# Modes of Reactivity of Cyclic Diynes: Probing the *syn*/*anti* Selectivity of Tetrathiacycloalkadiynes and Mono(alkyne)cobalt Complexes

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Cyclic tetrathiaalkadiynes in which two 1,4-dithiaalkyne units are connected with alkane bridges of length $n$ and $m$ [**A(*m.n*)**] were treated with [η$^2$-bis(*tert*-butylsulfonyl)acetylene]carbonyl(η$^5$-cyclopentadienyl)cobalt(I) (**8a**) and several substituted analogues (**8b**–**8e**) in order to probe the reactivity of electron-rich cyclic diynes. Both mono- [**B(*m.n*)**] and bis(cyclobutadiene) [**C(*m.n*)**] complexes were isolated as products of these reactions and the *anti*/*syn* ratio of **C(*m.n*)** was determined. For $m$, $n < 4$ the *syn* isomers dominate and this is attributed to the configuration of the intermediate metallacycle which is correlated with the conformations of the rings in the mono(cyclobutadiene) products **B(*m.n*)**. This analysis was corroborated by X-ray structural investigations of the products.

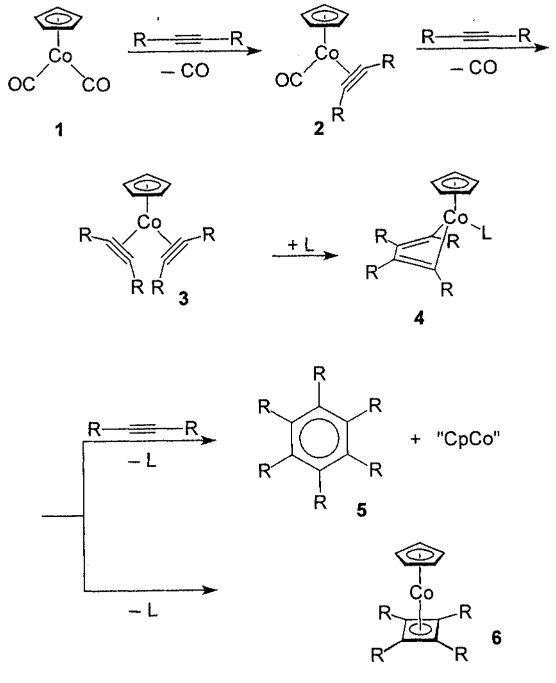
## Introduction

Dicarbonyl(η$^5$-cyclopentadienyl)cobalt [CpCo(CO)$_2$] (**1**) is a very convenient and efficient reagent for the di- and trimerisation of alkynes.[1] Two different mechanisms have been proposed for this reaction. One involves (alkyne)dicobalt complexes[2] whereas the other assumes that the reaction occurs on one CpCo fragment only.[3–5] The latter seems to be preferred at low temperatures whereas polynuclear complexes may play a role at higher temperatures.[2] The mechanism involving only one CpCoL$_2$ unit, in which the ligands are replaced successively by the alkyne to yield a 16-electron metallacycle which is converted to an 18-electron species **4** by an additional ligand L, is outlined briefly in Scheme 1.

The fact that derivatives of **2** and **4** have been isolated at room temperature[6–9] and that the alkynes react either to cyclobutadiene (**6**)[10] or to aromatic species (**5**)[4] support this mechanism.

Recently, we found a mild and efficient procedure to isolate congeners of **2** by treating **1** with bis(*tert*-butylsulfonyl)acetylene (BTSA, **7**).[7] The resulting complex **8** reacts under very mild conditions with electron-rich alkynes to yield the cyclobutadiene complexes **9**. The reactions with dithiaalkynes (R = SR′ in Scheme 2) were especially efficient.[11]

In view of the complex mechanism of cyclobutadiene formation (Scheme 1) it is of general interest to test the reactivity of electron-rich cyclic diynes with the electrophile **8**, and to see if there is any preference for one of the two possible products (*syn* or *anti*). For cyclic tetrathiadiynes **A(*m.n*)** the anticipated products **B(*m.n*)R**, and *syn*- and *anti*-**C(*m.n*)R** are shown in Scheme 3.



Scheme 1

## Results

We used the recently prepared cyclic tetrathiadiynes **A(2.2)** to **A(5.5)**[12] and [η$^2$-bis(*tert*-butylsulfonyl)acetylene]-

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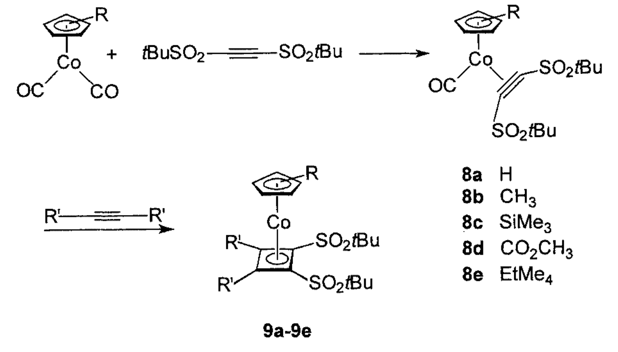
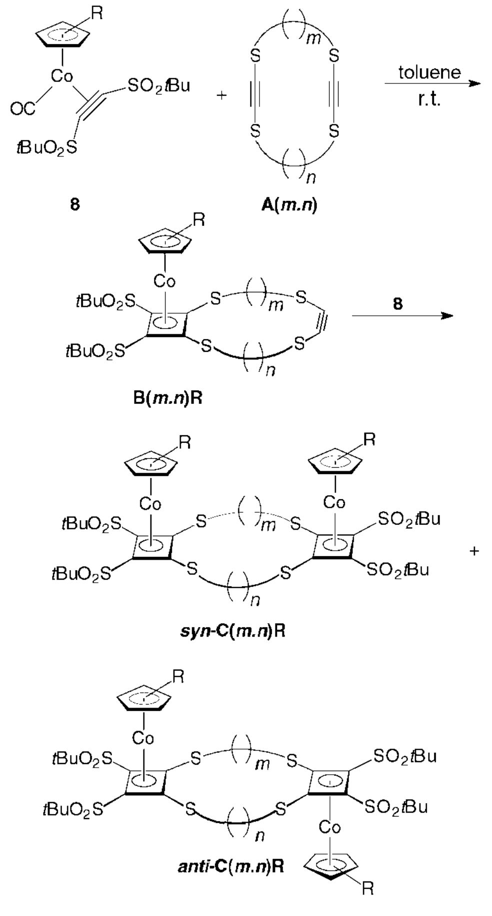


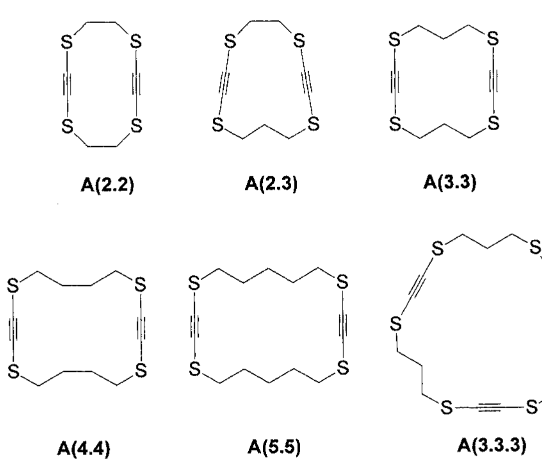
Scheme 2



Scheme 3

carbonyl(η$^5$-cyclopentadienyl)cobalt(I) (**8a**) and several analogues **8b**−**8e** substituted at the Cp ring[7] as starting materials.

The cyclic tetrathiadiynes **A(*m.n*)** were treated with **8a**−**8e** in 1:1 and 2:1 ratios at room temperature in toluene as solvent to give the 1:1 and 2:1 cyclobutadienes. The yields of the products **B(*m.n*)R** and **C(*m.n*)R** are reported in Table 1.



Because the solubility of the cyclobutadiene complexes decreases with reduced ring size we treated cycles **A(2.2)** and **A(2.3)** with **8c** only. The SiMe$_3$ substituent in the products ensured reasonable solubilities. The yields listed in Table 1 were obtained as follows: The reaction was monitored by thin layer chromatography, and as soon as no monoalkyne complex was present or no further reaction could be detected, we removed the solvent in vacuo and separated the products by column chromatography. In the case of **A(5.5)** the *syn*/*anti* ratio was determined by NMR spectroscopy since the stereoisomers could not be separated.

When the reaction was carried out such that **8**/**A** = 1:1, good yields of **B(*m.n*)R** were obtained (30−60%), whereas the yields of the 2:1 products were low. A closer look (Table 2) at the distributions of the *anti*/*syn*-**C(*m.n*)** product ratios shows a considerable variation.

In the case of the twelve-membered ring system **A(2.2)**, the *syn* isomer of **C(2.2)SiMe$_3$** was formed predominantly in about 13% yield. For **A(2.3)** and **A(3.3)** the *syn* isomers dominated, whereas for **A(4.4)** the *anti* isomer of **C(4.4)R** was preferred. Only when both triple bonds were separated by pentamethylene chains [**A(5.5)**] was the *anti*/*syn* ratio of the product [**C(5.5)**] found to be 1. These results reveal that thermodynamic factors are not important for the *anti*/*syn* selectivity observed, because the *anti*-**C(*m.n*)R** isomers should be more stable than the *syn* isomers due to steric reasons. We believe that it is the conformation of the large ring of the monosubstituted product **B(*m.n*)R** which primarily influences the *anti*/*syn* ratio of **C(*m.n*)R**. The *anti*/*syn* selectivity in the reactions of **A(3.3)** and **A(4.4)** with **8a**−**8c** (Table 3) allows estimation of the influence of the substituents on the Cp ring. The *anti*/*syn* ratio of the products **C(3.3)** and **C(4.4)** remains essentially constant for **C(3.3)R** and increases in the case of **C(4.4)R** with increasing size of R.

Reaction of triyne **A(3.3.3)** with a large excess of **8c** gave the trinuclear cobalt complexes *anti*-**C(3.3.3)SiMe$_3$** and all-*syn*-**C(3.3.3)SiMe$_3$** in 56 and 13% yield, respectively. In the former, two of the three cobalt centres are above the plane of the ring, whereas in the latter, all three cobalt atoms are on the same side.

Table 1. Yields of the products **B(*m.n*)R** and **C(*m.n*)R** as a function of the ratio of starting materials [**8**: **A(*m.n*)**]

| | Ratio **8**/**A** | Isomer | R = H | R = Me | R = SiMe$_3$ | R = CO$_2$Me | R = EtMe$_4$ |
|---|---|---|---|---|---|---|---|
| **A(2.2)** | 1:1 | mono | | | 41 | | |
| | | *anti* | | | <1 | | |
| | | *syn* | | | 5 | | |
| | 2:1 | mono | | | 60 | | |
| | | *anti* | | | <1 | | |
| | | *syn* | | | 13 | | |
| **A(2.3)** | 1:1 | mono | | | 41 | | |
| | | *anti* | | | <1 | | |
| | | *syn* | | | <1 | | |
| | 2:1 | mono | | | 8 | | |
| | | *anti* | | | 23 | | |
| | | *syn* | | | 32 | | |
| **A(3.3)** | 1:1 | mono | 27 | 18 | 57 | 12 | 19 |
| | | *anti* | 8 | 13 | 14 | 28 | <1 |
| | | *syn* | 14 | 32 | 11 | 12 | <1 |
| | 2:1 | mono | 11 | <1 | 10 | 1 | 13 |
| | | *anti* | 14 | 16 | 16 | 15 | 5 |
| | | *syn* | 26 | 58 | 25 | 33 | <1 |
| **A(4.4)** | 1:1 | mono | 34 | 43 | 57 | 41 | |
| | | *anti* | <1 | <1 | <1 | <1 | |
| | | *syn* | <1 | <1 | <1 | 8 | |
| | 2:1 | mono | 20 | <1 | 10 | 3 | 9 |
| | | *anti* | 26 | 53 | 31 | 29 | <1 |
| | | *syn* | 16 | 19 | 11 | 29 | <1 |
| **A(5.5)** | 1:1 | mono | 22 | 30 | | 48 | |
| | | *anti* | 3 | 9 | | <1 | |
| | | *syn* | 3 | 9 | | <1 | |
| | 2:1 | mono | 13 | <1 | | <1 | |
| | | *anti* | 16 | 28 | | 32 | |
| | | *syn* | 16 | 28 | | 32 | |

Table 2. Averaged *anti*/*syn* ratios of the isomers obtained in the reaction of bis(cyclopentadienylcobalt) complexes with the tetrathiadiynes **A(2.2)** to **A(5.5)**

| Diyne | A(2.2) | A(2.3) | A(3.3) | A(4.4) | A(5.5) |
|---|---|---|---|---|---|
| *anti*/*syn* | < 1:13 | 1:1.4 | 1:2 | 2 :1 | 1:1 |

Table 3. Yield of *syn* and *anti* **C(3.3)R** and **C(4.4)R** as a function of the substituents R

| | | **8a** (H) | **8b** (CH$_3$) | **8c** (SiMe$_3$) |
|---|---|---|---|---|
| **C(3.3)** | anti | 14 | 16 | 16 |
| | syn | 26 | 58 | 25 |
| **C(4.4)** | anti | 26 | 53 | 31 |
| | syn | 16 | 19 | 11 |

## X-ray Investigations

Isolation of single crystals of mono- and disubstitution products of the 12-, 13-, 14- and 16-membered rings **A(2.2)**, **A(2.3)**, **A(3.3)** and **A(4.4)** allowed a detailed study of their molecular structures using X-ray techniques. The molecular structures of **B(2.2)SiMe$_3$** and *syn*-**C(2.2)SiMe$_3$** are shown in Figure 1.

As can be seen from the conformation of the 12-membered ring of the monoadduct, the triple bond is situated relatively close (472 pm) to the cyclobutadiene (Cb) ring. The distances between the metal atom and the centres of the Cp ring and the Cb ring are 167 and 168 pm, respectively. Owing to the sizeable SiMe$_3$ substituent, the Cp and Cb rings are not parallel but are tilted by 8.3°. It is interesting to note that the torsion angle between the CH$_2$−S bonds at the triple bond of **B(2.2)SiMe$_3$** is 93.0°. In *syn*-**C(2.2)SiMe$_3$** (Figure 1) the two Cb rings are separated by 538 pm and 645 pm, corresponding to an angle between the two Cb planes of 42.7°.

The structure of **B(2.3)SiMe$_3$** in the crystal (Figure 2) shows that the 13-membered ring is more remote from the Cb ring (556 pm) and also from the CpSiMe$_3$ group. The interplanar angle between the Cp and Cb rings (4.1°) is smaller than in **B(2.2)SiMe$_3$**.

The X-ray structure of the *anti*-**C(2.3)SiMe$_3$** isomer is also shown in Figure 2. In this structure, both Cb rings are tilted towards each other by 62.0°.

The X-ray analysis of single crystals of **B(3.3)SiMe$_3$** revealed two molecules as asymmetric unit. The quality of the data was somewhat marginal and, while the distances and angles must therefore be viewed with caution, only the conformation of the 14-membered ring could be elucidated (Figure 3).

