Replacement of One CO Unit in Dicarbonyl(η^5-cyclopentadienyl)cobalt Derivatives by Bis(*tert*-butylsulfonyl)acetylene

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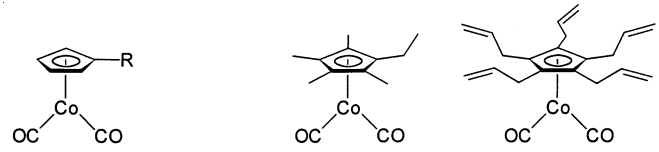
The reaction of dicarbonyl(η^5-cyclopentadienyl)cobalt (**1**) and some of the Cp-ring substituted congeners with bis(*tert*-butylsulfonyl)acetylene (BTSA) results in the replacement of one CO group by the BTSA moiety. The variation of the yields and reaction times indicates a dependence of the reactivity of **1**−**6** with BTSA as a function of substituents. X-ray investigations of the products show that the alkyne unit is strongly bound to the metal.

So far, substitution reactions at dicarbonyl(η^5-cyclopentadienyl)cobalt [$CpCo(CO)_2$] (**1**)[1][2][3] with alkynes could not be stopped at the monosubstitution stages, although such complexes have been postulated as intermediates.[4] In the reported cases follow-up reactions led to cyclobutadiene complexes, cyclopentadienone complexes or benzene derivatives.[5][6][7][8][9][10][11] In order to contribute to the clarification of the mechanism of dimerization or trimerization of alkynes we investigated the reaction of $CpCo(CO)_2$ with alkynes having electron-acceptor groups. Acceptor groups were chosen because we thought that replacement of only one CO group could best be accomplished by a triple bond with stronger acceptor properties than diphenyl acetylene. Therefore bis(*tert*-butylsulfonyl)acetylene (BTSA) was our first choice because this compound has been found to be a powerful dienophile.[12][13] This led us to investigate the ligand properties of BTSA. In this paper we report experiments with **1**[3] and the substituted congeners dicarbonyl(η^5-methylcyclopentadienyl)- (**2**)[14], dicarbonyl(η^5-trimethylsilylcyclopentadienyl)- (**3**)[15][16], dicarbonyl(η^5-methoxycarbonylcyclopentadienyl)- (**4**)[17], dicarbonyl-(η^5−1-ethyl-2,3,4,5-tetramethylcyclopentadienyl)- (**5**)[18][19], and dicarbonyl(η^5-pentaallylcyclopentadienyl)cobalt (**6**)[20].



R = H, CH_3, $Si(CH_3)_3$, CO_2CH_3

1 **2** **3** **4** **5** **6**

Results and Discussion

The reaction of BTSA with **1**−**6** was accomplished by stirring solutions of **1**−**6** and BTSA in methylene chloride at room temperature. After 2−11 days the reaction was complete and the corresponding products could be isolated (Scheme 1). The monoalkyne complexes **7**−**12**, respectively, were obtained in yields between 36% and 85%. In addition to yields we list in Table 1 the reaction time which was required for complete conversion of starting materials. The data show that **4** having an electron withdrawing substituent on the Cp ring results in reduced yield (**10**, 39%) and increased reaction time (11 d) as compared to **1**. The lower yield encountered in the case of **12** we ascribe to steric effects. However, we can not exclude that the mechanism of the substitution might be different as compared to the other examples, because the five vinyl groups might act as ligands with formation of intermediate chelate complexes, which finally react to the observed, less strained product **12**.

Scheme 1

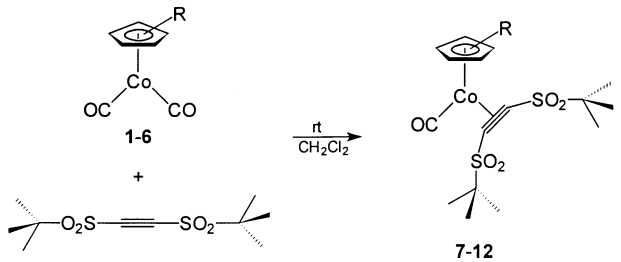


Table 1. reaction times, yields, and selected spectroscopical features of **7**−**12**

