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REACTION OF DINUCLEAR THIOLATO-BRIDGED COBALT COMPOUNDS WITH ACTIVATED ALKYNES. FORMATION AND X-RAY STRUCTURE OF AN UNUSUAL TRINUCLEAR COBALT COMPLEX, $[Co_3(\eta^5\text{-}C_5H_5)_3(SMe)_2(CF_3C{\equiv}CCF_3)_2]$

F.Y. PÉTILLON *, J.L. LE QUÉRÉ, F. LE FLOCH-PÉRENNOU, J.E. GUERCHAIS,
Laboratoire de Chimie, Electrochimie et Photochimie Moléculaires, Associé au CNRS, LA 322, Equipe de Chimie Inorganique Moléculaire, Faculté des Sciences et Techniques, Université de Bretagne Occidentale, 29283 Brest Cedex (France)

and P. L'HARIDON
Laboratoire de Chimie Minérale C, LA 254, Université de Rennes I, 35042 Rennes (France)

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Summary

The reaction of $[Co_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}SR)_2]$ (**1**, R = Me or Ph) in tetrahydrofuran with alkynes $R'\text{-}C{\equiv}C\text{-}R''$ ($R'{=}R''{=}CF_3$, CO_2Me or CN) gives products of the type $[Co_3(\eta^5\text{-}C_5H_5)_3(R'C_2R'')_2(\mu\text{-}SR)(\mu_3\text{-}SR)]$ (**2**). The nature of these novel cobalt-containing metallacycles has been determined from an X-ray crystal-structure study of the product with R = Me and R' = R'' = CF_3. This complex crystallizes in space group $P2_1/n$ with $a = 25.699(6)$, $b = 9.003(9)$, $c = 13.093(4)$ Å, $\beta = 94.47(2)°$ and $Z = 4$. On the basis of 1670 reflections with $I \geqslant 3\sigma(I)$, the structure was refined by full-matrix least-squares techniques to $R = 0.035$ and $R_w = 0.045$. The Co–Co distance of 2.451(2) Å indicates a metal–metal bond between two cobalt atoms, and the third cobalt atom is σ-bonded to the two carbons of a butadiene-like fragment with Co–C distances of 1.933(8) and 1.929(6) Å. No reaction was observed on heating or photolysing complexes of type **1** with tetrafluoroethylene or alkynes containing R' and R'' groups less electron-withdrawing than CF_3, CO_2Me, or CN.

Introduction

In recent years there has been considerable interest in the chemistry of binuclear transition-metal complexes, especially those containing metal–metal bonds [1]. Reactions of binuclear complexes with alkynes and alkenes have been extensively studied, and shown to include: (i) oxidative addition occurring at a dimetal centre leading to metal–metal bond breaking [2], (ii) oxidative addition at two non-bonded metal atoms with metal–metal bond formation[3]; and (iii) a neutral addition at a single

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metal center with replacement of two-electron ligands by π donor alkynes or alkenes [4].

As part of our interest in the reactivity of thio-bridged binuclear complexes [4b,5], we investigated the reactions of the cobalt compounds $[\{Co(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ (R = Me, Ph) with various alkynes and the alkene C_2F_4. We describe below the synthesis and characterization of a new type of trinuclear cobalt complex, $[Co_3(\eta^5\text{-}C_5H_5)_3(SR)_2(R'C_2R'')_2]$ (**2**), formed in such reactions.

Results

The complex $[\{(\eta^5\text{-}C_5H_5)Co(\mu\text{-}SMe)\}_2]$ (**1a**) reacted with the alkynes R'C≡CR'' (R' = R'' = CF_3 or CO_2Me) to give dark green air-sensitive crystals of **2** (**2a**, R' = R'' = CF_3; **2b**, R' = R'' = CO_2Me). Black crystals of **2c** were formed when the unstable thiophenyl complex $[\{(\eta^5\text{-}C_5H_5)Co(\mu\text{-}SPh)\}_2]$ (**1b**) was stirred at room temperature with dicyanoacetylene. Complexes **1** were unreactive under both thermal (~ 40°C) and photochemical conditions towards trifluoropropyne, monocyanoacetylene, diphenylacetylene and tetrafluoroethylene.

The ^1H NMR spectrum of **2a** exhibits four singlets at 4.90, 4.55, 2.42, and 2.15 ppm (relative intensities 10/5/3/3) clearly indicating that this compound contains three cyclopentadienyl and two thiolato groups per molecule. The IR spectrum shows two medium olefinic bands at 1572 and 1525 cm^{-1}. The ion of highest mass in the mass spectrum corresponds to the molecular ion $[(C_5H_5)_3Co_3(SMe)_2(CF_3C_2CF_3)_2]^+$, and ions due to the fragmentation of this species are observed with a particularly intense peak corresponding to $[Cp_2Co_2(CCF_3)_2]^+$. The ^{19}F NMR spectrum shows strong F–F coupling (~ 16 Hz), suggesting that CF_3 groups have a *cis* configuration. From their spectroscopic properties we deduce a similar geometry for **2b**, **2c** and **2a**.

