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Nature of previously reported thermally unstable products derived from the reaction of $[Co_2(CO)_8]$ with PhSSPh, EtSSEt or PhSeSePh and of the reactions of these products with alkynes or isocyanides

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Thermally unstable red complexes previously isolated from the reaction of $[Co_2(CO)_8]$ with REER (E = S, R = Ph or Et; E = Se, R = Ph) and assigned the structure $[Co_3(\mu_3\text{-}ER)(CO)_9]$ have been reformulated as the trinuclear complexes $[Co_3(\mu_3\text{-}E)R(CO)_8]$ (E = S, R = Ph **1a** or Et **1b**; E = Se, R = Ph **1c**) on the basis of their spectroscopic properties and the nature of their reactions with alkynes and isocyanides. Thus the complexes $[Co_3(\mu_3\text{-}E)R(CO)_8]$ **1a**–**1c** react with PhC≡CH to give $[Co_3(\mu_3\text{-}E)\{PhCCHC(O)R\}(CO)_7]$ **2a**–**2c** respectively (E = S, R = Ph **2a** or Et **2b**; E = Se, R = Ph **2c**). It is proposed that **2a**–**2c** are formed *via* migration of the R group in **1a**–**1c** from the metal to a carbonyl carbon atom to give an acyl group. Subsequent insertion of PhC≡CH into the metal–acyl group bond is followed by co-ordination of the acyl oxygen to give a five-membered metallacyclic ring. The reaction of $Bu^tN{\equiv}C$ with **1a**–**1c** gave the complexes $[Co_3(\mu_3\text{-}E)(\mu\text{-}Bu^tN{=}CR)(CO)_7]$ **3a**–**3c** respectively (E = S, R = Ph **3a** or Et **3b**; E = Se, R = Ph **3c**) and a similar reaction pathway is proposed. The structures of complexes **2a** and **3a** have been determined by single-crystal X-ray diffraction studies.

The reaction of $[Co_2(CO)_8]$ with dialkyl and diaryl disulfides, RSSR, was first studied more than thirty years ago by Klumpp and co-workers.[1,2] The products obtained were found to depend on the nature of the R groups and, for R = Ph, the two thermally stable products of the reaction were originally formulated as $[Co_6S(SPh)_5(CO)_{10}]$ and $[Co_3(SPh)_5(CO)_4]$; a further air-sensitive and thermally unstable red product was formulated as the SPh-capped tricobalt complex $[Co_3(\mu_3\text{-}SPh)(CO)_9]$.[1] For R = *p*-tolyl an analogous unstable red complex, formulated as $[Co_3(\mu_3\text{-}SC_6H_4Me\text{-}p)(CO)_9]$ and obtained in less than 1% yield, was the only reaction product,[1] whereas the reaction between EtSSEt and $[Co_2(CO)_8]$[2] led to three stable complexes formulated as $[Co_3(\mu_3\text{-}S)(\mu_3\text{-}SEt)(CO)_6]$, $[Co_4(SEt)_7(CO)_5]$ and $[Co_4(SEt)_3(CO)_7]$ but no thermally unstable red product was reported.

Several of the stable cluster complexes obtained in the above reactions were later structurally characterised by X-ray analysis and reformulated in the light of the structural evidence,[3,4] but the nature of the thermally unstable red complex obtained in the reactions with R = Ph or *p*-tolyl and formulated as $[Co_3(\mu_3\text{-}SR)(CO)_9]$ remained unclear. Recently the reaction of $[Co_2(CO)_8]$ with bis(perfluorophenyl) disulfide, $C_6F_5SSC_6F_5$, has been studied and the product structurally characterised as the trinuclear complex $[Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8]$.[5] We now present spectroscopic and chemical evidence that all the thermally unstable red products obtained in the reaction of RSSR with $[Co_2(CO)_8]$ and originally formulated as $[Co_3(\mu_3\text{-}SR)(CO)_9]$ are analogous to the above trinuclear pentafluorophenyl complex and should be reformulated as $[Co_3(\mu_3\text{-}S)R(CO)_8]$. We show also that a similar unstable red complex can be obtained in the reaction of EtSSEt with $[Co_2(CO)_8]$, even though such a product was not reported in the original investigation. Only traces of the originally reported complexes $[Co_4(SEt)_7(CO)_5]$ and $[Co_4(SEt)_3(CO)_7]$, later reformulated as $[Co_3(SEt)_5(CO)_4]$[3] and $[Co_6S(SEt)_4(CO)_{11}]$[4] respectively, were obtained under the milder reaction condition employed in the present study. Finally we show that diphenyl diselenide gives a corresponding product when it is treated with $[Co_2(CO)_8]$. The chemical evidence which supports these conclusions is provided by the nature of the reactions of the unstable red products with PhC≡CH and with Bu^tNC.

