Structural and Cobalt-59 Nuclear Magnetic Resonance Study of Heterosite Reactivities of Alkynes in Ru–Co Carbonyl–Nitrosyl Clusters*

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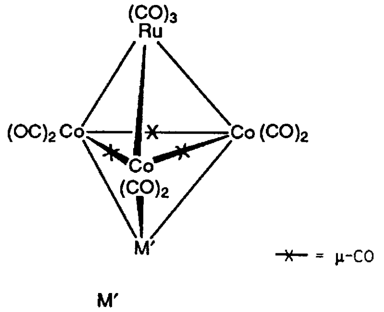
The reactions of the tetrahedral mixed-metal cluster $[NEt_4][RuCo_3(CO)_{12}]$ **1** with $[NO][BF_4]$ afforded the nitrosyl-substituted cluster $[RuCo_3(CO)_{11}(NO)]$ **3** in high yield. The latter reacts with excess alkynes RC_2R' to give $[RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}RC{\equiv}CR')]$ (R = R' = Ph **4a**; R = Ph, R' = H **4b**; R = R' = H **4c**) *via* specific insertion in a Co–Co bond, together with a small amount of the corresponding trinuclear cluster $[RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}CR')]$ (R = R' = Ph **5a**; R = Ph, R' = H **5b**; R = R' = H **5c**). All the complexes have been characterised by IR, UV/VIS, ^1H and ^{59}Co NMR spectroscopy. The crystal structures of **3** and **4b** have been determined by X-ray diffraction methods. Complex **3** exhibits a $RuCo_3$ tetrahedron and the linear nitrosyl ligand is axially bonded to one of the Co atoms of the Co_3 base. The structure of **4b** consists of a $RuCo_3$ butterfly in which the ruthenium atom occupies a hinge position, the alkyne ligand having been incorporated into the cluster core to generate a *closo*-$RuCo_3C_2$ octahedral framework.

Mixed-metal clusters of the transition metals are ideal systems to study the selectivity of their interactions with inorganic or organic reagents. One can anticipate that reactions which lead to *e.g.* edge- or face-capping or metal–metal bond breaking will be particularly informative with regard to the metalloselectivity involved in stoichiometric or catalytic transformations. We have recently reported [1a,b] the reactions of the tetrahedral cluster $[NEt_4][RuCo_3(CO)_{12}]$ 1 with the complexes MLCl (M = Cu, Ag or Au) or $HgBr_2$ which occur in toluene at room temperature and afford pentanuclear trimetallic clusters in high yields. Their structure consists of a $RuCo_3$ tetrahedron of which the Co_3 face is capped by the electrophilic metal fragment M′, as does the proton in $[RuCo_3H(CO)_{12}]$ 2.[1a,c,2]



M′
Cu(PPh₃)
Ag(PPh₃)
Au(PPh₃)
HgBr

Here we describe the reaction of 1 with NO^+ as an electrophile, which results in CO substitution at a cobalt site and formation of $[RuCo_3(CO)_{11}(NO)]$ 3. We have reported preliminary results on the ^{59}Co and ^{99}Ru NMR study of this reaction and the comparison with the reactivity of $[FeCo_3(CO)_{12}]^-$.[3] Nitrosylation by NO^+ has often been used to prepare low-oxidation state nitrosyl clusters,[4] which have been a subject of long standing interest.[5] Previous work has shown that 1 reacts with diphenylacetylene with selective opening of a Co–Co bond and formation of the butterfly cluster $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}RC{\equiv}CR')]^-$ 6.[6] Despite the considerable amount of work on the reactions of carbonyl clusters with alkynes, only few examples have been reported of metalloselective reactions.[7] In order to evaluate the influence of the NO ligand on the reactivity of 3 by comparison with that of 1 or 2, we report here its reactions with alkynes.

Results and Discussion

(*a*) *Synthesis of* $[RuCo_3(CO)_{11}(NO)]$ 3.—Treatment of 1 with an equimolar amount of $[NO][BF_4]$ in dichloromethane at 0 °C gave $[RuCo_3(CO)_{11}(NO)]$ 3 in high yield [equation (1)]. Cluster 3 was characterised by elemental analysis, IR,

$$\underset{\mathbf{1}}{[NEt_4][RuCo_3(CO)_{12}]} + [NO][BF_4] \longrightarrow \underset{\mathbf{3}}{[RuCo_3(CO)_{11}(NO)]} + CO + [NEt_4][BF_4] \quad (1)$$

UV/VIS and ^{59}Co NMR spectroscopy (see Experimental section). Its detailed molecular structure was established by X-ray diffraction (Fig. 1) and confirmed the tetrahedral core structure, with the linear nitrosyl ligand axially bonded to one of the Co atoms (see below) being also characterised in the IR spectrum by its ν(NO) frequency at 1820 cm⁻¹. The ^{59}Co NMR

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

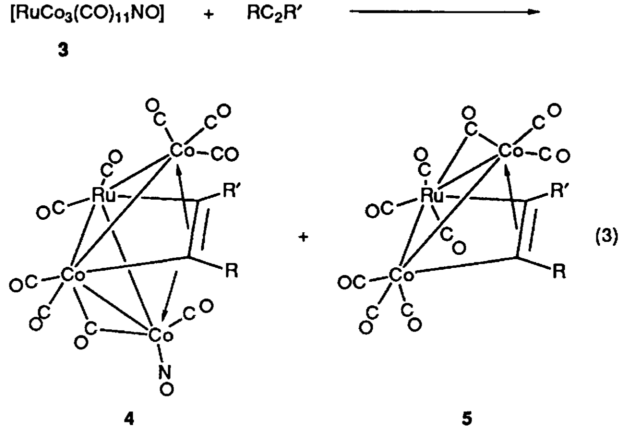
spectrum will be discussed below. When the reaction of **1** with [NO][BF$_4$] was performed at room temperature for a longer period of time, fragmentation occurred with formation of [Co(CO)$_3$(NO)], [Ru$_3$(CO)$_{12}$] and [RuCo$_2$(CO)$_{11}$],[8a] but **3** was not observed. Pure **3** is only moderately stable in CH$_2$Cl$_2$ under nitrogen, as evidenced by thin-layer chromatography, IR and ^{59}Co NMR spectroscopy. After *ca.* 0.5 h its fragmentation products [Co(CO)$_3$(NO)] and [RuCo$_2$(CO)$_{11}$] begin to form [equation (2)]. This transformation may be easily monitored

$$\underset{\mathbf{3}}{[\mathrm{RuCo_3(CO)_{11}(NO)}]} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{RuCo_2(CO)_{11}}] + [\mathrm{Co(CO)_3(NO)}] + \text{unidentified products} \quad (2)$$

by ^{59}Co and ^{99}Ru NMR spectroscopy.[3] Owing to its limited stability, **3** cannot be purified by chromatography and is best crystallised from toluene–hexane.

