

Ferrocenylalkynes as ligands in transition metal complexes

Elise Champeil and Sylvia M. Draper*

Chemistry Department, University of Dublin, Trinity College, Dublin 2, Ireland.
E-mail: suidraper@tcd.ie

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Several ferrocenylalkynes have been prepared and their reaction with dicobalt octacarbonyl led to the formation of $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})]$ **1**, $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,4-bis(ferrocenyl)butadiyne})]$ **2**, $[(\text{Co}_2(\text{CO})_6)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mu\text{-}\eta^2\text{:}\eta^2\text{-1,4-bis(ferrocenyl)butadiyne})]$ **3**, $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-1-ferrocenylethynyl-2-hydro-1,2-dihydro-[60]fullerene})]$ **4**, $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,1'-bis(phenylethynyl)ferrocene})]$ **5** and $[(\text{Co}_2(\text{CO})_6)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mu\text{-}\eta^2\text{:}\eta^2\text{-1,1'-bis(phenylethynyl)ferrocene})]$ **6**. The $[\text{Mo-Co}]$ -alkyne adducts $[\text{MoCo}(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})]$ **7** and $[\text{MoCo}(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,4-bis(ferrocenyl)butadiyne})]$ **8** were obtained from complexes **1**, **2** and **3**. The molecular structures of compounds **2**, **3**, **6** and **7** were determined by X-ray diffraction, only **6** has the cyclopentadienyl rings of the ferrocene unit eclipsed. The reaction of **1** with bis(diphenylphosphino)methane (dppm) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) resulted in the formation of $[\text{Co}_2(\text{CO})_4(\mu\text{-}\eta^1\text{:}\eta^1\text{-dppm})(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})]$ **9** and $[(\text{Co}_2(\text{CO})_4)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-dppf})(\eta^1\text{-}\mu\text{-}\eta^1\text{-dppf})(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})_2]$ **10**, respectively. The reaction of HPPH_2 with **7** gave the monosubstituted product $[\text{MoCo}(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})]$ **11**. The bis(phosphido)-bridged complex $[\text{Co}_2(\text{CO})_6(\mu\text{-PPh}_2)_2]$ undergoes regiospecific insertion with ethynylferrocene to give $[\text{Co}_2(\text{CO})_4\{(\mu\text{-}\eta^4\text{-PPh}_2\text{CHCRC(O)})\}(\mu\text{-PPh}_2)]$ (R = ferrocene) **12**, which was characterized by X-Ray diffraction and contains a five-membered metallacyclic ring.

Introduction

Compounds generated from the reaction of alkynes with transition metal carbonyls have found considerable utility. None more so, perhaps, than those complexes based on a Co_2C_2 core. The resurgence of interest in the cobalt carbonyl catalysed $[2 + 2 + 1]$ cycloaddition of alkyne, alkene and carbon monoxide (the Pauson–Khand cycloaddition) for the preparation of cyclopentenones has generated a host of new alkyne co-ordinated metal carbonyl complexes.¹ These have successfully extended the synthetic versatility of the reaction, which can be photolytically activated,² polymer supported³ and/or stereoselective.⁴ As part of our work⁵ on the metallisation of alkynes we describe here a systematic study into the modification of ferrocene substituted $\text{M}_1\text{M}_2[\text{alkyne}]$ complexes.

We chose ferrocene as a template for two reasons. It has established synthetic versatility and imparts improved crystallinity to its compounds. Here we report the molecular structures of $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,4-bis(ferrocenyl)butadiyne})]$ **2**, $[(\text{Co}_2(\text{CO})_6)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mu\text{-}\eta^2\text{:}\eta^2\text{-1,4-bis(ferrocenyl)butadiyne})]$ **3**, and $[(\text{Co}_2(\text{CO})_6)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mu\text{-}\eta^2\text{:}\eta^2\text{-1,1'-bis(phenylethynyl)ferrocene})]$ **6** which enable us to assess the structural changes imposed on changing the position and substituents on the ferrocenylalkyne.

Extended alkyne π -systems *e.g.* to give dendritic macromolecules, are of interest because of the possibility of charge transfer along the conjugated backbone.⁶ Ferrocene is an electron donating group, widely used in the construction of compounds with non-linear optical properties.⁷ In this work, we report the synthesis of $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{:}\eta^2\text{-1-ferrocenylethynyl-2-hydro-1,2-dihydro[60]fullerene})]$ **4**, a compound with potential non-linear optical properties, where the ferrocenyl donor group is linked *via* an electron-rich backbone to a polyaromatic acceptor moiety.

In addition, the attachment of adjacent organometallic moieties *via* alkyne linkages results in electronic interactions between metal atoms and the potential for tunable redox behaviour.⁸ The inclusion of a ferrocenyl moiety has allowed us

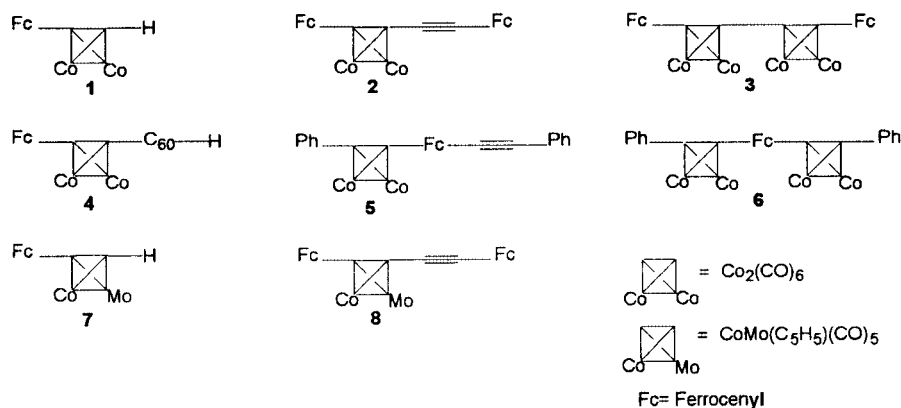
to link three different metal centres all with their own unique electronic requirements: $\text{M}^1\text{M}^2[\text{ferrocenylalkyne}]$ ($\text{M}^1 = \text{Mo}$, $\text{M}^2 = \text{Co}$). In the case of asymmetrical alkynes this differentiates the four apices of the metal–alkyne core and the complex is rendered chiral. Work in this area has shown that the use of similar diastereomerically pure complexes in the Pauson–Khand reaction can give rise to organic products with no sign of the other diastereoisomer in each case.⁹

Another approach to the development of asymmetric variants of the Pauson–Khand reaction has been to render the Co–Co core of the dicobalt hexacarbonyl adduct chiral by replacing carbonyl ligands with chiral substituents. Some recent examples have used chiral phosphines as ligands in order to increase the stereocontrol of the reaction.¹⁰ Here we report the synthesis of a number of phosphine substituted metal carbonyl moieties using 1,1'-bis(diphenyldiphenylphosphino)methane and bis(diphenylphosphino)ferrocene. The products are phosphine dependent giving the chelated $[\text{Co}_2(\text{CO})_4(\mu\text{-}\eta^1\text{:}\eta^1\text{-dppm})(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})]$ **9** and bridged $[(\text{Co}_2(\text{CO})_4)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-dppf})(\eta^1\text{-}\mu\text{-}\eta^1\text{-dppf})(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})_2]$ **10**, cobalt carbonyl species. Reaction of the mixed Mo–Co complex **7** with diphenylphosphine generated the monocarbonyl substituted $[\text{MoCo}(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-ethynylferrocene})]$ **11**. The reaction of the bis(phosphido)-bridged cobalt carbonyl species resulted in an inserted phosphametallacycle $[\text{Co}_2(\text{CO})_4\{(\mu\text{-}\eta^4\text{-PPh}_2\text{CHCRC(O)})\}(\mu\text{-PPh}_2)]$ (R = ferrocene) **12**. The later is reminiscent of an intermediate generated from the Pauson–Khand process.

