

Reactions of the μ -alkyne-dicobalt complexes $[\text{Co}_2(\text{CO})_6(\mu\text{-CF}_3\text{-C}\equiv\text{C-R})]$ ($\text{R} = \text{CF}_3, \text{H}$) with $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$: substitution and insertion leading to novel thiolato-alkyne tetra- and tricobalt clusters

Kenneth W. Muir ^{a,*}, René Rumin ^b, François Y. Pétilion ^{b,*}

^a Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, UK

^b UMR CNRS 6521, Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, B.P. 809, 29285 Brest Cedex, France

Received 3 April 2001; accepted 10 May 2001

Abstract

The bis(μ -thiolato)dicobalt complex $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (**1**) reacts with alkyne-cobalt complexes $[\text{Co}_2(\text{CO})_6(\mu\text{-F}_3\text{CC}\equiv\text{CR})]$ (**2**) to give tri- and tetranuclear cobalt cluster compounds. When $\text{R} = \text{CF}_3$ the main product is $[\text{Co}_2(\text{CO})_4(\mu\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-Co}_2\text{Cp}_2(\mu\text{-SMe})_2\}]$ (**3**) but the trinuclear cluster $[\text{Co}_3\text{Cp}(\text{CO})_4(\mu\text{-SMe})_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$ (**4**) is also obtained in low yield. When $\text{R} = \text{H}$ the products are the isomeric clusters $[\text{Co}_3\text{Cp}(\text{CO})_4(\mu\text{-SMe})_2(\mu\text{-CF}_3\text{C}_2\text{H})]$ (**5** and **6**), $[\text{Co}_3\text{Cp}_2(\text{CO})_3(\mu\text{-SMe})(\mu\text{-CF}_3\text{C}_2\text{H})]$ (**7**) and $[\text{CpCo}(\text{CO})_2]$. The solid state structures of **3**, **4**, **5** and **7** have been established by X-ray analysis. The 50 electron triangular cluster **4** has weak Co–Co bonds [2.573(1), 2.800(1), 2.838(1) Å]. The alkyne ligand bridges the shortest of these bonds in perpendicular fashion. **5** and **7** contain open chain tricobalt units [Co–Co 2.39–2.57 Å] more typical of 50 electron M_3 species. In these complexes the alkyne is π -bonded to the central metal atom and σ -bonded to both terminal cobalt atoms. Variable temperature NMR indicates that **5**, **6** and **7** each exist in solution as interconverting isomers which differ in the configuration at one sulphur atom. For **5** the activation parameters [$\Delta H^\ddagger = 64 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -85 \text{ J K}^{-1} \text{ mol}^{-1}$] were obtained spectroscopically. In the solid, molecules of **7** contain an asymmetrically bridging carbonyl [Co–C 1.833(4) and 2.050(3) Å] which is not detectable in the solution spectra. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Triangular clusters; Bridging alkynes; X-ray structures

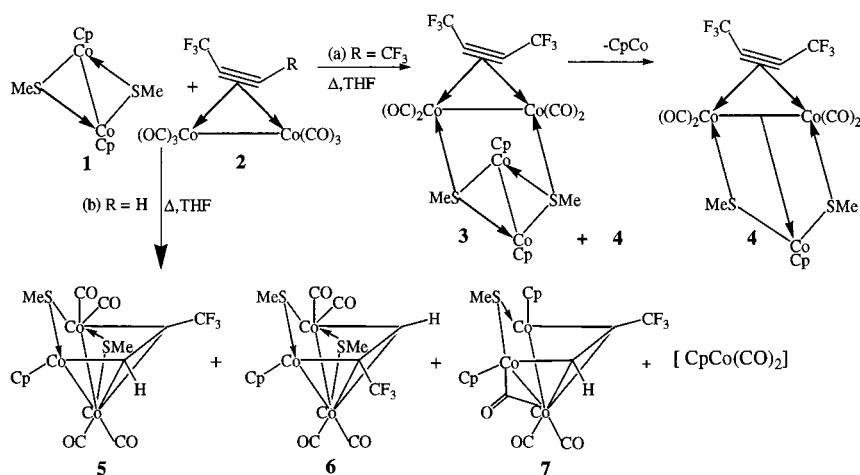
1. Introduction

We describe here the synthesis and characterisation of some new cobalt cluster complexes obtained by reacting the μ -thiolato-dicobalt complex $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (**1**) with alkyne-cobalt complexes $[\text{Co}_2(\text{CO})_6(\mu\text{-F}_3\text{CC}\equiv\text{CR})]$ (**2a** $\text{R} = \text{CF}_3$; **2b** $\text{R} = \text{H}$). We have previously shown that alkyne-dicobalt hexacarbonyl complexes are useful synthons for the fabrication of tri- and tetranuclear clusters [1]: they can readily be prepared using a wide variety of mono- and di-substituted acetylenes and the choice of acetylene, in particular its

electronegativity and retro-dative properties, is often important in determining the architecture of the final product cluster [2,3]. This work also represents an extension from molybdenum [4] and iron [5] to cobalt of our studies of sulphur-rich metal clusters as models for important biological and catalytic processes. A recent review by Went on reactions of polynuclear cobalt-alkyne complexes emphasises how easily $[\text{Co}_2(\text{CO})_6(\mu\text{-F}_3\text{CC}\equiv\text{CCF}_3)]$ can undergo decarbonylation under thermal conditions; this reaction has been exploited mainly to replace carbonyl by phosphine, phosphite or arsine, and other ligands have received little attention [6]. Went also gives a helpful summary of the structural features of $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}\equiv\text{CR}')]$ species. Current knowledge of Cp-stabilised cluster complexes of Group 9 metals has also been summarised [7]. Finally, we

* Corresponding authors. Tel.: +44-141-3300-5345; fax: +44-141-330-4888.

E-mail address: ken@chem.gla.ac.uk (K.W. Muir).



Scheme 1. Syntheses and proposed structures of complexes 3–7.

note that the complexes we now describe are stable, even though they contain highly electronegative alkynes apparently behaving as four-electron donor ligands. The explanation of this apparent paradox in terms of retro-dative bonding was given in response to a question at a conference devoted to the Walden inversion half a century ago [8].

2. Results and discussion

2.1. Reaction of $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (1) with $[\text{Co}_2(\text{CO})_6(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$ (2a): synthesis and spectroscopic characterization of complexes 3 and 4

The reaction of the bis-thiolato-compound $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (1) with 1 equivalent of $[\text{Co}_2(\text{CO})_6(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$ (2a) was carried out under reflux in tetrahydrofuran for 2 h. It afforded the tetranuclear metal complex $[\text{Co}_2(\text{CO})_4(\mu\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-Co}_2\text{Cp}_2(\mu\text{-SMe})_2\}]$ (3) as the major product (87%) (Scheme 1). Careful separation by column chromatography yielded one additional by-product, the trinuclear cluster $[\text{Co}_3\text{Cp}(\text{CO})_4(\mu\text{-SMe})_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$ (4) (6%).