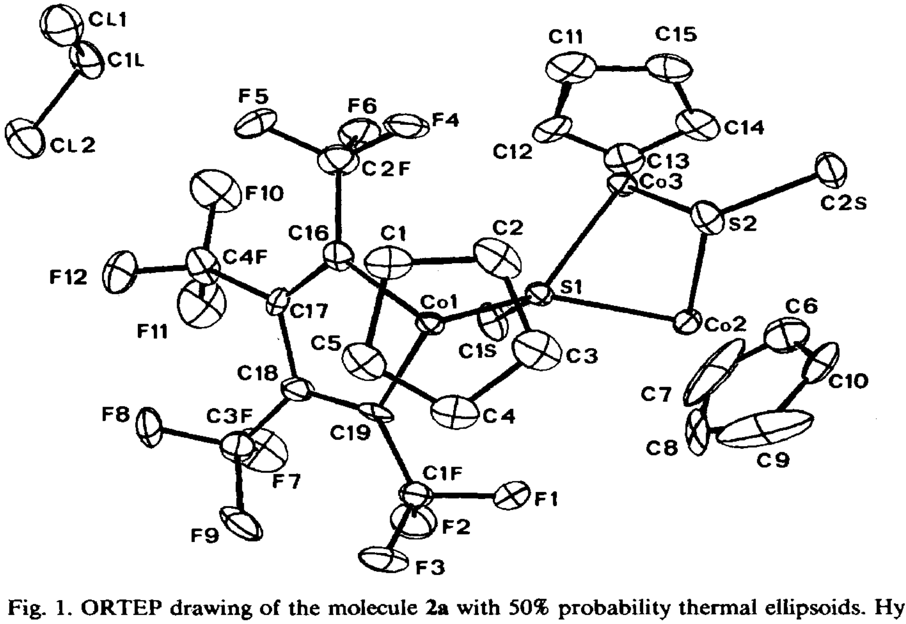


Fig. 1. ORTEP drawing of the molecule **2a** with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The complex **2a** was therefore formulated as $[(\eta^5\text{-}C_5H_5)_3Co_3(SMe)_2(CF_3C_2CF_3)_2]$, but since the structure could be not be unambiguously assigned from spectral and analytical data, an X-ray study was undertaken and the perspective view of the molecule, is given, together with the atom numbering in Fig. 1. **2a** shows it to be a trinuclear complex. The molecular skeleton can be described as a four-membered ring of Co and S atoms linked to a colbaltacyclopentadiene unit.

Atoms Co(2), Co(3), S(1) and S(2) are in a "butterfly" conformation, atoms S(1) and S(2) subtending similar *cis* angles of 84.9(1)° and 85.41(8)° at Co(2) and Co(3) respectively (see Table 2). The coordination of Co(2) and Co(3) can be described as piano-stool, with S(1),Co(3)or(2),S(2) as the three legs and the cyclopentadienyl unit as the three-fold upper part. Two cobalt atoms are close to each other (Co(2)–Co(3) 2.451(2) Å), in contrast to the two others, Co(1)–Co(2) and Co(1)–Co(3) (3.96 and 3.99 Å, respectively) (see Table 1). The short Co(2)–Co(3)distance is close to that (2.438–2.519 Å) in $[(\eta^5\text{-}C_5H_5)_3Co_3(CO)_3]$ [6]. This can be attributed to an important metal–metal interaction, and the presence of a metal–metal bond is the