Results and Discussion

(*a*) Reaction of $[Co_2(CO)_8]$ with PhSSPh, EtSSEt or PhSeSePh

These reactions when carried out in hexane solution at room temperature give red products which, on the basis of their spectroscopic properties and further reactions with alkynes or isocyanides (see below), may be formulated as the trinuclear complexes $[Co_3(\mu_3\text{-}E)R(CO)_8]$ (E = S, R = Ph **1a** or Et **1b**; E = Se, R = Ph **1c**) (Scheme 1). Thus the overall pattern of five ν(CO) absorption bands seen in the IR spectrum of each of the complexes **1a**–**1c** (Table 1) is closely similar to that of the analogous complex $[Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8]$.[5] In the ^1H NMR spectra of **1b** the ethyl protons give rise to two separate multiplets (δ 2.85 and 2.60) due to the diastereotopic CH_2 protons and to a doublet of doublets (δ 1.58) due to the CH_3 protons. The diastereotopic nature of the CH_2 group can be understood in terms of the asymmetry of the $Co_3(\mu_3\text{-}S)(CO)_8$ moiety to which the Et group is attached. The structure originally proposed for **1a**, $[Co_3(\mu_3\text{-}SPh)(CO)_9]$, is not similarly asymmetric and if **1b** had a structure analogous to **1a** it would not give rise to a diastereotopic CH_2 group.

Partial decomposition on attempted recrystallisation precluded analytically pure samples of complex **1a**–**1c** being obtained but the FAB mass spectra showed peaks at *m*/*z* values corresponding to the respective molecular ions and to fragment ions obtained by stepwise loss of carbonyl ligands from the molecular ions.

(*b*) Reaction of $[Co_3(\mu_3\text{-}E)R(CO)_8]$ (E = S, R = Ph 1a or Et 1b; E = Se, R = Ph 1c) with PhC≡CH

The complexes **1a**–**1c** were treated in hexane with 1 equivalent of PhC≡CH to give $[Co_3(\mu_3\text{-}E)\{PhCCHC(O)R\}(CO)_7]$ (E = S, R = Ph **2a** or Et **2b**; E = Se, R = Ph **2c**) as red crystalline solids. The products have been characterised by microanalysis, mass spectrometry and IR, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (see

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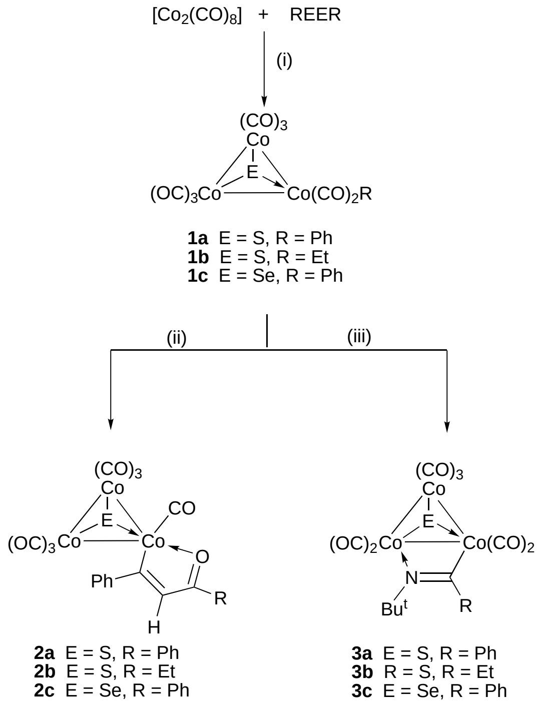
Table 1 Infrared and ^{1}H NMR data for the new complexes