The black product 3 was characterised by a combination of spectroscopic and X-ray diffraction techniques (see respectively Sections 3 and 2.3). 3 (Fig. 1) contains the $\text{Co}_2(\text{CO})_4(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ unit found as a building block in many dinuclear cobalt carbonyl complexes [6] and is derived by replacing two of the carbonyl ligands of the starting hexacarbonyl compound 2a by the two thiolato sulphur atoms of the unsaturated bis(μ -thiolato) species 1 which displays here its ability to act as a four-electron donor ligand. The $^1\text{H-NMR}$ spectrum of 3 at room temperature contains a singlet methyl resonance at δ 2.70 and a broad signal at δ 4.91 in the cyclopentadienyl region. At low temperature (253 K) the cyclopentadienyl resonance splits into two peaks

which broaden on heating, finally collapsing at 296 K. The activation barrier of the observed dynamic process was estimated from the chemical shift difference ($\Delta\nu = 49$ Hz) and the coalescence temperature (296 K) [9]. The value of the energy barrier associated with site exchange is low ($\Delta G^\ddagger = 60.6 (\pm 1.0)$ kJ mol $^{-1}$). Since no line-change involving the Me resonances was noticed over the temperature range 250–303 K, the fluxionality observed for the cyclopentadienyl ligands evidently does not affect the methyl groups under the same conditions. The exchange process most probably reflects the onset of a movement of the alkyne about the Co–Co bond which replaces the transannular interaction between the $\text{CpCo}(2)$ and $\text{C}(3)\text{CF}_3$ groups with an equivalent $\text{CpCo}(3)\cdots\text{C}(2)\text{CF}_3$ interaction. At the same time the C(5) and C(6) carbonyl ligands exchange position at the cobalt centres.

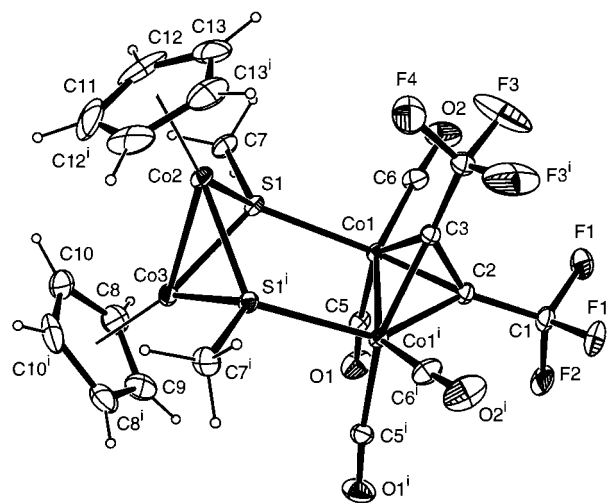


Fig. 1. A view of the structure of 3 showing 10% probability ellipsoids.

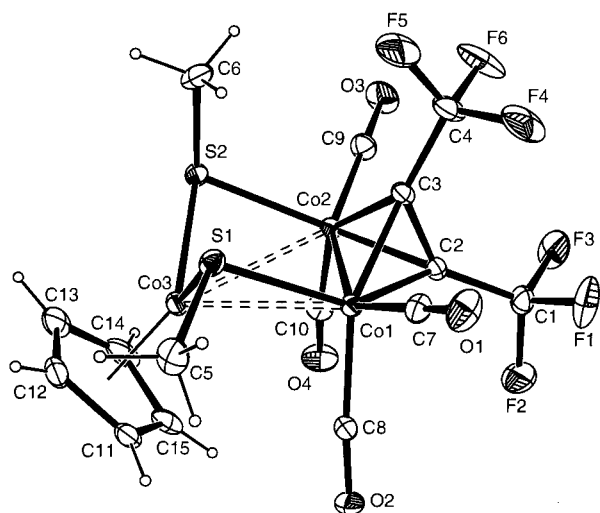


Fig. 2. A view of the structure of **4** showing 10% probability ellipsoids.

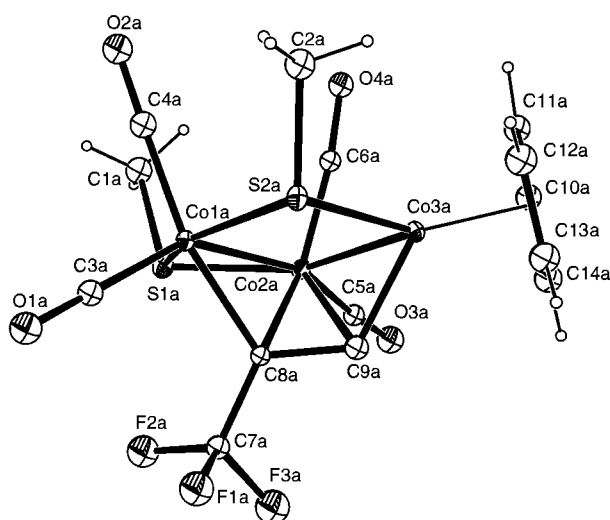


Fig. 3. A view of one of the two independent molecules of **5** showing 10% probability ellipsoids. The hydrogen atom attached to C9a was not located.

There is strong evidence that formation of the tricobalt complex **4** from **3** involves loss of CpCo in a stoichiometrically clean fragmentation reaction (Scheme 1). Indeed, in dichloromethane solution **3** gave **4** as the only metal carbonyl derivative. On standing at -20°C in CDCl_3 , almost 15% of **3** transformed into **4** in 24 h.

The cluster **4** was fully characterised by microanalysis, IR, and ^1H -, ^{19}F - and ^{13}C -NMR spectroscopy (see Section 3), and its molecular structure was also confirmed by an X-ray diffraction study (see Fig. 2 and Section 2.3). The presence of the μ -alkyne carbon atoms in **4** is clearly indicated by the appearance in the ^{13}C -NMR spectrum of two quartets ($^2J_{\text{C-F}} = 45\text{--}48$ Hz) at δ 73.8 and 69.8 ppm. The CO region of the

low-temperature (233 K) ^{13}C -NMR spectrum revealed four singlets between 198.7 and 195.9 ppm (intensity ratio 1:1:1:1) in the region typical for two $\text{Co}(\text{CO})_2$ groups. The ^1H - and ^{13}C -NMR spectra show the presence of only one cyclopentadienyl ligand in **4**. Resonances for two inequivalent SMe groups are present in the ^1H -NMR spectrum: one Me group is shifted highfield (δ 0.50 ppm) indicating that it is subject to a strong shielding cone effect. Mass spectroscopy confirmed the proposed trinuclear structure of the complex **4**: the upper part of the spectrum consists of the molecular ion $[\text{M}]^+$ and of the ions of the sequence $[\text{M} - n\text{CO}]^+$ ($n = 1\text{--}4$).

