INTRAMOLECULAR CARBYNE–CARBYNE COUPLING ON EXPOSURE OF $[\mu_3-\eta^1-CR^1][\mu_3-\eta^1-CR^2][CpCo]_3$ CLUSTERS TO SULPHUR AND SELENIUM: A NOVEL SYNTHESIS OF 1-COBALTA-2,5-DIHETEROCYCLOPENT-3-ENES

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Abstract—The trinuclear cobalt biscarbyne clusters $[\mu_3-\eta^1-CR^1][\mu_3-\eta^1-CR^2][CpCo]_3$ (1) react with sulphur (or selenium) to give the CpCo dithiolenes (or selenolenes) 2. This degradation is thought to proceed via electrophilic attack of the chalcogen, a step modelled by the addition of CH₃S⁺ to 1a to furnish 6, characterized by X-ray crystallography. Labelling experiments aimed at elucidating the mechanistic features of the formation of 2 were inconclusive because of the occurrence of CpCo-scrambling.

Sulphur is a well-known poison to catalysts of industrial significance.¹ Here we present a report on the reaction of trinuclear cobalt μ_3 - η^1 -biscarbyne clusters with sulphur and selenium which causes the disassembly of the metal framework and the intramolecular coupling of the carbyne fragments to yield cobaltadithiolenes and -selenolenes, respectively, a process that is of possible relevance to surface-mediated transformations.² There is a considerable body of literature dealing with the events that occur when transition metal clusters are exposed to sulphur.^{2(c),3} Some of these lead to metalladithiolenes,⁴ molecules of structural and electronic interest, often by mechanisms which are

obscure. The results summarized in this manuscript are unique and add to the diversity of the reactivity patterns that are possible in such processes.

This investigation was inspired by the observation that the clusters $[\mu_3-\eta^1-CR^1][\mu_3-\eta^1-CR^2]$ [CpCo]₃ (1), readily available by the reaction of CpCo(CO)₂⁵ or CpCo(CH₂=CH₂)₂⁶ with alkynes, are remarkably resilient to oxidation with O₂.⁷ However, exposure to an excess of elemental sulphur for two days in boiling chloroform provided the mononuclear η^5 -cyclopentadienylcobalt dithiolenes 2 [eq. (1)] in unusually high yield (Table 1). While the generation of the known⁸ bis- μ_3 -sulphido species 3 (10% yield) was only ascertained in the case of the reaction of 1b, it is assumed to be a byproduct in all the other degradations. The structural assignments of 2 were based on the characteristic⁴ spectral and the analytical data.

(1)



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Cluster	\mathbf{R}^1	R ²	R ³	x	1-Colbata-2,5-dihetero- cyclopent-3-ene % Yield
1a ⁵	CH ₃ CH ₂ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂	Н	S	2a , 99
1b ⁵	C ₆ H ₅	C ₆ H ₅	Н	S	2b , 99
1c ⁵	$C_2Si(CH_3)_3$	$C_2Si(CH_3)_3$	Н	S	2c , 33
1d	C ₆ H ₅	C_2H_5	Н	S	2d , 98
1e	C ₆ H ₅	C_6D_5	Н	S	2e , 95
1f ⁵	CO ₂ CH ₃	CO ₂ CH ₃	Η	S	2f , 90
1g	C ₆ H ₅	C ₆ H ₅	CH ₃	S	2g , 97
1a ⁵	CH ₃ CH ₂ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂	Н	Se	5, 97

Table 1. Results of the reaction of 1 with sulphur

Phenyl. alkoxycarbonyl and remarkably. appended ethynyl groups, appear to be tolerated by the reaction conditions, the latter albeit not completely. It is probably of mechanistic significance that the sulphurization of 1c gives 2c and none of **2h**, a feasible product should any of the reacting metal species undergo migration along the triple bonds.9 That the ethynyl substituents are not entirely inert is evidenced by the isolation of a small amount (5%) of the unusual bisdithiolene 4. Its structure follows from spectral and analytical data. Thus, the ¹H NMR spectrum exhibited the expected four singlet signals and a parent ion at m/z 594 in conjunction with a fragmentation pattern consistent with that of other dithiolene complexes was seen in the mass spectrum. The formation of 4 can

The mechanistic details of the conversion of 1 to 2 were of obvious interest. ¹H NMR monitoring of the progress of the degradation in the presence of either sulphur or selenium did not allow the detection of any intermediates. A clue to the intramolecular nature of the coupling of the two carbyne fragments as observed in 2 was provided by the reaction of 1d which did not furnish any crossover products. A more rigorous experiment involved deuterium-labelled 1e which resulted in 2e cleanly, the absence of deuterium scrambling being readily ascertained by mass spectral analysis. At the time of its discovery,^{2(d)} such a bond-forming reaction between cluster-bound carbyne units had only one precedence in related double-decker clusters.9(b) Since then, several of these unusual couplings have



be envisioned to involve the intermediacy of 2c, in which one of the triple bonds functions as an internal trap for the excess cyclopentadienylcobalt fragments generated from the starting cluster.

As a demonstration of the potential generality of the chalcogen degradation reaction, selenium transformed **1a** to **5** in virtually quantitative yield, although relatively higher temperatures were needed compared with the analogous sulphur reaction. been observed, not only featuring trinuclear CpCosystems¹⁰ but also others.¹¹

Considering that alkynes convert to compounds of type 2 in the presence of CpCo and sulphur (or selenium),^{4(a)} the possibility of the intermediacy of the free alkyne $R^1C \equiv CR^2$ derived from 1 had to be considered as a mechanistic pathway in the present work. However, admixture of external 5-decyne to 1b followed by addition of sulphur resulted in the formation of only 2b, ruling out any mechanisms in which carbyne-carbyne coupling followed by alkyne dissociation was responsible for the observed products.