It is interesting that the room-temperature reaction of [NO][BF$_4$] with the isostructural cluster [NEt$_4$][FeCo$_3$(CO)$_{12}$] has previously been found to give rise to [FeCo$_2$(μ_3-NH)(CO)$_9$] in 14% yield, but no NO-containing intermediate could be observed.[9] We have repeated this reaction under our conditions, starting from [NEt$_4$][FeCo$_3$(CO)$_{12}$], and monitored it by ^{59}Co NMR spectroscopy. We confirm the previous findings and the iron analogue of **3** was not detected. On the other hand, reaction of [CoRu$_3$(CO)$_{13}$]$^-$ with NO$^+$ produced the nitrido cluster [CoRu$_3$N(CO)$_{12}$] in low yield.[9]

(*b*) *Synthesis of the Butterfly Clusters* [RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-RC≡CR′)] **4**.—Cluster **3** readily reacts with diphenylacetylene, phenylacetylene or acetylene in hexane at room temperature to afford the new clusters [RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-RC≡CR′)] **4** together with a variable amount of the trinuclear clusters [RuCo$_2$(CO)$_9$(μ_3-η^2-RC≡CR′)] **5** according to equation (3).



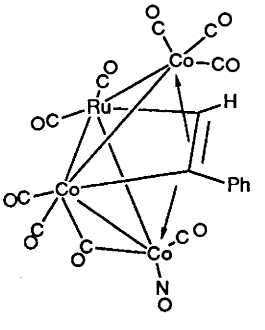
That CO substitution by an alkyne ligand converts a tetrahedral cluster into a butterfly is a general observation.[7] The more interesting aspect associated with a mixed-metal system is the possible metalloselectivity of such a transformation. This has been investigated in [Co$_2$Ru$_2$(CO)$_{13}$],[8b] [W$_2$Ir$_2$(CO)$_{10}$(cp)$_2$] (cp = η-C$_5$H$_5$)[10] and [Co$_2$Rh$_2$(CO)$_{12}$][11] systems where the weaker metal–metal bond was broken, as anticipated. With the tetrahedral cluster **1** we have previously observed[6] that a Co–Co bond is selectively broken by C$_2$Ph$_2$, as expected, yielding the anionic butterfly cluster [RuCo$_3$(CO)$_{10}$(μ_4-η^2-PhC≡CPh)]$^-$ **6** in which the Ru atom occupies a hinge position [equation (4)].

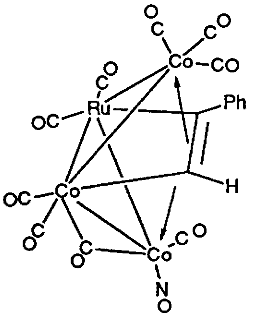
In contrast, the reaction of [FeRu$_3$H$_2$(CO)$_{13}$] with alkynes

$$\underset{\mathbf{1}}{[\mathrm{NEt_4}][\mathrm{RuCo_3(CO)_{12}}]} + \mathrm{C_2Ph_2} \longrightarrow \underset{\mathbf{6}}{[\mathrm{NEt_4}][\mathrm{RuCo_3(CO)_{10}}(\mu_4\text{-}\eta^2\text{-PhC{\equiv}CPh})]} + 2\mathrm{CO} \quad (4)$$

afforded FeRu$_3$C$_2$ skeletal isomers resulting from the rupture of Fe–Ru or Ru–Ru bonds of the precursor. The interconversion between these isomers was investigated.[12]

Clusters **4** and **5** have been characterised by elemental analysis and by IR, UV/VIS and ^{1}H NMR spectroscopy (see Experimental section). A ^{59}Co NMR characterisation was also performed and is detailed below. The reaction with the unsymmetrical alkyne PhC≡CH produces two isomers. The ^{1}H NMR spectrum of the **4b**/**4b′** mixture shows two singlets at δ 9.84 and 8.52 in a 4:1 intensity ratio. The C–H protons in these isomers are in different chemical environments: in one isomer the C–H group is attached to Ru, while in the other it is attached to a cobalt centre.


4b

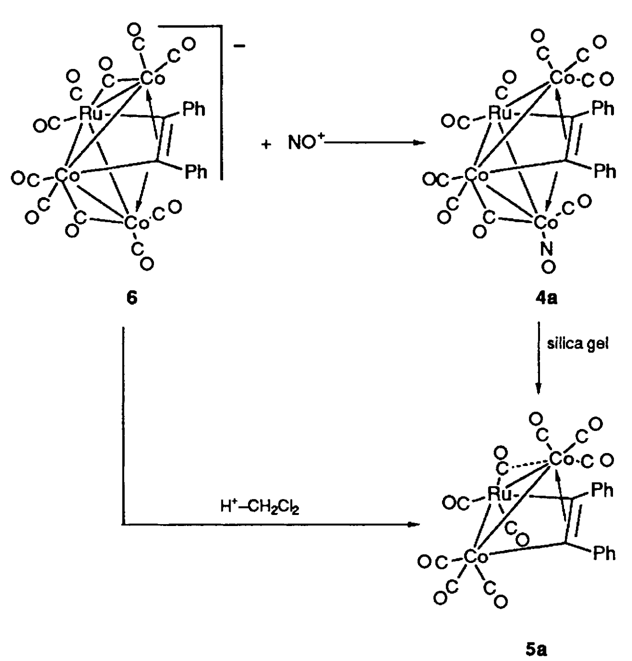

4b′

Attempts to separate isomers **4b** and **4b′** by chromatography over silica gel failed, in contrast to the case of [FeRu$_3$(CO)$_{12}$(μ_4-η^2-PhC≡CMe)] where separation of the isomers resulting from a different orientation of the alkyne ligand with respect to the Fe–Ru hinge of the butterfly core was possible.[12]

The results of an X-ray diffraction study on a single crystal of one isomer of [RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-PhC≡CH)] **4b** are discussed below (Fig. 2). The infrared pattern in the 1800–2100 cm^{-1} region is very similar for clusters **4**. It shows typically three absorptions for the bridging carbonyls and one for the ν(NO) stretch. They are also closely related to those of the precursor **3**.

Owing to the presence of the nitrosyl ligand in **3**, there are now two types of Co–Co bonds in this cluster which would be susceptible to open as a result of the alkyne insertion. From the position of the NO ligand in **4**, which is bonded to a wing-tip cobalt atom, we conclude that a (ON)Co–Co(CO) bond and not the (OC)Co–Co(CO) bond of **3** was selectively broken by the alkyne ligand. Further studies are needed to know whether the observed NO-induced labilisation of an adjacent metal–metal bond is a general phenomenon.

