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Study of ferrocenyl-substituted $Co_2(CO)_6$-bispropargylic alcohol complexes as substrates for the formation of chains and macrocycles

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ABSTRACT

Treatment of [Fc-1-R^1-1′-R^2] (R^1 = H, R^2 = CH(O); R^1 = H, R^2 = CMe(O); R^1 = R^2 = CMe(O)) with LiC≡C-CH_2OLi (prepared *in situ* from HC≡CCH_2OH and *n*-BuLi) affords the ferrocenyl-substituted but-2-yne-1,4-diol compounds of general formula [Fc-1-R^1-1′-{CR(OH)C≡CCH_2OH}] (R^1 = R = H (**1a**); R^1 = H, R = Me (**1b**); R^1 = CMe(O), R = Me (**1c**)) in low to high yields, respectively (where Fc = Fe(η^5-C_5H_4)$_2$). In the case of the reactions of [Fc-1-R^1-1′-R^2] (R^1 = H, R^2 = CH(O); R^1 = R^2 = CMe(O)), the by-products [Fc-1-R^1-1′-{CR(OH)$(CH_2)_3CH_3$}] (R^1 = R = H (**2a**); R^1 = CMe(O), R = Me (**2c**)) along with minor quantities of [Fc-1,1′-{CMe(OH)$(CH_2)_3CH_3$}$_2$] (**3**) are also isolated; a hydrazide derivative of dehydrated **2c**, [1-(CMe=$CHCH_2CH_2CH_3$)–1′-(CMe=NNH-2,4-$(NO_2)_2C_6H_3$)] (**2c′**), has been crystallographically characterised. Interaction of **1** with $Co_2(CO)_8$ smoothly generates the alkyne-bridged complexes [Fc-1-R^1-1′-{$Co_2(CO)_6$-μ-η^2-CR(OH)C≡CCH_2OH}] (R^1 = R = H (**4a**); R^1 = H, R = Me(**4b**); R^1 = CMe(O), R = Me (**4c**)) in good yield. Reaction of **4a** with PhSH, in the presence of catalytic quantities of $HBF_4 \cdot OEt_2$, gives the mono- [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2–CH(SPh)C≡CCH_2OH}] (**5**) and bis-substituted [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CH(SPh)C≡CCH_2SPh}] (**6**) straight chain species, while with $HS(CH_2)_nSH$ (*n* = 2,3) the eight- and nine-membered dithiomacrocylic complexes [Fc-1-H-1′-{*cyclo*-$Co_2(CO)_6$-μ-η^2-CH($S(CH_2)_n$–)C≡CCH_2S–}] [*n* = 2 (**7a**), *n* = 3 (**7b**)] are afforded. By contrast, during attempted macrocyclic formation using **4b** and $HSCH_2CH_2OCH_2CH_2SH$ dehydration occurs to give [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-C(=CH_2)C≡CCH_2OH}] (**8**). Single crystal X-ray diffraction studies have been reported on **2c′**, **4b**, **4c**, **7b** and **8**.

1. Introduction

The capacity of the Nicholas reaction to facilitate the substitution of dicobalt hexacarbonyl-coordinated propargylic alcohols (and ethers) with a range of functional groups has proved a powerful and versatile tool in organic synthesis [1]. In general a Lewis acid such as, $HBF_4 \cdot OEt_2$, $BF_3 \cdot OEt_2$ or trifluoromethane sulfonic acid is used to promote the formation of a $Co_2(CO)_6$-stabilised propargylic cation which can then undergo attack by the corresponding nucleophile. In the same way, symmetrical $Co_2(CO)_6$-monoynediols (A, Fig. 1) and $\{Co_2(CO)_6\}_2$-diynediols can undergo substitution reactions at both propargylic carbon centres to afford linear chains [2,3]. On the other hand, use of such cobalt carbonyl-coordinated diol substrates in combination with bifunctional nucleophiles has led to the development of high yielding routes to a wide variety of alkyne-containing macrocycles incorporating an assortment of donor groups [3b,3c–7].

Herein we report the preparation of a new family of unsymmetrical 1-ferrocenyl-substituted $Co_2(CO)_6$-but-2-yne-1,4-diol compounds (**4**, Fig. 1), with a view to probing the ability of the ferrocenyl substituent to modulate the acid-catalysed reactivity of the independent propargylic centres towards thiol- and dithiol-based nucleophiles. This synthetic investigation has, in part, been stimulated by Reutov and Gruselle's report (based on NMR studies) of the aptitude of a ferrocenyl group in tandem with an alkyne-bridged dicobalt hexacarbonyl unit to jointly influence the stability of an adjacent carbocation [8]. Furthermore, effective routes to systems of type **4** and its derivatives are of added interest due to the presence of two organometallic functionalities that have independently shown anti-cancer properties [9,10].

2. Results and discussion

2.1. Route to [Fc-1-R^1-1′-{CR(OH)C≡CCH_2OH}] (**1**)

Treatment of the dilithiated propargyl alcohol (prepared *in situ* from the reaction of HC≡CCH_2OH with 2 equiv. of *n*-BuLi) with an

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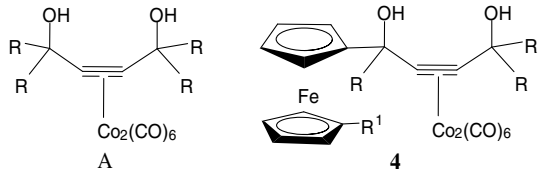
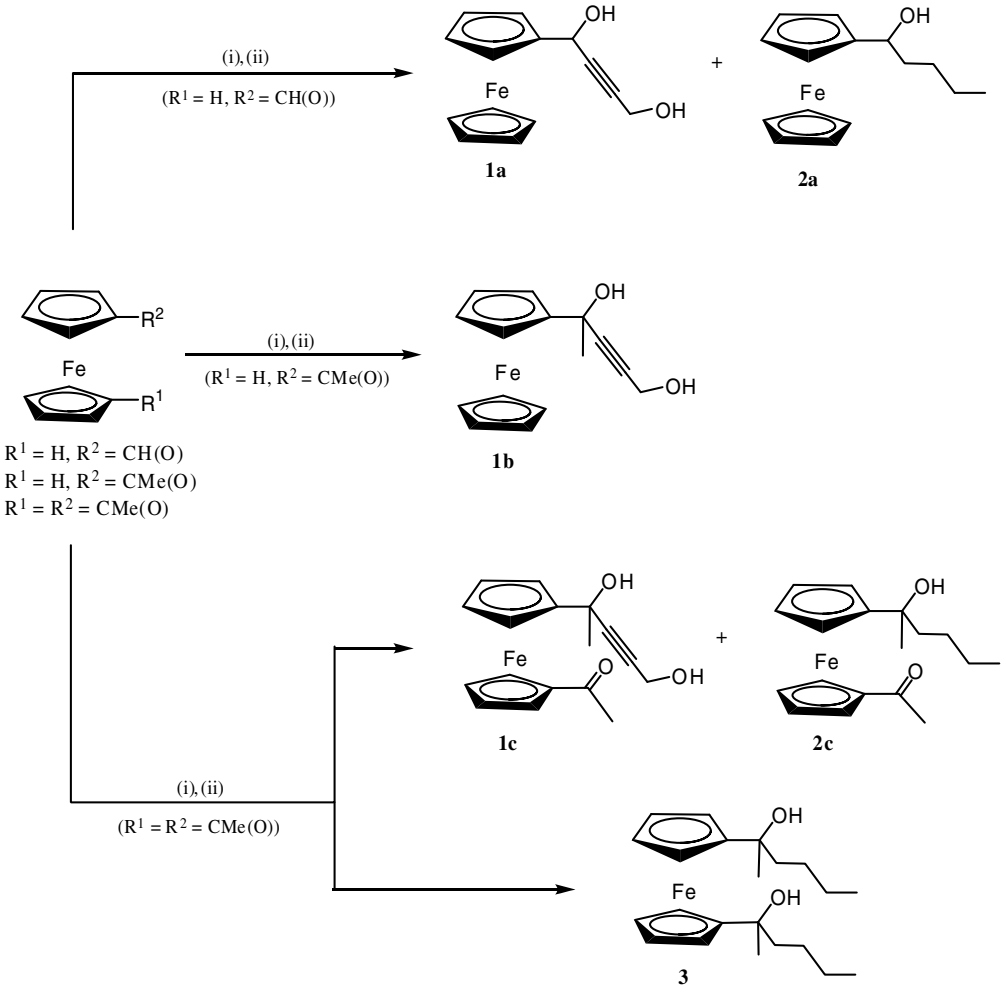


Fig. 1. Symmetrical and unsymmetrical but-2-yne-1,4-diol-$Co_2(CO)_6$ complexes [R = H, Me; R^1 = H, CMe(O)].

equimolar quantity of ferrocenecarboxaldehyde in tetrahydrofuran at −78 °C gave, on work-up, [Fc-1-H-1′-{CH(OH)C≡CCH_2OH}] (**1a**) as the major product and [Fc-1-H-1′-{$CH(OH)(CH_2)_3CH_3$}] (**2a**) (Fc = $Fe(\eta^5\text{-}C_5H_4)_2$) as the minor one, in good overall yield (Scheme 1). Under similar reaction conditions, acetylferrocene afforded [Fc-1-H-1′-{CMe(OH)C≡CCH_2OH}] (**1b**) as the sole isolable product in low yield (Scheme 1). In contrast, the attempted reaction of LiC≡C-CH_2OLi with 1,1′-diacetylferrocene in a 3:1 ratio gave, on work-up, [Fc-1-{CMe(O)–1′-{$CMe(OH)(CH_2)_3CH_3$}] (**2c**) as the major product and [Fc-1-{CMe(O)}-1′-{CMe(OH)C≡CCH_2OH}] (**1c**) as the minor product, along with trace quantities of [Fc-1,1′-{$CMe(OH)(CH_2)_3$-CH_3}$_2$] (**3**) (Scheme 1). All the new ferrocene-containing compounds have been characterised by ^1H and ^{13}C NMR spectroscopy and ESI mass spectrometry (Section 4). In addition, a hydrazide derivative of **2c** has been characterised by single crystal X-ray diffraction.