TABLE 1

SELECTED DISTANCES (Å) IN **2a**

Bonding distances			
Co(2)–Co(3)	2.451(2)	C(2)–C(3)	1.420(15)
Co(2)–S(1)	2.188(3)	C(3)–C(4)	1.384(13)
Co(2)–S(2)	2.188(3)	C(4)–C(5)	1.38(2)
Co(2)–C(6)	2.02(3)	C(6)–C(7)	1.31(2)
Co(2)–C(7)	2.01(2)	C(6)–C(10)	1.31(2)
Co(2)–C(8)	2.049(13)	C(7)–C(8)	1.34(3)
Co(2)–C(9)	2.04(2)	C(8)–C(9)	1.46(3)
Co(2)–C(10)	2.028(14)	C(9)–C(10)	1.39(2)
Co(3)–S(1)	2.177(2)	C(11)–C(12)	1.45(2)
Co(3)–S(2)	2.177(2)	C(11)–C(15)	1.44(3)
Co(1)–S(1)	2.229(3)	C(12)–C(13)	1.33(2)
Co(1)–C(1)	2.102(12)	C(13)–C(14)	1.407(13)
Co(1)–C(2)	2.100(6)	C(14)–C(15)	1.37(3)
Co(1)–C(3)	2.120(7)	C(16)–C(2F)	1.508(12)
Co(1)–C(5)	2.018(11)	C(17)–C(4F)	1.518(12)
Co(1)–C(16)	1.933(8)	C(18)–C(3F)	1.514(9)
Co(1)–C(19)	1.929(6)	C(19)–C(1F)	1.441(15)
S(1)–C(1S)	1.812(7)	C(1F)–F(1)	1.389(13)
S(2)–C(2S)	1.810(9)	C(1F)–F(2)	1.369(13)
C(16)–C(17)	1.374(8)	C(1F)–F(3)	1.315(12)
C(17)–C(18)	1.472(12)	C(1L)–Cl(1)	1.745(12)
C(18)–C(19)	1.374(12)	C(1L)–Cl(2)	1.762(8)
C(1)–C(2)	1.41(2)		
C(1)–C(5)	1.446(11)		
Non-bonding distances			
Co(1)–Co(2)	3.96	C(4)–F(1)	3.002(15)
Co(1)–Co(3)	3.99	S(1)–S(2)	2.953(2)
C(1L)–F(9)	3.195(15)	S(1)–C(16)	3.015(12)
C(1L)–F(10)	3.237(13)	S(1)–F(1)	3.313(5)
C(1)–C(16)	2.869(11)	Cl(1)–F(10)	3.237(13)
C(5)–C(19)	2.927(14)	Cl(2)–F(9)	3.443(8)

simplest explanation for the diamagnetism observed. The thiolato bridges are very nearly symmetrical with respect to the Co(2)–Co(3) axis. The S(1) atom linked to all three Co atoms is tetracoordinated and is almost symmetrically placed with respect to Co(1), Co(2) and Co(3) (the distances are 2.229(3), 2.188(3) and 2.177(2) Å, respectively). The angles around S(1) and S(2) clearly indicate a tetrahedral environment, as is usual in thiolato-bridged dinuclear complexes. Both S(1)–Me and S(2)–Me bonds are in equatorial positions, which correspond to the less sterically hindered geometry. Atoms Co(1), S(1), S(2), C(1S) and C(2S) are coplanar and their mean plane is perpendicular to Co(1), Co(2) and Co(3).

The second fragment of the molecule is a cobaltacycle, with the cobalt also bonded to the sulfur S(1) ligand and to the cyclopentadienyl ring (C(1)–C(5)). The geometry around Co(1) is approximatively of the octahedral type if three facial sites are regarded as occupied by a cyclopentadienyl ligand. The cobaltacycle can be viewed as a delocalized diene with the cobalt σ bonded to the two carbon atoms C(16) and C(19) of the ring. The Co(1)-sp^2 carbon C(19) and C(16) distances of 1.929(6) and 1.933(8) Å, respectively, are slightly shorter than those observed in similar complexes such as the cobaltacyclopentadiene $[(\eta^5\text{-}C_5H_5)(PPh_3)\overline{CoC(C_6F_5)=C(C_6F_5)C(C_6F_5)=C}(C_6F_5)]$ (1.994(11) Å) [7], the cobaltacyclopentene $[(\eta^5\text{-}C_5H_5)(PPh_3)\overline{CoCPh=C(CO_2Me)CH(CO_2Me)C}H(CO_2Me)]$ (1.947(11) Å) [8] and the [μ-{1–3η-1,3-diphenyl-2,4-(dimethoxycarbonyl)butene-1,4-diyl-C^1,C^4(Co^1) : C^1,C^3(Co^2)}(μ-carbonyl)(η^5-cyclopentadienyl)dicarbonyldicobalt(*Co*–

