

# Pentafluoro- $\lambda^6$ -sulfanylacetylene complexes of cobalt <sup>\*</sup>

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## Abstract

The reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{R}-\text{C}\equiv\text{C}-\text{SF}_5$  gives 1:1, 1:2, and 1:3 type products, depending on R. For R = H all three products can be isolated. According to the single-crystal structure determinations, the 1:1 product has the known di-cobalt-tetrahedrane structure, the 1:2 product is a cobaltacyclopentadiene cobalt, whereas the 1:3 product has been previously identified as a “fly-over bridge” complex. Sterically more crowded  $\text{F}_3\text{C}-\text{C}\equiv\text{C}-\text{SF}_5$  and  $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{SF}_5$  give only the 1:1 reaction. The product of  $\text{F}_3\text{C}-\text{C}\equiv\text{C}-\text{SF}_5$  reacts further with  $\text{H}-\text{C}\equiv\text{C}-\text{SF}_5$  to a 1:3 product, made up of different alkyne molecules.

*Keywords:* Cobalt; Sulfur; Fluorine; Pentafluorosulfanylacetylene complexes

## 1. Introduction

The reaction of  $\text{Co}_2(\text{CO})_8$  with alkynes has been well investigated [1]. A series of 1:1 products is well known; they have inevitably a dicobalttetrahedrane structure. There are also a few isolated 1:3 products known [1]. In these a chain of six carbon atoms is formed from three alkyne molecules which winds around the two cobalt atoms. This configuration has been called a “fly-over bridge” complex. These complexes are sources for 1, 2, 4-substituted benzenes, if alkynes  $\text{H}-\text{C}\equiv\text{C}-\text{R}$  are used. Only one example of a 1:2 product is known in the literature; this was obtained when  $\text{Co}_2(\text{CO})_8$  was reacted with highly reactive cyclooctyne. Its structure can be described as a half-sandwich complex made up of cobalt and a cobaltacyclopentadienyl ring [2].

$\text{SF}_5$ -substituted alkynes are quite unreactive. This is certainly a consequence of the sterical protection by the rigid  $\text{SF}_5$  group, but also of its electronegativity, so that these alkynes must be regarded as electron poor.  $\text{F}_5\text{S}-\text{C}\equiv\text{C}-\text{SF}_5$  as an extreme example does not even react with undiluted  $\text{SbF}_5$  at room temperature [3]. Therefore it was not surprising that the reaction between  $\text{Co}_2(\text{CO})_8$  and  $\text{F}_5\text{S}-\text{C}\equiv\text{C}-\text{SF}_5$  stops at the tetra-

hedrane stage, and the product has been identified among other methods by a single-crystal structure determination [4,5]. With  $\text{H}-\text{C}\equiv\text{C}-\text{SF}_5$  all three reactions are observed, and the compounds can be isolated. The 1:3 product has been identified as a fly-over bridge complex; its degradation with bromine serves as a source for otherwise not obtainable 1, 2, 4-( $\text{SF}_5$ )<sub>3</sub> benzene [4].

## 2. Results and discussion

In this work we consider the identification of the 1:1 and 1:2 products. The 1:1 compound is not unexpectedly a dicobalttetrahedrane complex. The result of its crystal structure determination is shown in Fig. 1 and later in Table 3. Bond lengths and angles are quite similar to those of other dicobalttetrahedranes [1]. The 1:2 compound, however, is formed only in very small amounts, and, besides the previously mentioned complex with cyclooctyne, no other example was known. The crystal structure determination resulted in a cobaltacyclopentadienyl cobalt complex, as shown in Fig. 2 and later in Table 5. The molecule has almost perfect mirror symmetry. The cobaltacyclopentadienyl ring is essentially planar (the sum of angles is 537°). In general the structure is very similar to that of the product with cyclooctyne. The two  $\text{SF}_5$  groups are

<sup>\*</sup> Dedicated to Herbert Schumann on the occasion of his 60th birthday.

