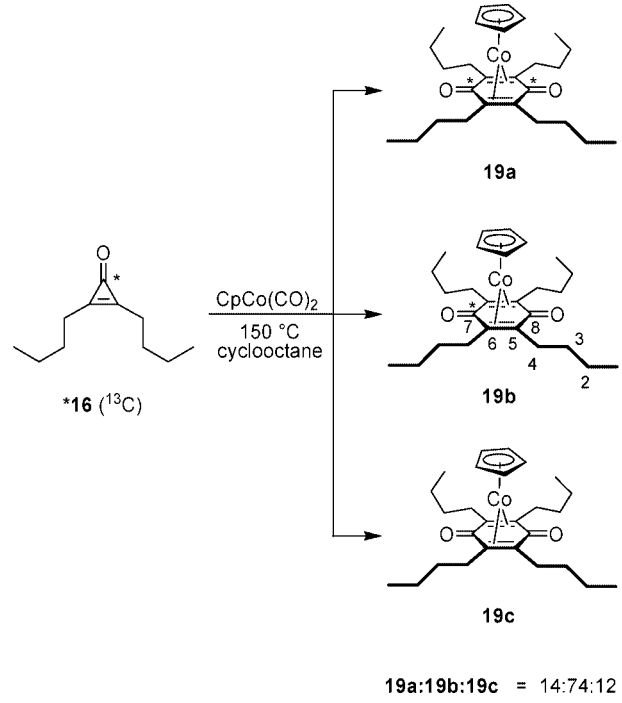
In Figure 2 we show the molecular structure of **23**. It can be described as a CpCo-complexed *p*-benzoquinone in which both double bonds are bridged by dodeca-6-yne bridges. As in the case of **17** and **19** the CO groups are bent away from the metal out of the plane spanned by the four remaining sp^2 carbon atoms.

To elucidate the reaction mechanism, we heated di(*n*-butyl)cyclopropenone (**16**) and a 10-fold surplus of 4-octyne (**24**) with $CpCo(CO)_2$ in cyclooctane under reflux conditions. As the main product we isolated the CpCo-complexed 2,3-di(*n*-butyl)-5,6-di(*n*-propyl)-*p*-benzoquinone **25** and the CpCo-capped 2,3-di(*n*-butyl)-4,5-di(*n*-propyl)cyclopentadienone **26**. The assignments of the structures of both species are based on their spectroscopic properties. The ^{13}C NMR spectrum of **25** shows 11 signals as expected, and in the ^{1}H NMR spectrum of **25** one can assign the six signals between 1 and 3 ppm to the anticipated resonances of the *n*-propyl and *n*-butyl groups as observed for **17** and **19**. The structural assignment of **25** is confirmed by

Scheme 5



Scheme 6

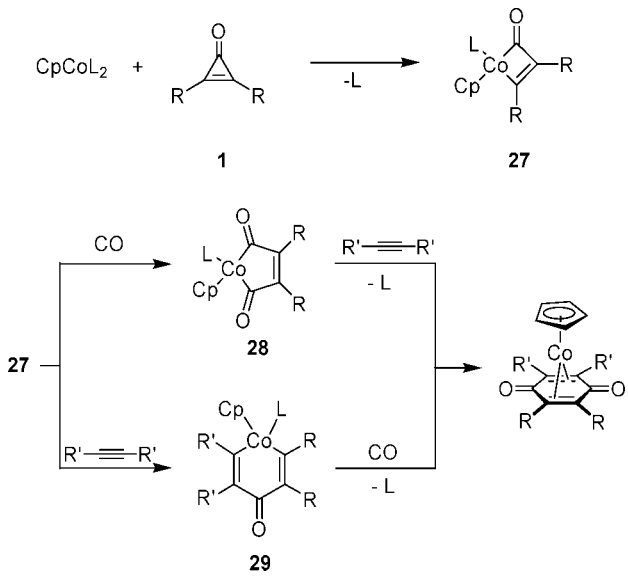


19a:19b:19c = 14:74:12

X-ray investigations on single crystals. They reveal very similar molecular parameters to those observed for **17** and **19**. Due to a missing plane of symmetry, the NMR data of **26** are more complex, especially the signals originating from the methylene groups (Scheme 5).