TABLE 2

SELECTED ANGLES (°) IN **2a**

S(1)–Co(3)–S(2)	85.41(8)	Co(2)–Co(3)–S(2)	56.05(7)
S(1)–Co(2)–S(2)	84.9(1)	Co(3)–S(1)–C(1S)	108.6(3)
S(1)–Co(1)–C(16)	92.6(3)	Co(3)–S(2)–C(2S)	110.3(3)
S(1)–Co(1)–C(19)	95.4(3)	Co(3)–Co(2)–S(1)	55.64(6)
S(1)–Co(1)–C(1)	132.2(3)	Co(3)–Co(2)–S(2)	55.63(6)
S(1)–Co(1)–C(2)	98.0(3)	C(16)–C(17)–C(18)	112.8(7)
S(1)–Co(2)–C(7)	111.2(5)	C(17)–C(18)–C(19)	114.2(6)
S(1)–Co(2)–C(10)	172.5(3)	C(16)–C(2F)–F(4)	111.8(8)
C(1)–Co(1)–C(16)	90.5(4)	C(16)–C(2F)–F(5)	114.5(9)
C(1)–Co(1)–C(19)	132.3(4)	C(16)–C(2F)–F(6)	112.(1)
C(16)–Co(1)–C(19)	83.3(3)	F(4)–C(2F)–F(5)	106.2(9)
Co(1)–S(1)–Co(2)	127.65(9)	F(4)–C(2F)–F(6)	104.4(8)
Co(1)–S(1)–Co(3)	130.0(1)	F(5)–C(2F)–F(6)	107.4(9)
Co(1)–S(1)–C(1S)	107.5(3)	H(1L)–C(1L)–H(2L)	110.(1)
Co(1)–C(16)–C(17)	114.5(6)	Cl(1)–C(1L)–Cl(2)	111.9(7)
Co(1)–C(16)–C(2F)	121.8(5)	C(Y1)–Co(1)–C(19) [a]	123.73
Co(1)–C(19)–C(18)	113.6(7)	C(Y1)–Co(1)–C(16)	125.98
Co(1)–C(19)–C(1F)	122.2(6)	C(Y1)–Co(1)–S(1)	124.76
Co(2)–S(1)–Co(3)	68.30(7)	C(Y2)–Co(2)–S(1)	139.57
Co(2)–S(1)–C(1S)	109.6(4)	C(Y2)–Co(2)–S(2)	135.46
Co(2)–S(2)–Co(3)	68.31(7)	C(Y2)–Co(2)–Co(3)	141.83
Co(2)–S(2)–C(2S)	110.8(4)	C(Y3)–Co(3)–S(1)	137.96
Co(2)–Co(3)–S(1)	56.06(7)	C(Y3)–Co(3)–S(2)	136.55
		C(Y3)–Co(3)–Co(2)	141.55

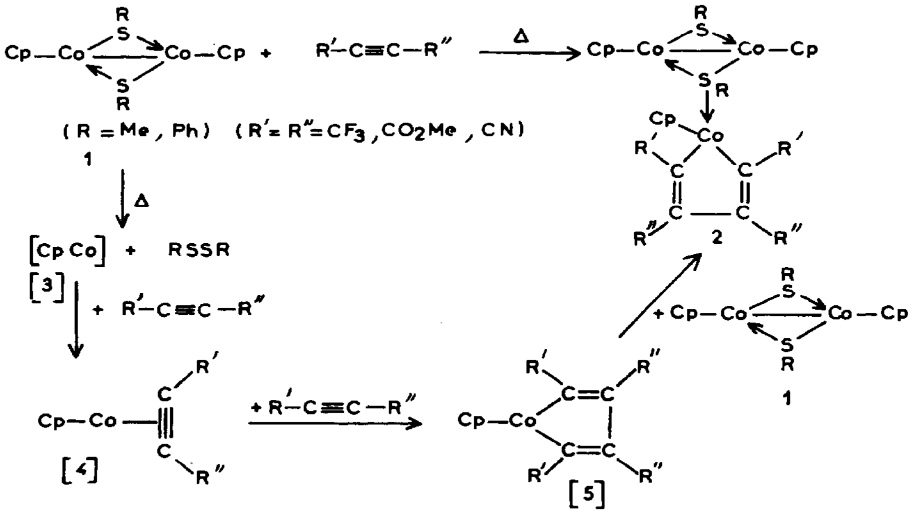
[a] C(Y) is the centre of the cyclopentadienyl groups.

Co)] (1.963(5) Å) [9]. As expected, the C–C distances in the ring fall mainly into two sets: C(16)–C(17) and C(18)–C(19) are 1.374(8) and 1.374(12) Å, respectively, indicative of a double bond, and C(17)–C(18) is 1.472(12) Å, corresponding to a single C–C bond [6,7]. The Co(1), C(16), C(17), C(18) and C(19) atoms are nearly coplanar, and their mean plane forms a dihedral angle of 119.2° with the Co(1),Co(2),Co(3) mean plane.

A particularly remarkable feature of the structure of **2a** is the short distance (2.953(2) Å) between the bridging S atoms; such a value is indicative of a weakly bonding S...S interaction [10]. However no unusual intermolecular nonbonded contacts are observed in the structure.

Discussion

No X-ray crystallographic structure determination has been carried out for complexes **1**, but their spectroscopic data are close to those for the rhodium compound $[\{Rh(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ ($R = C_6H_5$), which has been characterized by X-ray diffraction [11], and a similar structure can be assumed for the cobalt complexes. Such a structure is characterized by a single metal–metal bond and two bridging alkyl- or aryl-thio groups, and is similar to that of $[\{Fe(CO)_3(\mu\text{-}SR)\}_2]$ [12]. It is noteworthy that the original molecule $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}SMe)_2Co(\eta^5\text{-}C_5H_5)]$ is retained in the structure of complexes of type **2**. We therefore propose Scheme 1 to account for our observations.