The established^{7,10} nucleophilicity of clusters of the type 1 made it appear reasonable to assume that whatever form of sulphur¹² attacked them, it was of an electrophilic nature. To establish the feasibility of this notion, which has precedence in the literature,¹³ dimethyl(methylthio)sulphonium tetrafluoroborate,¹⁴ a source of CH₃S⁺, was allowed to react with 1a in nitromethane for 1 h [eq. (2)]. This treatment afforded a black crystalline salt, **6**, whose slight compression of the Co1-carbyne of approximately 0.015 Å and elongation of the Co2,3-carbyne carbon bonds of nearly 0.1 Å is evident.

Although perhaps of dubious relevance with respect to the mechanism of the conversion of 1 to 2, 6 did convert to 2a (78%) on exposure to sulphur under the conditions used to degrade 1a to the same product.

While it was clear that intramolecular carbynecarbyne coupling was occurring in the reactions of 1 with sulphur (and presumably also selenium), the molecularity of this process with respect to the CpCo unit remained to be established. To this end,



structure was initially assigned based only on spectral and analytical data. In particular, the chemical ionization mass spectrum showed a parent ion at m/z 584 for the cationic portion of the salt. More diagnostic was the ¹H NMR spectrum which exhibited two singlets in the chemical shift range typical for cyclopentadienyl ligands ($\delta = 5.08, 4.81$ ppm) in a ratio of 1:2. Of further note was the apparent non-equivalence of the two butyl groups, best indicated by the two distinct triplets assigned to the two sets of terminal methyl protons. Assuming the geometry about the sulphur atom to be tetrahedral, these data would be consistent with the structure of an edge-on bound methylsulphonium salt as depicted by 6. To corroborate this assignment and to rule out other feasible structural alternatives, an X-ray structural analysis was carried out, the results of which confirmed the initial formulation (Fig. 1, Table 2).

On inspection of the structural parameters, it is interesting to note that the sulphur has indeed adopted a tetrahedral geometry and the molecule has attained C_{2v} -symmetry. The Co2—Co3 distance has lengthened to 2.738 Å, an increase of almost 0.4 Å from that observed in $[\mu_3-\eta^1-\text{CH}]_2[\text{CpCo}]_3$.¹⁵ The Co2,3—Co1 distances are 2.38 Å, relatively unchanged from those seen in the parent system. A



Fig. 1. ORTEP drawing of 6. Ellipsoids are scaled to represent the 50% probability surface. There is some disorder at the terminus of one of the butyl substituents.

	Intramolec	ular angles		Intramolecular distances			
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Distance	
Co2	Co1	Co3	70.10(1)	Col	Co2	2.387(1)	
C16	Co1	C21	86.12(11)	Co1	Co3	2.380(1)	
Co2	Col	Cp1 ^a	145.0	Co2	Co3	2.738(1)	
Co3	Col	Cp1	144.9	S	Co2	2.219(1)	
C16	Co1	Cp1	136.8	S	Co3	2.218(1)	
C21	Co1	Cpl	137.1	S	C16	2.729(2)	
Col	Co2	Co3	54 84(1)	S	C21	2.614(3)	
Col	Co2	S	106 64(2)	C16	Col	1.829(2)	
C16	Co2	C21	79.59(10)	C16	Co2	1.944(2)	
Col	Co2	$Cp2^a$	127.7	C16	Co3	1.959(2)	
Co3	Co2	Cp2	177.1	C21	Col	1.817(2)	
S	Co2	Cp2	125.4	C21	Co2	1.946(2)	
	Co2	Cp2	136.6	C21	Co3	1.956(3)	
C21	Co2	Cp2	134.3	Col	C 1	2.076(3)	
Cal	Col	-r- Co2	55 06(1)	Col	C2	2.093(3)	
Col	C03	C02	106.86(2)	Co1	C3	2.076(3)	
	Co3	S C21	100.00(2)	Col	C4	2.056(3)	
C10	C03	C_{21}	120.0	Col	C5	2.064(3)	
Co1	C03	Cp3	129.0	Col		1.715	
C02	Co3	Cp3	1/4.9	Col		2 025(3)	
5	C03	Cp3	123.7	C02	C0	2.033(3)	
C16	Co3	Cp3	139.3	C02	C/	2.035(3)	
C21	003	Срэ	133.0	C02	Co	2.103(3)	
Col	C16	Co2	78.43(9)	Co2	C9	2.060(3)	
Co1	C16	Co3	77.80(9)	C02	C_{10}	2.004(3)	
Co2	C16	Co3	89.10(10)	02	Cp2	1.721	
Col	C16	C17	133.21(19)	Co3	C11	2.098(3)	
Co2	C16	C17	125.71(18)	Co3	C12	2.082(3)	
Co3	C16	C17	133.47(19)	Co3	C13	2.078(3)	
Col	C21	Co2	78.65(10)	Co3	C14	2.072(3)	
Col	C21	Co3	78.12(10)	Co3	C15	2.054(3)	
Co2	C21	Co3	89.11(11)	Co3	Cp3 ^a	1.725	
Col	C21	C22	133.45(20)	S	C26	1.812(3)	
Co2	C21	C22	128.52(19)	C16	C17	1.505(3)	
Co3	C21	C22	130.28(19)	C17	C18	1.503(4)	
Co2	S	Co3	76 19(2)	C18	C19	1.503(4)	
Co2	5	C26	111 17(11)	C19	C20	1.476(5)	
C02	5	C26	110.21(11)	C21	C22	1.502(4)	
C16	C17	C18	117 5(2)	C21 C22	C22	1.502(4)	
C10 C17	C18	C19	113 9(3)	C22	C23	1.519(5)	
C18	C19	C20	116.6(3)	C23	C24	1.330(3)	
C10	C12	C20	115 3(2)	C24 C24	C25	1.508(8) 1.173(12)	
C21	C22	C23	113.2(3) 110.7(4)	C24	C25	1.175(12)	
C22	C23	C24 C25	110.7(4)	B	Fl	1.365(4)	
C23	C24	C25	110.7(4)	B	F2	1.340(4)	
C23	C24	C25	129.7(8)	B	F3	1.358(5)	
C5	Cl	C2	108.7(4)	B	F4	1.346(5)	
C1	C2	C3	108.3(4)	CI	C2	1.36/(6)	
C2	C3	C4	109.3(4)	C2	C3	1.329(6)	
C3	C4	C5	106.8(4)	C3	C4	1.390(6)	
C4	C5	C1	106.9(4)	C4	CS	1.384(6)	
C10	C6	C7	109.3(4)	CS	CI	1.3/3(0)	
C6	C7	C8	110.8(4)	C6	C 7	1.326(6)	
C7	C8	C9	109.4(4)	C7	C8	1.279(6)	
C8	C9	C10	106.2(4)	C8	C9	1.345(7)	
C9	C10	C6	104.3(4)	C9	C10	1.438(7)	