A further insight into the reaction mechanism for the benzoquinone formation was provided by using di(*n*-butyl)cyclopropenone labeled with ^{13}C at the CO group as reaction component for the reaction with $CpCo(CO)_2$ (Scheme 6). The expected *m*/*z* ratios for **19a** (*m*/*z* 458.3), **19b** (*m*/*z* 457.3), and **19c** (*m*/*z* 456.3) were determined by electron impact (EI+) mass spectrometry. The ratio **19a**:**19b**:**19c** amounts to 14:74:12. This reveals as main product the one that has only one ^{13}C nucleus per molecule. The second CO group stems from the $CpCo(CO)_2$ reagent. The ^{13}C NMR spectrum has to be analyzed in terms of a superposition of spectra of different isotopomers. Differences for the resonances of the alkyl (C1−C4) and the Cp carbon atoms are not observed for **19a**−**19c**; the carbonyl group (C7, C8) resonates at 157.5 ppm. However, for the ^{13}C resonance of C5 and C6 of **19a**−**19c** we encounter a splitting of the signal with a ^{1}J coupling constant of 48 Hz for the carbon atom adjacent to the labeled carbon atom and

Scheme 7



a coupling constant of $^2J = 2$ Hz for the next carbon atom (see Scheme 6).

Discussion

To rationalize the isolation of the benzoquinone complexes **17**, **19**, **22**, **23**, and **25** as well as the cyclopentadienone complexes **18**, **20**, and **26**, we assume a sequence that is reminiscent of that shown in Scheme 1. We suppose as first key intermediate the metallacyclobutenone **27** (Scheme 7), which is related to **5** (Scheme 1). At the reaction temperature of 150 °C we can assume that the cyclopropenone decomposes at least partly into CO and alkyne. Recent studies of the decarbonylation reaction of cyclopropenone by transient spectroscopy and DFT calculations support a stepwise mechanism.[17,18] The calculations suggest an activation energy of 32.2 kcal/mol; the fragments CO and phenylacetylene are 4.2 kcal/mol more stable than phenylcyclopropenone. The intermediate **27** may react either with CO to yield **28** or with the alkyne to afford **29**. Related species to **28** are **12**[5] and **13** (Scheme 2). Although for both species only 16 e are counted in the valence shell, we found for **12** no evidence for any interaction between the olefinic double bond and the metal by our X-ray investigations.

With both intermediates **28** and **29** we can rationalize the formation of the CpCo-capped benzoquinone complexes by insertion of either an alkyne unit in **28** or a CO unit in **29** (Scheme 7). A pathway via **28** is favored by findings of Liebeskind et al.[19] It was shown that metallacyclopent-3-ene-2,5-diones react with alkynes on treatment with $AgBF_4$ in CH_3CN to the corresponding quinones.[19] This pathway was postulated earlier to explain the observation that alkynes react with metal carbonyls to produce quinones or quinone complexes in a number of cases.[20] A congener of **29** was discussed as an intermediate when studying the mechanism of the hydrogenation of alkynes with $Os_3(CO)_{10}(\mu\text{-H})_2$ using *para*-hydrogen as probe.[21] Related clusters with a metallacyclohexa-2,5-dien-4-one fragment[22,23] further support our assumption that also **29** is a reasonable candidate as an intermediate in the *p*-benzoquinone formation. Recent quantum chemical calculations on CpCo-mediated reactions of cyclopropenones support the mechanism via intermediate **28**.[24]

Conclusion

The reaction of dialkyl cyclopropenones **7** and **16** as well as the bicyclic derivative **21** with $CpCo(CO)_2$ or CpCo(cod) yielded as main product CpCo-complexed *p*-benzoquinone derivatives and in case of **7** and **16** as minor product CpCo-capped cyclopentadienone derivatives. The trapping experiment between di(*n*-butyl)cyclopropenone and 4-octyne as well as the product distribution of the reaction of ^{13}C-labeled di(*n*-butyl)cyclopropenone with $CpCo(CO)_2$ revealed that only 1 equiv of cyclopropenone was incorporated as an intact species. The second unit was incorporated as CO and an alkyne unit. By using an organometallic species that reacts with cyclopropenone to a congener of **27** at much lower activation energy than $CpCoL_2$ we can envisage catalytic processes with cyclopropenone as building blocks, such as Pauson−Khand reactions. Candidates are likely to be found in group VIIIc.