SCHEME 1

The major feature is that during the reaction one molecule of **1** is decomposed, releasing dimethyl of diphenyl disulfide (as suggested by: (i) the characteristic smell of R–S–S–R when the reaction vessel is opened, (ii) the recovery of $C_6H_5\text{-}S\text{-}S\text{-}C_6H_5$) and leading to electron-deficient units [3] which react with one molecule of alkyne to give a π complex [4]. Complex **4** adds on one more molecule of alkyne to give a cobaltacycle (**5**). Such a metallacycle is readily formed in reactions of low-valent compounds with alkynes. The electrophilic sixteen-electron compound

5 then reacts with one mole of the starting material (acting as a nucleophilic ligand) to give complex **2**.

In these complexes the SR ligand together with the four CF_3 groups provide an effective shield for the two double bonds in the cobaltacycle, which may explain the stability of the complexes.

The reactions of alkynes or alkenes with thio-bridged dimeric complexes containing a metal–metal bond have previously been studied. They mainly give μ-bridged alkyne or alkene compounds [2,13], involving an oxidative addition leading to metal–metal bond breaking. In such complexes the C–C bond is either perpendicular to the metal–metal axis, as in $[Co_2(CO)_6(RC_2R)]$ [14], or parallel as in $[\{Fe(\mu\text{-}SCF_3)(CO)_3\}_2]$ [2a,b]. Davidson and Sharp [15] examined the reaction of $[\{(\eta^5\text{-}C_5H_5)Co(SR)\}_2]$ (R = CF_3 or C_6F_5) with hexafluorobut-2-yne and noticed that there was no reaction below 340 K; above this temperature only the monomeric $[(\eta^5\text{-}C_5H_5)Co\{C_6(CF_3)_6\}]$ was formed. No trace of such a complex was observed in our reactions of complexes in which the R substituents of the SR groups, viz. Me and Ph are less electron-withdrawing.

Trinuclear complexes were also obtained by Poilblanc et al. [3a,16] by treating the dinuclear complex $[\{Ir(\mu\text{-St-Bu})(CO)_2\}_2]$ which does not contain a metal–metal bond with hexafluorobut-2-yne or dimethylacetylenedicarboxylate. These complexes $[Ir_3(\mu\text{-St-Bu})_3(\mu\text{-}C_2R_2)(CO)_6]$ [3a] (R = CF_3, CO_2Me) and $[Ir_3(\mu\text{-St-Bu})_3(\mu\text{-}C_2F_4)(\eta\text{-}C_2F_4)(CO)_5]$[16] are formed by an oxidative addition of alkyne to Ir atoms. However their structures are somewhat different from those of complexes **2**. Thus the three Ir atoms are linked by three sulfur atom to give a thiolate-bridged "crown-like" iridium compound, whereas in **2** Co(1), Co(2) and Co(3) are linked only by two sulfur atoms. Moreover no metallacycle is formed with alkynes in the case of the iridium complexes.

The present study shows the activation by a thiolato group of an electron-deficient alkyne cobalt unit can give rise to multimetallic complexes which form a special class of complexes with potential multicentered reactivity.

Experimental

General comments and spectroscopic data

Preparations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and degassed before use. Infrared spectra were obtained with a Pye-Unicam SP2000 spectrophotometer. Mass spectra were recorded on a Ribermag Mass-1500; NMR spectra in $CDCl_3$ solution on Jeol FX 100 spectrometer (^1H, ^{13}C and ^{19}F) were referenced to Me_4Si and $CFCl_3$. Chemical analyses were performed by the Analytische Laboratorien (H. Malissa and G. Reuter), Germany.

Syntheses $[\{Co(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ (1)

$[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ was a commercial product. $[\{Co(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ (R = Me, **1a**) was prepared by a slight modification of a published procedure (10% yield) [17]. In this, tetrahydrofuran solutions of the dicarbonylcyclopentadienyl cobalt (0.01 mol) with an excess of dimethyldisulphide were photolyzed (Hanau TQ 150 mercury vapor lamp) at room temperature for about 15 h then the solvent was removed under vacuum. The dark-green thiolatocobalt dimer **1a** was separated

(35–55% yield) from the starting material by chromatography on Florisil with dichloromethane/hexane as eluent. Complex **1a** was identified from its mass spectrum and IR and ^{1}H NMR spectra. $[\{Co(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ (R = Ph, **1b**) was prepared in the same way as **1a**; a good yield was obtained, but the product decomposed very quickly at room temperature. Attempts to prepare the dimeric $[\{Co(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ (R = t-Bu^t, Et) by irradiating or heating mixtures of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ and $(RS)_2$ (R = t-Bu^t, Et) failed.

