# CpCo-Stabilized Cyclopentadienones from Cyclobutadiene Complexes: Experimental and Theoretical Investigations

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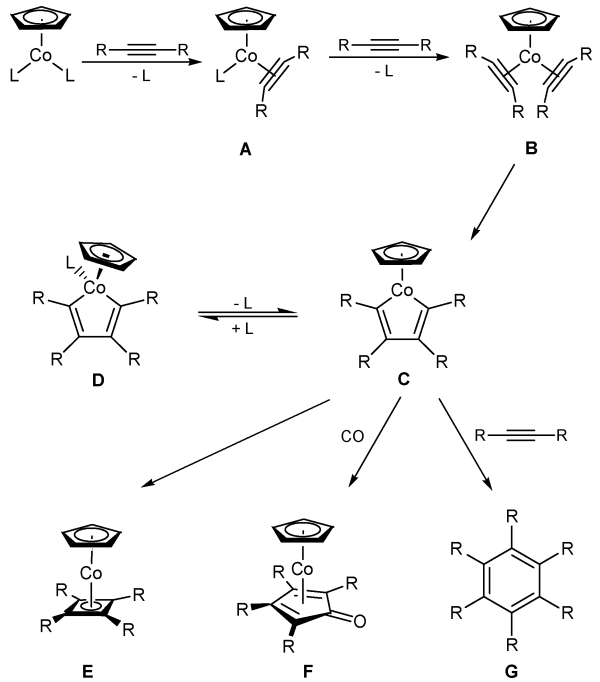
The reaction of 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (**7**) with $C_5H_4(CO_2Me)Co(CO)_2$ (**8**) and $C_5H_4(SiMe_3)Co(CO)_2$ (**10**) led to the tricyclic cyclopentadienone complexes **9** and **11**. In both species the CO was inserted into a former triple bond. This observation led to the preparation of the tetrathiaalkyl- and tetrathiaaryl-substituted $C_5H_4(CO_2Me)Co$-capped cyclobutadiene complexes **23** and **27**−**30**. When these compounds were heated under a pressurized CO atmosphere at 170 °C, the corresponding cyclopentadienone complexes **9**, **15**, and **31**−**33** were formed. Model calculations at the B3LYP level of theory on tetrasubstituted (R = $CH_3$, SH, $(CH_2)_3$, S−$CH_2$−S) CpCo-capped cyclobutadiene complexes showed that the substitution, especially by SH and S−$CH_2$−S, considerably lowered the energy of the assumed intermediate metallacycles **35** and **36**, which opens the possibility of reaction.

## Introduction

Transition-metal-induced oligomerization reactions of triple bonds have comprised a pivotal part of organic synthesis since the seminal work of Reppe.[1] The di-, tri-, and tetramerizations of triple bonds allow short and efficient syntheses of homo- and heterocyclic ring systems. A reagent which is frequently used in these reactions is ($\eta^5$-cyclopentadienyl)dicarbonylcobalt(I), [$CpCo(CO)_2$].[2] The reaction of this compound with alkynes leads—depending on the reaction conditions—to CpCo-stabilized cyclobutadienes,[3] to cyclopentadienone complexes,[4] or even to benzene derivatives.[5] For the mechanisms of these reactions there have been two proposals reported in the literature. Brintzinger suggested the intermediacy of dicobalt complexes, which could be isolated.[6,7] A second mechanism was put forward by Rausch et al., which assumes intermediates with only one cobalt nucleus.[8] In this latter proposal it is assumed that both ligands (L) on the metal are exchanged in a stepwise fashion by one alkyne unit each (Scheme 1).

**Scheme 1**




This gives rise to the intermediates **A** and **B**. From **B** the 16e and 18e cobaltols **C** and **D** can emerge. From **C** the cyclobutadiene complex **E**, the cyclopentadienone

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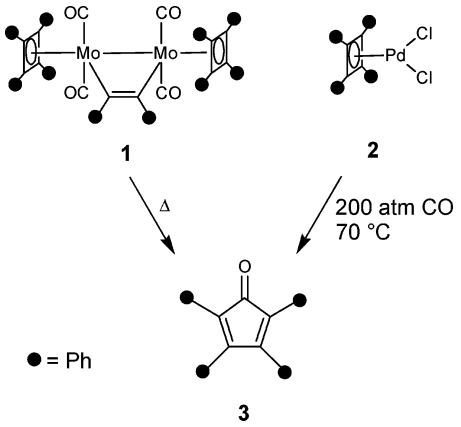
**Scheme 2**




complex **F**, and the benzene derivative **G** can be formed. This mechanism is supported by the observations that intermediates of types **A** and **D** could be isolated.[9−11]

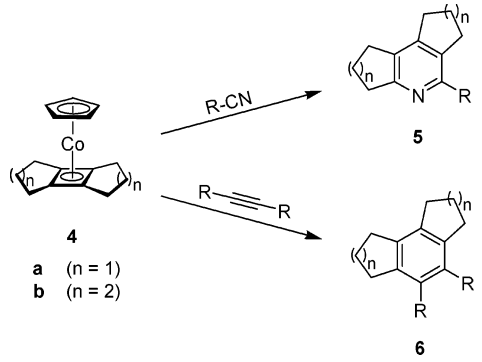
Although **B** and **C** could not be isolated, there is experimental evidence for their intermediacy. Studies on the pyrolysis of cyclobutadiene complexes in the gas phase by Vollhardt et al. excluded a $C_s$-symmetrical intermediate but favored a bis(alkyne) complex of type **B**.[12] On the basis of isomerization reactions an activation energy of 51.7 kcal/mol was reported.[12] This result was supported by quantum-mechanical calculations by Albright et al., which revealed that a direct rearrangement of the cyclobutadiene complex **E** into **C** is a symmetry-forbidden process and, therefore, a high activation energy is required.[13] This led to the conclusion that cyclobutadiene complexes are unreactive species which are involved neither in the cyclopentadienone nor in the benzene formation (Scheme 1).

However, the view that metal-stabilized cyclobutadiene complexes are rather unreactive has to be altered. Already in 1964 it was shown by Hübel[14] and also by Santarella[15] that the cyclobutadiene complexes **1** and **2** lead to tetraphenylcyclopentadienone **3** (Scheme 2).