2.2. Reaction of $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (**1**) with $[\text{Co}_2(\text{CO})_6(\mu\text{-CF}_3\text{C}_2\text{H})]$ (**2b**): synthesis, spectroscopic characterisation of complexes **5–7** and kinetic considerations

Treatment of **1** with 1 equivalent of **2b** in refluxing tetrahydrofuran for 2 h gave a mixture containing the trinuclear complexes **5** (22%), **6** (23%) and **7** (18%), and the degradation product $[\text{CpCo}(\text{CO})_2]$ (19%). The four compounds were cleanly separated by chromatography. An unbalanced reaction for the synthesis is shown in Scheme 1. Complexes **5** and **7** were obtained as crystalline solids and have been characterised both by spectroscopy and by X-ray diffraction studies (see Figs. 3 and 4), whereas **6** was isolated as a solid paste which did not yield diffraction-quality crystals. In a formal sense, insertion of a $(\text{Cp})\text{CoSMe}$ unit into either the $\text{Co}\text{--}\text{C}(\text{H})$ or the $\text{Co}\text{--}\text{C}(\text{CF}_3)$ bond of **2b** gives respectively **5** or **6** after a further transfer of a SMe group to the $\text{Co}_2(\text{CO})_4$ framework. In contrast, **7** has a structure resulting from the insertion of a $\text{Co}(\text{CO})_3(\text{HC}\equiv\text{CCF}_3)$ fragment into the $\text{Co}\text{--}\text{Co}$ bond of **1**.

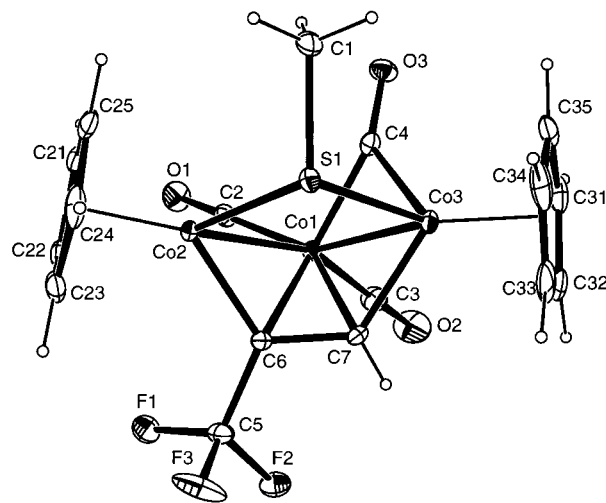


Fig. 4. A view of the structure of **7** showing 10% probability ellipsoids.

Table 1
Comparison of selected NMR chemical shift data (δ)^a for trinuclear-trifluoropropyne-cobalt complexes (**5**–**7**)

Compound	¹⁹ F		¹ H				¹³ C{ ¹ H}		
	CF ₃	=CH	C ₅ H ₅	SCH ₃	SCH ₃	C ₅ H ₅	CF ₃	C–CF ₃	=CH
5a	–53.25(s)	11.10(s)	5.06(s)	2.19(s) 2.01(s)	27.7(s) ^b 23.85(s)	85.5(s)	127.4 (q, ¹ J _{CF} = 276.0) ^b	150.3 (q, ² J _{CF} = 40.0) ^b	162.9(s) ^b
5b	–53.63(s)	11.23(s)	5.06(s)	1.29(s) 2.00(s)	24.5(s) ^b 23.85(s)	85.5(s)	127.7 (q, ¹ J _{CF} = 276.0) ^b	158.0(q) ^b	171.25(s) ^b
6a	–54.54(s)	7.53(s)	5.05(s)	2.31(s) 1.95(s)	25.45(s) 28.45(s)	82.8(s)	128.0 (q, ¹ J _{CF} = 278.0)	156.2 (q, ² J _{CF} = 34.0)	151.6(s)
6b	–55.55(s)	7.69(s)	5.04(s)	1.28(s) 1.95(s)	25.25(s) 28.45(s)	82.8(s)	127.1 (q, ¹ J _{CF} = 278.0)	164.6 (q, ² J _{CF} = 35.0)	159.25(s)
7a	–54.59(s)	11.49(s)	4.77(s) 4.67(s)	2.40(s)	29.3(s) ^b	88.35(s) ^b 83.10(s)	127.85 (q, ¹ J _{CF} = 275.0) ^b	150.15(q) ^b	163.9(s) ^b
7b	–53.86(s)	11.62(s)	4.75(s) 4.63(s)	1.23(s)	23.2(s) ^b	88.85(s) ^b 83.05(s)	127.95 (q, ¹ J _{CF} = 275.0) ^b	157.0(q) ^b	168.8(s) ^b

^a Measured in CDCl₃ solution at 293 K unless stated by footnote b. *J* in Hz.

^b In (CD₃)₂CO at 293 K.

NMR (¹H, ¹⁹F, ¹³C) spectrometry indicated that complex **5** exists in solution as two interconverting isomers. Since the NMR patterns of these isomers are very similar, except for the methyl regions (see Table 1), it is probable that only the methyl groups are responsible for the isomerisation process. Moreover, the ¹H-NMR spectrum clearly showed that only one of the two SMe groups is involved in the stereoisomerism, since only one methyl resonance was shifted to high field when **5a** was transformed into **5b** (Table 1), indicating that the two diastereoisomers differ only in the orientation of one SMe group, which can be either in or out of the shielding cone of the cyclopentadienyl group. As shown in Chart 1, the isomerism probably depends upon the relative dispositions of the cyclopentadienyl ligand and the methyl group attached to the S atom which bridges (Cp)Co and Co(CO)₂ groups (i.e. S2a in Fig. 3). The choice of S2a, rather than S1a, as the source of the isomerism is based on the observation that very similar changes in the ¹H-NMR patterns of **5** and **7** (see Table 1) occur when the isomers interconvert and that **7** contains only one SMe group, which bridges a dicobalt unit in a manner corresponding to S2a in **5**. The **5a**:**5b** ratios were found to depend on the solvent polarity: the more polar solvent favoured the *anti*-isomer (e.g. **5a**:**5b** = 1:1.04 in CDCl₃, 1:0.92 in (CD₃)₂CO and 1:0.66 in CD₃CN). The *syn*-isomer was the only product obtained in the solid state. CD₂Cl₂ solutions of **5b** at 193 K displayed a single ¹H-NMR pattern in accordance with the structure found for this complex by X-ray analysis (see below). Under these conditions, **5a** isomerised over several hours to give an equilibrium mixture of **5a** and **5b** in the ratio 1:1.04. The conversion of **5a** to **5b** can be regarded as the result of inversion at sulphur. The exchange process responsible for the **5a** →