It should be pointed out that **4a** can also be obtained from **6** by the reaction with NO$^+$, selective CO substitution occurring on a wing-tip cobalt atom. Other electrophiles, like H$^+$, were observed to fragment compound **6** in the trinuclear cluster [RuCo$_2$(CO)$_9$(μ_3-η^2-PhC≡CPh)] **5a**, by loss of the 12-electron fragment [Co(CO)]$^-$.[6] A similar fragmentation could account for the formation of clusters **5** from **4** when column chromatography on silica gel was used to separate the reaction mixture. However, direct formation of **5** was also observed in equation (3). This could be explained by the lability of **3** which, in the course of the reaction, would give [RuCo$_2$(CO)$_{11}$] [by loss of a Co(NO) fragment, equation (2)], which is known to react readily with alkynes to afford clusters of type **5** [equation (5)].[13] As for **4b**, two isomers were observed for **5b** and studied by ^{59}Co NMR spectroscopy (see below).

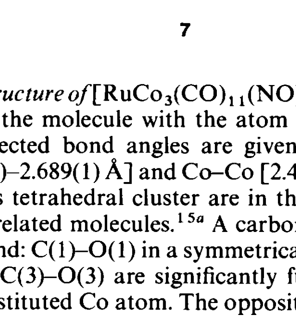


Scheme 1

$$[RuCo_2(CO)_{11}] + RC{\equiv}CR' \longrightarrow [RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}CR')] + 2CO \quad (5)$$

5

Finally, we found that the hydrido cluster **2** reacted with excess C_2Ph_2 to give a butterfly cluster **7** with a μ_4-η^2-PhC≡CPh and a μ-η^2-PhC=CPh(H) ligand. The latter results from formal insertion of the alkyne into a metal–hydrogen bond. The $FeCo_3$ analogue of **7** has been reported[14] and was obtained similarly. When **2** was treated with 1 equivalent of C_2Ph_2, a monoalkyne cluster could not be identified and only **7** was isolated. In contrast, **3** only led to a monoalkyne cluster, even in the presence of excess alkyne.



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(*c*) *Crystal Structure of* $[RuCo_3(CO)_{11}(NO)]$ **3**.—Fig. 1 represents a view of the molecule with the atom numbering. Bond lengths and selected bond angles are given in Table 1. The Ru–Co [2.665(1)–2.689(1) Å] and Co–Co [2.490(1)–2.513(1) Å] distances in this tetrahedral cluster are in the range found for these bonds in related molecules.[15a] A carbonyl ligand bridges each Co–Co bond: C(1)–O(1) in a symmetrical manner whereas C(2)–O(2) and C(3)–O(3) are significantly further away from the nitrosyl-substituted Co atom. The opposite was observed in $[FeCo_3H(CO)_{11}(PPh_2H)]$ where two CO bridges were closer to the phosphine-substituted Co atom.[15b] A carbonyl ligand bridges also the Co(3)–Ru bond in a asymmetrical manner, being 0.376 Å closer to Co(3) while the difference in metal radius between Ru and Co is only 0.07 Å. The reasons for the observed asymmetry are not clear since a symmetrical CO bridge would give a local electron bookkeeping of 18 electrons on both Co(3) and Ru metal atoms. Note however that in **1** the negative charge is not localised on the Ru, making the latter formally a 17-electron atom. The axial disposition of the nitrosyl ligand is as anticipated. The Co–N distance [1.644(5) Å] is similar to that in $[Co_4(NCMe_3)_4(NO)_4]$[16a] and slightly shorter than in dinuclear $[\{Co(\mu\text{-}PPh_2)(CO)(NO)\}_2]$.[16b]

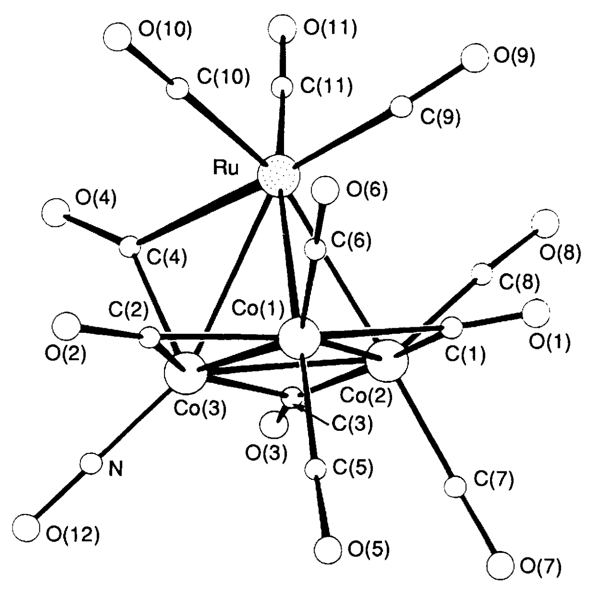


Fig. 1 View of the molecular structure of compound **3** showing the numbering scheme used

(*d*) *Crystal Structure of* $[RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CH)]$ **4b**.—Fig. 2 represents a view of the molecule together with the numbering scheme used. Bond distances and selected bond angles are given in Table 2. The structure consists of a $RuCo_3$ butterfly in which the ruthenium atom occupies a hinge position. The dihedral angle between the wings is 114.1°, which compares with the corresponding angles observed in the related compounds $[RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)]^-$ **6** (115.2°)[6] or $[RuCo_3(CO)_9(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}Bu^tC{\equiv}CH)]$ (115.2°) **8**.[17] The alkyne is co-ordinated to all metal atoms, parallel to the Co(1)–Ru hinge, forming a distorted *closo*-$RuCo_3C_2$ octahedron. This 60-electron butterfly cluster **4b** bears a strong structural resemblance to $[Co_4(CO)_{10}(C_2R_2)]$ (R = Et[18a] or H[18b]) and $[Ru_4(CO)_{10}(C_2R_2)]$ (R = Ph[19a] or Me[19b]) but there is no plane of symmetry passing through the acetylenic carbon atoms, Co(1) and Ru, since a wing-tip cobalt atom is co-ordinated by the linear nitrosyl ligand and the Co(1)–Co(3) edge is bridged by a symmetrical carbonyl group. In addition, two carbonyls bridge unsymmetrically the two Ru–Co(2) and Ru–Co(3) adjacent edges [Ru–C(6) 2.124(10) and Co(2)–C(6) 1.877(9), Ru–C(8) 2.100(10) and Co(3)–C(8) 1.895(9) Å]. Cluster **4b** is thus inherently chiral. Its structure is fully consistent with Wade's[20] skeletal electron counting rules, which predict a *closo*-M_4C_2 octahedral structure for seven skeletal electron pairs. This resembles the situation found in the related clusters **6**[6] or **8**.[17] A comparison (Table 3) shows that, within the precision of the structural determinations, the Ru–Co and Co–Co bond lengths are very similar in these isoelectronic clusters. The Co(3)–N distance of 1.638(7) Å in **4b** is similar to that observed in the precursor **3** [1.644(5) Å]. The alkyne can best be viewed as a four-electron donor to the cluster framework. The value of 1.397(9) Å for the alkyne C–C bond in **4b** is in excellent agreement with that found in cluster **6**, but is shorter than those generally reported for such μ_4-η^2-alkyne type clusters.[7]