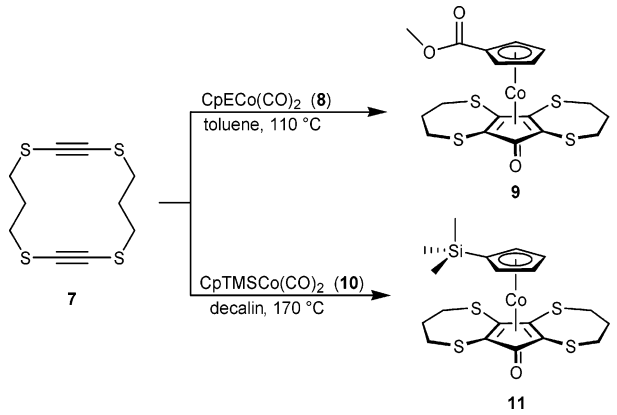
Furthermore, we could transform the CpCo-stabilized cyclobutadiene complexes **4a** and **4b** into the aromatic species **5** and **6** by heating with benzonitrile and dimethyl acetylenedicarboxylate (DMAD), respectively (Scheme 3).[16]

With this paper we intend to contribute further to an understanding of the reactivity of CpCo-stabilized cyclobutadiene complexes. We report on the results of an experimental and quantum-chemical study of one part of the mechanism shown in Scheme 1: namely, the reaction of cyclobutadiene complexes **E** with carbon monoxide, leading to the cyclopentadienone complexes **F**.

**Scheme 3**




**Scheme 4**




## Results and Discussion

In our investigation of the reaction between cyclic tetrathia-substituted diynes and $CpCo(CO)_2$ derivatives we found that the reaction of **7**[17] and $C_5H_4(CO_2Me)$-$Co(CO)_2$ (**8**) in toluene affords the cyclopentadienone complex **9** in 6% yield (Scheme 4).

When the solvent is changed to decalin and higher temperature is applied, the yield can be increased up to 33% for **9**. The same holds for the reaction of **7** and $C_5H_4(SiMe_3)Co(CO)_2$ (**10**) (Scheme 4). The cyclopentadienone complex **11** is formed in 36% yield in this reaction.

Interestingly the CO is inserted into one of the former triple bonds of the diyne **7**, which was proven by means of X-ray crystallography (Figure 1). Otherwise, one would expect the CO to be inserted between the two former triple bonds.

To find out whether the cyclopentadienone formation summarized in Scheme 4 is limited to cyclic tetrathiadiynes only or is dependent on substituents at the Cp ring, we reacted bis(methylthio)acetylene (**12**)[18] with the $CpRCo(CO)_2$ species **8**, **10**, and **13** under the same conditions (Scheme 5). It was found that the ester group provides the highest yields of the corresponding cyclo-

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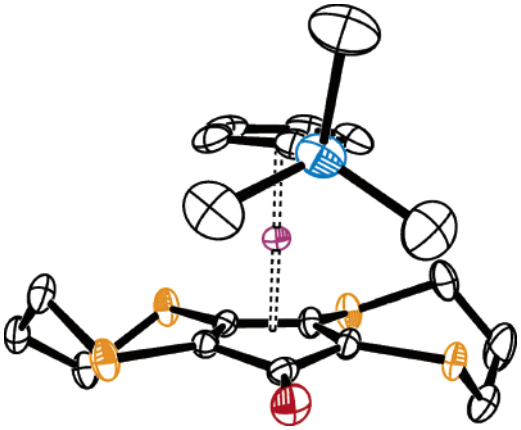
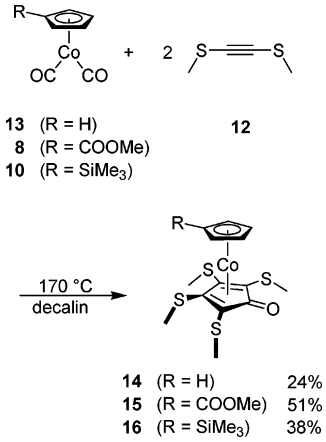


**Figure 1.** ORTEP representation of complex **11** (50% ellipsoid probability). Hydrogen atoms are omitted for the sake of clarity. Color scheme: red, O; blue, Si; orange, S; purple, Co.

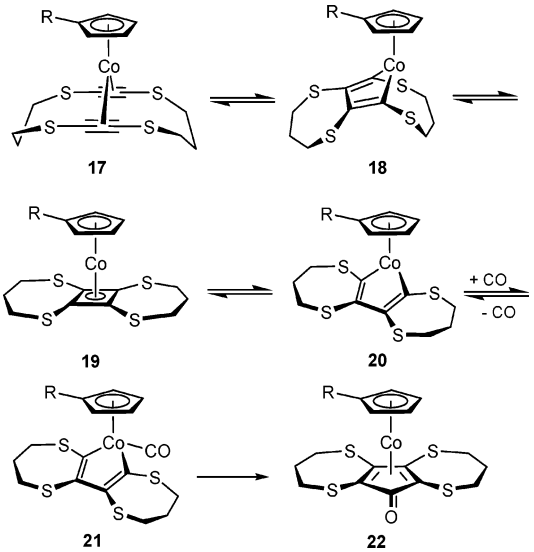
**Scheme 5**




pentadienone complexes **14**–**16** (Scheme 5). Therefore, we continued our investigations with this substituent at the Cp ring.

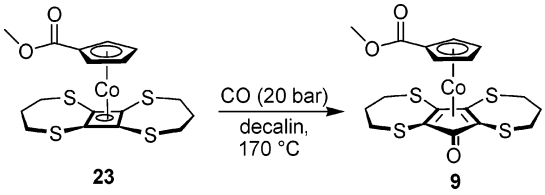
To rationalize the unexpected experimental result summarized in Scheme 4, we assume that this reaction proceeds via the mechanism shown in Scheme 6.

**Scheme 6**




In analogy to Rausch's mechanism (Scheme 1) the bis(alkyne) complex **17** is formed first, starting from a cyclic diyne. From this bis(alkyne) complex only the cobaltol **18** can be formed directly. Now an isomerization step has to occur, which could proceed via the intermediate cyclobutadiene complex **19**. From there both cobaltols **18** and **20** can be reached. For the formation of the cyclopentadienone complex **22** the cobaltol **20** has to be an intermediate in the reaction pathway. In complex **20** one former triple bond is broken and the CpCo fragment is inserted. This 16e complex is able to react with CO to afford the 18e cobaltol **21**. A rearrangement of **21** would lead to the final product **22**. To prove that a cyclobutadiene complex such as **19** is an active intermediate in the formation of the cyclopentadienone complexes, we dissolved complex **23**[19] in decalin and heated the solution to 170 °C under an atmosphere of 20 bar of CO (Scheme 7). We obtained cyclopentadienone complex **9** in 42% yield as the only product.