5b interconversion is thought to be slow, since no fluxional phenomena could be detected on the NMR (¹⁹F, ¹H) time scale over the temperature range 193–293 K in CD₂Cl₂. First-order rate constants for the **5a** → **5b** interconversion reaction at four different temperatures in the range 218–234 K were therefore derived from the changes in the ¹⁹F-NMR spectra with time (see Section 3.4). The activation parameters were calculated from the Eyring plot shown in Fig. 5: $\Delta H^\ddagger = 64 (\pm 1) \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -85 (\pm 1) \text{ u.e.}$ The value of the energy barrier ($\Delta G_{298\text{K}}^\ddagger = 89 \text{ kJ mol}^{-1}$) is high compared to those reported for inversion at bridging sulphur in many dinuclear complexes ($\Delta G^\ddagger \sim 45\text{--}62 \text{ kJ mol}^{-1}$) [5,10], but it is of the order of that determined ($\Delta G^\ddagger \sim 74 \text{ kJ mol}^{-1}$) for [W₂(η⁵-C₅H₄Prⁱ)₂Cl₄(μ-H)(μ-SMe)] [11].

Complex **6** was unequivocally characterised in solution by IR and ¹H-, ¹⁹F- and ¹³C-NMR spectroscopy and by comparison with complex **5**. Indeed, the close similarity between **6** and **5** in chemical behaviour (solutions of both complexes contain two interconverting isomers) and in their NMR spectra (see Table 1) strongly suggest that both compounds contain a similar

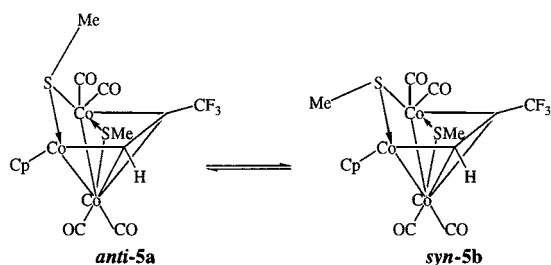


Chart 1.

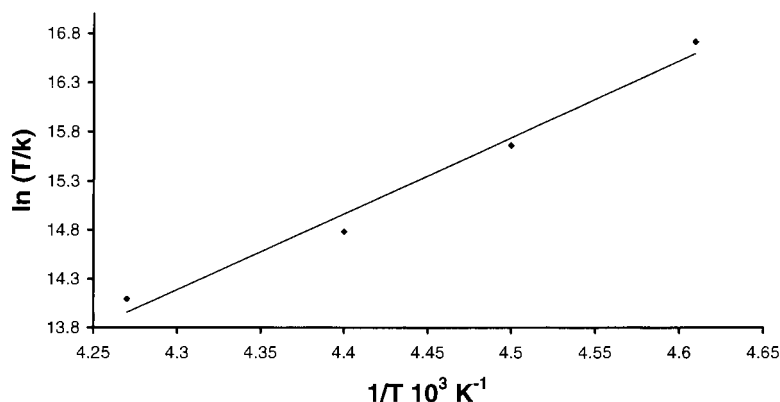


Fig. 5. Eyring plot for the reaction in which **5a** isomerises to give **5b**.

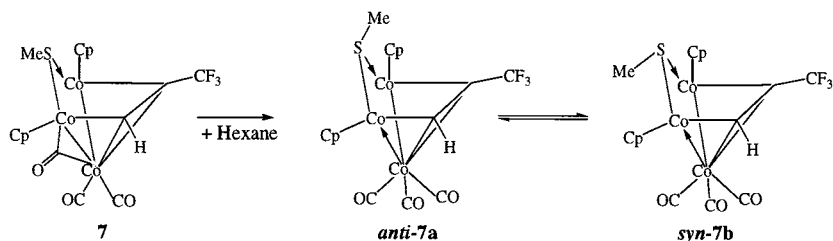


Chart 2.

$\text{CoC(H)C(CF}_3\text{)CoS(Me)}$ cyclobaltathiapentene ring π -bonded to a Co(CO)_2 group. It is likely that **6** differs from **5** by an interchange of the positions of the alkyne CH and CCF_3 groups. This view is supported by the significant shift to high field of the CH resonance ($\delta \sim 7.6$ ppm) in the $^1\text{H-NMR}$ spectrum of **6**, where the CH bridges two Co(CO)_2 groups, relative to that ($\delta \sim 11.2$ ppm) in the spectrum of **5**, where the CH links Co(Cp) and Co(CO)_2 units. As stated above, the room-temperature $^1\text{H-}$, $^{19}\text{F-}$ and $^{13}\text{C-NMR}$ spectra of **6** (Table 1) are consistent with the presence of two interconverting isomers, which will be referred to as **6a** and **6b**. The very close similarities between the $^1\text{H-NMR}$ spectra of **6** and **5** in the methyl regions (Table 1) suggest strongly that the conversion of **6a** to **6b** again involves inversion of the sulphur atom of the $(\text{Cp})\text{Co}(\mu\text{-SMe})\text{Co(CO)}_2$ unit, the *anti*-position of the methyl and the cyclopentadienyl groups in **6a** being replaced by a *syn* arrangement in **6b**.

The IR spectra of **7** in the $\nu(\text{CO})$ region (see Section 3) show that the structure in the solid differs slightly from that obtained in solution. To aid clarity the structure in solution will be referred to as **7'**. A bridging carbonyl [$\nu(\text{CO}) = 1845 \text{ cm}^{-1}$] was found in the single-crystal X-ray study (see below), whereas no peak attributable to bridging CO was observed in solution (Chart 2). Otherwise, spectroscopic data for **7'** are consistent with the structure of **7** obtained by X-ray analysis. Like **5** and **6**, **7'** exists in solution as interconverting isomers **7'a** and **7'b**. NMR spectra of **7'a** and **7'b**

are very similar, with significant differences only in the methyl regions, suggesting that **7'a** and **7'b** correspond respectively to *anti*- and *syn*-isomers (Chart 2). In the room-temperature $^1\text{H-NMR}$ spectrum the distinct isomers **7'a** and **7'b** give rise to methyl singlets at δ 2.40 and 1.23, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum a set of two singlets at δ 163.9 and 168.8 and two quartets at δ 150.15 and 157.0 belong to the bridging C_2 group and have chemical shifts close to those of the corresponding atoms in **5a** and **5b**. Like **5** and **6**, the **7'a:7'b** ratios depend on the solvent polarity: the more polar solvent again favours the *anti*-isomer (e.g. **7'a:7'b** = 1:0.96 in CDCl_3 , 1:0.92 in $(\text{CD}_3)_2\text{CO}$ and 1:0.75 in CD_3CN). Since CD_2Cl_2 solutions of crystals of **7** at low-temperature (193 K) displayed a double $^1\text{H-NMR}$ pattern similar to that detailed in Table 1, rates for **7'a** \rightarrow **7'b** interconversion could not be determined, but it is not unreasonable to suggest that ΔG^\ddagger for this process is of the same order as that obtained for the inversion at sulphur in **5**.