Table 2. Bond lengths (Å) and angles (°) for $\bf 6$

Intramolecular angles				Intramolecular distances			
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Distance	
C15	C11	C12	108.3(4)	C10	C6	1.344(7)	
C11	C12	C13	110.2(4)	C11	C12	1.326(6)	
C12	C13	C14	105.2(4)	C12	C13	1.380(6)	
C13	C14	C15	106.4(4)	C13	C14	1.398(7)	
C14	C15	C11	109.9(4)	C14	C15	1.372(7)	
Fl	В	F2	110.2(3)	C15	C11	1.325(6)	
F1	В	F3	109.6(3)				
F1	В	F4	109.5(4)				
F2	В	F3	108.9(4)				
F2	В	F4	108.8(3)				
F3	В	F4	109.8(3)				

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Table 2.	l continue	a

^aCp1, Cp2 and Cp3 are the centroids of the cyclopentadienide ligands.

another crossover experiment was devised involving methyl labelled 1g. To also address the possibility of a potentially regioselective (albeit mechanistically rather obscure) metal attachment pathway, this compound was reacted with sulphur in the presence of 1e. The outcome of this experiment revealed the occurrence of scrambling of the labelled CpCo unit to give 2b, 2e, 2g and 7 [see eq. (3)]. processes can be envisaged as a rationalc for this molecular reorganization: exchange of Cp, CpCo or CpCoS₂ (or $R^1R^2C_2$). The feasibility of the first option was made likely by literature precedence for Cp exchange¹⁷ and the fact that exposure of **2g** to nine equivalents of sodium cyclopentadienide in boiling THF afforded **2b** and starting material in a





Although one could have construed this result as being indicative of an intermolecular mechanism by which the metal units progressed to 2, a control experiment in which 2e and 2g were heated in chloroform to give an equilibrium mixture with 2b and 7 negated the validity of that conclusion. Transpositions of this type had been known in metalladithiolenes, 4,16 but had never been rigorously scrutinized mechanistically. The observation of scrambling in the transformation of 2e in the presence of 2g provided an opportunity to do so. Three

roughly equimolar ratio. This experiment suggested the possibility that trace quantities of anionic Cp could function as reactive intermediates in the observed scrambling. The second option had been implied in previous reports^{4,16} but was never proven. The possibility of alkyne exchange also had to be considered seriously, based on some literature analogies¹⁸ and the finding that **2b**, when treated with dimethyl butynedioate in boiling CH₂Cl₂ gave **2f** (18%), diphenylacetylene (45%) and dimethyl 4,5diphenylthiophene-2,3-dicarboxylate (10%).

To differentiate between these three modes, a series of crossover experiments was designed aimed at revealing the conservation (or lack thereof) of the presence of the various bonds which are involved. These utilized selenium as a label for sulphur and rhodium as a label for cobalt. To probe the possibility of alkyne exchange, a solution of 2g and 5 was heated to 90°C for 12 h, after which the reaction was stopped and the mixture separated by HPLC to give the respective pairs of dithiolenes 2b, 2g and diselenolenes 5, 8 [see eq. (4)]. These were then

eliminates the consideration of cyclopentadienyl ligand transfer in the degradation of 1, leaving only Cpmetal exchange as a viable mechanism. It therefore appears that the reaction of 2g with cyclopentadienylanion is mechanistically unrelated to the transformations which constitute the main body of this report.

Although the details by which cyclopentadienylmetal exchange occurs in these processes are not known, several possibilities present themselves. The first to be considered is a dissociative pathway in which 2 would split into cyclo-



analysed by both ¹H NMR and mass spectroscopy to reveal only exchange products in which the chalcogen had remained attached to the alkyne fragment. This finding ruled out the possibility that alkyne units were being transferred in these processes and suggested that the reaction of **2b** with dimethyl butynedioate followed an independent (and as yet unexplored) pathway.

