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Syntheses and some reactions of complexes containing carbon chains capped by ferrocenyl and $W(CO)_3Cp$ groups

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Abstract

The preparation and some reactions of $W\{(C{\equiv}C)_n\}(CO)Cp$ [$n = 1$–4 (**1**–**4**)] are described. For $n = 1$ and 2, Cu(I)-catalysed reactions between $Fc(C{\equiv}C)_nH$ ($n = 1$, 2) and $WCl(CO)_3Cp$ gave compounds **1** and **2**, respectively, while Cu(I)–Pd(0)-catalysed coupling between $FcC{\equiv}CI$ and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ gave **3**. Oxidative coupling of $FcC{\equiv}CC{\equiv}CH$ and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ gave **4**, together with both homo-coupled products. Electrochemical studies showed that the Fc/Fc^+ oxidation potential increases by about 50 mV for each $C{\equiv}C$ triple bond added to the carbon chain. Reactions with $Co_2(\mu\text{-dppm})_m(CO)_{8-2m}$ ($m = 0$, 1) gave complexes **6**–**10** in which the Co_2 fragment is attached to the sterically least-hindered $C{\equiv}C$ triple bond. The novel vinylidene cluster $Co_2W(\mu_3\text{-CCPhFc})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_5Cp$ (**5**) was also obtained from **1** and $Co_2(\mu\text{-dppm})(CO)_6$. Reactions of **1** with tetracyanoethene (tcne) gave the cyclobutenyl (**11**) and buta-1,3-dien-2-yl (**12**) complexes by cycloaddition to the $C{\equiv}C$ triple bond and subsequent ring-opening. In the presence of silica gel, **12** reacts with MeOH to give the chelating imino complex $W\{C[{=}C(CN)_2C(OMe){=}NH]CFc{=}C(CN)_2\}(CO)_2Cp$ (**13**). With **2** and **3**, addition of tcne to the $C{\equiv}C$ triple bond one removed from the tungsten centre gave buta-1,3-dien-2-yl complexes **14** and **15**. X-ray crystal structure determinations have been carried out on **2**, **5**, **7**, **8** and **10**–**14**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon chains; Cycloaddition; Ferrocene metal cluster; Tungsten

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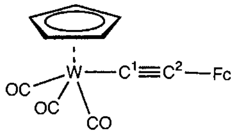
1. Introduction

During the 50 years that have passed since the announcements of the discovery of ferrocene [1,2], the development of its chemistry and subsequent utility has included the recognition of its redox properties and its subsequent employment as a reference compound for electrochemical measurements [3]. In the course of our studies of electronic communication along molecular scale wires, typified by the complex $\{Cp(Ph_3P)_2Ru\}$-$C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$, which shows a series of five 1-e oxidations [4], we and others [5] have employed the ferrocenyl group (Fc) as one of the end-capping groups in related complexes. In this paper, we describe the synthesis and properties of several complexes of the type $Fc(C{\equiv}C)_n\{W(CO)_3Cp\}$ ($n = 1$–4).



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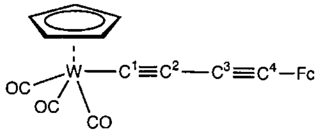

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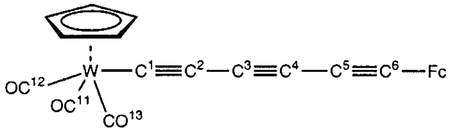

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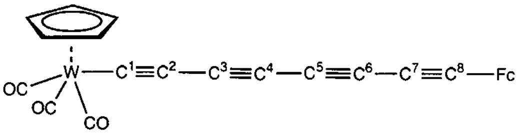

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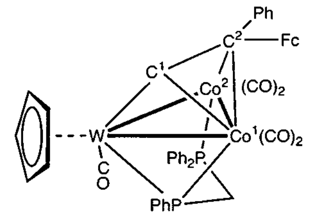

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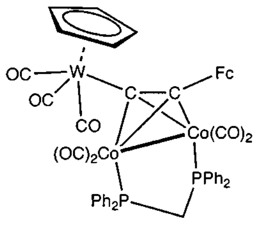

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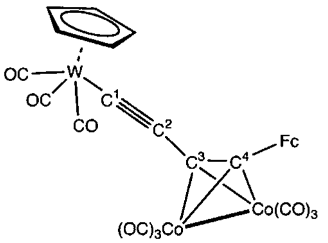