2.3. Molecular structures of **3** and **4**

Complex **3** is formed when two of the carbonyl ligands in **2a** are replaced by the lone pairs of the two sulphur atoms of **1** (Fig. 1, Table 2). No new metal–metal bonds are thereby formed, and the stereochemistries and cluster valence electron counts (CVE) of the metal atoms in the starting complexes are conserved.

Molecules of **3** lie across a crystallographic mirror plane which contains Co2, Co3 and the four alkyne carbon atoms. In consequence, the alkyne plane is exactly perpendicular to the Co1–Co1ⁱ bond and the sawhorse skeleton typical of [Co₂(CO)₆(μ-CF₃C₂CF₃)] (**2a**) [12] and its analogues [6] is retained. The Co1–Co1ⁱ distance [2.454(1) Å] is comparable with the values in **2a** [2.464(4) and 2.472(2) Å] and with a database-derived average of 2.467 Å for 70 [Co₂(CO)₆(μ-RC₂R)] complexes [6]. Similarly, the C2–C3 distance [1.346(7) Å] agrees with values for **2a** [1.355(7) and 1.360(7) Å]

Table 2
Bond lengths (Å) for **3**

Co(1)–C(6)	1.773(4)
Co(1)–C(5)	1.809(4)
Co(1)–C(2)	1.916(4)
Co(1)–C(3)	1.924(4)
Co(1)–S(1)	2.283(2)
Co(1)–Co(1) ⁱ	2.454(1)
Co(2)–C(12)	2.019(7)
Co(2)–C(11)	2.046(12)
Co(2)–C(13)	2.055(6)
Co(2)–S(1)	2.178(1)
Co(2)–Co(3)	2.436(1)
Co(3)–C(10)	2.043(6)
Co(3)–C(8)	2.049(6)
Co(3)–C(9)	2.065(8)
Co(3)–S(1)	2.181(1)
C(1)–C(2)	1.477(7)
C(2)–C(3)	1.346(7)
C(3)–C(4)	1.463(8)

Symmetry transformations used to generate equivalent atoms: (i) $-x+2, y, z$.

Table 3
Bond lengths (Å) for **4**

Co(1)–C(7)	1.775(5)
Co(1)–C(8)	1.794(5)
Co(1)–C(2)	1.937(4)
Co(1)–C(3)	1.941(4)
Co(1)–S(1)	2.234(1)
Co(1)–Co(2)	2.573(1)
Co(1)–Co(3)	2.800(1)
Co(2)–C(9)	1.769(5)
Co(2)–C(10)	1.795(5)
Co(2)–C(3)	1.937(4)
Co(2)–C(2)	1.933(4)
Co(2)–S(2)	2.233(1)
Co(2)–Co(3)	2.838(1)
Co(3)–C(13)	2.030(5)
Co(3)–C(12)	2.044(5)
Co(3)–C(14)	2.057(6)
Co(3)–C(11)	2.075(5)
Co(3)–C(15)	2.102(6)
Co(3)–S(1)	2.171(1)
Co(3)–S(2)	2.194(1)
C(1)–C(2)	1.472(7)
C(2)–C(3)	1.366(6)
C(3)–C(4)	1.463(6)

and the mean for all 70 alkyne complexes [1.339 Å]. Compared with a database-derived mean Co–C(alkyne) distance of 1.969 Å [6], the values in **2a** are short [mean 1.930(5) Å], reflecting the high electronegativity of the CF₃ group [12] and the consequent importance of retro-dative bonding in **2a** [8]; the Co1–C2 and Co1–C3 distances in **3** [1.916(4) and 1.924(4) Å] also show this shortening. The correlation noted between Co–C(alkyne) distances and alkyne C≡C–C angles [6] is complicated in **3** by a steric effect: while the C1–C2–C3 angle [138.8(5)°] agrees with the values in **2b** [137.4(4)–139.5(4)°] (cf. the mean of 142.6° for all 70 analogues) the C2–C3–C4 angle narrows to 133.7(5)° to relieve intramolecular Cp⋯CF₃ contacts.

Although the structure of **1** itself has not been determined, the portion of **3** derived from **1** is geometrically extremely similar to the corresponding parts of [Co₂Cp₂(μ-SMe)(μ₃-SMe)CoCp{(CCF₃)₄}] [13], a complex which also illustrates the Lewis base capabilities of the sulphur atoms of **1**. In **3** S1 is equidistant from Co2 and Co3 [2.178(1) and 2.181(1) Å] and 0.1 Å further from Co1 [2.283(2) Å]. The μ₃-bridging role of the SMe group in **3** appears to preclude low-energy inversion of the sulphur atom, consistent with the interpretation of the NMR spectrum (see Section 2.1).

Removal of Co2 and its associated Cp group from **3** to give **4** is achieved with remarkably little alteration in stereochemistry, as may be seen by comparing Fig. 1 with Fig. 2. Indeed, careful comparison of the structures (Tables 2 and 3) reveals only four changes of any significance. (i) The methyl groups on S1 and S2 are respectively *syn* and *anti* to the Co3 Cp ring in **4** whereas in **3** they are both *syn*; this difference is consistent with the NMR spectra of **4** discussed above. (ii) The Co1–Co2 bond length in **4** is 2.573(1) Å, 0.12 Å longer than the corresponding bond in **3**. (iii) The Co3 atom is respectively 2.800(1) and 2.838(1) Å from Co1 and Co2; although these distances are very long for Co–Co bonds, they are still more than 1 Å shorter than the corresponding distances in **3** which are clearly non-bonding. (iv) The Co1–S1 and Co2–S2 distances in **4** of 2.234(1) and 2.233(1) Å are 0.05 Å shorter than the comparable distances in **4**.

Since the dicobalt-hexafluorobut-2-yne portions of **3** and **4** are nearly identical it is logical to regard the alkyne as a four-electron donor in both molecules. All four metal atoms in **3** then have 18-electron configurations but **4** must then be regarded as rare example of a 50 CVE tricobalt cluster which has one weak and two very weak Co–Co bonds. According to Went, three metal atoms can form either a 50 CVE open chain with two strong metal–metal bonds or, more commonly, a triangular 48 CVE framework [6]. Presumably, the unusual pattern of M–M distances in **4** is a consequence of the anti-bonding nature of the HOMO.