Experimental Section

General Procedures. All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV light absorption data were recorded using a Hewlett-Packard 8452A spectrometer. IR spectra were recorded with a Bruker Vector 22. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^{1}H NMR at 300 or 500 MHz and ^{13}C NMR at 75 or 125 MHz) using C_6D_6 as solvent and internal standard (δ), if not otherwise noted. FAB mass spectra refer to data from a Jeol JMS-700 instrument. As matrix for the FAB experiments *m*-nitrobenzyl alcohol was used. All reactions were carried out in dried glassware under argon atmosphere using dried and oxygen-free solvents. Dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (**14**),[25] di(*n*-propyl)cyclopropenone (**7**),[12] di(*n*-butyl)cyclopropenone (**16**),[12] and bicyclo[12.1.0]pentadeca-1(14)-en-7-yn-15-one (**21**)[11] were prepared according to literature procedures.

General Procedure for the Reaction of Cyclopropenones with $CpCoL_2$ (L = CO, L_2 = 1,5-cyclooctadiene). A solution of the cyclopropenone derivative and $CpCoL_2$ was dissolved in 20

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mL of anhydrous cyclooctane and refluxed for 3 h (150 °C). The reaction was monitored by TLC. After cooling, the solvent was removed under vacuum and the residue was purified by column chromatography using ALOX III (neutral).

Preparation of ^{13}C-Labeled Di(*n*-butyl)cyclopropenone (*16). Starting materials: 0.5 mL (2.8 mmol) of 5-decyne, 1.0 g (8.3 mmol) of ^{13}C-labeled chloroform, and 50 mL of anhydrous THF. After addition of anhydrous chloroform the mixture was cooled to –78 °C. Using an injection pump, 18 mL (3.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) was added slowly at a rate of 7 mL/h. The mixture was stirred at −78 °C for 90 min. Then the temperature was gradually allowed to rise to 10 °C. For the workup 200 mL of 9 M sulfuric acid was added and the mixture was stirred for a few minutes. The organic layer was separated and the aqueous layer was extracted three times with dichloromethane (100 mL each). The combined organic layers were carefully neutralized with a saturated solution of $NaHCO_3$ in water and afterwards washed with brine. After drying over $MgSO_4$ the solvent was removed under vacuum. Purification by column chromatography (SiO_2, hexane/EtOAc, 2:1) yielded 214 mg (46%) of ***16** as a slightly brownish liquid. The rate of labeled cyclopropenone is 95%, calculated on comparison of mass spectra of unlabeled and labeled cyclopropenone. HRMS (EI+): calcd for $^{12}C_{10}{}^{13}CH_{18}O$ 167.1391 (M^+), found 167.1396. The remaining spectroscopic data are consistent with those obtained for the unlabeled di(*n*-butyl)cyclopropenone.