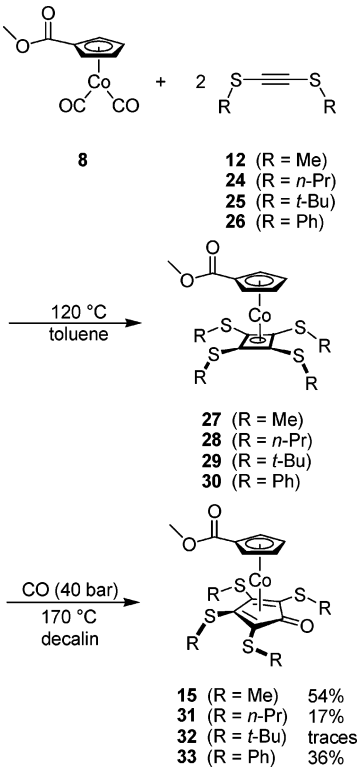
**Scheme 7**




As in the previous reactions (cf. Scheme 4), the CO is inserted in the same position with respect to the substituents. This leads to the assumption that a cobaltol intermediate analogous to **20** is formed during the reaction.

To find out whether the reaction sequence **17** → **22** (Scheme 6) depends on electronic and/or steric effects, we have prepared a variety of tetrathia-substituted cyclobutadiene complexes **27**–**30**[19] by reacting the dithia-substituted alkynes **12**[18] and **24**–**26**[20] with **8** (Scheme 8).

**Scheme 8**



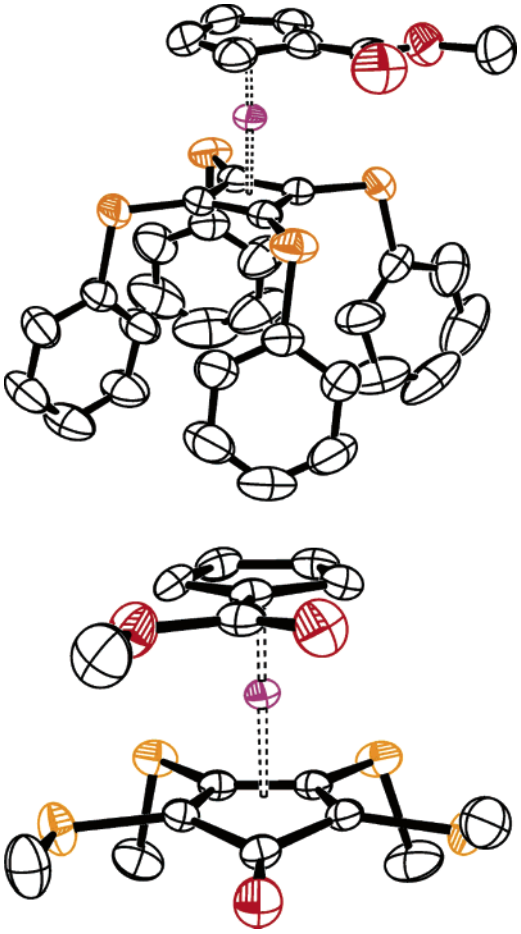


**Figure 2.** ORTEP representation of complexes **15** (bottom) and **30** (top) (50% ellipsoid probability). Hydrogen atoms are omitted for the sake of clarity. Color scheme: red, O; orange, S; purple, Co.

The complexes **27**−**30** were treated with 40 bar of CO in decalin and heated to 170 °C. As in the case of **23**, the corresponding cyclopentadienone complexes **15** and **31**−**33** were formed (Scheme 8). The obtained yields led us to conclude that the cyclopentadienone formation is easier with small substituents (Me in **15**) rather than with the bulky *tert*-butyl groups in **32**. In the latter case we could isolate 3 mg of the product; therefore, the identification is based on the high-resolution mass spectrometric data only.

**Structural Investigations.** Single crystals were available of the cyclobutadiene complexes of **27**[19] and **30** as well as of the cyclopentadienone complexes of **11** and **14**−**16**. The molecular structures of **15** and **30** are shown in Figure 2. For the cyclobutadiene complexes we find that the substituents at the sulfur centers are turned away from the CpCo moiety. In contrast, in the case of the cyclopentadienone complexes at least two groups are oriented parallel to the $\pi$ plane of the cyclopentadienone ring. This allows a good interaction between the 3p lone pairs at the sulfur atom and the $\pi$ system. The molecular parameters such as distances and angles recorded for **27** and **30** as well as for **9** and **14**−**16** parallel those reported for related systems.

**Theoretical Investigations.** To rationalize our experimental findings, we have carried out density functional theory (DFT) calculations[21] on the mechanism shown in Figure 3. To study the influence of electron-releasing substituents as well as ring strain, we have chosen neutral methyl groups (R = Me), electron-rich thiol groups (R = SH), bridging trimethylene chains (R∩R = $(CH_2)_3$), and, as a combination of ring strain and electron-donating character, S−$CH_2$−S chains (R∩R = S−$CH_2$−S).

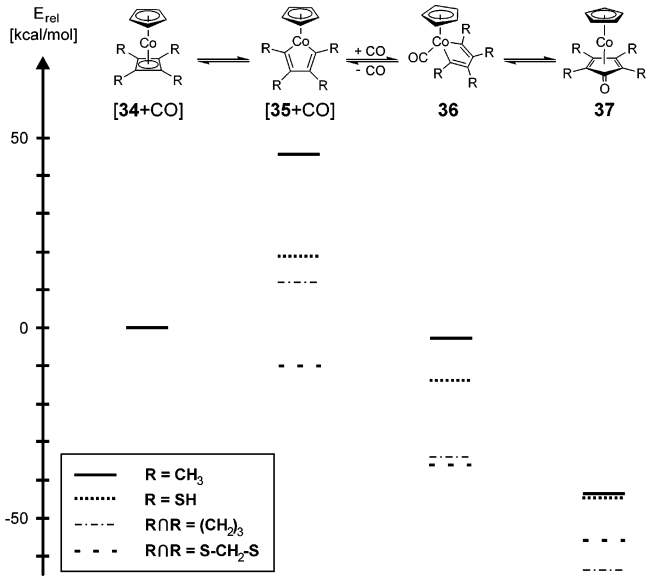



**Figure 3.** Calculated energies relative to the corresponding cyclobutadiene complex [**34** + CO].

**Table 1. Calculated Relative Energies (kcal/mol) of [34 + CO], [35 + CO], 36, and 37**

| | [**34** + CO] | [**35** + CO] | **36** | **37** |
|---|---|---|---|---|
| R = $CH_3$ | 0 | 45.7 | −3.0 | −44.5 |
| R = SH | 0 | 18.7 | −13.8 | −44.1 |
| R∩R = $(CH_2)_3$ | 0 | 11.9 | −34.0 | −63.6 |
| R∩R = S−$CH_2$−S | 0 | −10.1 | −35.7 | −55.6 |