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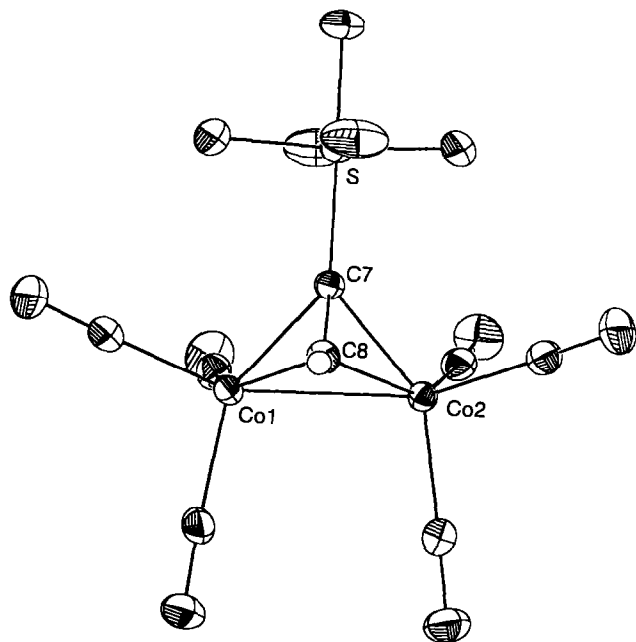
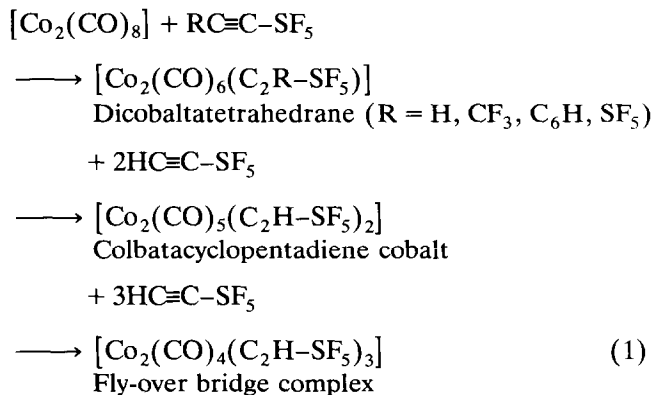


Fig. 1. ORTEP view of  $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{-SF}_5)]$ . The vibrational ellipsoids show 50% probability.

positioned in such a way that they avoid each other as much as possible.



Since now such a cobaltacyclopentadiene cobalt complex has been formed from extremely reactive cyclooctyne as well as from quite unreactive  $\text{H-C}\equiv\text{C-SF}_5$ , it can be assumed that it is always present if the reaction goes beyond the 1:1 stage. Only small yields may have prevented detection in all those cases where 1:3 products have been isolated. It can be assumed that the 1:1, 1:2 and 1:3 products are formed stepwise and that the incoming alkyne adds in a side-on manner to one cobalt atom. The step of reorientation to the final 1:2 and 1:3 products is obviously guided by sterical repulsion of the large  $\text{SF}_5$  groups. So in the reaction  $1:2 \rightarrow 1:3$  the alkyne molecule can only add in such a way that both terminal carbon atoms of the C(6) chain in the fly-over bridge complex carry  $\text{SF}_5$

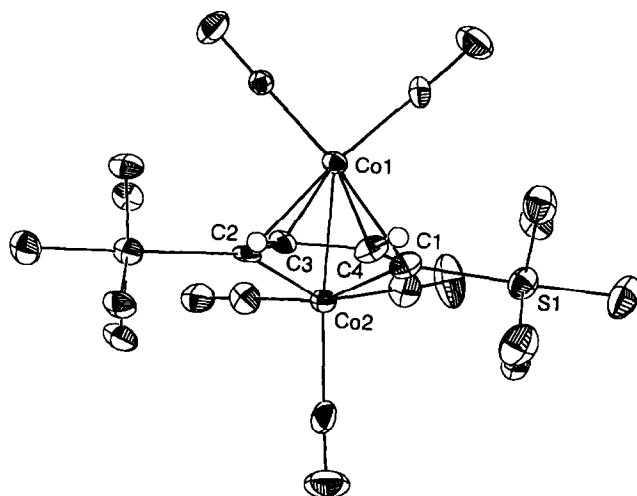
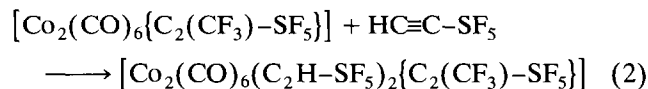


Fig. 2. ORTEP view of  $[\text{Co}_2(\text{CO})_5(\text{HC}_2\text{-SF}_5)_2]$ . The vibrational ellipsoids show 50% probability.

groups. This enforces the generation of 1, 2, 4-substituted benzenes upon degradation.



The reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{F}_3\text{C-C}\equiv\text{C-SF}_5$  and  $\text{C}_6\text{H}_5\text{-C}\equiv\text{C-SF}_5$  results only in the tetrahedrane even after long reaction times. The crystal structure of the first compound is shown in Fig. 3 and later in Table 7. The equatorial fluorine atoms on sulfur have quite large vibrational amplitudes. We assume that at  $-158^\circ\text{C}$  the free rotation of the  $\text{SF}_5$  group around the