Table 1 Selected bond distances (Å) and angles (°) in [$RuCo_3(CO)_{11}$-(NO)] **3** with estimated standard deviations (e.s.d.s) in parentheses

Ru–Co(1)	2.665(1)	Co(2)–C(8)	1.771(7)
Ru–Co(2)	2.689(1)	Co(3)–N	1.644(5)
Ru–Co(3)	2.679(1)	Co(3)–C(2)	2.100(6)
Co(1)–Co(2)	2.513(1)	Co(3)–C(3)	2.075(6)
Co(1)–Co(3)	2.490(1)	Co(3)–C(4)	1.839(6)
Co(2)–Co(3)	2.513(1)	O(1)–C(1)	1.156(7)
Ru–C(4)	2.215(6)	O(2)–C(2)	1.138(7)
Ru–C(9)	1.927(7)	O(3)–C(3)	1.157(6)
Ru–C(10)	1.910(7)	O(4)–C(4)	1.152(7)
Ru–C(11)	1.931(6)	O(5)–C(5)	1.127(7)
Co(1)–C(1)	1.939(6)	O(6)–C(6)	1.133(6)
Co(1)–C(2)	1.857(6)	O(7)–C(7)	1.120(7)
Co(1)–C(5)	1.814(6)	O(8)–C(8)	1.141(7)
Co(1)–C(6)	1.782(6)	O(9)–C(9)	1.124(7)
Co(2)–C(1)	1.949(6)	O(10)–C(10)	1.126(7)
Co(2)–C(3)	1.858(6)	O(11)–C(11)	1.128(7)
Co(2)–C(7)	1.795(7)	O(12)–N	1.144(6)
Co(2)–Co(1)–Ru	62.49(2)	Co(1)–C(1)–O(1)	140.9(5)
Co(3)–Co(1)–Ru	62.51(3)	Co(2)–C(1)–O(1)	138.5(5)
Co(1)–Co(2)–Ru	61.53(2)	Co(1)–C(2)–O(2)	152.7(5)
Co(3)–Co(2)–Ru	61.88(3)	Co(3)–C(2)–O(2)	129.6(5)
Co(1)–Co(3)–Ru	61.95(2)	Co(1)–C(5)–O(5)	178.1(6)
Co(2)–Co(3)–Ru	62.30(3)	Co(2)–C(7)–O(7)	178.7(6)
Co(1)–Ru–Co(2)	55.98(2)	Co(2)–C(3)–O(3)	150.9(5)
Co(1)–Ru–Co(3)	55.54(2)	Co(3)–C(3)–O(3)	129.9(5)
Co(2)–Ru–Co(3)	55.82(2)	Co(2)–C(8)–O(8)	176.3(7)
Co(1)–Co(3)–Co(2)	60.31(3)	Co(3)–C(4)–O(4)	142.5(5)
Co(1)–Co(2)–Co(3)	59.39(3)	Ru–C(4)–O(4)	135.4(5)
Co(2)–Co(1)–Co(3)	60.30(3)	Co(3)–N(1)–O(12)	177.6(6)
Co(1)–C(6)–O(6)	178.8(6)		

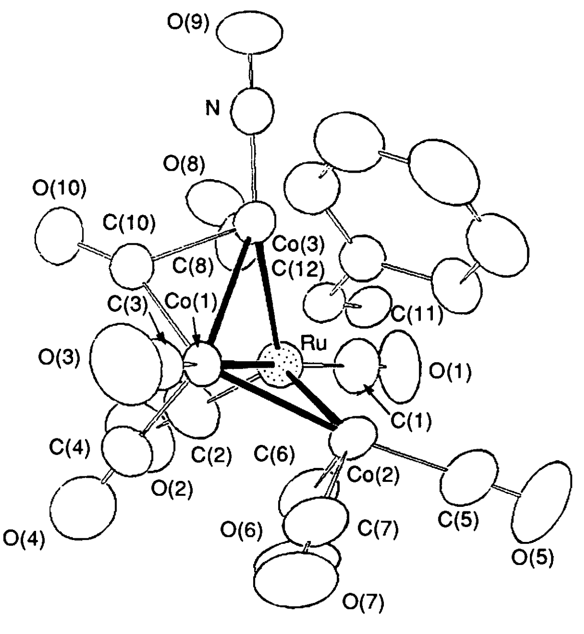


Fig. 2 View of the molecular structure of compound **4b** showing the numbering scheme used

(*e*) *Cobalt-59 NMR Spectra.*—We have recently shown[3,15] that ^{59}Co NMR spectroscopy may be very valuable to improve our knowledge about metallosite selectivity in cluster reactions. We have described[3] the direct monitoring by ^{59}Co NMR spectroscopy of reaction (1). The ^{59}Co NMR spectrum of **3** contains resonances at δ −2745 ($\Delta\nu_{\frac{1}{2}}$ 6700 Hz) and −486 ($\Delta\nu_{\frac{1}{2}}$ 7000 Hz). The latter value is characteristic of a cobalt atom bound to a nitrogen-donor ligand and compares with the value of δ −1110 for [$RuCo_3H(CO)_{11}(NMe_3)$].[15]

The two inequivalent Co nuclei of compounds **5** give rise to two ^{59}Co resonances and to two sets of resonances in the case of the mixture **5b**/**5b′** (Table 4). In order to assign these resonances, it is reasonable to assume that the cobalt atom Co(2) to which the alkyne is π-bonded should have a similar chemical shift in **5b** and **5b′**, irrespective of the alkyne orientation. This allows to assign the resonance at δ −2587 to Co(2). By analogy, we assign the resonances at δ −2444 and −2755 to Co(2) in **5a** and **5c**, respectively. This leads to the assignment of the Co(1) resonances in **5a** and **5c** and, by analogy, in **5b**/**5b′**. It is interesting that the chemical shift of Co(2) in **5b**/**5b′** is close to the mean of the corresponding resonances in **5a** and **5c**. From the peak integration, we find that the concentration of isomer **5b** is about three times that of **5b′** in the mixture **5b**/**5b′**.