Table 4
Bond lengths (Å) for **5**

	Molecule A	Molecule B		Molecule A	Molecule B
Co(1)–C(3)	1.76(2)	1.77(2)	Co(2)–S(1)	2.202(6)	2.210(6)
Co(1)–C(4)	1.78(2)	1.71(2)	Co(2)–Co(3)	2.514(4)	2.507(4)
Co(1)–C(8)	2.00(2)	1.95(2)	Co(3)–C(9)	1.90(2)	1.87(2)
Co(1)–S(1)	2.257(6)	2.247(6)	Co(3)–S(2)	2.208(5)	2.206(5)
Co(1)–S(2)	2.280(6)	2.277(6)	Co(3)···C(6)	2.50(2)	2.57(2)
Co(1)–Co(2)	2.398(3)	2.386(3)	S(1)–C(1)	1.81(2)	1.82(2)
Co(2)–C(6)	1.71(2)	1.73(2)	S(2)–C(2)	1.81(2)	1.84(2)
Co(2)–C(5)	1.74(2)	1.78(3)	C(7)–C(8)	1.47(3)	1.43(3)
Co(2)–C(8)	2.00(2)	2.02(2)	C(8)–C(9)	1.40(3)	1.45(2)
Co(2)–C(9)	2.04(2)	2.09(2)			

2.4. Molecular structures of **5** and **7**

The structures of the 50 CVE clusters **5** and **7** are based on a more conventional molecular framework and share several common features (see Figs. 3 and 4, Tables 4 and 5). Thus, both clusters have an open chain Co₃ unit, with one intramolecular non-bonding Co···Co distance of 3.3–3.4 Å which is bridged by a methylthiolate ligand whose S–Me bond is *syn* to the Cp–Co bond in **5** (see Chart 1) and to both Co–Cp bonds in **7** (see Chart 2). The terminal atoms of the tricobalt chain are also bridged in parallel fashion via σ -bonds by the CF₃C≡CH ligand which additionally is retro-datively bonded to the central metal atom. The σ -Co–C distances in **7** are comparable to the Co–C(alkyne) distances in **3** and **4**, while the Co1–C6 and Co1–C7 π -bond lengths [2.079(3) and 2.003(3) Å] are longer and slightly irregular. The Co–Co distances [2.570(1) and 2.483(1) Å] differ slightly, the shorter bond being asymmetrically bridged by the C4 carbonyl group [\angle Co1–C4–O3 and \angle Co3–C4–O3, respectively, 149.7(3) and 131.9(3)°]. The two independent molecules present in crystals of **5** are structurally indistinguishable. The analysis of **5** is less accuracy than that of **7** (see Section 3) and a detailed discussion of its bond lengths is not warranted. However, the shortening of the thiolato-bridged Co1–Co2 bond [2.398(3) and 2.386(3) Å] relative to the unbridged Co2–Co3 bond [2.514(3) and 2.507(3) Å] accords with a similar effect in **7**. Co–S bonds in **5** and **7** are in the range 2.202–2.210 Å, except for the Co1–S distances in **5** which are longer [2.247(6)–2.280(6) Å], reflecting the strong π -acidity of the CO ligands bonded to Co1.

3. Experimental

3.1. General procedures

All reactions were performed under either argon or nitrogen using standard Schlenk techniques, and sol-

vents were deoxygenated and dried by standard methods. Column chromatography was carried out with silica gel purchased from SDS and deoxygenated before use. Alkynes we purchased from Fluorochem Limited. Literature methods were used for the preparation of [Co₂Cp₂(μ -SMe)₂] [12] and [{Co(CO)₃]₂(μ -CF₃C≡CR)] (R = CF₃, H) [14]. All other reagents were commercial grade and were used as obtained. Yields are either with respect to the starting complex **2** for the preparation of **3–6** or with respect to compound **1** for the synthesis of **7** and [CpCo(CO)₂].

Infrared spectra were obtained with a Perkin–Elmer 1430 either in hexane–CH₂Cl₂ solutions or in KBr pellets in the ν (CO) region. The mass spectra were measured on a GC/MS Hewlett–Packard spectrometer at the Laboratoire de Biochimie, Faculté de Médecine (Brest). Chemical analyses were performed either by the ‘Océanographie Chimique’ Laboratory or by the ‘Spectroscopie Atomique’ Laboratory at the University of Brest. The NMR spectra (¹H, ¹³C, ¹⁹F), in CDCl₃ or (CD₃)₂CO solutions, were recorded on either a Bruker AC300 or DRX400 spectrometer and were referenced to SiMe₄ (¹H, ¹³C) or CFCl₃ (¹⁹F). Part of the NMR data for **5–7** are compared in Table 1. The remaining

Table 5
Bond lengths (Å) for **7**

Co(1)–C(2)	1.756(4)
Co(1)–C(3)	1.786(4)
Co(1)–C(4)	1.833(4)
Co(1)–C(7)	2.003(3)
Co(1)–C(6)	2.079(3)
Co(1)–Co(3)	2.4829(7)
Co(1)–Co(2)	2.5704(7)
Co(2)–C(6)	1.908(3)
Co(2)–S(1)	2.203(1)
Co(3)–C(7)	1.930(4)
Co(3)–C(4)	2.050(3)
Co(3)–S(1)	2.208(1)
S(1)–C(1)	1.818(4)
C(5)–C(6)	1.484(5)
C(6)–C(7)	1.375(5)

spectral data of these complexes are reported in this section.

3.2. Preparation of $[\text{Co}_2(\text{CO})_4(\mu\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-Co}_2\text{Cp}_2(\mu\text{-SMe})_2\}]$ (**3**) and $[\text{Co}_3\text{Cp}(\text{CO})_4(\mu\text{-SMe})_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$ (**4**)

To a THF solution (30 ml) of $[\{\text{Co}(\text{CO})_3\}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)]$ (**2a**) (896 mg, 2.0 mmol) was added 1 equivalent of $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (**1**) (684 mg), and the mixture was heated under reflux for ca. 2 h. The solution was then dissolved in CH_2Cl_2 , and subjected to silica gel chromatography. Elution with hexane– CH_2Cl_2 (4:1) gave two main dark-brown bands yielding **4** (70 mg, 6%) and **3** (1280 mg, 87%), respectively.