The mass spectra of **1a**–**1c** all show molecular ions in addition to peaks corresponding to M^++Na ions. In their ^{13}C NMR spectra, the alkynic carbon atoms are seen in each case as separate singlets in the range δ 98.1–85.8, while the independent propargyl carbon atoms appear more upfield (range: δ 66.4–50.7) with the ferrocene-linked carbon displaying the more positive of the two chemical shifts. The ^1H NMR spectra for **1a**–**1c** support the formulations with the propargyl CH_2 protons evident as doublets (**1a**, **1b**) or as a singlet (**1c**); the former multiplicity is the result of three-bond coupling to the hydroxyl proton. The proton at the carbon atom α to the ferrocene (*i.e.*, Fc*CH*OH) in **1a** gives rise to a doublet at 5.21 ($^3J_{H-H}$ 6.5 Hz) due to coupling to the OH proton, which is supported by the presence of a mutually coupled doublet at δ 3.42 for the hydroxyl proton itself.

Compounds **2a** and **3** have been reported previously [11,12], while **2c** has been assigned a related structure on the basis of a comparison of its spectroscopic data with those of **2a** and **3**. Thus, the mass spectrum of **2c** revealed a M^++Na peak while the IR and ^{13}C NMR spectra were consistent with the presence of an unreacted acetyl moiety. In order to allow access to a crystalline sample, **2c** was treated with $H_2NNH\text{-}2,4\text{-}C_6H_3(NO_2)_2$ in ethanol, in the presence of a catalytic amount of glacial acetic acid, to afford the yellow crystalline derivative [Fc-1-(CMe=$CHCH_2CH_2CH_3$)–1′-(CMe=NNH-2,4-$(NO_2)_2C_6H_3$)] (**2c′**) in high yield. Single crystals of **2c′** suitable for an X-ray diffraction study were grown from a hex-



Scheme 1. Reagents and conditions: (i) $LiCCCH_2OLi$ (1–3 equiv.), THF, −78 °C; (ii) $(CH_3)_2CHOH/H_2O$.

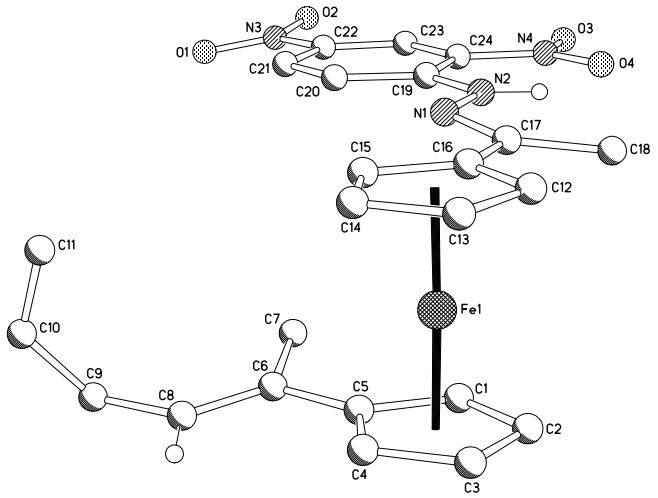


Fig. 2. Molecular structure of **2c′** with a partial atom labeling scheme; all hydrogen atoms, apart from $H2_N$ and H8, have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **2c′**

Range Fe(1)–C(1–4)	2.039(3)–2.044(3)	C(10)–C(11)	1.325(12)
Fe(1)–C(5)	2.059(3)	C(16)–C(17)	1.466(5)
Range Fe(1)–C(12–15)	2.039(3)–2.051(4)	C(17)–N(1)	1.295(4)
Fe(1)–C(16)	2.046(3)	N(1)–N(2)	1.388(4)
C(5)–C(6)	1.463(5)	N(2)–C(19)	1.345(4)
C(6)–C(8)	1.355(5)	C(22)–N(3)	1.459(5)
C(8)–C(9)	1.485(6)	C(24)–N(4)	1.445(4)
C(9)–C(10)	1.458(9)	Range N–O	1.218(5)–1.237(4)
C(5)–C(6)–C(8)	120.4(3)	C(17)–N(1)–N(2)	114.9(3)
C(6)–C(8)–C(9)	127.1(4)	N(1)–N(2)–C(19)	119.6(3)
C(16)–C(17)–N(1)	115.9(3)		

ane:chloroform mixture. A view of **2c′** is depicted in Fig. 2; selected bond lengths and angles are collected in Table 1.

The structure of **2c′** consists of a 1,1′-disubstituted ferrocene unit with one cyclopentadienyl ring containing a C(Me)=N–NH{2,4-$(NO_2)_2C_6H_3$} substituent and the other a C(Me)=$CHCH_2CH_2CH_3$ group. It is apparent that during the acid-catalysed condensation reaction to form **2c′** the hydroxyl group in **2c** has been eliminated by dehydration to yield an alkene [C(6)–C(8) 1.355(5) Å], with the *n*-propyl and ferrocene substituents adopting a *trans* configuration [tors.: C(5)–C(6)–C(8)–C(9) 179.2°]. The spectroscopic properties of **2c′** are consistent with the solid state structure being maintained in solution (see Experimental Section). In the ^{1}H NMR spectrum, the vinylic hydrogen atom takes the form of a poorly resolved triplet of doublets at δ 5.62 as a result of coupling to the neighbouring methylene group and the vinylic methyl group; the hydrazide NH proton is seen as a singlet at δ 11.26. The presence of a downfield signal at δ 154.7 in the ^{13}C NMR spectrum confirms the formation of the imine unit.

The isolation of **2a**, **2c** and **3** indicates that nucleophilic attack by a butyl group (from any unreacted *n*-BuLi) at the corresponding carbonyl-containing ferrocene represents a competing side reaction in this chemistry. The low yield observed for **1b** suggests that a similar reaction pathway is likely, leading in this case to products that are not amenable to chromatographic separation. Nevertheless, sufficient quantities of the desired alkynic species **1a**–**1c** were obtained in order to allow further studies (*vide infra*).

2.2. Preparation of [Fc-1-R^1-1′-{$Co_2(CO)_6$-μ-η^2-CR(OH)C≡CCH_2OH}] (**4**)

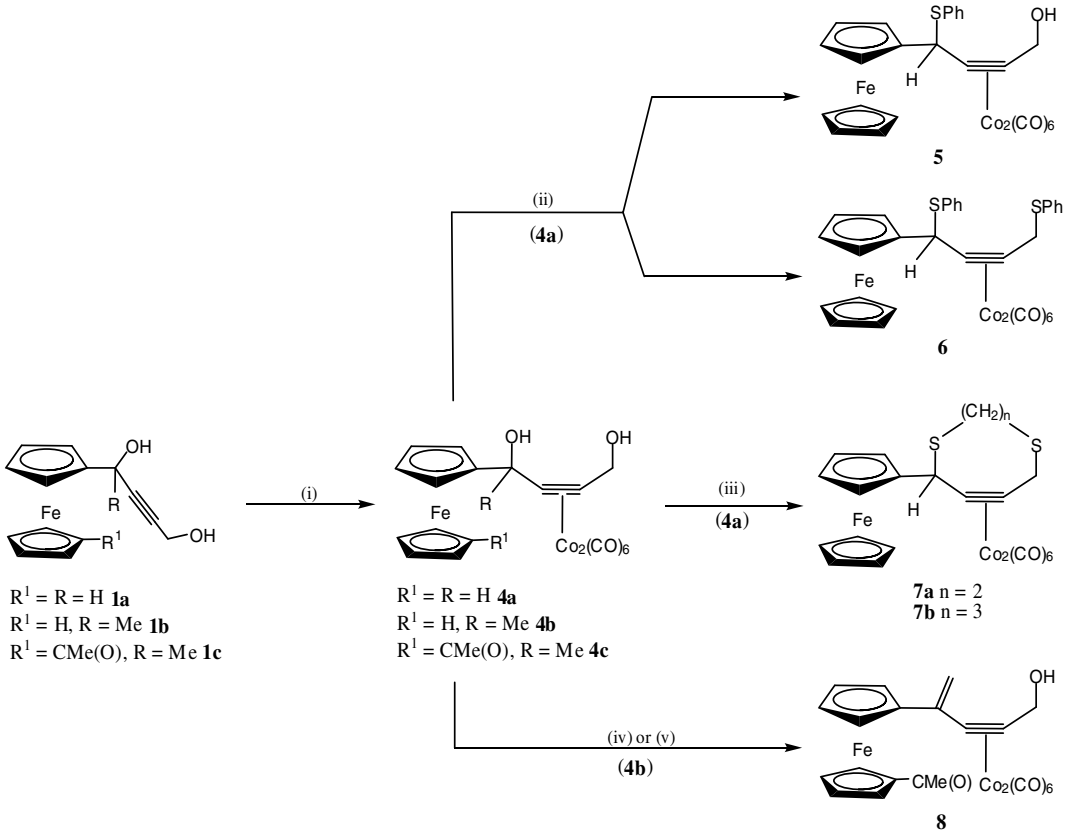
Interaction of **1a**–**1c** with a slight excess of $Co_2(CO)_8$ in dichloromethane at room temperature afforded [Fc-1-R^1-1′-{$Co_2(CO)_6$-μ-η^2-CR(OH)C≡CCH_2OH}] [R^1 = R = H (**4a**); R^1 = H, R = Me (**4b**); R^1 = CMe(O), R = Me (**4c**)] in high yields (Scheme 2). All the new complexes have been characterised by IR, ^{1}H and ^{13}C NMR spectroscopy and LSI mass spectrometry (Table 2 and Section 4). In addition, complexes **4b** and **4c** have been the subject of single crystal X-ray diffraction studies.