Results and discussion

(a) Synthesis of dicobalt hexacarbonyl complexes

The treatment of dicobalt octacarbonyl with alkynes proceeds *via* loss of two equivalents of CO to yield the corresponding metallatetrahedranes. In a similar manner the ferrocenylalkynes used here lead to complexes **1–6** (Scheme 1). The incorporation of one or two $\text{Co}_2(\text{CO})_6$ units and a consequent reduction in



Scheme 1

triple bond character is characterised by the downfield shift in the proton and carbon NMR spectra of the products. In particular, the deshielding of the C_{60} methine proton of 1-ferrocenylethynyl-2-hydro-1,2-dihydro[60]fullerene (δ_H 7.13), ascribed to the presence of the triple bond, was lost upon complexation and a signal more reminiscent of C_{60} alkyl or phenyl derivative ($RC_{60}H$) is now observed (δ_H 6.04 for $R = Me$ and δ_H 6.81 for $R = Ph$).¹¹ The synthesis and spectroscopic characterisation (IR, 1H NMR) of complexes **2** and **3** have been reported previously.¹²

The IR spectra of **1–6** showed the expected absorptions in the carbonyl region.⁷ Compound **4** exhibits the lowest $\nu_1(A_1)$ stretching frequencies of all the complexes. This would be expected in a situation where there is an increase in electron density around the cobalt atoms of **4**, and the dicobalt unit is acting as an electron sink.

In general, in complexes **9–12** where CO ligands are replaced by poorer π -accepting phosphines, the $\nu(CO)$ IR absorption bands are lower than in the unsubstituted carbonyl complexes.¹³ For complexes **9**, **10** and **11**, where structural comparisons can be made, a trend is observed where the higher the degree of phosphine substitution, the lower the $\nu(CO)$ frequencies. The $\nu_1(A_1)$ shift of the carbonyl complexes compared to their phosphine derivatives is 50 cm^{-1} for monosubstitution in **12**, 65 cm^{-1} for disubstitution in **9** and 80 cm^{-1} for trisubstitution in **10**.

(b) Crystal structures of dicobalt hexacarbonyl complexes **2**, **3** and **6**

Single crystals of compounds **2**, **3** and **6** were obtained from saturated solutions of the compounds in dichloromethane (**2** and **3**) or hexane (**6**). The molecular structures of **2**, **3** and **6** are depicted in Figs. 1, 2 and 3. In all cases the Co–Co bond lengths are shorter ($2.46\text{--}2.47\text{ \AA}$) than those observed in the parent carbonyl (2.52 \AA).¹⁴ This observation agrees with previously reported dicobalt systems bridged by perpendicular alkynes.¹⁵ A common feature of all the molecular structures obtained is the presence of distorted Co_2C_2 cores. The asymmetry of the dimetallatetrahedranes is most clearly seen in the disparity of the (ferrocene)Co–Co bond lengths of **3** (C(11)–Co(1) $1.983(9)\text{ \AA}$, C(11)–Co(2) $1.946(9)\text{ \AA}$).

The interaction of the $Co_2(CO)_6$ units lengthens the alkyne bond consistent with the loss of $C\equiv C$ bond character resulting from the delocalisation of electron density onto the Co_2 unit. The deviation from sp hybridisation on metallisation is also apparent *e.g.* in the pivotal angles of C(11) and C(12) in **2** (C(10)–C(11)–C(12), $141.5(13)^\circ$, C(11)–C(12)–C(13), $141.6(12)^\circ$). These angles, within crystallographic error, are generally independent of the substituents attached to the alkyne but in **3** the pivotal angle (C(10)–C(11)–C(12), $136.7(8)^\circ$) is the smallest yet reported. This might be expected when the

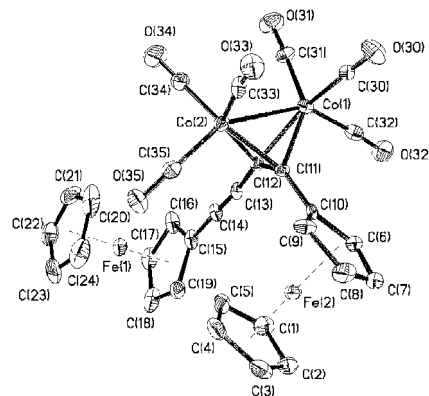


Fig. 1 ORTEP drawing of the structure of **2** (thermal ellipsoids have been drawn at the 20% probability level, hydrogen atoms have been omitted for clarity).

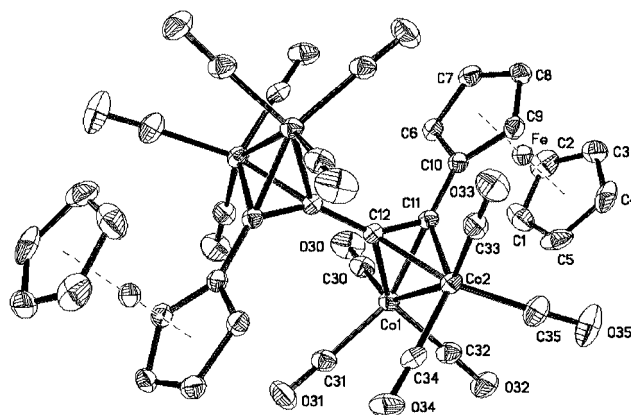


Fig. 2 ORTEP drawing of the structure of **3** (thermal ellipsoids have been drawn at the 20% probability level, hydrogen atoms have been omitted for clarity).

presence of the second $Co_2(CO)_6$ fragment is considered. Despite this difference, the C–C bond lengths of the Co_2C_2 tetrahedranes in **2**, **3** and **6** vary very little (**2**: $1.33(2)\text{ \AA}$, **3**: $1.322(12)\text{ \AA}$, **6**: $1.335(4)$ and $1.332(4)\text{ \AA}$). The free alkyne unit in **3** retains its linearity as expected and the relevant bond length is consistent with the retention of significant triple bond character (C(13)–C(14) $1.20(2)\text{ \AA}$).

An interesting feature of the molecular structures is the position of the ferrocenyl units. In **2** they exhibit an orthogonal relationship whereas in **3** they are related by the crystallographic centre of symmetry that lies at the centre of the butadiene. In both these structures the Cp rings of each ferrocene unit are staggered (average 9°). Compound **6**, however, crystallises in a configuration where the Cp rings of the linking ferrocene are eclipsed; this appears to reduce any

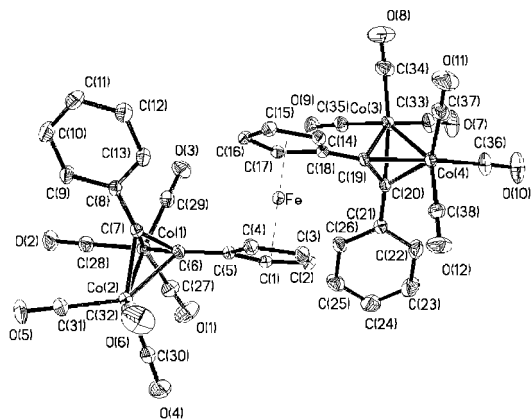


Fig. 3 ORTEP drawing of the structure of **6** (thermal ellipsoids have been drawn at the 20% probability level, hydrogen atoms have been omitted for clarity).

steric interactions between the phenyl substituents on the alkyne. Interestingly the Cp rings in unmetallated 1,1'-bis-(phenylethynyl)ferrocene are also eclipsed¹⁶ but in this case the molecule crystallises with a *cis* arrangement of the phenylethynyl ligands. Clearly the increased steric requirements on metallisation lead to the twisting of substituents away from each other but not to the extent that a 180° or *trans* arrangement is observed.