The three inequivalent cobalt atoms in clusters **4** give rise to

Table 2 Selected bond distances (Å) and angles (°) in [$RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CH)$] **4b** with e.s.d.s in parentheses

Ru–Co(2)	2.561(1)	Co(1)–C(4)	1.784(9)
Ru–Co(3)	2.540(1)	Co(1)–C(10)	1.887(8)
Ru–Co(1)	2.700(1)	Co(1)–C(12)	2.005(7)
Co(2)–Co(1)	2.479(1)	N–O(9)	1.150(8)
Co(3)–Co(1)	2.484(1)	C(7)–O(7)	1.103(10)
Ru–C(6)	2.124(10)	C(5)–O(5)	1.122(10)
Ru–C(2)	1.917(10)	C(3)–O(3)	1.120(9)
Ru–C(1)	1.907(10)	C(4)–O(4)	1.126(11)
Ru–C(8)	2.100(10)	C(10)–O(10)	1.163(9)
Ru–C(11)	2.174(7)	C(6)–O(6)	1.155(10)
Co(2)–C(7)	1.782(10)	C(2)–O(2)	1.127(11)
Co(2)–C(5)	1.785(9)	C(1)–O(1)	1.107(10)
Co(2)–C(6)	1.877(9)	C(8)–O(8)	1.172(12)
Co(2)–C(11)	2.024(7)	C(11)–C(12)	1.397(9)
Co(2)–C(12)	2.113(6)	C(12)–C(13)	1.479(10)
Co(3)–N	1.638(7)	C(13)–C(14)	1.405(10)
Co(3)–C(10)	1.986(8)	C(13)–C(18)	1.366(10)
Co(3)–C(8)	1.895(9)	C(14)–C(15)	1.390(11)
Co(3)–C(11)	2.107(6)	C(15)–C(16)	1.349(13)
Co(3)–C(12)	2.094(7)	C(16)–C(17)	1.352(13)
Co(1)–C(3)	1.814(9)	C(17)–C(18)	1.369(11)
Co(2)–Co(1)–Ru	59.08(3)	Co(2)–C(5)–O(5)	177.7(9)
Co(3)–Co(1)–Ru	58.49(3)	Co(2)–C(7)–O(7)	175.9(8)
Co(1)–Co(2)–Ru	64.77(3)	Co(2)–C(6)–O(6)	142.5(8)
Co(1)–Co(3)–Ru	65.02(3)	Ru(6)–C(6)–O(6)	137.9(7)
Co(1)–Ru–Co(2)	56.14(3)	Co(3)–N–O(9)	179.7(7)
Co(1)–Ru–Co(3)	56.48(3)	Co(3)–C(8)–O(8)	138.3(8)
Co(2)–Ru–Co(3)	88.55(4)	Ru–C(8)–O(8)	142.8(7)
Co(2)–Co(1)–Co(3)	91.71(4)	Ru–C(1)–O(1)	179.6(8)
Co(1)–C(3)–O(3)	178.6(9)	Ru–C(2)–O(2)	177.7(8)
Co(1)–C(4)–O(4)	176.6(8)	Ru–C(11)–Co(2)	75.1(2)
Co(3)–C(10)–O(10)	132.9(7)	Ru–C(11)–Co(3)	72.8(2)
Co(1)–C(10)–O(10)	147.3(7)	Co(1)–C(12)–Co(2)	74.0(2)
		Co(1)–C(12)–Co(3)	74.6(2)

Table 3 Comparison of the main structural features of [$RuCo_3(CO)_9$-(NO)(μ_4-η^2-PhC≡CH)] **4b**, [$RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)$]$^-$ **6** and [$RuCo_3(CO)_9(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}Bu^tC{\equiv}CH)$] **8**

Complex	**4b**	**6**	**8**
Co(1)–Co(2)	2.479(1)	2.481(2)	2.567(1)
Co(1)–Co(3)	2.484(1)	2.518(2)	2.494(1)
Co(2) ··· Co(3)	3.561(2)	3.549(2)	3.517(2)
Ru–Co(1)	2.700(1)	2.725(2)	2.776(1)
Ru–Co(2)	2.561(1)	2.525(2)	2.558(1)
Ru–Co(3)	2.540(1)	2.493(2)	2.399(1)
Ru–C(11)	2.174(7)	2.13(1)	2.187(1)
Co(1)–C(12)	2.005(7)	2.14(1)	2.009(4)
Co(2)–C(11)	2.024(7)	2.07(1)	2.086(4)
Co(2)–C(12)	2.113(6)	2.14(1)	
Co(3)–C(11)	2.107(6)	2.12(1)	2.122(4)
Co(3)–C(12)	2.094(7)	2.06(1)	
C(11)–C(12)	1.397(9)	1.34(1)	1.424(5)
Dihedral angle (°)	114.1	115.2	115.2

three ^{59}Co resonances. As found for the isomer mixture **5b**/**5b′**, we also observe two sets of cobalt resonances for the **4b**/**4b′** mixture (Table 5). Their assignment is facilitated by the typical resonance for Co(3) which carries the NO ligand (δ +47 and +57). In the mixture **4b**/**4b′**, the Co(2) resonance should not be very sensitive to the orientation of the alkyne with respect to the Ru–Co(1) hinge. It is found at δ −1625 and −1650, respectively, those at δ −2030 and −1903 being therefore assigned to the corresponding Co(1) nuclei. This leads now to the assignment of the resonances in **4a** and **4c**, which in turn allows the precise assignment of the resonances for **4b**/**4b′** since their intensities also reflect their different proportions (see Fig. 3). We note again that the chemical shifts of the Co(2) and Co(3) nuclei in the mixture **4b**/**4b′** are close to the mean of those found in **4a** and **4c**. The ratio **4b**/**4b′** appears to be very sensitive to experimental conditions and was found to vary from sample to sample.

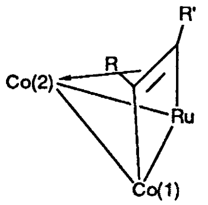
When comparing the cobalt chemical shifts between clusters **4** and **6**, we note that the nitrosyl group has a significant effect on all three cobalt resonances, the largest being obviously for that of Co(3) (Table 5). This 'NO effect' includes here a narrowing of the resonances. In contrast, the NO ligand in **3** induced only a slight effect on the resonances of the adjacent Co nuclei (δ −2745 in **3** and −2760 in **2**[15b]).

Experimental

Schlenk-tube techniques were used throughout the experiments and all reactions were performed under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The clusters $[NEt_4][RuCo_3(CO)_{12}]$ **1**,[21] $[RuCo_3H(CO)_{12}]$ **2**[15b] and $[NEt_4][RuCo_3(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)]$ **6**[6] were prepared as reported. Nitrosyl tetrafluoroborate and all alkynes were commercial samples and were used as received. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin Elmer 398 spectrophotometer. An FT-Bruker SY 200 spectrometer was used for the ^{1}H NMR recordings ($CDCl_3$ solution). The UV/VIS spectra were recorded on a Beckman Acta CIII spectrophotometer (CH_2Cl_2 solutions).