Single crystals of **4b** and **4c** suitable for the X-ray determinations were grown from a hexane:dichloromethane mixture at room temperature. The structures of **4b** and **4c** are similar and will be discussed together. A perspective view of **4c** is depicted in Fig. 3; selected bond distances and angles for both **4b** and **4c** are listed in Table 3. The molecular structures consist of a $HOCH_2C$≡CC(OH)(Me)–R chain [R = Fc (**4b**), (η^5-C_5H_4)(η^5-C_5H_4CMeO)Fe (**4c**)] in which each alkynic group is perpendicularly bound by a dicobalt hexacarbonyl unit. The Co_2C_2 cores adopt the expected tetrahedral arrangements with the Co–Co and C(alkyne)–C(alkyne) bond distances falling within the normal ranges [13,14]; the coordinated carbonyl ligands display the expected linear geometries. The C–C≡C *bend-back* angles [C(7)–C(8)–C(9) 136.3(3) (**4b**), 143.3(4) (**4c**); C(10)–C(9)–C(8) 136.3(2) (**4b**), 142.0(4) (**4c**)°] within each complex are similar in magnitude and comparable with those found in the related complexes [$Co_2(CO)_6$(μ-η^2-$HOCR_2CCCR_2OH$)] [R = H 136.64(av)°, Me 141.72(av)°] [15] and [$Co_2(CO)_6$(μ-η^2-HOCHRCC-CHROH)] [R = Me 137.49(av)°, Et 136.97(av)°, Ph 135.6(av)°] [15a,16]. The relative disposition of the hydroxyl groups within the $HOCH_2C$≡CC(OH)(Me)–R chains in **4b** and **4c** do, however, show some differences. In **4b** the two oxygen atoms are disposed in such a way that the hydrogen atom on O(8) can undergo an intramolecular interaction [O(8)···O(7) 2.679 Å] with O(7). In **4c** no comparable hydrogen bond is evident with the corresponding oxygen atoms positioned far apart [O(8)···O(7) 6.161 Å]. Inspection of the packing picture for **4b** and **4c** reveals the presence of a number of intermolecular contacts with the closest interaction involving a hydroxyl hydrogen atom in one molecule with either a neighbouring hydroxyl oxygen [O(7)···O(8A) 2.651 Å (**4b**)] or with a neighbouring ketonic oxygen atom [O(7)···O(9A) 2.571 Å (**4c**)].

The IR spectra of **4a**–**4c** display the characteristic set of bands for dicobalt hexacarbonyl-coordinated monoyne moieties [4,5,13], while their LSI mass spectra display molecular ions (and M^++Na peaks) along with fragmentation peaks corresponding to the loss of successive carbonyl groups. In their ^{1}H NMR spectra resonances corresponding to the cyclopentadienyl protons are accompanied by signals due to the coordinated –C(OH)RC≡CCH_2OH chains [R = H (**4a**), R = Me (**4b, 4c**)]. For example, the C≡CCH_2OH protons are all observed around δ 4.7 with those in **4b** taking the form of a doublet ($^3J_{H-H}$ 5.7 Hz) while in **4c** the methylene protons are inequivalent resulting in a multiplet; the expected mutually coupled hydroxyl protons are also evident. In the ^{13}C NMR spectrum of **4a** the inequivalent alkynic carbon atoms are shifted downfield on coordination (*c.f.*, **1a**) as are the signals due to the propargylic carbon atoms [δ 63.8 (Fc*C*HOH) and 63.7 (C≡*C*CH_2OH)]. Notably, the Fc*C*HOH carbon signal in **4a** is shifted by only 2.5 ppm on coordination to the $Co_2(CO)_6$ moiety, compared to the 13 ppm shift for the –C≡*C*CH_2OH carbon signal, indicating that the ferrocene moiety activates the adjacent propargyl site (Fc*C*HOH) even in the free alkyne (**1a**) [8].

2.3. Acid-catalysed reaction of **4** with sulfur-based nucleophiles

In order to explore the capability of **4** to undergo nucleophilic substitution reactions, **4a** was initially chosen as the substrate



Scheme 2. Reagents and conditions: (i) $Co_2(CO)_8$, CH_2Cl_2, RT; (ii) $HBF_4 \cdot OEt_2$ (cat.), C_6H_5SH, CH_2Cl_2, −78 °C; (iii) $HBF_4 \cdot OEt_2$ (cat.), $HS(CH_2)_nSH$, CH_2Cl_2, −78 °C; (iv) $HBF_4 \cdot OEt_2$ (cat.), $HS(CH_2)_2O(CH_2)_2SH$, CH_2Cl_2, −78 °C; (v) $HBF_4 \cdot OEt_2$ (cat.), CH_2Cl_2, −78 °C.

Table 2
Selected characterisation data for the cobalt carbonyl-containing complexes **4**–**8**

Complex	ν(CO) (cm^{-1})[a]	^{1}H NMR[b]	LSI mass spectrum
4a	2028(vs), 2056(vs), 2094(m)	δ 5.59 (d, 1H, C_5H_4CHOH, $^3J_{H-H}$ 1.9), 4.73 (m, 2H, CH_2) 4.33–4.32 (m, 1H, C_5H_4), 4.27–4.26 (m, 1H, C_5H_4), 4.26 (s, 5H, C_5H_5), 4.25–4.19 (m, 2H, C_5H_4), 2.82 (d, 1H, $CHOH$, $^3J_{H-H}$ 1.9), 2.46 (m, 1H, CH_2OH).	M^++H (557), M^+−OH (539), M^+−nCO (n = 2–6)
4b	2027(vs), 2056(vs), 2092(m)	δ 4.68 (d, 2H, $C{\equiv}CCH_2OH$, $^3J_{H-H}$ 5.7), 4.31 (s, 1H, C_5H_4), 4.20 (s, 5H, C_5H_5), 4.16–4.11 (m, 3H, C_5H_4), 3.00 (s, 1H, C_5H_4CMeOH), 2.87 (t, 1H, CH_2OH, $^3J_{H-H}$ 5.7), 1.91 (s, 3H, CH_3).	M^++Na (593), M^+ (570), M^+−OH (553), M^+−nCO (n = 2–6)
4c	2028(vs), 2056(vs), 2093(vs)	δ 4.94 (t, 1H, C_5H_4, $^3J_{H-H}$ 1.3), 4.76 (t, 1H, C_5H_4, $^3J_{H-H}$ 1.3), 4.74–4.71 (m, 2H, CH_2OH, $^3J_{H-H}$ 6.3, $^3J_{H-H}$ 4.6), 4.62–4.61 (m, 1H, C_5H_4), 4.58 (m, 1H, C_5H_4), 4.33 (m, 1H, C_5H_4), 4.32–4.31 (m, 1H, C_5H_4), 4.17–4.16 (m, 1H, C_5H_4), 4.15–4.14 (m, 1H, C_5H_4), 3.47 (s, 1H, C_5H_4COH) 3.16 (dd, 1H, $CCCH_2OH$, $^3J_{H-H}$ 6.3, $^3J_{H-H}$ 4.6), 2.41 (s, 3H, $C_5H_4COCH_3$), 1.99 (s, 3H, $C_5H_4C(OH)CH_3$).	M^++Na (635), M^+−nCO (n = 2–5)
5	2029(vs), 2053(vs), 2062(s), 2092(m), 2099(m)	δ 7.57 (d, 2H, C_6H_5, $^3J_{H-H}$ 7.5), 7.43 (t, 2H, C_6H_5, $^3J_{H-H}$ 7.5), 7.31 (t, 1H, C_6H_5, $^3J_{H-H}$ 7.5), 5.50 (s, 1H, C_5H_4CHSPh), 4.39 (s, 1H, C_5H_4), 4.32 (s, 1H, C_5H_4), 4.27 (s, 1H, C_5H_4), 4.23 (s, 5H, C_5H_5), 4.21 (s, 1H, C_5H_4), 4.11 (d, 2H, CH_2OH, $^3J_{H-H}$ 7), 1.52 (t, 1H, CH_2OH, $^3J_{H-H}$ 7).	M^++Na (671), M^+ (648), M^+−nCO (n = 2–5)
6	2028(vs), 2056(vs), 2094(m)	δ 7.64–7.62 (m, 2H, C_6H_5), 7.40 (t, 2H, C_6H_5, $^3J_{H-H}$ 7.7), 7.29–7.19 (groups of m, 6H, $CH_2SC_6H_5$), 5.71 (s, 1H, C_5H_4CHSPh), 4.42 (m, 1H, C_5H_4), 4.32 (m, 1H, C_5H_4), 4.25 (m, 1H, C_5H_4), 4.21 (s, 5H, C_5H_5), 4.19–4.18 (m, 1H, C_5H_4), 3.87 (d, 1H, CH_2, $^3J_{H-H}$ 14), 3.76 (d, 1H, CH_2, $^3J_{H-H}$ 14).	M^++H (741), M^+−nCO (n = 3–6)
7a	2027(vs), 2058(vs), 2095(m)	δ 4.92 (s, 1H, $C_5H_4CHSCH_2$), 4.24–4.13 (groups of m, 9H, C_5H_4 and C_5H_5), 4.06–4.04 (m, 2H, $C{\equiv}CCH_2S$), 3.68–3.64 (m, 1H, SCH_2), 3.38–3.34 (m, 1H, SCH_2), 3.02–2.91 (m, 2H, SCH_2).	M^+ (614), M^+−nCO (n = 3–6)
7b	2027(vs), 2056(vs), 2096(m)	δ 5.06 (s, 1H, $C_5H_4CHSCH_2$), 4.36–4.18 (groups of m, 11H, C_5H_4, C_5H_5 and $C{\equiv}CCH_2S$), 3.06 (m, 2H, $(CH_2)_3$), 2.90–2.88 (m, 2H, $(CH_2)_3$), 2.43 (m, 1H, $(CH_2)_3$), 2.28 (m, 1H, $(CH_2)_3$).	M^++H (629), M^+−nCO (n = 2–6)
8	2027(vs), 2053(vs), 2091(s)	δ 5.76 (br. s, 1H, $C{=}CH_2$), 5.01 (br. s, 1H, $C{=}CH_2$), 4.99 (s, 2H, C_5H_4), 4.42 (s, 2H, CH_2), 4.30 (s, 2H, C_5H_4), 4.16 (s, 5H, C_5H_5), 1.93 (s, 1H, CH_2OH).	M^+−nCO (n = 1–5)

[a] Recorded in CH_2Cl_2 (apart from **6a** in THF) in 0.5 mm NaCl solution cells.
[b] ^{1}H NMR chemical shifts in ppm relative to $SiMe_4$ (0.0 ppm), coupling constants in Hz in $CDCl_3$ at 293 K.

and its reactivity towards a range of sulfur-based nucleophiles was examined. Thus, reaction of complex **4a** with one equivalent of PhSH in dichloromethane at −78 °C in the presence of a catalytic quantity of $HBF_4 \cdot OEt_2$ affords, on work-up, [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CH(SPh)C≡CCH_2OH}] (**5**) as the minor product and the bis-capped species [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CH(SPh)C≡CCH_2SPh}] (**6**) as the major product (Scheme 2). Use of the dithols $HS(CH_2)_nSH$ (n = 2, 3) in place of thiophenol in the above reaction affords the