Compound	**7**	**8**	**9**	**10**	**11**	**12**
Reaction time [d]	3	2	6	11	2	3
Yield [%]	73	85	78	39	63	36
$\tilde{\nu}_{C\equiv C}$[cm^{-1}]	1772	1778	1779	1777	1752	1734
$\tilde{\nu}_{CO}$[cm^{-1}]	2017	2023	2022	2031	2010	2002
^{13}C δ (C≡C)	93.72	104.55	91.60	91.33	103.43	103.21

  1434−1948/98/0505−0629 $ 17.50+.50/0

All resulting compounds (**7**−**12**) were characterized by their spectroscopic and analytical data. With the exception of **10** we were also able to grow single crystals allowing a more detailed study of the molecular parameters by using the X-ray technique. The molecular structures of **7** and **12** are shown in Figure 1.

Figure 1. Top: Molecular structure of one of both independent molecules of **7** in the unit cell. Bottom: Molecular structure of **12**. Ellipsoids are at the 50% probability level.

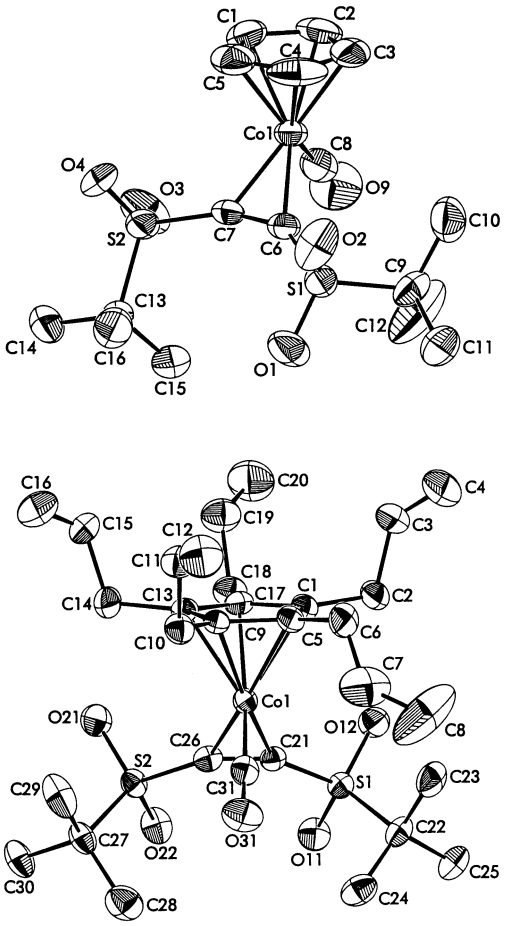


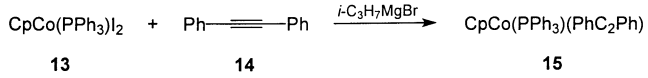
Table 2. Selected structural parameters of **7**−**9**, **11**, and **12**. The distances (*d*) are given in pm, the angles in degrees

Compound	**7**		**8**	**9**	**11**	**12**
d(C≡C)	126.4(5)	126.8(5)	127.0(3)	126.7(3)	126.9(3)	126.1(5)
d(≡C−Co)	194.2(3)	196.9(3)	194.7(3)	194.5(2)	195.2(2)	196.3(4)
	194.6(4)	196.8(3)	194.9(3)	195.9(2)	196.8(2)	196.4(4)
angle at C≡C−S	142.8(3)	142.2(3)	146.4(2)	145.0(2)	143.3(2)	140.9(3)
	158.5(3)	158.1(3)	158.9(2)	159.1(2)	155.9(2)	140.7(3)
torsion angle at S−C≡C−S	16(1)	13(1)	18(1)	15.6(1)	12.3(6)	3.0(1)
d(Co−CO)	176.1(4)	175.8(4)	177.0(3)	176.2(3)	175.3(2)	177.8(5)
d(C≡O)	113.5(5)	113.7(5)	113.1(4)	112.9(4)	113.9(2)	113.0(5)
d(Co−center of Cp)	170.2(2)	170.0(2)	169.6(2)	169.8(2)	170.2(1)	170.8(2)

The most relevant distances and angles of **7**−**9**, **11**, and **12** are listed in Table 2. A pronounced lengthening of the C−C bond of the alkyne unit was observed, from 119.1 pm in the uncomplexed state to 126.1−127.0 pm in the complexes. The deviation from linearity of up to 40° is considerable. These results are supported by vibrational spectra which show that the wave number for the uncomplexed BTSA unit (2160 cm^{-1} from Raman spectrum) is shifted to lower values (1734−1779 cm^{-1}).