Preparation of 17 and 18. Starting material: 139 mg (1.0 mmol) of **7**, 180 mg (1.0 mmol) of **14**, and 20 mL of cyclooctane. The raw material was purified by column chromatography using petroleum ether/diethyl ether (10:1 → 1:1) to afford two fractions: First fraction: 79 mg (39%) of **17** as a red crystalline solid (mp 183 °C). ^{1}H NMR (300 MHz): δ 1.17 (m, 12H, CH_3), 1.39–1.52 (m, 4H, CH_2), 1.88 (m, 4H, CH_2), 2.14–2.27 (m, 4H, CH_2), 3.03 (m, 4H, CH_2), 4.08 (s, 5H, CH_{Cp}). ^{13}C NMR (75 MHz): δ 15.0 (*C*H_3), 23.3 (*C*H_2), 32.4 (*C*H_2), 84.3 (*C*H_{Cp}), 95.0 (C_{sp^2}), 158.4 (*C*O). IR (KBr) 2964, 2949, 2928, 2866, 1593, 1573, 1461 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 252 (4.3), 272 (4.2), 304 (4.2), 384 (3.94), 442 (3.0). Anal. Calcd for $C_{25}H_{33}O_2Co$: C, 68.99; H, 8.31. Found: C, 68.69; H, 8.35. Second fraction: 15 mg (8%) of **18** as an orange solid (mp 102–103 °C). ^{1}H NMR (500 MHz): δ 0.87 (t, ^3J = 7.4 Hz, 6H, CH_3), 1.04 (t, ^3J = 7.4 Hz, 6H, CH_3), 1.31–1.44 (m, 4H, CH_2), 1.55–1.68 (m, 2H, CH_2), 1.80–1.86 (m, 2H, CH_2), 1.92–2.00 (m, 2H, CH_2), 2.03–2.09 (m, 2H, CH_2), 2.14–2.20 (m, 2H, CH_2), 2.62–2.68 (m, 2H, CH_2), 4.28 (s, 5H, CH_{Cp}). ^{13}C NMR (125 MHz): δ 15.0 (*C*H_3), 15.2 (*C*H_2), 23.2 (*C*H_2), 25.0 (*C*H_2), 28.6 (*C*H_2), 28.7 (*C*H_2), 80.9 (C_{Cpd}), 82.3 (*C*H_{Cp}), 92.1 (C_{Cpd}), 160.5 (s, *C*O). IR (KBr): 3077, 2959, 2933, 2870, 1574, 1466 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 288 (4.5), 362 (3.5), 412 (3.1). Anal. Calcd for $C_{22}H_{33}OCo$: C, 70.95; H, 8.93. Found: C, 70.81; H, 8.96.

Preparation of 19 and 20. Starting material: 98 mg (0.60 mmol) of **16**, 116 mg (0.50 mmol) of **15**, and 10 mL of cyclooctane. The raw material was purified by column chromatography using petroleum ether/diethyl ether (10:1) to yield two fractions. First fraction: 21 mg (16%) of **19** as an orange solid (mp 195 °C). ^{1}H NMR (300 MHz): δ 0.99 (m, 12H, CH_3), 1.51 (m, 12H, CH_2), 1.89 (m, 4H, CH_2), 2.22 (m, 4H, CH_2), 3.00 (m, 4H, CH_2), 4.00 (s, 5H, CH_{Cp}). ^{13}C NMR (75 MHz): δ 14.2 (*C*H_3), 24.1 (*C*H_2), 30.2 (*C*H_2), 32.3 (*C*H_2), 84.5 (*C*H_{Cp}), 95.1 (C_{sp^2}), 158.0 (*C*O). IR (KBr) 3075, 2957, 2870, 1572, 1570, 1462 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 236 (4.1), 252 (4.1), 304 (4.0), 392 (3.7), 430 (3.3). Anal. Calcd for $C_{27}H_{41}O_2Co$: C, 71.03; H, 9.05. Found: C, 70.95; H, 9.05. Second fraction: 8 mg (6%) of **20** as a dark red solid (mp 131 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.93 (m, 12H, CH_3), 1.37–1.38 (m, 14H, CH_2), 1.61–1.88 (m, 2H, CH_2), 1.91–1.96 (m, 2H, CH_2), 2.22–2.52 (m, 6H, CH_2), 4.57 (s, 5H, CH_{Cp}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4 (*C*H_3), 14.5 (*C*H_3), 24.0 (*C*H_2), 24.1 (*C*H_2), 26.0 (*C*H_2), 26.4 (*C*H_2), 32.3 (*C*H_2), 44.0 (*C*H_2), 82.6 (C_{Cpd}), 82.8 (*C*H_{Cp}), 92.9 (C_{Cpd}), 158.5 (*C*O). IR (KBr): 3069, 2958, 2931, 2858, 1573, 1465 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 220 (4.4), 228 (4.5), 342 (4.4), 360 (4.1), 400 (4.0). Anal. Calcd for $C_{26}H_{41}OCo$: C, 72.87; H, 9.64. Found: C, 72.66; H, 9.70.