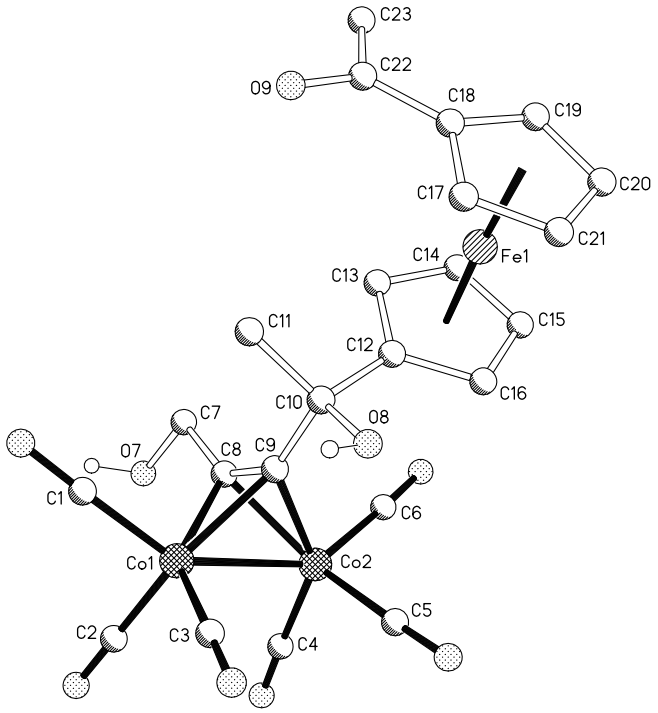


Fig. 3. Molecular structure of **4c** with a partial atom labeling scheme; all hydrogen atoms, apart from H7 and H8, have been omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for **4b** and **4c**

	4b	4c
Range Fe(1)–C(17, 19–21)	–	2.037(4)–2.067(5)
Fe(1)–C(18)	–	2.031(4)
Range Fe(1)–C(17–21)	2.037(3)–2.051(3)	–
Range Fe(1)–C(13–16)	2.036(3)–2.045(3)	2.025(5)–2.052(4)
Fe(1)–C(12)	2.041(3)	2.057(4)
C(12)–C(10)	1.507(4)	1.510(6)
C(10)–O(8)	1.437(3)	1.402(6)
C(10)–C(11)	1.521(4)	1.491(8)
C(10)–C(9)	1.507(4)	1.510(6)
C(9)–C(8)	1.345(4)	1.347(6)
C(8)–C(7)	1.491(4)	1.478(6)
C(7)–O(7)	1.433(3)	1.437(6)
C(22)–O(9)	–	1.236(7)
Co(1)–Co(2)	2.4764(5)	2.4776(8)
Co–C(carbonyl)	1.796(4)–1.825(3)	1.790(6)–1.832(5)
C–O(carbonyl)	1.133(3)–1.136(4)	1.122(6)–1.142(6)
Co–C(alkyne)	1.947(3)–1.979(3)	1.952(4)–1.976(4)
O(9)–C(22)-(C23)	–	122.1(5)
C(12)–C(10)–O(8)	110.7(2)	107.9(4)
C(12)–C(10)–C(11)	112.2(2)	111.8(4)
C(12)–C(10)–C(9)	108.1(2)	106.8(3)
C(10)–C(9)–C(8)	136.3(2)	142.0(4)
C(9)–C(8)–C(7)	136.3(3)	143.3(4)
C(8)–C(7)–O(7)	107.2(2)	112.3(4)

macrocyclic complexes [Fc-1-H-1′-{*cyclo*-$Co_2(CO)_6$-μ-η^2-$CH(S(CH_2)_n-)C{\equiv}CCH_2S$-}] [$n$ = 2 (**7a**), n = 3 (**7b**)] in moderate yield. Complexes **5**–**7** have all been characterised by IR, ^1H and ^{13}C NMR spectroscopy and LSI mass spectrometry (Table 2 and Section 4). In addition, complex **7b** has been the subject of a single crystal X-ray diffraction study.

Crystals of **7b** suitable for the X-ray diffraction determination were grown from hexane:dichloromethane solution. The molecular structure of **7b** is shown in Fig. 4; selected bond lengths and angles are collected in Table 4. There are two molecules (A and B) in the asymmetric unit which differ mainly in the conformation of the $S(CH_2)_3S$ bridging moiety. In molecule A the moiety is disposed on one side of the coordinated alkynic C–C vector (*cis*-isomer) while in molecule B the $S(CH_2)_3S$ unit is located across the coordinated C≡C bond (*trans*-isomer). The following discussion will be concerned with molecule A; any significant variations in B will be highlighted. The structure consists of a nine-membered –S–C–C–C–S-C–C≡C–C– dithiomacrocycle in which the alkynic moiety is η^2-bridged by a dicobalt hexacarbonyl unit. The Co_2C_2 core adopts the expected pseudo tetrahedral geometry with the bond parameters within the core falling in the normal ranges [13,14]. The Co_2C_2 cores in each isomer are slightly skewed: C(10)–C(9)–Co(1) 129.73(17)° *vs.* C(10)–C(9)–Co(2) 136.10(17)° (*trans*-isomer) and C(10)–C(9)–Co(1) 140.54(18)° *vs.* C(10)–C(9)–Co(2) 128.58(17)° (*cis*-isomer). The alkyne *bend-back* angles are comparable

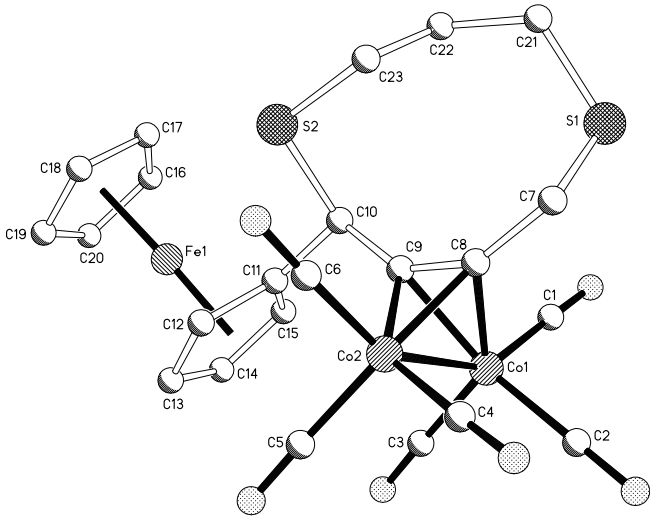


Fig. 4. Molecular structure of **7b** (molecule A) with a partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) for **7b**

	Molecule A	Molecule B
Range Fe(1)–C(12–15)	2.025(3)–2064(3)	2.035(3)–2.052(3)
Fe(1)–C(11)	2.070(2)	2.067(2)
Range Fe(1)–C(16–20)	2.037(3)–2.050(3)	2.039(3)–2.047(3)
C(11)–C(10)	1.507(3)	1.506(3)
C(10)–C(9)	1.509(3)	1.508(3)
C(9)–C(8)	1.341(3)	1.336(3)
C(8)–C(7)	1.494(3)	1.497(3)
C(7)–S(1)	1.816(3)	1.822(3)
S(1)–C(21)	1.787(3)	1.819(3)
C(21)–C(22)	1.524(4)	1.526(4)
C(22)–C(23)	1.518(4)	1.517(4)
C(23)–S(2)	1.809(3)	1.809(2)
S(2)–C(10)	1.830(2)	1.830(2)
Co(1)–Co(2)	2.4628(5)	2.4591(5)
Co–C(carbonyl)	1.795(3)–1.824(3)	1.793(4)–1.827(3)
C–O(carbonyl)	1.132(3)–1.137(3)	1.132(4)–1.141(4)
Co–C(alkyne)	1.956(2)–1.973(2)	1.967(3)–1.984(3)
S(1)–C(7)–C(8)	114.32(18)	116.17(18)
C(7)–C(8)–C(9)	148.7(2)	146.8(2)
C(8)–C(9)–C(10)	145.6(2)	141.7(2)
C(9)–C(10)–S(2)	114.21(17)	114.06(17)
C(10)–S(2)–C(23)	102.20(12)	102.31(11)
S(2)–C(23)–C(22)	114.6(2)	115.69(18)
C(23)–C(22)–C(21)	113.8(3)	113.3(2)
C(22)–C(21)–S(1)	117.0(2)	114.86(19)
C(21)–S(1)–C(7)	104.04(15)	102.75(13)
C(11)–C(10)–S(2)	107.75(16)	108.64(17)

[C(8)–C(9)–C(10) 145.6(2)° *vs.* C(7)–C(8)–C(9) 148.7(2)°] in size with the average value greater than that found in the previously reported eight-membered dithiomacrocyclic complex [{*cyclo*-Co_2-$(CO)_4$(μ-dppm)-μ-η^2-CH_2($S(CH_2)_2$–)C≡CCH_2S-}] [138.7(av)°] [4a]. No significant intermolecular interactions are apparent.

In the IR spectra of **5**–**7** the typical *ν*(CO) pattern of bands for dicobalt hexacarbonyl-bridged alkynes is observed [4,5,13]. All four complexes (**5**, **6**, **7a**, **7b**) show molecular ion peaks (and/or M^++H/M^++Na peaks) along with fragmentation corresponding to the loss of carbonyl groups. In the ^{1}H NMR spectrum of **5**, the presence of a doublet (three-bond coupling to the hydroxyl proton) for the C*H*$_2$OH protons and a singlet for the FcC*H*SPh proton confirms that the substitution has occurred selectively at the carbon atom α to the ferrocene unit. The ^{1}H NMR spectrum of **6** indicates that the C≡CC*H*$_2$SPh protons are inequivalent (analogously to **4a**) and appear as doublets at *δ* 3.87 and 3.76 with $^3J_{H-H}$ 14 Hz for each signal. The presence of the bridging $(CH_2)_n$ units in **7a** ($n = 2$) and **7b** ($n = 3$) is revealed by a series of multiplets between *δ* 3.68 and 2.28 in their ^{1}H NMR spectra. In the ^{13}C NMR spectra (recorded at 293 K) for **6** and **7b** only one type of carbonyl carbon resonance is evident while in **7a** two broad peaks are visible; the remaining signals are consistent with the proposed formulations.