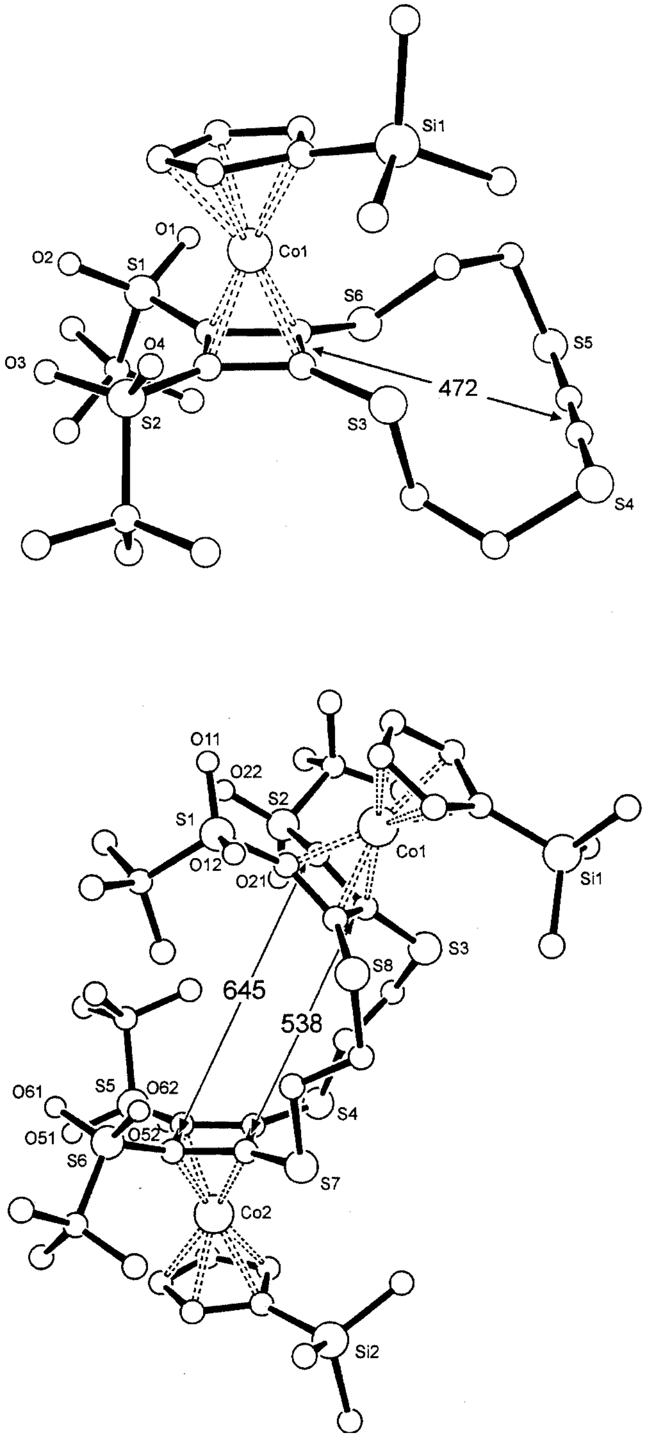


Figure 1. Molecular structures of **B(2.2)SiMe$_3$** and *syn*-**C(2.2)SiMe$_3$**; distances between the π-units defined by the arrows are given

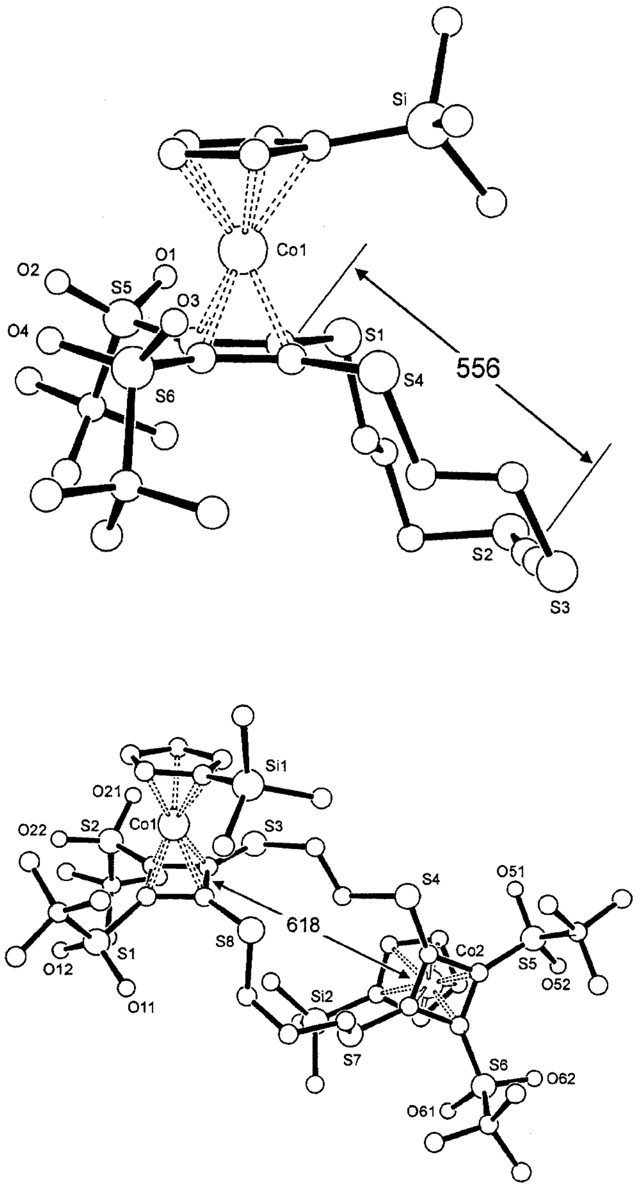


Figure 2. Molecular structures of **B(2.3)SiMe$_3$** and *anti*-**C(2.3)SiMe$_3$**; distances between the π-units defined by the arrows are given

The quality of the structure of *syn*-**C(3.3)SiMe$_3$** ($R_w$ = 0.147) is similar to that of **B(3.3)SiMe$_3$**, and therefore a structural diagram has not been included. However, it can be deduced that the conformation of *syn*-**C(3.3)SiMe$_3$** is similar to that of *anti*-**C(2.3)SiMe$_3$** insofar as the planes of the two cyclobutadiene rings are twisted by about 72°. All *tert*-butylsulfonyl groups are bent away from the SiMe$_3$CpCo moieties. Figure 3 also shows the structure of *anti*-**C(3.3)SiMe$_3$** in the crystal. As in the *syn* isomer the two Cb rings are twisted, but the twist angle is 54° (calculated as "torsion angle" between the two nearest Cb bonds of both rings), less than in the *syn* isomer. The distance between the cyclobutadiene rings in the *anti* isomer (685 pm) is larger than that found in *syn*-**C(3.3)SiMe$_3$** (661 pm). Both *tert*-butylsulfonyl moieties are bent away from the SiMe$_3$CpCo fragment.

The triple bond in **B(4.4)CH$_3$** (Figure 4) is relatively far remote from the cyclobutadiene ring (705 pm) and is nearly in plane with the cyclobutadiene ring. The large ring adopts an armchair conformation. In both *syn*- and *anti*-**C(4.4)CH$_3$** (Figure 4) a chair-like conformation of the central ring is maintained. A comparison of the structures of

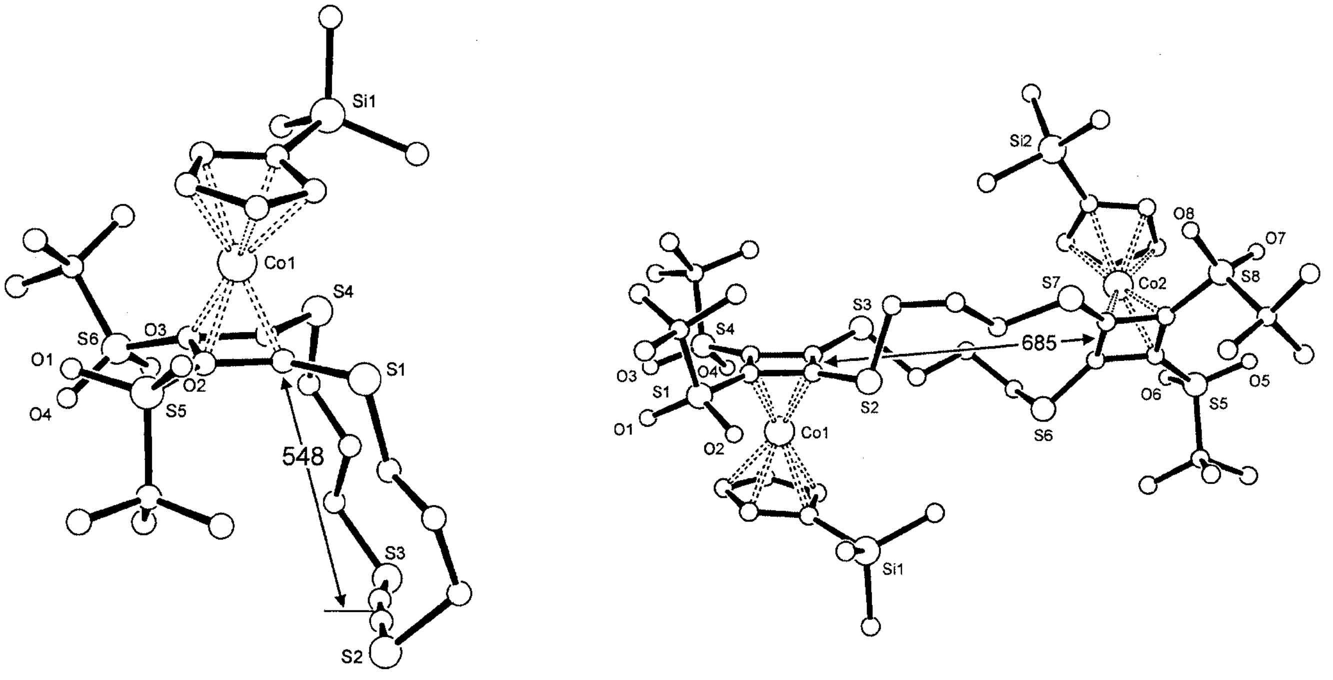


Figure 3. Molecular structures of **B(3.3)SiMe$_3$** (only one of both independent molecules is shown) and *anti*-**C(3.3)SiMe$_3$**; distances between the π-units defined by the arrows are given

**B(4.4)CH$_3$** and **C(4.4)CH$_3$** shows an increase in the distance between the former triple bonds [779 pm in *syn*-**C(4.4)CH$_3$**]. The "torsion angle" between the two nearest bonds of both cyclobutadiene units is 3.8°. All four *tert*-butylsulfonyl groups point away from the MeCpCo moieties. In *anti*-**C(4.4)CH$_3$** the central ring adopts a chair-like conformation. A crystallographic inversion center is found and consequently both cyclobutadiene rings are parallel to each other. As anticipated, the distance between both cyclobutadiene units (776 pm) is larger than in **B(4.4)CH$_3$**. The distance between the cobalt atoms is larger in the *anti* isomer (1080 pm) than in the *syn* isomer (1024 pm). The CpMe unit adopts a conformation which places the CH$_3$ group mostly between the SO$_2$ groups. Such a conformation has previously never been encountered for bulky SiMe$_3$ substituents.

Table 4 gives a comparison of the transannular distances *d* between the π units of **A(*m.n*)**, **B(*m.n*)R** and **C(*m.n*)R**, as well as the torsional angles α between the unsaturated bonds as defined in Figure 5. This shows that the transannular distance *d* between the triple bonds in **A(*m.n*)** is increased in the complexes. This increase is anticipated because it is due to the rehybridisation of the sp centres into sp$^2$ centres. Thus, the former C(sp)−C(sp)−S angles are reduced from 180 to about 120°. There are small torsion angles α between the triple bonds and the cyclobutadiene rings in the **B(*m.n*)R** complexes. It is interesting to note that the chair conformation of the 14-membered ring of **A(3.3)** is changed to a twisted conformation in both *syn*- and *anti*-**C(3.3)SiMe$_3$**, with α = 66.4 and 54.2°, respectively. The opposite is found in the case of the 16-membered ring of **A(4.4)**. Here the twisted conformation (α = 58.7°) is transformed into an armchair and a chair conformation, respectively, with small torsion angles. Figure 6 shows the molecular structure of the trinuclear cobalt complex all-*syn*-**C(3.3.3)SiMe$_3$**.

## Discussion

The rationalisation of our results is difficult since the system contains a number of unknowns. As outlined in Scheme 1 the metal-supported cyclobutadiene formation follows a sequence of several steps. A further complication arises from the unknown minimum energy conformation of the medium-sized ring in **B(*m.n*)** in solution. In order to rationalise the outcome of our experiments we assume that the transition state which determines the stereochemistry of the products is close in energy and structure to the intermediate metallacycle (e.g. **4** in Scheme 1) and rather different to the cyclobutadiene product. We furthermore assume that the barrier to ring inversion in the metallacycles is in the order of 5 kcal/mol.[8] Steric effects should therefore be important in determining the *syn*/*anti* ratios.

In order to discuss the reaction mechanism, two conformations of **B(*m.n*)**, **D1** and **D2** (Figure 7) must be considered. In **D1** the triple bond is situated on the same level with the cyclobutadiene system, whereas in **D2** it is placed below the cyclobutadiene ring. Which of the two geometries is favoured depends mainly on the conformations of the methylene chains and, to a minor extent, on the substituents at the Cp ring. The methylene chains favour a zig-zag arrangement, as demonstrated for several cyclic diynes[13] and especially for cyclic tetrathiadiynes[11] and tetrathiaenynes.[14] In these ring systems a staggered conformation is achieved.