To distinguish between Cp and Cpmetal exchange it was necessary to label the metal centre. This goal was reached by the preparation of rhodium dithiolene 9 via an adaptation of the Bönnemann– Schrauzer procedure.^{4(a)} Exposure of 9 to 10 (obtained in an analogous way from (η^{5} -CH₃C₅H₄) Co(CO)₂, 5-decyne, and S₈) in xylene at 130°C showed products 11 and 2g, determined by mass spectral analysis to be derived only from cyclopentadienylrhodium or methylcyclopentadienylcobalt exchange [see eq. (5)]. This experiment pentadienylcobalt and the corresponding dithioketone. While such a mechanism is attractive because of its topological simplicity, it seems unlikely, as the organometallic fragment produced contains a highly coordinatively unsaturated 14e configuration. Indeed, attempts to trap such a complex were unsuccessful. Thus, addition of disodium 1,2dicyanoethene-1,2-dithiolate to a heated solution of **2a** gave only recovered starting material.

A more likely scenario draws again from literature precedence which shows that metalladithiolenes are capable of forming diverse dimeric structures incorporating bridging enedithiolate ligands,¹⁸ all of which could be intermediates in the exchange reactions uncovered in this work.

Finally, although more of the details by which



clusters 1 transform in the presence of chalcogens remain to be established, it is likely that after sulphur has attacked one of the cobalt-cobalt bonds, migration into a carbyne-metal bond takes place, as observed for NO⁺ and HCO⁺,¹⁰ to, in the present case, furnish a cluster bound thioacyl group, a species that has been the result of a number of related reactions of metal clusters with sulphur or sulphurcontaining reagents.¹⁹

EXPERIMENTAL

General procedures

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF was purified by distillation from sodium-benzophenone ketyl under N₂ and hydrocarbon solvents by stirring over H₂SO₄ for several hours. This treatment was repeated until the H_2SO_4 remained colourless. The organic layer was washed five times with 5% aqueous bicarbonate, five times with H_2O_1 , twice with aqueous KMnO₄, again H₂O, then dried over MgSO₄, and distilled from CaH₂. Solvents and solutions were deoxygenated either by bubbling a vigorous stream of nitrogen through the liquid for several hours or by subjecting the latter to several freeze-evacuationthaw cycles. All reactions involving cobalt were executed in deoxygenated solvents and under an inert atmosphere. Melting points (open Pyrex capillary) are uncorrected. ¹H NMR spectra were recorded at 250 or 200 MHz on instruments equipped with Cryomagnets Inc. magnets and Nicolet model 1180 data collection systems. ¹H NMR data are tabulated in the order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; m, multiplet), coupling constant(s) in Hz and number of hydrogens (H). Chemical shifts are reported in ppm downfield from TMS, referenced to the residual proton peak of deuterated solvent as follows: δ CHCl₃, 7.24; C_6D_5H , 7.15; CD₃C(O)CD₂H, 2.04; CD₂HCN, 1.09 ppm. ¹³C NMR chemical shifts are reported in ppm downfield from TMS, referenced to the respective central peaks of the perdeuteriobenzene ($\delta = 127.0$ ppm) or deuteriochloroform triplet ($\delta = 77.0$ ppm). Infrared absorptions were measured on a Perkin-Elmer infrared spectrophotometer model number 681. Mass spectral data are tabulated as m/z (relative intensity) and were obtained with Atlas MS-12 (low resolution) or Consolidated 12-110B (high resolution) mass spectrometers. Elemental analyses were provided by the Microanalytical Laboratory in the College of Chemistry, University of California, Berkeley, California. All chromatography was

carried out with Alfa alumina (neutral) which had been deactivated by adding 5% H₂O w/w. High pressure liquid chromatography was performed with an Altex model 110A pump and an Altex model 153 UV detector using, linked in series, two Ultrasphere ODS 10 mm \times 25 cm, 5 μ particle columns (reverse phase). All crystallizations took place in hexane at -78° C.

General procedure for the preparation of $bis(\mu_3-\eta^1-alkylidyne)tris(\eta^5-cyclopentadienylcobalt)$ complexes⁵

Decalin (300 cm³) was placed in a 500 cm³ round bottom flask equipped with a magnetic stirbar and a reflux condenser stoppered with a rubber septum pierced by two 20 gauge syringe needles, one of which reaches a position just above level, the other functioning as a pressure release. The solvent was heated to reflux and exposed to a nitrogen purge for 2 h. A decalin solution (20 cm³) containing the alkyne (1 equiv) and $CpCo(CO)_2$ (3 equiv) was then added via syringe pump to the boiling solvent with continued nitrogen purge over 6 h. After boiling the resulting mixture for an additional 4 h, it was filtered through glass wool and the solvent removed via vacuum transfer. The residue was dissolved in CH₂Cl₂ and preadsorbed onto alumina, then chromatographed on alumina with hexane and hexaneether mixtures to afford the desired biscarbyne clusters.

$(\mu_3-\eta^1-Benzylidyne)(\mu_3-\eta^1-propylidyne)tris(\eta^5-cyclo-pentadienylcobalt)$ (1d)

Following the general protocol for the preparation of biscarbyne clusters, the following reagents were used: 1-phenyl-1-butyne (1 g, 7.69 mmol) and CpCo(CO)₂ (4.15 g, 23 mmol). This reaction afforded **1d** (1.56 g, 41%): maroon crystals, m.p. 155–157°C; IR (NaCl) 2960m, 2935m, 1415w, 1160w, 1005m, 800s cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 2.16 (t, J = 7 Hz, 3 H), 4.94 (s, 15 H), 5.19 (q, J = 7 Hz, 2 H), 7.41 (m, 3 H), 8.18 (br d, J = 7 Hz, 2 H); mass spectrum m/z 502 (M⁺, 89), 370 (60), 247 (32), 189 (100), 124 (17). Exact mass. Found: 501.9949. Calc. for C₂₅H₂₅Co₃: 501.9952. Analysis. Found: C, 60.00; H, 5.02. Calc. for C₂₅H₂₅Co₃: C, 59.76; H, 5.02%.