The resulting energies relative to the corresponding cyclobutadiene complexes [**34** + CO] are listed in Table 1 and depicted in Figure 3. The energy of the cyclobutadiene complexes [**34** + CO] is set to 0 kcal/mol. The influence of the substituents R is reflected in the change of energy in comparison to that for the methyl-substituted complexes (R = Me) which were chosen as reference compounds. It is apparent that the influence of the substituents R = SH, R∩R = $(CH_2)_3$, and R∩R = S−$CH_2$−S is stabilizing compared to that of R = Me. The largest influence results for the substituted cobaltol intermediates [**35** + CO]. Here the stabilization energies with regard to the methyl-substituted derivative are as follows: for R = SH, −27.0 kcal/mol; for the trimethylene-bridged derivative R = $(CH_2)_3$, −33.8 kcal/mol; for the derivative with bridging S−$CH_2$−S tethers R∩R = S−$CH_2$−S, −55.8 kcal/mol. In contrast to this observation the same substituents have significantly less effect on the relative energy of the cyclopentadienone complexes **37**.

Provided that the compounds **34** and **35** are in thermodynamic equilibrium, the stabilizing effect should

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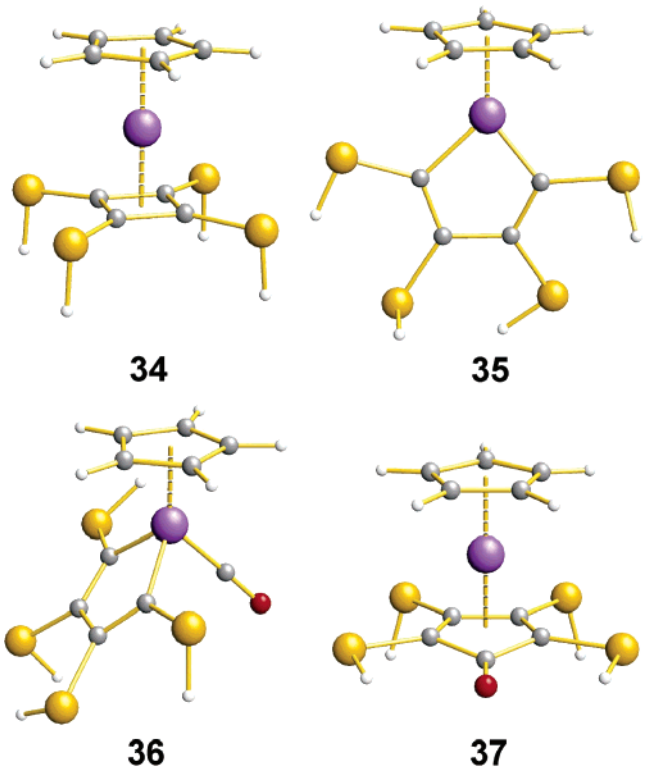


**Figure 4.** DFT (B3LYP) optimized structures **34**−**37** for R = SH.

lead to a shift of the equilibrium toward **35**. As cobaltol **35** is the reactive 16-electron species required for the reaction with a CO molecule, the reactivity toward CO should be enhanced by substituents that stabilize the transition state between **34** and **35**. Though we were not able to localize this transition state, we assume that substituents leading to a substantial stabilization of **35** are likely to stabilize the transition state as well. This assumption is in agreement with the strong endothermic reaction path and, therefore, a product-like transition state receptive to similar substituent effects such as **35**. The proposed large stabilizing effects of SH groups on **35** is in line with the experimentally found enhanced reactivity for the SR-substituted derivative of **34**. In the case of the 2-fold trimethylene-bridged derivative of **34**, the reactivity toward CO could be expected to be increased as well, and therefore a CO insertion leading to a cyclopentadienone complex should be possible. When ring strain and electron-donating sulfur atoms are combined, the most dramatic effect is to be expected. For this derivative (R∩R = S−$CH_2$−S) the cobaltol intermediate [**35** + CO] is located energetically lower than the respective cyclobutadiene complex [**34** + CO]. Therefore, we suspect that the attempted synthesis of the cyclobutadiene complex should finally yield the isolable cobaltol **35** instead. As until now there has existed no isolated, structurally investigated example of this reactive intermediate, the synthesis of this compound still remains a challenging goal.

In Figure 4 we show the optimized structures of **34**−**37** for R = SH. For **34** calculations predict a conformation in which the 3p orbital at each SH group is oriented perpendicular to the plane of the cyclobutadiene ring. This result mirrors the X-ray data of **27** and **30**. For the 16-valence-electron species **35** three of the four SH groups are oriented in such a way that the conjugation with the metallacycle and the occupied 3p orbitals at the SH groups is optimal. Similarly, the conjugation between the SH groups and the adjacent $\pi$ system of **36** is better than in **34**. In **37** the SH groups in positions $\alpha$ to the CO group of the cyclopentadienone ring show a conformation which allows 3p−$\pi$ interaction, whereas the SH groups at the $\beta$-position adopt the same conformation as in **34**. The conformations of the SH groups in **37** are very close to those crystallographically found in **14**−**16**.

## Conclusions

Our investigations on tetrathia-substituted CpCo-capped cyclobutadiene complexes revealed an enhanced reactivity of these complexes toward CO insertion. This observation can be rationalized by assuming an equilibrium between the cyclobutadiene complex and a metallacyclopentadiene species. This assumption is supported by DFT calculations on assumed intermediates. These calculations furthermore suggest that the metallacyclopentadiene complexes substituted with S−$CH_2$−S bridges should be stable enough to be isolated.