The isolation of the mixed SPh/OH species **5** from the acid-catalysed reaction of **4a** with thiophenol indicates that the presence of the ferrocenyl unit α- to a propargylic centre does indeed induce some selectivity during the transformation. It would therefore seem likely that appended ferrocenyl group affects the stability of the intermediate propargylic cation in such a way as to drive the selective nucleophilic attack [8]. A related stepwise formation of macrocycles **7** would also seem probable.

In an attempt to extend the ability of **4a** to act as template for the formation of ring systems, the reaction of **4b** with the bis(2-mercaptoethyl) ether, in the presence of catalytic amount of $HBF_4 \cdot OEt_2$, was investigated. On work-up complex [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-C(=CH_2)C≡CCH_2OH}] (**8**) could be isolated as the sole product in modest yield (Scheme 2). Complex **8** could also be isolated in comparable yield on treatment of **4b** with the acid catalyst in the absence of the bis(2-mercaptoethyl) ether. Complex **8** has been characterised by IR, ^{1}H and ^{13}C NMR spectroscopy and LSI mass spectrometry (Table 2 and Section 4). In addition, complex **8** has been the subject of a single crystal X-ray diffraction study.

Crystals of **8** suitable for the X-ray determination were grown from hexane:dichloromethane solution. The molecular structure is depicted in Fig. 5; selected bond lengths and angles are presented in Table 5. The structure consists of a FcC(=CH_2)C≡CCH_2OH chain in which the alkynic group is perpendicularly bound by a dicobalt hexacarbonyl unit. The bond lengths and angles of the almost tetrahedral Co_2C_2 core are all within the expected range [13,14]. The Co(1) atom is located slightly closer to the C(8) atom than to C(9), probably due to the steric demands of the ferrocene moiety [Co(1)–C(8) is 1.9631(18) Å *vs.* Co(1)–C(9) of 1.9939(18) Å]. The C(9)–C(10) and C(10)–C(12) bonds are shortened by *ca.* 0.03–0.04 Å compared to **4b**, consistent with increased communication between the ferrocene and dicobalt moieties *via* the more delocalised bridging C(=CH_2) moiety in **8**. The alkyne *bend-back* angles are similar [C(7)–C(8)–C(9) 145.53(18)° *vs.* C(10)–C(9)–C(8) 146.23(18)°] in size with the average value significantly larger than that found in **4b**. No significant intermolecular interactions are apparent.

The IR spectrum of **8** confirms the presence of a dicobalt hexacarbonyl moiety in the molecule with three characteristic *ν*(CO) bands [4,5,13]. The ^{1}H NMR spectrum of **8** is consistent with the solid state structure being maintained in solution with two broad singlets due to the inequivalent C=C*H*$_2$ protons visible at *δ* 5.76 and 5.01. The unreacted propargyl group C*H*$_2$OH protons gives rise to a peak at *δ* 4.42 while the CH_2O*H* proton is seen at *δ* 1.93.

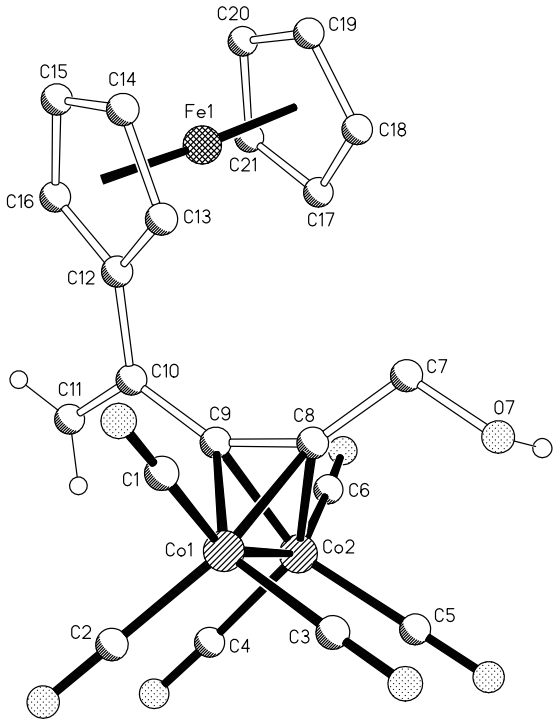


Fig. 5. Molecular structure of **8** with a partial atom labeling scheme; all hydrogen atoms, apart from H11A and H11B, have been omitted for clarity.

Table 5
Selected bond distances (Å) and angles (°) for **8**

Range Fe(1)–C(13–16)	2.037(2)–2.0476(19)	C(8)–C(7)	1.489(3)
Fe(1)–C(12)	2.0605(19)	C(7)–O(7)	1.415(3)
Range Fe(1)–C(17–21)	2.039(2)–2.045(2)	Co(1)–Co(2)	2.4635(4)
C(12)–C(10)	1.477(3)	Co–C(carbonyl)	1.792(2)–1.827(2)
C(10)–C(11)	1.337(3)	C–O(carbonyl)	1.129(3)–1.135(3)
C(10)–C(9)	1.466(3)	Co–C(alkyne)	1.9631(18)–1.9939(18)
C(9)–C(8)	1.343(3)		
C(12)–C(10) –C(9)	118.70(16)	C(10)–C(9)–C(8)	146.26(18)
C(12)–C(10)–C(11)	120.74(18)	C(9)–C(8)–C(7)	145.53(18)
C(11)–C(10)–C(9)	120.53(18)	C(8)–C(7)–O(7)	113.17(17)

Previous studies of dicobalt hexacarbonyl-coordinated propargyl alcohols with alkyl groups on the propargyl centre have shown that acid-catalysed dehydration reactions are commonplace [1a]. Therefore it would seem likely that during the reaction of **4b**, formation of an intermediate carbocation by protonation of the OH group α to the ferrocenyl group occurs preferentially (*cf.* reaction of **4a** to give **5**) before subsequent loss of H_2O to give **8**. Nevertheless, it is uncertain why no substitution chemistry occurs at the unsubstituted propargylic centre.

3. Conclusions

A family of ferrocenyl-containing but-2-yne-1,4-diols (**1a**–**1c**) has been successfully prepared and their alkynic moieties coordinated to dicobalt hexacarbonyl units (**4a**–**4c**). The capacity of **4a** to undergo acid-catalysed substitution reactions with mono- and di-thiols has been demonstrated leading to linear chain (**5** and **6**) and macrocyclic complexes (**7**). In the case of the chain products, initial substitution takes place at the ferrocenyl-substituted propargylic carbon atom. An attempt to form a macrocycle using the more sterically congested **4b** resulted only in dehydration to give

8; a pathway also, however, likely to involve preferential reactivity at the ferrocenyl-substituted propargylic carbon atom. The application of **7** and related macrocycles in the field of redox-active receptor molecules will be examined elsewhere [17].

4. Experimental

4.1. General procedures and materials

Unless otherwise stated all experiments were carried out under an atmosphere of dry, oxygen-free argon, using standard Schlenk line techniques and solvents freshly distilled from appropriate drying agent [18]. NMR spectra were recorded in $CDCl_3$ at ambient temperature using a Bruker DRX-500 or a AM-400 spectrometer with TMS as an external standard for ^1H and ^{13}C spectra; coupling constants are measured in Hertz (Hz). ^1H–^1H COSY, HMQC and HMBC NMR experiments were employed to obtain ^1H–^1H and ^1H–^{13}C correlated spectra [19]. Infrared spectra were, unless otherwise stated, recorded in dichloromethane solution in 0.5 mm NaCl solution cells, using a Perkin Elmer 1710 Fourier Transform Spectrometer. LSI (Liquid Secondary Ion) mass spectra were recorded on a Micromass Autospec high resolution double focusing mass spectrometer at the EPSRC National Mass Spectrometry Service Centre at the University of Wales, Swansea. Electrospray (ESI) mass spectra were recorded on a Micromass Quattro LC instrument at the University of Cambridge, Mass Spectrometry Services. Elemental analyses were performed either at the University of Cambridge or at the Science Technical Support Unit, London Metropolitan University. Column chromatography was performed on Kieselgel 60 (70–230 mesh ASTM). Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. All products are listed in order of decreasing R_f. The reagents, propargyl alcohol, *n*-butyl lithium (1.5M in hexane), ferrocenecarboxaldehyde, acetylferrocene, 1,1′-diacetylferrocene, 2,4-dinitrophenylhydrazine, dicobalt octacarbonyl, thiophenol, 1,2-ethanedithiol, 1,3-propanedithiol, bis(2-mercaptoethyl) ether and tetrafluoroboric acid (48 wt. % in diethyl ether) were obtained from Aldrich Chemical Co. and used without further purification.