$(\mu_3 - \eta^1 - Benzylidyne)(\mu_3 - \eta^1 - pentadeuteriobenzylidyne)$ tris $(\eta^5$ -cyclopentadienylcobalt) (1e)

Diphenylacetylene- d_5^{20} (1.0 g, 5.46 mmol) and CpCo(CO)₂ (3.0 g, 16.7 mmol) were converted to 1e (1.29 g, 42.5%) : maroon crystals ; mass spectrum m/z 555 (M⁺, 100), 370 (26), 189 (90), 124 (49).

$Bis(\mu_3 - \eta^1 - benzylidyne)tris(\eta^5 - methylcyclopentadienyl$ cobalt) (1g)

Diphenylacetylene (500 mg, 2.8 mmol) and (η^{5} -CH₃C₅H₄)Co(CO)₂ (1.6 g, 8.2 mmol) transformed to **1g** (1.2 g, 74%): maroon crystals, m.p. 131– 132°C; IR (NaCl) 2920w, 1570m, 1432m, 800s, 700s cm⁻¹; ¹H NMR (200 MHz, C₆D₆) δ 1.28 (s, 9 H), 4.21 (br s, 6 H), 4.38 (br s, 6 H), 7.45 (m, 6 H), 8.38 (br d, J = 8 Hz, 4 H); mass spectrum m/z 592 (M⁺, 46), 372 (100), 316 (30), 267 (33), 217 (49), 178 (24). Exact mass. Found : 592.0414. Calc. for C₃₂H₃₁Co₃: 592.0422. Analysis. Found : C. 65.20; H, 5.38. Calc. for C₃₂H₃₁Co₃ : C, 64.94; H, 5.29%.

General procedure for sulphur degradations

In a 50 cm³ round bottom flask equipped with a stirbar was placed CHCl₃ (35 cm³) and an excess of sulphur (~ 0.6 mmol) while N₂ was bubbled through the solution for several hours. The cluster (~ 0.2 mmol) was added, the mixture boiled for 2 days, alumina (5 g) added and the solvent removed on a rotary evaporator. The reaction mixture, thus preadsorbed, was placed on top of an alumina column and chromatographed using hexane and hexane–ether mixtures.

Degradation of $bis(\mu_3 - \eta^1 - pentylidyne)tris(\eta^5 - cyclo-pentadienylcobalt)$ (1a)

According to the above general procedure, **1a** (100 mg, 0.196 mmol) and sulphur (20 mg, 0.63 mmol) were transformed into **2a** (63 mg, 99%): purple crystals, m.p. 62–64°C; IR (NaCl) 2960m, 2940m, 1470w, 1410w, 1000m cm⁻¹; ¹H NMR (200 MHz, C₆D₆) δ 0.84 (t, J = 7.3 Hz, 6 H), 1.33 (quin, J = 7.5 Hz, 4 H), 1.78 (sex, J = 8 Hz, 4 H), 2.78 (t, J = 7.4 Hz, 4 H), 4.69 (s, 5 H); mass spectrum m/z 326 (M⁺, 77), 241 (39), 188 (83), 44 (100). Exact mass. Found: 326.0581. Calc. for C₁₅H₂₃CoS₂: 326.0556.

Degradation of $bis(\mu_3-\eta^1-benzylidyne)tris(\eta^5-cyclo$ pentadienylcobalt) (1b)

Complex **1b** (100 mg, 0.18 mmol) and sulphur (20 mg, 0.63 mmol) were allowed to react as above to furnish **2b** (66 mg, 99%) : blue crystals, m.p. 113–114°C; IR (KBr) 3050w, 1598m, 1490m, 1440m, 755s, 680s cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 4.71 (s, 5 H), 6.95 (m, 6 H), 7.45 (m, 4 H); ¹³C NMR (50 MHz, CDCl₃) δ 79.61, 127.14, 127.85, 129.02, 142.24, 168.82; mass spectrum *m*/*z* 366 (M⁺, 74), 188 (100), 178 (91), 124 (61). Analysis. Found : C,

62.72; H, 4.18; S, 17.2. Calc. for $C_{19}H_{15}CoS_2$: C, 62.28; H, 4.13; S, 17.5%.

A second more polar compound was then isolated and characterized as 3 (8 mg, 10%): black plates, m.p. > 250°C (ref. 8 > 250°C; ¹H NMR (250 MHz, CDCl₃) δ 4.65 (s); mass spectrum m/z 436 (M⁺, 11), 189 (79), 124 (100).

Degradation of $bis[\mu_3 - \eta^1 - (3 - trimethylsilyl) - 2 - propynylidyne]tris(cyclopentadienylcobalt) (1c)$

Following the general procedure, 1c (100 mg, 0.17 mmol) and sulphur (20 mg, 0.63 mmol) were converted to 2c (23 mg, 33%): aquamarine crystals, m.p. 115-116°C; IR (KBr) 2960w, 2060w, 1010w, 800w cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 0.23 (s, 9 H), 4.35 (s, 5 H); mass spectrum m/z 406 (M⁺, 20), 279 (35), 188 (41), 183 (33), 149 (94), 57 (100). Exact mass. Found: 406.0111. Calc. for C₁₇H₂₃CoS₂Si₂: 406.0111. A second more polar compound turned out to be 4 (5 mg, 5%): forest green crystals, m.p. 187–189°C; IR (NaCl) 2060w, 1460m, 730m cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 0.24 (s, 9 H), 0.28 (s, 9 H), 4.35 (s, 5 H), 4.42 (s, 5 H); mass spectrum m/z 594 (M⁺, 8.5), 522 (36), 366 (19), 189 (8.1), 44 (100). Exact mass. Found: 593.9274. Calc. for C₂₂H₂₈Co₂S₄Si₂: 593.9276.