## Experimental Section

**General Remarks.** 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 the solvent as an internal standard ($\delta$). 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 an argon atmosphere using dried and oxygen-free solvents. The reactions with carbon monoxide were performed in high-pressure vessels (Roth). Starting materials were prepared according to literature methods.[17,18,20,22]

**General Procedure for the Synthesis of the Cyclobutadiene Complexes.** $C_5H_4(CO_2Me)Co(CO)_2$ (**8**) and the alkyne were dissolved in toluene. The mixture was stirred at 120 °C for 3 days. After it was cooled to room temperature, the reaction mixture was separated by column chromatography (silica gel) using a gradient of *n*-hexane → diethyl ether as eluant.

**(a) ($\eta^5$-(Methoxycarbonyl)cyclopentadienyl)($\eta^4$-tetrakis(*n*-propylthio)cyclobutadiene)cobalt(I) (28).** This compound was prepared from $C_5H_4(CO_2Me)Co(CO)_2$ (**8**; 476 mg, 2.00 mmol) and alkyne **24** (697 mg, 4.00 mmol) in toluene (125 mL). Yield: 552 mg (52%) of a yellow-orange oil. $^1$H NMR (500 MHz, $C_6D_6$; $\delta$): 0.89 (t, $^3J$ = 7.4 Hz, 12H, C$H_3$), 1.59 (m, 8H, C$H_2$CH$_3$), 2.80 (t, $^3J$ = 7.4 Hz, 8H, SC$H_2$), 3.65 (s, 3H, OC$H_3$), 4.86 (ps, 2H, Cp *H*), 5.62 (ps, 2H, Cp *H*). $^{13}$C NMR (125 MHz, $C_6D_6$; $\delta$): 13.5 (*C*H$_3$), 23.7 (*C*H$_2$CH$_3$), 37.5 (S*C*H$_2$), 51.3 (O*C*H$_3$), 82.3 (Cbd *C*), 84.0 (Cp *C*H), 85.7 (Cp *C*H), 88.4 (Cp *C*−$CO_2$Me), 166.4 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 2961, 2931, 2872, 1717, 1467, 1281, 1143. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$): 238 (4.37), 316 (4.16), 356 (3.33). HR-MS (FAB+; *m/z*): calcd for $C_{23}H_{35}O_2S_4Co$ ($M^+$), 530.0852; found, 530.0827. Anal. Calcd for $C_{23}H_{35}O_2S_4Co$: C, 52.05; H, 6.65; S, 24.17. Found: C, 52.17; H, 6.65; S, 24.00.

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**(b) ($\eta^5$-(Methoxycarbonyl)cyclopentadienyl)($\eta^4$-tetrakis(*tert*-butylthio)cyclobutadiene)cobalt(I) (29).** This compound was prepared from $C_5H_4(CO_2Me)Co(CO)_2$ (**8**; 476 mg, 2.00 mmol) and alkyne **25** (810 mg, 4.00 mmol) in toluene (125 mL). Yield: 117 mg (10%) of a yellow solid (mp 69 °C). $^1$H NMR (500 MHz, $C_6D_6$; $\delta$): 1.42 (s, 36H, C(C$H_3$)$_3$), 3.91 (s, 3H, OC$H_3$), 5.08 (ps, 2H, Cp *H*), 5.49 (ps, 2H, Cp *H*). $^{13}$C NMR (125 MHz, $C_6D_6$; $\delta$): 17.2 (C(*C*H$_3$)$_3$), 29.5 (*C*(CH$_3$)$_3$), 50.8 (O*C*H$_3$), 81.9 (Cbd *C*), 83.2 (Cp *C*H), 84.6 (Cp *C*H), 88.0 (Cp *C*−CO$_2$Me), 166.1 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 2960, 2920, 2860, 1721, 1469, 1364, 1144. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 252 (4.45), 326 (4.11), 374 (2.95). HR-MS (FAB+; *m/z*): calcd for $C_{27}H_{43}O_2S_4Co$ (M$^+$), 586.1478; found, 586.1436. Anal. Calcd for $C_{27}H_{43}O_2S_4Co$: C, 55.26; H, 7.39; S, 21.86. Found: C, 55.66; H, 7.24; S, 21.43.

**(c) ($\eta^5$-(Methoxycarbonyl)cyclopentadienyl)($\eta^4$-tetrakis(phenylthio)cyclobutadiene)cobalt(I) (30).** This compound was prepared from $C_5H_4(CO_2Me)Co(CO)_2$ (**8**; 476 mg, 2.00 mmol) and alkyne **26** (969 mg, 4.00 mmol) in toluene (125 mL). Yield: 200 mg (15%) of a yellow solid (mp 128 °C). $^1$H NMR (500 MHz, $C_6D_6$; $\delta$): 3.94 (s, 3H, OC$H_3$), 5.01 (ps, 2H, Cp *H*), 5.48 (ps, 2H, Cp *H*), 6.91 (m, 8H, C(Ph) *H*), 7.15 (m, 8H, C(Ph) *H*), 7.21 (m, 4H, C(Ph) *H*). $^{13}$C NMR (125 MHz, $C_6D_6$; $\delta$): 52.0 (O*C*H$_3$), 82.5 (Cbd *C*), 84.7 (Cp *C*H), 86.2 (Cp *C*H), 87.9 (Cp *C*−CO$_2$Me), 126.7 (Ph *C*H$_{para}$), 128.4 and 130.2 (Ph *C*H$_{ortho/meta}$), 165.9 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 2961, 2931, 2872, 1723, 1622, 1470, 1278, 1145. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 262 (4.16), 366 (4.18), 434 (3.40). HR-MS (FAB+; *m/z*): calcd for $C_{35}H_{27}O_2S_4Co$ (M$^+$), 666.0226; found, 666.0225. Anal. Calcd for $C_{35}H_{27}O_2S_4Co$: C, 63.05; H, 4.08; S, 19.23. Found: C, 63.47; H, 4.16; S, 18.84.

**General Procedure for the Synthesis of the Cyclopentadienone Complexes via Cyclization.** $C_5H_4(CO_2Me)Co(CO)_2$ (**8**), $C_5H_4(SiMe_3)Co(CO)_2$ (**10**), or $CpCo(CO)_2$ (**13**) and the alkyne were dissolved in decalin (60 mL) and stirred at 170 °C for 2 days. After it was cooled to room temperature, the reaction mixture was separated by column chromatography (Alox III) using a gradient of *n*-hexane → dichloromethane → methanol as eluant.

