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FULL PAPER

Ferrocenylethynylnaphthalenes and acenaphthylenes; communication between ferrocenyl and cluster redox centres

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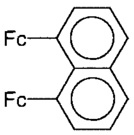
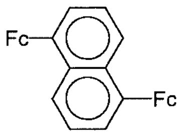
The synthesis and comparative investigation of the reactivity and communication between redox centres in *peri*-1,8- (**3**) and 1,5- (**4**) bis(ferrocenylethynyl)naphthalene and acenaphthylenes, and their $Co_2(CO)_{6-x}L_x$ derivatives, are described. The cofacial alkyne configuration in **3** encourages acenaphthylene formation; 1-ferrocenylacenaphthylene and triferrocenylbenzo[*a*]acenaphthylene directly from **3** and (*E*,*E*)-diferrocenyliodobut[*a*]acenaphthylene-1,2-diene **9**, diferrocenylcyclopent[*a*]acenaphthylen-8-one **10**, furan[*a*]acenaphthylene and γ-lactone[*a*]acenaphthylene from reactions with $^iPr_2NH_2^+I^-/Co_2(CO)_{6-x}L_x$. **9** has an (*E*,*E*) configuration (X-ray structure) and steric crowding causes significant distortion of the diene fragment. $Co_2(CO)_6$ and $Co_2(CO)_4(dppm)$ complexes with **4** but not **3** have been characterised. 1,5-$\{PhC_2Co_2(CO)_4[P(OMe)_3]_2\}_2C_{10}H_6$ has the phosphite ligands in pseudo-axial sites and there is an unusually short Co–Co bond (2.437 Å). Electrochemical and spectroscopic data show that there is effective communication between two ferrocenyl or two cluster redox centres, reinforced by the transannular interaction, but the ferrocenyl and cluster electrophores act independently of one another. The primary reduction centre for the acenaphthylenes is the *peri* ring system. The mixed valence $\mathbf{10}^+$ has been characterised.

Introduction

Efficient energy transfer between redox- or photo-active centres is an important goal for materials incorporating organometallic species because of their potential technological applications.[1] A considerable body of work has focused on the integration of redox-active cobalt clusters and ferrocene into rigid skeletons tethered by alkyne groups, with or without aromatic spacers.[2–6] While ferrocene has been used in a plethora of arrays, the recognition that communication can be established with metal clusters is relatively recent.[7] In some instances thermolysis of cluster arrays leads to materials with metallic properties.[8,9] For nanoscale devices it would be desirable to incorporate a photophore so that there is an alternative response other than that from an electrode. A fluorescence output is attractive for many reasons and it is our intention to synthesize arrays with metal cluster/ferrocenyl/fluorophore components. One type of array with interesting structural possibilities are those which result from self-assembly through cofacial interactions. Rosenblum and coworkers[10] have prepared a number of cofacial 1,8-ferrocenylnaphthalene molecules which, as discrete molecules or in polymers, demonstrate communication between the ferrocenyl redox centres. A photon-assisted electron-hopping process was postulated[11] as the mechanism for the increased electrical conductivity for iodine-doped compressed polymers. These systems have ferrocene bound directly to a 1,8-naphthalene skeleton **1a**.



1a



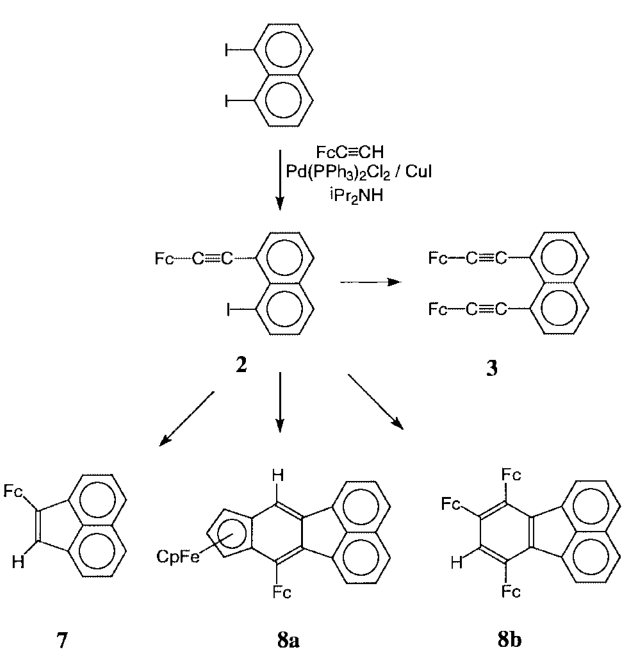
1b

In keeping with our emphasis on redox centres tethered to alkynes we have investigated the near-rigid 1,8-alkynylnaphthalene framework where the parallel acetylene groups at ≈244 pm offer the possibility of transannular interactions. This paper describes the synthesis and redox chemistry of 1,8-bis(ferrocenylethynyl)naphthalene derivatives and, for comparison, the 1,5-ethynylnaphthalene analogues and **1b** (its synthesis and structure has been reported recently[12]) which cannot participate in transannular interactions. The thermolysis or photolysis of *peri*-phenylalkynylnaphthalenes was shown some time ago[13] to lead to a variety of cyclobutadienes and fluoranthenes. More recently, phase-transfer transition metal/ion pair-mediated cycloaddition of phenylated diynes has been found[14] to generate a variety of polycyclic compounds depending on the distance between the cofacial ethynyl groups. By end-stopping the putative conjugated link involving a naphthalene ring system with ferrocenyl and/or suitably functionalised (alkyne)-dicobalt-hexacarbonyl units we create in-built sensors to gauge the effectiveness of communication between redox centers. The ferrocene redox system is well understood while the reaction of $Co_2(CO)_6$(alkyne) complexes with bis(diphenylphosphino)-methane (dppm) affords complexes of increased stability which have simple electrochemical responses not bedeviled by fast electrochemical–chemical–electrochemical (ECE) reactions.[4,7] Ferrocenylalkynylnaphthalenes therefore offer not only a potential route to conjugated emissive ring systems with ferrocenyl and/or cluster substituents, but also an opportunity to explore the concept that electronic interactions *via* a -C≡C- link may be largely unaffected by the orientation or aromaticity of the spacing group.

Results and discussion

1,8- and 1,5-Bis(ferrocenylethynyl)naphthalenes

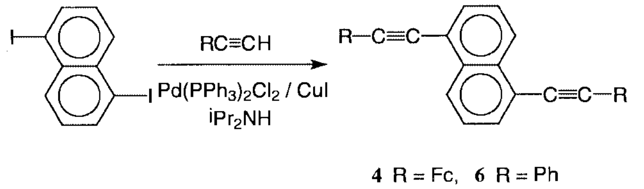
Orange 1,8-bis(ferrocenylethynyl)naphthalene **3** was synthesised in 43% yield *via* the palladium catalysed Cu^I coupling of ethynylferrocene and 1,8-diiodonaphthalene (Scheme 1). Yields of **3** were very dependent on the conditions employed for the coupling reaction, and the described procedure in a relatively concentrated solution at room temperature gives the best results. Lower yields of **3** are obtained under the more usual conditions for this type of coupling reaction—using elevated temperatures and dilute solutions—and a number of by-products were chromatographically identified, often in very small yield. Among those characterised were iodoferrocenylethynylnaphthalene **2**, 1-ferrocenylacenaphthylene **7** and cyclic rearrangement products **8a** and **8b**. It is clear that



Scheme 1

the formation of **3** involves a sequential coupling reaction *via* **2**. At elevated temperatures the second coupling step is in competition with, first, an intramolecular elimination of HI and cyclisation of **2** to give **7**, and, second, combined intramolecular elimination and alkynyl coupling to give **8**.

1,5-Bis(ferrocenylethynyl)naphthalene **4** was prepared in high yield from ethynylferrocene and 1,5-diiodonaphthalene (Scheme 2) using the same coupling conditions as for **3**. In comparison to the reaction with 1,8 compounds a 1,5 analogue of intermediate **2** was not detected nor were there any cycloaddition products. Both **3** and **4** are orange solids, stable in air and moderately soluble in organic solvents. Their NMR and electronic spectra are similar to their respective 1,8- and 1,5-phenylethynyl counterparts[13] **5** and **6**. The general upfield shift of δ_H for the 1,8 compounds is consistent with a transannular interaction but there is nothing in the electronic spectra to suggest a strong interaction. Fluorescence, noted[13] for **5**, was not observed with either **3** or **4**.



Scheme 2

Reactions of 3

Bossenbroek *et al.* found[13] that the thermolysis of 1,8-bis(phenylethynyl)naphthalene in diglyme at 130 °C gave a number of fluoroanthenes from 1,4 transannular reactions. In contrast, thermolysis in solution up to 130 °C for 24 hours left **3** unchanged.

Treatment of **3** with diisopropylammonium iodide in boiling toluene gave good yields of a 1,4 addition product, diferrocenyliodobut[*a*]acenapthylen-1,2-diene **9**, and two unidentified minor products. The low field δ_H(Fc) of **9** could be assigned to the Fc group adjacent to the iodine substituent and the (*E*,*E*) diene configuration suggested by the NMR data was confirmed by a single crystal X-ray structure (*vide infra*). The (*E*,*E*) configuration is consistent with the mechanism of formation from **3**. Protonation of one alkyne group of **3** creates a carbocation stabilised by the electron donor ferrocene which then undergoes *peri* ring closure to form the acenaphthylene; nucleophilic attack by I$^-$ at the carbocation of the acenaphthylene then gives **9** (Scheme 3).