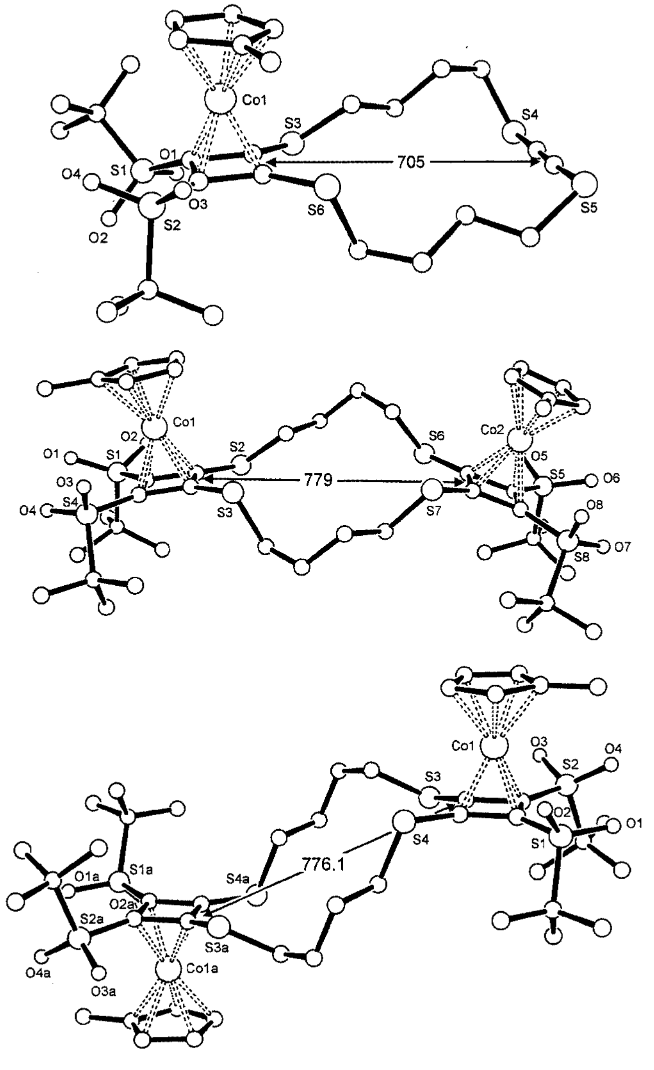


Figure 4. Molecular structures of **B(4.4)Me** (top), *syn*-**C(4.4)Me** (centre) and *anti*-**C(4.4)Me** (bottom); distances between the π-units defined by the arrows are given

Table 4. Transannular distances *d* [pm] and torsional angles α [°] for **A(*m.n*)**, **B(*m.n*)R** and **C(*m.n*)R** ($m = 2-4$, $n = 2-4$) as defined in Figure 5

| *m* | *n* | R | | **A(*m.n*)** | **B(*m.n*)R** | **C(*m.n*)R** | |
|---|---|---|---|---|---|---|---|
| | | | | | | *syn* | *anti* |
| 2 | 2 | $SiMe_3$ | *d* | 356 | 472 | 539 | – |
| | | | α | 0.0 | 5.8 | 20.9 | – |
| 2 | 3 | $SiMe_3$ | *d* | 405 | 556 | – | 61.8 |
| | | | α | 13.9 | 3.3 | – | 59.1 |
| 3 | 3 | $SiMe_3$ | *d* | 545 | 548/561 | 661/652 | 685 |
| | | | α | 0.0 | 9.6/10.6 | 66.4/89.7 | 54.2 |
| 4 | 4 | Me | *d* | 535 | 705 | 779 | 776 |
| | | | α | 58.7 | 1.6 | 3.8 | 0.0 |

The two conformations **D1** and **D2** yield two intermediates **E1** and **E2** (Figure 7). In **E1** the repulsion between the two Cp rings is minimised. Reaction via **E1** should lead to the *anti* isomer, whereas **E2** will give the *syn* isomer. The close distance between the triple bond and the cyclobutadiene ring (472 pm) and the bulky $SiMe_3$ substituent in **B(2.2)SiMe$_3$** should clearly favour **E1** even when the triple bond and cyclobutadiene ring are situated at the same level (Figure 1). The strong preference for *syn*-**C(2.2)SiMe$_3$** (Tables 1 and 2) can be rationalised by assuming that the energy difference between the conformation shown in Figure 1 and one close to that found for **B(2.3)SiMe$_3$** (Figure 2) should be small. This assumption is supported by X-ray studies of (*Z*)-1,4,7,10-tetrathiacyclododeca-2-en-8-yne (**9**).[14] The conformation of **9** is given in Figure 8 and resembles that of the enyne fragment of **B(2.3)SiMe$_3$**. In this conformation the triple bond is rather close to the *tert*-butyl groups, and therefore the metallacycle with the CpCo fragment on the *syn* side should be favoured. The same holds for **B(2.3)SiMe$_3$** and **B(3.3)SiMe$_3$**. Owing to the stair-like arrangement of double and triple bonds, and the close proximity of the *tert*-butyl groups and the triple bond, a *syn* product should be favoured as indicated in Table 2. The results summarised in Table 3 suggest that, for the reaction of **B(3.3)R** with **8a**−**8c**, a transition state similar to **E2** should be preferred, whereas in the reaction of **B(4.4)R** with **8a**−**8c**, a geometry closely related to **E1** should be favoured. These conclusions are in agreement with the structures of **B(3.3)SiMe$_3$** and **B(4.4)SiMe$_3$** in the crystal.

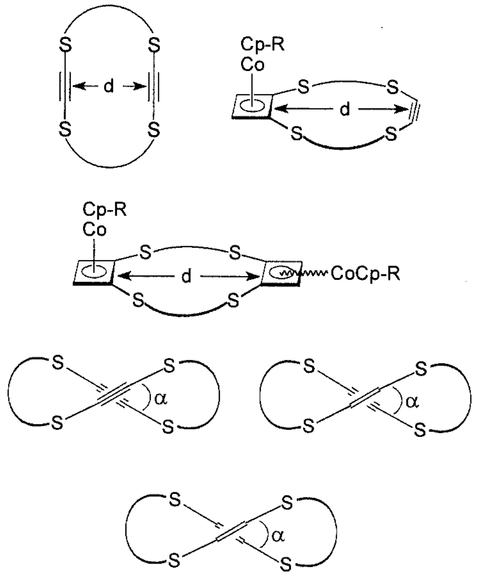


Figure 5. Definition of *d* and α for the values listed in Table 4

## Conclusions

In the beginning of our investigations we raised the question of the *syn*/*anti* selectivity in the twofold cyclobutadiene formation in nonconjugated cyclic diynes. We have been able to determine the *syn*/*anti* ratio in the reaction of the medium-sized rings **A(*m.n*)** ($n = 2-4$ and $m = 2-4$) by using highly reactive nucleophilic tetrathiaalkadiynes and strongly electrophilic mono(alkyne)cobalt complexes. No selectivity was observed for larger rings ($m$, $n > 4$). For smaller rings, *syn* selectivity was preferred for **A(2.2)**, **A(2.3)**

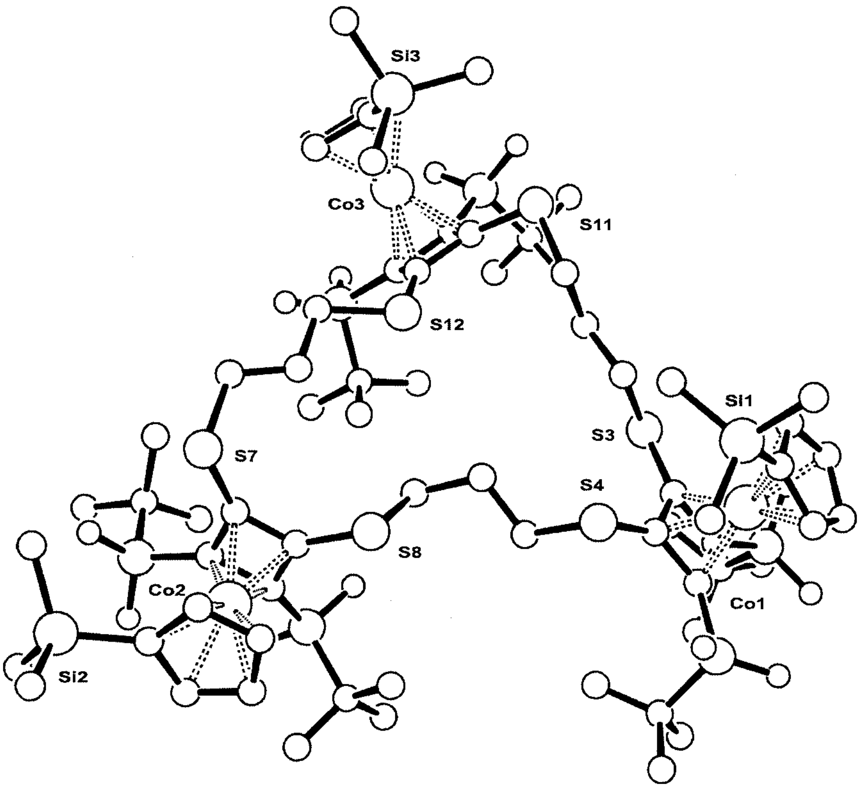


Figure 6. Molecular structure of all-*syn*-**C(3.3.3)SiMe$_3$**

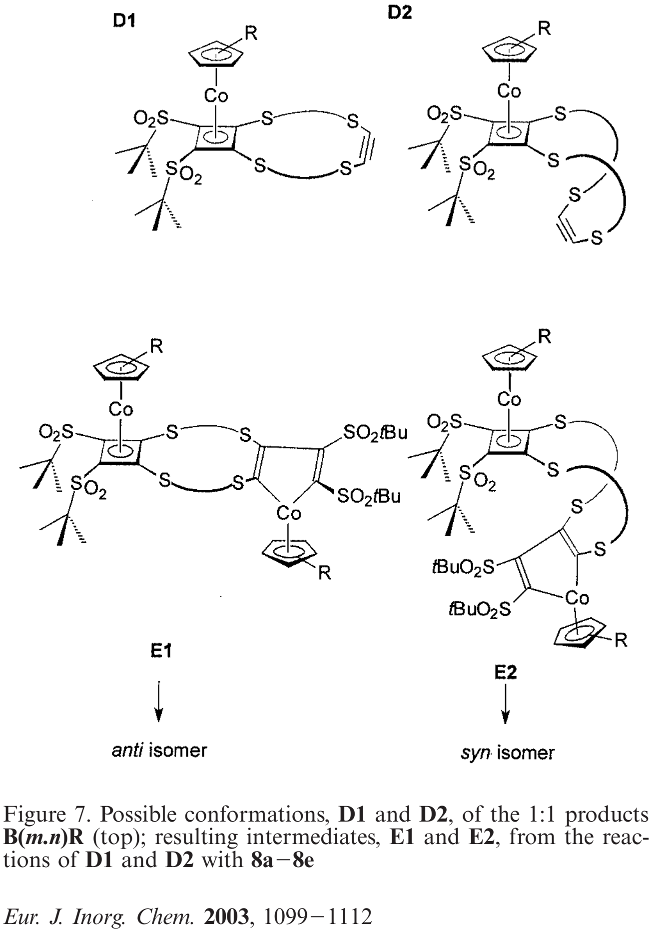


Figure 7. Possible conformations, **D1** and **D2**, of the 1:1 products **B(*m.n*)R** (top); resulting intermediates, **E1** and **E2**, from the reactions of **D1** and **D2** with **8a−8e**

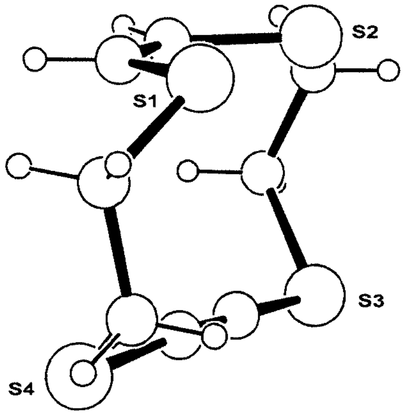


Figure 8. The conformation of (*Z*)-1,4,7,10-tetrathiacyclododeca-2-en-8-yne (**9**) in the crystal that resembles that of the enyne fragment of **B(2.3)SiMe$_3$**

and **A(3.3)**, whereas for **A(4.4)** *anti* selectivity prevails. Our X-ray investigations on the mono- and disubstituted complexes revealed that the selectivity is mainly determined by the conformation of the medium-sized chain. For short chains ($m$, $n < 4$) we found that the ring with the dithiaalkyne unit in **B(*m.n*)** is bent away from the CpCo moiety. This conformation favours the formation of the second metallacycle *syn* to the CpCo-stabilised cyclobutadiene complex. These studies suggest that a stepwise synthesis of cyclic oligomers[15] should be possible if the chain length between the triple bonds is small. For pure hydrocarbons the chain length should be below six CH$_2$ groups.

## Experimental Section

**General Methods:** Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon. Toluene was dried with sodium/benzophenone and distilled under argon before use. Petroleum ether and diethyl ether were distilled before use. Melting points are uncorrected. Materials used for column chromatography: Silica gel 60 (Machery−Nagel). $^1$H and $^{13}$C NMR: Bruker AS 200 ($^1$H at 200 MHz and $^{13}$C at 50.33 MHz), Bruker Avance 300 ($^1$H at 300 MHz and $^{13}$C at 75.47 MHz), Bruker Avance 500 ($^1$H at 500 MHz and $^{13}$C at 125.77 MHz) using the solvent as internal standard. The signals were assigned by NMR correlation techniques. IR: Bruker Vector 22 FT-IR. MS: Low resolution: ZAB-2F; high resolution: JEOL JMS-700. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Complexes **8a**−**8e**[7] and the tetrathiacyclodiynes **A(2.2)** to **A(5.5)**[12] were prepared according to literature methods.

**General Procedure for the Preparation of the Cyclobutadiene Complexes:** The mono(alkyne)cobalt complex was dissolved in toluene (150 mL) and the tetrathiacycloalkadiyne was added in one portion. The reaction mixture was stirred at room temperature. After completion of the reaction, the solvent was removed by rotary evaporation and the products were isolated by column chromatography ($SiO_2$; diethyl ether/petroleum ether, 1:1 → 2:1 → 5:1 → dichloromethane/methanol, 30:1).

**Reaction of A(2.2) with [CpSiMe$_3$Co(CO)(BTSA)] (8c). Reaction A: 8c** (134 mg, 0.27 mmol) and **A(2.2)** (70 mg, 0.30 mmol). Yield: 77 mg (41%) of **B(2.2)SiMe$_3$** and 15 mg (5%) of *syn*-**C(2.2)SiMe$_3$**. **Reaction B: 8c** (324 mg, 0.66 mmol) and **A(2.2)** (70 mg, 0.30 mmol). Yield: 126 mg (60%) of **B(2.2)SiMe$_3$** and 46 mg (13%) of *syn*-**C(2.2)SiMe$_3$**.

**B(2.2)SiMe$_3$:** Yellow solid, m.p. 186 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 0.36$ [s, 9 H, $Si(CH_3)_3$], 1.45 [s, 18 H, $C(CH_3)_3$], 2.97/3.60 (m, 8 H, $SCH_2$), 5.32/5.68 (pt, 4 H, CpH) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = -0.4$ [$Si(CH_3)_3$], 24.7 [$C(\mathit{C}H_3)_3$], 33.1/34.1 ($SCH_2$), 61.6 [$\mathit{C}(CH_3)_3$], 78.3 [$\mathit{C}(Cb)SO_2t\mathrm{Bu}$], 81.6 [$\mathit{C}$(Cb)S], 87.3 (≡C), 88.5/90.1 [$\mathit{C}$(Cp)H], 93.7 [$\mathit{C}(Cp)SiMe_3$] ppm. IR (KBr): $\tilde{\nu} = 2966\ \mathrm{cm}^{-1}$, 2929, 1631, 1358, 1309, 1250, 1121. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 316 nm (4.35). MS (FAB+): 694 [$M^+$]. HRMS (FAB+): [$M^+$] $C_{26}H_{39}CoO_4S_6Si$: calcd. 694.0274; found 694.0244. $C_{26}H_{39}CoO_4S_6Si$ (695.0): calcd. C 44.93, H 5.66, S 27.68; found C 45.22, H 5.74, S 27.39.

***syn*-C(2.2)SiMe$_3$:** Yellow solid, m.p. 230 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 0.32$ [s, 18 H, $Si(CH_3)_3$], 1.41 [s, 36 H, $C(CH_3)_3$], 2.79/3.51 (m, 8 H, $SCH_2$), 4.95/5.61 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = -0.3$ [$Si(CH_3)_3$], 24.6 [$C(\mathit{C}H_3)_3$], 36.7 ($SCH_2$), 61.9 [$\mathit{C}(CH_3)_3$], 77.5 [$\mathit{C}(Cb)SO_2t\mathrm{Bu}$], 81.2 [$\mathit{C}$(Cb)S], 88.8/91.5 [$\mathit{C}$(Cp)H], 94.7 [$\mathit{C}(Cp)SiMe_3$] ppm. IR (KBr): $\tilde{\nu} = 2955\ \mathrm{cm}^{-1}$, 1633, 1307, 1123. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 258 (4.77), 316 nm (4.70). MS (FAB+): 1156 [$M^+$], 1083 [$M^+ - t\mathrm{BuO}$]. HRMS (FAB+): [$M^+$] $C_{44}H_{70}Co_2O_8S_8Si_2$: calcd. 1156.1039; found 1156.1047. $C_{44}H_{70}Co_2O_8S_8Si_2\cdot 0.25C_4H_{10}O$ (1176.1): calcd. C 45.96, H 6.21, S 21.81; found C 46.10, H 6.15, S 22.08.