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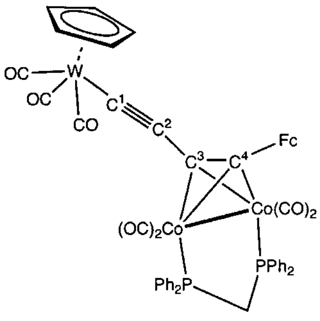

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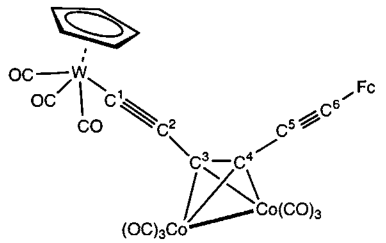

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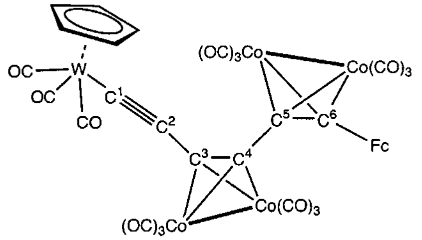

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2. Results

2.1. Syntheses of $Fc(C{\equiv}C)_nW(CO)_3Cp$ [n = 1 (**1**), 2 (**2**), 3 (**3**), 4 (**4**)]

2.1.1. n = 1

The copper(I)-catalysed reaction between $FcC{\equiv}CH$ and $WCl(CO)_3Cp$ was carried out in a mixed THF–diethylamine solvent and afforded orange $W(C{\equiv}CFc)(CO)_3Cp$ (**1**) in 55% yield, which was readily characterised spectroscopically. Thus, its IR $\nu(CO)$ spectrum contained the expected two-band pattern for the $W(CO)_3Cp$ group, together with a single weak $\nu(C{\equiv}C)$ absorption at 2099 cm^{-1}. Resonances in the ^1H- and ^{13}C-NMR spectra (Table 1 lists the ^{13}C-NMR details) were readily assigned to the Fc [singlet (δ_H 4.14, δ_C 69.57) and multiplet resonances (δ_H 4.04, 4.25, δ_C 65–70) for the Cp and C_5H_4 groups, respectively] and CpW groups (singlet at δ 91.6). The two CO resonances (at δ 229.89 and 211.53) showed 62 and 72 Hz couplings to ^{183}W. These features are common to most of the complexes described herein. The two carbons of the acetylenic chain resonated at δ 125.81 and 67.90 and are assigned to C(1) and C(2), respectively, by comparison to similar complexes [5]; neither showed coupling to tungsten. Finally, the electrospray (ESMS) mass spectrum to contained $[M]^+$ at m/z 514, which fragmented by loss of CO groups. Although crystals diffracted X-rays, we have been unable to refine the structure unambiguously.

2.1.2. n = 2

A similar reaction between $FcC{\equiv}CC{\equiv}CH$ and $WCl(CO)_3Cp$ gave red $W(C{\equiv}CC{\equiv}CFc)(CO)_3Cp$ (**2**) in 79% yield, which was characterised by an X-ray structure determination (see below). Its spectroscopic properties include the characteristic two-band $\nu(CO)$ pattern and two $\nu(C{\equiv}C)$ bands at 2253 and 2186 cm^{-1} in the IR spectrum, and the expected resonances in the ^1H- and ^{13}C-NMR spectra. Resonances at δ 111.84 [for C(1)] and between δ 65 and 73.3 are due to the four carbons of the diyne chain, but the latter could not be unambiguously assigned. The base peak in the ESMS is $[M]^+$ at m/z 566.

2.1.3. n = 3

This complex (**3**) was obtained by a copper(I)–palladium(0) catalysed coupling between $FcC{\equiv}CI$ and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ as a bright orange solid in 72% yield. The IR spectrum of **3** contained three $\nu(C{\equiv}C)$ bands between 2181 and 2040 cm^{-1}, and the usual two-band $\nu(CO)$ pattern. In the ^{13}C-NMR spectrum, C(1) resonates at δ 112.17, but the five resonances of the other carbons of the triyne chain appearing between δ 71.4 and 60.63 could not be assigned with certainty. In the ESMS, $[M]^+$ at m/z 590 is the base peak.