Compound	$\tilde{\nu}$(CO)^a/cm^{-1}	^{1}H NMR (δ)^b
1a	2098m, 2064s, 2054vs, 2041m, 2031w	7.87–6.81 (m, Ph)
1b	2098m, 2061vs, 2051s, 2037m, 2017w	2.85 (m, 1 H, $CH\mathit{H}CH_3$), 2.60 (m, 1 H, $C\mathit{H}HCH_3$), 1.58 [dd, ^3J(HH) 7.32, 3 H, $CH_2C\mathit{H}_3$]
1c	2096m, 2062s, 2050vs, 2036m, 2026 (sh)	7.88–7.20 (m, Ph)
2a	2083m, 2053vs, 2029s, 2017w	7.78–6.99 (m, 10 H, Ph), 6.98 (s, 1 H, $PhCC\mathit{H}COPh$)
2b	2080w, 2057w, 2046w, 2044s, 2032w, 2015w	7.38–7.17 (m, 5 H, Ph), 6.80 (s, 1 H, $PhCC\mathit{H}COEt$), 2.85 [q, ^3J(HH) 7.41, 2 H, $\mathit{C}H_2CH_3$], 1.27 [t, ^3J(HH) 7.43, 3 H, $CH_2C\mathit{H}_3$]
2c	2083m, 2051vs, 2027s	8.20–7.21 (m, 10 H, Ph and 1 H, $PhCC\mathit{H}COPh$)
3a	2078m, 2033s, 2012m	7.6–7.0 (m, 3 H, Ph), 6.78 [d, ^3J(HH) 6.0, 1 H, Ph], 6.80 [d, ^3J(HH) 6.5, 1 H, Ph], 0.99 (s, 9 H, Bu^t)
3b	2157w, 2125w, 2026m, 2013vs, 2001s, 1989 (sh)	2.91 [sextet, ^3J(HH) 7.4, 1 H, $CH\mathit{H}CH_3$], 2.58 [sextet, ^3J(HH) 7.4, 1 H, $C\mathit{H}HCH_3$], 1.23 [t, ^3J(HH) 7.4, 3 H, CH_3], 1.17 (s, Bu^t)
3c	2074m, 2029s, 2010m	7.4–7.1 (m, 3 H, Ph), 6.82 [d, ^3J(HH) 6.1, 1 H, Ph], 6.70 [d, ^3J(HH) 7.3, 1 H, Ph], 0.97 (s, 9 H, Bu^t)

^{a} Recorded in CH_2Cl_2 solution. ^{b} Proton chemical shifts relative to $SiMe_4$ (δ 0), coupling constants in Hz in $CDCl_3$ at 293 K.



Scheme 1 Preparation and structures of the new complexes. (i) Hexane; (ii) PhCCH, hexane; (iii) Bu^{t}NC, hexane

Table 1 and Experimental section). Complex **2a** has also been the subject of a crystal structure determination.

The molecular structure of complex **2a** is shown in Fig. 1 and selected bond parameters are presented in Table 2. The apical sulfur atom is linked to all three metal atoms, with Co(1) being additionally co-ordinated by a C(Ph)CHC(Ph)O ligand in such a manner that a five-membered metallacyclic ring is formed. The cobalt atom to which this ligand is bonded is also co-ordinated by a terminal carbonyl group, the other two cobalt atoms being bonded to three terminal carbonyl groups each. The Co(2)–Co(3) bond [2.5582(11) Å] between the cobalt atoms not forming part of the metallacyclic ring is the longest of the three metal–metal bonds [Co(1)–Co(2) 2.5342(9), Co(1)–Co(3) 2.5163(11) Å]. The Co(1)–S bond distance [2.1316(14) Å] is slightly shorter than the other two Co–S bonds [Co(2)–S 2.1650(14), Co(3)–S 2.149(2) Å]. There are not many previously reported metallacyclic rings systems of the type present in **2a**. Those that have been reported are part of either mono- or di-nuclear cobalt complexes.[6] Bond distances within the metallacyclic ring in **2a** are within the range previously found for analogous complexes and include a dative carbon–oxygen bond length, Co(1)–O(15), of 1.953(3) Å and a cobalt-carbon σ bond, Co(1)–C(17), of 1.926(4) Å.[7]

The overall patterns of the IR spectra in the ν(CO) region of each of the complexes **2a**–**2c** are similar. The ^{1}H NMR spectra show, in addition to phenyl resonances (**2a** and **2c**) and ethyl proton resonances (**2b**) at δ 2.85 (quartet) and δ 1.27 (triplet), resonances at around δ 7 are due to the alkenic proton.

A plausible pathway for the reaction leading to complexes **2a**–**2c** is illustrated in Scheme 2. It is proposed that the first step in the reaction is the migration of the alkyl/aryl group from the cobalt atom to a carbonyl carbon atom to give an acyl group. This is presumably followed by co-ordination of the PhC≡CH to the unsaturated 16-electron cobalt centre and regioselective insertion of the alkyne into the metal–acyl bond. Co-ordination of the acyl oxygen atom to the metal centre would then give the complexes **2a**–**2c**.

(*c*) Reaction of [$Co_3(\mu_3$-E)R(CO)$_8$] (E = S, R = Ph 1a or Et 1b; E = Se, R = Ph 1c) with Bu^{t}NC

The complexes **1a**–**1c** were treated in hexane with 1 equivalent of Bu^{t}NC to give [$Co_3(\mu_3$-E)(μ-Bu^{t}N=CR)(CO)$_7$] (E = S, R = Ph **3a** or Et **3b**; E = Se, R = Ph **3c**). The products were characterised by a combination of microanalysis, mass spectrometry and IR, ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy (see Table 1 and Experimental section). Since the complexes are chiral the two protons of the CH_2 group in **3b** are in different environments. This results in the CH_2 protons giving rise to two overlapping quartets and the methyl protons to two overlapping doublets. Complex **3a** has been the subject of a single-crystal structure determination.