**Reaction of A(2.3) with [CpSiMe$_3$Co(CO)(BTSA)] (8c). Reaction A: 8c** (127 mg, 0.26 mmol) and **A(2.3)** (70 mg, 0.30 mmol). Yield: 76 mg (41%) of **B(2.3)SiMe$_3$**. **Reaction B: 8c** (307 mg, 0.62 mmol) and **A(2.3)** (70 mg, 0.30 mmol). Yield: 15 mg (8%) of **B(2.3)SiMe$_3$**, 74 mg (23%) of *anti*-**C(2.3)SiMe$_3$** and 106 mg (32%) of *syn*-**C(2.3)SiMe$_3$**.

**B(2.3)SiMe$_3$:** Yellow solid, m.p. 200 °C (dec.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 0.35$ [s, 9 H, $Si(CH_3)_3$], 1.49 [s, 18 H, $C(CH_3)_3$], 2.15 (m, 2 H, $CH_2C\mathit{H}_2CH_2$), 2.60/2.98 (m, 2 H, $CH_2CH_2C\mathit{H}_2SC{\equiv}$), 2.74/2.98 (m, 2 H, $SCH_2C\mathit{H}_2SC{\equiv}$), 3.19 (m, 2 H, $SC\mathit{H}_2CH_2SC{\equiv}$), 3.31/3.47 (m, 2 H, $C\mathit{H}_2CH_2CH_2SC{\equiv}$), 5.06/5.70 (pt, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, $CD_2Cl_2$): $\delta = -0.3$ [$Si(CH_3)_3$], 25.38/25.42 [$C(\mathit{C}H_3)_3$], 30.9 ($CH_2\mathit{C}H_2CH_2$), 35.3 ($SCH_2\mathit{C}H_2SC{\equiv}$), 36.2 ($CH_2CH_2\mathit{C}H_2SC{\equiv}$), 36.5 ($\mathit{C}H_2CH_2CH_2SC{\equiv}$), 37.0 ($S\mathit{C}H_2CH_2SC{\equiv}$), 62.4 [$\mathit{C}(CH_3)_3$], 77.9/78.9 [$\mathit{C}(Cb)SO_2t\mathrm{Bu}$], 82.9 [$\mathit{C}(Cb)SCH_2CH_2S$], 83.8 [$\mathit{C}(CBD)SCH_2CH_2CH_2$], 86.0 ($SCH_2CH_2S\mathit{C}{\equiv}$), 89.1 ($CH_2CH_2CH_2S\mathit{C}{\equiv}$), 89.3/89.4/91.4 [$\mathit{C}$(Cp)H], 95.3 [$\mathit{C}(Cp)SiMe_3$] ppm. IR (KBr): $\tilde{\nu} = 2970\ \mathrm{cm}^{-1}$, 2930, 1632, 1356, 1307, 1248, 1192, 1163, 1121. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 258 (4.19), 314 nm (4.08). MS (FAB+): 708 [$M^+$], 635 [$M^+ - t\mathrm{BuO}$]. HRMS (FAB+): [$M^+$] $C_{27}H_{41}CoO_4S_6Si$: calcd. 708.0430; found 708.0470. $C_{27}H_{41}CoO_4S_6Si$ (709.0): calcd. C 45.74, H 5.83, S 27.13; found C 45.86, H 5.82, S 27.08.

***anti*-C(2.3)SiMe$_3$:** Yellow solid, m.p. 235 °C (dec.). $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta = 0.30$ [s, 18 H, $Si(CH_3)_3$], 1.41/1.45 [s, 36 H, $C(CH_3)_3$], 1.94 (m, 2 H, $CH_2C\mathit{H}_2CH_2$), 3.08 (m, 4 H, $C\mathit{H}_2CH_2C\mathit{H}_2$), 3.18/3.45 (m, 4 H, $SCH_2CH_2S$), 5.08/5.16 (pt, 4 H, CpH), 5.63 (m, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, $CD_2Cl_2$): $\delta = -0.4$ [$Si(CH_3)_3$], 24.68/24.74 [$C(\mathit{C}H_3)_3$], 28.2 ($CH_2\mathit{C}H_2CH_2$), 35.9 ($\mathit{C}H_2CH_2\mathit{C}H_2$), 36.2 ($S\mathit{C}H_2\mathit{C}H_2S$), 61.8/61.9 ($\mathit{C}(CH_3)_3$], 77.2/79.0 [$\mathit{C}(Cb)SO_2t\mathrm{Bu}$], 78.5 [$\mathit{C}(Cb)SCH_2CH_2CH_2$], 84.6 [$\mathit{C}(CBD)SCH_2CH_2S$], 88.3/89.2/90.2/90.7 [$\mathit{C}$(Cp)H], 94.2 [$\mathit{C}(Cp)SiMe_3$] ppm. IR (KBr): $\tilde{\nu} = 2956\ \mathrm{cm}^{-1}$, 2932, 1632, 1474, 1357, 1309, 1250, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 258 (4.47), 314 nm (4.38). MS (FAB+): 1170 [$M^+$], 1097 [$M^+ - SiMe_3$], 1024 [$M^+ - 2\ SiMe_3$]. HRMS (FAB+): [$M^+$] $C_{45}H_{72}Co_2O_8S_8Si_2$: calcd. 1170.1195; found 1170.1246. $C_{45}H_{72}Co_2O_8S_8Si_2$ (1171.6): calcd. C 46.13, H 6.19, S 21.90; found C 46.29, H 6.26, S 21.87.

***syn*-C(2.3)SiMe$_3$:** Yellow solid, m.p. 244 °C (dec.). $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta = 0.35$ [s, 18 H, $Si(CH_3)_3$], 1.45/1.46 [s, 36 H, $C(CH_3)_3$], 2.04 (m, 2 H, $CH_2C\mathit{H}_2CH_2$), 3.00/3.42 (m, 4 H, $C\mathit{H}_2CH_2C\mathit{H}_2$), 3.19/3.42 (m, 4 H, $SCH_2CH_2S$), 5.16/5.73 (pt, 8 H, CpH) ppm. $^{13}$C NMR (125 MHz, $CD_2Cl_2$): $\delta = -0.4$ [$Si(CH_3)_3$], 25.21/25.29 [$C(\mathit{C}H_3)_3$], 29.1 ($CH_2\mathit{C}H_2CH_2$), 36.0 ($\mathit{C}H_2CH_2\mathit{C}H_2$), 36.1 ($S\mathit{C}H_2\mathit{C}H_2S$), 62.3/62.5 [$\mathit{C}(CH_3)_3$], 77.4/78.6 [$\mathit{C}(Cb)SO_2t\mathrm{Bu}$], 80.8 [$\mathit{C}(Cb)SCH_2CH_2S$], 81.9 [$\mathit{C}(Cb)SCH_2CH_2CH_2$], 89.5/90.2/91.5 [$\mathit{C}$(Cp)H], 94.5 [$\mathit{C}(Cp)SiMe_3$] ppm. IR (KBr): $\tilde{\nu} = 2967\ \mathrm{cm}^{-1}$, 1632, 1474, 1357, 1309, 1250, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 258 (4.18), 316 nm (4.07). MS (FAB+): 1170 [$M^+$], 1097 [$M^+ - SiMe_3$]. HRMS (FAB+): [$M^+$] $C_{45}H_{72}Co_2O_8S_8Si_2$: calcd. 1170.1195; found 1170.1218. $C_{45}H_{72}Co_2O_8S_8Si_2.0.5\ C_4H_{10}O$ (1208.7): calcd. C 46.71, H 6.42, S 21.22; found C 46.83, H 6.32, S 21.59.

**Reaction of A(3.3) with [CpCo(CO)(BTSA)] (8a). Reaction A: 8a** (117 mg, 0.28 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 49 mg (27%) of **B(3.3)H**, 11 mg (8%) of *anti*-**C(3.3)H** and 20 mg (14%) of *syn*-**C(3.3)H**. **Reaction B: 8a** (296 mg, 0.71 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 21 mg (11%) of **B(3.3)H**, 44 mg (14%) of *anti*-**C(3.3)H** and 84 mg (26%) of *syn*-**C(3.3)H**.

**B(3.3)H:** Yellow solid, m.p. 157 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.47$ [s, 18 H, $C(CH_3)_3$], 2.21 (m, 4 H, $CH_2C\mathit{H}_2CH_2$), 2.76 (m, 4 H, $CH_2SC{\equiv}$), 3.20 (m, 4 H, $SC\mathit{H}_2CH_2CH_2SC{\equiv}$), 5.40 (s, 5 H, CpH) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 25.2$ [$C(\mathit{C}H_3)_3$], 30.5 ($CH_2\mathit{C}H_2CH_2$), 35.3/36.9 ($SCH_2$), 62.1 [$\mathit{C}(CH_3)_3$], 78.7 [$\mathit{C}(Cb)SO_2t\mathrm{Bu}$], 84.6 [$\mathit{C}(Cb)SCH_2$], 86.3 [$\mathit{C}$(Cp)], 87.0 (C≡) ppm. IR (KBr): $\tilde{\nu} = 2929\ \mathrm{cm}^{-1}$, 1632, 1309, 1121. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 250 (4.14), 314 nm (3.93). MS (FAB+): 650 [$M^+$], 577 [$M^+ - t\mathrm{BuO}$]. HRMS (FAB+): [$M^+$] $C_{25}H_{35}CoO_4S_6$: calcd. 650.0192; found 650.0197. $C_{25}H_{35}CoO_4S_6$ (650.9): calcd. C 46.13, H 5.42; found C 46.08, H 5.71.

***anti*-C(3.3)H:** Yellow solid, m.p. 286 °C (dec.). $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.46$ [s, 36 H, $C(CH_3)_3$], 2.10 (m, 4 H, $CH_2C\mathit{H}_2CH_2$), 3.18 (m, 8 H, S*C*H$_2$), 5.42 (s, 10 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 25.2 [C(*C*H$_3$)$_3$], 29.0 (CH$_2$*C*H$_2$CH$_2$), 37.0 (S*C*H$_2$), 62.2 [*C*(CH$_3$)$_3$], 78.7 [*C*(Cb)SO$_2$*t*Bu], 83.6 [*C*(Cb)SCH$_2$], 86.3 [*C*(Cp)] ppm. IR (KBr): ṽ = 2961 cm$^{-1}$, 2929, 1727, 1632, 1307, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 248 (4.35), 310 (4.10), 358 nm (3.38). MS (FAB+): 1140 [M$^+$], 967 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{40}H_{58}Co_2O_8S_8$: calcd. 1040.0561; found 1040.0560. $C_{40}H_{58}Co_2O_8S_8$ (1041.3): calcd. C 46.14, H 5.61, S 24.64; found C 46.07, H 5.64, S 24.44.

***syn*-C(3.3)H:** Yellow solid, m.p. 290 °C (dec.). $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.47 [s, 36 H, C(CH$_3$)$_3$], 2.12 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 3.26 (m, 8 H, SC*H*$_2$), 5.41 (s, 10 H, CpH) ppm. IR (KBr): ṽ = 2925 cm$^{-1}$, 2854, 1307, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 252 (4.27), 310 (3.99), 356 nm (3.23). MS (FAB+): 1140 [M$^+$], 967 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{40}H_{58}Co_2O_8S_8$: calcd. 1040.0561; found 1140.0580. $C_{40}H_{58}Co_2O_8S_8$ (1041.3): calcd. C 46.14, H 5.61, S 24.64; found C 46.04, H 5.89, S 24.45.

**Reaction of A(3.3) with [CpMeCo(CO)(BTSA)] (8b). Reaction A: 8b** (122 mg, 0.28 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 34 mg (18%) of **B(3.3)Me**, 20 mg (13%) of *anti*-**C(3.3)Me** and 47 mg (32%) of *syn*-**C(3.3)Me**. **Reaction B: 8b** (305 mg, 0.71 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 54 mg (16%) of *anti*-**C(3.3)Me** and 191 mg (58%) of *syn*-**C(3.3)Me**.

**B(3.3)Me:** Yellow solid, m.p. 172 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.47 [s, 18 H, C(CH$_3$)$_3$], 2.10 (s, 3 H, CpC*H*$_3$), 2.19 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 2.73 (m, 4 H, CH$_2$SC≡), 3.17 (m, 4 H, SC*H*$_2$CH$_2$CH$_2$SC≡), 5.14/5.31 (pt, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 12.9 (Cp*C*H$_3$), 25.2 [C(*C*H$_3$)$_3$], 30.5 (CH$_2$*C*H$_2$CH$_2$), 35.4/36.1 (S*C*H$_2$), 62.1 [*C*(CH$_3$)$_3$], 78.3 [*C*(Cb)SO$_2$*t*Bu], 82.7 [*C*(Cb)SCH$_2$], 85.5/86.8 [*C*(Cp)H], 87.0 (C≡), 101.2 [*C*(Cp)CH$_3$] ppm. IR (KBr): ṽ = 2928 cm$^{-1}$, 1634, 1476, 1356, 1305, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ [nm] (log ε) = 254 (4.23), 314 (4.06), 366 (3.38). MS (FAB+): 664 [M$^+$], 591 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{26}H_{37}CoO_4S_6$: calcd. 664.0348; found 664.0359.

***anti*-C(3.3)Me:** Yellow solid, m.p. 277 °C (dec.). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.46 [s, 36 H, C(CH$_3$)$_3$], 2.09 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 2.12 (s, 6 H, CpC*H*$_3$), 3.18 (m, 8 H, SC*H*$_2$), 5.22/5.34 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 12.9 (Cp*C*H$_3$), 25.2 [C(*C*H$_3$)$_3$], 29.1 (CH$_2$*C*H$_2$CH$_2$), 36.6 (S*C*H$_2$), 62.2 [*C*(CH$_3$)$_3$], 77.9 [*C*(Cb)SO$_2$*t*Bu], 82.4 [*C*(Cb)SCH$_2$], 85.3/86.7 [*C*(Cp)H], 101.1 [*C*(Cp)CH$_3$] ppm. IR (KBr): ṽ = 2971 cm$^{-1}$, 2929, 1633, 1476, 1349, 1308, 1194, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 252 (4.52), 312 (4.34), 356 nm (3.74). MS (FAB+): 1068 [M$^+$], 995 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{42}H_{62}Co_2O_8S_8$: calcd. 1068.0874; found 1068.0881. $C_{42}H_{62}Co_2O_8S_8$ (1069.3): calcd. C 47.18, H 5.84, S 23.99; found C 47.08, H 5.87, S 23.71.