Table 1 Selected bond lengths [Å] and angles [°] for **9**

C(1)–C(20)	1.343(9)	C(23)–Fe(1)	2.050(7)
C(1)–C(11)	1.499(9)	C(24)–Fe(1)	2.040(7)
C(1)–C(2)	1.509(9)	C(25)–Fe(1)	2.039(7)
C(2)–C(30)	1.356(9)	Fe(1)–C(26)	2.049(7)
C(2)–C(3)	1.486(8)	Fe(1)–C(27)	2.055(7)
C(3)–C(4)	1.375(10)	Fe(1)–C(28)	2.055(7)
C(3)–C(12)	1.408(10)	Fe(1)–C(29)	2.056(7)
C(4)–C(5)	1.408(9)	Fe(1)–C(210)	2.030(8)
C(5)–C(6)	1.365(11)	C(30)–C(31)	1.463(10)
C(6)–C(7)	1.403(10)	C(31)–Fe(2)	2.051(7)
C(7)–C(8)	1.428(10)	C(32)–Fe(2)	2.034(7)
C(7)–C(12)	1.413(9)	C(33)–Fe(2)	2.028(7)
C(8)–C(9)	1.354(10)	C(34)–Fe(2)	2.037(7)
C(9)–C(10)	1.431(9)	C(35)–Fe(2)	2.032(6)
C(10)–C(11)	1.372(10)	Fe(2)–C(36)	2.043(7)
C(11)–C(12)	1.427(10)	Fe(2)–C(37)	2.044(7)
C(20)–I(1)	2.128(7)	Fe(2)–C(38)	2.021(7)
C(20)–C(21)	1.485(9)	Fe(2)–C(39)	2.038(8)
C(21)–Fe(1)	2.056(6)	Fe(2)–C(310)	2.040(7)
C(22)–Fe(1)	2.034(7)		
C(20)–C(1)–C(11)	129.4(7)	C(1)–C(20)–C(21)	128.2(6)
C(20)–C(1)–C(2)	124.9(6)	C(1)–C(20)–I(1)	120.8(5)
C(11)–C(1)–C(2)	105.6(5)	C(21)–C(20)–I(1)	110.9(5)
C(30)–C(2)–C(1)	124.9(6)	C(2)–C(30)–C(31)	124.6(6)
C(30)–C(2)–C(3)	126.0(6)		

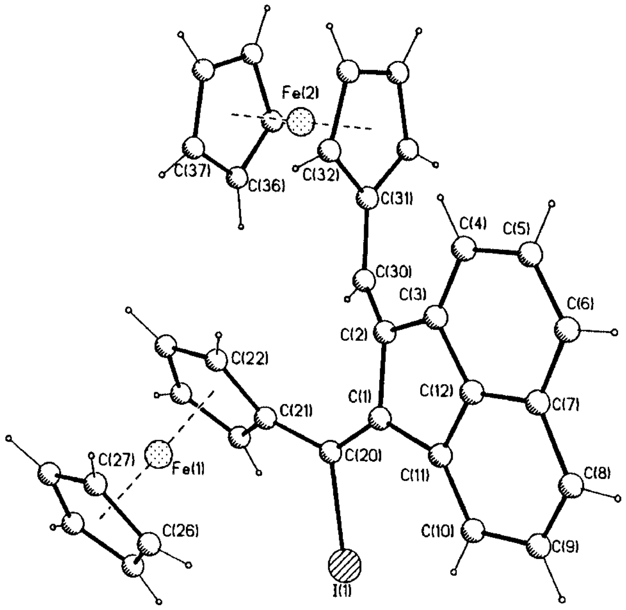
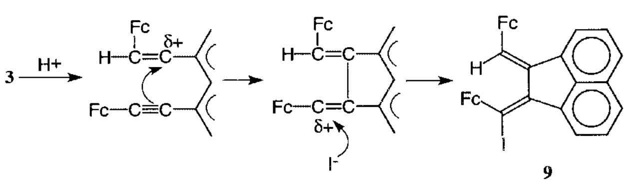


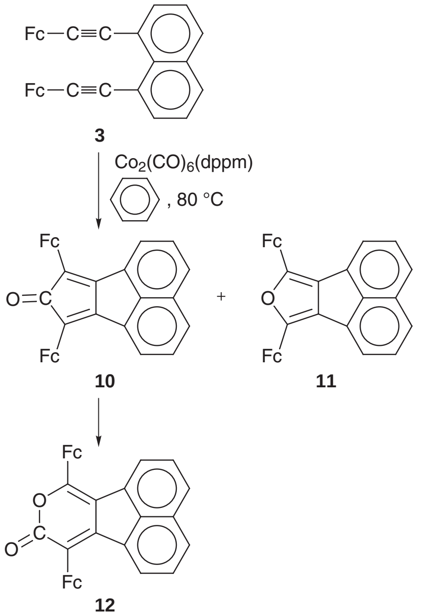
Fig. 1 Single crystal X-ray structure of **9**.



Scheme 3

Selected bond length and angle data for **9** are given in Table 1. A perspective view of the molecule in Fig. 1 defines the atom numbering scheme. The shortest intermolecular contact not involving hydrogen atoms is 3.38(1) Å between C(4) and C(6) ($-x$, $-y+1$, $-z$). The structure of **9** consists of an acenaphthylene moiety with methylidene substituents *exo* to the five-membered ring. One methylidene carbon atom carries an iodo and a ferrocenyl substituent with a ferrocenyl residue on the other. The configuration of the substituents in the butadiene fragment is confirmed as (*E*,*E*) by the structural investigation. This configuration minimises steric interactions between the two ferrocenyl moieties, placing them on opposite sides of the acenaphthylene ring plane. The planes of the C(21)–C(25) and C(31)–C(35) cyclopentadiene rings are inclined at angles of 85.0(3)° to one another and at 34.0(3)° and 83.4(2)° respectively to the plane of the acenaphthylene unit. Further indications of steric crowding in the molecule are signaled by significant twisting of the C(20)–C(1)–C(2)–C(30) diene fragment (torsion angle 28(1)°). In particular, C(30) is twisted out of the acenaphthylene plane by 0.653(9) Å with C(20) displaced by 0.226(9) Å in the opposite direction. Bond distances in the acenaphthylene unit are normal with the exception of C(1)–C(2) which, at 1.509(8) Å, is significantly longer than the 1.45 Å found in butadiene but shorter than those observed in 7,9-bis(trimethylsilyl)-8*H*-cyclopenta[*a*]acenaphthylen-8-one[15] and in a number of acenaphthylene systems with C–C single bonded substituents at C(1) and C(2).[16] The C(20)–I(1) distance, 2.128(7) Å, is within experimental error of that observed in 4-iodo-1,2,3,4-tetraphenyl-1,3-butadienylbromodiphenyltin.[17] Bond lengths and angles within each of the ferrocenyl fragments are unremarkable and each pair of η^5-cyclopentadiene rings is almost parallel (interplanar angles: C(21)–C(25)/C(26)–C(210) 0.9(6)°; C(31)–C(35)/C(36)–C(310) 2.5(5)°). The cyclopentadiene rings of both ferrocenyl moieties are approximately eclipsed with mean C(m)–C(1g)–C(2g)–C(n) torsion angles of 6.7(3)° for C(21)–C(210) and 12.2(2)° for C(31)–C(310) (C(1g) and C(2g) are the cyclopentadiene ring centroids).

There was no evidence for $Co_2(CO)_x$ complexes in reactions of $Co_2(CO)_8$ or $Co_2(CO)_6$(dppm) with the cofacial alkyne **3**, undoubtedly because the cofacial arrangement in **3** makes it difficult sterically to add metal carbonyl entities across the alkyne bond. Conversely, it is an ideal arrangement for the formation of cycloaddition products of the type well known[18] in metal carbonyl–alkyne chemistry. Thus, 1,4-cycloaddition products with an acenaphthylene skeleton, cyclopent[*a*]acenapthen-8-one **10** (major product) and furan[*a*]acenaphthylene **11**, were isolated from these reactions (Scheme 4). Acenaphthylenones have been isolated from Rh-catalysed reactions of 1,8-bis(ethynyl)naphthylenes[14] and cyclopentadienones are commonly found in $Co_2(CO)_8$ reactions with alkynes.[19] However, the furan is unusual. A logical mechanism leading to **10** and **11** is the addition of one $Co_2(CO)_x$ moiety across one alkyne, *peri*-cyclisation followed by CO insertion and elimination of cobalt(0).