2.1.4. $n = 4$

An oxidative coupling reaction between FcC≡CC≡CH and W(C≡CC≡CH)$(CO)_3$Cp was carried out under Hay conditions [Cu(I)–tmed–acetone, O_2, r.t.]. The expected mixture of the three possible coupling products was readily separated by preparative TLC, giving Fc$(C{\equiv}C)_4$W$(CO)_3$Cp (**4**) in 24% yield, together with known Fc$(C{\equiv}C)_4$Fc (22%) [6] and $\{W(CO)_3Cp\}_2C_4$ (24%) [7]. The IR spectrum of **4** contained several ν(C≡C) bands between 2184 and 2011 cm^{-1}, together with ν(CO) absorptions at 2047 and 1961 cm^{-1}. In the ^{13}C-NMR spectrum, seven singlets between δ 60.6 and 80.4 arise from the carbons C(2)–C(8) of the tetrayne chain, together with C(1) at δ 112.16. More readily assignable peaks are at δ 91.68 (WCp) and 70.31 (FeCp). It was necessary to add $[Ag(NCMe)_4]^+$ as an aid to ionisation in the ESMS, whereupon ions at m/z 1336 ($[2M + Ag]^+$) and 655 ($[M + MeCN]^+$) were found.

2.2. Reactions with dicobalt carbonyls

We have previously reported on the utility of simple η^2-alkyne adducts containing $Co_2(CO)_6$ or $Co_2(\mu$-dppm$)(CO)_4$ fragments in identifying or confirming the nature of metal complexes containing di- or poly-ynyl ligands [8]. In most cases, the $Co_2(CO)_6$ groups can be removed oxidatively to regenerate the original complex. In view of the difficulties in obtaining structural characterisation of complexes **1**–**4**, we have examined their reactions with the dicobalt carbonyl precursors.

2.2.1. Reaction between W(C≡CFc)$(CO)_3$Cp and $Co_2(\mu$-dppm$)(CO)_6$

The reaction between **1** and $Co_2(\mu$-dppm$)(CO)_6$ was carried out in benzene at 80 °C for 16 h. Two complexes were separated from the reaction mixture by preparative TLC. The faster moving band contained a dark red compound, which was characterised by a single-crystal X-ray structure determination as the cluster vinylidene $Co_2W(\mu_3$-CCPhFc$)(\mu_3$-PPhCH$_2$PPh$_2)$-$(CO)_5$Cp (**5**). Spectroscopic properties were in accord with the solid-state structure, with several ν(CO) bands between 2014 and 1899 cm^{-1} in the IR spectrum. In the ^{1}H-NMR spectrum, singlet resonances at δ 5.11 (WCp) and 3.66 (FeCp) were accompanied by multiplets assigned to CH_2, C_5H_4 and Ph protons. The ^{13}C-NMR spectrum contained resonances for vinylidene carbons at δ 103.88 [C(1)] and 70.23 [C(2)], singlet resonances at δ 86.87 (WCp) and 68.92 (FeCp) and the

Table 1
Selected ^{13}C-NMR data [δ (J_{CW}, Hz)]

Complex	δ(WCp) [a]	δ(FeCp) [a]	$\delta(FeC_5H_4)$ [b]	δW(CO)	δ(CC) [c]	Other resonances
1	91.60	69.57	65.61, 67.50, 70.84	229.89t (62), 211.53t (72)	125.81, 67.90	
2	91.60	69.94	64.94, 68.68, 71.97	228.07t (61), 210.65t (72)	111.84,73.30,72.59, 67.89	
3	91.67	70.20	63.29, 69.23, 72.44	227.22t (61), 210.33t (72)	112.17, 71.40, 66.13, 63.83, 60.95, 60.09	
4	91.68	70.31	65.67, 69.69, 73.02	210.19s	112.16, 80.38, 71.39, 70.48, 64.45, 62.70, 62.12, 60.63	
5	86.87	68.92	65.40, 68.21, 69.44		103.88, 70.23	29.70 (CH_2P), 125.69–131.92 (Ph)
6	92.81					126.33–137.22 (Ph)
7	91.76	69.67	69.94, 69.91	228.41s, 210.34s	124.82, 93.21, 85.69	
8	91.63	69.19	67.87, 69.64, 69.82	218.44s, 210.84s	97.71, 90.85, 22.55, 14.01	29.62 (CH_2P), 127.80–133.51 (Ph)
9	91.75	69.85	69.17, 70.02	227.21s, 210.35s	112.46, 87.72, 85.31, 84.34, 72.55, 72.5	198.74 (br) [Co(CO)]
10	91.73	69.73	68.72, 70.95	228.41s, 210.06s	112.45	199.24 (br) [Co(CO)]
11	91.88	70.54	67.82, 70.83, 73.84	228.40s, 212.83s	155.15	44.35, 46.88 [2 × s, $C(CN)_2$], 110.61, 111.28 (2 × s, CN)
12	93.95	72.69	71.09, 73.03, 74.71	221.22s, 216.39s	67.81, 29.67	28.66, 29.33 [2 × s, $C(CN)_2$], 113.68, 115.09 (2 × s, CN)
14	92.56	72.49	71.01, 73.37, 75.43	221.21s, 210.20s	170.18, 147.73, 88.03	31.54, 31.89 [2 × s, $C(CN)_2$], 111.36, 112.89, 113.11, 114.23 (4 × s, CN)
15	92.12	72.67	70.93, 72.84, 73.70	222.85s, 209.27s	169.66, 148.53, 105.26, 71.53	75.84, 76.14 [2 × s, $C(CN)_2$], 110.92, 111.48, 112.87, 113.42 (4 × s, CN)