***syn*-C(3.3)Me:** Yellow solid, m.p. 290 °C (dec.). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.47 [s, 36 H, C(CH$_3$)$_3$], 2.10 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 2.12 (s, 6 H, CpC*H*$_3$), 3.19 (m, 8 H, SC*H*$_2$), 5.23/5.35 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 12.9 (Cp*C*H$_3$), 25.2 [C(*C*H$_3$)$_3$], 29.1 (CH$_2$*C*H$_2$CH$_2$), 36.6 (S*C*H$_2$), 62.2 [*C*(CH$_3$)$_3$], 77.9 [*C*(Cb)SO$_2$*t*Bu], 82.4 [*C*(Cb)SCH$_2$], 85.3/86.7 [*C*(Cp)H], 101.0 [*C*(Cp)CH$_3$] ppm. IR (KBr): ṽ = 2973 cm$^{-1}$, 2929, 1634, 1476, 1353, 1307, 1193, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 242 (4.57), 318 (4.26), 372 nm (3.65). MS (FAB+): 1168 [M$^+$], 995 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{42}H_{62}Co_2O_8S_8$: calcd. 1068.0874; found 1068.0867. $C_{42}H_{62}Co_2O_8S_8$ (1069.3): calcd. C 47.18, H 5.84, S 23.99; found C 46.90, H 5.88, S 23.85.

**Reaction of A(3.3) with [CpSiMe$_3$Co(CO)(BTSA)] (8c). Reaction A: 8c** (138 mg, 0.28 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 115 mg (57%) of **B(3.3)SiMe$_3$**, 23 mg (14%) of *anti*-**C(3.3)SiMe$_3$** and 18 mg (11%) of *syn*-**C(3.3)SiMe$_3$**. **Reaction B: 8c** (348 mg, 0.71 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 22 mg (10%) of **B(3.3)SiMe$_3$**, 57 mg (16%) of *anti*-**C(3.3)SiMe$_3$** and 93 mg (25%) of *syn*-**C(3.3)SiMe$_3$**.

**B(3.3)SiMe$_3$:** Yellow solid, m.p. 159 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.31 [s, 9 H, Si(CH$_3$)$_3$], 1.47 [s, 18 H, C(CH$_3$)$_3$], 2.21 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 2.71 (m, 4 H, CH$_2$SC≡), 3.13 (m, 4 H, SC*H*$_2$CH$_2$CH$_2$SC≡), 5.10/5.75 (pt, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 0.4 [Si(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 30.6 (CH$_2$*C*H$_2$CH$_2$), 35.4/36.3 (S*C*H$_2$), 62.3 [*C*(CH$_3$)$_3$], 78.2 [*C*(Cb)SO$_2$*t*Bu], 82.9 [*C*(Cb)SCH$_2$], 87.2 (C≡), 89.4/90.9 [*C*(Cp)H], 94.6 [*C*(Cp)SiMe$_3$] ppm. IR (KBr): ṽ = 2929 cm$^{-1}$, 1650, 1358, 1304, 1250, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 258 (4.18), 314 nm (4.04). MS (FAB+): 722 [M$^+$], 649 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{28}H_{43}CoO_4S_6Si$: calcd. 722.0587; found 722.0587.

***anti*-C(3.3)SiMe$_3$:** Yellow solid, m.p. 204 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.31 [s, 18 H, Si(CH$_3$)$_3$], 1.47 [s, 36 H, C(CH$_3$)$_3$], 2.03 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 3.13 (m, 8 H, SC*H*$_2$), 5.20/5.74 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 0.3 [Si(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 29.5 (CH$_2$*C*H$_2$CH$_2$), 36.8 (S*C*H$_2$), 62.4 [*C*(CH$_3$)$_3$], 78.3 [*C*(Cb)SO$_2$*t*Bu], 82.4 [*C*(Cb)SCH$_2$], 89.2/90.7 [*C*(Cp)H], 94.2 [*C*(Cp)SiMe$_3$] ppm. IR (KBr): ṽ = 2963 cm$^{-1}$, 1632, 1309, 1250, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 258 (4.45), 316 nm (4.32). MS (FAB+): 1184 [M$^+$], 1111 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{46}H_{74}Co_2O_8S_8Si_2$: calcd. 1184.1352; found 1184.1340. $C_{46}H_{74}Co_2O_8S_8Si_2$ (1185.7): calcd. C 46.60, H 6.29, S 21.64; found C 46.79, H 6.25, S 21.51.

***syn*-C(3.3)SiMe$_3$:** Yellow solid, m.p. 230 °C (dec.). $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.35 [s, 18 H, Si(CH$_3$)$_3$], 1.48 [s, 36 H, C(CH$_3$)$_3$], 2.01 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 3.19 (m, 8 H, SC*H*$_2$), 5.22/5.75 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 0.4 [Si(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 28.8 (CH$_2$*C*H$_2$CH$_2$), 36.5 (S*C*H$_2$), 62.5 [*C*(CH$_3$)$_3$], 77.9 [*C*(Cb)SO$_2$*t*Bu], 82.1 [*C*(Cb)SCH$_2$], 89.2/90.5 [*C*(Cp)H], 94.2 [*C*(Cp)SiMe$_3$] ppm. IR (KBr): ṽ = 2954 cm$^{-1}$, 1632, 1308, 1249, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 258 (4.45), 314 nm (4.32). MS (FAB+): 1184 [M$^+$], 1111 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{46}H_{74}Co_2O_8S_8Si_2$: calcd. 1184.1352; found 1184.1382. $C_{46}H_{74}Co_2O_8S_8Si_2$ (1185.7): calcd. C 46.60, H 6.29, S 21.64; found C 46.47, H 6.32, S 21.51.

**Reaction of A(3.3) with [CpCOOMeCo(CO)(BTSA)] (8d). Reaction A: 8d** (133 mg, 0.28 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 24 mg (12%) of **B(3.3)COOMe**, 45 mg (28%) of *anti*-**C(3.3)COOMe** and 19 mg (12%) of *syn*-**C(3.3)COOMe**. **Reaction B: 8d** (294 mg, 0.62 mmol) and **A(3.3)** (70 mg, 0.27 mmol). Yield: 47 mg (15%) of *anti*-**C(3.3)COOMe** and 103 mg (33%) of *syn*-**C(3.3)COOMe**.

**B(3.3)COOMe:** Yellow solid, m.p. 146 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.48 [s, 18 H, C(CH$_3$)$_3$], 2.20 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 2.74 (m, 4 H, CH$_2$SC≡), 3.26 (m, 4 H, SC*H*$_2$CH$_2$CH$_2$SC≡), 3.90 (s, 3 H, COOCH$_3$), 5.63/5.73 (pt, 4 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 25.4 [C(*C*H$_3$)$_3$], 30.4 (CH$_2$*C*H$_2$CH$_2$), 34.8/35.1 (S*C*H$_2$), 52.9 (COO*C*H$_3$), 62.5 [*C*(CH$_3$)$_3$], 78.9 [*C*(Cb)SO$_2$*t*Bu], 84.9 [*C*(Cb)SCH$_2$], 87.1 (C≡), 87.6/89.0 [*C*(Cp)H], 90.4 [*C*(Cp)COOMe], 166.0 (C=O) ppm. IR (KBr): ṽ = 2966 cm$^{-1}$, 1724, 1472, 1366, 1308, 1193, 1148, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 318 (4.02), 366 nm (3.42). MS (FAB+): 709 [M + H$^+$], 635 [M$^+$ − *t*BuO]. HRMS (FAB+): [M + H$^+$] $C_{27}H_{38}CoO_6S_6$: calcd. 709.0325; found 709.0326.

***anti*-C(3.3)COOMe:** Yellow solid, m.p. 226 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.47 [s, 36 H, C(CH$_3$)$_3$], 2.03 (m, 4 H, CH$_2$C*H*$_2$CH$_2$), 3.29 (m, 8 H, SC*H*$_2$), 3.91 (s, 6 H, COOCH$_3$), 5.65/5.84 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 25.1 [C(*C*H$_3$)$_3$], 28.8 (CH$_2$*C*H$_2$CH$_2$), 35.4 (S*C*H$_2$), 53.0 (COO*C*H$_3$), 62.6

[*C*(CH$_3$)$_3$], 79.2 [*C*(Cb)SO$_2t$Bu], 84.3 [*C*(Cb)SCH$_2$], 87.2/89.0 [*C*(Cp)H], 90.4 [*C*(Cp)COOMe], 166.0 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2933 cm$^{-1}$, 1722, 1632, 1473, 1367, 1309, 1194, 1148. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 254 (4.43), 314 (4.26), 356 nm (3.55). MS (FAB+): 1157 [M + H$^+$], 1083 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] C$_{44}$H$_{62}$Co$_2$O$_{12}$S$_8$: calcd. 1156.0671; found 1156.0709. C$_{44}$H$_{62}$Co$_2$O$_{12}$S$_8$ (1157.4): calcd. C 45.66, H 5.40, S 22.16; found C 45.80, H 5.39, S 22.07.

***syn*-C(3.3)COOMe:** Yellow solid, m.p. 254 °C (dec.). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.47 [s, 36 H, C(CH$_3$)$_3$], 2.06 (m, 4 H, CH$_2$C*H$_2$*CH$_2$), 3.24 (m, 8 H, SC*H$_2$*), 3.85 (s, 6 H, COOCH$_3$), 5.64/5.83 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 25.2 [C(*C*H$_3$)$_3$], 29.4 (CH$_2$*C*H$_2$CH$_2$), 35.6 (S*C*H$_2$), 52.9 (COO*C*H$_3$), 62.5 [*C*(CH$_3$)$_3$], 79.3 [*C*(Cb)SO$_2t$Bu], 84.7 [*C*(Cb)SCH$_2$], 87.2/89.0 [*C*(Cp)H], 90.4 [*C*(Cp)COOMe], 166.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2934 cm$^{-1}$, 1722, 1634, 1473, 1367, 1308, 1194, 1148, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 242 (4.60), 320 (4.28), 366 nm (3.65). MS (FAB+): 1157 [M + H$^+$], 1083 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] C$_{44}$H$_{62}$Co$_2$O$_{12}$S$_8$: calcd. 1156.0671; found 1156.0702. C$_{44}$H$_{62}$Co$_2$O$_{12}$S$_8$ (1157.4): calcd. C 45.66, H 5.40, S 22.16; found C 45.51, H 5.41, S 22.26.

**Reaction of E(3.3) with [EtMe$_4$CpCo(CO)(BTSA)] (5). Reaction A: 8e** (140 mg, 0.28 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 40 mg (19%) of **B(3.3)EtMe$_4$**. **Reaction B: 8e** (360 mg, 0.71 mmol) and **A(3.3)** (80 mg, 0.31 mmol). Yield: 29 mg (13%) of **B(3.3)EtMe$_4$** and 20 mg (5%) of *anti*-**C(3.3)EtMe$_4$**.

**B(3.3)EtMe$_4$:** Yellow solid, m.p. 169 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.98 (t, $^3J$ = 7.6 Hz, 3 H, CH$_2$C*H$_3$*), 1.42 (s, 18 H, C(CH$_3$)$_3$], 1.92/1.93 (s, 12 H, CpC*H$_3$*), 2.13 (m, 4 H, CH$_2$C*H$_2$*CH$_2$), 2.51 (q, $^3J$ = 7.6 Hz, 2 H, C*H$_2$*CH$_3$), 2.57/2.84 (m, 4 H, CH$_2$SC≡), 2.73/3.22 (m, 4 H, SC*H$_2$*CH$_2$CH$_2$SC≡) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 10.0/10.3 (Cp*C*H$_3$), 14.4 (CH$_2$*C*H$_3$), 18.4 (*C*H$_2$CH$_3$), 25.7 [C(*C*H$_3$)$_3$], 30.8 (CH$_2$*C*H$_2$CH$_2$), 35.9/36.2 (SCH$_2$), 62.3 [*C*(CH$_3$)$_3$], 77.2 [*C*(Cb)SO$_2t$Bu], 78.4 [*C*(Cb)SCH$_2$], 87.2 (C≡), 95.7/96.7 [*C*(Cp)CH$_3$], 101.0 [*C*(Cp)CH$_2$CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2967 cm$^{-1}$, 2926, 1630, 1303, 1117. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 268 (4.22), 320 (4.21), 370 (3.31). MS (FAB+): 734 [M$^+$]. HRMS (FAB+): [M + H$^+$] C$_{31}$H$_{48}$CoO$_4$S$_6$: calcd. 735.1209; found 735.1209.

***anti*-C(3.3)EtMe$_4$:** Yellow solid, m.p. 263 °C (dec.). $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.97 (t, $^3J$ = 7.6 Hz, 6 H, CH$_2$C*H$_3$*), 1.42 [s, 36 H, C(CH$_3$)$_3$], 1.90/1.91 (s, 24 H, CpC*H$_3$*), 2.48 (q, $^3J$ = 7.6 Hz, 2 H, C*H$_2$*CH$_3$), 2.73 (m, 4 H, CH$_2$C*H$_2$*CH$_2$), 2.59/3.20 (m, 8 H, SC*H$_2$*) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 10.0/10.2 (Cp*C*H$_3$), 14.3 (CH$_2$*C*H$_3$), 18.3 (*C*H$_2$CH$_3$), 25.8 [C(*C*H$_3$)$_3$], 35.2 (CH$_2$*C*H$_2$CH$_2$), 36.7 (S*C*H$_2$), 62.3 [*C*(CH$_3$)$_3$], 77.2 [*C*(Cb)], 77.6 [*C*(Cb)], 95.8/96.7 [*C*(Cp)CH$_3$], 101.2 [*C*(Cp)CH$_2$CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2968 cm$^{-1}$, 2929, 1632, 1457, 1349, 1306, 1193, 1118. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 268 (4.54), 320 (4.56), 370 nm (3.69). MS (FAB+): 1208 [M$^+$]. HRMS (FAB+): [M + H$^+$] C$_{52}$H$_{83}$Co$_2$O$_8$S$_8$: calcd. 1209.2518; found 1209.2535.

**Reaction of A(4.4) with [CpCo(CO)(BTSA)] (8a). Reaction A: 8a** (105 mg, 0.25 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 57 mg (34%) of **B(4.4)H**. **Reaction B: 8a** (267 mg, 0.64 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 38 mg (20%) of **B(4.4)H**, 81 mg (26%) of *anti*-**C(4.4)H** and 48 mg (16%) of *syn*-**C(4.4)H**.

**B(4.4)H:** Yellow solid, m.p. 206 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.47 [s, 18 H, C(CH$_3$)$_3$], 1.84 (m, 4 H, C*H$_2$*CH$_2$CH$_2$SC≡), 2.00 (m, 4 H, CH$_2$C*H$_2$*CH$_2$SC≡), 2.68 (m, 4 H, CH$_2$SC≡), 3.17 (m, 4 H, C*H$_2$*CH$_2$CH$_2$CH$_2$SC≡), 5.41 (s, 5 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 25.2 [C(*C*H$_3$)$_3$], 27.8 (CH$_2$*C*H$_2$SC≡), 28.7 (*C*H$_2$CH$_2$CH$_2$SC≡), 35.8 (*C*H$_2$SC≡), 37.3 (*C*H$_2$CH$_2$CH$_2$CH$_2$SC≡), 62.0 [*C*(CH$_3$)$_3$], 77.9 [*C*(Cb)SO$_2t$Bu], 84.3 [*C*(Cb)SCH$_2$], 85.9 [*C*(Cp)], 86.6 (C≡) ppm. IR (KBr): $\tilde{\nu}$ = 2929 cm$^{-1}$, 1633, 1306, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 250 (4.20), 316 (4.00), 356 nm (3.31). MS (FAB+): 678 [M$^+$], 605 [M$^+$ − *t*BuO]. HRMS (FAB+): [M + H$^+$] C$_{27}$H$_{40}$CoO$_4$S$_6$: calcd. 679.0583; found 679.0616. C$_{27}$H$_{39}$CoO$_4$S$_6$.CH$_3$OH (711.0): calcd. C 47.31, H 6.09, S 27.08; found C 47.27, H 5.92, S 26.95.