4.2. Synthesis of ***1a*** and ***2a***

To a solution of $HC{\equiv}CCH_2OH$ (1.36 ml, 1.31 g, 23.36 mmol) in tetrahydrofuran (200 ml) at −78 °C was added *n*-BuLi (31.0 ml, 46.72 mmol, 2 equiv.) dropwise. The viscous mixture was left to stir for a further 2 h at −78 °C. A solution of ferrocenecarboxaldehyde (5.00 g, 23.36 mmol, 1 equiv.) in tetrahydrofuran (50 ml) was slowly added and the reaction mixture left to stir for 0.5 h at −78 °C. On warming to room temperature, the mixture was stirred for a further 0.5 h. Isopropanol (20 ml) was added and the resulting mixture stirred for 0.5 h before being poured onto a water–ice mixture (200 ml). The organic layer was collected and the aqueous layer extracted with chloroform (3 × 50 ml). The combined organic fractions were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The oily residue was dissolved in the minimum amount of dichloromethane, adsorbed on silica and applied to the top of a chromatography column. Elution with hexane:ethyl acetate (4:1) afforded [Fc-1-H-1′-{CH(OH)$(CH_2)_3CH_3$}] (**2a**) (0.629 g, 2.31 mmol, 10%). Further elution with hexane:ethyl acetate (1:1) yielded [Fc-1-H-1′-{CH(OH)C≡CCH_2OH}] (**1a**) (4.128 g, 15.29 mmol, 66%) as a yellow solid. Compound **2a**: ^1H NMR (400 MHz, $CDCl_3$): δ 4.30 (m, 1H, C_5H_4CHOH), 4.23 (m, 1H, C_5H_4), 4.17 (s, 5H, C_5H_5), 4.16–4.14 (m, 3H, C_5H_4), 1.97 (d, 1H, CHO*H*, $^3J_{H-H}$ 3.5), 1.66–1.61 (m, 2H, CH(OH)CH_2), 1.45–1.25 (m, 4H, –$CH_2CH_2CH_3$), 0.90 (t, 3H, CH_3, $^3J_{H-H}$ 7.3). MS (LSIMS): (M for $C_{15}H_{20}OFe$: 272): M^+: 272; M^+-H_2O: 255. MS (ESI): (M for $C_{15}H_{20}OFe$: 272): MNa^+: 295; M^+: 272; M^+-H_2O: 255. Compound **1a**: ^1H NMR (500 MHz, CD_3CN): δ 5.21 (d, 1H, C_5H_4CHOH, $^3J_{H-H}$ 6.5), 4.37 (m, 1H, C_5H_4), 4.28 (m, 1H, C_5H_4), 4.27 (d, 2H, $CCCH_2$, $^3J_{H-H}$ 1.6), 4.20 (s, 5H, C_5H_5), 4.17–4.15 (m, 2H, C_5H_4), 3.42 (d, 1H, CHO*H*, $^3J_{H-H}$ 6.5), 3.18 (t, 1H, CH_2OH, $^3J_{H-H}$ 1.6). HMQC: 5.21 (61.3), 4.37 (67.7), 4.28 (68.8), 4.27 (50.7), 4.20 (69.8), 4.17–4.15 (68.8, 69.0). ^{13}C NMR (125 MHz, CD_3CN): δ 90.2, 85.8 (C, C≡C), 83.9 (C, C_5H_4), 69.8 (CH, C_5H_5), 69.0, 68.83, 68.79, 67.71 (CH, C_5H_4), 61.3 (CH, C_5H_4CHOH), 50.7 (CH_2OH). MS (LSIMS): (M for $C_{14}H_{14}O_2Fe$: 270): MNa^+: 293; M^+: 270; MH^+-H_2O: 255. Anal. Calc. for $C_{14}H_{14}O_2Fe$: C, 62.25; H, 5.22; Found: C, 62.34; H, 5.25%.

4.3. Synthesis of ***1b***

To a solution of $HC{\equiv}CCH_2OH$ (0.78 ml, 0.751 g, 13.4 mmol) in tetrahydrofuran (100 ml) at −78 °C was added *n*-BuLi (18.0 ml, 27.0 mmol, 2 equiv.) dropwise. The viscous mixture was left to stir for 2 h at −78 °C. A solution of acetylferrocene (2.05 g, 9.0 mmol, 0.67 equiv.) in tetrahydrofuran (50 ml) was added, the reaction mixture left to stir for 0.5 h at −78 °C and then allowed to warm slowly to room temperature and stirred for a further 5 h. Isopropanol (20 ml) was introduced and the resulting mixture stirred for 0.5 h before being poured onto a water–ice mixture (200 ml). The organic layer was collected and the aqueous layer was extracted with chloroform (3 × 50 ml). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The oily residue was dissolved in the minimum amount of dichloromethane, adsorbed onto silica and applied to top of a chromatography column. Elution with hexane:ethyl acetate (4:1) afforded [Fc-1-H-1′-{CMe(OH)C≡CCH_2OH}] (**1b**) (0.957 g, 2.31 mmol, 10%) as a yellow solid. Compound **1b**: ^1H NMR (400 MHz, $CDCl_3$): δ 4.49–4.38 (d, 2 H, C≡CCH_2OH, $^3J_{H-H}$ 6.2), 4.35 (m, 1H, C_5H_4), 4.31–4.30 (m, 1H, C_5H_4), 4.23 (s, 5H, C_5H_5), 4.20–4.19 (m, 1H, C_5H_4), 4.17–4.16 (m, 1H, C_5H_4), 2.51 (q, 1H, C_5H_4CMeOH, $^4J_{H-H}$ 0.3), 1.70 (d, 3H, CH_3, $^4J_{H-H}$ 0.3), 1.56 (t, 1H, CH_2OH, $^3J_{H-H}$ 6.2). MS (ESI): (M for $C_{15}H_{16}O_2Fe$: 284): MNa^+: 307; M^+: 284.

4.4. Syntheses of ***1c***, ***2c*** and ***3***

To a solution of $HC{\equiv}CCH_2OH$ (3.25 ml, 3.1 g, 55.56 mmol) in tetrahydrofuran (300 ml) at −78 °C was added *n*-BuLi (85 ml, 127.5 mmol, 2.3 equiv.) dropwise. The viscous mixture was left to stir for 2 h at −78 °C. A solution of 1,1′-diacetylferrocene (5.0 g, 18.5 mmol, 0.33 equiv.) in tetrahydrofuran (100 ml) was slowly added, the resulting mixture left to stir at −78 °C for 0.5 h and then allowed to warm slowly to room temperature and stirred for a further 5 h. Isopropanol (20 ml) was added and the mixture stirred for 0.5 h before being poured onto a water–ice mixture (200 ml). The organic layer was collected and the aqueous layer extracted with chloroform (3 × 50 ml). The combined organic extracts were dried over $MgSO_4$, filtered and all volatiles removed under reduced pressure. The oily residue was re-dissolved in the minimum amount of dichloromethane, adsorbed onto silica and applied to the top a chromatography column. Elution with hexane:ethyl acetate (2:1) afforded trace amounts of a mixture composed of ferrocene and [Fc-1,1′-{CMe(OH)$(CH_2)_3CH_3$}$_2$] (**3**). Further elution with hexane:ethyl acetate (2:1) afforded minor quantities of **3** (0.045 g, 0.12 mmol, <1%) as a yellow oil. Subsequent elution with hexane:ethyl acetate (1:1) afforded [Fc-1-{CMe(O)–1′-{CMe(OH)$(CH_2)_3CH_3$}] (**2c**) (3.346 g, 10.23 mmol, 55%) as a yellow oil. Elution with hexane:ethyl acetate (1:1) gave unreacted 1,1′-diacetylferrocene (0.575 g). Finally, elution with ethyl acetate afforded [Fc-1-{CMe(O)}-1′-{CMe(OH)C≡CCH_2OH}] (**1 c**) (0.440 g, 1.22 mmol, 7%) as a yellow oily solid. Compound **3**: ^1H NMR (400 MHz, $CDCl_3$): δ 4.33 (m, 1H, C_5H_4), 4.19 (m, 1H,

C_5H_4), 4.15–4.11 (groups of m, 5H, C_5H_4), 3.98 (m, 1H, C_5H_4), 3.87 (s, 1H, O*H*), 3.46 (s, 1H, O*H*), 1.72–1.54 (m, 4H, $C_5H_4C(OH)CH_2$), 1.54 (s, 3H, $C_5H_4C(OH)CH_3$), 1.44 (s, 3H, $C_5H_4C(OH)CH_3$), 1.26–1.24 (m, 4H, $CH_2CH_2CH_3$), 1.18–1.16 (m, 4H, $CH_2CH_2CH_3$), 0.88 (t, 3H, $CH_2CH_2CH_3$, $^3J_{H-H}$ 7.0), 0.80 (t, 3H, $CH_2CH_2CH_3$, $^3J_{H-H}$ 7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 100.0 (C, C_5H_4), 99.0 (C, C_5H_4), 71.3 (C, C_5H_4COH), 71.0 (C, C_5H_4COH), 67.4, 67.3, 67.19, 67.18, 67.1, 66.7, 66.3, 66.1 (CH, C_5H_4), 45.5, 43.8 (CH_2,$CMe(OH)CH_2CH_2CH_2CH_3$), 29.1, 28.4 (CH_3, $C(OH)CH_3$), 26.7, 26.4 (CH_2, $CMe(OH)CH_2CH_2CH_2CH_3$), 23.2, 23.0 (CH_2,$CMe(OH)CH_2CH_2CH_2CH_3$), 14.1, 14.0 (CH_3,$CH_2CH_2CH_2CH_3$). MS (ESI): (M for $C_{22}H_{34}O_2Fe$: 386): MNa^+: 409; M^+: 386; MH^+-nH_2O (n = 1,2): 369, 351. Compound **2c**: ^1H NMR (500 MHz, $CDCl_3$): δ 4.83–4.82 (m, 1H, C_5H_4), 4.75–4.74 (m, 1H, C_5H_4), 4.53–4.52 (t, 2H, C_5H_4, $^3J_{H-H}$ 2.0), 4.21–4.20 (m, 1H, C_5H_4), 4.20–4.19 (m, 1H, C_5H_4), 4.13–4.12 (m, 1H, C_5H_4), 4.04–4.03 (m, 1H, C_5H_4), 2.37 (s, 3H, $C_5H_4COCH_3$), 2.19 (s, 1H, O*H*), 1.58–1.50 (m, 2H, $C(OH)CH_2$), 1.48 (s, 3H, $C_5H_4C(OH)CH_3$), 1.23–1.14 (groups of m, 4H, $CH_2CH_2CH_3$), 0.83–0.80 (t, 3H, $CH_2CH_2CH_3$, $^3J_{H-H}$ 7.0). HMQC (125 MHz, $CDCl_3$): 4.83–4.82 (coupled to C at 70.3), 4.75–4.74 (coupled to C at 69.8), 4.53–4.52 (coupled to C at 72.6, 72.5), 4.21–4.20 (m, 1H, C_5H_4, coupled to C at 69.3), 4.20–4.19 (coupled to C at 67.8), 4.13–4.12 (coupled to C at 69.0), 4.04–4.03 (coupled to C at 68.2), 2.37 (coupled to C at 27.5), 1.58–1.50 (coupled to C at 44.0), 1.48 (coupled to C at 28.2), 1.23–1.14 (coupled to C at 26.5, 23.0), 0.83–0.80 (coupled to C at 14.0). ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.0 (C, $C_5H_4COCH_3$), 101.6 (C, C_5H_4), 79.3 (C, C_5H_4), 72.6, 72.5 (CH, C_5H_4), 70.8 (C, C_5H_4COH), 70.3, 69.8, 69.3, 69.0, 68.2, 67.8 (CH, C_5H_4), 44.0 (CH_2, $CMe(OH)CH_2CH_2CH_2CH_3$), 28.2 (CH_3, $C(OH)CH_3$), 27.5 (CH_3, $C_5H_4COCH_3$), 26.5 (CH_2, $CMe(OH)CH_2CH_2CH_2CH_3$), 23.0 (CH_2, $CMe(OH)CH_2CH_2CH_2CH_3$), 14.0 (CH_3, $CMe(OH)CH_2CH_2CH_2CH_3$). MS (ESI): (M for $C_{18}H_{24}O_2Fe$: 328): MNa^+: 351; MH^+-nH_2O (n = 1, 2): 311, 293. Compound **1c**: ^1H NMR (400 MHz, $CDCl_3$): δ 4.84 (s, 1H, C_5H_4), 4.78 (s, 1H, C_5H_4), 4.56 (s, 2H, CH_2OH), 4.35 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.18 (s, 1H, C_5H_4), 4.15 (s, 1H, C_5H_4), 2.36 (s, 3H, $C_5H_4COCH_3$), 1.61 (s, 3H, $C_5H_4C(OH)(CCCH_2OH)$ CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4 (C, $COCH_3$), 98.1, 88.4 (C, C≡C), 82.1 (C, C_5H_4COMe), 79.33 (C, C_5H_4COH), 73.6, 73.4, 71.5, 70.5, 69.6, 69.4, 68.5, 67.5 (CH, C_5H_4), 66.4 (C, C_5H_4COH), 50.7 (CH_2, C≡CCH_2OH), 32.2 (CH_3, $C_5H_4COCH_3$), 27.6 (CH_3, $C(OH)CH_3$). MS (ESI): (M for $C_{17}H_{18}O_3Fe$: 326): MNa^+: 349; MH^+: 327; MH^+-nH_2O (n = 1, 2): 309, 291.