Analogous results were reported by Yamazaki et al. for a related complex obtained by treating the diiodide of bis(triphenylphosphane)(η^5-cyclopentadienyl)cobalt (**13**) with tolane and isopropylmagnesium bromide.[21] The monosubstituted product **15** shows a C-C triple-bond stretching frequency of 1818 cm^{-1} which is considerably higher than that found in our examples.

Scheme 2



The complexes **7**−**12** are interesting intermediates on our endeavors to isolate a CpCo complex with two alkyne units and CpCo-capped push-pull cyclobutadiene complexes.

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Experimental Section

General Methods. Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon. Solvents were dried and distilled under argon before use; THF, diethylether, *n*-pentane, and *n*-hexane from sodium, dichloromethane from CaH_2. − Melting points are uncorrected. − Materials used for column chromatography: Silica gel 60 (Macherey-Nagel), alumina (Merck). − ^{1}H-NMR and ^{13}C-NMR: Bruker AS 200 (^{1}H at 200 MHz and ^{13}C at 50.33 MHz), Bruker WH 300 (^{1}H at 300 MHz, ^{13}C at 75.47 MHz) using the solvent as internal standard. − IR: Bruker Vector 22 FT-IR. − UV: Hewlett Packard HP8452A. − MS: Low resolution: ZAB-2F; high resolution: JEOL JMS-700. − Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. − The dicarbonyl(η^5-cyclopentadienyl)cobalt complexes **1**[3], **2**[14], **3**[15][16], **4**[17], and **5**[18][19] were prepared according to literature methods.

Dicarbonyl(η^5-pentaallylcyclopentadienyl)cobalt (**6**). Iodine (2.60 g, 10.2 mmol) was added at r.t. in portions to a stirred solution of 3.50 g (10.2 mmol) of dicobaltoctacarbonyl in 250 ml of anhydrous THF. The solution turned to a dark green color with vigorous foaming. After stirring for 1 h at room temperature, the solution was cooled to −40 °C and 6.17 g (20.3 mmol) of potassium pentaallylcyclopentadienide[20] was added. The reaction mixture was allowed to warm to room temperature overnight. After additional stirring for 1 d at room temperature the solvent was removed in vacuo, the residue dissolved in dichloromethane and chromatographed (alumina, 6% water, 30 × 3 cm). Elution with *n*-hexane yielded 2.51 g (33%) of **6** as a dark red, air-sensitive oil. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.92−2.96 (m, 10 H, CH_2), 4.81−5.00 (m, 10 H, =CH_2), 5.61−5.81 (m, 5 H, =CH). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 29.10 (CH_2), 99.62 (Cp-C), 115.40 (=CH), 137.21 (=CH_2), 183.85 (C≡O). − IR (film): $\tilde{\nu}$ = 3078 cm^{-1}, 3007, 2978, 2915, 2843, 2010, 1944, 1637, 1440, 1414, 1286, 993, 911,

617, 556. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 222 nm (5.00). − MS (EI, 70 eV): *m/z* = 352 [M^+ − CO], 324 [M^+ − 2CO].

General Procedure for the Preparation of the Carbonyl(η⁵-cyclopentadienyl)(η²-bis[tert-butylsulfonyl]acetylene)cobalt(I) Complexes. The dicarbonyl(η⁵-cyclopentadienyl)cobalt complex was added at ambient temperature to a solution of bis(*tert*-butylsulfonyl)acetylene (BTSA) in 50 ml of dichloromethane. After stirring for 2−11 d at r.t. the solvent was removed in vacuo and the product was isolated by silica gel chromatography (silica gel, *n*-pentane/diethyl ether).