Reactions of $[\{Co(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)\}_2]$ (1) with alkynes and an alkene

*1. Reaction of **1a** with hexafluorobut-2-yne: preparation of $[Co_3(\eta^5\text{-}C_5H_5)_3(SMe)_2(CF_3C_2CF_3)_2]$ (**2a**).* In a typical procedure, ca. 1/g of **1a** (3×10^{-3} mol) was placed in a thick glass reaction vessel fitted with a Teflon stopcock. The vessel was evacuated, cooled to −178°C, and freshly distilled tetrahydrofuran (ca. 50 cm^3) and the alkyne (6×10^{-3} mol) were condensed into it. The mixture was allowed to warm slowly to room temperature and then stirred at 35°C for 24h. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 and chromatographed. Elution with hexane/CH_2Cl_2 (2/1) gave a green band, from which the product **2a** was isolated in about 40% yield. Further elution with CH_2Cl_2 gave the green starting compound **1a**. Complex **2a** is soluble in common organic solvents, but the solutions are very air-sensitive. Green crystals of **2a** suitable for X-ray analysis were crystallized from degassed hexane/CH_2Cl_2 mixture at −40°C. Compound **2a** crystallized with one molecule of dichloromethane, which was readily removed by pumping. Anal. Found: C, 37.9; H, 2.6; Co, 22.1; F, 29.0; S, 8.3. $C_{25}H_{21}Co_3F_{12}S_2$ calcd.: C, 38.0; H, 2.6; Co, 22.4; F, 28.9; S, 8.1%. Selected IR data (Nujol): ν(C=C) 1572, 1525 cm^{-1}; ν(C–F) 1215, 1190, 1160, 1130 cm^{-1}. The mass spectrum showed ions corresponding to: $[M]^+$ 790; $[(C_5H_5)_2Co_2(CF_3C_2CF_3)_2]^+$ 572; $[(C_5H_5)CoC(CF_3)\text{=}C(CF_3)C(CF_3)\text{=}C(CF_3)]^+$ 448; $[(C_5H_5)_2Co_2(SMe)_2]^+$ 342; $[\{C(CF_3)(SMe)\}_2]^+$ 256. ^{1}H NMR, δ: 4.90 (s, 10H, C_5H_5); 4.55 (s, 5H, C_5H_5); 2.42 (s, 3H, SMe); 2.15 (s, 3H, SMe). $^{13}C\{^1H\}$NMR, δ: 126.9 (qu., J(C–F) 275 Hz, CF_3): 118.4 (qu., J(C–F) 281 Hz, CF_3); 112.7 (qu., ^2J(C–F) 43.5 Hz, C=C); 88.8 (s, C_5H_5); 78.3 (s, $2C_5H_5$); 33.3 (s, SMe); 23.2 (s, SMe). ^{19}F NMR, δ: 57.9(m, unresolved); 48.0(m, unresolved).

*2. Reaction of **1a** with dimethyl acetylenedicarboxylate: preparation of $[Co_3(\eta^5\text{-}C_5H_5)_3(SMe)_2(CO_2MeC_2CO_2Me)_2]$ (**2b**).* The reaction was carried out as described above for compound **2a** using $CO_2MeC{\equiv}CO_2Me$. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2. The solution was chromatographed over Florisil, and elution with CH_2Cl_2/THF (9/1) gave **2b** as a green powder. Complex **2b** is very air-sensitive and was characterised only by its spectral data. Selected IR data (Nujol): ν(C=O) 1695, 1680 cm^{-1}; ν(C=C) 1525, 1510 cm^{-1}. ^{1}H NMR, δ: 4.82 and 4.80 (2s, 15H, C_5H_5); 3.80 and 3.52 (2s, 6H, CO_2Me); 2.80 (s, 3H, SMe); 2.25 (s, 3H, SMe).

*3. Reaction of **1b** with hexafluorobut-2-yne.* On heating of $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}SPh)_2Co(\eta^5\text{-}C_5H_5)]$ (**1b**) with $CF_3C_2CF_3$, in tetrahydrofuran for about 48 h gave no trinuclear cobalt compound. A complicated mixture of products was obtained, and no well-defined complex could be identified.

*4. Reaction of **1b** with dicyanoacetylene: preparation of $[Co_3(\eta^5\text{-}C_5H_5)_3(SPh)_2(CNC_2CN)_2]$ (**2c**).* Complex **1b** (0.60 g) and dicyanoacetylene (synthesised as described by Moureu and Bongrand [18]) were stirred together in tetrahydrofuran at room temperature for 24 h. An insoluble black solid (0.10 g) was removed by filtration, and the filtrate was evaporated under vacuo. The residue was extracted with dichloromethane, and addition of hexane to the dichloromethane extract gave a black powder (0.15g) of **2c**. The compound was recrystallized [19] from a mixture of dichloromethane/hexane at low temperature under nitrogen. The mass spectrum does not show the molecular ion, but includes $[(C_5H_5)_2Co_2(SPh)_2(CNC_2CN)]^+$ 542; $[(C_5H_5)_2Co_2(SPh)_2]^+$ 466; $[\{C(CN)(SPh)\}_2]^+$ 294. Selected IR data (Nujol): ν(CN) 2020, 2170 cm^{-1}; ν(C=C) 1560 cm^{-1}. ^1H NMR, δ; 7.53–7.10 (m, SPh); 5.23 (s, 10H, C_5H_5); 5.03 (s, 5H, C_5H_5).