Preparation of ^{13}C-Labeled 19. Starting material: 200 mg (1.2 mmol) of ^{13}C-labeled di(*n*-butyl)cyclopropenone, 216 mg (1.2 mmol) of **14**, and 20 mL of cyclooctane. The reaction was stirred at 180 °C for 3 h. The raw material was purified by column chromatography (ALOX, diethyl ether/methanol, 10:1) to yield 38 mg (14%) of **19**. ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9 (C1), 23.8 (C2), 30.0 (C3), 31.9 (C4), 85.1 (C_{Cp}), 95.9 (C6, d, $^1J_{(C6,C7)}$ = 48 Hz), 95.9 (C5, d, $^2J_{(C5,C7)}$ = 2 Hz), 157.3 (C8), 157.5 (C7). HRMS (EI+): calcd for $^{12}C_{26}{}^{13}CH_{41}O_2Co$ 457.2470 (M^+), found 457.2456. The remaining spectroscopic data are consistent with those obtained for the unlabeled compound.

Preparation of 22. Starting material: 107 mg (0.50 mmol) of **21**, 160 mg (0.90 mmol) of **14**, and 10 mL of cyclooctane. The raw material was purified by column chromatography to yield 72 mg (37%) of **22** as a red crystalline solid (mp > 150 °C, dec). ^{1}H NMR (300 MHz): δ 1.24 (m, 2H, CH_2), 1.54 (m, 4H, CH_2), 1.77 (m, 6H, CH_2), 1.90 (m, 2H, CH_2), 2.20 (m, 2H, CH_2), 2.86 (m, 4H, CH_2), 4.72 (s, 5H, CH_{Cp}). ^{13}C NMR (125 MHz): δ 27.2 (*C*H_2), 29.2 (*C*H_2), 34.0 (*C*H_2), 36.1 (*C*H_2), 40.2 (*C*H_2), 87.7 (C_{sp^2}), 89.5 (*C*H_{Cp}), 145.3 (*C*O), 146.8 (C_{sp}). The ^{13}C resonance of the CO ligand could not be detected. IR (KBr): 2933, 2846, 1972, 1667, 1443 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 250 (4.1), 308 (3.6), 398 (3.4). Anal. Calcd for $C_{22}H_{25}O_3Co$: C, 66.67; H, 6.36. Found: C, 66.63; H, 6.40.

Reaction of 21 with 15. Starting material: 99 mg (0.46 mmol) of **21**, 106 mg (4.6 mmol) of **15**, and 8 mL of cyclooctane. The raw material was purified by column chromatography using petroleum ether/diethyl ether (5:1) to yield two fractions. First fraction: 18 mg (10%) of **22**. Second fraction: 5 mg (4%) of **23** as an orange crystalline solid (mp 202 °C, dec). ^{1}H NMR (500 MHz): δ 1.30–2.30 (m, 36H, CH_2), 3.20 (m, 4H, CH_2), 4.10 (s, 5H, CH_{Cp}). ^{13}C NMR (125 MHz): δ 19.1 (*C*H_2), 21.7 (*C*H_2), 25.1 (*C*H_2), 27.4 (*C*H_2), 30.0 (*C*H_2), 30.7 (*C*H_2), 31.8 (*C*H_2), 31.8 (*C*H_2), 34.4 (*C*H_2), 34.4 (*C*H_2), 38.4 (*C*H_2), 81.4 (C_{sp}), 85.5 (*C*H_{Cp}), 96.1 (C_{sp^2}), 192.3 (*C*O). IR (film): 2927, 2854, 1628, 1593, 1579, 1552, 1458 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 236 (4.0), 254 (4.0), 294 (3.9), 384 (3.6), 426 (2.8). HRMS (FAB+): calcd for $C_{35}H_{45}O_2Co$ 557.2829 (M^+), found 557.2834.