[a] Singlets.

[b] Resonances for three ring carbons of C_5H_4 group.

[c] Resonances for carbon chain.

dppm CH_2 resonance at δ 29.7. In the ESMS of a solution containing NaOMe, the highest mass ions were at m/z 1123 ($[M+Na]^+$) and 1016 ($[M-3CO]^+$).

The second complex appears to be the heptacarbonyl precursor of **5**, namely $W\{\eta^1:\eta^2\text{-}C_2Fc[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_3Cp$ (**6**), as indicated by microanalytical and some spectroscopic data. The IR spectrum contains three terminal and one bridging $\nu(CO)$ bands between 1986 and 1812 cm^{-1}, while the ^1H- and ^{13}C-NMR spectra contain the expected singlets for the WCp and FeCp groups. In the ESMS, the only significant ions correspond to $[M-nCO]^+$ ($n=5$–7), between m/z 1016 and 960.

2.2.2. Reaction between $W(C\equiv CC\equiv CFc)(CO)_3Cp$ and $Co_2(CO)_8$ or $Co_2(\mu\text{-dppm})(CO)_6$

The reaction between **2** and $Co_2(CO)_8$ afforded the simple adduct $W\{\eta^1:\eta^2\text{-}C\equiv CC_2Fc[Co_2(CO)_6]\}(CO)_3Cp$ (**7**) as black crystals in 60% yield. A single-crystal X-ray structure determination confirmed that the Co_2 fragment is attached to the sterically least-congested C≡C triple bond, i.e. that carrying the Fc group. Spectroscopic data are in accord with the solid-state structure and deserve no further comment here; the negative ion ESMS contains $[M+OMe]^-$ at m/z 883, which fragments by loss of up to nine CO groups.

Similarly, a dark red solid (**8**) was obtained from the reaction between **2** and $Co_2(\mu\text{-dppm})(CO)_6$ in 42% yield. An X-ray determination showed this to have a structure analogous to that of **7**, as suggested by the elemental analysis and spectroscopic data. In this case, we suggest that resonances at δ 97.7, 90.85, 22.55 and 14.01 can be assigned to C(1), C(2), C(3) and C(4), respectively, the latter two being shifted upfield by coordination to the Co_2 fragment. The ESMS contains the ions $[M-nCO]^+$ ($n=2$–7).

2.2.3. Reaction between $W\{(C\equiv C)_3Fc\}(CO)_3Cp$ and $Co_2(CO)_8$

Two black compounds were obtained from the reaction between **3** and $Co_2(CO)_8$. Separation by preparative TLC gave the monoadduct, $W\{C\equiv CC_2[Co_2(CO)_6]\text{-}C\equiv CFc\}(CO)_3Cp$ (**9**), as the slower-moving band, in 38% yield, and the bis-adduct $W\{C\equiv CC_2[Co_2(CO)_6]C_2Fc[Co_2(CO)_6]\}(CO)_3Cp$ (**10**) in 21% yield, characterised by a single-crystal X-ray structure determination. Spectroscopic data are in agreement with the structures proposed or found. For **9**, $\nu(C\equiv C)$ for the uncoordinated C≡C triple bonds was at 2134 cm^{-1}, while the NMR spectra contained singlets at δ_H 5.69 and 4.28 and δ_C 91.75 and 69.85 for the WCp and FeCp groups, respectively. Several resonances between δ_C 69 and 113 are assigned to the carbons of the C_6 chain, although only the resonance at δ 112.46 can be confidently assigned to C(1). A quadrupole-broadened singlet at δ 198.74 arises from the Co(CO) groups. In the ESMS $[M]^+$ is found at m/z 876. Compound **10** has similar spectroscopic properties, the $\nu(CO)$ region containing two more bands, while there is no $\nu(C\equiv C)$ absorption for an uncoordinated C≡C triple bond. In the ^{13}C-NMR spectrum, the carbons of the C_6 chain were not resolved, singlets at δ_C 91.73 and 69.73 being assigned to the WCp and FeCp groups, respectively. The Co(CO) groups again resonate as a broad singlet at δ 199.24. The negative ion ESMS of a solution containing NaOMe contained $[M+OMe]^-$ at m/z 1192.