Scheme 4

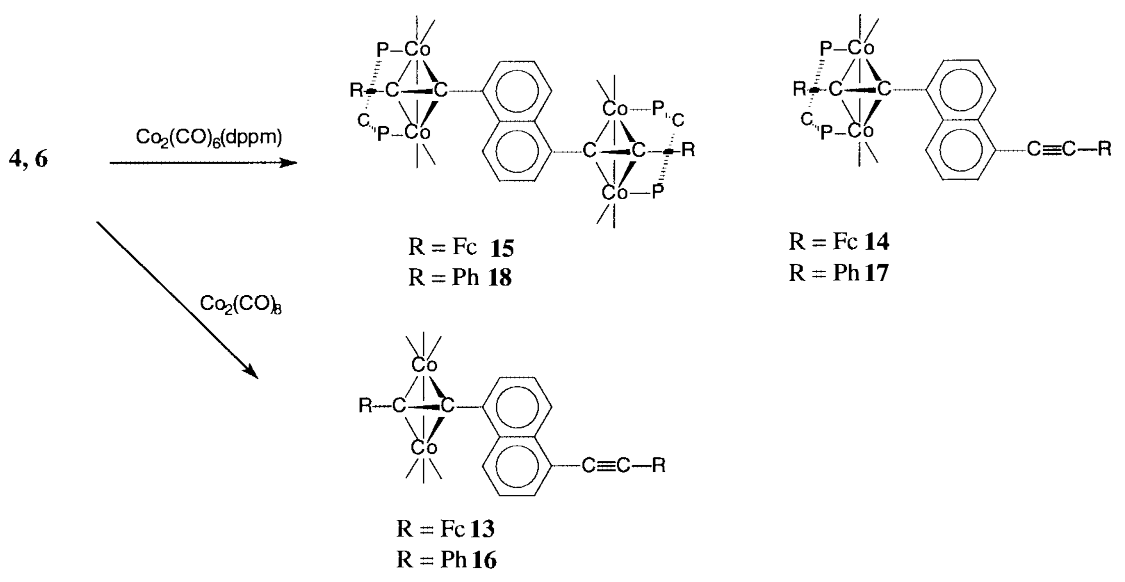
In contrast to the $Co_2(CO)_x$ reactions with **3**, the reaction of $Fe(CO)_5$ with 1,8-bis(phenylethynyl)naphthalene **5** at 130 °C gave[13] an acecyclonone and its $Fe(CO)_3$ adduct, but no furan. These results for **5** suggested that an acecyclonone can function as a diene ligand but the ferrocenylacecyclonone **10** did not coordinate to $PdCl_2$, or μ_3-$PhCCo_3(CO)_9$.[20] However, in the presence of a metal carbonyl species or on standing in solution **10** underwent an unusual conversion to give the acepyranone **12** and traces of a compound with one further oxygen atom. A formyl intermediate has been invoked[14] to explain the formation of a furanone in ion-pair-catalysed carbonylations of 9,10-ethynylphenanthrenes but the mechanism of CO insertion into **10** is puzzling.

$Co_2(CO)_xL_y$ complexes of 1,5-bis(ferrocenylethynyl)naphthalene

In contrast to **3**, $Co_2(CO)_6$(dppm) cleanly reacts with **4** to give the thermally stable **14** and **15** which had typical IR and NMR parameters for this type of dppm complex[4] (Scheme 5). The $Co_2(CO)_6$ analogues were surprisingly unstable and only **13** was identified spectroscopically. This instability was also found for the $Co_2(CO)_6$ complexes **16**, the $Co_2(CO)_4$(dppm) complexes **17**, **18** and $\{[PhC_2Co_2(CO)_6]_2nap\}$ **19** (nap = 1,5-naphthalene) but not with a monodentate phosphite, $P(OMe)_3$, as the phosphorus donor (Scheme 6). It is difficult to account for this thermal instablity. Although it has been found that $Co_2(CO)_x$ addition across two adjacent alkyne bonds is sterically prohibited with Fc termini[4] there appears to be no steric impediment in the 1,5 derivatives. It is pertinent to note that the decomposition pathway is the loss of the Co_2 units; this is exacerbated in anthracene derivatives.[21] Given the low oxidation potentials of these derivatives (see below) it is conceivable that partial oxidation creates a radical cation which reduces the π-acceptor capability of the ethynyl tether leading to the elimination of the Co_2 unit.

A noteworthy feature of the ^{31}P NMR specific to derivatives with only one Co_2 unit and a Ph alkyne substituent, **17** and $\{1,5\text{-}[PhC_2Co_2(CO)_6]C_{10}H_6[PhC_2Co_2(CO)_4(dppm)]\}$ **24**, was the variable temperature profile (Fig. 2). There is coalescence of two ^{31}P resonances due to chelating dppm at room temperature but clearly two structures between −35 °C and −65 °C with one dominating at −75 °C; no other ^{31}P resonances are seen in this temperature range. For steric reasons dppm must be in an equatorial–equatorial configuration[4] but there are two conformers differing in the orientation of the dppm ligand with respect to the Ph and naphthalene alkyne substituents.

The single crystal X-ray structure of **22** is shown in Fig. 3; the molecule has a crystallographically imposed centre of symmetry and Fig. 3 displays the numbers for the unique atoms only. Selected bond length and angle data are given in Table 2. The structure consists of well separated molecules with the closest intermolecular contact not involving H atoms at 3.07(4) Å between O(11) and O(25B).[22] The phenyl and naphthalene ring systems are inclined in a transverse fashion when viewed down the C(1)≡C(2) vector with an angle of 57.1(8)° between the mean planes. It is likely that this staggered conformation minimises repulsive interactions between the ring H atoms and the equatorial CO ligands.[23] The pseudo-tetrahedral C_2Co_2 cluster core deviates slightly from idealised C_{2v} symmetry with a Co(1)–Co(2)/C(1)≡C(2) interline angle of 2.8(8)° and small variations in the Co–C bond distances [Co(1)–C(1) 1.93(2) Å; Co(1)–C(2) 1.98(2) Å; Co(2)–C(1) 1.98(2) Å; Co(2)–C(2) 1.95(1) Å] which may reflect the effect of the asymmetry of the alkyne unit on the frontier molecular orbitals involved in binding the Co_2C_2 core.[24] The phosphite ligands each occupy a pseudo-axial coordination site on each of the adjacent cobalt atoms, an accepted preference for substitution in these molecules. Other structural paramenters are similar to classical



Scheme 5

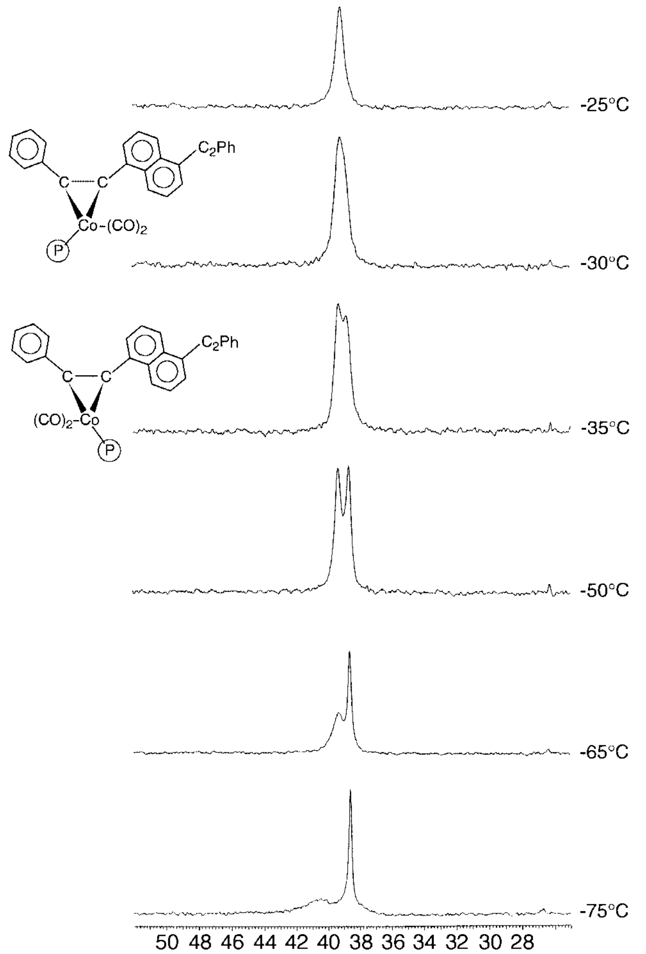
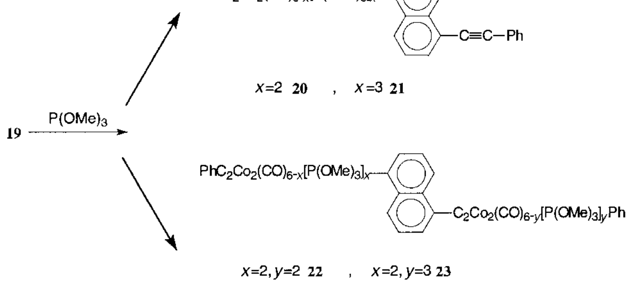


Fig. 2 Variable temperature ^{31}P NMR of **17**.

'sawhorse' arrangements except the length of the Co(1)–Co(2) bond which at 2.437(3) Å is significantly shorter than the axially substituted $H_2C_2Co_2(CO)_4(PMe_3)_2$ (2.464(1) Å)[25] and $(CHO)_2C_2Co_2(CO)_4(PPh_3)_2$ (2.456(3) Å)[26] and indeed appears to be the shortest reported Co–Co vector for alkyne dicobalt complexes. The reason for this is not obvious as there is no evidence for significant steric strain in the molecule or specific electronic effects.



Scheme 6

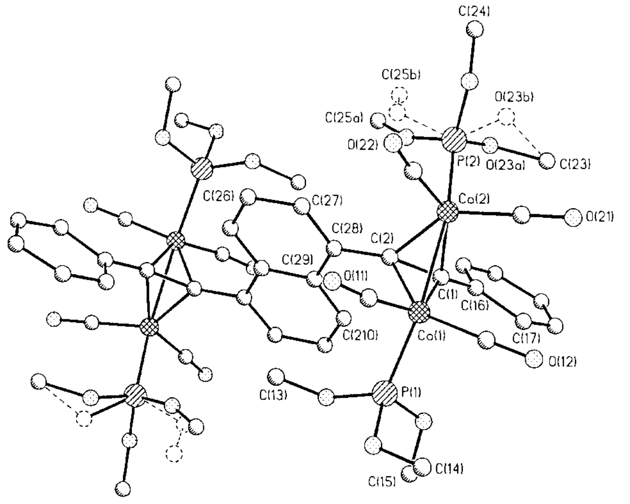


Fig. 3 Single crystal X-ray structure of **22**.