Degradation of $(\mu_3-\eta^1-benzylidyne)(\mu_3-\eta^1-propyli$ dyne)tris(cyclopentadienylcobalt) (1d)

Reaction of 1d (100 mg, 0.20 mmol) with sulphur (20 mg, 0.63 mmol) afforded 2d (62 mg, 98%) : blue crystals, m.p. 110–111°C; IR (KBr) 3100w, 2950w, 1455m, 1430m, 1405m, 835m, 742m, 740m cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.31 (t, J = 7 Hz, 3 H), 2.83 (q, J = 7 Hz, 2 H), 4.67 (s, 5 H), 7.11 (m, 3 H), 7.43 (m, 2 H); ¹³C NMR (50 MHz, CDCl₃) 16.43, 31.09, 79.28, 127.31, 127.97, 128.45, 142.70, 167.69, 174.12; mass spectrum m/z 318 (M⁺, 36), 188 (100), 149 (13), 124 (35). Analysis. Found : C, 56.28; H, 4.71; S, 19.76. Calc. for C₁₅H₁₅CoS₂: C, 56.59; H, 4.76; S, 20.14%.

Degradation of 1e

Complex 1e (100 mg, 0.18 mmol) and sulphur (20 mg, 0.63 mmol) transformed to 2e (66 mg, 99%): blue crystals, m.p. 113–114°C; mass spectrum m/z 371 (M⁺, 45), 188 (100), 183 (33).

Degradation of 1f

Complex 1f (100 mg, 0.195 mmol) and sulphur (20 mg, 0.63 mmol) converted to 2f (58 mg, 90%): red violet crystals, m.p. 112–114°C; IR (KBr)

2950m, 2910m, 1710s, 1365m cm⁻¹; ¹H NMR (250 MHz, C_6D_6) δ 3.52 (s, 6 H), 4.40 (s, 5 H); mass spectrum *m*/*z* 330 (M⁺, 75), 188 (100), 168 (39), 124 (82). Exact mass. Found: 329.9429. Calc. for $C_{11}H_{11}CoO_4S_2$: 329.9449.

Degradation of 1g

Complex 1g (100 mg, 0.17 mmol) and sulphur (20 mg, 0.63 mmol) provided 2g (62 mg, 97%) : blue crystals, m.p. 165–166°C; IR (KBr) 3050w, 1595m, 1475m, 1460m, 1420m, 1020m, 745m, 690m cm⁻¹; ¹H NMR (250 MHz, C_6D_6) δ 1.80 (s, 3 H), 4.52 (br, s, 2 H), 4.66 (br, s, 2 H), 6.95 (m, 6 H), 7.48 (m, 4 H); mass spectrum *m*/*z* 380 (M⁺, 82), 202 (100), 178 (45). Exact mass. Found : 380.0106. Calc. for $C_{20}H_{17}CoS_2$: 380.0076.

Degradation of 1a with selenium

Complex 1a (100 mg, 0.196 mmol) was dissolved in toluene (25 cm³) in a 50 cm³ round bottom flask containing a stirbar. The solution was purged with nitrogen for 2 h and selenium (1.0 g, 13 mmol) added. The reaction mixture was heated for 2 days, the solvent removed and the residue purified by chromatography on alumina eluting with hexane and hexane-ether mixtures to furnish 5 (78 mg, 94%): dark violet crystals, m.p. 72-73°C; IR (KBr) 2975w, 2915w, 1450w, 1410w, 1009m, 995m cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 0.847 (t, J = 7 Hz, 6 H), 1.27 (m, 4 H), 1.83 (m, 4 H), 3.01 (t, J = 7Hz, 4 H) 4.59 (s, 5 H); mass spectrum m/z 422 (M⁺, 9.0), 420 (8.2), 286 (23), 284 (770), 124 (62), 44 (100). Exact mass. Found: 421.9474. Calc. for C₁₅H₂₃CoSe₂: 421.9461. Analysis. Found : C, 42.93; H, 5.61. Calc. for $C_{15}H_{23}CoSe_2$: C, 42.87; H, 5.53%.

Preparation of the sulphonium salt 6

In a 100 cm³ round bottom flask equipped with a stirbar, 1a (275 mg, 0.539 mmol) dissolved in nitromethane (50 cm³) was added to dimethyl-(thiomethyl)sulphonium tetrafluoroborate (105 mg, 0.54 mmol) and the mixture stirred at ambient temperature for 2 h. The solvent was removed via vacuum transfer and the residue triturated with benzene to remove any residual starting material. The remainder was dissolved in acetone and the product crystallized by vapour diffusion using hexane over 2 days leading to 6 (320 mg, 92%): black prisms, m.p. $> 300^{\circ}$ C; ¹H NMR (250 MHz, CD₃CN) δ 1.21 (s, 3 H), 1.28 (t, J = 8 Hz, 3 H), 1.36 (t, J = 7 Hz, 3 H), 2.05 (m, 4 H), 2.53 (m, 2 H), 2.99 (m, 2 H), 4.81 (s, 10 H), 5.08 (s, 5 H), 5.27 (m, 4 H); CI mass spectrum m/z 557 (M⁺ of cation,

1.7), 473 (1.7), 431 (5.7), 189 (100). Analysis. Found: C, 47.32; H, 5.36; S, 4.53. Calc. for $C_{26}H_{36}BCo_3F_4S: C, 48.46; H, 5.64; S, 4.53\%$.