Carbonyl(η⁵-cyclopentadienyl)(η²-bis[tert-butylsulfonyl]acetylene)cobalt(I) (**7**); Starting material: 300 mg (1.67 mmol) of dicarbonyl(η⁵-cyclopentadienyl)cobalt (**1**), 890 mg (3.34 mmol) of BTSA. Reaction time: 3 d. Silica gel chromatography (*n*-pentane/diethyl ether, 1:2). Yield: 508 mg (73%) of **7** as an orange solid, m.p. 110°C (decomposition). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 18 H, CH_3), 5.29 (s, 5 H, Cp-H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.38 [C(*C*H_3)$_3$], 61.52 [*C*(CH_3)$_3$], 86.93 (Cp-C), 93.72 (≡C). − IR (KBr): $\tilde{\nu}$ = 3119 cm^{-1}, 2979, 2936, 2866, 2017, 1772, 1476, 1395, 1295, 1116. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 256 nm (4.14). − MS (EI, 70 eV): *m/z* = 390 [M^+ − CO], 270, 245, 214, 141, 124. − HRMS (FAB+): [M + H^+] $C_{16}H_{24}CoO_5S_2$: calcd. 419.0319; found 419.0332. − $C_{16}H_{23}CoO_5S_2$ (418.425): calcd. C 45.93, H 5.54; found C 45.79, H 5.61.

Carbonyl(η⁵-methylcyclopentadienyl)(η²-bis[tert-butylsulfonyl]acetylene)cobalt(I) (**8**); Starting material: 330 mg (1.70 mmol) of dicarbonyl(η⁵-methylcyclopentadienyl)cobalt (**2**), 906 mg (3.40 mmol) of BTSA. Reaction time: 2 d. Silica gel chromatography (*n*-pentane/diethyl ether, 3:1). Yield: 624 mg (85%) of **8** as an orange solid, m.p. 91°C (decomposition). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 3 H, Cp-CH_3), 1.53 (s, 18 H, C(CH_3)$_3$), 5.13/5.52 (pt, 4 H, Cp-H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 11.55 (Cp-CH_3), 23.55 [C(*C*H_3)$_3$], 61.54 [*C*(CH_3)$_3$], 83.24/90.22 (Cp-C), 97.70 [Cp(*C*)-CH_3], 104.55 (≡C). − IR (KBr): $\tilde{\nu}$ = 3119 cm^{-1}, 2978, 2932, 2867, 2023, 1778, 1475, 1365, 1297, 1117. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 nm (4.32). − MS (FAB+): *m/z* = 433 [M + H^+], 405. − HRMS (FAB+): [M + H^+] $C_{17}H_{26}CoO_5S_2$: calcd. 433.0554; found 433.0554. − $C_{17}H_{25}CoO_5S_2$ (432.452): calcd. C 47.22, H 5.83; found C 47.03, H 5.86.

Carbonyl(η⁵-trimethylsilylcyclopentadienyl)(η²-bis[tert-butylsulfonyl]acetylene)cobalt(I) (**9**): Starting material: 420 mg (1.67 mmol) of dicarbonyl(η⁵-trimethylsilylcyclopentadienyl)cobalt (**3**), 890 mg (3.34 mmol) of BTSA. Reaction time: 6 d. Silica gel chromatography (*n*-pentane/diethyl ether, 1:1). Yield: 639 mg (78%) of **9** as a yellow solid, m.p. 116°C (decomposition). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.34 [s, 9 H, Si(CH_3)$_3$], 1.49 [s, 18 H, C(CH_3)$_3$], 5.20/5.35 (b, 4 H, Cp-H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = −0.62 [Si(CH_3)$_3$], 23.43 [C(*C*H_3)$_3$], 61.58 [*C*(CH_3)$_3$], 91.60 (≡C), 91.94/92.05 (Cp-C), 94.35 [Cp(*C*)-Si]. − IR (KBr): $\tilde{\nu}$ = 3092 cm^{-1}, 2980, 2956, 2867, 2022, 1779, 1459, 1393, 1295, 1115. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 nm (4.14). − MS (FAB+): *m/z* = 491 [M + H^+], 463, 389. − HRMS (FAB+): [M^+] $C_{19}H_{31}CoO_5S_2Si$: calcd. 490.0714; found 490.0779. − $C_{19}H_{31}CoO_5S_2Si$ (490.608): calcd. C 46.52, H 6.37; found C 46.55, H 6.46.

Carbonyl(η⁵-methoxycarbonylcyclopentadienyl)(η²-bis[tert-butylsulfonyl]acetylene)cobalt(I) (**10**): Starting material: 357 mg (1.50 mmol) of dicarbonyl(η⁵-methoxycarbonylcyclopentadienyl)-cobalt (**4**), 800 mg (3.00 mmol) of BTSA. Reaction time: 11 d. Silica gel chromatography (*n*-pentane/diethyl ether, 1:1). Yield: 280 mg (39%) of **10** as an orange solid, m.p. 114°C (decomposition).