Syntheses.—$[RuCo_3(CO)_{11}(NO)]$ **3**. Solid $[NO][BF_4]$ (0.110 g, 0.941 mmol) was added to a suspension of **1** (0.505 g, 0.652 mmol) in CH_2Cl_2 (50 cm^3) at 0 °C. A progressive colour change takes place from light red to violet red, while **1** reacts and

Table 4 Cobalt-59 NMR chemical shifts (δ) and half-height linewidths ($\nu_{\frac{1}{2}}$) for clusters **5**[a]



			Co(1)		Co(2)	
Cluster	R	R′	δ	($\nu_{\frac{1}{2}}$/Hz)	δ	($\nu_{\frac{1}{2}}$/Hz)
5a	Ph	Ph	−1 983	(7 500)	−2 444	(12 000)
5b	Ph	H	−1 957	(5 100)	−2 587	(7 000)[b]
5b′	H	Ph	−2 092	(8 850)	−2 587	(7 000)[b]
5c	H	H	−2 050	(4 800)	−2 755	(4 100)

[a] Spectra recorded in $CDCl_3$; reference $K_3[Co(CN)_6]$ in D_2O. [b] This linewidth is not significant since two resonances are overlapping.

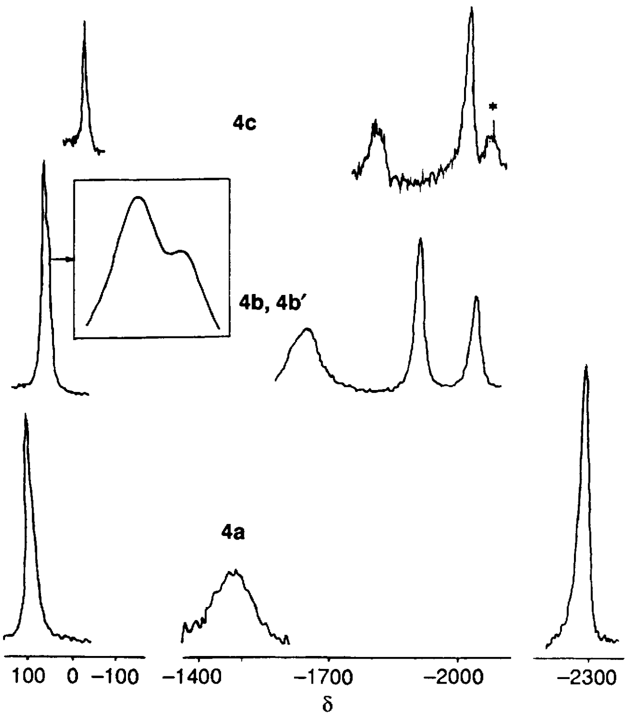
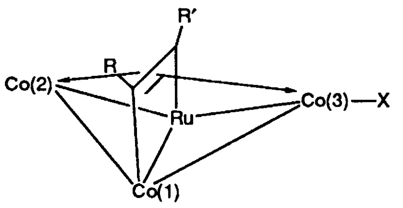


Fig. 3 Cobalt-59 NMR spectra of clusters **4** in $CDCl_3$. The resonances of **4b**/**4b′** around δ 50 are expanded in the box. The spectra are presented in several parts when measured at different frequencies. The asterisk denotes the low-field resonance of **5c** present

Table 5 Cobalt-59 chemical shifts (δ) and half-height linewidths ($\nu_{\frac{1}{2}}$) for clusters **4** and **6***



				Co(1)		Co(2)		Co(3)	
Cluster	R	R′	X	δ	($\nu_{\frac{1}{2}}$/Hz)	δ	($\nu_{\frac{1}{2}}$/Hz)	δ	($\nu_{\frac{1}{2}}$/Hz)
4a	Ph	Ph	NO	−2 285	(2 500)	−1 489	(8 000)	+82	(1 600)
4b	Ph	H	NO	−2 030	(2 200)	−1 625	(4 500)	+47	(1 100)
4b′	H	Ph	NO	−1 903	(2 000)	−1 650	(4 500)	+57	(1 000)
4c	H	H	NO	−2 014	(20 800)	−1 801	(4 400)	−29	(900)
6	Ph	Ph	CO	−1 750	(4 200)	−1 364	(11 700)	−1 364	(11 700)

* Spectra recorded in $CDCl_3$; reference $K_3[Co(CN)_6]$ in D_2O.

dissolves. After stirring was maintained for 2 h, the reaction mixture was filtered. The solution was evaporated to dryness under reduced pressure (during this time, volatile [Co(CO)$_3$(NO)] is eliminated) and the solid was extracted with toluene at room temperature. A saturated toluene solution afforded dark red (almost black) crystals at −10 °C. Compound **3** (0.243 g, 60%) (Found: C, 21.25; N, 2.00. Calc. for $C_{11}Co_3NO_{12}Ru$: C, 21.45; N, 2.25%): decomp. 123–124 °C; IR (hexane) ν(CO) 2100m, 2067s, 2057s, 2030m, 1934m, 1909m and 1867m, ν(NO) 1820m cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}/nm 320, 400 and 500; ^{59}Co and ^{99}Ru NMR data have been reported elsewhere.[3]

After separation of **3**, the filtrate was separated by chromatography over silica gel (230–400 mesh) using hexane as eluent and afforded four bands. The first two yellow bands correspond, respectively, to [Co(CO)$_3$(NO)] and [Ru$_3$(CO)$_{12}$], whereas the two following red bands afforded [RuHCo$_3$(CO)$_{12}$] **2** and [RuCo$_2$(CO)$_{11}$], respectively.

This reaction was monitored by ^{59}Co NMR spectroscopy by taking small fractions (≈1.5 cm^3) of the reaction mixture at 0 °C into a 10 mm NMR tube to which ≈0.5 cm^3 of CDCl$_3$ was added. Measurement time was *ca.* 0.25 h.

[RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-PhC≡CPh)] **4a**. A solution of **3** (0.290 g, 0.471 mmol) in hexane (30 cm^3) was added to a suspension of C_2Ph_2 (0.100 g, 0.561 mmol) in hexane (30 cm^3). After being stirred for 3 h at *ca.* 40 °C the solution was filtered and placed at −15 °C. Two compounds were obtained by fractional crystallisation. The least soluble was **4a** as black microcrystals (0.158 g, 45%), the other was [RuCo$_2$(CO)$_9$(μ_3-η^2-PhC≡CPh)] **5a** (0.101 g, 29%) as red crystals.[6,13a] Compound **4a** (Found: C, 37.55; H, 1.25; N, 1.75. Calc. for $C_{23}H_{10}Co_3NO_{10}Ru$: C, 37.40; H, 1.35; N, 1.90%): m.p. 109–111 °C; IR (hexane) ν(CO) 2086m, 2059s, 2043s, 2031m, 2020w, 1915s, 1887m and 1871m, ν(NO) 1805s cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}/nm 320, 420 and 514; ^{1}H NMR (CDCl$_3$), δ 7.19–6.67 (m, C_6H_5).

Cluster **4a** was also obtained by reaction of [NEt$_4$][RuCo$_3$(CO)$_{10}$(μ_4-η^2-PhC≡CPh)] (0.428 g, 0.494 mmol) with excess of [NO][BF$_4$] (0.096 g, 0.822 mmol) in CH_2Cl_2 (30 cm^3). After being stirred for 2.5 h at room temperature the solution was filtered and evaporated under reduced pressure. The solid residue was extracted with hexane (6 × 20 cm^3) and the solution placed overnight at −15 °C, affording **4a** as black needles (0.220 g, 60%) and some **5a** as red crystals.

[RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-PhC≡CH)] **4b**/**4b′**. A solution of **3** (0.221 g, 0.358 mmol) in hexane (30 cm^3) was added to a suspension of PhC$_2$H (0.046 g, 0.450 mmol) in hexane (30 cm^3). After being stirred overnight at room temperature the solution was filtered and evaporated under reduced pressure. The resulting solid was chromatographed over silica gel, using hexane as eluent, which afforded four bands. The first fast-moving yellow band of [Co(CO)$_3$(NO)] was followed by a second yellow band of [Ru$_3$(CO)$_{12}$]. Further elution with hexane gave first a red band of [RuCo$_2$(CO)$_9$(μ_3-η^2-PhC≡CH)] **5b**[13a] and then a dark red band, which afforded deep violet crystals of **4b** (0.087 g, 35%) (Found: C, 31.10; H, 1.10; N, 2.05. Calc. for $C_{17}H_6Co_3NO_{10}Ru$: C, 30.85; H, 0.90; N, 2.10%): m.p. 97–99 °C; IR (hexane) ν(CO) 2094m, 2063s, 2053s, 2038m, 2021w, 2000w, 1920s, 1892m and 1877m, ν(NO) 1812s cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}/nm 320, 420 and 507; ^{1}H NMR (CDCl$_3$), δ 9.84 (s, 0.8 H, CH of one isomer), 8.52 (s, 0.2 H, CH of the other isomer, see text), 7.25–6.96 (m, C_6H_5).

[RuCo$_3$(CO)$_9$(NO)(μ_4-η^2-HC≡CH)] **4c**. Gaseous acetylene was bubbled into a solution of **3** (0.304 g, 0.493 mmol) in hexane (60 cm^3). After being stirred for 8 h at room temperature the solution was filtered and evaporated under reduced pressure. The resulting solid was chromatographed over silica gel, using hexane–toluene (9:1) as eluent, which afforded four bands. The first fast-moving yellow band of [Co(CO)$_3$(NO)] was followed by a red band of [RuCo$_2$(CO)$_9$(μ_3-η^2-HC≡CH)] **5c**.[13b] Further elution with hexane–toluene gave a brown-red band [unknown product, IR (hexane) ν(CO) 2100m, 2072vs, 2032vs, 2020(sh) and 1915w cm^{-1}] followed by a deep red band, which afforded deep violet microcrystals of **4c** (0.202 g, 70%) (Found: C, 22.40; H, 0.30; N, 2.25. Calc. for $C_{11}H_2Co_3NO_{10}Ru$: C, 22.55; H, 0.35; N, 2.40%): m.p. 82–83 °C; IR (hexane) ν(CO) 2090m, 2060s, 2048s, 2033m, 2017w, 1918s, 1891m and 1876m, ν(NO) 1810s cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}/nm 320, 420 and 490; ^{1}H NMR (CDCl$_3$), δ 10.15 (d, ^3J = 2, CH), 8.67 (d, ^3J = 2 Hz, CH).

Reaction of Diphenylacetylene with [RuCo$_3$H(CO)$_{12}$] **2**.—A solution of **2** (0.142 g, 0.230 mmol) in hexane (50 cm^3) was added to a suspension of C_2Ph_2 (0.187 g, 1.050 mmol) in hexane (20 cm^3). After being stirred for 17 h at reflux the solution was filtered. The filtrate was placed overnight at 0 °C and gave deep violet microcrystals of [RuCo$_3$(CO)$_9$(C_2Ph_2H)(C_2Ph_2)] **7** (0.137 g, 58%).

After separation of **7**, the filtrate was chromatographed over silica gel (230–400 mesh), using hexane–toluene (10:1) as eluent and afforded four bands. The first pink band (unknown product) was followed by a red band of **5a**, and further elution gave a mixture of [RuCo$_3$H(CO)$_{12}$] **2** and **7**, followed by the fourth band containing pure **7**. Compound **7** (Found: C, 50.60; H, 2.45. Calc. for $C_{37}H_{21}Co_3O_9Ru$: C, 50.05; H, 2.40%): m.p. 190–193 °C; IR (hexane) ν(CO) 2078m, 2050s, 2040s, 2020w, 2000w, 1988w, 1875m and 1855m cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max}/nm 300, 347, 447 and 510; ^{1}H NMR (CDCl$_3$), δ 7.10–6.50 (m, 20 H, Ph) and 4.96 (s, 1 H, CH).

NMR Measurements.—All ^{59}Co NMR spectra have been recorded on a Bruker AM 400 instrument at 94.941 MHz using 10 mm tubes. Except when indicated, all compounds were dissolved in CDCl$_3$. The temperature was 24 °C and the sample concentrations were between 0.01 and 0.02 mol dm^{-3}. The reference was K$_3$[Co(CN)$_6$] saturated in D$_2$O. The chemical shifts were measured by the substitution method and the necessary lock corrections were applied.[22] The following parameters were used: sweep width 125 kHz; 4 K points; pulse width 5 μs corresponding to a flip angle of about 30°. As the sweep width was sometimes lower than the extent of the spectrum, different measurements have been performed at different excitation frequencies.

Single-crystal X-Ray Structure Determinations for Clusters **3** *and* **4b**.—*General conditions.* A single crystal of each compound was obtained by slow crystallisation from a hexane solution at −15 °C. Diffraction measurements were carried out at room temperature on a Nonius CAD-4 four-circle diffractometer, using graphite-monochromatised Mo-Kα radiation (λ = 0.710 73 Å) and the ω–2θ scan technique. All the reflections with θ in the range 1–25° were measured. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. The intensity of three reflections was monitored every hour of exposure and showed no evidence of decay. For all subsequent computations the Enraf-Nonius SPD package was used.[23] Intensity data were corrected for Lorentz polarisation and for absorption using the DIFABS program.[24]

Crystal data. **3**: $C_{11}Co_3NO_{12}Ru$, M = 615.99, size 0.10 × 0.22 × 0.14 mm, monoclinic, space group $P2_1/n$, a = 13.580(4), b = 8.598(2), c = 15.422(5) Å, β = 105.47(3)°, U = 1735.4 Å^3, Z = 4, F(000) = 1176, D_c = 2.36 g cm^{-3}, μ(Mo-Kα) = 37.2 cm^{-1}.

4b: $C_{17}H_6Co_3NO_{10}Ru$, M = 662.11, size irregular, monoclinic, space group $P2_1/n$, a = 11.438(9), b = 13.033(6), c = 14.345(9) Å, β = 100.72(4)°, U = 2101 Å^3, Z = 4, F(000) = 1280, D_c = 2.09 g cm^{-3}, μ(Mo-Kα) = 30.7 cm^{-1}.