Redox chemistry

3, 4 and Lewis base derivatives. The sequence of compounds just described provides an opportunity to investigate whether communication between identical redox centres or between ferrocene and a $Co_2(CO)_x$ cluster through alkyne bonds takes place with a naphthalene spacer, and whether this is reinforced by cofacial interactions. Electrochemical data are given in Table 3 and Figs. 4–6. Cyclic and square wave voltammetric data were recorded at different scan rates and temperatures in the range 1.5 V to −1.5 V for all compounds but only oxidation processes are given in Table 2 due to the complicated ECE reactions

Table 2 Selected bond lengths [Å] and angles [°] for **22**

Co(1)–Co(2)	2.4368(19)	C(22)–O(22)	1.178(13)
Co(1)–C(1)	1.934(10)	Co(2)–P(2)	2.131(3)
Co(1)–C(2)	1.978(9)	P(2)–O(23A)	1.622(16)
Co(1)–P(1)	2.135(3)	P(2)–O(24)	1.600(13)
P(1)–O(13)	1.582(6)	P(2)–O(25B)	1.601(17)
P(1)–O(15)	1.582(7)	P(2)–O(25A)	1.66(2)
P(1)–O(14)	1.621(6)	C(1)–C(2)	1.346(11)
Co(1)–C(11)	1.757(14)	C(1)–C(16)	1.476(13)
C(11)–O(11)	1.181(12)	C(2)–C(28)	1.495(11)
Co(1)–C(12)	1.743(10)	C(26)–C(27)	1.411(11)
C(12)–O(12)	1.180(10)	C(26)–C(210)[1]	1.361(11)
Co(2)–C(1)	1.982(9)	C(27)–C(28)	1.380(12)
Co(2)–C(2)	1.945(7)	C(28)–C(29)	1.419(12)
Co(2)–C(21)	1.741(10)	C(29)–C(210)	1.391(12)
C(21)–O(21)	1.189(11)	C(29)–C(29)[1]	1.441(15)
Co(2)–C(22)	1.759(14)	C(210)–C(26)[1]	1.361(11)
C(11)–Co(1)–P(1)	97.1(4)	C(29)–C(28)–C(2)	123.3(9)
C(12)–Co(1)–P(1)	96.5(3)	C(210)–C(29)–C(28)	122.9(8)
P(1)–Co(1)–Co(2)	154.47(10)	C(27)–C(28)–C(2)	116.2(8)
O(11)–C(11)–Co(1)	172.1(13)	C(27)–C(28)–C(29)	120.6(8)
O(12)–C(12)–Co(1)	177.5(10)	C(28)–C(27)–C(26)	119.9(9)
C(21)–Co(2)–P(2)	97.3(4)	C(210)–C(29)–C(29)[1]	118.5(11)
C(22)–Co(2)–P(2)	93.8(4)	C(28)–C(29)–C(29)[1]	118.6(11)
P(2)–Co(2)–Co(1)	153.40(12)	C(26)[1]–C(210)–C(29)	122.2(8)
C(2)–C(1)–C(16)	142.1(9)		
C(1)–C(2)–C(28)	143.0(9)		

Symmetry transformations used to generate equivalent atoms: [1] $-x + 1$, $-y$, $-z + 1$.

Table 3 Electrochemical data[a,b]

Compound[c]	$E_{1/2}$/V	$\Delta E_{1/2}$/mV	$E_{1/2}$/V	$\Delta E_{1/2}$/mV
1,8-Fc_2nap **1a**[10]	0.46	195	—	
1,5-Fc_2nap **1b**[30]	0.56	95	—	
3	0.61	109	—	
4	0.65	60	—	
Fc-(C≡C)$_2$-Fc	0.58	110	—	
10	0.55	140	*−1.00*[d]	
11	0.56	160	*−1.25*[d]	
Fc-Co_2C_2-Fc	0.46	220	*1.14*	
Fc-Co_2C_2-Ph	0.47	—	*1.00*	—
[Fc-Co_2C_2-]$_2$-C≡C-	0.48	40	*1.11*	*80*
15	0.44	90	*0.94*	*70*
[Ph-Co_2C_2]$_2$-C≡C-	—	—	*0.62*	*180*
Ph-[Co_2C_2]$_2$-Ph	—	—	*0.51*	*450*
17	—	—	*0.70*	—
22	—	—	*0.51*	*128*
23	—	—	*0.20, 0.58*[e]	

[a] Potentials referenced against decamethylferrocene; $E_{1/2}$ from square wave voltammetry; at 20 °C, in CH_2Cl_2; data only in the range 1.5 V to 0.00 V except for **10**, **11**. [b] Data in italics refer to cluster component. [c] -Co_2C_2- represents a $Co_2(CO)_4$(dppm) unit. [d] Reduction of acecyclonone or furan unit. [e] Non-equivalent $Co_2[P(OMe)_3]_x$ units; $x = 3$ is 0.20 V process.

which are always observed upon reduction of Lewis base complexes.[7,27] The first reduction of naphthalene in **3** and **4** occurs as a multielectron irreversible wave at ≈−1.25 V as is normal with benzoid aromatics.[28] Irreversible multielectron reduction waves at more negative potentials were not studied. Simulation of the square wave plots was used to calculate small (<80 mV) peak-to-peak separations.

The ferrocenyl derivatives **3** and **4** display two chemically reversible diffusion-controlled one-electron couples assigned to the ferrocenyl redox centres (Fig. 4). Both $E_{1/2}$ values for the removal of the first electron are anodic of $E_{1/2}[\mathrm{Fc}]^{+/0}$ (Table 3) but the difference of 40 mV is not significant.

$$[\mathbf{3}]^{+/+} \overset{0.72\ \mathrm{V}}{\Longleftrightarrow} [\mathbf{3}]^{+/0} \overset{0.61\ \mathrm{V}}{\Longleftrightarrow} [\mathbf{3}] \overset{-1.1\ \mathrm{V}}{\Rightarrow} [\mathbf{3}]^{0/-1}$$

The peak separation $\Delta E_{1/2}$ is of more interest as it is a measure of the communication along the conjugated array[29] and the order is **1a** > **3** > **1b** > **4**. The influence of cofacial interactions which reinforce the communication is clearly seen from this sequence. For the molecules where the ferrocenyl group is directly bound to the naphthalene spacer (**1a**/**1b**) the cofacial or transannular effect in $\Delta E_{1/2}$ is 100 mV; interpolation of the alkyne reduces this to 49 mV (**3**/**4**). Rosenblum and coworkers found[10] a similar decrease in communication between the Fc termini as they were separated by 1,8-Fc-naphthalene units. These effects have been attributed to a 'distance' factor if the energy transfer is in a rigid conjugated linkage; that is, they are essentially electrostatic in origin.[30] If this was the explanation then one would expect communication to be almost terminated when the conjugation is reduced by the addition of a $Co_2(CO)_4$(dppm) across the triple bond, yet $\Delta E_{1/2}$ *increases* by 30 mV from **4** to **15**. $\Delta E_{1/2}$[**4**] is similar in magnitude to $\Delta E_{1/2}$[Fc-(C≡C)$_3$-Fc],[21] a molecule where -C≡C- is the spacer, but for dppm complexes the naphthalene representative $\Delta E_{1/2}$[**15**] is larger than $\Delta E_{1/2}$\{$Fc_2C_2[Co_2(CO)_4(dppm)]_2$-(C≡C-)\}.[4] Naphthalene is clearly as effective as a -C≡C- group in modulating communication, but while gross trends in $\Delta E_{1/2}$ do give an indicative measure of 'communication', small fluctuations may well be due to electrochemical as well as electronic factors. We conclude that the relative importance of intramolecular *versus* intermolecular through-space interactions is yet to be determined.

With the coordination of a $Co_2(CO)_4$(dppm) entity to the alkyne an additional oxidation probe becomes accessible as does the possibility of synergic interaction between the cluster and ferrocenyl redox centres. **15** has two asymmetric two-electron waves (at $E_p \approx 0.5$ V and 1.0 V) under normal cyclic voltammetric conditions, assigned to the ferrocenyl and cluster centres respectively, which with square wave voltammetry resolve into four reversible one-electron waves (Fig. 5). These potentials are very similar to other complexes with a Fc_2C_2-[Co_2(dppm)] unit[4] (Table 3) and a $\Delta E_{1/2}$ of 70 mV for the intracluster communication confirms the effectiveness of naphthalene as a link. Previous work[4,7,31] has shown that the increased electron density associated with coordination of phosphorus ligands makes the $Co_2(CO)_{6-x}P_x$ cluster a readily oxidisable centre. The cluster potential is simply a function of the number of phosphorus donor atoms per cluster unit and this is readily seen by comparing **15** > **22** and the difference of 0.38 V in $E_{1/2}{}^{+/0}$ for the non-equivalent clusters in **23**. Because of the instability of many derivatives of **6** there is not a coherent series of $E_{1/2}$ for comment although the $\Delta E_{1/2}$ for **22** of 128 mV indicates that the naphthalene spacer is an effective intracluster transmitter. The ligation sphere of the cluster has little effect on $E_{1/2}$[Fc] implying that the redox centres are acting independently of each other.