3 (black solid). Anal. Found: C, 32.4; H, 2.1; Co, 31.8. Calc. for $\text{C}_{20}\text{H}_{16}\text{Co}_4\text{F}_6\text{O}_4\text{S}_2$ (734.17): C, 32.72; H, 2.19; Co, 32.11%. IR (CH_2Cl_2): $\nu(\text{CO})$ 2057 m, 2037 s, 2012 s cm^{-1} . $^1\text{H-NMR}$ (CDCl_3 , -20°C): δ 5.00 (s, C_5H_5), 4.83 (s, C_5H_5), 2.70 (s, 2 SCH_3). $^{19}\text{F-NMR}$ (CDCl_3 , -20°C): δ -56.04 (q, $^5J_{\text{F-F}} = 2.5$ Hz, CF_3), -48.9 (q, $^5J_{\text{F-F}} = 2.5$ Hz, CF_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CDCl_3 , -20°C): δ 202.8 (s, CO), 196.6 (s br, 3CO), 128.5 (q, $^1J_{\text{C-F}} = 271.0$ Hz, CF_3), 125.5 (q, $^1J_{\text{C-F}} = 268.0$ Hz, CF_3), 93.1 (m, 2 C-CF_3), 85.1 (s, 2 C_5H_5), 32.1 (s, 2 SCH_3).

4 (black solid). Anal. Found: C, 29.8; H, 1.9; Co, 28.8. Calc. for $\text{C}_{15}\text{H}_{11}\text{Co}_3\text{F}_6\text{O}_4\text{S}_2$ (610.15): C, 29.53; H, 1.82; Co, 28.98%. IR (CH_2Cl_2): $\nu(\text{CO})$ 2058 m, 2037 s, 2005 s cm^{-1} . $^1\text{H-NMR}$ (CDCl_3 , RT): δ 5.15 (s, C_5H_5), 3.24 (s, SCH_3), 0.50 (s, SCH_3). $^{19}\text{F-NMR}$ (CDCl_3 , RT): δ -52.47 (q, $^5J_{\text{F-F}} = 2.5$ Hz, CF_3), -48.9 (q, $^5J_{\text{F-F}} = 2.5$ Hz, CF_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CDCl_3 , -40°C): δ 198.7, 197.6, 196.5, 195.9 (s, CO), 129.2 (q, $^1J_{\text{C-F}} = 281.0$ Hz, CF_3), 125.6 (q, $^1J_{\text{C-F}} = 284.0$ Hz, CF_3), 85.1 (s, C_5H_5), 73.8 (q, $^2J_{\text{C-F}} = 48.0$ Hz, C-CF_3), 69.8 (q, $^2J_{\text{CF}} = 45.0$ Hz, C-CF_3), 26.8 (s, SCH_3), 17.3 (s, SCH_3). Mass spectrum: m/z 610 $[\text{M}]^+$, 582, 554, 526, 498 $[\text{M}^+ - n\text{CO}]$ ($n = 1-4$).

3.3. Preparation of $[\text{Co}_3(\text{CO})_4\text{Cp}(\mu\text{-SMe})_2(\mu\text{-CF}_3\text{C}_2\text{H})]$ (**5** and **6**) and $[\text{Co}_3(\text{CO})_3\text{Cp}_2(\mu\text{-CF}_3\text{C}_2\text{H})]$ (**7**)

A 100 ml Schlenk flask was charged with 1140 mg (3 mmol) of $[\{\text{Co}(\text{CO})_3\}_2(\mu\text{-CF}_3\text{C}_2\text{H})]$ (**2b**), 1026 mg (3 mmol) of $[\text{Co}_2\text{Cp}_2(\mu\text{-SMe})_2]$ (**1**) and 30 ml of THF. This solution was heated under reflux for 2 h with constant stirring. The progress of the reaction was followed by $^{19}\text{F-NMR}$ until complex **2b** totally disappeared. The solvent was removed in vacuo. The solid residue was dissolved in 10 ml of CH_2Cl_2 –pentane and chromatographed over a silica gel column. Using pentane as

Table 6
Crystal data and details of refinements

Compound	3	4	5	7
Empirical formula	$\text{C}_{20}\text{H}_{16}\text{Co}_4\text{F}_6\text{O}_4\text{S}_2$	$\text{C}_{15}\text{H}_{11}\text{Co}_3\text{F}_6\text{O}_4\text{S}_2$	$\text{C}_{14}\text{H}_{12}\text{Co}_3\text{F}_3\text{O}_4\text{S}_2$	$\text{C}_{17}\text{H}_{14}\text{Co}_3\text{F}_3\text{O}_3\text{S}$
Formula weight	734.17	610.15	542.15	532.13
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$\text{Cmc}2_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	10.4188(7)	10.0976(9)	9.8127(9)	8.7571(7)
b (Å)	13.7862(8)	16.2642(9)	13.646(2)	10.051(1)
c (Å)	17.9176(9)	13.149(1)	14.306(3)	12.097(1)
α (°)			76.87(2)	84.00(1)
β (°)		99.10(1)	85.16(1)	71.42(1)
γ (°)			82.85(1)	66.68(1)
Z	4	4	4	2
μ (mm^{-1})	2.764	2.572	2.932	2.810
Crystal size (mm)	$0.58 \times 0.48 \times 0.13$	$0.48 \times 0.20 \times 0.04$	$0.15 \times 0.10 \times 0.05$	$0.20 \times 0.20 \times 0.02$
Habit and colour	Black plate	Red plate	Red block	Red plate
θ maximum (°)	35.0	28.5	23.3	30.0
Reflections collected	3981	6651	6433	8159
Unique reflections $[R_{\text{int}}]$	3290 [0.015]	5189 [0.029]	5343 [0.115]	5379 [0.012]
Reflections with $I > 2\sigma(I)$	2159	3092	2519	3369
Absorption correction	ψ -scan	Analytical	None	ψ -scan
Max. and min. transmission	0.664 and 0.441	0.904 and 0.372		0.656 and 0.495
Data/parameters	3290/180	5189/272	5343/259	5378 /249
R_1 and wR_2 [$I > 2\sigma(I)$] ^a	0.035, 0.089	0.041, 0.091	0.089, 0.224	0.046, 0.105
R_1 and wR_2 (all data)	0.065, 0.098	0.102, 0.111	0.225, 0.296	0.092, 0.116
Flack parameter	0.05(4)			
$\Delta\rho$ ($\text{e} \text{ \AA}^{-3}$)	0.76 to -0.31	0.57 to -0.35	1.21 to -1.13	0.73 to -0.57

^a Refinements were on F^2 . $R_1 = \sum \|F_{\text{obs}}\| - \|F_{\text{calc}}\| / \sum \|F_{\text{obs}}\|$. $wR_2 = \{\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / \sum wF_{\text{obs}}^4\}^{1/2}$.

eluent gave $[\text{CoCp}(\text{CO})_2]$ as the first fraction which was evaporated to dryness under vacuum (yield 200 mg of black–red crystals, 18.5%). Elution with pentane– CH_2Cl_2 (9:1) gave a red–brown band containing **6** (yield 370 mg of red–brown pasty solid, 23%) and a dark-violet band containing **5** (yield 360 mg of brown–violet crystals, 22%). Further elution with pentane– CH_2Cl_2 (4:1) produced a violet band of **7** (290 mg, 18%). Recrystallisation of **5** from cooled dichloromethane–pentane resulted in pure crystals of **5a**.