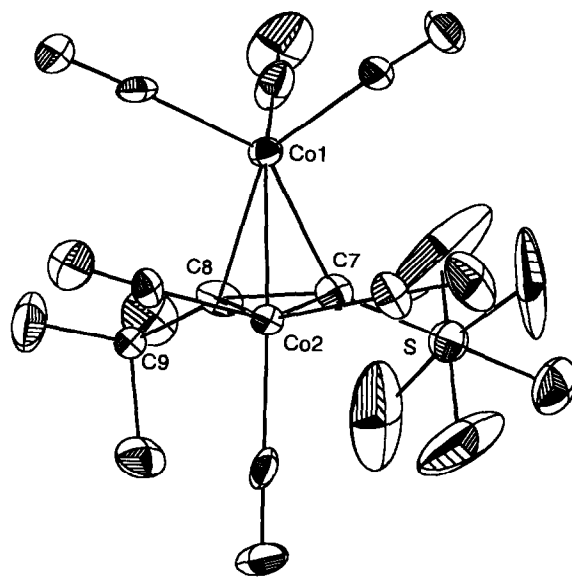


Fig. 3. ORTEP view of  $[\text{Co}_2(\text{CO})_6(\text{F}_3\text{C-C}_2\text{-SF}_5)]$ . The vibrational ellipsoids show 50% probability. The large vibrational amplitudes of the equatorial fluorine atoms indicate partial rotational disorder of this group at  $-158^\circ\text{C}$ .

Table 1  
Crystal structure experimental data

	[Co <sub>2</sub> (CO) <sub>6</sub> (HC <sub>2</sub> -SF <sub>5</sub> )]	[Co <sub>2</sub> (CO) <sub>5</sub> (HC <sub>2</sub> -SF <sub>5</sub> ) <sub>2</sub> ]	[Co <sub>2</sub> (CO) <sub>6</sub> (F <sub>3</sub> C-C <sub>2</sub> -SF <sub>5</sub> )]
Formula	C <sub>8</sub> HCo <sub>2</sub> F <sub>5</sub> O <sub>6</sub> S	C <sub>9</sub> H <sub>2</sub> Co <sub>2</sub> F <sub>10</sub> O <sub>5</sub> S <sub>2</sub>	C <sub>6</sub> Co <sub>2</sub> F <sub>8</sub> O <sub>6</sub> S
Molecular weight	437.81	561.78	506.01
Color	Orange	Brown-red	Orange
Size (mm)	0.4 × 0.4 × 0.3	0.4 × 0.2 × 0.2	0.4 × 0.4 × 0.3
<i>a</i> (pm)	964.5(2)	1192.9(4)	773.2(2)
<i>b</i> (pm)	1268.1(4)	1356.0(8)	1395.5(4)
<i>c</i> (pm)	1085.7(1)	1948.8(11)	1422.7(7)
$\beta$ (°)	100.19(1)		94.17(3)
Volume (10 <sup>6</sup> pm <sup>3</sup> )	1307.0(5)	3152(2)	1535(1)
Temperature (°C)	-148	-158	-158
<i>Z</i>	4	8	4
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>Pbca</i> (No. 61)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
$\mu$ (cm <sup>-1</sup> )	7.05	6.88	6.08
$\theta$ range (°)	2-30	2-25	2-25
Indices	$\pm h, k, l$	$+h, +k, +l$	$\pm h, k, l$
Number of measured reflections	4102	2912	2223
Number of independent reflections	3608	2539	2003
Number of reflections with $F \geq 3\sigma(F)$	3231	1950	1605
Number of parameters	203	253	235
<i>R</i> ; <i>R</i> <sub>w</sub>	0.022; 0.026	0.066; 0.052	0.058; 0.064
Weighting scheme	1.66[ $\sigma^2(F) + 0.0005F^2$ ]	2.05/ $\sigma^2(F)$	2.17/[ $\sigma^2(F) + 0.005F^2$ ]

S-C bond has been frozen to a partially disordered orientation.

However, this tetrahedrane reacts with excess HC≡C-SF<sub>5</sub> in very long reaction times (months at room temperature) to [Co<sub>2</sub>(CO)<sub>4</sub>(HC<sub>2</sub>-SF<sub>5</sub>)<sub>2</sub>(F<sub>3</sub>C-C<sub>2</sub>-SF<sub>5</sub>)], the first of such SF<sub>5</sub>-substituted fly-over bridge complexes formed from different alkynes. This compound exists in two isomers. The inverted reaction of [Co<sub>2</sub>(CO)<sub>6</sub>(HC<sub>2</sub>-SF<sub>5</sub>)] with F<sub>3</sub>C-C<sub>2</sub>-SF<sub>5</sub> gives only alkyne exchange. Such exchange has been described before [1].

The sterically most crowded tetrahedrane carrying two SF<sub>5</sub> groups, however, is completely inert against further reaction or alkyne exchange. Similarly F<sub>5</sub>S-C≡C-SF<sub>5</sub> does not react with any dicobalttetrahedrane.