4.5. Synthesis of **2c′**

To a solution of **2c** (1.0 g, 3.05 mmol) in absolute ethanol (300 ml) (0.670 g, 3.4 mmol) was added 2,4-$(NO_2)_2C_6H_3NHNH_2$ followed by five drops of glacial acetic acid. The mixture was refluxed overnight and left to stir for 2 days at room temperature. The dark red crystalline precipitate formed during this period was filtered and washed with absolute ethanol (2 × 50 ml) to afford deep red crystalline [Fc-1-(CMe=$CHCH_2CH_2CH_3$)–1′-(CMe=NNH-2,4-$(NO_2)_2C_6H_3$)] (**2c′**) (1.441 g, 2.94 mmol, 97%). Compound **2c′**: ^1H NMR (500 MHz, $CDCl_3$): δ 11.26 (s, 1H, N*H*), 9.15 (d, 1H, C_6H_3, $^3J_{H-H}$ 2.6), 8.31 (dd, 1H, C_6H_3, $^3J_{H-H}$ 9.6, $^3J_{H-H}$ 2.5), 7.98 (d, 1H, C_6H_3, $^3J_{H-H}$ 9.6), 5.62 (td, 1H, C=CH–$CH_2CH_2CH_3$, $^3J_{H-H}$ 7.3, $^3J_{H-H}$ 1.3), 4.65 (t, 2H, C_5H_4, $^3J_{H-H}$ 1.9), 4.39 (t, 2H, C_5H_4, $^3J_{H-H}$ 1.9), 4.35 (t, 2H, C_5H_4, $^3J_{H-H}$ 1.9), 4.19 (t, 2H, C_5H_4, $^3J_{H-H}$ 1.9), 2.25 (s, 3H, $C_5H_4C(=N-)CH_3$), 1.97 (q, 2H, C=CH–$CH_2CH_2CH_3$, $^3J_{H-H}$ 7.3), 1.85 (d, 3H, $C_5H_4C(CH_3)$=$CHCH_2CH_2CH_3$, $^3J_{H-H}$ 1.3), 1.36 (sextet, 2H, C=CH–$CH_2CH_2CH_3$, $^3J_{H-H}$ 7.3), 0.88 (t, 3H, C=CH–$CH_2CH_2CH_3$, $^3J_{H-H}$ 7.3). COSY: δ 9.15 (weakly to 8.31), 8.31 (9.15, 7.98), 7.98 (8.31), 5.62 (1.97; weakly to 1.85), 4.65 (4.39), 4.39 (4.65), 4.35 (4.19), 4.19 (4.35), 1.97 (5.62, 1.36), 1.85 (weakly to 5.62), 1.36 (1.97, 0.88), 0.88 (1.36). HMQC: δ 9.15 (123.6), 8.31 (129.6), 7.98 (116.5), 5.62 (125.2), 4.65 (68.1), 4.39 (71.6), 4.35 (66.3), 4.19 (69.4), 2.25 (14.4), 1.97 (30.4), 1.85 (15.2), 1.36 (22.7), 0.88 (13.8). HMBC: δ 9.15 (144.3, 137.5, 129.6, 128.9, 123.6), 8.31 (144.3, 137.5, 123.6), 7.98 (137.5, 128.9, 116.5), 5.62 (91.1, 30.4, 22.7, 15.2), 4.65 (82.6, 71.6, 68.1), 4.39 (82.6, 71.6, 68.1), 4.35 (91.1, 69.4, 66.3), 4.19 (91.1, 69.4, 66.3), 2.25 (154.7, 82.6, 14.4), 1.97 (129.8, 125.2, 22.7, 13.8), 1.85 (129.8, 125.2, 91.1, 15.2), 1.36 (125.2, 30.4, 13.8), 0.88 (30.4, 22.7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7 (C, C=N), 144.3 (C, C_6H_3), 137.5 (C, C_6H_3), 129.8 (C, C=CH), 129.6 (CH, C_6H_3), 128.9 (C, C_6H_3), 125.2 (CH, C=CH), 123.6 (CH, C_6H_3), 116.5 (CH, C_6H_3), 91.1 (C, C_5H_4CMe=CH), 82.6 (C, C_5H_4CMe=N), 71.6, 69.4, 68.1, 66.3 (CH, C_5H_4), 30.4 (CH_2, CH_3C=$CHCH_2CH_2CH_3$), 22.7 (CH_2, CH_3C=$CHCH_2CH_2CH_3$), 15.2 (CH_3, $C_5H_4C(CH_3)$=C), 14.4 (CH_3, $C_5H_4C(CH_3)$=N), 13.8 (CH_3, CH_3C=$CHCH_2CH_2$ CH_3). MS (LSIMS): (M for $C_{24}H_{26}O_4FeN_4$: 490): MNa^+: 514; MH^+: 491. Anal. Calc. for $C_{24}H_{26}O_4FeN_4$: C, 58.79; H, 5.31; N, 11.43; Found: C, 58.97; H, 5.23; N 11.19%.

4.6. Synthesis of **4**

(a) **4a**: To a solution of **1a** (3.923 g, 14.5 mmol) in dichloromethane (500 ml) at room temperature was added $Co_2(CO)_8$ (5.0 g, 14.6 mmol, 1 equiv.) in small portions. Evolution of CO gas was accompanied by a rapid change in the colour of the solution from light yellow to dark red. The solution was allowed to stir at room temperature for 6 h. All volatiles were removed under reduced pressure and the residue re-dissolved in the minimum amount of dichloromethane, adsorbed onto silica and added to the top of a chromatography column. Elution with hexane:ethyl acetate (5:1) afforded dark red [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CH(OH)C≡CCH_2OH}] (**4a**) (6.750 g, 12.1 mmol, 84%) as the sole major product. Compound **4a**: MS (ESI): (M for $C_{20}H_{14}O_8FeCo_2$: 556): MNa^+: 579; M^+: 556; M^+-OH: 539; M^+-nCO (n = 2–5): 500–416. Compound **4a**: ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (C, CO), 99.2, 94.6 (C, C≡C), 93.4 (C, C_5H_4), 71.3 (CH, C_5H_4), 68.6 (CH, C_5H_5), 68.3 (CH, C_5H_4), 67.3 (CH, C_5H_4), 63.8 (CH, C_5H_4CHOH), 63.7 (CH_2OH). Anal. Calc. for $C_{20}H_{14}O_8FeCo_2$: C, 43.19; H, 2.52; Found: C, 43.01; H, 2.71%.

(b) **4b**: To a solution of **1b** (0.957 g, 3.37 mmol) in dichloromethane (200 ml) at room temperature was added $Co_2(CO)_8$ (1.268 g, 3.70 mmol, 1 equiv.) in small portions. Evolution of CO gas was accompanied by a rapid change in the colour of the solution from light yellow to dark red. The resulting dark red solution was stirred at room temperature for 6 h and the solvent then removed under reduced pressure. The residue was re-dissolved in the minimum amount of dichloromethane, adsorbed onto silica and applied to the top of a chromatography column. Elution with hexane:ethyl acetate (5:1) afforded dark red [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CMe(OH)C≡CCH_2OH}] (**4b**) (1.644 g, 2.88 mmol, 86%). Compound **4b**: Anal. Calc. for $C_{21}H_{16}O_8FeCo_2$: C, 44.23; H, 2.81; Found: C, 44.51; H, 2.78%.

(c) **4c**: To a solution of **1c** (0.440 g, 1.35 mmol) in dichloromethane (200 ml) at room temperature was added $Co_2(CO)_8$ (0.870 g, 2.54 mmol) in small portions. The resulting dark red was stirred at room temperature for 6 h and the solvent then removed under reduced pressure. The residue was re-dissolved in the minimum amount of dichloromethane, adsorbed onto silica and added to the top of a chromatography column. Elution with hexane:ethyl acetate (2:1) afforded red-orange [Fc-1-{CMe(O)}-1′-{$Co_2(CO)_6$-μ-η^2-CMe(OH)C≡CCH_2OH}] (**4c**) (0.426 g, 0.64 mmol, 47%). Compound **4c**: ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.9 (C, Fc$COCH_3$), 199.2 (C, CO), 105.7, 101.3 (C, C≡C), 94.5 (C, C_5H_4COMe), 79.4 (C, C_5H_4COH), 73.2 (C, C_5H_4COH), 73.0, 72.9, 71.3, 70.0, 69.8, 69.5, 68.0, 67.7 (CH, C_5H_4), 63.8 (CH_2, C≡CCH_2OH), 31.3 (CH_3, $C_5H_4COCH_3$), 27.6 (CH_3, $C(OH)CH_3$). Anal. Calc. for $C_{23}H_{18}O_9FeCo_2$: C, 45.12; H, 2.94; Found: C, 44.98; H, 3.05%.