The molecular structure of complex **3a** is shown in Fig. 2 and selected bond parameters are listed in Table 3. The molecular geometry closely resembles that previously reported for [$Co_3(\mu_3$-S)(μ-Bu^{t}CNC$_6$H$_{11}$)(CO)$_7$].[8] The three cobalt atoms are capped by an apical sulfur atom with an edge-bridging imino unit [C(11), N, C(12), C(13)] co-ordinating Co(1) and Co(2) through N and C(12) respectively. The Co(3) atom is co-ordinated by three terminal carbonyl groups while the other two cobalt atoms are additionally co-ordinated by two terminal carbonyl groups each. As compared to [$Co_3(\mu_3$-S)(CO)$_9$],[9] the displacement in **3a** of two CO groups donating a total of four electrons by the three-electron donor bidentate ligand Bu^{t}N=CR leads to a distortion of the Co_3S core and two sets of metal–metal bond lengths are present. Both Co(1)–Co(3) [2.575(2) Å] and Co(2)–Co(3) [2.545(2) Å] are in the expected range for Co–Co bond distances in trinuclear capped clusters. However the Co(1)–Co(2) bond distance [2.411(2) Å] is the shortest ever observed in such clusters apart from some S-capped tricobalt complexes with cyclopentadienyl ligands.[10] As a result the base of the pyramid is no longer an equilateral triangle and the Co(1)–S–Co(2) angle of 67.93(9)° is significantly narrower than Co(1)–S–Co(3) or Co(2)–S–Co(3) which are respectively 72.83(10) and 71.75(10)°. The imino unit C(11), N, C(12), C(13)

Table 2 Selected bond lengths (Å) and angles (°) for [$Co_3(\mu_3$-S)-{PhCCHC(O)Ph}$(CO)_7$] **2a** with estimated standard deviation in parentheses

Co(1)–C(17)	1.926(4)	Co(1)–O(15)	1.953(3)
Co(1)–S	2.1316(14)	Co(1)–Co(3)	2.5163(11)
Co(1)–Co(2)	2.5342(9)	Co(2)–S	2.1650(14)
Co(2)–Co(3)	2.5582(11)	Co(3)–S	2.149(2)
C(8)–C(14)	1.471(6)	C(14)–O(15)	1.276(5)
C(14)–C(16)	1.414(6)	C(16)–C(17)	1.369(6)
C(17)–C(18)	1.476(6)		
C(17)–Co(1)–O(15)	84.3(2)	C(17)–Co(1)–S	111.82(13)
O(15)–Co(1)–S	152.19(10)	C(17)–Co(1)–Co(3)	100.50(3)
C(15)–Co(1)–Co(3)	101.76(9)	S–Co(1)–Co(3)	54.31(4)
C(17)–Co(1)–Co(2)	160.71(13)	C(15)–Co(1)–Co(2)	103.56(9)
S–Co(1)–Co(2)	54.47(4)	Co(3)–Co(1)–Co(2)	60.87(3)
S–Co(2)–Co(1)	53.25(4)	S–Co(2)–Co(3)	53.33(4)
Co(1)–Co(2)–Co(3)	59.22(3)	S–Co(3)–Co(1)	53.68(4)
S–Co(3)–Co(2)	53.92(4)	Co(1)–Co(3)–Co(2)	59.91(3)
Co(1)–S–Co(3)	72.01(5)	Co(1)–S–Co(2)	72.28(5)
Co(3)–S–Co(2)	72.75(5)	O(15)–C(14)–C(16)	117.0(4)
O(15)–C(14)–C(8)	118.4(4)	C(14)–O(15)–Co(1)	112.4(3)
C(17)–C(16)–C(14)	116.3(4)	C(16)–C(17)–C(18)	121.5(4)
C(16)–C(17)–Co(1)	110.0(3)	C(18)–C(17)–Co(1)	128.5(3)