(c) Synthesis of heterobimetallic complexes

The chiral heterobimetallic MoCoC₂ adducts **7** and **8** were obtained from complexes **1** and **2** respectively, *via* replacement of a Co(CO)₃ vertex by the isolobal moiety MoCp(CO)₂¹⁷ (Scheme 1). Complex **3** lost an additional Co₂(CO)₆ in the substitution resulting in an alternative route to **8**. Interestingly, it has been reported that only one of the CC bonds of 4,4'-dipyridylbutadiyne reacts with Cp₂Mo₂(CO)₄, even in the presence of an excess of the metal complex.¹⁸

The ¹³C{¹H} NMR spectra of **7** and **8** exhibit three terminal carbonyl resonances as seen with other heterobimetallic species with a MoCoC₂ core.¹⁹ These consist of two sharp downfield signals typical of molybdenum-bound carbonyls and one broad upfield shift typical of cobalt-bound carbonyls (δ 203.0, 226.2, 225.7 for **7** and δ 202.5, 224.5, 224.4 for **8**). This implies that the two carbonyl groups on the molybdenum atom are inequivalent in solution. Hence, the ligands on the molybdenum are either non-fluxional at 293 K or, alternatively, a fluxional process can be invoked involving a series of twists of the three ligands which maintains the inequivalence.²⁰ The IR spectra of compounds **7** and **8** show seven stretching frequencies in the carbonyl region. This high number of bands is probably due to the presence of isomers in solution.

(d) Crystal structure of **7**

Single crystals of **7** were obtained from a saturated dichloromethane solution. The molecular structure of **7** is depicted in Fig. 4. The presence of a cobalt atom and a molybdenum atom means the cluster is chiral.²¹ Evidence of the presence of two enantiomers is given by the fact that crystallisation occurs in a centrosymmetric space group. Only one of these is shown in Fig. 4. The replacement of one Co(CO)₃ moiety by MoCp(CO)₂ decreases the symmetry of the metal acetylene linkage resulting in a more distorted tetrahedron than that observed for compounds **2**, **3** and **6** (C(11)–Mo 2.140(4) Å, C(12)–Mo 2.167(4) Å, C(11)–Co 2.025(4) Å, C(12)–Co 1.951(4) Å). The CoMoC₂ tetrahedron opens up so as to incorporate the two different metal centres (C(11)–C(12) 1.342(6) Å, C(11)–Co–C(12) 47.94(10)°, C(11)–Mo–C(12) 45.84(11)°). It appears that the distortion resulting from mixed metal complexation renders the reaction of both alkynes unfavourable in this case.

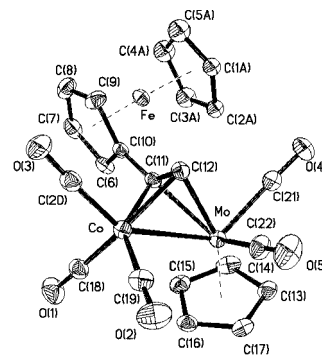


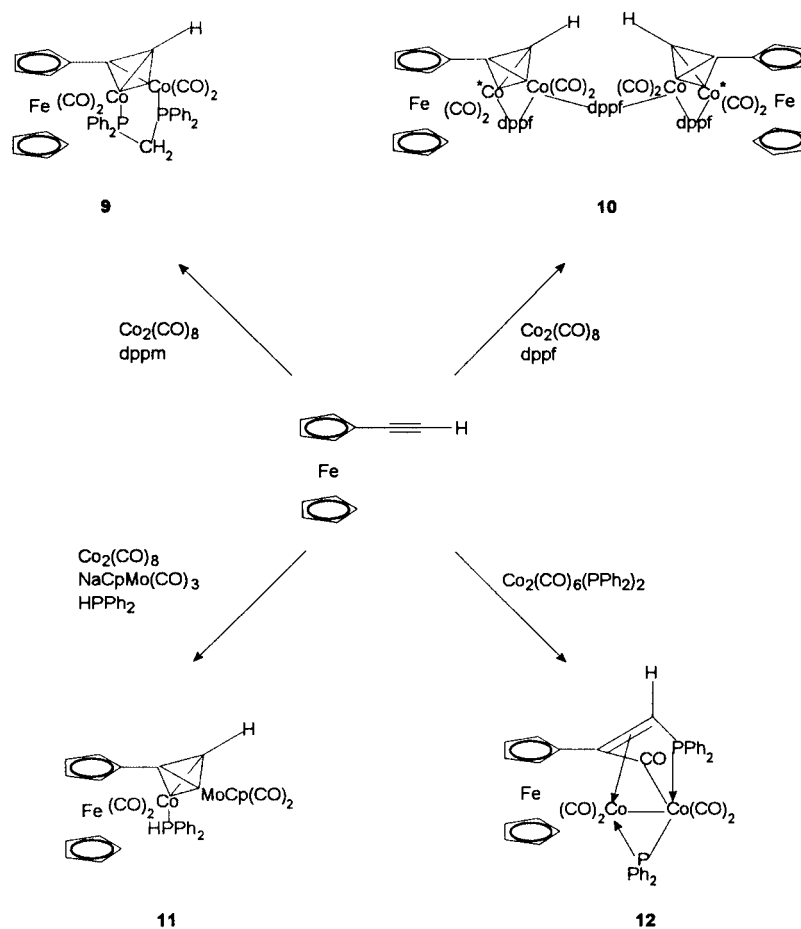
Fig. 4 ORTEP drawing of the structure of one enantiomer of **7** (thermal ellipsoids have been drawn at the 30% probability level, hydrogen atoms have been omitted for clarity). There was considerable rotational disorder of the unbound Cp ring. This was modelled as two Cp rings with refined occupancies of 55.8 and 44.2% and the carbon atoms were held isotropic.

(e) Phosphine substituted complexes

The facile substitution of carbonyl ligands by phosphines in dicobalt hexacarbonyl complexes²² prompted us to investigate the reaction of **1** with dppm and dppf. The small bite angle of dppm was expected to lead to the formation of a bridged dicobalt complex. Indeed, the addition of dppm to **1** in a 1 : 1 ratio lead to the formation of dark-red, air-stable **9**. The ³¹P{¹H} NMR spectrum of compound **9** exhibits a single resonance at δ 41.5 consistent with the coordination of both phosphorus atoms in the same chemical environment. Metal coordination results in a 62.5 ppm upfield shift of the ³¹P{¹H} NMR signal compared to the free ligand. Further evidence for the structure proposed is provided by the solution IR spectrum which exhibits four terminal stretching frequencies.