Crystal structure determination of 6

Shiny black crystals were grown from an acetone-hexane bilayer. One of these was cleaved and a fragment of dimensions $\sim 0.21 \times 0.23 \times$ 0.32 mm mounted on a glass fibre in air using polychromate cement. Crystal parameters at 25° C: a =8.8230(6), b = 20.331(25), c = 15.3307(14) Å, $\beta = 101.088(7)^{\circ}$, $V = 2699 \text{ Å}^3$, space group $P2_1/c$; weight = 644.24 amu, Z = 4, $d_{calc} = 1.585$ g cm⁻³, $\mu_{calc} = 109.36$ cm⁻¹. Data measurement parameters: diffractometer, Enraf-Nonius CAD-4; monochromatic radiation, Mo- K_{α} ($\lambda = 0.71073$ Å); highly-orientated graphite $(2\theta_m = 12.2)$ perpendicular mode, assumed 50% perfect; detector, crystal scintillation counter with PHA; aperture \rightarrow crystal = 173 mm, vertical aperture = 3.0 mm, horizontal aperture = $2 + 1 \tan(\theta) \operatorname{mm}(\operatorname{variable});$ reflections measured : $+H+K\pm L$; 2θ range 3-45°; scan type θ -2 θ ; scan speed, 0.66-6.7 (θ , ° min⁻¹; scan width, $\Delta \theta = 0.55 + 0.347 \tan \theta$; background, measured over an additional 0.25 ($\Delta \theta$) added to each end of the scan; number of reflections collected, 3916; number of unique reflections, 3525; intensity standards, 553, 239, 0 12 1; measured every 2 h of X-ray exposure time; no decay in intensity was observed; orientation, three reflections were checked after every 250 measurements; no reorientation was necessary during data collection ; unit cell parameters and their esds were derived from a least-squares fit to the setting angles of the unresolved Mo- K_{α} components of 24 reflections with 2θ near 28°; the esds of all parameters are given in parentheses, right-justified to the least significant digits.

Structure solution and refinement : the 3916 raw intensity data were converted to values of the structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the azimuthal scan data revealed a $\pm 5\%$ variation in intensity. At the end of refinement an absorption correction was performed based on the measured shape and size of the crystal and a $10 \times 10 \times 8$ Gaussian grid of internal points. The maximum transmission factors were 0.84 and 0.70, respectively. Rejection of systematically absent and redundant data yielded 3525 unique data.

The three cobalt atoms were located by analysis of a three-dimensional Patterson map. Location of the other non-hydrogen atoms proceeded via standard Fourier and least-squares techniques. Analysis of the disorder for C25—C25' was performed by applying different occupancies until the isotropic thermal parameters were approximately equal. Over a broad range of occupancy distributions there was no significant change in the residuals. Prior to the last cycles of least squares refinement the idealized positions of all hydrogen atoms (except those on C24 and C25) were calculated and their contribution included in structure factor calculations. The final residuals for 315 variables refined against 2953 data for which $F^2 > 3\sigma(F^2)$, R = 3.32%, $R_w = 4.93\%$, and GOF = 2.401. The R value for all 3525 data was 4.40%.

The quantity minimized by the least-squares program was $\Sigma w(|F_0| - |F_c|)^2$, where w is the weight of a given observation. The *p*-factor used to reduce the weight of intense reflections was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all non-hydrogen values corrected for both the real and imaginary components of anomalous dispersion. Inspection of the residuals ordered in ranges of $|F_0|$ and parity, and value of the individual indices showed no unusual features or trends. There was no evidence of secondary extinction in the low-angle, high intensity data. Reflections with low sin θ/λ were systematically poor in fit, probably due to the observed disorder. The largest peak in the final difference Fourier map had an electron density of $0.55 e^- Å^{-3}$. The atomic positional and thermal parameters as well as structure factor tables have been deposited with the editor as supplementary material.

Notes on the structure of 6. Molecules of the cationic part are well separated from each other and from their counterion. There are no particularly close contacts between molecules. Each cation core has approximate 2 mm (C_{2v}) symmetry. One plane is defined by the three cobalt atoms, the sulphur and the cyclopentadiene centroids, Cp1, Cp2 and Cp3. An orthogonal plane includes Cp1, Co1, S, C16, C21 and the methyl carbon C26. The three Cp ligands are all planar. The torsional angles of the rings about the Co-centroid vector differ quite significantly from the mirror ideal values. The internal distances in the Cp ligands show clear systematic and random errors due to the very large amplitudes of vibrational motion about the Co-centroid axis. Thermal motion effects and those of disorder are also evident at the distal ends of the carbyne ligands, e.g. C19-C20, C24-C25 and C24-C25'. The sulphur is bridging Cp2 and Cp3 in the plane of Co1, Co2 and Co3 and displays a pyramidal environment. A Co2-Co3 distance of 2.738(1) Å is consistent with the absence of any significant metalmetal bond. Comparison of the three Co-C(carbyne) bonds indicates a strengthening of the linkage to the unique metal centre Co1, at the expense of the other two. There is also a slight and probably *not* significant, difference in the Co—Cp distances between the two types of chemically non-equivalent cobalt atoms. The C₃H₉ ligands adopt basically an extended *trans* configuration, their planes oriented in different directions (probably due to packing forces); C16—C20 aligns roughly parallel to the plane defined by Co2, C16 and C21, and C21— C25 is approximately parallel to that incorporating Co1, C16 and C21.