4.7. Reaction of **4a** with C_6H_5SH

To a solution of **4a** (0.564 g, 1.01 mmol) and PhSH (0.12 ml, 1.173 mmol, 1.1 equiv.) in dichloromethane (200 ml) at −78 °C was added five drops of 48% $HBF_4 \cdot OEt_2$. After warming to 0 °C an excess of $NaHCO_3$ was added. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent removed on a rotary evaporator. The residue was re-dissolved in the minimum amount of dichloromethane and the solution applied to the base of TLC plates. Elution with hexane:ethyl acetate (3:1) afforded the deep red oily [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CH(SPh)C≡CCH_2SPh}] (**6**) (0.359 g, 0.485 mmol, 48%) and some deep red oily [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-CH(SPh)C≡CCH_2OH}] (**5**) (0.097 g, 0.149 mmol, 15%). Compound **6**: ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.0 (C, CO), 136.7 (C, C_6H_5), 136.4 (C, C_6H_5), 129.7 (CH, C_6H_5), 129.4 (CH, C_6H_5), 128.8 (CH, C_6H_5), 128.4 (CH, C_6H_5), 126.7 (CH, C_6H_5), 125.9 (CH, C_6H_5), 104.8, 94.3 (C, C≡C), 90.9 (C, C_5H_4), 69.4 (C_5H_5), 69.0, 68.2, 67.2, 67.1 (C_5H_4), 51.7 (C_5H_4CHSPh), 38.4 (C≡CCH_2SPh).

4.8. Reaction of **4a** with $HS(CH_2)_nSH$

(a) $n = 2$: To a solution of **4a** (0.655 g, 1.2 mmol) and $HS(CH_2)_2SH$ (0.10 ml, 1.2 mmol, 1 equiv.) in dichloromethane (200 ml) at −78 °C was added five drops of 48% $HBF_4 \cdot OEt_2$. On warming to 0 °C an excess of $NaHCO_3$ was added. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent removed on a rotary evaporator. The residue was re-dissolved in the minimum amount of dichloromethane and the solution applied to the base of TLC plates. Elution with hexane:ethyl acetate (6:1) afforded a deep red oily solid [Fc-1-H-1′-{*cyclo*-$Co_2(CO)_6$-μ-η^2-CH(S(CH_2)$_2$–)C≡CCH_2S–}] (**7a**) (0.407 g, 0.66 mmol, 55%) as the sole product. Compound **7a**: ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4, 199.1 (C, CO), 106.5, 98.0 (C, C≡C), 90.9 (C, C_5H_4), 69.3 (CH, C_5H_5), 68.8, 68.5, 67.0, 66.6 (CH, C_5H_4), 52.4 (C_5H_4CHSCH_2), 38.3 (C≡CCH_2), 37.0 (FcCHSCH_2), 36.8 (FcCHSCH_2CH_2).

(b) $n = 3$: To a solution of **4a** (0.694 g, 1.25 mmol) and $HS(CH_2)_3SH$ (0.125 ml, 1.25 mmol, 1 equiv.) in dichloromethane (200 ml) at −78 °C under argon was added five drops of 48% $HBF_4 \cdot OEt_2$. After warming to 0 °C an excess of $NaHCO_3$ was added. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent removed on a rotary evaporator. The residue was re-dissolved in the minimum amount of dichloromethane and the solution applied to the base of TLC plates. Elution with hexane:ethyl acetate (6:1) afforded deep red [Fc-1-H-1′-{*cyclo*-$Co_2(CO)_6$-μ-η^2-CH(S(CH_2)$_3$–)C≡CCH_2S-}] (**7b**) (0.345 g, 0.55 mmol, 44%). Compound **7b**: ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.9 (C, CO), 104.61, 97.3 (C, C≡C), 90.6 (C, C_5H_4), 69.5 (CH, C_5H_4), 69.3 (CH, C_5H_5), 68.1, 67.5, 67.1 (CH, C_5H_4), 47.1 (CH, FcCHSCH_2), 39.1 (CH_2,C≡CCH_2S), 32.4 (CH_2, FcCHSCH_2), 31.5 (CH_2, FcCHSCH_2CH_2CH_2S), 30.3 (CH_2, FcCHSCH_2CH_2CH_2S). Anal. Calc. for $C_{23}H_{18}O_6Co_2$ FeS_2: C, 43.96; H, 2.87; Found: C, 44.15; H, 2.80%.

4.9. Reaction of **4b** with or without $HS(CH_2)_2O(CH_2)_2SH$

(a) To a solution of **4b** (0.800 g, 1.40 mmol) and $HS(CH_2)_2$-$O(CH_2)_2SH$ (0.20 ml, 1.7 mmol) in dichloromethane (200 ml) at −78 °C was added five drops of 48% $HBF_4 \cdot OEt_2$. After warming to room temperature an excess of $NaHCO_3$ was added. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent removed on a rotary evaporator. The residue was re-dissolved in the minimum amount of dichloromethane and the solution applied to the base of TLC plates. Elution with hexane:ethyl acetate (6:1) afforded [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2–C(=CH_2)C≡CCH_2OH}] (**8**) (0.178 g, 0.32 mmol, 15%) as a deep red solid. Compound **8**: Anal. Calc. for $C_{23}H_{16}O_8Co_2$ Fe: C, 46.49; H, 2.70; Found: C, 46.71; H, 2.89%.

(b) To a solution of the complex **4b** (1.07 g, 1.88 mmol) in dichloromethane (200 ml) at −78 °C was added five drops of 48% $HBF_4 \cdot OEt_2$. After warming to 0 °C and stirring overnight, an excess of $NaHCO_3$ was added to the mixture. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent removed on a

Table 6
Crystallographic and data processing parameters for **2c′**, **4b**, **4c**, **7b** and **8**

Complex	**2c′**	**4b**	**4c**	**7b**	**8**
Formula	$C_{24}H_{26}FeN_4O_4.CHCl_3$	$C_{21}H_{16}Co_2FeO_8$	$C_{23}H_{18}Co_2FeO_9$	$C_{23}H_{18}Co_2FeO_6S_2$	$C_{21}H_{14}Co_2FeO_7$
M	609.71	570.05	612.08	628.20	552.03
Crystal size (mm^3)	0.23 × 0.21 × 0.07	0.23 × 0.23 × 0.12	0.25 × 0.14 × 0.07	0.16 × 0.16 × 0.14	0.32 × 0.32 × 0.23
Temperature (K)	180(2)	180(2)	180(2)	180(2)	180(2)
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)2(1)2(1)$	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$
a (Å)	10.4515(2)	7.8929(2)	7.5737(2)	10.85610(10)	13.5757(5)
b (Å)	11.7754(2)	10.9312(2)	11.6787(4)	12.9819(2)	7.7001(2)
c (Å)	13.0045(4)	25.4756(6)	14.2589(5)	34.3721(5)	20.7497(8)
α (°)	109.9290(10)	90	109.987(2)	90	90
β (°)	92.5470(10)	90	92.598(2)	91.1600(10)	108.6810(10)
γ (°)	113.6780(10)	90	91.024(2)	90	90
U ($Å^3$)	1347.06(5)	2198.01(9)	1183.28(7)	4843.16(11)	2054.78(12)
Z	2	4	2	8	4
D_{calc} ($Mg\ m^{-3}$)	1.503	1.723	1.718	1.723	1.784
F(000)	628	1144	616	2528	1104
μ(Mo Kα) (mm^{-1})	0.896	2.188	2.041	2.155	2.334
Reflections collected	16893	17667	15141	54650	11594
Independent reflections	6140	5003	5406	11048	4609
R_{int}	0.456	0.0581	0.0449	0.0443	0.0381
Restraints/parameters	7/341	0/296	0/ 318	0/613	1/ 283
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.609$, $wR_2 = 0.1592$	$R_1 = 0.0326$, $wR_2 = 0.0611$	$R_1 = 0.0470$, $wR_2 = 0.1403$	$R_1 = 0.0342$, $wR_2 = 0.0784$	$R_1 = 0.0276$, $wR_2 = 0.0688$
All data	$R_1 = 0.0878$, $wR_2 = 0.1776$	$R_1 = 0.0482$, $wR_2 = 0.0656$	$R_1 = 0.0782$, $wR_2 = 0.1800$	$R_1 = 0.0500$, $wR_2 = 0.0846$	$R_1 = 0.0327$, $wR_2 = 0.0719$
Goodness of fit on F^2 (all data)	1.039	1.029	1.120	1.071	1.033

Data in common: graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum(wF_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2+(aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, where *a* is a constant adjusted by the program; goodness of fit = $[\sum(F_o^2 - F_c^2)2/(n-p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

rotary evaporator. The residue was dissolved in the minimum amount of dichloromethane and the solution applied to the base of TLC plates. Elution with hexane:ethyl acetate (6:1) afforded [Fc-1-H-1′-{$Co_2(CO)_6$-μ-η^2-C(=CH_2)C≡CCH_2OH}] (**8**) (0.195 g, 0.35 mmol, 19%) as a deep red solid.

4.10. Crystallographic studies

Single crystal X-ray diffraction data for **2c′**, **4b**, **4c**, **7b** and **8** were collected using a Nonius-Kappa CCD diffractometer, equipped with an Oxford Cryosystems cryostream and employing Mo Kα (λ = 0.71073 Å) irradiation from a sealed tube X-ray source. Cell refinement, data collection and data reduction were performed with the programs DENZO [20] and COLLECT [21] and multi-scan absorption corrections were applied to all intensity data with the program SORTAV [22]. All structures were solved and refined with the programs SHELXS97 and SHELXL97 [23], respectively. Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for all other H atoms. Details of the data collection, refinement and crystal data are listed in Table 6.

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Appendix A. Supplementary material

CCDC 672415, 672416, 672417, 672418 and 672419 contain the supplementary crystallographic data for for compounds **2c′**, **4b**, **4c**, **7b** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.05.011.

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