The ligand dppf has been shown to be flexible in relation to its coordination to metal carbonyl complexes, it has proven ability to both bridge and link Co(CO)₂ moieties.²³ The reaction of **1** with an excess (1.5 equivalents) of dppf, resulted in the isolation of a dark brown product **10**. Although **10** is highly air-sensitive and unstable in solution (no elemental analysis could be obtained), comparison of its spectroscopic data with similar compounds²⁴ suggests the structure presented in Scheme 2 as the linked η^1 - μ - η^1 cluster: [(Co₂(CO)₄(μ - η^1 : η^1 -dppf)₂(η^1 - μ - η^1 -dppf)(μ - η^2 : η^2 -ethynylferrocene)₂]. The ³¹P{¹H} NMR exhibits two signals in the region expected for metal coordinated phosphorus atoms, a doublet (³J(PP) 97 Hz, 4P) at δ 43.4 and a broad singlet (2P) at δ 34.4. These are shifted 60.4 ppm upfield for the doublet and 51.4 ppm upfield for the singlet compared to free dppf. The ³¹P{¹H} NMR spectrum of a similar compound with the same [(Co₂(CO)₄(μ - η^1 : η^1 -dppf)₂(η^1 - μ - η^1 -dppf)] core also shows two signals in the same region (a broad singlet (4P) at δ 42.1 and a triplet (³J(PP) 50 Hz, 2P) at δ 32.2).²⁴ In both cases the ³¹P nuclei attached to the “outer” Co atoms (labelled Co* in Scheme 2) resonate at lower field. However, different coupling patterns are observed. In Robinson’s case each “outer” P atom couples to the two nearest “inner” ones (t, ³J(PP) 50 Hz) whereas in **10** no coupling is observed for the “outer” P atoms but the “inner” P atoms couple to give a doublet (d, ³J(PP) 97 Hz). The signals in the ¹H NMR spectrum of **10** integrate for an ethynylferrocene : dppf ratio of 2 : 3 consistent with the structure proposed.

Several groups have explored the reaction of diphenylphosphine with metallic complexes containing an [M¹M²C₂] core (where M¹ = Co and M² = Mo or Co). The formation of phosphido-bridged complexes *via* P–H cleavage has literature precedence.²⁵ However, in the reaction of **7** with diphenylphosphine no cleavage of the P–H bond was observed irrespective of temperature or reaction time. Instead, diphenylphosphine coordinated to the cobalt moiety to give **11**. The ³¹P NMR proton coupled spectrum of **11** exhibits only one signal that is



Scheme 2

shifted 74 ppm upfield compared to free diphenylphosphine. This signal is a doublet of doublets ($^1J(\text{PH})$ 348 Hz, $^3J(\text{PH})$ 27.1 Hz) assigned to the HPPH_2 and HCCHPPH_2 interactions respectively. The ^{13}C NMR spectrum of compound **11** exhibits four terminal carbonyl resonances. Two at higher chemical shift are assigned to Mo-bound carbonyls and two at a lower chemical shift are assigned to cobalt-bound carbonyls. These data imply that none of the CO ligands are equivalent. The appearance of six carbonyl stretches in the IR spectra of **11** can be explained in a similar manner as that for **7** and **8**.

An alternative synthetic strategy is to react bis(phosphido)-bridged complexes such as $[\text{Co}_2(\text{CO})_6(\mu\text{-PPh}_2)_2]$ with alkynes. Here we report the first reaction of $[\text{Co}_2(\text{CO})_6(\mu\text{-PPh}_2)_2]$ with ethynylferrocene which affords **12** in 72% yield. As expected, ethynylferrocene reacted regiospecifically *i.e.* for steric reasons, only the product isomer with the more bulky alkyne substituent (ferrocene) attached to the carbon atom remote from the PPh_2 group was formed.²⁶

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the broad resonance at δ 43.6 was assigned to P(1) (for atom numbering see crystal structure below), the phosphido bridging ligand, while the broad resonance at δ 160.4 was assigned to P(2), the phosphorus atom involved in the five-membered phosphametallocycle. Both phosphorus signals are shifted upfield (157.1 ppm for P(1) and 273.9 ppm for P(2)) with respect to the ^{31}P signal in $[\text{Co}_2(\text{CO})_6(\mu\text{-PPh}_2)_2]$. In the ^{13}C NMR spectrum, the most downfield signal (δ 212.8) was assigned to the inserted CO; C(11) and C(12) appear as doublets with $^2J(\text{CP})$ 36 and $^1J(\text{CP})$ 43 Hz, respectively.

In the ^1H NMR spectrum, the signal at δ 5.63 due to the acetylenic H appears as a triplet ($^2J(\text{HP})$ 4 Hz). It is deshielded compared to the analogous H atom in **1** due to the enhanced double bond character of C(12)–C(11).

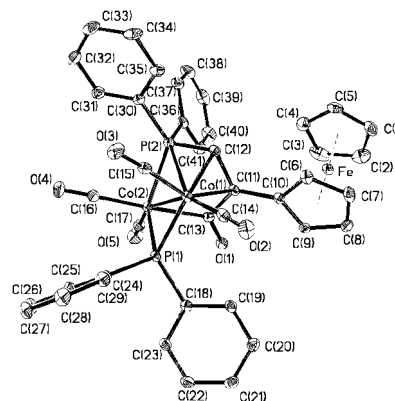


Fig. 5 ORTEP drawing of the structure of one enantiomer of **12** (thermal ellipsoids have been drawn at the 20% probability level, hydrogen atoms have been omitted for clarity); **12** crystallised with one molecule of CH_2Cl_2 per asymmetric unit. This has been omitted from the drawing.

The IR spectrum shows the presence of four terminal CO groups (four bands below 1850 cm^{-1}) and one bridging carbonyl ($\nu(\text{CO})$ at 1657 cm^{-1}) consistent with the solid state structure.

(f) Crystal structure of **12**

Dark brown crystals of **12** were obtained from a saturated dichloromethane solution. The molecular structure of **12** is shown in Fig. 5. Compound **12** crystallised with one dichloromethane molecule in space group $P\bar{1}$. C(11) has four different substituents attached to it. Therefore the molecule is chiral

Table 1 Crystallographic data for compounds **2**, **3**, **6**, **7** and **12**

	2	3	6	7	12
Empirical formula	C ₃₀ H ₁₈ Co ₂ Fe ₂ O ₆	C ₃₆ H ₁₈ Co ₄ Fe ₂ O ₁₂	C ₃₈ H ₁₈ Co ₄ FeO ₁₂	C ₂₂ H ₁₅ CoFeMoO ₅	C ₄₂ H ₃₂ C ₁₂ Co ₂ FeO ₅ P ₂
<i>M_w</i>	704.00	989.92	958.09	570.06	923.23
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.6378(7)	9.064(9)	10.914(3)	8.2046(8)	10.597(9)
<i>b</i> /Å	11.5265(7)	9.311(4)	12.113(2)	8.7356(7)	11.004(5)
<i>c</i> /Å	22.328(2)	11.82(2)	14.919(2)	14.869(2)	18.059(8)
<i>a</i> /°	90	81.84(12)	93.710(11)	78.365(7)	74.86(4)
<i>β</i> /°	90	88.1(2)	107.05(2)	87.176(8)	88.66(5)
<i>γ</i> /°	90	65.13(7)	96.54(2)	78.197(7)	71.27(5)
<i>V</i> /Å ³	2737.8(4)	896(2)	1863.3(6)	1021.7(2)	1921(2)
<i>Z</i>	4	2	2	2	2
<i>μ</i> /cm ^{−1}	2.272	2.661	2.186	2.139	1.494
2 θ_{max} /°	49.93	49.8	51.6	49.94	49.94
No. of data	2176	3289	6494	3738	6438
Unique data	2176	3081	6148	3482	6206
No. of parameters	361	244	496	275	494
<i>R</i> 1 ^a	0.0467	0.987	0.0297	0.0318	0.0373
<i>wR</i> 2 ^b	0.1292	0.223	0.065	0.0658	0.0974

^a *R*1 = $|F_o| - F_c|/\Sigma F_o$, ^b *wR*2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

and as crystallisation occurs in a centrosymmetric space group, a racemic mixture of both enantiomers is present in the crystal.