***anti*-C(4.4)H:** Yellow solid, m.p. 293 °C (dec.). $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.46 [s, 36 H, C(CH$_3$)$_3$], 1.88 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 3.08 (m, 8 H, CH$_2$S), 5.37 (s, 10 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 25.2 [C(*C*H$_3$)$_3$], 29.0 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 37.3 (*C*H$_2$S), 62.1 [*C*(CH$_3$)$_3$], 78.3 [*C*(Cb)SO$_2t$Bu], 84.4 [*C*(Cb)SCH$_2$], 86.1 [*C*(Cp)] ppm. IR (KBr): $\tilde{\nu}$ = 2971 cm$^{-1}$, 2931, 1633, 1308, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 250 (4.44), 314 (4.24), 356 nm (3.66). MS (FAB+): 1068 [M$^+$], 995 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] C$_{42}$H$_{62}$Co$_2$O$_8$S$_8$: calcd. 1068.0874; found 1068.0872. C$_{42}$H$_{62}$Co$_2$O$_8$S$_8$ (1069.34): calcd. C 47.17, H 5.84, S 23.99; found C 47.01, H 5.86, S 23.77.

***syn*-C(4.4)H:** Yellow solid, m.p. 273 °C (dec.). $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.46 [s, 36 H, C(CH$_3$)$_3$], 1.87 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 3.06 (m, 8 H, C*H$_2$*S), 5.37 (s, 10 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 25.1 [C(*C*H$_3$)$_3$], 29.0 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 37.1 (*C*H$_2$S), 62.1 [*C*(CH$_3$)$_3$], 78.3 [*C*(Cb)SO$_2t$Bu], 84.0 [*C*(Cb)SCH$_2$], 86.3 [*C*(Cp)] ppm. IR (KBr): $\tilde{\nu}$ = 2931 cm$^{-1}$, 1632, 1308, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 248 (4.49), 312 (4.28), 354 nm (3.59). MS (FAB+): 1068 [M$^+$], 995 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] C$_{42}$H$_{62}$Co$_2$O$_8$S$_8$: calcd. 1068.0874; found 1068.0900.

**Reaction of A(4.4) with [CpMeCo(CO)(BTSA)] (8b). Reaction A: 8b** (109 mg, 0.25 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 74 mg (43%) of **B(4.4)Me**. **Reaction B: 8b** (276 mg, 0.64 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 164 mg (53%) of *anti*-**C(4.4)Me** and 59 mg (19%) of *syn*-**C(4.4)Me**.

**B(4.4)Me:** Yellow solid, m.p. 174 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.45 [s, 18 H, C(CH$_3$)$_3$], 1.81 (m, 4 H, C*H$_2$*CH$_2$CH$_2$SC≡), 1.98 (m, 4 H, C*H$_2$*CH$_2$SC≡), 2.10 (s, 3 H, CpC*H$_3$*), 2.65 (m, 4 H, CH$_2$SC≡), 3.10 (m, 4 H, C*H$_2$*CH$_2$CH$_2$CH$_2$SC≡), 5.19/5.30 (pt, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 12.9 (Cp*C*H$_3$), 25.2 [C(*C*H$_3$)$_3$], 27.8/28.7 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 35.8/36.8 (SCH$_2$), 62.0 [*C*(CH$_3$)$_3$], 77.2 [*C*(Cb)SO$_2t$Bu], 83.1 [*C*(Cb)SCH$_2$], 85.9/86.5 [*C*(Cp)H], 86.6 (C≡), 100.8 [*C*(Cp)CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2964 cm$^{-1}$, 2927, 1632, 1475, 1455, 1305, 1236, 1193, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 254 (4.19), 316 (4.07), 358 nm (3.46). MS (FAB+): 692 [M$^+$], 619 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] C$_{28}$H$_{41}$CoO$_4$S$_6$: calcd. 693.0739; found 693.0750. C$_{28}$H$_{41}$CoO$_4$S$_6$. 0.25 C$_4$H$_{10}$O (711.5): calcd. C 48.96, H 6.16, S 27.04; found C 48.78, H 6.01, S 26.93.

***anti*-C(4.4)Me:** Yellow solid, m.p. 266 °C (dec.). $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.46 [s, 36 H, C(CH$_3$)$_3$], 1.85 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 2.10 (s, 6 H, CpC*H$_3$*), 3.04 (m, 8 H, SC*H$_2$*), 5.14/5.29 (pt, 8 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 12.8 (Cp*C*H$_3$), 25.2 [C(*C*H$_3$)$_3$], 29.0 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 36.6 (S*C*H$_2$), 62.1 [*C*(CH$_3$)$_3$], 77.3 [*C*(Cb)SO$_2t$Bu], 82.5 [*C*(Cb)SCH$_2$], 85.4/86.7 [*C*(Cp)H], 101.0 [*C*(Cp)CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2970 cm$^{-1}$, 2930, 1633, 1475, 1456, 1355, 1307, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 252 (4.59), 314 (4.27), 354 nm (3.73). MS (FAB+): 1096 [M$^+$], 1023 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] C$_{44}$H$_{66}$Co$_2$O$_8$S$_8$: calcd. 1096.1188; found 1096.1172.

***syn*-C(4.4)Me:** Yellow solid, m.p. 266 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.46 [s, 36 H, C(CH$_3$)$_3$], 1.85 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 2.10 (s, 6 H, CpC*H$_3$*), 3.04 (m, 8 H, SC*H$_2$*), 5.14/5.29 (pt, 8 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 12.8 (Cp*C*H$_3$), 25.2 [C(*C*H$_3$)$_3$], 29.1 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 36.6

(S*C*H$_2$), 62.1 [*C*(CH$_3$)$_3$], 77.8 [*C*(Cb)SO$_2$*t*Bu], 82.5 [*C*(Cb)SCH$_2$], 85.4/86.8 [*C*(Cp)H], 101.0 [*C*(Cp)CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2970 cm$^{-1}$, 2929, 1633, 1476, 1456, 1355, 1308, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 252 (4.53), 314 (4.38), 354 nm (3.70). MS (FAB+): 1096 [M$^+$], 1023 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{44}H_{66}Co_2O_8S_8$: calcd. 1096.1188; found 1096.1188. $C_{44}H_{66}Co_2O_8S_8$ (1097.4): calcd. C 48.16, H 6.06, S 23.38; found C 48.22, H 6.07, S 23.26.

**Reaction of A(4.4) with CpSiMe$_3$Co(CO)(BTSA) (8c). Reaction A: 8c** (123 mg, 0.25 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 107 mg (57%) of **B(3.3)SiMe$_3$. Reaction B: 8c** (314 mg, 0.64 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 22 mg (10%) of **B(4.4)SiMe$_3$**, 104 mg (31%) of *anti*-**C(4.4)SiMe$_3$** and 38 mg (11%) of *syn*-**C(4.4)SiMe$_3$**.

**B(4.4)SiMe$_3$:** Yellow solid, m.p. 193 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.34 [s, 9 H, Si(CH$_3$)$_3$], 1.46 [s, 18 H, C(CH$_3$)$_3$], 1.79 (m, 4 H, C*H$_2$*CH$_2$CH$_2$SC≡), 1.95 (m, 4 H, C*H$_2$*CH$_2$SC≡), 2.65 (m, 4 H, CH$_2$SC≡), 2.98/3.15 (m, 4 H, C*H$_2$*CH$_2$CH$_2$CH$_2$SC≡), 5.26/5.73 (pt, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 0.3 [Si(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 27.7 (*C*H$_2$CH$_2$CH$_2$SC≡), 28, 6 (*C*H$_2$CH$_2$SC≡), 35.7 (CH$_2$SC≡), 37.2 (*C*H$_2$CH$_2$CH$_2$CH$_2$SC≡), 62.2 [*C*(CH$_3$)$_3$], 76.8 [*C*(Cb)SO$_2$*t*Bu], 84.0 [*C*(Cb)SCH$_2$], 86.6 (C≡), 88.9/90.2 [*C*(Cp)H], 94.3 [*C*(Cp)SiMe$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2929 cm$^{-1}$, 1633, 1456, 1307, 1248, 1192, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 258 (4.16), 318 (4.05), 362 nm (3.41). MS (FAB+): 750 [M$^+$], 677 [M$^+$ − SiMe$_3$]. HRMS (FAB+): [M$^+$] $C_{30}H_{47}CoO_4S_6Si$: calcd. 750.0900; found 750.0909. $C_{30}H_{47}CoO_4S_6Si.0.25\ C_4H_{10}O$ (769.6): calcd. C 48.38, H 6.48, S 25.00; found C 48.56, H 6.41, S 25.21.

***anti*-C(4.4)SiMe$_3$:** Yellow solid, m.p. 202 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.35 [s, 18 H, Si(CH$_3$)$_3$], 1.47 [s, 36 H, C(CH$_3$)$_3$], 1.88 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 2.99 (m, 8 H, C*H$_2$*S), 5.15/5.73 (pt, 8 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = −0.4 [Si(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 28.2 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 36.4 (S*C*H$_2$), 61.6 [*C*(CH$_3$)$_3$], 77.3 [*C*(Cb)SO$_2$*t*Bu], 82.8 [*C*(Cb)SCH$_2$], 88.5/89.8 [*C*(Cp)H], 93.8 [*C*(Cp)SiMe$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2931 cm$^{-1}$, 1457, 1355, 1310, 1249, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 328 (4.34), 360 (3.69), 370 nm (3.77). MS (FAB+): 1212 [M$^+$], 1139 [M$^+$ − SiMe$_3$]. HRMS (FAB+): [M + H$^+$] $C_{48}H_{79}Co_2O_8S_8Si_2$: calcd. 1213.1743; found 1213.1743. $C_{48}H_{78}Co_2O_8S_8Si_2.0.5\ C_4H_{10}O$ (1250.8): calcd. C 48.02, H 6.69, S 20.51; found C 48.29, H 6.65, S 20.26.

***syn*-C(4.4)SiMe$_3$:** Yellow solid, m.p. 274 °C (dec.). $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.32 [s, 18 H, Si(CH$_3$)$_3$], 1.48 [s, 36 H, C(CH$_3$)$_3$], 1.85 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 3.00 (m, 8 H, C*H$_2$*S), 5.12/5.72 (pt, 8 H, CpH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 0.3 [Si(CH$_3$)$_3$], 25.3 [C(*C*H$_3$)$_3$], 28.8 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 37.3 (S*C*H$_2$), 62.3 [*C*(CH$_3$)$_3$], 77.9 [*C*(Cb)SO$_2$*t*Bu], 84.0 [*C*(Cb)SCH$_2$], 89.2/90.4 [*C*(Cp)H], 99.8 [*C*(Cp)SiMe$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2931 cm$^{-1}$, 1633, 1457, 1356, 1309, 1249, 1121. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 260 (4.48), 316 (4.37), 360 nm (3.69). MS (FAB+): 1212 [M$^+$], 1139 [M$^+$ − SiMe$_3$]. HRMS (FAB+): [M + H$^+$] $C_{48}H_{79}Co_2O_8S_8Si_2$: calcd. 1213.1743; found 1213.1741. $C_{48}H_{78}Co_2O_8S_8Si_2.0.5\ C_4H_{10}O$ (1250.8): calcd. C 48.02, H 6.69, S 20.51; found C 47.78, H 6.64, S 20.32.

**Reaction of A(4.4) with CpCOOMeCo(CO)(BTSA) (8d). Reaction A: 8d** (120 mg, 0.25 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 75 mg (41%) of **B(4.4)COOMe**, and 12 mg (8%) of *syn*-**C(4.4)COOMe**. **Reaction B: 8d** (304 mg, 0.64 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 6 mg (3%) of **B(4.4)COOMe**, 97 mg (29%) of *anti*-**C(4.4)COOMe** and 97 mg (29%) of *syn*-**C(4.4)COOMe**.

**B(4.4)COOMe:** Yellow solid, m.p. 155 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.45 [s, 18 H, C(CH$_3$)$_3$], 1.81 (m, 4 H, C*H$_2$*CH$_2$CH$_2$SC≡), 1.97 (m, 4 H, C*H$_2$*CH$_2$SC≡), 2.65 (m, 4 H, CH$_2$SC≡), 3.17 (m, 4 H, C*H$_2$*CH$_2$CH$_2$CH$_2$SC≡), 3.89 (s, 3 H, COOCH$_3$), 5.65/5.82 (pt, 4 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 25.1 [C(*C*H$_3$)$_3$], 28.0/28.6 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 35.70/35.73 (SCH$_2$), 52.9 (COO*C*H$_3$), 62.4 [*C*(CH$_3$)$_3$], 78.1 [*C*(Cb)SO$_2$*t*Bu], 85.7 [*C*(Cb)SCH$_2$], 86.5 (C≡), 86.9/88.8 [*C*(Cp)H], 90.4 [*C*(Cp)COOMe], 166.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2931 cm$^{-1}$, 1724, 1632, 1472, 1308, 1146. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 240 (4.35), 324 (4.05), 364 nm (3.41). MS (FAB+): 736 [M$^+$], 633 (M$^+$ − *t*BuO). HRMS (FAB+): [M + H$^+$] $C_{29}H_{42}CoO_6S_6$: calcd. 737.0638; found 737.0639. $C_{29}H_{41}CoO_6S_6{\cdot}CH_3OH$ (769.0): calcd. C 46.86, H 5.90, S 25.02; found C 46.51, H 5.78, S 25.29.

***anti*-C(4.4)COOMe:** Yellow solid, m.p. 246 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.47 (s, 36 H, C(CH$_3$)$_3$], 1.86 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 3.13 (m, 8 H, C*H$_2$*S), 3.86 (s, 6 H, COOCH$_3$), 5.63/5.79 (pt, 8 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 24.4 (C(*C*H$_3$)$_3$], 28.1 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 35.0 (S*C*H$_2$), 52.7 (COO*C*H$_3$), 61.7 [*C*(CH$_3$)$_3$], 77.9 [*C*(Cb)SO$_2$*t*Bu], 85.0 [*C*(Cb)SCH$_2$], 86.4/88.2 [*C*(Cp)H], 90.7 [*C*(Cp)COOMe], 166.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2934 cm$^{-1}$, 1721, 1633, 1473, 1367, 1308, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ [nm] (log ε) = 240 (4.64), 322 (4.35), 366 nm (3.76). MS (FAB+): 1184 [M$^+$], 1111 (M$^+$ − *t*BuO). HRMS (FAB+): [M + H$^+$] $C_{46}H_{67}Co_2O_{12}S_8$: calcd. 1185.1062; found 1185.1056. $C_{46}H_{66}Co_2O_{12}S_8$ (1185.4): calcd. C 46.61, H 5.61, S 21.64; found C 46.66, H 5.66, S 21.56.

***syn*-C(4.4)COOMe:** Yellow solid, m.p. 193 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 1.45 [s, 36 H, C(CH$_3$)$_3$], 1.85 (m, 8 H, CH$_2$C*H$_2$*C*H$_2$*CH$_2$), 3.12 (m, 8 H, C*H$_2$*S), 3.89 (s, 6 H, COOCH$_3$), 5.61/5.77 (pt, 8 H, CpH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 25.1 (C(*C*H$_3$)$_3$], 28.8 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$), 35.5 (S*C*H$_2$), 52.9 (COO*C*H$_3$), 62.5 [*C*(CH$_3$)$_3$], 78.4 [*C*(Cb)SO$_2$*t*Bu], 85.1 [*C*(Cb)SCH$_2$], 87.4/88.9 [*C*(Cp)H], 90.5 [*C*(Cp)COOMe], 166.0 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2934 cm$^{-1}$, 1721, 1633, 1473, 1367, 1308, 1122. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 242 (4.66), 320 (4.35), 366 nm (3.68). MS (FAB+): 1184 [M$^+$], 1111 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{46}H_{66}Co_2O_{12}S_8$: calcd. 1184.0984; found 1184.0986. $C_{46}H_{66}Co_2O_{12}S_8$ (1185.4): calcd. C 46.61, H 5.61, S 21.64; found C 46.59, H 5.62, S 21.49.