Acecyclonone 10. Cyclic and square wave voltammograms of the acecyclonone **10** show a sequence of chemically reversible one-electron Nernstian processes (Fig. 6). Two at 0.55 V and 0.69 V are assigned to the ferrocenyl couple (*cf.* **1** and **3**) and the reduction process at −1.00 V to the formation of an acecyclonone radical anion (Scheme 7). A $\Delta E_{1/2}$ of 137 mV for the oxidation processes is evidence of effective communication between the ferrocene substituents. An interesting question is whether the odd electron in $\mathbf{10}^{\bullet -}$ is located largely on the naphthalene or in an orbital encompassing the acecyclonone unit. Unlike the first reduction step for benzenoid aromatics,[28] $E_{1/2}[\mathbf{10}]^{0/-1}$ is chemically reversible in all solvents and is 0.25 V positive of the multielectron couple $E_p[\mathbf{4}]^{0/-1}$. Monomeric cyclopentadienones[32] however undergo a reversible one-electron reduction at comparable potentials to $E_{1/2}[\mathbf{10}]^{0/-1}$ ($E_{1/2}$ for diphenylcyclopent[*a*]acenapthylen-8-one **25** is −0.89 V) and, although $E_{1/2}[\mathbf{10}]^{0/-1}$ is unexpectedly higher than $E_{1/2}[\mathbf{25}]^{0/-1}$,

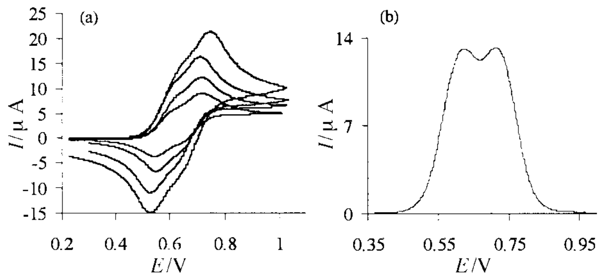


Fig. 4 Electrochemistry of **3** in CH_2Cl_2, Pt, 0.1 M $^nBu_4NPF_6$. (a) Cyclic voltammograms at, with increasing *i*, 100, 200, 400, 800 mV s^{-1}; (b) experimental and fitted square wave voltammogram, 100 mV s^{-1}.

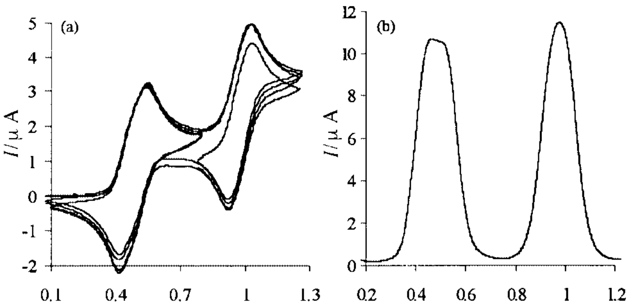


Fig. 5 Electrochemistry of **15** in CH_2Cl_2, Pt, 0.1 M $^nBu_4NPF_6$, 100 mV s^{-1}. (a) Cyclic voltammograms switched at different potentials; (b) experimental and fitted square wave voltammogram.

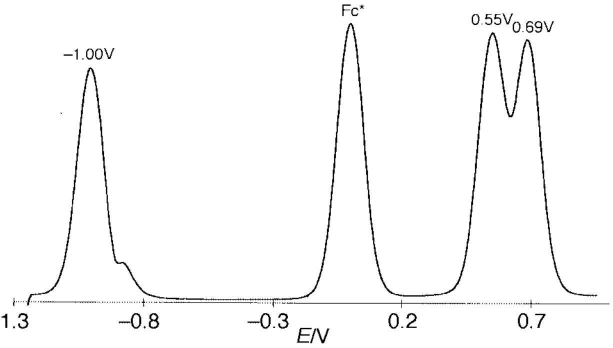


Fig. 6 Electrochemistry of **10** in CH_2Cl_2, Pt, 0.1 M $^nBu_4NPF_6$, 100 mV s^{-1}.

these data support an acecyclonone-centred radical anion for **10**$^{\bullet-}$. A tricobaltcarbon cluster cyclopentadienone has a quasi-reversible reduction at −0.95 V, close to that for **10**, but in this case the redox behaviour is influenced by that of the cluster.[33]

Spectroscopic work was undertaken to define the redox orbitals for the oxidation processes. Of interest was the broad electronic absorption band at 720 nm ($\varepsilon = 3100$) which is a typical of ethynylferrocenyl or naphthalene compounds (Fig. 7) and the ferrocenyl absorption has also red-shifted to 470 nm. These observations suggest a small HOMO–LUMO gap and hence extensive delocalisation within the acecyclonone unit. Furthermore, the low energy band is unaffected by the polarity of the solvent implying that the ground and excited state dipoles are similar.

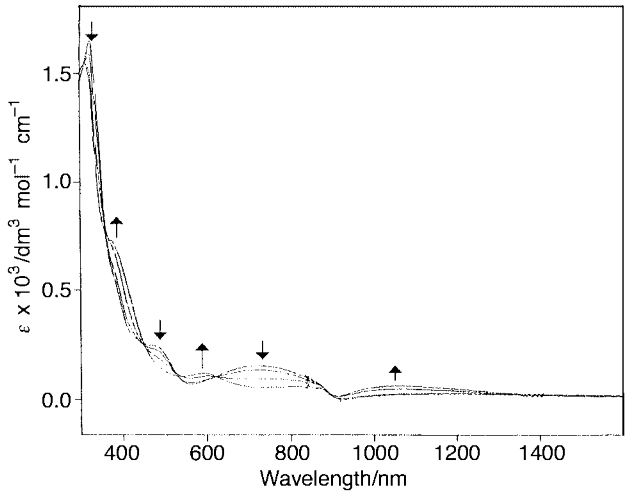


Fig. 7 Electronic spectrum of **10** (360–1600 nm) in OTTLE; CH_2Cl_2, 0.1 M $^nBu_4NPF_6$; arrows show changes as oxidation occurs at 0.55 V.

Oxidation of **10** at the first oxidation potential in an optically transparent thin layer electrode (OTTLE), or with one mole of Ag^+, produced the mixed valence species **10**$^+$ which exhibits a broad absorption at 1050 nm (Fig. 7). The mixed valence parameter $a = 0.23$ for a through-bond interaction confirms that there is good communication between the ferrocenyl centres.

Furan 11. **11** has two reversible one-electron oxidation processes at 0.56 V and 0.72 V and a irreversible reduction wave at ≈ -1.25 V (Fig. 6). Despite furans being π-electron rich relative to cyclopentadienones the ferrocenyl potentials of **10** and **11** are almost identical but the increased delocalisation of a furan ring results in a larger $\Delta E_{1/2}$ for **10**. It is likely that the irreversible reduction step for **11** involves a dimerisation reaction, typical of furans.[28]

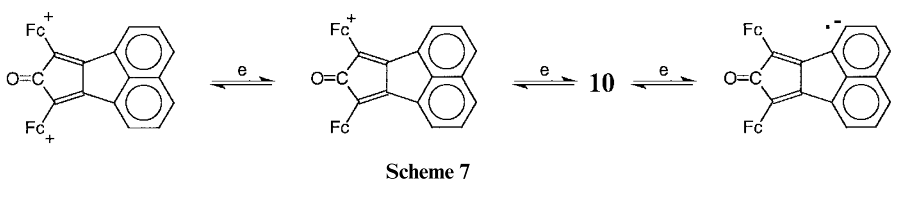
Conclusion

Compared to the phenyl analogue **5** the *peri*-ferrocenylethynylnaphthalene **3** is remarkably stable. Nevertheless, transannular interactions in **3** allow, *via* 1,4 addition reactions, an elaboration of the polyaromatic framework to give a variety of acenaphthylenes with ferrocenyl substituents. In turn, the acenaphthylenes can be used as templates for array synthesis and the incorporation of cluster substituents. There is a marked difference between the 1,4-addition reactions of the two *peri* naphthalenes **3** and **5**; products from the latter are based on a benzo[*k*]fluoroanthene skeleton. The formation of this structure requires a cyclobutadiene intermediate, an intermediate which would be difficult to accommodate for reactions of **3** due to the steric congestion, evident in the structure of **9**, from the two Fc substituents.

Further examples of cofacial-assisted polycyclic synthesis are being studied with particular emphasis on the quenching of fluorescence when there are metal cluster and ferrocene substituents.

Experimental

Solvents were dried and distilled by standard procedures, and all reactions were performed under nitrogen. 1,5 and 1,8-Diiodonaphthalene[13] and ethynylferrocene[34] were prepared by literature methods. Other commercial reagents were used as



Scheme 7

received. IR spectra were recorded on a Digilab FX60 or Perkin Elmer 1600 series FT-IR spectrometer, NMR on a Varian VXR 300 MHz or Gemini 200 MHz spectrometer (^{1}H NMR were referenced to $CDCl_3$, ^{31}P to external 85% H_3PO_4) and electronic spectra on Jasco V 550 or Perkin Elmer Lambda 9 UV-vis spectrophotometers. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago. Mass spectra were recorded on a Kratos MS80RFA instrument with an Iontech ZN11NF atom gun. Electrochemical measurements were performed in CH_2Cl_2 using a three-electrode cell with a polished disc, Pt (2.27 mm^2) or GC as the working electrode; solutions were $\approx 10^{-3}$ M in electroactive material and 0.10 M or 0.15 M (square wave voltammetry) in supporting electrolyte (triply recrystallised $^n Bu_4NPF_6$). Data were recorded on an EG & G PAR 273A computer-controlled potentiostat. Scan rates of 0.05–10 V s^{-1} were typically employed for cyclic voltammetry and for Osteryoung square-wave voltammetry, square-wave step heights of 1–5 mV, a square amplitude of 15–25 mV with a frequency of 30–240 Hz. All potentials are referenced to decamethylferrocene (0.0765 V against SCE); sublimed ferrocene was $E_{1/2}$ 0.468 V. The OTTLE cell had a Pt gauze working electrode and 1 mm spacer controlled by a home-built potentiostat; the solvent was CH_2Cl_2.