The two Co atoms are bridged by a diphenylphosphido ligand while Co(1) is incorporated in a five-membered metalacyclic ring consisting of P(2)C(12)=C(11)C(13)Co(1). The C(11)=C(12) bond is η^2 -coordinated to the second Co(2) atom. The overall structure is very similar to that already reported for [Co₂(CO)₄{(μ- η^4 -PPh₂CHCPhC(O))}(μ-PPh₂)].²⁷ The P(2)C(12)=C(11)C(13) system is folded so as to make the Co–Co and the C(11)–C(12) axes almost perpendicular. The C(11)–C(12) bond length at 1.424(4) Å is shorter than in the analogous literature system. The asymmetry of the Co(1)–P(1)Co(2) bridge, however, is comparable to that reported, with the Co(2)–P(1) distance being shorter (2.169(1) Å) than the Co(1)–P(1) distance (2.194(1) Å). Ferrocene substitution in comparison to phenyl substitution causes a marginal reduction in the steric strain of the five-membered metallocycle. This is illustrated by the relevant bond angles (C(11)–C(12)–P(2) 112.0(3)°, C(12)–C(11)–C(13) 115.0(3)°, Co(1)–C(13)–C(11) 110.3(2)°, Co(1)–P(2)–C(12) 95.2(1)°). The carbons of the Cp rings are staggered as seen before in **2** and **3** by *ca.* 9°.

Conclusion

This work illustrates the coordination of several ferrocenylalkynes to [Co–Co] and [Co–Mo] moieties. The various acetylenic ligands synthesised react readily with Co₂(CO)₈, NaMoCp(CO)₃ and Co₂(CO)₆(PPh₂)₂. However, the coordination of two [Co–Mo] units to two adjacent triple bonds proved too sterically demanding. In the solid state, the ferrocenyl fragments of the complexes synthesised show high flexibility and adopt a configuration which minimises steric interactions. Further work will examine a way to modify the electronic properties of such compounds in order to investigate their redox and NLO behaviour. This work has shown that phosphine substitution on the cobalt atom of such complexes proceeds easily. For instance, the electronic environment of the metal atoms could be modified *via* replacement of some carbonyls by suitable chiral phosphine ligands. An alternative method would be to modify the sphere of coordination by incorporating M(L)_{*n*} building blocks (M = Ni, Fe; L = Cp, CO) to form alkyne bridged clusters of higher nuclearity and differing electronic properties.

Experimental

General comments

Unless otherwise stated, all reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Chromatographic separations were undertaken in air except for compound **6** where dry and degassed solvents were used under a nitrogen atmosphere were used. CHCl₃-*d* and acetone-*d*₆ were distilled from molecular sieves. IR spectra were recorded on a Perkin-Elmer Paragon spectrophotometer. NMR spectra were recorded on DPX 400 spectrometer operating at 400.13 MHz for ¹H, 100.61 MHz for ¹³C and 161.97 MHz for ³¹P nuclei, respectively. ¹H and ¹³C NMR were referenced relative to SiMe₄, ³¹P NMR chemical shifts are given relative to 85% orthophosphoric acid with downfield shifts reported as positive. Analyses were performed by the analytical service at University College Dublin. The ferrocenylalkynes were prepared following reported literature procedures.^{16,28} The C₆₀ ethynyl ligand was synthesised using a modified literature procedure (THF was used as the solvent system).²⁹

X-Ray crystallographic data collection and refinement of the structures

Single crystals of **2**, **3**, **6**, **7** and **12** were mounted in glass capillaries. Data were collected on an Enraf-Nonius CAD-4 diffractometer (Mo-Kα, λ = 0.71073 Å radiation, graphite monochromator, ω -2 θ scan mode) at 20 °C. Unit cell dimensions were refined with 25 reflections. The final cell parameters were determined using the Celdim routine. An empirical absorption correction based on azimuthal scans of 6–8 reflections was applied to the data collected for **6** and **7**. The crystal data and experimental parameters for **2**, **3**, **6**, **7** and **12** are summarised in Table 1.

The data were processed using the WINGX software packages. The structures were solved by automatic direct methods using SHELXS-86³⁰ and were refined by full-matrix least-squares analysis on *F*² with SHELXL93.³¹ All structures were readily solved and refined by direct methods. All non-hydrogen atoms were refined anisotropically except the carbon atoms of the unbound Cp ring in **12**. In this case the rotational disorder was modelled as two Cp rings with refined occupancies of 55.8 and 44.2% and the carbon atoms were held isotropic.

The relatively high *R*₁ value for **3** was a result of the data collection (tube fading) and not poor crystal quality.

Crystals of **12** contain one molecule of dichloromethane per asymmetric unit. This dichloromethane solvent molecule was found to be well defined and the chlorine and carbon atoms were refined anisotropically.

The hydrogen atoms bound to C(12) in **7** and **12** were located from difference Fourier maps and refined isotropically. All other CH hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Diagrams of the structures were drawn using ORTEX.³²

CCDC reference numbers 151896–151900.

See <http://www.rsc.org/suppdata/dt/b0/b008803j/> for crystallographic data in CIF or other electronic format.

Synthesis of [Co₂(CO)₈(μ, η²: η²-ethynylferrocene)] **1**

Dicobalt octacarbonyl (1.32 g, 4 mmol) was added to a solution of ethynylferrocene (0.84 g, 4 mmol) in hexane (100 ml). The reaction was allowed to proceed for 12 h at room temperature. After removal of the solvent, compound **1** was purified by flash chromatography (SiO₂, hexane) followed by crystallisation from hexane (1.785 g, 90%) (Found: C, 43.31; H, 1.98; Fe, 11.04; Co, 24.02. C₁₈H₁₀O₆FeCo₂ requires C, 43.59; H, 2.03; Fe, 11.26; Co, 23.76%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2092s, 2066w, 2051s, 2021s, 2010m and 1983w (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.3 (1 H, s, H_{acetylenic}), 4.37 (2 H, s, H_{Cp}), 4.34 (2 H, s, H_{Cp}) and 4.18 (5 H, s, H_{Cp}); $\delta_{\text{C}}(\text{CDCl}_3)$ 203 (6 C, br, CO), 84.3 (1 C, (C–C)[Co–Co]), 79.9 (1 C, (C–C)[Co–Co]), 73.8 (1 C, C_{quat/Cp}), 70.2 (2 C, C_{Cp}), 69.7 (5 C, C_{Cp}) and 69 (2 C, C_{Cp}).