### 3. Experimental details

The general procedures used were as follows. NMR spectra: JEOL F 90 Q instrument; <sup>1</sup>H, 89.55 MHz; <sup>19</sup>F, 84.25 MHz. Tetramethylsilane and CFC<sub>3</sub> were used as external or internal standards. Mass spectroscopy (MS): Varian MAT 711 instrument; electron impact with 80 eV excitation energy. The mass units and their intensities refer to the most abundant isotopes. IR spectra: Perkin-Elmer 983 instrument; samples were prepared in KBr. Crystal structures: Enraf-Nonius CAD 4 diffractometer; Mo K $\alpha$  irradiation; graphite monochromator. The cell constants were obtained by fine orientation of 25 reflections with usually 12° <  $\theta$  < 25°.

Intensities were obtained using a  $\omega$ -2 $\theta$  scan, allowing a maximum of 60 s for one reflection and is thereof for background measurements. Lorentz polarization and absorption corrections [6] were applied, but no extinction correction. The structures were solved by direct methods [7] and refined using the program SHELX 76 with difference Fourier maps for locating lighter atoms [8]. Hydrogen atoms were located similarly and refined

Table 2  
Positional parameters for [Co<sub>2</sub>(CO)<sub>6</sub>(HC<sub>2</sub>-SF<sub>5</sub>)]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Co(1)	0.2156(0)	0.1212(0)	0.9007(0)	1.24
Co(2)	0.1582(0)	0.2610(0)	1.0417(0)	1.14
S	0.4721(0)	0.3127(0)	0.9494(0)	1.42
F(1)	0.4178(1)	0.4018(1)	0.8512(2)	3.43
F(2)	0.5061(1)	0.2401(1)	0.8394(1)	2.77
F(3)	0.5406(1)	0.2257(1)	1.0470(1)	3.02
F(4)	0.4531(1)	0.3879(1)	1.0607(2)	3.78
F(5)	0.6245(1)	0.3610(1)	0.9575(1)	2.43
O(1)	0.3405(2)	0.0580(1)	0.6830(1)	2.69
O(2)	-0.0691(2)	0.0299(1)	0.8264(1)	2.52
O(3)	0.3789(2)	-0.0139(1)	1.0965(2)	2.73
O(4)	-0.1337(1)	0.1950(1)	1.0519(2)	2.48
O(5)	0.1397(2)	0.4877(1)	1.0945(2)	2.59
O(6)	0.3294(2)	0.1960(1)	1.2830(1)	2.49
C(1)	0.2912(2)	0.0813(1)	0.7664(2)	1.85
C(2)	0.0412(2)	0.0623(1)	0.8550(2)	1.75
C(3)	0.3142(2)	0.0344(1)	1.0197(2)	1.82
C(4)	-0.0232(2)	0.2220(1)	1.0481(2)	1.67
C(5)	0.1453(2)	0.4007(1)	1.0744(2)	1.73
C(6)	0.2590(2)	0.2194(1)	1.1928(2)	1.63
C(7)	0.3016(2)	0.2572(1)	0.9398(2)	1.19
C(8)	0.1751(2)	0.2700(1)	0.8646(2)	1.39

Table 3  
Important bond lengths (pm) and bond angles (°) of [Co<sub>2</sub>(CO)<sub>6</sub>(HC<sub>2</sub>-SF<sub>5</sub>)]

Bond lengths	
Co(1)–Co(2)	246.9(0)
Co(1)–C(7)	192.9(2)
Co(1)–C(8)	195.2(2)
Co(2)–C(7)	191.8(2)
Co(2)–C(8)	196.1(2)
S–F	157.6(1)–159.0(1)
S–C(7)	177.5(2)
C(7)–C(8)	135.2(2)
C–O	112.8(2)–113.4(2)
Bond angles	
Co(2)–Co(1)–C(8)	51.0(0)
Co(1)–Co(2)–C(7)	50.3(0)
Co(1)–Co(2)–C(8)	50.7(0)
C(7)–Co(2)–C(8)	40.8(1)
F–S–F	87.3(1)–89.9(1)
Co–C–O	175.1(2)–178.5(2)
Co(1)–C(7)–Co(2)	79.9(1)
Co(1)–C(7)–C(8)	70.6(1)
Co(2)–C(7)–C(8)	71.3(1)
Co(1)–C(8)–Co(2)	78.2(1)
Co(1)–C(8)–C(7)	68.7(1)
Co(2)–C(8)–C(7)	67.9(1)

isotropically. Experimental details of the crystal structure determinations are collected in Table 1; the results are presented in Tables 2–7.