**Reaction of A(4.4) with EtMe$_4$CpCo(CO)(BTSA) (8e). Reaction A: 8e** (126 mg, 0.25 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 17 mg (9%) of **B(4.4)EtMe$_4$. Reaction B: 8e** (322 mg, 0.64 mmol) and **A(4.4)** (80 mg, 0.28 mmol). Yield: 30 mg (14%) of **B(4.4)EtMe$_4$**.

**B(4.4)EtMe$_4$:** Yellow solid, m.p. 184 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.98 (t, $^3J$ = 7.5 Hz, 3 H, CH$_2$C*H$_3$*), 1.41 [s, 18 H, C(CH$_3$)$_3$], 1.75 (m, 4 H, C*H$_2$*CH$_2$CH$_2$SC≡), 1.93 (m, 4 H, C*H$_2$*CH$_2$SC≡), 1.92/1.94 (s, 12 H, CpC*H$_3$*), 2.51 (q, $^3J$ = 7.5 Hz, 2 H, C*H$_2$*CH$_3$), 2.62/2.70 (m, 4 H, CH$_2$SC≡), 2.70/3.03 (m, 4 H, C*H$_2$*CH$_2$CH$_2$CH$_2$SC≡) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 10.0/10.3 (Cp*C*H$_3$), 14.4 (CH$_2$*C*H$_3$), 18.4 (*C*H$_2$CH$_3$), 25.7 [C(*C*H$_3$)$_3$], 28.0 (*C*H$_2$CH$_2$CH$_2$SC≡), 28.8 (*C*H$_2$CH$_2$SC≡), 35.8 (*C*H$_2$SC≡), 37.1 (*C*H$_2$CH$_2$CH$_2$CH$_2$SC≡), 62.3 [*C*(CH$_3$)$_3$], 76.4 [*C*(Cb)SO$_2$*t*Bu], 78.6 [*C*(Cb)SCH$_2$], 86.7 (C≡), 95.5/96.5 [*C*(Cp)CH$_3$], 100.9 [*C*(Cp)CH$_2$CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2964 cm$^{-1}$, 2928, 2867, 1456, 1357, 1307, 1237, 1193, 1117, 1024. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log ε) = 266 (4.26), 322 (4.29), 364 nm (3.40). MS (FAB+): 762 [M$^+$], 689 [M$^+$ − *t*BuO]. HRMS (FAB+): [M$^+$] $C_{33}H_{51}CoO_4S_6$: calcd. 762.1444; found 762.1474. $C_{33}H_{51}CoO_4S_6{\cdot}0.5CH_3OH$ (795.1): calcd. C 51.65, H 6.86, S 24.69; found C 51.80, H 6.64, S 24.59.

**Reaction of A(5.5) with CpCo(CO)(BTSA) (8a). Reaction A: 8a** (84 mg, 0.20 mmol) and **A(5.5)** (70 mg, 0.22 mmol). Yield: 31 mg (22%) of **B(5.5)H** and 12 mg (5%) of a mixture of *anti*-**C(5.5)H** and *syn*-**C(5.5)H**. **Reaction B: 8a** (213 mg, 0.51 mmol) and **A(5.5)** (80 mg, 0.22 mmol). Yield: 20 mg (13%) of **B(5.5)H** and 75 mg (31%) of a mixture of *anti*-**C(5.5)H** and *syn*-**C(5.5)H**.

**B(5.5)H:** Yellow solid, m.p. 132 °C. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.47$ [s, 18 H, $C(CH_3)_3$], 1.59 (m, 4 H, $CH_2CH_2CH_2SC{\equiv}$), 1.76 (m, 4 H, $CH_2CH_2CH_2CH_2SC{\equiv}$), 1.83 (m, 4 H, $CH_2CH_2SC{\equiv}$), 2.63 (m, 4 H, $CH_2SC{\equiv}$), 3.02 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 5.35 (s, 5 H, CpH) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta = 25.2$ [$C(CH_3)_3$], 28.1 ($CH_2CH_2CH_2SC{\equiv}$), 29.6 ($CH_2CH_2SC{\equiv}$), 30.4 ($CH_2CH_2CH_2CH_2SC{\equiv}$), 36.2 ($CH_2SC{\equiv}$), 37.6 ($CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 62.0 [$C(CH_3)_3$], 78.3 [$C(Cb)SO_2t$Bu], 84.3 [$C(Cb)SCH_2$], 86.2 [C(Cp)], 86.6 ($C{\equiv}$) ppm. IR (KBr): $\tilde{\nu} = 2964\ cm^{-1}$, 2928, 2855, 1456, 1349, 1310, 1193, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 248 (3.48), 312 (4.01), 356 nm (3.35). MS (FAB+): 706 [$M^+$], 633 [$M^+ - t$BuO]. HRMS (FAB+): [$M^+$] $C_{29}H_{43}CoO_4S_6$: calcd. 706.0818; found 706.0825.

**Data for the Mixture of *anti*-C(5.5)H and *syn*-C(5.5)H:** Yellow solid. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.45$ [s, 72 H, $C(CH_3)_3$], 1.63 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 1.72 (m, 16 H, $CH_2CH_2CH_2CH_2CH_2$), 3.05 (m, 16 H, $CH_2CH_2CH_2CH_2CH_2$), 5.36 (s, 10 H, CpH), 5.37 (s, 10 H, CpH) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta = 25.1$ [$C(CH_3)_3$], 28.8 ($CH_2CH_2CH_2CH_2CH_2$), 29.5 ($CH_2CH_2CH_2CH_2CH_2$), 37.7/37.8 ($CH_2CH_2CH_2CH_2CH_2$), 62.03/62.05 [$C(CH_3)_3$], 78.1/78.2 [$C(Cb)SO_2t$Bu], 84.38/84.43 [$C(Cb)SCH_2$], 85.98/86.00 [C(Cp)] ppm. IR (KBr): $\tilde{\nu} = 2971\ cm^{-1}$, 2931, 2858, 1458, 1351, 1309, 1194, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 250 (4.45), 314 (4.25), 362 nm (3.54). MS (FAB+): 1096 [$M^+$], 1023 [$M^+ - t$BuO]. HRMS (FAB+): [$M^+$] $C_{44}H_{66}Co_2O_8S_8$: calcd. 1096.1187; found 1096.1215. $C_{44}H_{66}Co_2O_8S_8$ (1097.4): calcd. C 48.16, H 6.06, S 23.38; found C 48.28, H 6.03, S 23.27.

**Reaction of A(5.5) with CpMeCo(CO)(BTSA) (8b). Reaction A: 8b** (87 mg, 0.20 mmol) and **A(5.5)** (70 mg, 0.22 mmol). Yield: 44 mg (30%) of **B(5.5)Me** and 39 mg (17%) of a mixture of *anti*-**C(5.5)Me** and *syn*-**C(5.5)Me**. **Reaction B: 8b** (220 mg, 0.51 mmol) and **A(5.5)** (70 mg, 0.22 mmol). Yield: 137 mg (55%) of a mixture of *anti*-**C(5.5)Me** and *syn*-**C(5.5)Me**.

**B(5.5)Me:** Yellow solid, m.p. 122 °C. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.47$ [s, 18 H, $C(CH_3)_3$], 1.59 (m, 4 H, $CH_2CH_2CH_2SC{\equiv}$), 1.75 (m, 4 H, $CH_2CH_2CH_2CH_2SC{\equiv}$), 1.82 (m, 4 H, $CH_2CH_2SC{\equiv}$), 2.09 (s, 3 H, $CpCH_3$), 2.63 (m, 4 H, $CH_2SC{\equiv}$), 2.99 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 5.12/5.28 (pt, 4 H, CpH) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta = 12.8$ ($CpCH_3$), 25.2 [$C(CH_3)_3$], 28.1 ($CH_2CH_2CH_2SC{\equiv}$), 29.6 ($CH_2CH_2SC{\equiv}$), 30.4 ($CH_2CH_2CH_2CH_2SC{\equiv}$), 36.2 ($CH_2SC{\equiv}$), 37.1 ($CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 62.0 [$C(CH_3)_3$], 77.8 [$C(Cb)SO_2t$Bu], 83.0 [$C(Cb)SCH_2$], 85.3/86.7 [C(Cp)H], 86.6 ($C{\equiv}$), 100.9 [$C(Cp)CH_3$] ppm. IR (KBr): $\tilde{\nu} = 2959\ cm^{-1}$, 2929, 2857, 1475, 1456, 1354, 1309, 1222, 1194, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 254 (4.25), 314 (4.08), 360 nm (3.32). MS (FAB+): 720 [$M^+$], 647 [$M^+ - t$BuO]. HRMS (FAB+): [$M^+$] $C_{30}H_{45}CoO_4S_6$: calcd. 720.0974; found 720.0984.

**Data for the Mixture of *anti*-C(5.5)Me and *syn*-C(5.5)Me:** Yellow solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta = 1.44$ (s, 72 H, $C(CH_3)_3$], 1.69 (m, 24 H, $CH_2CH_2CH_2CH_2CH_2$), 2.08 (s, 6 H, $CpCH_3$), 2.09 (s, 6 H, $CpCH_3$), 3.05 (m, 16 H, $CH_2CH_2CH_2CH_2CH_2$), 5.15/5.28 (pt, 16 H, CpH) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta = 12.82/12.83$ ($CpCH_3$), 25.2 [$C(CH_3)_3$], 28.9 ($CH_2CH_2CH_2CH_2CH_2$), 29.5 ($CH_2CH_2CH_2CH_2CH_2$), 37.7 ($CH_2CH_2CH_2CH_2CH_2$), 62.03/62.04 [$C(CH_3)_3$], 77.43/77.54 [$C(Cb)SO_2t$Bu], 83.2 [$C(Cb)SCH_2$], 85.0/86.5 [C(Cp)H], 100.8 [$C(Cp)CH_3$] ppm. IR (KBr): $\tilde{\nu} = 2969\ cm^{-1}$, 2929, 2858, 1476, 1457, 1353, 1311, 1194, 1123. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 254 (4.59), 314 (4.43), 360 nm (3.65). MS (FAB+): 1124 [$M^+$], 1051 [$M^+ - t$BuO]. HRMS (FAB+): [$M + H^+$] $C_{46}H_{71}Co_2O_8S_8$: calcd. 1125.1579; found 1125.1584. $C_{46}H_{70}Co_2O_8S_8$ (1125.5): calcd. C 49.09, H 6.27, S 22.79; found C 49.25, H 6.23, S 22.70.

**Reaction of A(5.5) with CpCOOMeCo(CO)(BTSA) (8d). Reaction A: 8d** (96 mg, 0.20 mmol) and **A(5.5)** (70 mg, 0.22 mmol). Yield: 48 mg (31%) of **B(5.5)COOMe**. **Reaction B: 8d** (242 mg, 0.51 mmol) and **A(5.5)** (70 mg, 0.22 mmol). Yield: 165 mg (61%) of a mixture of *anti*-**C(5.5)COOMe** and *syn*-**C(5.5)COOMe**.

**B(5.5)COOMe:** Orange oil. $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta = 1.47$ [s, 18 H, $C(CH_3)_3$], 1.60 (m, 4 H, $CH_2CH_2CH_2SC{\equiv}$), 1.78 (m, 8 H, $CH_2CH_2CH_2CH_2SC{\equiv}$), 2.63 (m, 4 H, $CH_2SC{\equiv}$), 3.07 (m, 4 H, $CH_2CH_2CH_2CH_2CH_2SC{\equiv}$), 3.88 (s, 3 H, $COOCH_3$), 5.62/5.74 (pt, 4 H, CpH) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 25.1$ [$C(CH_3)_3$], 28.0 ($CH_2CH_2CH_2SC{\equiv}$), 29.5/30.3 ($CH_2CH_2CH_2CH_2SC{\equiv}$), 36.0/36.2 ($CH_2S$), 52.8 ($COOCH_3$), 62.4 [$C(CH_3)_3$], 78.6 [$C(Cb)SO_2t$Bu], 85.4 [$C(Cb)SCH_2$], 86.6 ($C{\equiv}$), 87.3/88.9 [C(Cp)H], 90.4 [$C(Cp)CH_3$], 166.1 ($COOCH_3$) ppm. IR (KBr): $\tilde{\nu} = 2929\ cm^{-1}$, 1720, 1472, 1308, 1283, 1192, 1147. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 240 (4.99), 320 (4.66), 364 nm (3.47). MS (FAB+): 764 [$M^+$], 691 [$M^+ - t$BuO]. HRMS (FAB+): [$M^+$] $C_{31}H_{45}CoO_6S_6$: calcd. 764.0872; found 764.0891.

**Data for the Mixture of *anti*-C(5.5)COOMe and *syn*-C(5.5)COOMe:** Yellow solid. $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta = 1.46$ [s, 72 H, $C(CH_3)_3$], 1.68 (m, 24 H, $CH_2CH_2CH_2CH_2CH_2$), 3.11 (m, 16 H, $CH_2CH_2CH_2CH_2CH_2$), 3.85 (s, 6 H, $COOCH_3$), 3.90 (s, 6 H, $COOCH_3$), 5.63/5.79 (pt, 16 H, CpH) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 24.4$ [$C(CH_3)_3$], 28.84/28.87 ($CH_2CH_2CH_2CH_2CH_2$), 29.4 ($CH_2CH_2CH_2CH_2CH_2$), 36.14/36.26 ($CH_2CH_2CH_2CH_2CH_2$), 52.76/52.88 ($COOCH_3$), 62.44/62.47 [$C(CH_3)_3$], 78.32/78.45 [$C(Cb)SO_2t$Bu], 85.65/85.88 [$C(Cb)SCH_2$], 87.03/87.10/88.78/ 88.81 [C(Cp)H], 90.31/90.34 [$C(Cp)COOCH_3$], 166.13 ($COOCH_3$) ppm. IR (KBr): $\tilde{\nu} = 2932\ cm^{-1}$, 1720, 1650, 1472, 1367, 1309, 1193, 1147, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log ε) = 242 (4.56), 322 (4.25), 364 nm (3.58). MS (FAB+): 1212 [$M^+$], 1139 [$M^+ - t$BuO]. HRMS (FAB+): [$M + H^+$] $C_{48}H_{71}Co_2O_{12}S_8$: calcd. 1213.1375; found 1213.1399. $C_{48}H_{70}Co_2O_{12}S_8$ (1213.5): calcd. C 47.51, H 5.81; found C 47.19, H 5.83.