Conversion of 6 to 2a

The salt 6 (25 mg, 0.039 mmol) and sulphur (10 mg, 0.39 mmol) in acetonitrile were heated to reflux for 48 h. The solvent was removed on a rotary evaporator and the residue chromatographed on alumina to afford 2a (10 mg, 78%).

Mixed degradation of 1e and 1g

Complexes 1e (50 mg, 0.084 mmol) and 1g (50 mg, 0.091 mmol) were allowed to react with sulphur (20 mg, 0.63 mmol) under standard conditions. The so-generated mixture was analysed by mass spectroscopy to reveal the presence of equimolar amounts of 2b, e, g and 7.

Reaction of 2e with 2g

In a 25 cm³ round bottom flask, a CHCl₃ solution (10 cm^3) containing **2e** (10 mg, 0.027 mmol) and **2g** (10 mg, 0.026 mmol) was heated to reflux for 24 h. The reaction mixture was filtered through alumina and the products analysed by mass spectroscopy to reveal the parent ions of the four dithiolenes **2b**, e, g and 7 present in roughly equal intensity.

Reaction of 2g with NaCp · DME complex

Methylcyclopentadienylcobalt(diphenyldithiolene) 2g (50 mg, 0.13 mmol) was dissolved in THF (15 cm³), NaCp \cdot DME (200 mg, 1.12 mmol) added and the reaction mixture boiled for 24 h. The solvent was then removed on a rotary evaporator and the residue chromatographed on alumina to afford 2b and 2g as a roughly equimolar mixture, analysed by mass spectroscopy.

Reaction of dimethyl butynedioate with cyclopentadienylcobalt(diphenyldithiolene) (2b)

The dithiolene **2b** (50 mg, 0.136 mmol) was dissolved in CH_2Cl_2 (15 cm³) and the solution heated to reflux. A first portion of dimethyl butynedioate (200 mg, 0.141 mmol) was added, followed after 12 h by a second (200 mg, 0.070 mmol), and after 36 h a third (200 mg, 0.070 mmol). After 48 h, the solvent was removed and the reaction mixture purified by chromatography on silica gel eluting with hexane and hexane-ether mixtures. The first compound to be isolated was diphenylacetylene (11 mg, 45%), the second the fluorescent dimethyl 4,5-diphenylthiophene-2,3-dicarboxylate (5 mg, 10%): m.p. 90–92°C (ref. 21 92°C); mass spectrum m/z 352 (M⁺), and the third the red violet **2f** (8 mg, 18%).

Crossover between 2g and 5

A mixture of 2g (5 mg, 0.013 mmol) and 5 (5 mg, 0.012 mmol) was dissolved in benzene (1 cm³) and heated in a sealed tube for 24 h at 110°C. The crude product was filtered through alumina and purified by reverse phase HPLC, eluting with acetonitrile to give mixtures of 2b and g and 5 and 8, respectively, analysed by mass spectroscopy.

η^{5} - Cyclopentadienylrhodium(3,4 - diphenyldithio - lene) (9)

A cyclooctane solution (10 cm^3) containing $CpRh(CO)_2^{22}$ (1.0 g, 4.4 mmol) and diphenylacetylene (794 mg, 4.4 mmol) was added via syringe pump over 0.66 h to a boiling solution of sulphur (600 mg, 18.75 mmol) in cyclooctane (100 cm³). After heating to reflux for an additional 1.5 h, the solution was cooled to room temperature, the solvent removed and the residue chromatographed on alumina eluting with hexane and hexane-ether mixtures to provide 9 (458 mg, 25%): red-violet crystals, m.p. $> 250^{\circ}$ C; IR (KBr) 1600m, 1495m, 1442s, 1070m, 919m, 758s, 690s cm⁻¹; ¹H NMR (250 MHz, acetone-d₆) δ 7.20 (br s, 10 H), 5.78 (s, 5 H); mass spectrum m/z 410 (M⁺, 55), 232 (2), 178 (100), 176 (23), 149 (25). Exact mass. Found: 409.9668. Calc. for C₁₉H₁₅RhS₂: 409.9659.

η^5 -Methylcyclopentadienylcobalt(3,4-dibutyldithiolene) (10)

A cyclooctane solution (10 cm^3) containing $(\eta^5-CH_3C_5H_4)Co(CO)_2$ (1.0 g, 5.15 mmol) was added over 0.66 h via a syringe pump to boiling cyclooctane (75 cm³) containing sulphur (330 mg, 10.3 mmol) and 5-decyne (700 mg, 5.15 mmol). The mixture was heated for an additional hour, the solvent removed and the residue purified by chromatography to afford **10** (472 mg, 27%): purple crystals, m.p. 116–118°C; IR(NaCl) 2960m, 2910m, 1460m, 1020w cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 0.85 (t, J = 7 Hz, 6 H), 1.32 (m, 4 H), 1.72 (s, 3 H), 1.84 (m, 4 H), 3.03 (t, J = 7 Hz, 4 H), 4.56 (br s, 2 H), 4.57 (br s, 2 H); mass spectrum m/z 340 (M⁺, 61), 225 (40), 202 (65), 44 (100). Exact mass. Found : 340.0747. Calc. for C₁₆H₂₅CoS₂: 340.0730.

Crossover between 9 and 10

A solution of 9 (5 mg, 0.015 mmol) and 10 (5 mg 0.012 mmol) in *m*-xylene (5 cm³) was heated to reflux for 48 h. An aliquot was filtered through alumina and the solvent removed under reduced pressure. The residue was then analysed by mass spectroscopy, revealing the presence of approximately equimolar amounts of 9, 10, 11 and 2g.

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