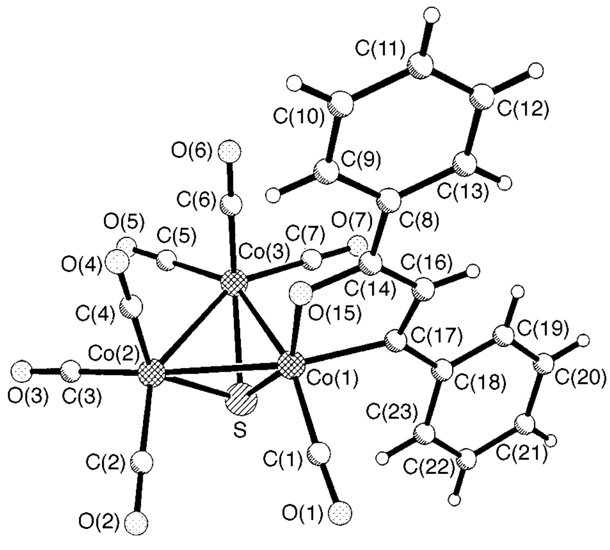
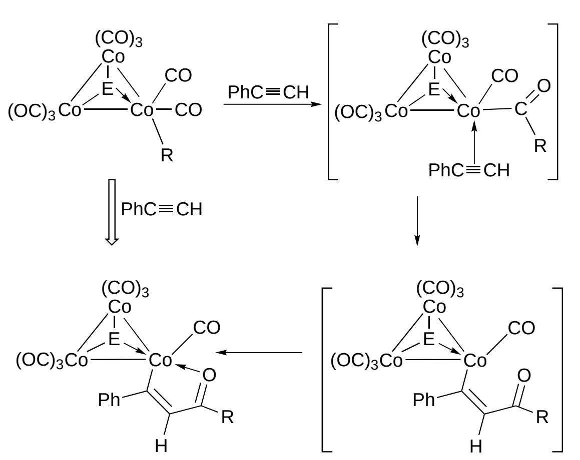


Fig. 1 Molecular structure of [$Co_3(\mu_3$-S){PhCCHC(O)Ph}$(CO)_7$] **2a** including the atom numbering scheme



Scheme 2 Possible reaction pathway for the formation of complexes **2a**–**2c** from **1a**–**1c**

Table 3 Selected bond lengths (Å) and angles (°) for [$Co_3(\mu_3$-S)-(μ-Bu^{t}NCPh)$(CO)_7$] **3a** with estimated standard deviation in parentheses

Co(1)–N	2.010(8)	Co(1)–S	2.155(3)
Co(1)–Co(2)	2.411(2)	Co(1)–Co(3)	2.575(2)
Co(2)–C(12)	1.964(9)	Co(2)–S	2.160(3)
Co(2)–Co(3)	2.545(2)	Co(3)–S	2.183(3)
N–C(12)	1.285(12)		
N–Co(1)–S	95.0(2)	N–Co(1)–Co(2)	74.9(2)
S–Co(1)–Co(2)	56.13(9)	N–Co(1)–Co(3)	135.3(2)
S–Co(1)–Co(3)	54.08(9)	Co(2)–Co(1)–Co(3)	61.28(6)
C(12)–Co(2)–S	95.8(3)	C(12)–Co(2)–Co(1)	71.9(3)
S–Co(2)–Co(1)	55.94(9)	C(12)–Co(2)–C(3)	134.2(3)
S–Co(2)–Co(3)	54.54(8)	Co(1)–Co(2)–Co(3)	62.55(6)
S–Co(3)–Co(2)	53.71(9)	S–Co(3)–Co(1)	53.09(8)
Co(2)–Co(3)–Co(1)	56.17(5)	Co(1)–S–Co(2)	67.93(9)
Co(1)–S–Co(3)	72.83(10)	Co(2)–S–Co(3)	71.75(10)
C(12)–N–C(11)	130.0(8)	C(12)–N–Co(1)	101.6(6)
C(11)–N–Co(1)	128.4(7)	N–C(12)–C(13)	130.6(9)
N–C(12)–Co(2)	111.1(7)		

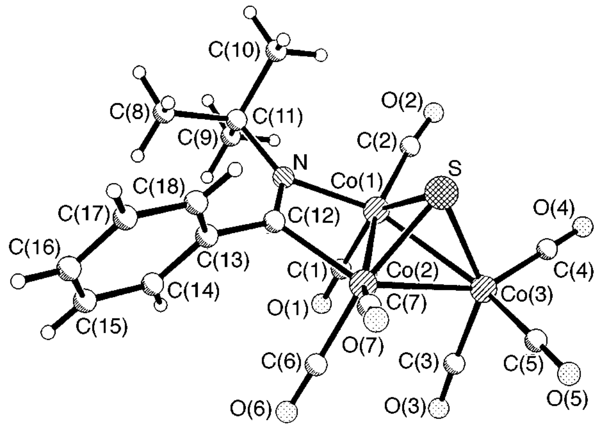


Fig. 2 Molecular structure of [$Co_3(\mu_3$-S)(μ-Bu^{t}NCPh)$(CO)_7$] **3a** including the atom numbering scheme

is slightly twisted (torsion angle 8.2°). The dihedral angle between the mean plane through these atoms and the Co_3 triangular core is 170.6°; the plane through the atoms C(13), C(12), N lies closer to the plane through the Co_3 triangle (dihedral angle 5.7°) than that through C(12), N, C(11) (10.3°). The planar co-ordination around C(12) and N indicates sp^2 hybridisation which is consistent with the C(12)–N bond distance of 1.285(12) Å (within the range of C–N double-bond distances).[11]