5. Reactions of ***1a*** *and* ***1b*** *with trifluoropropyne, monocyanoacetylene, diphenylacetylene and tetrafluoroethylene.* No reaction was observed on extended irradiation or warming in tetrahydrofuran solutions containing compounds **1a** or **1b** and the title alkynes ($CF_3C{\equiv}CH$, $CNC{\equiv}CH$ and $C_6H_5C{\equiv}C_6H_5$) or tetrafluoroethylene ($CF_2{=}CF_2$). Unchanged **1a** or **1b** recovered in 80–90% yield.

X-Ray structure analysis of **2a**

X-Ray data. At room temperature crystals **2a** diffracted for only a few minutes, and quickly became amorphous. This is because the product readily loses the molecule of solvent, and this disrupts the crystal. The X-ray study thus had to be made at low-temperature. The diffraction data were collected at −120°C with an Enraf–Nonius CAD-4 automatic four circle diffractometer equipped with an Enraf–Nonius cooling apparatus. The single crystal was cooled by a stream of cold nitrogen. Unfortunately during the recording of the data ($l = -1$) the crystal was ejected by the nitrogen stream, and so only one-eighth of the reflecting sphere was collected instead of one-fourth, normally required for a monoclinic crystal. However, owing to the technical difficulties (the epoxy-resin used polymerizes extensively at low temperature) and the low stability of the crystal, we went on to derive the structure from the limited data obtained. Obviously a higher accuracy would be gained with more data, but the R factor reached is acceptable, and we have obtained an adequate description of the molecular structure of the complex.

Unit cell dimensions were determined from a least-squares fit of 25 reflections by using Mo-K_α radiation with a graphite monochromator. The cell constants and other pertinent data are shown in Table 3. The density of 1.85 g/cm^3, observed at room temperature by flotation in the cyclohexane/tetrabromoethane solutions is obviously lower than that of 1.92 g/cm^3 calculated for 4 formula units in the low temperature cell, and this is because at room temperature **2a** loses readily its solvating molecule of dichloromethane. Intensity data for reflections with $\theta < 25$°C were collected using the ω–2θ scan method. The intensities of three standard reflections (224, 50$\bar{9}$, 703) were monitored every hour, the crystal orientations were checked every 400 reflections; no significant change was observed.

A total of 2893 reflections were recorded up to 2θ(Mo) 50°. The intensities were corrected for Lorentz and polarisation effects and reduced to observed structure factor amplitudes, with use of a p value of 0.05. After processing, only 1670 unique reflections with $I > 3\sigma(I)$ were used in subsequent calculations. No absorption corrections were made because of the relatively low absorption coefficient: μ 20.2 cm^{-1} for Mo-K_α.

Solution and refinement of the structure. The structure was solved by using both three-dimensional Patterson function results and multisolution provided the Multan program which yielded positions for Co and S atoms. Subsequent refinements using full-matrix least squares and difference Fourier syntheses enabled us to determine the positions of all remaining non-hydrogen atoms. Atomic scattering factors were taken from International Tables, for X-ray crystallography [20] for cell atoms. A least squares refinement with nonhydrogen atoms in the structure led to $R = 0.12$. Then the heavier atoms (Co, S and Cl) were refined with the carbon atoms kept fixed and the remaining non-hydrogen atoms were refined with the heavier atoms kept fixed, and this cycle was repeated to convergence at $R = 0.070$. At this stage the positions of hydrogen atoms were determined, and the refinement was performed keeping these atoms in rigid positions; R was then reduced from 0.07 to 0.056. In this model the hydrogen bonded-carbon atoms deviated from their previous positions, and so they were calculated with a carbon–hydrogen distance of 1.0 Å. At this point, 406 variable parameters were refined (excluding hydrogen atoms) with a depending factor for shifts of 0.3. The final values of R and R_w [21] were 0.035 and 0.045, respectively. Final positional are listed in Table 4. Idealized positions of the hydrogen atoms, relevant least-squares plane data for selected atomic groups, tables of structure factors and thermal parameters and a table of all positional parameters with their estimated standard deviations are available from the authors.