Reaction of Di(*n*-butyl)cyclopropenone (16) with 14 in the Presence of 4-Octyne (24). Starting material: 170 mg (1.0 mmol) of **16**, 1.10 g (10.0 mmol) of **24**, 180 mg (1.0 mmol) of **14**, and 40 mL of cyclooctane. The raw material was purified by column chromatography using petroleum ether/diethyl ether (10:1 → 1:1) to afford two fractions. First fraction: 138 mg (32%) of **25** as a red crystalline solid. ^{1}H NMR (500 MHz): δ 0.98 (m, 6H, CH_3), 1.07 (m, 6H, CH_3), 1.40–1.55 (m, 8H, CH_2), 1.79 (m, 2H, CH_2), 1.87 (m, 2H, CH_2), 2.17–2.23 (m, 4H, CH_2), 2.91–3.01 (m, 4H, CH_2), 3.96 (s, 5H, CH_{Cp}). ^{13}C NMR (125 MHz): δ 13.7 (*C*H_3), 14.9 (*C*H_3), 23.2 (*C*H_2), 23.7 (*C*H_2), 23.7 (*C*H_2), 29.8 (*C*H_2), 31.9 (*C*H_2), 32.3 (*C*H_2), 84.1 (C_{sp}), 94.5 (C_{sp^2}), 94.7 (C_{sp^2}), 158.0 (*C*O). IR (KBr): 2960, 2931, 2871, 1573, 1460 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 254 (4.3), 304 (4.1), 384 (3.8), 432 (2.9). Anal. Calcd for $C_{25}H_{37}O_2Co$: C, 70.08; H, 8.70. Found: C, 70.27; H, 8.65. Second fraction: 50 mg (13%) of **26** as a red oil. ^{1}H NMR (300 MHz): δ 0.90 (m, 9H, CH_3), 1.04 (m, 3H, CH_3), 1.24–1.68 (m, 10H, CH_2), 1.77–2.28 (m, 8H, CH_2), 2.61–2.76 (m, 2H, CH_2), 4.29 (s, 5H, CH_{Cp}). ^{13}C NMR (75 MHz): δ 14.0 (*C*H_3), 14.2 (*C*H_3), 15.0 (*C*H_3), 15.2 (*C*H_3), 23.2 (*C*H_2), 24.2 (*C*H_2), 25.0 (*C*H_2), 26.1 (2*C*H_2), 28.5 (*C*H_2), 28.7 (*C*H_2), 32.1 (*C*H_2), 33.8 (*C*H_2), 81.1 (C_{Cpd}), 82.3 (*C*H_{Cp}), 92.0 (C_{Cpd}), 92.2 (C_{sp^2}), 160.1 (*C*O). IR (KBr): 2958, 2933, 2871, 1558, 1457 cm^{-1}. UV/vis (CH_2Cl_2) (λ_{max}, nm (log ϵ)): 288 (4.0), 392 (3.0), 418 (2.6). HRMS (FAB+): calcd for $C_{24}H_{37}O_2Co$ 401.2238 (M^+), found 401.2254.

Table 1. Crystal Data and Details of the Refinement Procedure for 12, 17, 18, 19, 22, 23, and 25