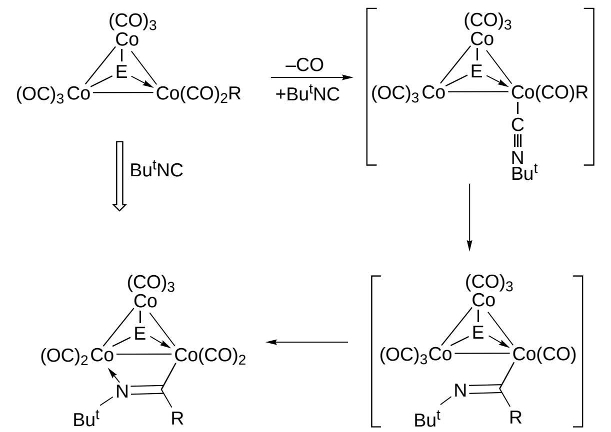
A plausible reaction pathway for the formation of complexes **3a**–**3c** from **1a**–**1c** is illustrated in Scheme 3. It is proposed that a carbonyl ligand on the metal atom to which the R group is attached is substituted by the Bu^{t}NC ligand. Migration of the R group from the cobalt to the carbon atom of the isocyanide group is then followed by co-ordination of the nitrogen atom of the resulting imino group to the other metal centre. This must be accompanied by migration of a CO ligand from one cobalt atom to the other to maintain the requirements of the EAN rule for each centre. Complexes similar to **3a**–**3c** have been synthesized previously *via* the reaction of [$Co_2(CO)_8$] with the thioamides R′C(S)NHR″ (R′ = Me or Ph, R″ = C_6H_{11}).[8]

Experimental

Unless otherwise stated all reactions were carried out under a nitrogen atmosphere. Solvents were distilled from the appropriate drying agent prior to use.[12] Products are presented in order of decreasing R_f values. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. The instrumentation used to obtain the spectroscopic data has been described previously.[13]

Reactions of [$Co_2(CO)_8$]

With PhSSPh. To a solution of [$Co_2(CO)_8$] (1.0 g, 2.924



Scheme 3 Possible reaction pathway for the formation of complexs **3a**–**3c** from **1a**–**1c**

mmol) in hexane (100 cm^3) was added PhSSPh (0.213 g, 0.974 mmol) and the resulting solution stirred at room temperature for 2 h. After removal of solvent the residue was taken up in the minimum volume of dichloromethane and adsorbed onto silica. The silica was pumped dry and added to the top of a silica chromatography column. Elution with hexane–dichloromethane (4:1) gave red [$Co_3(\mu_3$-S)Ph(CO)$_8$] **1a**. ^{13}C NMR (CDCl$_3$, 20 °C, ^{1}H composite pulse decoupled): δ 208.4 (CO), 208.2 (CO) and 133.6–125.1 (m, Ph). FAB mass spectrum: *m*/*z* 510 (M^+) and $M^+ - n$CO (n = 1–6). The yield of unrecrystallised product was 1.0 g.

With EtSSEt. To a solution of [$Co_2(CO)_8$] (1.0 g, 2.924 mmol) in hexane (100 cm^3) was added EtSSEt (0.120 cm^3, 0.974 mmol) in three equal portions at 10 min intervals and the resulting solution was then stirred at room temperature for 5 h. Work-up as for complex **1a** gave red [$Co_3(\mu_3$-S)Et(CO)$_8$] **1b** followed by trace amounts of the known complexes [Co_3(SEt)$_5$-(CO)$_4$]^3 and [Co_6S(SEt)$_4$(CO)$_{11}$].^{4} The identity of both the known complexes was confirmed by IR spectroscopy. Complex **1b**: FAB mass spectrum *m*/*z* 462 (M^+) and $M^+ - n$CO (n = 1–4). The yield of unrecrystallised product **1b** was 0.5 g.

With PhSeSePh. To a solution of [$Co_2(CO)_8$] (1.0 g, 2.924 mmol) in hexane (100 cm^3) was added PhSeSePh (0.304 g, 0.974 mmol) and the resulting solution stirred at room temperature for 2 h. Work-up as for **1a** gave red [$Co_3(\mu_3$-Se)Ph(CO)$_8$] **1c**. ^{13}C NMR (CDCl$_3$, 20 °C, ^{1}H composite pulse decoupled: δ 134.7–124.2 (m, Ph). FAB mass spectrum: *m*/*z* 558 (M^+) and $M^+ - n$CO (n = 1–8). The yield of unrecrystallised product was 0.65 g.