Synthesis of [Co₂(CO)₈(μ-η²: η²-1,4-bis(ferrocenyl)butadiyne)] **2**

Dark purple crystals of **2** were from a saturated solution of dichloromethane at 195 K (0.985 g, 70%) (Found: C, 50.75; H, 2.18; Fe, 16.04; Co, 17.06. Calc. for C₃₀H₁₈O₆Fe₂Co₂: C, 51.18; H, 2.58; Fe, 15.87; Co, 16.74%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2090m, 2078w, 2055vs, 2032vs, 2024s and 1981w (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.51 (2 H, t, *J*(HH) 2 Hz, H_{Cp}), 4.41 (2 H, t, *J*(HH) 2 Hz, H_{Cp}), 4.39 (5 H, s, H_{Cp}), 4.16 (2 H, t, *J*(HH) 2 Hz, H_{Cp}), 4.34 (2 H, t, *J*(HH) 2 Hz, H_{Cp}) and 4.30 (5H, s, H_{Cp}); $\delta_{\text{C}}(\text{CDCl}_3)$ 198.3 (6 C, br, CO), 99.2 (1 C, (C–C)[Co–Co]), 93.8 (1 C, (C–C)[Co–Co]), 84.8 (1 C, C_{acetylenic}), 83.3 (1 C, C_{acetylenic}), 71.2 (2 C, C_{Cp}), 70.6 (1 C, C_{quat/Cp}), 69.5 (5 C, C_{Cp}), 69.4 (2 C, C_{Cp}), 69.3 (5 C, C_{Cp}), 69.1 (1 C, C_{quat/Cp}), 69.0 (2 C, C_{Cp}) and 68.8 (2 C, C_{Cp}).

Synthesis of [(Co₂(CO)₈)₂(μ-η²: η², μ-η²: η²-1,4-bis(ferrocenyl)-butadiyne)] **3**

Dark green crystals of **3** were obtained from a saturated solution of dichloromethane at 195 K (1.742 g, 88%) (Found: C, 43.42; H, 2.35; Fe, 10.89; Co, 23.57. Calc. for C₃₆H₁₈O₁₂Fe₂Co₄: C, 43.68; H, 1.83; Fe, 11.28; Co, 23.81%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2096w, 2077m, 2056vs, 2033m, 2022s and 1975w (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.45 (4 H, t, *J*(HH) 2 Hz, H_{Cp}), 4.35 (4 H, t, *J*(HH) 2 Hz, H_{Cp}) and 4.27 (10 H, s, H_{Cp}); $\delta_{\text{C}}(\text{CDCl}_3)$ 198.7 (12 C, br, CO), 100.5 (2 C, (C–C)[Co–Co]), 96.4 (2 C, (C–C)[Co–Co]), 87.8 (2 C, C_{quat/Cp}), 70.6 (4 C, C_{Cp}), 69.1 (10 C, C_{Cp}) and 68.2 (4 C, C_{Cp}).

Synthesis of [Co₂(CO)₈(μ-η²: η²-1-ferrocenylethynyl-2-hydro-1,2-dihydro[60]fullerene)] **4**

1-Ferrocenylethynyl-2-hydro-1,2-dihydro[60]fullerene (0.072 g, 0.077 mmol) was stirred with one equivalent (0.026 g, 0.077 mmol) of dicobalt octacarbonyl in 100 ml of toluene at room temperature for 12 h, the solvent was removed and **4** was purified by flash chromatography (SiO₂, CS₂-hexane 1 : 1) (0.079 g, 85%) (Found: C, 76.45; H, 1.24. C₇₈H₁₀O₆FeCo₂ requires C, 77.00; H, 0.83%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2080w, 2061vs, 2053vs, 2038w, 2028w and 1982w (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.13 (1 H, s, C₆₀H), 4.83

(2 H, s, H_{Cp}), 4.54 (5 H, s, H_{Cp}) and 4.26 (2 H, s, H_{Cp}); $\delta_{\text{C}}(\text{CDCl}_3\text{--CS}_2)$ 198.93 (6 C, br, CO), 154.55, 152.57, 147.44, 147.16, 146.35, 146.31, 146.27, 146.21, 146.10, 146.07, 145.08, 145.52, 145.40, 145.32, 145.26, 144.62, 144.39, 144.10, 142.58, 142.54, 142.23, 142.02, 141.94, 141.83, 141.60, 140.33, 139.99, 136.00, 135.06 (C₆₀ core), 92.41 (1 C, (C–C)[Co–Co]), 84.77 (1 C, (C–C)[Co–Co]), 71.6 (1 C, C_{quat/Cp}), 70.66 (2 C, C_{Cp}), 70.15 (5 C, C_{Cp}), 70.04 (2 C, C_{Cp}), 67.64 (1 C, quaternary sp³-C in the C₆₀ core) and 63.02 (1 C, CH in the C₆₀ core); λ_{\max}/nm (cyclohexane) 203, 245, 253, 316 and 373.

Synthesis of [Co₂(CO)₈(μ-η²: η²-1,1'-bis(phenylethynyl)-ferrocene)] **5**

1,1'-Bis(phenylethynyl)ferrocene (0.046 g, 0.12 mmol) was dissolved in 50 ml of dichloromethane. One equivalent of Co₂(CO)₈ (0.041 g, 0.12 mmol) was added and the reaction mixture was allowed to stir overnight at room temperature. TLC analysis revealed two spots attributed to compound **5** (*R*_f = 0.5) and **6** (*R*_f = 0.3). Products were separated by flash chromatography (SiO₂, hexane–dichloromethane 4 : 1). Dark purple crystals of **5** were obtained from a saturated solution of hexane–dichloromethane 1 : 1 at 195 K (0.058 g, 72%) (Found: C, 57.63; H, 3.08. C₃₂H₁₈O₆FeCo₂ requires C, 57.18; H, 2.70%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2085s, 2050vs, 2025vs, 2020s, 2007w and 1980w (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.93–7.91 (2 H, m, H_{phenyl}), 7.53–7.34 (8 H, m, H_{phenyl}), 4.57 (2 H, t, *J*(HH) 1.76 Hz, H_{Cp}), 4.53 (2 H, t, *J*(HH) 2.04 Hz, H_{Cp}) and 4.25 (2 H, t, *J*(HH) 1.76 Hz, H_{Cp}); $\delta_{\text{C}}(\text{CDCl}_3)$ 199.3 (6 C, br, CO), 138.4 (1 C, C_{quat/phenyl}), 131.4, 129.7, 128.9, 128.3, 127.9 (10 C, C_{phenyl}), 123.6 (1 C, C_{quat/phenyl}), 91.6 (1 C, (C–C)[Co–Co]), 91.0 (1 C, (C–C)[Co–Co]), 87.4 (1 C, C_{quat/Cp}), 86.6 (1 C, C_{acetylenic}), 86.3 (1 C, C_{acetylenic}), 72.6 (2 C, C_{Cp}), 72.2 (2 C, C_{Cp}), 71.5 (2 C, C_{Cp}), 70.8 (2 C, C_{Cp}) and 66.4 (1 C, C_{quat/Cp}).