**(a) Cyclopentadienone Complex 9.** This compound was prepared from $C_5H_4(CO_2Me)Co(CO)_2$ (**8**; 358 mg, 1.50 mmol) and tetrathiacyclodiyne **7** (390 mg, 1.50 mmol) in decalin (60 mL). Yield: 233 mg (33%) of a deep red oil. $^1$H NMR (500 MHz, $CDCl_3$; $\delta$): 2.22 (m, 4H, $CH_2CHHCH_2$), 3.12 (m, 2H, SC*H*H), 3.24−3.33 (m, 6H, C*H*HC$H_2$C*HH*), 3.90 (s, 3H, OC$H_3$), 5.07 (ps, 2H, Cp *H*), 5.31 (ps, 2H, Cp *H*). $^{13}$C NMR (125 MHz, $CDCl_3$; $\delta$): 31.1 (*C*H$_2$), 32.1 (*C*H$_2$), 32.4 (*C*H$_2$), 52.3 (O*C*H$_3$), 84.5 (Cpd *C*), 85.6 (Cp *C*H), 88.6 (Cpd *C*), 89.6 (Cp *C*H), 93.9 (Cp *C*−CO$_2$Me), 151.5 (Cpd *C*O), 164.5 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 2925, 2223, 1719, 1603, 1470, 1369, 1280, 1193, 1146. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 246 (3.93), 360 (4.10), 408 (3.14). HR-MS (FAB+; *m/z*): calcd for $C_{18}H_{20}O_3S_4Co$ (M$^+$ + H), 470.9627; found, 470.9635.

**(b) Cyclopentadienone Complex 11.** This compound was prepared from $C_5H_4(SiMe_3)Co(CO)_2$ (**10**; 290 mg, 1.13 mmol) and tetrathiacyclodiyne **7** (295 mg, 1.13 mmol) in decalin (60 mL). Yield: 192 mg (36%) of a deep red solid (mp 212 °C). $^1$H NMR (300 MHz, $CDCl_3$; $\delta$): 0.28 (s, 9H, Si(C$H_3$)$_3$), 2.13 (m, 2H, $CH_2CHHCH_2$), 2.27 (m, 2H, $CH_2CHHCH_2$), 2.99−3.11 (m, 8H, C*HH*C$H_2$C*HH*), 4.76 (ps, 2H, Cp *H*), 4.94 (ps, 2H, Cp *H*) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$; $\delta$): −0.9 (Si(*C*H$_3$)$_3$), 31.1 (*C*H$_2$), 32.9 (S*C*H$_2$), 33.6 (S*C*H$_2$), 81.9 (Cpd *C*), 88.5 (Cp *C*H), 90.2 (Cp *C*H), 90.5 (Cp *C*−TMS), 94.3 (Cpd *C*), 153.2 (Cpd *C*O). IR (KBr; cm$^{-1}$): 2919, 1603, 1412, 1298, 1248, 839. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 248 (4.10), 320 (3.84), 356 (4.23), 426 (3.24). HR-MS (FAB+; *m/z*): calcd for $C_{19}H_{26}OS_4SiCo$ (M$^+$ + H), 484.9968; found, 484.9939. Anal. Calcd for $C_{19}H_{25}OS_4SiCo$: C, 47.08; H, 5.20; S, 26.46. Found: C, 47.25, H, 5.23; S, 26.48.

**(c) ($\eta^5$-Cyclopentadienyl)($\eta^4$-tetrakis(methylthio)cyclopentadienone)cobalt(I) (14).** This compound was prepared from $CpCo(CO)_2$ (**13**; 304 mg, 1.69 mmol) and alkyne **12** (400 mg, 3.38 mmol) in decalin (50 mL). Yield: 158 mg (24%) of a red solid (mp 106 °C). $^1$H NMR (300 MHz, $CDCl_3$; $\delta$): 2.37 (s, 6H, SC$H_3$), 2.64 (s, 6H, SC$H_3$), 4.93 (s, 5H, Cp *H*). $^{13}$C NMR (75 MHz, $C_6D_6$; $\delta$): 15.7 (S*C*H$_3$), 19.1 (S*C*H$_3$), 84.2 (Cp *C*H), 86.8 (Cpd *C*), 93.2 (Cpd *C*), 157.0 (*C*O). IR (KBr; cm$^{-1}$): 2987, 1688, 1612, 1415, 1302. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 258 (4.14), 350 (4.19), 438 (3.32). HR-MS (FAB+; *m/z*): calcd for $C_{14}H_{18}OS_4Co$ (M$^+$ + H), 388.9543; found, 388.9573. Anal. Calcd for $C_{14}H_{17}OS_4Co$: C, 43.28; H, 4.41; S, 33.02. Found: C, 43.57; H, 4.49; S, 32.81.

**(d) ($\eta^5$-Methoxycyclopentadienyl)($\eta^4$-tetrakis(methylthio)cyclopentadienone)cobalt(I) (15).** This compound was prepared from $C_5H_4(CO_2Me)Co(CO)_2$ (**8**; 180 mg, 0.76 mmol) and alkyne **12** (178 mg, 1.51 mmol) in decalin (50 mL). Yield: 172 mg (51%) of a red solid (mp 124 °C). $^1$H NMR (300 MHz, $C_6D_6$; $\delta$): 2.03 (s, 6H, SC$H_3$), 2.35 (s, 6H, SC$H_3$), 3.52 (s, 3H, OC$H_3$), 4.71 (ps, 2H, Cp *H*), 5.02 (ps, 2H, Cp *H*). $^{13}$C NMR (75 MHz, $C_6D_6$; $\delta$): 14.4 (S*C*H$_3$), 18.1 (S*C*H$_3$), 52.0 (O*C*H$_3$), 85.1 (Cp *C*H), 86.4 (Cp *C*H), 87.8 (Cpd *C*), 88.5 (Cp *C*−CO$_2$Me), 92.8 (Cpd *C*), 156.1 (Cpd *C*O), 164.5 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 3095, 2979, 1715, 1601, 1461, 1369, 1141. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 241 (4.35), 362 (4.29), 428 (3.43). HR-MS (FAB+; *m/z*): calcd for $C_{16}H_{20}O_3S_4Co$ (M$^+$ + H), 446.9628; found, 446.9609. Anal. Calcd for $C_{16}H_{19}O_3S_4Co \times 0.1\ C_6H_{14}$: C, 43.81; H, 4.52; S, 28.18. Found: C, 43.73; H, 4.43; S, 27.99.