TABLE 3

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY

Compound	$[Co_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-SMe})_2(CF_3C_2CF_3)_2]$, CH_2Cl_2
FW	875.2
Formula	$C_{26}H_{23}Cl_2Co_3F_{12}S_2$
Cryst. system	monoclinic
Space group	$P2_1/n$
Cell parameters (at −120°C)	
a	25.699(6) Å
b	9.003(9) Å
c	13.093(4) Å
β	94.47(2)°
V	3020 Å^3
Z	4
Density, g/cm^3	1.92(calcd. for −120°C), 1.85 (measured by flotation at RT)
Cryst. dimens.	0.35×0.20×0.12 mm
Temperature	−120°C
radiation	Mo-K_α ($\lambda = 0.7107$ Å)
μ(Mo-K_α)	20.2 cm^{-1}
θ_{max}(Mo-K_α)	25°
Scan width	1.30+0.35 tg θ(deg)
Counter aperture	2.40+0.5 tg θ(mm)
Reflections measured	$h(0-30)$, $k(0-10)$, $l(-15---1)$
$F(000)$	1736
No. of unique data, $I > 3\sigma(I)$	1670
No. of parameters refined	406
Final R [a] values	$R = 0.035$, $R_w = 0.045$
Quality of fit s [b]	1.15

[a] $R = \Sigma(k|F_0| - |F_c|)/\Sigma k|F_0|$; $R_w = [\Sigma w(k|F_0| - |F_c|)^2/\Sigma wk^2F_0^2]^{1/2}$. [b] $s = [\Sigma w(|F_0| - |F_c|)^2/(N_{obsd.} - N_{parameters})]^{1/2}$.

TABLE 4

ATOMIC COORDINATES FOR **2a** [a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.91020(3)	0.1391(1)	0.17737(6)	C(1F)	0.8234(3)	−0.0499(9)	0.2373(5)
Co(2)	0.83662(4)	0.1526(1)	−0.10195(7)	C(2F)	0.9416(3)	0.4505(9)	0.2352(6)
Co(3)	0.87524(4)	0.3971(1)	−0.06932(7)	C(3F)	0.0154(3)	0.134(1)	0.4292(5)
S(1)	0.85746(7)	0.2415(2)	0.0511(1)	C(4F)	0.8750(3)	0.4289(8)	0.4203(5)
S(2)	0.91678(7)	0.2115(2)	−0.1323(1)	F(1)	0.8219(2)	−0.0878(5)	0.1342(3)
C(1)	0.9925(3)	0.1239(9)	0.2024(5)	F(2)	0.7713(2)	−0.0315(6)	0.2510(3)
C(2)	0.9774(3)	0.1145(9)	0.0966(5)	F(3)	0.8368(2)	−0.1754(5)	0.2849(4)
C(3)	0.9451(3)	−0.0114(9)	0.0788(5)	F(4)	0.9696(2)	0.4278(5)	0.1540(3)
C(4)	0.9393(3)	−0.0797(8)	0.1724(6)	F(5)	0.9759(2)	0.4927(6)	0.3116(4)
C(5)	0.9654(3)	0.0034(9)	0.2483(5)	F(6)	0.9112(2)	0.5669(5)	0.2081(3)
C(6)	0.7816(6)	0.166(2)	−0.222(1)	F(7)	0.7675(2)	0.1893(7)	0.4166(4)
C(7)	0.7585(5)	0.157(2)	−0.136(1)	F(8)	0.8367(2)	0.1801(6)	0.5204(3)
C(8)	0.7713(4)	0.025(2)	−0.0923(7)	F(9)	0.8098(2)	−0.0148(6)	0.4399(3)
C(9)	0.8095(7)	−0.048(1)	−0.153(1)	F(10)	0.8879(3)	0.5622(6)	0.3884(4)
C(10)	0.8115(4)	0.051(1)	−0.2346(7)	F(11)	0.8248(2)	0.4436(6)	0.4438(4)
C(11)	1.0942(5)	0.387(1)	0.0455(7)	F(12)	0.9028(2)	0.4016(6)	0.5067(3)
C(12)	1.1476(4)	0.3993(9)	0.0159(6)	C(1L)	0.9245(4)	0.859(1)	0.5107(6)
C(13)	1.1804(3)	0.4398(9)	0.0953(6)	Cl(1)	0.98804(9)	0.7870(3)	0.5083(2)
C(14)	1.1516(4)	0.4573(9)	0.1817(6)	Cl(2)	0.89194(9)	0.7840(3)	0.6127(2)
C(15)	1.1000(4)	0.4267(9)	0.1526(6)	C(1S)	0.7986(3)	0.305(1)	0.1065(5)
C(16)	0.9099(3)	0.3165(8)	0.2593(5)	C(2S)	0.9218(3)	0.240(1)	−0.2685(5)
C(17)	0.8794(3)	0.3082(8)	0.3410(5)				
C(18)	0.8489(3)	0.1706(8)	0.3422(5)				
C(19)	0.8544(3)	0.0803(8)	0.2596(5)				

[a] Estimated standard deviations in the least significant digits are given in parentheses.

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