Preparation of 1,8-diferrocenylethynylnaphthalene 3 and 1,8-iodoferrocenylethynylnaphthalene 2

Ethynylferrocene (0.61 g, 2.9 mmol) and 1,8-diiodonaphthalene (0.41 g, 1.1 mmol) were stirred in diisopropylamine (6 ml) with $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) for 3 hours at 20 °C. The precipitate was collected and washed with water then $CHCl_3$/hexane and dried *in vacuo* giving **3** as an orange powder (43%). **3** was soluble in benzene and chlorinated solvents, and was also slightly soluble in hexane. Found: C, 74.76; H, 4.22; M^+ 544. $C_{34}H_{24}Fe_2$ requires: C, 75.03; H, 4.44%; M 544. δ_H ($CDCl_3$): 4.17 [t (J = 1.8 Hz), 4H, Fc-*H*], 4.20 (s, 10H, -C_5H_5), 4.41 [t (J 1.8 Hz), 4H, Fc-*H*], 7.43 (m, 2H, naph. *H*), 7.8 (m, 4H, naph. *H*). λ_{max}(CH_2Cl_2, nm): 241 (51 200), 270 (14 700), 340 (14 500), 430 (2300).

The solution and washings obtained after the collection of **3** were reduced in volume and separated on preparative TLC silica plates using a hexane : CH_2Cl_2 (3 : 1) eluent. Band 1: unreacted ethynylferrocene (150 mg). Band 2 gave orange crystals of **2** (33%) after recrystallisation from hexane. Found: C, 57.48; H, 3.32; M^+ 462. $C_{22}H_{15}FeI$ requires: C, 57.18; H, 3.27%, M 462. δ_H ($CDCl_3$): 4.29 [t (J = 1.8 Hz), 2H, Fc-*H*], 4.30 (s, 5H, -C_5H_5), 4.63 [t (J = 1.8 Hz), 2H, Fc-*H*], 7.09, 7.42 [2 × (m, 1H, naph. *H*)], 7.8 (m, 3H, naph. *H*), 8.06 (m, 1H, naph. *H*).

1-Ferrocenylacenaphthylene 7

Ethynylferrocene (1 g, 4.8 mmol) and 1,8-diiodonaphthalene (0.6 g, 1.6 mmol) were refluxed in diisopropylamine (75 ml) with $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) for 40 min. Solvent was removed *in vacuo* and the reaction mixture separated as previously using TLC with hexane : CH_2Cl_2 (3 : 1). Band 2, recrystallised from hexane gave orange crystals of **7** (3% yield). C, 77.93; H, 4.53; M^+ 336, M − $CpFe^+$ 215. $C_{22}H_{16}Fe$ requires: C, 78.59; H, 4.80%; M 336. δ_H ($CDCl_3$): 4.12 (s, 5H, -C_5H_5), 4.26, 4.79 {2 × [t (J = 1.9 Hz), 2H, Fc-*H*]}, 6.99 (s, 1H, acenap*H*), 7.5–7.9 (m, 5H, naph. *H*), 8.06 [d (J = 7 Hz), 1H, naph. *H*]. Band 4, grey solid **8a**: Found: mass spectrum (EI), M^+ 544. $C_{34}H_{24}Fe_2$ requires: M 544. δ_H ($CDCl_3$): 4.06 (s, 5H, -C_5H_5), 4.13 (s, 5H, -C_5H_5), 4.4–4.9 (m, Fc-*H*), 7.3–7.7 (m, naph. 5*H*), 8.85 [d (J = 7 Hz), 1H, naph. *H*]. Band 5, dark red solid **8b**. Found: mass spectrum (EI), M^+ 754. $C_{46}H_{34}Fe_3$ requires: M 754. δ_H ($CDCl_3$): 4.08, 4.35, 4.37 [3 × (s, 5H, -C_5H_5)], 4.3–4.8 (m, Fc-H), 7.0–8.2 (m), 9.0 (d), 9.64 (d, naph. *H*).

Preparation of 1,5-bis(ferrocenylethynyl)naphthalene 4

1,5-Diiodonaphthalene (220 mg, 0.6 mmol) and ethynylferrocene (480 mg, 2.3 mmol) were added to $PdCl_2(PPh_3)_2$ (8 mg, 2 mol%) and CuI (2 mg, 2 mol%) in 10 ml diisopropylamine. The reaction mixture was heated to reflux temperature for 15 min during which time an orange solid precipitated. This solid was collected, dissolved in hot benzene and crystallised to give **4** as an orange powder (73%). $C_{34}H_{24}Fe_2$ requires: C, 75.03; H, 4.44%; M 544. Found: C, 74.44; H, 4.42; M^+ 544. δ_H ($CDCl_3$): 4.29 (s, 10H, -C_5H_5), 4.29 (t, J = 1.8 Hz, 4H, Fc-*H*), 4.61 (t, J = 1.8 Hz, 4H, Fc-*H*), 7.5, 7.7, 8.4 [3 × (m, 2H, naph. *H*)]. λ_{max}(CH_2Cl_2, nm): 239 (48 400), 270 (13 000), 341 (17 200), 430 (2600).

Reaction of 3 with $Co_2(CO)_6$(dppm)

3 (100 mg, 0.18 mmol) and $Co_2(CO)_6$(dppm) (250 mg, 0.37 mmol) were heated to reflux temperature in benzene for 20 min. The solvent was removed under vacuum and the reaction mixture separated using preparative TLC (silica); hexane : CH_2Cl_2 (1 : 1). The residue from the first band (yellow, R_f = 0.6) was crystallised from hexane to give orange crystals of the furan **11** (9%). $C_{34}H_{24}Fe_2$ requires: C, 72.89; H, 4.32%; M 560. Found: C, 73.08; H, 4.26; M^+ 560. δ_H ($CDCl_3$): 4.20 (s, 10H, -C_5H_5), 4.46, 4.99 {2 × [t (J = 2.0 Hz), 4H, Fc-*H*]}, 7.62 (m, 2H, naph. *H*), 7.74 [d (J = 8 Hz), 2H, naph.], 7.92 [d (J = 7 Hz), 2H, naph.].

Band 2 (dark green, R_f = 0.5) was removed and eluted with CH_2Cl_2 from which dark green needles of **10** (74%) were obtained on evaporation. $C_{35}H_{24}Fe_2O$ requires: C, 73.46; H, 4.23%; M 572. Found: C, 73.53; H, 4.53; M^+ 572. δ_H ($CDCl_3$): 4.22 (s, 10H, -C_5H_5), 4.54, 5.07 {2 × [t (J = 1.8 Hz), 4H, Fc-*H*]}, 7.63 (m, 2H, naph.), 7.84 [d (J = 8 Hz), 2H, naph.], 8.23 [d (J = 7 Hz), 2H, naph.]. $\nu_{C=O}$ (CH_2Cl_2, cm^{-1}): 1712. λ_{max}(CH_2Cl_2, nm): 256 (34800), 336 (21500), 475 (4800), 720 (3100).

Band 3 (dark green) was identified by IR and ^{1}H NMR as $Co_4(CO)_8(dppm)_2$.[35] Solutions of **11** in chlorinated solvents slowly decomposed to the dark red lactone **12**. Found: M^+ 588. $C_{35}H_{24}Fe_2O_2$ requires: M 588. δ_H ($CDCl_3$): 4.26, 4.36 [2 × (s, 5H, -C_5H_5)], 4.52, 4.57, 4.94, 5.04 {4 × [t (J = 1.9 Hz), 2H, Fc-*H*]}, 7.5 (m, 2H, naph. *H*), 7.73, 7.87, 7.97, 8.18 {4 × [d (J = 7 Hz), 1H, naph. *H*]}. $\nu_{C=O}$ (CH_2Cl_2, cm^{-1}): 1741, $\nu_{C=C}$ 1644.

HI addition product 9

3 (105 mg, 0.2 mmol) was heated to reflux temperature in toluene with $^iPr_2NH_2{}^+I$ (195 mg, 0.85 mmol) for 1 hour. Solvent was removed *in vacuo* and preparative TLC with hexane : CH_2Cl_2 (3 : 1) used to separate the reaction mixture. Band 1 recrystallised from hexane to give dark red crystals of **9**. Its conformation was determined by X-ray crystallography. Found: C, 61.44; H, 3.74; M^+ 672. $C_{34}H_{25}Fe_2I$ requires: C, 60.76; H, 3.75%; M 672. δ_H ($CDCl_3$): 4.02, 4.28 [2 × (s, 5H, -C_5H_5)], 4.28 (m, 4H, Fc-*H*), 4.55, 4.81 [2 × (t, 2H, Fc-*H*)], 6.66 (s, 1H, C=C*H*), 7.3–7.8 (m, 5H, naph), 8.97 [d (J = 7 Hz), 1H, naph.].

Attempts to characterise the other red band, 2, which is most likely another conformer of **9**, were unsuccessful.