Table 4  
Positional parameters for [Co<sub>2</sub>(CO)<sub>5</sub>(HC<sub>2</sub>-SF<sub>5</sub>)<sub>2</sub>]

Atom	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Co(1)	0.0320(1)	0.1101(1)	0.1046(1)	1.14
Co(2)	0.0100(1)	0.2803(1)	0.1485(1)	1.21
S(1)	0.0241(3)	0.2873(2)	–0.0247(2)	1.93
S(2)	–0.1346(2)	0.1237(2)	0.2509(2)	1.52
F(11)	0.0301(6)	0.3941(5)	0.0083(3)	2.21
F(12)	0.1543(5)	0.2709(5)	–0.0088(3)	2.00
F(13)	0.0649(6)	0.3366(5)	–0.0940(3)	3.03
F(14)	0.0212(6)	0.1848(5)	–0.064(3)	2.61
F(15)	–0.1024(6)	0.3073(5)	–0.0469(4)	3.02
F(21)	–0.1407(5)	0.2314(5)	0.2814(3)	2.11
F(22)	–0.0111(4)	0.1099(4)	0.2787(3)	1.44
F(23)	–0.1343(5)	0.0117(4)	0.2275(3)	1.76
F(24)	–0.1777(5)	0.0866(5)	0.3237(3)	2.22
F(25)	–0.2633(5)	0.1313(5)	0.2291(3)	1.88
O(11)	0.1007(7)	–0.0473(6)	0.1939(4)	2.28
O(12)	0.2057(7)	0.0520(6)	0.0095(5)	2.64
O(21)	–0.1603(8)	0.4385(7)	0.1398(5)	3.50
O(22)	0.1005(6)	0.3045(6)	0.2884(4)	2.02
O(23)	0.2250(7)	0.3704(7)	0.1094(4)	3.06
C(1)	–0.0203(9)	0.2281(8)	0.0553(6)	1.52
C(2)	–0.0849(9)	0.1648(8)	0.1676(6)	1.34
C(3)	–0.1479(9)	0.1237(8)	0.1106(6)	1.25
C(4)	–0.1098(9)	0.1615(8)	0.0484(6)	1.47
C(11)	0.0722(9)	0.0151(8)	0.1587(5)	1.27

Table 5  
Important bond lengths (pm) and bond angles (°) of [Co<sub>2</sub>(CO)<sub>5</sub>(HC<sub>2</sub>-SF<sub>5</sub>)<sub>2</sub>]

Bond lengths	
Co(1)–Co(2)	247.6(3)
Co(1)–C(1)	197(1)
Co(1)–C(2)	200(1)
Co(1)–C(3)	216(1)
Co(1)–C(4)	213(1)
Co(2)–C(1)	198(1)
Co(2)–C(2)	197(1)
Co(2)–C(21)	187(1)
S–F	158(1)–160(1)
C–O	109(2)–115(2)
C(1)–C(4)	141(2)
C(2)–C(3)	145(2)
C(3)–C(4)	139(2)
Bond angles	
C(1)–Co(1)–C(2)	77.1(5)
C(1)–Co(1)–C(3)	69.0(4)
C(1)–Co(1)–C(4)	39.8(4)
C(2)–Co(1)–C(3)	40.6(4)
C(2)–Co(1)–C(4)	68.9(4)
C(3)–Co(1)–C(4)	37.9(4)
C(12)–Co(1)–C(11)	90.1(5)
F–S–F	85.8(5)–90.3(5)
C(1)–Co(2)–C(2)	77.5(5)
Co(2)–C(1)–C(4)	117.1(8)
Co(2)–C(2)–C(3)	117.3(8)
Co(2)–C(3)–C(4)	75.1(7)
C(2)–C(3)–C(4)	111(1)
C(1)–C(4)–C(3)	114(1)

Table 6  
Positional parameters for [Co<sub>2</sub>(CO)<sub>6</sub>(F<sub>3</sub>C–C<sub>2</sub>-SF<sub>5</sub>)]

Atom	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Co(1)	0.1353(1)	0.6296(1)	0.6855(1)	1.09
Co(2)	–0.0693(1)	0.7269(1)	0.5852(1)	1.18
S	–0.0146(3)	0.8158(2)	0.8085(2)	2.16
F(1)	0.4295(6)	0.8215(4)	0.6877(4)	2.45
F(2)	0.2477(7)	0.9144(4)	0.6113(4)	3.17
F(3)	0.3701(8)	0.7952(4)	0.5408(4)	3.45
F(4)	–0.1131(19)	0.8898(8)	0.7520(6)	12.34
F(5)	0.1003(14)	0.7537(8)	0.8761(6)	8.64
F(6)	0.1482(4)	0.8812(7)	0.8080(7)	9.40
F(7)	–0.0611(8)	0.8732(4)	0.8993(4)	3.55
F(8)	–0.1654(13)	0.7538(9)	0.8242(7)	10.20
O(1)	0.4359(9)	0.6197(5)	0.8231(5)	2.59
O(2)	0.2595(8)	0.5116(5)	0.5326(5)	2.43
O(3)	–0.1088(8)	0.5134(5)	0.7865(6)	3.60
O(4)	0.0180(8)	0.6553(5)	0.3990(6)	2.46
O(5)	–0.2116(11)	0.9159(5)	0.5321(6)	4.10
O(6)	–0.3888(8)	0.6242(5)	0.6246(5)	2.64
C(1)	0.3215(12)	0.6217(6)	0.7705(7)	1.80
C(2)	0.2144(10)	0.5548(6)	0.5931(7)	1.35
C(3)	–0.0139(11)	0.5547(7)	0.7463(7)	2.33
C(4)	–0.0184(11)	0.6833(6)	0.4694(8)	1.44
C(5)	–0.1584(13)	0.8434(7)	0.5519(7)	2.24
C(6)	–0.2704(11)	0.6641(6)	0.6066(7)	1.66
C(7)	0.0377(10)	0.7531(5)	0.7097(7)	1.35
C(8)	0.1557(10)	0.7600(5)	0.6435(7)	1.44
C(9)	0.2975(10)	0.8282(5)	0.6144(7)	1.21