Synthesis of [(Co₂(CO)₈)₂(μ-η²: η², μ-η²: η²-1,1'-bis(phenylethynyl)ferrocene)] **6**

1,1'-Bis(phenylethynyl)ferrocene (0.046 g, 0.12 mmol) was dissolved in 50 ml of dichloromethane. Two equivalents of Co₂(CO)₈ (0.082 g, 0.24 mmol) were added and the reaction mixture was allowed to stir overnight at room temperature. TLC analysis revealed the formation of **6** (*R*_f = 0.3). The product was purified by flash chromatography (SiO₂, hexane–dichloromethane 4 : 1). Green crystals of **6** were obtained from a saturated solution of hexane at 195 K (0.094 g, 82%) (Found: C, 47.26; H, 1.79; Co, 24.41; Fe, 5.66. C₃₈H₁₈O₁₂Co₄Fe requires C, 47.64; H, 1.89; Co, 24.6; Fe, 5.83%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2084m, 2050vs, 2026s, 2019s, 2004w and 1983w (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.85–7.83 (4 H, m, H_{phenyl}), 7.50–7.39 (6H, m, H_{phenyl}), 4.55 (4 H, t, *J*(HH) 2.02 Hz, H_{Cp}) and 4.34 (4 H, t, *J*(HH) 2.02 Hz, H_{Cp}); $\delta_{\text{C}}(\text{CDCl}_3)$ 198.5 (12 C, br, CO), 138.4 (2 C, C_{quat/phenyl}), 129.6, 128.9, 128.0 (10 C, C_{phenyl}), 91.8 (2 C, (C–C)[Co–Co]), 91.0 (2 C, (C–C)[Co–Co]), 86.0 (2 C, C_{quat/Cp}), 72.2 (4 C, C_{Cp}) and 70.6 (4 C, C_{Cp}).

Synthesis of [MoCo(CO)₅(η⁵-C₅H₅)(μ-η²: η²-ethynylferrocene)] **7**

To a solution of **1** (0.42 g, 2 mmol) in 60 ml of THF was added a solution of NaCpMo(CO)₃ prepared as follows: 0.54 g (1.11 mmol) of Cp₂Mo₂(CO)₆ in 20 ml of THF was added to an amalgam (0.1 g of sodium with 5 g of mercury). The reaction was complete after 1 h at reflux. After removal of the solvent, the red residue was chromatographed (SiO₂, hexane–dichloromethane 3 : 1). Further crystallisation from dichloromethane afforded pure **7** (0.638 g, 56%) (Found: C, 45.8; H, 3.17; Fe, 9.31. C₂₂H₁₅O₅FeCoMo requires C, 46.35; H, 2.65; Fe, 9.79%; $\nu_{\max}/\text{cm}^{-1}$ (CO) 2067w, 2050m, 2027s, 2014s, 2000vs, 1982s and 1944m (hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.01 (1 H, s, H_{acetylenic}), 5.39 (5 H, s, H_{MoCp}), 4.21 (2 H, s, H_{FeCp}), 4.20 (1 H, s, H_{FeCp}), 4.17 (5 H, s, H_{FeCp}) and 4.14 (1 H, s, H_{FeCp}); $\delta_{\text{C}}(\text{CDCl}_3)$ 226.2 (1 C, s,

MoCO), 225.7 (1 C, s, MoCO), 203 (3 C, br, CoCO), 91.1 (5 C, C_{MoCp}), 82.8 (1 C, br, (C–C)[Mo–Co]), 79.8 (1 C, (C–C)[Mo–Co]), 70 (1 C, C_{FeCp}), 69.3 (6 C, C_{FeCp}), 68.6 (1 C, C_{quat/FeCp}), 68.1 (1 C, C_{FeCp}) and 67.9 (1 C, C_{FeCp}).

Synthesis of [MoCo(CO)₅(η⁵-C₅H₅)(μ-η²: η²-1,4-bis(ferrocenyl)-butadiene)] 8

0.1 g (0.14 mmol) of **2** were added to a solution of NaMoCp(CO)₃ prepared as above but using 0.069 g (0.14 mmol) of Cp₂Mo₂(CO)₆. The mixture was allowed to stir for 0.5 h in refluxing THF. After removal of the solvent, the red residue was chromatographed (SiO₂, hexane–dichloromethane 3 : 1) (0.065 g, 60%), (Found: C, 52.14; H, 3.53; Fe, 14.17. C₃₄H₂₃O₅Fe₂CoMo requires C, 52.48; H, 2.98; Fe, 14.35%; ν_{max}/cm⁻¹ (CO) 2064w, 2051m, 2006vs, 1990s, 1983s, 1967w and 1950m (hexane); δ_H(CDCl₃) 5.39 (5 H, s, H_{MoCp}), 4.56 (1 H, t, J(HH) 1.6 Hz, H_{FeCp}), 4.48 (1 H, t, J(HH) 1.6 Hz, H_{FeCp}), 4.39 (4 H, t, J(HH) 1.6 Hz, H_{FeCp}), 4.38 (5 H, s, H_{FeCp}) and 4.28 (10 H, s, H_{FeCp}); δ_C(CDCl₃) 224.5 (1 C, s, MoCO), 224.4 (1 C, s, MoCO), 202.5 (3 C, br, CoCO), 95.1 (1 C, C_{acetylenic}), 91.2 (5 C, C_{MoCp}), 87.2 (1 C, br, (C–C)[Mo–Co]), 85.7 (1 C, C_{acetylenic}), 75.1 (1 C, br, (C–C)[Mo–Co]), 71.2, 71.1, 69.1, 68.4, 67.8, 67.5 (8 C, C_{FeCp}), 69.5 (5 C, C_{FeCp}), 68.9 (5 C, C_{FeCp}), 68.4 (1 C, C_{quat/Cp}) and 65.8 (1 C, C_{quat/Cp}).

Synthesis of [Co₂(CO)₄(μ-η¹: η¹-dppm)(μ-η²: η²-ethynyl-ferrocene)] 9

Ligand dppm (0.12 g, 0.302 mmol) and **1** (0.15 g, 0.302 mmol) were stirred in 75 ml of dichloromethane at room temperature for 4 h. The resulting red product was isolated by flash chromatography (SiO₂, hexane–ethyl acetate 3 : 1) and purified by crystallisation from acetone (0.179 g, 72%) (Found: C, 59.40; H, 3.94; Fe, 6.54; Co, 14.08. C₄₁H₃₃O₄P₂FeCo₂ requires C, 59.66; H, 4.03; Fe, 6.76; Co, 14.28%; ν_{max}/cm⁻¹ (CO) 2019m, 1989s, 1962s and 1943 (sh) (hexane); δ_H(acetone-*d*₆) 7.52 (8 H, m, H_{phenyl}), 7.30 (12 H, m, H_{phenyl}), 6.09 (1 H, t, ³J(HP) 6.8 Hz, H_{acetylenic}), 4.39 (2 H, t, J(HH) 1.6 Hz, H_{Cp}), 4.26 (2 H, t, J(HH) 2 Hz, H_{Cp}), 4.19 (5 H, s, H_{Cp}), 4.05 (1 H, dt, J 10.8, 6 Hz, CH₂) and 3.47 (1 H, dt, J 10.8, 6 Hz, CH₂); δ_C(acetone-*d*₆) 209.6 (4 C, br, CO), 137.5 (2 C, t, ¹J(CP) 20 Hz, C_{quat/phenyl}), 137.4 (2 C, t, ¹J(CP) 20 Hz, C_{quat/phenyl}), 132.6 (4 C, t, ²J(CP) 6 Hz, C_{phenyl}), 132.3 (4 C, t, ²J(CP) 6 Hz, C_{phenyl}), 130.1 (1 C, C_{phenyl}), 130 (1 C, C_{phenyl}), 128.7 (4 C, t, ³J(CP) 5 Hz, C_{phenyl}), 127.8 (4 C, t, ³J(CP) 005 Hz, C_{phenyl}), 90.8 (1 C, (C–C)[Co–Co]), 76.4 (1 C, br, (C–C)[Co–Co]), 70.4 (2 C, C_{Cp}), 69.9 (5 C, C_{Cp}), 68.4 (2 C, C_{Cp}), 67.7 (1 C, C_{quat/Cp}) and 40.3 (1 C, t, ¹J(CP) 22 Hz, CH₂); δ_P(acetone-*d*₆) 41.5 (1 P, s).