Reactions of PhC≡CH

With [$Co_3(\mu$-S)Ph(CO)$_8$] 1a. To a solution of complex **1a** (0.30 g, 0.588 mmol) in dichloromethane (50 cm^3) was added PhC≡CH (0.06 cm^3, 0.57 mmol) and the resulting solution stirred at room temperature for 4 h. The solvent was then removed on a rotary evaporator, the residue taken up in the minimum volume of dichloromethane and absorbed onto silica. The silica was pumped dry and added to the top of a silica chromatography column. Elution with hexane gave brown [$Co_3(\mu_3$- S){PhCCHC(O)Ph}(CO)$_7$] **2a** (0.072 g, 20%) (Found: C, 43.03; H, 1.85. $C_{22}H_{11}Co_3O_8S$ requires C, 43.14; H, 1.80%). ^{13}C NMR (CDCl$_3$, 20 °C, ^{1}H composite pulse decoupled): δ 142.4–137.9 (m, Ph) and 131.2–125.2 [m, μ-Ph*CC*(H)C(O)]. FAB mass spectrum: *m*/*z* 613 (M^+) and $M^+ - n$CO (n = 1–7).

With [$Co_3(\mu$-S)Et(CO)$_8$] 1b. To a solution of complex **1b** (0.30 g, 0.649 mmol) in hexane (50 cm^3) was added PhC≡CH (0.07 cm^3, 0.64 mmol) and the resulting solution stirred at room temperature for 3 h. Work-up as for **2a** gave brown [$Co_3(\mu_3$-S){PhCCHC(O)Et}(CO)$_7$] **2b** (0.15 g, 40%) (Found: C, 38.21; H, 1.85. $C_{18}H_{11}Co_3O_8S$ requires C, 38.30; H, 1.95%); FAB mass spectrum *m*/*z* 565 (M^+) and $M^+ - n$CO (n = 1–7).

With [$Co_3(\mu$-Se)Ph(CO)$_8$] 1c. To a solution of complex **1c** (0.30 g, 0.538 mmol) in hexane (50 cm^3) was added PhC≡CH (0.06 cm^3, 0.54 mmol) and the resulting solution stirred at room temperature for 3 h. Work-up as for **2a** gave brown [Co_3-(μ_3-Se){PhCCHC(O)Ph(CO)$_7$] **2c** (0.16 g, 45%) (Found: C, 40.18; H, 1.85. $C_{22}H_{11}Co_3O_8Se$ requires C, 40.06; H, 1.70%); FAB mass spectrum *m*/*z* 660 (M^+) and $M^+ - n$CO (n = 1–6).

Reactions of Bu^{t}NC

With [$Co_3(\mu$-S)Ph(CO)$_8$] 1a. To a solution of complex **1a** (0.30 g, 0.588 mmol) in hexane (50 cm^3) was added Bu^{t}NC (0.06 cm^3, 0.58 mmol) and the resulting solution stirred at room temperature for 3 h. The solvent was then removed on a rotary evaporator, the residue taken up in the minimum volume of dichloromethane and adsorbed onto silica. The silica was pumped dry and added to the top of a silica chromatography column. Elution with hexane–dichloromethane (3:2) gave brown [$Co_3(\mu_3$-S)(μ-Bu^{t}NCPh)(CO)$_7$] **3a** (0.22 g, 65%) (Found: C, 38.18; H, 2.42. $C_{18}H_{14}Co_3NO_7S$ requires C, 38.23; H, 2.50%). ^{13}C NMR (CDCl$_3$, 20 °C, ^{1}H composite pulse decoupled): δ 208.9 (CO), 148.3 (Ph*C*N), 129.0–126.6 (m, Ph), 121.5 (s, Ph), 121.0 (s, Ph), 63.9 (Me$_3$*C*) and 30.95 Me. FAB mass spectrum: *m*/*z* 565 (M^+) and $M^+ - n$CO (n = 1–7).

With [$Co_3(\mu$-S)Et(CO)$_8$] 1b. To a solution of complex **1b** (0.30 g, 0.649 mmol) in hexane (50 cm^3) was added Bu^{t}NC (0.07 cm^3, 0.64 mmol) and the resulting solution stirred at room temperature for 2 h. Work-up as for **3a** except for the use of hexane–dichloromethane (4:1) as the solvent gave brown [$Co_3(\mu_3$-S)(μ-Bu^{t}NCEt)(CO)$_7$] **3b** (0.18 g, 55%) (Found: C, 32.30; H, 2.85. $C_{14}H_{14}Co_3NO_7S$ requires C, 32.50; H, 2.71%). ^{13}C NMR (CDCl$_3$, 20 °C, ^{1}H composite pulse decoupled): δ 208.7 (CO), 146.3 (Et*C*N), 60.8 (Me$_3$*C*), 40.9 (*C*H$_2$CH$_3$), 31.0 [(*C*H$_3$)$_3$C] and 11.8 (*C*H$_3$CH$_2$). FAB mass spectrum: *m*/*z* 517 (M^+) and $M^+ - n$CO (n = 1–6).