Table 7  
Important bond lengths (pm) and bond angles (°) of  $[\text{Co}_2(\text{CO})_6(\text{F}_3\text{C}-\text{C}_2-\text{SF}_5)]$

Bond lengths	
Co(1)–Co(2)	246.3(2)
Co(1)–C(7)	192.7(8)
Co(1)–C(8)	193.0(8)
Co(2)–C(7)	193.4(9)
Co(2)–C(8)	192.8(8)
S–F	148 (1)–158(1)
F(1)–C(9)	141 (1)
F(2)–C(9)	127 (1)
F(3)–C(9)	131 (1)
C–O	112 (2)–113(2)
C(7)–C(8)	136 (1)
Bond angles	
Co(2)–Co(1)–C(7)	50.5(3)
Co(2)–Co(1)–C(8)	50.3(2)
F–S–F	85 (1)–90(1)
C(7)–Co(1)–C(8)	41.3(4)
C(7)–Co(2)–C(8)	41.2(4)
Co(1)–C(7)–Co(2)	79.3(3)
Co(1)–C(7)–C(8)	69.4(5)
Co(2)–C(7)–C(8)	69.2(5)
Co(1)–C(8)–Co(2)	79.3(3)
Co(1)–C(8)–C(7)	69.3(5)
Co(2)–C(8)–C(7)	69.6(5)
C(7)–C(8)–C(9)	139.4(7)

### 3.1. Materials

Bis-pentafluoro- $\lambda^6$ -sulfanylethyne was obtained from  $\text{BrSF}_5$  and  $\text{H}-\text{C}\equiv\text{C}-\text{SF}_5$  [9]; the latter was obtained according to [10].  $\text{F}_3\text{C}-\text{C}\equiv\text{C}-\text{SF}_5$  was made from  $\text{BrSF}_5$  and  $\text{H}-\text{C}\equiv\text{C}-\text{CF}_3$  [9].  $\text{Co}_2(\text{CO})_8$  (Merck Schuchardt) was sublimed before use. Solvents were dried and stored under argon.  $[\text{Co}_2(\text{CO})_6(\text{HC}_2-\text{SF}_5)]$  and  $[\text{Co}_2(\text{CO})_5(\text{HC}_2-\text{SF}_5)_2]$  were prepared from  $\text{Co}_2(\text{CO})_8$  and  $\text{H}-\text{C}\equiv\text{C}-\text{SF}_5$  in *n*-hexane at 25°C, as previously described [4].

### 3.2. Preparation of $[\text{Co}_2(\text{CO})_6(\text{F}_3\text{C}-\text{C}_2-\text{SF}_5)]$

0.90 g (4.1 mmol) of  $\text{F}_3\text{C}-\text{C}\equiv\text{C}-\text{SF}_5$  and 0.50 g (1.5 mmol) of  $\text{Co}_2(\text{CO})_8$  are refluxed in *n*-hexane for 2 h. After pumping off all volatiles in high vacuum the solid is recrystallized from pentane. 0.64 g (86% yield) of orange product is obtained (melting point (m.p.), 149°C (sublimed), 152°C (decomposition). Chromatography on silica gel:  $R_F$  values: 0.46 (pentane), 0.80 pentane–diethylether (9:1), 0.98 (pentane–diethylether (1:1)).

$^{19}\text{F}$  NMR (84 MHz, pentane):  $\delta$  multiplet 80.11–81.02 ( $\text{ab}_4$  type,  $\text{SF}_5$ ), –53.92 ( $\text{CF}_3$ ) ppm.

MS:  $m/z$  506 ( $\text{M}^+$ , 4.8%), 478 ( $[\text{M}-\text{CO}]^+$ , 33.6%), 450 ( $[\text{M}-2\text{CO}]^+$ , 4.6%), 366 ( $[\text{M}-5\text{CO}]^+$ , 6.0%), 351 ( $[\text{Co}_2(\text{CO})_5\text{C}_3\text{F}_3]^+$ , 2.6%), 338 ( $[\text{M}-6\text{CO}]^+$  and/or  $[\text{Co}_2(\text{CO})_4\text{C}_2\text{SF}_4]^+$ , 18.4%), and smaller fragments.