Synthesis of [(Co₂(CO)₄)(μ-η¹: η¹-dppf)(η¹-μ-η¹-dppf)-(μ-η²: η²-ethynylferrocene)] 10

Ligand dppf (0.3 g, 0.54 mmol) was added to a solution of **1** (0.18 g 0.36 mmol) in 150 ml of dichloromethane. The solution was stirred overnight at room temperature. Compound **10** was purified by column chromatography (SiO₂, hexane–ethyl acetate 3 : 1) (0.199 g, 45%), ν_{max}/cm⁻¹ (CO) 2003vs, 1977vs, 1962 (sh) and 1920 (sh) (hexane); δ_H(acetone-*d*₆) 7.12–7.05 (60 H, m, H_{phenyl}), 6.07 (2 H, t, ³J(HP) 14 Hz, H_{acetylenic}), 4.53 (4 H, s, H_{Cp}), 4.45 (4 H, s, H_{Cp}), 4.39 (8 H, s, H_{Cp}), 4.25 (4 H, s, H_{Cp}), 4.11 (4 H, s, H_{Cp}), 4.04 (10 H, s, H_{Cp}), 3.72 (4 H, s, H_{Cp}) and 3.95 (4 H, s, H_{Cp}); δ_P(acetone-*d*₆) 43.4 (4 P, d, ³J(PP) 97 Hz, PCo) and 34.4 (2 P, br, PCo*).

Synthesis of [MoCo(CO)₄(η⁵-C₅H₅)(PPh₂)(μ-η²: η²-ethynyl-ferrocene)] 11

HPPH₂ (0.10 g, 0.56 mmol) was added to compound **7** (0.15 g, 0.28 mmol) in 50 ml of toluene. The solution was heated at 338 K for 48 h. After removal of the solvent under vacuum, the residue was dissolved in degassed hexane–dichloromethane

(14 : 15) and purified by column chromatography under nitrogen (SiO₂, hexane–dichloromethane 14 : 15) (0.167 g, 82%) (Found: C, 55.00; H, 3.94. C₃₃H₂₆O₄PFeCoMo requires C, 54.43; H, 3.60%; ν_{max}/cm⁻¹ (CO) 2017s, 2005m, 1970vs, 1946s, 1932vs and 1866m (hexane); δ_H(acetone-*d*₆) 7.63–7.40 (10 H, m, H_{phenyl}), 6.05 (1 H, t, ³J(HP) 9.2 Hz, H_{acetylenic}), 5.79 (1 H, d, ¹J(HP) 348 Hz, HPPH₂), 5.62 (5 H, s, H_{MoCp}), 4.47 (1 H, m, H_{FeCp}), 4.25 (1 H, m, H_{FeCp}), 4.14 (1 H, m, H_{FeCp}), 4.09 (1 H, m, H_{FeCp}) and 4.04 (5 H, s, H_{FeCp}); δ_C(acetone-*d*₆) 237.1 (1 C, s, MoCO), 233.7 (1 C, s, MoCO), 227.5 (1 C, CoCO), 227.4 (1 C, CoCO), 133.9 (1 C, d, ¹J(CP) 12 Hz, C_{quat/phenyl}), 133.8 (1 C, d, ¹J(CP) 12 Hz, C_{quat/phenyl}), 133.2 (2 C, d, ²J(CP) 10 Hz, C_{phenyl}), 132.6 (2 C, d, ²J(CP) 10 Hz, C_{phenyl}), 130.6 (1 C, C_{phenyl}), 130.4 (1 C, C_{phenyl}), 129.3 (2 C, d, ³J(CP) 3 Hz, C_{phenyl}), 129.2 (2 C, d, ³J(CP) 3 Hz, C_{phenyl}), 92.4 (5 C, C_{MoCp}), 83.9 (1 C, (C–C)[Mo–Co]), 82.08 (1 C, br, (C–C)[Mo–Co]), 70.88 (1 C, C_{quat/FeCp}), 70.82 (1 C, C_{FeCp}), 69.6 (1 C, C_{FeCp}), 66.9 (1 C, C_{FeCp}), 69.7 (5 C, C_{FeCp}) and 70.3 (1 C, C_{FeCp}); δ_P(proton coupled, acetone-*d*₆) 35.2 (1 P, dd, ^{1,3}J(PH) 348, 27.1 Hz).

Synthesis of [Co₂(CO)₄(μ-η⁴-PPh₂CHCRC(O))(μ-PPh₂)] (R = ferrocene) 12

A 500 ml Berghol autoclave was charged with toluene (50 ml) and Co₂(CO)₈ (0.8 g, 2.3 mmol). HPPH₂ (0.8 ml, 4.3 mmol) was then added to it. The autoclave was sealed, purged with CO, pressured to 80 atm, and heated to 383 K for 24 h. When the sample was required, the CO pressure was released and the toluene solution of [Co₂(CO)₆(μ-PPh₂)₂] decanted. Ethynyl-ferrocene (0.48 g, 2.3 mmol) was then dissolved in 50 ml of toluene to which the previous solution of [Co₂(CO)₆(μ-PPh₂)₂] was added. The resulting mixture was allowed to stir 15 h at 293 K. After removal of the solvent *in vacuo*, **12** was isolated by chromatography (SiO₂, hexane–dichloromethane 1 : 1). Crystallisation from dichloromethane afforded pure **12** (1.38 g, 72%) (Found: C, 55.76; H, 4.20; P, 6.82; Fe, 6.14; Co, 12.06. C₄₁H₃₀O₅P₂FeCo₂CH₂Cl₂ requires C, 54.64; H, 3.49; P, 7.71; Fe, 6.05; Co, 12.77%; ν_{max}/cm⁻¹ (CO) 2045m, 2016vs, 2006m, 1975m and 1657w (hexane); δ_H(acetone-*d*₆) 8.35–7.29 (20 H, m, H_{phenyls}), 5.63 (1 H, t, ²J(HP) 4 Hz, H_{acetylenic}), 4.28 (1 H, s, H_{Cp}), 4.03 (1 H, s, H_{Cp}), 4.01 (2 H, s, H_{Cp}) and 3.55 (5 H, s, H_{Cp}); δ_C(acetone-*d*₆) 212.8 (1 C, s, [PPh₂CHCRC(O)]), 208.5 (2 C, s, CoCO), 201.7 (2 C, s, CoCO), 147.5–127.2 (20 C, C_{phenyls}), 70.06 (1 C, C_{quat/Cp}), 68.2 (5 C, C_{Cp}), 68 (1 C, C_{Cp}), 67.3 (2 C, C_{Cp}), 66.5 (1 C, C_{Cp}), 85.45 (1 C, dd, ^{1,2}J(CP) 43, 36 Hz, (C–C)[Co–Co]) and 42.5 (1 C, dd, ^{1,2}J(CP) 43, 36 Hz, CPPH₂); δ_P(acetone-*d*₆) 160.4 (1 P, br, CPPH₂) and 43.6 (1 P, br, CoPPh₂Co).

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