**Reaction of A(3.3.3) with [CpSiMe$_3$Co(CO)(BTSA)] (8c). Synthesis of A(3.3.3):** A suspension of lithium acetylide in THF and a solution of 1,3-dithiocyanatopropane in THF were added simultaneously at −40 °C to THF (1 L) over a period of 4 h. After complete addition, the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed by rotary evaporation and polymers and salts were removed by flash filtration [$SiO_2$; 3% $NEt_3$(v/v), toluene]. After removal of the solvent, the product was isolated by column chromatography [$SiO_2$; 3% $NEt_3$ (v/v), *n*-hexane/toluene, 3:1]. Starting material: Dilithium acetylide, prepared from *n*BuLi (60 mmol) in THF (250 mL) and 1,3-dithiocyanatopropane (4.51 g, 28.5 mmol) in THF (250 mL). Yield: 107 mg (3%) of **A(3.3.3)**.

**A(3.3.3):** Colourless solid, m.p. 100 °C. $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta = 2.24$ (quint, 6 H, $SCH_2CH_2$), 2.81 (t, $^{3}J = 7.1$ Hz, 12 H, $SCH_2$) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 28.5$ ($SCH_2CH_2$), 34.4 ($SCH_2$), 86.2 ($C{\equiv}$) ppm. IR (KBr): $\tilde{\nu} = 2929\ cm^{-1}$, 2058, 1437. MS (EI+): 390 [$M^+$], 204, 88. HRMS (EI+): [$M^+$] $C_{15}H_{18}S_6$: calcd. 389.9733; found 389.9725. $C_{15}H_{18}S_6$ (390.7): calcd. C 46.11, H 4.64, S 49.25; found C 46.22, H 4.70, S 48.99.

Starting material: **A(3.3.3)** (60 mg, 0.15 mmol) and **8c** (453 mg, 0.92 mmol). Yield: 154 mg (56%) of *anti*-**C(3.3.3)SiMe$_3$**, 36 mg (13%) of *all-syn*-**C(3.3.3)SiMe$_3$**.

***anti*-C(3.3.3)SiMe$_3$:** Yellow solid, m.p. 103 °C (dec.). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.29 [s, 9 H, $Si(CH_3)_3$], 0.32 [s, 18 H, $Si(CH_3)_3$], 1.47 [s, 48 H, $C(CH_3)_3$], 1.99 (m, 6 H, $CH_2CH_2CH_2$), 3.03 (m, 12 H, $SCH_2$), 5.19/5.73 (pt, 12 H, CpH) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = −0.2 [$Si(CH_3)_3$], 24.7 [$C(CH_3)_3$], 29.5 ($CH_2CH_2CH_2$), 29.6 ($CH_2CH_2CH_2$), 36.1 ($SCH_2$), 36.1 ($SCH_2$), 36.3 ($SCH_2$), 61.8 [$C(CH_3)_3$], 61.8 [$C(CH_3)_3$], 61.9 [$C(CH_3)_3$], 76.4 [$C$(Cb)$SO_2t$Bu], 76.5 [$C$(Cb)$SO_2t$Bu], 76.6 [$C$(Cb)$SO_2t$Bu], 82.9 [$C$(Cb)$SCH_2$], 83.6 [$C$(Cb)$SCH_2$], 83.6 [$C$(Cb)$SCH_2$], 88.5/88.6/88.6/89.6/89.8/90.3 [$C$(Cp)H], 93.7/93.9 [$C$(Cp)$SiMe_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2958 cm$^{-1}$, 1631, 1351, 1122. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ [nm] (log $\varepsilon$) = 258 (4.34), 316 (4.22). MS (FAB+): 1778 [M$^+$]. HRMS (FAB+): [M + Na$^+$] $C_{69}H_{111}Co_3O_{12}S_{12}Si_3Na$: calcd. 1799.1926; found 1799.1908. $C_{69}H_{111}Co_3O_{12}S_{12}Si_3$ (1778.5): calcd. C 46.60, H 6.29, S 21.64; found C 46.96, H 6.41, S 21.49.

***all-syn*-C(3.3.3)SiMe$_3$:** Yellow solid, m.p. 105 °C (dec.). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 0.35 [s, 27 H, $Si(CH_3)_3$], 1.46 [s, 48 H, $C(CH_3)_3$], 1.98 (m, 6 H, $CH_2CH_2CH_2$), 3.04 (m, 6 H, SCH$H$), 3.07 (m, 6 H, SCH$H$), 5.21/5.72 (pt, 12 H, CpH) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = −0.2 [$Si(CH_3)_3$], 24.7 [$C(CH_3)_3$], 29.5 ($CH_2CH_2CH_2$), 36.1 ($SCH_2$), 61.8 [$C(CH_3)_3$], 76.4 [$C$(Cb)$SO_2t$Bu], 83.4 [$C$(Cb)$SCH_2$], 88.5/90.0 [$C$(Cp)H], 94.0 [$C$(Cp)$SiMe_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2956 cm$^{-1}$, 1631, 1309, 1250, 1121. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 258 (4.60), 316 (4.47), 364 (3.69), 408 nm (3.40). MS (FAB+): 1778 [M$^+$]. HRMS (FAB+): [M$^+$] $C_{69}H_{112}Co_3O_{12}S_{12}Si_3$: calcd. 1777.2106; found 1777.2108. $C_{69}H_{111}Co_3O_{12}S_{12}Si_3$.0.25 $C_4H_{10}O$ (1797.0): calcd. C 47.15, H 6.51, S 20.98; found C 46.97, H 6.56, S 20.76.

**X-ray Diffraction Analyses:** Reflections were collected using Nonius CAD4, Bruker Smart CCD and Bruker APEX diffractometers (Mo-$K_\alpha$ radiation, graphite monochromator). Intensities were corrected for Lorentz and polarisation effects. Numerical (face indexing) or empirical absorption corrections were applied using SADABS.[16] 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 ($F^2$). Hydrogen atom positions were calculated according to stereochemical aspects. In **B(2.3)SiMe$_3$** the *tert*-butyl groups (6:4) and the thiaalkyne side chain (7:3) were disordered. In *syn*-**C(2.2)SiMe$_3$** one ethano moiety was disordered (1:1:1). In *syn*-**C(3.3)SiMe$_3$** two methylene units were disordered (3:1). The minor positions were refined isotropically. Structure solution and refinement were carried out using the SHELXTL software package.[16] Tables 5 and 6 contain the crystallographic data, details of the data collection and the refinement procedure. ORTEP drawings were obtained using ORTEP-3 for Windows.[17] CCDC-193187 to -193198 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 5. Crystallographic data for **B(2.2)SiMe$_3$**, **B(2.3)SiMe$_3$**, **B(3.3)SiMe$_3$**, **B(4.4)Me**, *syn*-**C(2.2)SiMe$_3$** and *anti*-**C(2.3)SiMe$_3$**

| | **B(2.2)SiMe$_3$** | **B(2.3)SiMe$_3$** | **B(3.3)SiMe$_3$** | **B(4.4)Me** | *syn*-**C(2.2)SiMe$_3$** | *anti*-**C(2.3)SiMe$_3$** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{26}H_{39}CoO_4S_6Si$ | $C_{27}H_{41}CoO_4S_6Si$ | $C_{28}H_{43}CoO_4S_6Si$ | $C_{28}H_{41}CoO_4S_6$ | $C_{44}H_{70}Co_2O_8S_8Si_2$ | $C_{45}H_{72}Co_2O_8S_8Si_2$ |
| Formula mass [g/mol] | 695.01 | 708.98 | 723.06 | 692.96 | 1157.60 | 1171.63 |
| Crystal colour | orange | orange | yellow | dark yellow | orange | orange |
| Crystal size [mm] | 0.24 × 0.20 × 0.17 | 0.40 × 0.20 × 0.15 | 0.48 × 0.14 × 0.12 | 0.42 × 0.38 × 0.15 | 0.42 × 0.18 × 0.13 | 0.30 × 0.17 × 0.16 |
| Crystal shape | polyhedron | polyhedron | polyhedron | polyhedron | polyhedron | polyhedron |
| Temperature [K] | 200(2) | 293(2) | 200(2) | 200(2) | 200(2) | 200(2) |
| Crystal system | triclinic | orthorhombic | orthorhombic | triclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | Pbca | $Pca2_1$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ |
| Z | 2 | 8 | 8 | 2 | 4 | 4 |
| $a$ [Å] | 11.3932(2) | 32.031(8) | 20.8028(3) | 10.7867(3) | 14.3890(3) | 15.9129(1) |
| $b$ [Å] | 11.4211(1) | 16.732(5) | 9.8930(2) | 11.9069(4) | 27.0985(5) | 20.7595(2) |
| $c$ [Å] | 13.6488(1) | 12.517(3) | 33.4337(2) | 13.5096(4) | 15.5620(3) | 17.3414(2) |
| $\alpha$ [°] | 68.160(1) | 90 | 90 | 108.122(1) | 90 | 90 |
| $\beta$ [°] | 79.717(1) | 90 | 90 | 94.780(1) | 115.870(1) | 102.561(2) |
| $\gamma$ [°] | 81.728(1) | 90 | 90 | 99.355(1) | 90 | 90 |
| $V$ [Å$^3$] | 1616.23(3) | 6708(3) | 6880.73(18) | 1610.45(8) | 5459.85(18) | 5591.49(9) |
| $D_{calcd.}$ [g/cm$^3$] | 1.428 | 1.404 | 1.396 | 1.429 | 1.408 | 1.392 |
| $\mu$ [mm$^{-1}$] | 0.986 | 0.951 | 0.929 | 0.954 | 1.004 | 0.981 |
| $h_{min}/h_{max}$ | −13/13 | 0/42 | −24/24, | −12/12 | −18/18 | −18/18 |
| $k_{min}/k_{max}$ | −13/13 | 0/22 | −11/11, | −13/14 | −35/35 | −24/24 |
| $l_{min}/l_{max}$ | −15/14 | 0/16 | −40/40 | −15/16 | −20/20 | −19/20 |
| Refl. collected | 12061 | 8064 | 48399 | 12022 | 56008 | 41137 |
| Refl. unique | 5384 | 8064 | 11929 | 5349 | 12514 | 9678 |
| Refl. observed | 4756 | 3877 | 9825 | 4866 | 9065 | 7489 |
| Parameter | 352 | 407 | 722 | 359 | 604 | 604 |
| $S$ (Gof) on $F^2$ | 1.04 | 1.01 | 1.14 | 1.03 | 1.02 | 1.07 |
| $R(F)$ | 0.025 | 0.054 | 0.066 | 0.023 | 0.045 | 0.033 |
| $R_w(F^2)$ | 0.063 | 0.142 | 0.163 | 0.058 | 0.093 | 0.065 |
| $(\Delta\rho)_{max}$ [eA$^{-3}$] | 0.30 | 0.94 | 1.94 | 0.30 | 0.89 | 0.31 |
| $(\Delta\rho)_{min}$ [eA$^{-3}$] | −0.28 | −0.47 | −0.50 | −0.25 | −0.98 | −0.34 |

Table 6. Crystallographic data for *syn*- and *anti*-**C(3.3)SiMe$_3$**, *syn*- and *anti*-**C(4.4)Me**, **A(3.3.3)** and all-*syn*-**C(3.3.3)SiMe$_3$**

| | *syn*-**C(3.3)SiMe$_3$** | *anti*-**C(3.3)SiMe$_3$** | *syn*-**C(4.4)Me** | *anti*-**C(4.4)Me** | **A(3.3.3)** | all-*syn*-**C(3.3.3)SiMe$_3$** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{46}H_{74}Co_2O_8S_8Si_2$[a] | $C_{46}H_{74}Co_2O_9S_8Si_2$[b] | $C_{44}H_{66}Co_2O_8S_8$ | $C_{58}H_{82}Co_2O_8S_8$[c] | $C_{15}H_{18}S_6$ | $C_{69}H_{111}Co_3O_{12}S_{12}Si_3$ |
| Formula mass [g/mol] | 1185.65 | 1185.65 | 1097.40 | 1097.40 | 390.65 | 1778.40 |
| Crystal colour | orange | orange | yellow | yellow | colorless | yellow |
| Crystal size [mm] | 0.22 × 0.17 × 0.16 | 0.23 × 0.21 × 0.13 | 0.48 × 0.20 × 0.11 | 0.48 × 0.10 × 0.09 | 0.15 × 0.08 × 0.06 | 0.23 × 0.15 × 0.05 |
| Crystal shape | polyhedron | polyhedron | polyhedron | needle | polyhedron | plate |
| Temperature [K] | 200(2) | 200(2) | 200(2) | 200(2) | 200(2) | 203(2) |
| Crystal system | Triclinic | orthorhombic | tetragonal | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $Pna2_1$ | $P4_2/n$ | $P2_1/c$ | $P\bar{1}$ | $C2/c$ |
| Z | 4 | 4 | 8 | 2 | 2 | 8 |
| $a$ [Å] | 17.3542(1) | 11.0539(1) | 31.6670(3) | 9.8439(1) | 5.1841(2) | 42.073(4) |
| $b$ [Å] | 17.7849(3) | 49.9314(1) | 31.6670(3) | 25.6281(4) | 11.0558(2) | 15.933(1) |
| $c$ [Å] | 22.0769(3) | 10.5457(1) | 9.9244(1) | 12.2894(1) | 16.4672(5) | 30.183(3) |
| $\alpha$ [°] | 112.615(1) | 90 | 90 | 90 | 80.108(2) | 90 |
| $\beta$ [°] | 108.785(1) | 90 | 90 | 94.812(1) | 83.827(2) | 113.086(2) |
| $\gamma$ [°] | 91.480(1) | 90 | 90 | 90 | 87.066(2) | 90 |
| $V$ [Å$^3$] | 5866.94(13) | 5820.56(8) | 9952.18(17) | 3089.45(6) | 923.87(5) | 18612(3) |
| $D_{calcd.}$ [g/cm$^3$] | 1.371 | 1.389 | 1.465 | 1.378 | 1.404 | 1.269 |
| $\mu$ [mm$^{-1}$] | 0.939 | 0.947 | 1.052 | 0.858 | 0.731 | 0.885 |
| $h_{min}/h_{max}$ | −20/20 | −13/13 | −37/37 | −11/11 | −6/6 | −56/56 |
| $k_{min}/k_{max}$ | −20/21 | −57/60 | −36/36 | −29/31 | −14/14 | −21/20 |
| $l_{min}/l_{max}$ | −25/26 | −12/12 | −12/11 | −14/14 | −21/21 | −40/35 |
| Refl. collected | 44201 | 42573 | 75080 | 22631 | 9565 | 68596 |
| Refl. unique | 19571 | 9823 | 8896 | 5339 | 4202 | 23118 |
| Refl. observed | 12704 | 8924 | 6897 | 4316 | 2495 | 11339 |
| Parameter | 1256 | 633 | 574 | 404 | 190 | 919 |
| $S$ (Gof) on $F^2$ | 1.03 | 1.03 | 1.03 | 1.06 | 0.99 | 0.93 |
| $R(F)$ | 0.061 | 0.032 | 0.045 | 0.045 | 0.045 | 0.073 |
| $R_w(F^2)$ | 0.147 | 0.070 | 0.097 | 0.106 | 0.083 | 0.168 |
| $(\Delta\rho)_{max}$ [eA$^{-3}$] | 0.77 | 0.54 | 0.63 | 1.22 | 0.30 | 1.54 |
| $(\Delta\rho)_{min}$ [eA$^{-3}$] | −0.78 | −0.39 | −0.63 | −0.31 | −0.37 | −0.46 |

[a] The single crystal contained 2 independent molecules and 1.75 molecules of methanol in the asymmetric unit (not completely occupied). [b] The single crystal contained 1 molecule of methanol in the asymmetric unit. [c] The single crystal contained 1 molecule of disordered toluene in the unit cell.

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