IR (KBr):  $\nu$  2955(sh, w), 2923(w), 2853(w), 2547(w), 2510(w), 2360(w), 2127(s), 2095(vs), 2066(vs), 1553(m),

1384(w), 1217(m), 1146(m), 969(m), 946(m), 919(w), 845(s), 749(m), 706(m), 683(m), 659(m), 644(m), 594(m), 569(m), 522(m), 515(m), 507(m), 492(m), 441(m), 421(sh, w)  $\text{cm}^{-1}$ .

### 3.3. Preparation of 1-(pentafluoro- $\lambda^6$ -sulfanyl)-2-phenyl-2,2-difluoroethane ( $\text{C}_6\text{H}_5-\text{CF}_2-\text{CH}_2-\text{SF}_5$ )

2.16 g (8.8 mmol) of  $\text{C}_6\text{H}_5-\text{CO}-\text{CH}_2-\text{SF}_5$  [11], dissolved in 13 g of  $\text{CFCl}_3$ , is treated in a 100 ml stainless steel autoclave with 0.5 g (25 mmol) of anhydrous HF and 4.6 g (42.5 mmol) of  $\text{SF}_4$  for 6 days at room temperature. Excess pressure is relieved into a hood, water is added, and after neutralization with  $\text{K}_2\text{CO}_3$  the lower organic phase is separated and dried. Fractional vacuum condensation through –78 and –196°C cold traps afford 1.65 g (70% yield) of colorless crystals in the –78°C trap (m.p., 9.5°C; boiling point (b.p.), 22.8°C at 0.001 bar)

$^{19}\text{F}$  NMR:  $\delta$  80.34, 70.96 ( $\text{ab}_4$  type,  $\text{SF}_5$ ), –98.24 ppm.  $^4J_{\text{CF}-\text{SFb}} = 13.5$  Hz;  $^2J_{\text{SFa}-\text{SFb}} = 147.2$  Hz.

$^1\text{H}$  NMR:  $\delta$  3.99, 7.32 ppm.  $^3J_{\text{CH}_2-\text{SFb}} = 27$  Hz;  $^3J_{\text{CH}_2-\text{CF}_2} = 13.5$  Hz.

MS;  $m/z$  268 ( $\text{M}^+$ , 53%), 141 ( $\text{CH}_2-\text{SF}_5^+$ , 34%), 127 ( $\text{C}_6\text{H}_5-\text{CF}_2^+$  or  $\text{SF}_5^+$ , 100%), and smaller fragments.

IR (KBr, film):  $\nu$  3056(vw), 3038(vw), 2982(vw), 2920(vw), 2854(vw), 1605(vw), 1495(vw), 1452(m), 1412(w), 1340(w), 1317(m), 1255(s), 1208(w), 1175(m), 1156(m), 1110(m), 1093(m), 1066(s), 1051(s), 1022(m), 998(s), 923(w), 904(m), 858(vs), 832(vs), 793(m), 769(s), 750(m), 696(s), 669(w), 658(m), 633(m), 624(s), 603(s), 565(m), 550(w)  $\text{cm}^{-1}$ .

### 3.4. Preparation of 1-(pentafluoro- $\lambda^6$ -sulfanyl)-2-phenylethyne ( $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{SF}_5$ )

1 g (3.7 mmol) of  $\text{C}_6\text{H}_5-\text{CF}_2-\text{CH}_2-\text{SF}_5$  is treated in 10 ml of *n*-pentane with 2.5 g of powdered KOH under stirring and slow warming from –20°C to room temperature. Control by  $^{19}\text{F}$  NMR shows the end of the reaction after a few hours. Fractional vacuum condensation of the organic layer through –60 and –196°C cold traps affords 0.64 g (75% yield) of colourless crystals (m.p., –8.5°C; b.p., 20.7°C at 0.002 bar).

$^{19}\text{F}$  NMR:  $\delta$  76.61, 83.40 ( $\text{ab}_4$  type,  $\text{SF}_5$ ) ppm.  $^2J_{\text{SFa}-\text{SFb}} = 154.7$  Hz.

$^1\text{H}$  NMR:  $\delta$  7.13 ppm.

MS:  $m/z$  228 ( $\text{M}^+$ , 64%), 209 ( $\text{M}^+-1$ , 13%), 127 ( $\text{SF}_5^+$ , 3%), 120( $\text{C}_6\text{H}_5-\text{C}_2\text{F}^+$ , 100%), and smaller fragments.