Data collection, structure solution and refinement. In the case of **3**, 3041 independent reflections were measured of which 1931 having $F_o > 3\sigma(F_o)$ were considered observed and used in the analysis. In the case of **4b**, 4028 independent reflections were measured and 2970 unique. The structures were solved using direct methods and Fourier difference techniques and refined by blocked full-matrix least squares for all non-hydrogen atoms

Table 6 Fractional atomic coordinates for cluster **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru	0.025 60(3)	0.225 37(5)	0.169 44(3)
Co(1)	−0.110 45(5)	0.259 77(8)	0.264 62(4)
Co(2)	0.037 93(5)	0.445 13(8)	0.295 95(4)
Co(3)	0.063 21(5)	0.166 38(8)	0.345 81(4)
O(1)	−0.157 4(3)	0.575 8(5)	0.195 2(3)
O(2)	−0.097 5(3)	−0.074 6(5)	0.296 8(3)
O(3)	0.243 0(3)	0.371 1(5)	0.406 9(3)
O(4)	0.185 1(3)	−0.026 1(6)	0.266 2(3)
O(5)	−0.210 6(3)	0.331 9(5)	0.407 0(3)
O(6)	−0.283 6(3)	0.190 3(5)	0.111 6(3)
O(7)	0.021 7(4)	0.664 6(6)	0.435 6(3)
O(8)	0.111 6(4)	0.652 7(6)	0.178 0(3)
O(9)	−0.105 7(4)	0.424 3(6)	0.018 7(3)
O(10)	−0.056 2(3)	−0.072 9(6)	0.071 0(3)
O(11)	0.210 1(3)	0.251 7(6)	0.092 1(3)
O(12)	0.131 5(4)	0.006 7(6)	0.508 1(3)
N	0.105 6(4)	0.072 9(5)	0.441 6(3)
C(1)	−0.105 0(4)	0.476 4(6)	0.231 3(3)
C(2)	−0.077 8(4)	0.054 0(6)	0.296 0(3)
C(3)	0.158 6(4)	0.359 0(7)	0.365 8(3)
C(4)	0.126 0(4)	0.068 7(7)	0.268 8(4)
C(5)	−0.171 5(4)	0.302 1(6)	0.353 2(3)
C(6)	−0.216 9(4)	0.218 4(6)	0.171 3(3)
C(7)	0.028 5(4)	0.579 1(7)	0.382 6(4)
C(8)	0.083 5(4)	0.567 3(7)	0.222 7(4)
C(9)	−0.057 4(4)	0.355 3(7)	0.076 4(3)
C(10)	−0.025 8(4)	0.037 9(7)	0.107 2(3)
C(11)	0.143 1(4)	0.245 9(7)	0.122 2(3)

Table 7 Fractional atomic coordinates for cluster **4b** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru	0.369 50(6)	0.178 86(5)	0.566 47(5)
Co(1)	0.171 26(8)	0.285 36(8)	0.491 97(7)
Co(2)	0.289 94(9)	0.330 87(9)	0.649 50(7)
Co(3)	0.351 17(9)	0.288 41(8)	0.417 76(7)
O(1)	0.610 2(6)	0.115 1(6)	0.675 3(6)
O(2)	0.268 0(7)	−0.038 0(6)	0.551 2(7)
O(3)	−0.030 7(6)	0.422 0(6)	0.423 6(6)
O(4)	0.023 9(6)	0.120 1(6)	0.543 3(5)
O(5)	0.427 1(7)	0.425 3(7)	0.819 0(5)
O(6)	0.266 4(8)	0.140 9(6)	0.747 4(5)
O(7)	0.064 2(6)	0.383 9(8)	0.699 1(5)
O(8)	0.470 2(7)	0.098 5(6)	0.392 4(5)
O(9)	0.425 4(7)	0.361 9(7)	0.255 5(5)
O(10)	0.144 3(6)	0.191 2(6)	0.303 2(5)
N	0.395 1(6)	0.331 6(6)	0.322 6(5)
C(1)	0.521 9(8)	0.138 9(7)	0.635 4(7)
C(2)	0.307 9(8)	0.041 5(7)	0.557 4(8)
C(3)	0.047 0(7)	0.370 8(7)	0.450 5(6)
C(4)	0.081 4(8)	0.182 4(7)	0.521 1(6)
C(5)	0.375 4(8)	0.387 1(8)	0.754 0(6)
C(6)	0.295(1)	0.193 9(7)	0.690 8(6)
C(7)	0.148 7(9)	0.363 9(8)	0.676 8(6)
C(8)	0.424 7(8)	0.157 6(7)	0.435 9(7)
C(10)	0.189 1(7)	0.231 7(7)	0.373 1(6)
C(11)	0.404 6(6)	0.342 4(6)	0.557 9(5)
C(12)	0.300 1(6)	0.392 0(6)	0.514 6(5)
C(13)	0.286 1(6)	0.502 4(6)	0.490 4(5)
C(14)	0.321 7(7)	0.578 2(6)	0.559 7(6)
C(15)	0.303 1(8)	0.681 7(6)	0.538 2(7)
C(16)	0.252 4(8)	0.710 4(7)	0.449 4(8)
C(17)	0.221 2(8)	0.638 9(7)	0.380 8(7)
C(18)	0.236 1(8)	0.536 6(7)	0.401 8(6)

which were assigned anisotropic thermal parameters. Hydrogen atoms in **4b** were placed in calculated positions (C–H 0.95 Å) and were refined isotropically. The function minimised was $\Sigma(w|F_o| - |F_c|)^2$, where the weight $w = 4F_o^2/[\sigma^2(F_o) - (0.07|F_o|^2)]$. Final R and R' values were 0.0233 and 0.0317 for **3**, and 0.074 and 0.062 for **4b**. The neutral scattering factors used for all atoms and anomalous dispersion coefficients were obtained from standard sources.[25] The atomic coordinates for **3** and **4b** are listed in Tables 6 and 7 respectively, with the corresponding standard deviations.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for compounds **3** and **4b**.

Conclusion

In conclusion, we have observed that the tetrahedral [$MCo_3H(CO)_{12}$] (M = Fe or Ru) clusters provide interesting systems for the study of metalloselective substitution reactions. Whereas donor ligands such as phosphines, thioethers, amines or nitrosyl selectively substitute a Co-bound carbonyl while keeping the tetrahedral structure,[15] alkynes act as four-electron donors and lead to the corresponding butterfly clusters by rupture of a Co–Co bond. In the case of the nitrosyl cluster **3**, we conclude from the X-ray structure of **4b** that it is the Co–Co bond between the unsubstituted and the NO-substituted cobalt atoms which was selectively broken by the alkyne. The directing role of the NO ligand deserves further studies. The sensitivity of ^{59}Co NMR spectroscopy to changes in the co-ordination sphere of the metal makes it a particularly useful tool in this series of clusters for which well resolved resonances were obtained, allowing also the study of isomeric mixtures.

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