**(e) ($\eta^5$-(Trimethylsilyl)cyclopentadienyl)($\eta^4$-tetrakis(methylthio)cyclopentadienone)cobalt(I) (16).** This compound was prepared from $C_5H_4(SiMe_3)Co(CO)_2$ (**10**; 192 mg, 0.76 mmol) and alkyne **12** (178 mg, 1.51 mmol) in decalin (50 mL). Yield: 133 mg (38%) of an orange solid (mp 103 °C). $^1$H NMR (300 MHz, $CDCl_3$; $\delta$): 0.32 (s, 9H, Si(C$H_3$)$_3$), 2.37 (s, 6H, SC$H_3$), 2.65 (s, 6H, SC$H_3$), 4.77 (ps, 2H, Cp *H*), 5.07 (ps, 2H, Cp *H*). $^{13}$C NMR (75 MHz, $CDCl_3$; $\delta$): −0.6 (Si*C*), 15.5 (S*C*H$_3$), 19.1 (S*C*H$_3$), 85.6 (Cpd *C*), 87.9 (Cp *C*H), 88.7 (Cp *C*H), 92.8 (*C*), 93.3 (*C*), 157.9 (*C*O). IR (KBr; cm$^{-1}$): 3087, 2951, 1610, 1601, 1423, 1303, 1159. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 256 (4.05), 354 (4.11), 414 (3.31), 424 (3.25), 440 (3.16). HR-MS (FAB+): calcd for $C_{17}H_{26}OSiS_4Co$ (M$^+$ + H), 460.9968; found, 460.9987. Anal. Calcd for $C_{17}H_{25}OSiS_4Co$: C, 44.32; H, 5.47. Found: C, 44.83; H, 5.58.

**General Procedure for the Synthesis of Cyclopentadienone Complexes via CO Insertion.** A solution of the cyclobutadiene complex in decalin (80 mL) was stirred at 170 °C under a CO atmosphere in a high-pressure vessel for 15 h. After it was cooled to room temperature, the reaction mixture was separated by column chromatography (Alox III) using a gradient of *n*-hexane → dichloromethane → methanol as eluant.

**(a) Cyclopentadiene Complex 9.** This compound was prepared from the cyclobutadiene complex **16** (90 mg, 0.20 mmol) and CO (20 bar) in decalin (80 mL). Yield: 40 mg (42%). For analytical data, see above.

**(b) ($\eta^5$-Methoxycyclopentadienyl)($\eta^4$-tetrakis(methylthio)cyclopentadienone)cobalt(I) (15).** This compound was prepared from the cyclobutadiene complex **27** (280 mg, 0.67 mmol) and CO (40 bar) in decalin (80 mL). Yield: 162 mg (54%). For analytical data, see above.

**(c) ($\eta^5$-Methoxycyclopentadienyl)($\eta^4$-tetrakis(*n*-propylthio)cyclopentadienone)cobalt(I) (31).** This compound was prepared from the cyclobutadiene complex **28** (159 mg, 0.30 mmol) and CO (40 bar) in decalin (80 mL). Yield: 28 mg (17%) of a red solid (mp 143 °C). $^1$H NMR (500 MHz, $C_6D_6$; $\delta$): 0.86 (t, $^3J$ = 7.4 Hz, 6H, C$H_3$), 0.98 (t, $^3J$ = 7.4 Hz, 6H, C$H_3$), 1.47 (m, 4H, C$H_2$CH$_3$), 1.71 (m, 4H, C$H_2$CH$_3$), 2.73 (m, 2H, SC$H_2$), 2.86 (m, 2H, SC$H_2$), 3.18 (m, 2H, SC$H_2$), 3.68 (s, 3H, OC$H_3$), 3.95 (m, 2H, SC$H_2$), 4.62 (ps, 2H, Cp *H*), 5.28 (ps, 2H, Cp *H*). $^{13}$C NMR (125 MHz, $C_6D_6$; $\delta$): 13.5 (*C*H$_3$), 13.7 (*C*H$_3$), 23.6 (*C*H$_2$CH$_3$), 24.1 (*C*H$_2$CH$_3$), 33.2 (S*C*H$_2$), 37.4 (S*C*H$_2$), 51.7 (O*C*H$_3$), 86.4 (Cp *C*H), 87.3 (Cp *C*H), 88.7 (Cp *C*−CO$_2$Me), 89.0 (Cpd *C*), 92.0 (Cpd *C*), 156.6 (Cpd *C*O), 164.7 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 3091, 2975, 1605, 1430, 1354, 1134. UV−vis ($CH_2Cl_2$;