IR (KBr, film):  $\nu$  3085(vw), 3061(vw), 2223(vs), 1488(m), 1443(m), 1364(w), 1240(w), 1226(m), 1027(m), 866(vs), 800(vs), 755(vs), 686(s), 613(s), 583(s), 571(s), 536(m), 492(m), Raman (488 Nm, 36 mW),  $\text{cm}^{-1}$ : 3073(m), 2226(s), 1601(s), 1496(w), 1241(m), 1229(m),

1179(m), 1161(w), 1029(w), 1000(s), 894(m), 799(w), 791(w), 696(m), 623(w), 613(w), 584(w), 538(m), 370(w), 233(m), 142(m)  $\text{cm}^{-1}$ .

### 3.5. Preparation of $[\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{-C}_2\text{-SF}_5)]$

0.18 g (0.79 mmol) of  $\text{C}_6\text{H}_5\text{-C}\equiv\text{C-SF}_5$  and 0.24 g (0.7 mmol) of  $\text{Co}_2(\text{CO})_8$  are refluxed in 7.8 g of *n*-hexane. Chromatography over a silica gel column and evaporation of the major part of the solvent affords 0.3 g (83% yield) of red-brown crystalline product after cooling.

$^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  79.58, 75.51 ( $\text{ab}_4$  type,  $\text{SF}_5$ ) ppm.  $^2J_{\text{SFa-SFb}} = 144.3$  Hz.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.9 ppm.

MS:  $m/z$  514 ( $\text{M}^+$ , 7%), 486 ( $\text{M}^+ - \text{CO}$ , 34%), 458 ( $\text{M}^+ - 2\text{CO}$ , 26%), 430 ( $\text{M}^+ - 3\text{CO}$ , 31%), and smaller fragments, based on 278 ( $\text{Co}_2\text{C}_2(\text{C}_6\text{H}_5)\text{F}^+$ , 100%). High resolution:  $\text{M}^+(\text{C}_{14}\text{H}_5\text{Co}_2\text{F}_5\text{O}_6\text{S})$  found: 513.83989. Calc.: 513.83909.

UV ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda$  220, 256, 360, 520 nm. IR (KBr):  $\nu$  3433(w), 2921(vw), 2109.5(vs), 2077(vs), 2046.5(vs), 2038(vs), 1638(w), 1553(w), 1474(w), 1440(w), 1382(w), 1328(vw), 1198(w), 1125(w), 969(w), 902(w), 830(s), 797(s), 762(m), 733(m), 689(w), 658(w), 635(m), 606(m), 583(m), 565(m), 504(m), 488(m), 444(w), 346(w)  $\text{cm}^{-1}$ .

### 3.6. Preparation of $[\text{Co}_2(\text{CO})_4(\text{HC}_2\text{-SF}_5)_2(\text{F}_3\text{C-C}_2\text{-SF}_5)]$

0.529 g (1.05 mol) of  $\text{Co}_2(\text{CO})_6(\text{F}_3\text{C-C}_2\text{-SF}_5)$  are dissolved in 20 ml of *n*-hexane, and 0.73 g (4.8 mol) of  $\text{H-C}\equiv\text{C-SF}_5$  is added by condensation. After 4 months at room temperature the non-volatile residue is separated by column chromatography on silica gel with petrol-ether of boiling point 40–60°C and recrystallization from *n*-pentane gives 0.37 g (47% yield) of dark-blue crystalline product (m.p., 102°C).

$^{19}\text{F}$  NMR:  $\delta$  83.4, 67.0–76.4 ( $\text{ab}_4$  type, 4  $\text{SF}_5$ ,  $J_{\text{ab}} = 130\text{--}140$  Hz);  $-60.6$  ( $J_{\text{FF}} = 14.7$  Hz),  $-55.3$  ( $J_{\text{FF}} = 13.4$  Hz) (two  $\text{CF}_3$  groups coupling to equatorial fluorine on sulfur) ppm.

$^1\text{H}$  NMR:  $\delta$  4.18, 6.66, 6.93, 7.26 ppm.

MS:  $m/z$  754( $\text{M}^+$ , 0.5%), 726 ( $[\text{M} - \text{CO}]^+$ , 4.2%), 707 ( $[\text{M} - \text{CO} - \text{F}]^+$ , 0.3%), 698 ( $[\text{M} - 2\text{CO}]^+$ , 0.6%), 627 ( $[\text{M} - \text{SF}_5]^+$ , 0.5%), and smaller fragments.

IR (KBr):  $\nu$  3099(w), 2921(w), 2118(s), 2093(vs), 2080(s), 2072(s), 2066(s), 1637(w), 1417(w), 1302(m), 1265(m), 1254(m), 1211(m), 1184(m), 1141(m), 1028(w), 949(m), 899(m), 834(vs), 805(s), 759(m), 716(w), 695(w), 662(m), 654(m), 637(m), 587(s), 553(m), 543(m), 533(m), 515(m), 478(w), 443(w), 414(w), 395(w), 346(w).

### 3.7. Crystal structures

Further details of the crystal structures can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), upon quoting the deposition number CSD 58466, the name of authors and the journal citation.

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