	12	**17**	**18**	**19**	**22**	**23**	**25**
empirical formula	$C_{53}H_{42}Cl_3O_2P_2Rh$	$C_{23}H_{33}CoO_2$	$C_{22}H_{33}CoO$	$C_{27}H_{41}CoO_2$	$C_{22}H_{25}CoO_3$	$C_{35}H_{45}CoO_2$	$C_{24}H_{37}CoO$
fw	982.07	400.42	372.41	456.53	396.35	556.64	400.47
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pc	$P2_1/c$
unit cell dimensions							
a [Å]	13.409(1)	9.4714(1)	7.8086(5)	9.357(6)	16.9392(2)	26.0685(8)	20.1199(3)
b [Å]	16.825(1)	24.4828(3)	18.988(1)	24.95(2)	8.7139(1)	6.9916(2)	24.7482(7)
c [Å]	20.694(2)	9.5828(2)	27.209(2)	11.073(7)	13.2461(2)	16.7394(5)	9.3578(2)
α [deg]	83.193(2)	90	90	90	90	90	90
β [deg]	73.888(2)	108.918(1)	90.422(2)	91.56(5)	111.162(1)	108.551(1)	90.924(1)
γ [deg]	87.966(2)	90	90	90	90	90	90
Z	4	4	4	4	4	4	8
V [Å^3]	4453.7(7)	2102.09(6)	4064.1(5)	2584(3)	1823.36(4)	2892.4(2)	4658.9(1)
D_{calc} [g/cm^3]	1.465	1.265	1.223	1.174	1.444	1.278	1.142
abs coeff [mm^{-1}]	0.678	0.830	0.853	0.683	0.960	0.623	0.746
max./min. transmn	0.94/0.89	0.98/0.78	0.96/0.80	0.80/0.65	0.93/0.74	-	0.97/0.82
θ range for data collection (deg)	1.96/28.36	1.66/26.65	1.31/24.71	1.63/25.00	1.29/25.64	1.28/25.51	1.01/20.84
index ranges	$-17 \le h \le 17$, $-22 \le k \le 22$, $-27 \le l \le 27$	$-11 \le h \le 11$, $-30 \le k \le 30$, $-11 \le l \le 11$	$-9 \le h \le 9$, $-22 \le k \le 22$, $-32 \le l \le 32$	$-11 \le h \le 11$, $0 \le k \le 29$, $0 \le l \le 13$	$-19 \le h \le 19$, $-10 \le k \le 10$, $-15 \le l \le 15$	$-31 \le h \le 31$, $-8 \le k \le 8$, $-20 \le l \le 20$	$-20 \le h \le 20$, $-24 \le k \le 24$, $-9 \le l \le 9$
no. of reflns collected	46 760	19 964	32 190	4547	13 027	18 690	26 591
no. of indep reflns	21 909	4286	6889	4547	3152	9118	4888
no. of reflns obsd	16 325	3338	5166	3599	2606	6964	2652
goodness-of-fit on F^2	1.18	1.02	1.01	1.03	1.05	1.05	1.03
$R(F)$	0.086	0.033	0.038	0.044	0.028	0.084	0.060
$R_w(F^2)$	0.159	0.069	0.072	0.099	0.061	0.209	0.136
$(\Delta\rho)$max., $(\Delta\rho)$min. (e Å^{-3})	1.15, −1.19	0.25, −0.31	0.33, −0.28	0.38, −0.36	0.27, −0.27	1.39, −0.39	0.92, −0.47

X-ray Diffraction Analyses. The reflections were collected with a Bruker Smart CCD diffractometer at 200 K (**17**, **22**, **23**, **25**), a Bruker APEX diffractometer at 100 K (**18**) and at 200 K (**12**), and a Siemens-Stoe AED2 diffractometer at 213 K (**19**), all equipped with a Mo Kα radiation source and a graphite monochromator. Intensities were corrected for Lorentz and polarization effects, and an absorption correction was applied using psi-scans (**19**) or SADABS based on the Laue symmetry of the reciprocal space (**12**, **17**, **18**, **22**, **25**). In the case of **23** no absorption correction was applied due to the low-quality data set. The structures were solved by direct methods; the structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique against F^2. The hydrogen atom locations were either calculated according to stereochemical aspects (**12**, **17**, **23**, **25**) or refined isotropically (**18**, **22**) or treated in a mixed manner (**19**). Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[26] Table 1 contains the crystallographic data and details of the data collection and the refinement procedure. The structure determination of **23** was rather problematic. The crystals were pseudomerohedrically twinned (23%), and furthermore there was about 6% whole molecule disorder in both independent molecules. This led to results that can be considered as proof of constitution, but the low quality does not justify the depiction of the anisotropic displacement parameters. They are not meaningful and partially nonpositive definite. Thus, we decided to show the structure in ball-and-stick representation. CCDC-673226 (**12**), −665713 (**17**), −665714 (**18**), −665715 (**19**), −665716 (**22**), −665717 (**23**), and −665718 (**25**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(26) Sheldrick, G. M. *SHELXTL (5.10)*; Bruker Analytical X-Ray Division: Madison, WI, 1997.

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Supporting Information Available: NMR data of **17**–**20**, **22**, **23**, **25**, and **26**. Mass spectra of **16** and **19**, labeled and unlabeled. Crystal data (cif files) for compounds **12**, **17**−**19**, **22**, **23**, and **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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