**Table 2. Crystallographic Data and Details of the Refinement Procedure of 11, 14−16, and 30**

| | 11 | 14 | 15 | 16 | 30 |
|---|---|---|---|---|---|
| empirical formula | $C_{19}H_{25}OS_4SiCo$ | $C_{14}H_{17}OS_4Co$ | $C_{16}H_{19}O_3S_4Co$ | $C_{17}H_{25}OS_4SiCo$ | $C_{35}H_{27}O_2S_4Co$ |
| formula wt | 484.65 | 388.48 | 446.48 | 460.66 | 666.74 |
| cryst syst | triclinic | triclinic | monoclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| $Z$ | 2 | 6 | 4 | 4 | 2 |
| unit cell dimens | | | | | |
| $a$ (Å) | 8.8194(1) | 9.1494(3) | 16.4714(6) | 7.9711(1) | 10.3437(6) |
| $b$ (Å) | 8.8964(1) | 12.4455(5) | 8.3209(3) | 14.6145(2) | 10.4068(6) |
| $c$ (Å) | 14.4346(2) | 22.3392(8) | 15.0158(5) | 17.7756(1) | 14.8969(9) |
| α (deg) | 76.275(1) | 79.022(1) | 90 | 90 | 93.530(1) |
| $\beta$ (deg) | 86.030(1) | 83.800(1) | 114.331(1) | 95.805(1) | 93.912(1) |
| $\gamma$ (deg) | 84.964(1) | 79.226(1) | 90 | 90 | 102.042(1) |
| $V$ (Å$^3$) | 1094.59(2) | 2446.3(2) | 1875.23(11) | 2060.13(4) | 1559.9(2) |
| $D_{calcd}$ (g/cm$^3$) | 1.47 | 1.58 | 1.58 | 1.49 | 1.42 |
| abs coeff (mm$^{-1}$) | 1.23 | 1.56 | 1.37 | 1.30 | 0.85 |
| cryst shape | polyhedron | polyhedron | polyhedron | needle | prism |
| cryst size (mm$^3$) | 0.42 × 0.34 × 0.10 | 0.21 × 0.10 × 0.02 | 0.41 × 0.10 × 0.07 | 0.50 × 0.12 × 0.10 | 0.31 × 0.20 × 0.15 |
| $\theta$ range for data collecn (deg) | 2.3−27.5 | 0.9−25.6 | 1.4−27.5 | 1.8−27.5 | 2.0−28.3 |
| index ranges | $-11 \le h \le 11$ | $-11 \le h \le 11$ | $-21 \le h \le 21$ | $-10 \le h \le 10$ | $-13 \le h \le 13$ |
| | $-11 \le k \le 11$ | $-15 \le k \le 15$ | $-10 \le k \le 10$ | $-18 \le k \le 18$ | $-13 \le k \le 13$ |
| | $-18 \le l \le 18$ | $-27 \le l \le 27$ | $-19 \le l \le 19$ | $-23 \le l \le 23$ | $-19 \le l \le 19$ |
| no. of rflns collected | 11 392 | 23 034 | 18 886 | 21 109 | 16 316 |
| no. of indep rflns | 4985 | 9560 | 4300 | 4731 | 7629 |
| no. of obsd rflns | 4434 | 5088 | 3175 | 3843 | 6124 |
| max/min transmissn | 0.89/0.63 | 0.97/0.74 | 0.91/0.60 | 0.88/0.56 | 0.88/0.78 |
| no. of data/restraints/params | 4985/11/251 | 9560/0/553 | 4300/0/222 | 4731/0/224 | 7629/0/380 |
| goodness of fit on $F^2$ | 1.06 | 0.95 | 1.04 | 1.04 | 1.02 |
| $R(F)$ | 0.026 | 0.049 | 0.032 | 0.027 | 0.038 |
| $R_w(F^2)$ | 0.065 | 0.067 | 0.061 | 0.057 | 0.097 |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å$^{-3}$) | 0.48, −0.39 | 0.49, −0.44 | 0.31, −0.33 | 0.32, −0.27 | 0.48, −0.26 |

$\lambda_{max}$/nm (log $\epsilon$)): 239 (4.31), 360 (4.01), 431 (3.27). HR-MS (FAB+; *m/z*): calcd for $C_{24}H_{36}O_3S_4Co$ ($M^+$ + H), 559.0879; found, 559.0859. Anal. Calcd for $C_{24}H_{35}O_3S_4Co$: C, 51.59; H, 6.31; S 22.96. Found: C, 51.61; H, 6.40; S, 22.89.

**(d) ($\eta^5$-Methoxycyclopentadienyl)($\eta^4$-tetrakis(phenylthio)cyclopentadienone)cobalt(I) (33).** This compound was prepared from the cyclobutadiene complex **30** (113 mg, 0.17 mmol) and CO (40 bar) in decalin (80 mL). Yield: 43 mg (36%) of a red solid (mp 139 °C). $^1$H NMR (300 MHz, $CDCl_3$; $\delta$): 3.99 (s, 3H, OC*H*$_3$), 4.98 (pt, 2H, Cp *H*), 5.34 (pt, 2H, Cp *H*), 6.75−6.88 (m, 8H, C(Ph) *H*), 6.89−6.97 (m, 2H, C(Ph) *H*), 7.04−7.18 (m, 6H, C(Ph) *H*), 7.41−7.47 (m, 4H, C(Ph) *H*). $^{13}$C NMR (75 MHz, $CDCl_3$; $\delta$): 52.6 (O*C*H$_3$), 84.0 (Cpd *C*), 85.7 (Cp *C*H), 88.2 (Cp *C*H), 89.0 (Cp *C*−CO$_2$Me), 97.2 (Cpd *C*), 127.0 (Ph *C*H$_{para}$), 127.5 (Ph *C*H$_{para}$), 128.5 (Ph *C*H$_{ortho/meta}$), 128.6 (Ph *C*H$_{ortho/meta}$), 130.1 (Ph *C*H$_{ortho/meta}$), 131.9 (Ph *C*H$_{ortho/meta}$), 159.5 (Cpd *C*O), 165.9 (*C*O$_2$Me). IR (KBr; cm$^{-1}$): 3092, 2975, 1599, 1454, 1365, 1138. UV−vis ($CH_2Cl_2$; $\lambda_{max}$/nm (log $\epsilon$)): 237 (4.11), 363 (4.59), 359 (3.18). HR-MS (FAB+; *m/z*): calcd for $C_{36}H_{27}O_3S_4Co$ ($M^+$), 694.0175; found, 694.0204. Anal. Calcd for $C_{36}H_{27}O_3S_4Co$: C, 62.24; H, 3.91. Found: C, 62.48; H, 4.08.

**X-ray Diffraction Analyses.** The reflections were collected with a Bruker Smart CCD diffractometer (Mo Kα radiation, graphite monochromator). The data were collected at 200 K except for **30** which was recorded at 296 K. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS,[23] based on the Laue symmetry of the reciprocal space. 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 ($F^2$). The hydrogen atom locations were calculated according to stereochemical aspects. Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[23] ORTEP drawings were obtained using the ORTEP-3 for Windows program by Farrugia.[24] Table 2 contains the crystallographic data and details of the data collection and refinement procedure. In the case of **14**, we found three crystallographically independent molecules in the asymmetric unit, which is rather unusual. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) +44-1223/336-033; e-mail, data_request@ccdc.cam.ac.uk), on quoting the deposition numbers CCDC-261360 (**11**), CCDC-261361 (**14**), CCDC-261362 (**15**), CCDC-261363 (**16**), and CCDC-261364 (**30**).

**Computational Details.** All the calculations were performed using the GAUSSIAN98 program package.[25] The structures were fully optimized by Becke's three-parameter hybrid functional[26] combined with the Lee−Yang−Parr[27] correlation functional (abbreviated as B3LYP) level of density functional theory, using the 6-311G(d) basis set[28] for C, O, S, and H. For Co we have chosen Wachters' (14s, 9p, 5d) basis set[29] augmented with a 4f polarization function. All stationary points have been identified as local minima (number of imaginary frequencies, NImag = 0). For graphical displays we used the MOLEK-9000 program.[30]

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**Supporting Information Available:** Crystal data (CIF files) for compounds **11**, **14**−**16**, and **30** and Gaussian archive entries of all calculated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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