5 (brown–violet solid). Anal. Found: C, 31.3; H, 2.4; Co, 32.8. Calc. for $\text{Co}_3\text{C}_{14}\text{H}_{12}\text{F}_3\text{O}_4\text{S}$ (542.14): C, 31.02; H, 2.23; Co, 32.61%. IR (hexane): $\nu(\text{CO})$ 2064 m, 2024 s, 1944 m cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , r.t.): δ (CO), 206.3 (s), 199.0 (s), 198.3 (s), 196.6 (s).

6 (red–brown pasty solid). Elemental analyses were tried under nitrogen on independently prepared samples with identical NMR data, but unreliable data were obtained probably because the pasty nature of **6**. IR (hexane): $\nu(\text{CO})$ 2060 m, 2020 s, 1956 s cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , -10°C): δ 205.0 (s br, CO), 199.5 (s, CO), 198.0 (s, 2 CO).

7 (dark-violet solid). Anal. Found: C, 38.7; H, 2.8; Co, 32.9. Calc. for $\text{Co}_3\text{C}_{17}\text{H}_{14}\text{F}_3\text{O}_3\text{S}$ (532.13): C, 38.37; H, 2.65; Co, 32.22%. IR (hexane): $\nu(\text{CO})$ 2034 s, 1998 s cm^{-1} . IR (in KBr pellets): $\nu(\text{CO})$ 2040 m, 2006 s, 1995 sh, 1950 s, 1845 s cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , r.t.): δ 212–200 (m, 3CO). Mass spectrum: m/z 532 $[\text{M}]^+$.

3.4. Kinetic measurements: **5a**–**5b** isomerisation reactions

The kinetic runs were monitored by ^{19}F -NMR (282.39 MHz). A 0.2 M solution of isomer **5a** was prepared by placing 0.050 g of the complex in cooled (195 K) CD_2Cl_2 . The tube was then inserted into the magnet and taken to the desired temperature. The progress of the reaction was followed by monitoring the decreasing intensity of the ^{19}F -NMR resonance of **5a** and the increasing intensity of the signal of **5b**. Plots of $\ln\{x_e/(x_e - x)\}$ against time (where x and x_e are the percentages of **5b** before and at the point when thermodynamic equilibrium was reached) were linear. The slope of this line gave the first-order rate constant.

3.5. Crystal structure analysis of **3**, **4**, **5** and **7**

Measurements were made on a Nonius CAD4 diffractometer with Mo– K_α radiation, $\lambda = 0.71073 \text{ \AA}$, using standard procedures [15]. In general, non-hydrogen atoms were refined with anisotropic displacement tensors. H-atom positions were determined from stereochemical considerations or difference maps and subsequently rode on parent C atoms [16]. Further details are given in Table 6. For **5** the crystals were of poor quality and less than optimum size; only Co and

S atoms were allowed anisotropic displacement tensors because of the small number of observed intensities.

4. Supplementary material

Crystallographic information files (CIF files) for each structure have been deposited with the Cambridge Structural Database, deposition numbers CCDC 160747–160750 for **3**, **4**, **5** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the CRNS (France), EPSRC (UK), and the Universities of Brest and Glasgow.

References

- [1] R. Rumin, P. Abiven, F.Y. Pétillon, K.W. Muir, *J. Organomet. Chem.* 555 (1998) 89 and references cited therein.
- [2] P. Schollhammer, E. Guénin, S. Poder-Guillou, F.Y. Pétillon, J. Talarmin, K.W. Muir, P. Baguley, *J. Organomet. Chem.* 539 (1997) 193.
- [3] For example: (a) E. Sappa, A. Tiripiccio, B. Braunstein, *Coord. Chem. Rev.* 65 (1985) 219. (b) E. Sappa, *J. Cluster Sci.* 5 (1994) 211 and references cited therein. (c) N.M. Aghatabay, J.L. Davidson, U. Dullweber, G. Douglas, K.W. Muir, *J. Chem. Soc. Dalton Trans.* (1999) 3883.
- [4] For a recent review see F.Y. Pétillon, P. Schollhammer, J. Talarmin, K.W. Muir, *Coord. Chem. Rev.* 178–180 (1998) 203.
- [5] P. Madec, K.W. Muir, F.Y. Pétillon, R. Rumin, Y. Scaon, P. Schollhammer, J. Talarmin, *J. Chem. Soc. Dalton Trans.* (1999) 2371.
- [6] M.J. Went, *Adv. Organomet. Chem.* 41 (1997) 69.
- [7] H. Wade, S. Gebert, *Coord. Chem. Rev.* 143 (1995) 535.
- [8] M.J.S. Dewar, *Bull. Soc. Chim. Fr.* 18 (1951) C71.
- [9] H. Shanan-Atidi, K.H. Bar-Eli, *J. Chem. Phys.* 74 (1970) 961.
- [10] (a) S.D. Killops, S.A.R. Knox, *J. Chem. Soc. Dalton Trans.* (1978) 1260; (b) I.B. Benson, S.A.R. Knox, P.J. Naish, A.J. Welsh, *J. Chem. Soc. Dalton Trans.* (1981) 2235.
- [11] Q. Feng, M. Ferrer, M.L.H. Green, P. Mountford, V.S.B. Mtetwa, K. Prout, *J. Chem. Soc. Dalton Trans.* (1991) 1397.
- [12] F. Baert, A. Guelzim, P. Coppens, *Acta Crystallogr. Sect. B* 40 (1984) 590.
- [13] F.Y. Pétillon, J.L. Le Quéré, F. Le Floc'h-Pérennou, J.E. Guerschais, P. L'Haridon, *J. Organomet. Chem.* 281 (1985) 305.
- [14] R.S. Dickson, P.J. Fraser, *Adv. Organomet. Chem.* 12 (1974) 323.
- [15] P. Schollhammer, F.Y. Pétillon, J. Talarmin, K.W. Muir, *J. Organomet. Chem.* 560 (1998) 245.
- [16] Programs used: G.M. Sheldrick, SHELX-97. Programs for Crystal Structure Analysis (Release 97-2), Institut für Anorganische Chemie der Universität, Göttingen, Germany, 1998. L.J. Farrugia, WinGX-A Windows Program for Crystal Structure Analysis, *J. Appl. Crystallogr.* 32 (1999) 837.