Table 3. Crystallographic data of **7**, **8**, **9**, **11**, and **12**

Compound	**7**	**8**	**9**	**11**	**12**
Empirical formula	$C_{16}H_{23}CoO_5S_2$	$C_{17}H_{25}CoO_5S_2$	$C_{19}H_{31}CoO_5S_2Si$	$C_{22}H_{35}CoO_5S_2$	$C_{31}H_{43}CoO_5S_2$
Molecular mass [g/mol]	418.425	432.452	490.608	502.586	618.748
Solvent	*n*-pentane/diethyl ether	*n*-pentane/diethyl ether	*n*-pentane/diethyl ether	*n*-pentane/diethyl ether	*n*-pentane/diethyl ether
Crystal size [mm]	0.20×0.60×0.60	0.55×0.65×0.75	0.70×0.55×0.45	0.40×0.40×0.20	0.30×0.23×0.18
Crystal color	red	red	orange	red	orange
Crystal shape	irregular	prism	prism	irregular	needle
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	10.510(3)	9.601(3)	9.807(2)	15.270(4)	19.582(3)
b [Å]	12.431(3)	9.822(4)	9.920(1)	13.751(1)	9.518(1)
c [Å]	14.628(3)	12.710(4)	13.051(2)	11.961(2)	17.493(2)
α [°]	97.14(2)	70.04(3)	97.56(1)	90	90
β [°]	94.50(2)	78.31(3)	100.54(1)	100.28(2)	105.0920(10)
γ [°]	89.91(2)	63.07(3)	92.55(1)	90	90
V [Å^3]	1890.5(7)	1002.8(6)	1234.3(3)	2471.2(7)	3147.91(7)
$D_{calcd.}$ [Mg/m^3]	1.47	1.43	1.32	1.35	1.31
Z	4	2	2	4	4
F(000)	872	452	516	1064	1312
Temperature [K]	293	293	293	263	200
h_{min} / h_{max}	−12 / 12	0 / 12	−2 / 11	0 / 20	−23 / 23
k_{min} / k_{max}	−15 / 14	−10 / 12	−11 / 11	0 / 18	−11 / 11
l_{min} / l_{max}	0 / 17	−15 / 16	−15 / 15	−15 / 15	−12 / 20
μ [mm^{-1}]	1.15	1.09	0.94	0.89	0.71
Refl. collected	7161	4374	5504	6152	14195
Refl. unique	7062	4374	4343	5940	5328
Refl. observed	5603	3837	3844	4569	4309
Variables	434	227	281	282	358
R(*F*)	0.049	0.048	0.034	0.032	0.053
$R_w(F^2)$	0.116	0.121	0.089	0.079	0.127
S (Gof) on F^2	1.07	1.10	1.15	1.06	1.10
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.44	0.34	0.40	0.49	0.80
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.55	−1.09	−0.26	−0.42	−0.59

– ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.51 [s, 18 H, $C(CH_3)_3$], 3.87 (s, 3 H, OCH_3), 5.37/5.79 (b, 4 H, Cp-H). – ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 23.55 [$C(CH_3)_3$], 52.40 (OCH_3), 61.90 [$C(CH_3)_3$], 88.87/89.57 (Cp-C), 90.31 [Cp(*C*)-CO_2Me], 91.33 (≡C), 164.44 (C=O). – IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1}, 2977, 2868, 2031, 1777, 1726, 1477, 1374, 1300, 1196, 1149, 1119. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 260 nm (4.27). – MS (FAB+): *m*/*z* = 477 [M + H^+], 449. – HRMS (FAB+): [M + H^+] $C_{18}H_{26}CoO_7S_2$: calcd. 477.0452; found 477.0436.