Reaction of 4 with $Co_2(CO)_8$ and $Co_2(CO)_6$(dppm)

4 (110 mg, 0.2 mmol) and $Co_2(CO)_8$ (140 mg, 0.4 mmol) were stirred at room temperature for 20 min. The solvent was removed under vacuum and the reaction mixture separated using preparative TLC (silica plates; CH_2Cl_2 : hexane (1 : 1)). A small amount of the monocluster species **13** was characterised by ^{1}H NMR and IR. δ_H ($CDCl_3$): 4.30 (s, 5H, -C_5H_5), 4.31 (s, 5H, -C_5H_5), 4.31 (2H, Fc-*H*), 4.47 (t, J = 1.9 Hz, 2H, Fc-*H*), 4.58 (t, J = 1.9 Hz, 2H, Fc-*H*), 4.61 (t, J = 1.9 Hz, 2H, Fc-*H*), 7.5–7.8 (m, 3H, naph. *H*), 8.3, 8.4, 8.7 [3 × (m, 1H, naph. *H*)]. ν_{CO} (CH_2Cl_2, cm^{-1}): 2085 (s), 2050 (vs), 2021 (vs) cm^{-1}.

4 (54 mg, 0.1 mmol) and $Co_2(CO)_6$(dppm) (150 mg, 2.2 mmol) were heated to reflux temperature in benzene for 20 min. The solvent was removed under vacuum and the reaction mixture separated using preparative TLC (silica plates; CH_2Cl_2 : hexane (1 : 1)). Band 3 crystallised from CH_2Cl_2 layered with hexane to give brown **14** (10%). δ_H ($CDCl_3$): 3.2 (m, 2H, P-CH_2-P), 3.93 (s, 5H, -C_5H_5), 4.26 (t, J = 1.8 Hz, 4H, Fc), 4.31 (2H, Fc), 4.32 (s, 5H, -C_5H_5), 4.53 (2H, Fc), 4.64 (t, J = 1.8 Hz, 2H, Fc), 7.0–7.7 (m, 23H, 20 C_6H_5, 3 naph.), 7.7, 8.4, 8.6 [3 × (m, 1H, naph.)]. δ_P ($CDCl_3$): 37 (s). ν_{CO} (CH_2Cl_2, cm^{-1}): 2017 (s), 1990 (vs), 1963 (s), 1947 (w). Band 4 likewise gave green-black crystals of **15** (20%). Found: C, 62.20; H, 4.17; P, 6.94. $C_{92}H_{68}Co_4Fe_2O_8P_4$ requires: C, 62.33; H, 3.87; P, 6.99%. δ_H ($CDCl_3$): 3.2 (m, 4H, P-CH_2-P), 4.07 (s, 10H, -C_5H_5), 4.27 (t, J = 1.7 Hz, 4H, Fc-*H*), 4.57 (br s, 4H, Fc-*H*), 7.0–7.7 (m, 44H, 40 phenyl + 4 naph. *H*), 8.6 (m, 2H, naph. *H*). δ_p ($CDCl_3$): 37.0 (m). ν_{CO} (CH_2Cl_2 cm^{-1}): 2014 (s), 1989 (vs), 1961 (s), 1945 (w).

Complexes of 6

16: has been reported elsewhere.[5] **19**: $P(OMe)_3$ (0.37 g, 3 mmol) was added to **16** (0.23 g, 0.25 mmol) in 50 ml toluene, and stirred at 50 °C for 30 min. The solvent was removed and the products separated by column chromatography (SiO_2 with CH_2Cl_2). Band 1 (red **20**, R_f = 0.92) was crystallised from MeOH (16%). Found: C, 53.90; H, 4.27; P, 7.47. $C_{36}H_{34}Co_2O_{10}P_2$ requires: C, 53.62; H, 4.25; P, 7.68%. δ_H($CDCl_3$): 3.12 (m, $^3J_{P-H}$ = 11 Hz, 18H, -OCH_3), 7.2–8.4 (complex, 16H, naph. + phenyl). δ_P($CDCl_3$): 162 (s). ν_{CO}(hexane, cm^{-1}): 2029 (vs), 1977 (s), 1953 (w). Band 2 (red **21**, R_f = 0.85), was crystallised from CH_2Cl_2 : hexane (59%). Found: C, 43.18; H, 3.88; P, 9.74. $C_{46}H_{52}Co_4O_{20}P_4$ requires: C, 43.01; H, 4.08; P, 9.65%. δ_H($CDCl_3$): 3.12 (m, $^3J_{P-H}$ = 11 Hz, 36H, -OCH_3), 7.2 (m, 8H, phenyl + naph.), 7.62 (d, J = 8 Hz, 4H, phenyl), 7.99 (d, J = 7 Hz, 2H, naph.), 8.2 (m, 2H, naph.). δ_P($CDCl_3$): 163 (br). ν_{CO}(CH_2Cl_2 cm^{-1}): 2022 (vs), 1967 (vs). Band 3 (red-brown **22**, R_f = 0.75) crystallised from CH_2Cl_2 : hexane (7%). Found: C, 51.06; H, 4.81; P, 10.17; 846 (M^+ − 2CO). $C_{38}H_{43}Co_2O_{12}P_3$ requires: C, 50.57; H, 4.80; P, 10.30%; 874 *M*. δ_H($CDCl_3$): 3.02 (m, $^3J_{P-H}$ = 11 Hz, 9H, -OCH_3), 3.26 (m, $^3J_{P-H}$ = 10 Hz, 9H, -OCH_3), 3.37 (d, $^3J_{P-H}$ = 11 Hz, 9H, -OCH_3), 7.1–8.7 (complex, 16H, naph. + phenyl). δ_P($CDCl_3$): 158, 162, 166 (1 : 1 : 1, 3P). ν_{CO}(CH_2Cl_2, cm^{-1}): 1994 (vs), 1948 (vs). Band 4 (red **23**, R_f = 0.55) was crystallised from CH_2Cl_2 : hexane (10%). Found: C, 41.71; H, 4.65; P, 11.13; 1324 (M^+ − 2CO). $C_{48}H_{61}Co_4O_{22}P_5$ requires: C, 41.76; H, 4.45; P, 11.22%; 1380 *M*. δ_H($CDCl_3$): 3.02 (m, $^3J_{P-H}$ = 9 Hz, 9H, -OCH_3), 3.12 (br s, 18H, -OCH_3), 3.25 (m, $^3J_{P-H}$ = 9 Hz, 9H, -OCH_3), 3.39 (d, $^3J_{P-H}$ = 11 Hz, 9H, -OCH_3), 7.1–7.3 (m, 8H, 6 phenyl + 2 naph.), 7.60, 7.71 [2 × (d, J = 7 Hz, 2H, phenyl)], 8.0, 8.1, 8.2, 8.6 [4 × (m, 1H, naph.)]. δ_P($CDCl_3$): 160, 163, 167 (1 : 3 : 1, 5P). ν_{CO}(CH_2Cl_2 cm^{-1}): 2023 (vs), 1992 (vs), 1966 (vs), 1947 (s).

17: This was prepared by the reaction of dppm with **19** or $Co_2(CO)_6$(dppm) with **6** in boiling toluene and benzene respectively. The solvent was removed and the products separated by preparative TLC (SiO_2, 1 : 1 hexane : CH_2Cl_2) and crystallised from CH_2Cl_2 : hexane. Band 1, R_f = 0.6, brown **17**. Found: C, 70.15; H, 4.46; P, 6.47. $C_{55}H_{38}Co_2O_4P_2$ requires: C, 70.08; H, 4.06; P, 6.57%. δ_H($CDCl_3$): 3.3 (m, 2H, P-CH_2-P), 7.0–7.8 (complex, 34H, 30 phenyl + 4 naph.), 8.02, 8.40 [2 × (d, J = 8 Hz, 1H, naph.)]. ^{31}P NMR δ_P($CDCl_3$): 39 (br). ν_{CO}(hexane, cm^{-1}): 2025 (s), 2001 (vs), 1978 (s), 1956 (w). The product band 2 (R_f = 0.4, brown) was unstable, and was characterised as **18** on the basis of ^{31}P NMR and IR. ^{31}P NMR δ_P($CDCl_3$): 36 (s). ν_{CO}(hexane cm^{-1}): 2021 (s), 1996 (vs), 1970 (s). The reaction of **17** with $Co_2(CO)_8$ in hexane gave **24**. Found: C, 59.65; H, 3.41; P, 5.08%. $C_{61}H_{38}Co_4O_{10}P_2$ requires: C, 59.63; H, 3.12; P, 5.04%. δ_H($CDCl_3$): 3.2 (m, 2H, P-CH_2-P), 7.0–7.7 (complex, 33H, 30 phenyl + 3 naph.), 7.78, 7.84, 8.15 [3 × (d, J = 8 Hz, 1H, naph.)]. δ_P($CDCl_3$): 39 (br). ν_{CO}(hexane, cm^{-1}): 2088 (m), 2054 (s), 2026 (vs), 2001 (s), 1978 (s), 1956 (w).