With [$Co_3(\mu$-Se)Ph(CO)$_8$] 1c. To a solution of complex **1c** (0.30 g, 0.538 mmol) in hexane (50 cm^3) was added Bu^{t}NC (0.06 cm^3, 0.54 mmol) and the resulting solution stirred at room temperature for an hour. Work-up as for **3a** gave brown [Co_3-(μ_3-Se)(μ-Bu^{t}NCPh)(CO)$_7$] **3c** (0.16 g, 50%) (Found: C, 35.33; H, 2.32. $C_{18}H_{14}Co_3NO_7Se$ requires C, 35.29; H, 2.29%). ^{13}C NMR (CDCl$_3$, 20 °C, ^{1}H composite pulse decoupled): δ 208.2 (CO), 146.3 (Ph*C*N), 128.7–123.3 (m, Ph), 121.3 (s, Ph), 120.8 (s, Ph), 63.8 (Me$_3$*C*) and 30.9 [(*C*H$_3$)$_3$C]. FAB mass spectrum: *m*/*z* 612 (M^+) and $M^+ - n$CO (n = 1–7).

Crystallography

Data for [$Co_3(\mu_3$-S){PhCCHC(O)Ph}(CO)$_7$] **2a** and [$Co_3(\mu_3$-S)-(μ-Bu^{t}NCPh)(CO)$_7$] **3a** were collected by the ω–2θ scan method on a Rigaku AFC7R (**2a**) or AFC5R (**3a**) four-circle diffractometer. Three standard reflections were monitored at intervals of 200 reflections. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections ($20 < 2\theta < 22.5°$). Semiempirical absorption corrections based on ψ-scan data were applied.^{14,15}

The structures were solved by direct methods (SIR 92^{16}) and subsequent Fourier-difference syntheses and refined anisotropically on all non-H atoms by full-matrix least squares on F^2 (SHELXL 93^{17}). Hydrogen atoms were placed in idealised positions and refined using a riding model or as rigid methyl groups. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. Full details are given in Table 4.

Table 4 Crystal data for $[Co_3(\mu_3\text{-}S)\{PhCCHC(O)Ph\}(CO)_7]$ **2b** and $[CO_3(\mu_3\text{-}S)(\mu\text{-}Bu^tNCPh)(CO)_7]$ **3a** *

	$[Co_3(\mu_3\text{-}S)\{PhCCHC(O)Ph\}(CO)_7]$ **2a**	$[Co_3(\mu_3\text{-}S)(\mu\text{-}Bu^tNCPh)(CO)_7]$ **3a**
Molecular formula	$C_{22}H_{11}Co_3O_8S$	$C_{18}H_{14}Co_3NO_7S$
M	612.16	565.15
a/Å	11.422(2)	8.797(2)
b/Å	13.324(2)	15.793(3)
c/Å	7.872(2)	8.5066(11)
α/°	91.42(2)	104.259(13)
β/°	98.71(2)	101.344(13)
γ/°	93.640(10)	83.24(2)
U/Å^3	1181.1(4)	1120.04(4)
D_c/Mg m^3	1.721	1.676
Crystal size/nm	0.20 × 0.10 × 0.10	0.3 × 0.3 × 0.1
Crystal habit	Red brown	Dark red plate
F(000)	608	564
μ/mm^{-1}	2.215	2.326
Maximum, minimum relative transmission	0.999, 0.807	0.997, 0.888
Data collection range/°	$5.24 < 2\theta < 45.04$	$5.02 < 2\theta < 45.0$
Index ranges	$0 \leqslant h \leqslant 12, -14 \leqslant k \leqslant 14, -8 \leqslant l \leqslant 8$	$0 \leqslant h \leqslant 9, -16 \leqslant k \leqslant 16, -9 \leqslant l \leqslant 8$
Reflections measured	3295	3157
Independent reflections (R_{int})	3102 (0.019)	2931 (0.039)
Parameters, restraints	309, 0	271, 0
w*R*2 (all data)	0.086	0.2068
x, *y*	0.0327, 0.278	0.100, 0.00
$R1[I > 2\sigma(I)]$	0.035	0.053
Observed reflections	2389	1986
Goodness of fit on F^2 (all data)	1.057	1.296
Maximum shift/σ	0.001	0.000
Peak, hole in final difference map/e Å^{-3}	0.343, −0.231	0.837, −1.479
Decay (%)	0	7

* Data in common: graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, *T* = 293(2) K; triclinic, space group $P\bar{1}$; $Z = 2$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where *x* and *y* are constants adjusted by the program; goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$ where *n* is the number of reflections and *p* the number of parameters.

CCDC reference number 186/871.

See http://www.rsc.org/suppdata/dt/1998/775/ for crystallographic files in .cif format.

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