Carbonyl(η^5–1-ethyl-2,3,4,5-tetramethylcyclopentadienyl)(η^2-bis[tert-butylsulfonyl]acetylene)cobalt(I) (**11**): Starting material: 396 mg (1.50 mmol) of dicarbonyl(η^5-1-ethyl-2,3,4,5-tetramethylcyclopentadienyl)cobalt (**5**), 800 mg (3.00 mmol) of BTSA. Reaction time: 2 d. Silica gel chromatography (*n*-pentane/diethyl ether, 3:1). Yield: 476 mg (63%) of **11** as an orange solid, m.p. 92°C (decomposition). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.01 (t, 3 H, CH_2CH_3, ^3J = 7.5 Hz), 1.47 [s, 18 H, $C(CH_3)_3$], 1.83 (s, 6 H, Cp-CH_3), 1.85 (s, 6 H, Cp-CH_3), 2.41 (q, 2 H, CH_2, ^3J = 7.5 Hz). – ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 9.28/9.43 (Cp-CH_3), 13.84 (CH_2CH_3), 17.81 (CH_2), 23.43 [$C(CH_3)_3$], 61.41 [$C(CH_3)_3$], 98.29/99.67 [Cp(*C*)-CH_3], 103.43 (≡C), 105.22 [Cp(*C*)-CH_2CH_3]. – IR (KBr): $\tilde{\nu}$ = 2974 cm^{-1}, 2914, 2871, 2010, 1752, 1458, 1380, 1291, 1115. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 272 nm (4.80). – MS (FAB+): *m*/*z* = 503 [M + H^+], 475. – HR-MS (FAB+): [M + H^+] $C_{22}H_{36}CoO_5S_2$: calcd. 503.1336; found 503.1452. – $C_{22}H_{35}CoO_5S_2$ (502.586): calcd. C 52.58, H 7.02; found C 52.38, H 7.11.

Carbonyl(η^5-pentaallylcyclopentadienyl)(η^2-bis[tert-butylsulfonyl]acetylene)cobalt(I) (**12**): Starting material: 304 mg (0.80 mmol) of dicarbonyl(η^5-pentaallylcyclopentadienyl)cobalt (**6**), 426 mg (1.60 mmol) of BTSA. Reaction time: 3 d. Silica gel chromatography (*n*-pentane/diethyl ether, 5:1). Yield: 180 mg (36%) of **12** as a yellow solid, m.p. 106°C (decomposition). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 18 H, CH_3), 3.11–3.16 (td, 10 H, CH_2, ^3J = 6.2 Hz, ^4J = 1.6 Hz), 4.92–5.02 (dd, 5 H, CH=CH_{cis}H, $^3J_{trans}$ = 17.0 Hz, $^2J_{gem}$ = 1.4 Hz), 4.98–5.04 (dd, 5 H, CH=CH_{trans}H, $^3J_{cis}$ = 10.2 Hz, $^2J_{gem}$ = 1.4 Hz), 5.71–5.86 (tdd, 5 H, C*H*=CH_2, $^3J_{trans}$ = 17.0 Hz, $^3J_{cis}$ = 10.2 Hz, ^3J = 6.2 Hz). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.52 [$C(CH_3)_3$], 28.94 (CH_2), 61.91 [$C(CH_3)_3$], 101.50 (Cp-C), 103.21 (≡C), 116.81 (=CH_2), 135.14 (-CH=). – IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1}, 2979, 2937, 2870, 2002, 1734, 1637, 1453, 1415, 1365, 1301, 1118, 993, 914, 636. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 294 nm (4.47). – MS (FAB+): *m*/*z* = 619 [M + H^+], 591. – HRMS (FAB+): [M + H^+] $C_{31}H_{44}CoO_5S_2$: calcd. 619.1962; found 619.2037. – $C_{31}H_{43}CoO_5S_2$ (618.748): calcd. C 60.18, H 7.00; found C 60.22, H 7.07.

X-ray Diffraction Analyses: The reflections were collected with a Nonius-CAD4 diffractometer (**11**), a Siemens Nicolet-Syntex-R3 diffractometer (**7**, **8**, **9**) and a Siemens CCD diffractometer (**12**). Intensities were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (**7**, **8**, **9**, **12**: SHELXS-86[22]; **11**: SIR-92[23]). The structural parameters of the nonhydrogen atoms were refined anisotropically according to a full-matrix-least-squares technique (F^2). The hydrogen atoms were refined with fixed thermal parameters or calculated parameters. Refinement was carried out with SHELXL-93[24]. Table 3 contains the crystallographic data and details of the refinement procedure. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallograhic Data center as supplementary publication no CCDC–100891. Copies of data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB12 IEZ, UK [fax: int. code +44 (0)1223/336/033, email: deposit@ccdc.ac.uk].

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