Table 4 Crystal data and structure refinement for **9** and **22**

	9	**22**
Chemical formula	$C_{34}H_{25}Fe_2I$	$C_{46}H_{52}O_{20}P_4Co_4$
Formula weight	672.14	1284.48
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
Absorption coefficient/mm^{-1}	2.400	1.399
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0559$, $wR2 = 0.1481$	$R1 = 0.0685$ $wR2 = 0.1200$
R indices (all data)	$R1 = 0.0663$	$R1 = 0.2202$
Unit cell dimensions: *a*/Å	10.4784(6)	13.515(5)
b/Å	10.5404(6)	13.242(6)
c/Å	12.5099(8)	30.181(7)
α/°	81.6260(10)	90
β/°	88.6560(10)	90
γ/°	67.2300(10)	90
Volume/Å^3	1259.59(13)	5402(3)
Temperature/K	145(2)	166(2)
Z	2	4
Reflections collected	5549	7916
Independent reflections	3372 [*R*(int) = 0.0525]	4753 [*R*(int) = 0.1563]

X-Ray data collection, reduction and structure solution for 9 and 22

Crystal data for **9** and **22** are given in Table 4. Compound **9** was recrystallised from hexane and a dark red block was used for data collection. Data for **9** were collected on a Bruker SMART CCD diffractometer, with exposures over 0.3° using graphite monochromated Mo-Kα radiation, and processed using SAINT[36] with empirical absorption corrections applied using SADABS.[37] Crystals of **22** were obtained from CH_2Cl_2 : hexane. Data were collected from a weakly diffracting ruby coloured hexagonal plate on a Siemens R3m/V, four circle, fully automated diffractometer; data were processed and empirical absorption corrections applied using SHELXTL.[38] The structures were solved by direct methods, SHELXS-96[38] for **9** and SHELXS-86[38] for **22**, and refined by full-matrix least squares on F^2 using SHELXL-97[38] for **9** and SHELXL-93[38] for **22**. All non-hydrogen atoms were refined anisotropically and hydrogen atoms included in calculated positions in both structures. The structure of **22** has a crystallographically imposed centre of symmetry located at the centroid of the naphthalene residue; refinement therefore involved only one half of the molecular unit. High and increasing temperature factors on the O(23), O(25) and C(25) atoms of the phosphite ligand bound to Co(2) in the structure of **22** indicated possible disorder. This was resolved by refining two unique positions for these atoms with their occupancy factors f and f'' refined such that $f' = 1 - f$. The final value of f refined to 0.58(2). Selected bond length and bond angle data are given in Table 1 for **9** and Table 2 for **22**.

CCDC reference number 186/1506.

See http://www.rsc.org/suppdata/dt/1999/2487/ for crystallographic files in .cif format.

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References

1 J. E. Sheets, C. E. Carracher and C. U. Pittman (Editors), *Metal containing Polymeric Systems*, Plenum, New York, 1985;

F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101; I. Manners, *Chem. Br.*, 1996, 46; M. D. Ward, *Chem. Ind.*, 1996, 568; D. Astruc, *Acc. Chem. Res.*, 1997, **30**, 383; U. H. F. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969; J. K. Young and J. S. Moore, *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995, ch. 12; J. M. Tour, *Chem. Rev.*, 1996, **96**, 537.

2 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.

3 B. H. Robinson, J. Simpson and G. H. Worth, *Organometallics*, 1992, **11**, 3863; S. M. Elder, B. H. Robinson and J. Simpson, *J. Organomet. Chem.*, 1990, **398**, 165.

4 C. J. McAdam, N. W. Duffy, B. H. Robinson and J. Simpson, *Organometallics*, 1996, **16**, 3935; C. J. McAdam, N. W. Duffy, B. H. Robinson and J. Simpson, *J. Organomet. Chem.*, 1997, **527**, 179; N. W. Duffy, C. J. McAdam, B. H. Robinson and J. Simpson, *J. Organomet. Chem.*, 1998, **565**, 19; N. W. Duffy, C. J. McAdam, B. H. Robinson and J. Simpson, *J. Organomet. Chem.*, 1999, **573**, 36.

5 N. W. Duffy, C. J. McAdam, C. Nervi, D. Osella, M. Ravera, B. H. Robinson and J. Simpson, *Inorg. Chim. Acta*, 1996, **247**, 99.

6 M. S. Khan, A. K. Kakkar, N. J. Long, J. Lewis, P. R. Raithby, P. Nguyen, T. B. Marder, F. Wittmann and R. H. Friend, *J. Mater. Chem.*, 1994, **4**, 1227; B. F. G. Johnson, J. Lewis, P. R. Raithby and D.A. Wilkinson, *J. Organomet. Chem.*, 1991, **408**, C9; J. Lewis, B. Lin, M. S. Khan, M. R. A. Al-Mandhary and P. R. Raithby, *J. Organomet. Chem.*, 1994, **484**, 161; M. C. B. Colbert, D. Hodgson, J. Lewis, N. J. Long and P. R. Raithby, *Polyhedron*, 1995, **14**, 2759.

7 B. H. Robinson and J. Simpson, in *Paramagnetic Organometallic Species in Activation/Selectivity Catalysis*, ed. M. Chanon, Kluwer, Dordrecht, The Netherlands, 1989, p. 357.

8 G. H. Worth, B. H. Robinson and J. Simpson, *Appl. Organomet. Chem.*, 1990, **4**, 481.

9 D. S Shephard, T. Maschmeyer, G. Sankar, J. M. Thomas, D. Ozkaya, B. F. G. Johnson, R. Raja, R. D. Oldroyd and R. G. Bell, *Eur. J. Chem.*, 1998, **4**, 1214; D. S. Shephard, T. Maschmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R. D. Oldroyd and R. G. Bell, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2242.

10 R. Arnold, S. A. Matchett and M. Rosenblum, *Organometallics*, 1988, **7**, 2261; R. Arnold, B. M. Foxman, M. Rosenblum and W. B. Euler, *Organometallics*, 1988, **7**, 1253.

11 M. Rosenblum, H. M. Nugent, K.-S. Jang, M. M. Labes, W. Cahalane, P. Klemarczyk and W. M. Reiff, *Macromolecules*, 1995, **28**, 6330.

12 C. J. McAdam, B. H. Robinson and J. Simpson, *Acta Crystallogr., Sect. C*, 1996, **52**, 2404.

13 B. Bossenbroek, D. C. Sanders, H. M. Curry and H. Shechter, *J. Am. Chem. Soc.*, 1969, **91**, 371.

14 W. Baidossi, H. Schumann and J. Blum, *Tetrahedron*, 1996, **52**, 8349 and refs. therein.

15 Y. Badrich, J. Blum and H. Schumann, *J. Mol. Catal.*, 1994, **90**, 231.

16 T. R. Welberry, *Acta Crystallogr., Sect. B*, 1971, **27**, 360; C. Courseille, B. Busetta, M. Hospital and A. Castellan, *Cryst. Struct. Commun.*, 1972, **1**, 337; G. I. Borodkin, S. M. Nagi, Y. V. Gatilov and V. G. Shubin, *Dokl. Akad. Nauk SSSR*, 1985, **280**, 881; A. D. Schluter, M. Loffler and V. Enkelman, *Nature* (*London*), 1994, **368**, 831.

17 C. R. A. Muchmore and M. J. Heeg, *Acta Crytsallogr., Sect. C*, 1990, **46**, 1743.

18 J. A. Casalnuovo and N. E. Schore, in *Modern Acetylene Chemistry*, ed. P. J. Strang and F. Diederich, VCH, Weinheim, 1995, ch. 5; M. J. Went, *Adv. Organomet. Chem.*, 1997, **41**, 69.

19 R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 1974, **12**, 323.

20 P. E. Elder and B. H. Robinson, *J. Organomet. Chem.*, 1972, **36**, C45.

21 C. J. McAdam, MSc Thesis, University of Otago, 1996.

22 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.

23 D. Gregson and J. A. K. Howard, *Acta Crystallogr., Sect. C*, 1983, **39**, 1024.

24 D. L. Thorn and R. Hoffman, *Inorg. Chem.*, 1978, **17**, 126.

25 J.-J. Bonnet and R. Mathieu, *Inorg. Chem.*, 1978, **17**, 1973.

26 A. Meyer, A. Gorgues, Y. Le Floc'h, Y. Pineau, J. Guillevic and J. Y. Le Marouille, *Tetrahedron Lett.*, 1981, **22**, 5181.

27 C. M. Arewgoda, P. H. Rieger, B. H. Robinson, J. Simpson and S. J. Visco, *J. Am. Chem. Soc.*, 1982, **104**, 5633; L. V. Casagrande, T. Chen, P. H. Rieger, B. H. Robinson, J. Simpson and S. J. Visco, *Inorg. Chem.*, 1984, **23**, 2019.

28 M. M Baizer and H. Lund, *Organic Electrochemistry*, Marcel Dekker, New York, 1983.

29 A. Bard and L. R. Faulkner, *Electrochemical Methods*: *Fundamentals and Applications*, Wiley, New York, 1980.

30 A. C. Ribou, J.-P. Launay, M. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735; A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K.-H. Ongania, K. Wurst and J.-P. Launay, *Organometallics*, 1997, **19**, 392 and refs. therein.

31 R. P. Aggarwal, N. G. Connelly, M. C. Crespo, B. J. Dunne, P. M. Hopkins and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1992, 655.

32 J. Kopilov and D. H. Evans, *J. Electroanal. Chem.*, 1986, **280**, 381.

33 G. H. Worth, B. H. Robinson and J. Simpson, *J. Organomet. Chem.*, 1990, **387**, 337.

34 T. S. Abram and W. E. Watts, *Synth. React. Inorg. Metal–Org. Chem.*, 1976, **6**, 31.

35 E. C. Lisic and B. E. Hanson, *Inorg. Chem.*, 1986, **25**, 812.

36 SMART (Control) and SAINT (Integration) software, Bruker AXS, Madison, WI, 1994.

37 SADABS (correction for area detector data), Bruker AXS, Madison, WI, 1995 and 1997.

38 G. M. Sheldrick, SHELXS-86, 1986; SHELXL-93, 1993; SHELXS-96, 1996; SHELXL-97, 1997; University of Göttingen, Germany; SHEXTL-plus, 1990, Siemens Analytical X-ray Instruments, Madison, WI, USA.

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