2.3. Reactions with tetracyanoethene

Cycloaddition of tetracyanoethene (tcne) to C≡C triple bonds to give cyclobutenyls and subsequent ring-opening to buta-1,3-dien-2-yl complexes are other characteristic reactions of σ-alkynyl or poly-ynyl ligands on transition metals [9]. In this case, the di- or poly-ynyl ligands cannot be regenerated from the cyanocarbon ligand, but the reactions offer further confirmation of the presence of the former.

2.3.1. With $W(C\equiv CFc)(CO)_3Cp$

Addition of tcne to **1** in dichloromethane solution resulted in a change in colour from orange to red after a few minutes. The solution gave an orange solid in 74% yield, which was shown to be the corresponding cyclobutenyl complex $W\{C{=}CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (**11**) by an X-ray structural study. Characteristic spectral properties include weak $\nu(CN)$ bands at 2390 and 2338 cm^{-1}, the usual $\nu(CO)$ pattern at 2042 and 1963 cm^{-1}, and singlet resonances for WCp and FeCp groups at δ_H 4.29 and 5.83, and δ_C 70.54 and 91.88, respectively. The cyclobutenyl ring carbons resonate around δ 68–74, the $C(CN)_2$ atoms at δ ca. 45, and the CN groups at δ ca. 110. The ESMS of a solution containing NaOMe contained $[M+Na]^+$ at m/z 693.

On heating a solution of **11** in refluxing THF for 6 h, the colour deepened, and preparative TLC enabled separation of the blue buta-1,3-dien-2-yl complex $W\{C[{=}C(CN)_2]CFc{=}C(CN)_2\}(CO)_3Cp$ (**12**), again characterised by a crystallographic study. Spectroscopic data include $\nu(CN)$ at 2222 cm^{-1}, $\nu(CO)$ at 2049 and 1960 cm^{-1} and singlet resonances for the FeCp and WCp groups at δ_H 4.45 and 5.51, respectively. Butadienyl carbons are found between δ_C ca. 68 and 75, the CN carbons at δ_C ca. 114 and the $C(CN)_2$ carbons at δ_C 22.66 and 29.33. The molecular ion is found at m/z 670 in the ESMS.

When **12** was extracted from TLC silica gel with methanol, the colour changed to red. Purification and crystallisation gave the methanol adduct $W\{C[{=}C(CN)_2C(OMe){=}NH]CFc{=}C(CN)_2\}(CO)_2Cp$ (**13**), as

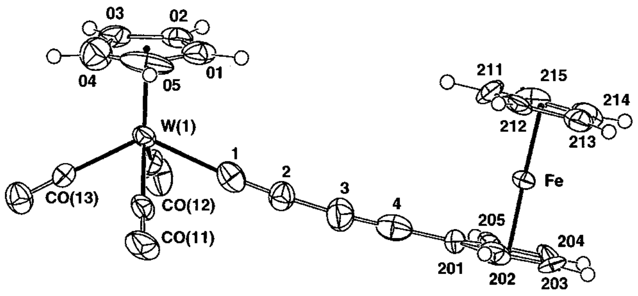


Fig. 1. Plot of a molecule of $W(C{\equiv}CC{\equiv}CFc)(CO)_3Cp$ (**2**), showing atom numbering scheme. In this and subsequent figures, 50% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

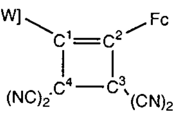
shown by a single-crystal X-ray structure determination. Addition of methanol to one of the CN groups of the $=C(CN)_2$ unit adjacent to the tungsten has occurred. Full spectroscopic data were not obtained, the IR spectrum containing ν(CN) at 2220 cm^{-1} and two strong ν(CO) bands at 1969 and 1897 cm^{-1}, while the ^1H-NMR spectrum contained singlet resonances at δ 4.52 and 5.08 for FeCp and WCp groups, respectively, and at δ 4.05 for the OMe protons. In the ESMS $[M]^+$ is found at m/z 674.

2.3.2. With $W(C{\equiv}CC{\equiv}CFc)(CO)_3Cp$

Dark green crystals of $W\{C{\equiv}CC[{=}C(CN)_2]CFc{=}C(CN)_2\}(CO)_3Cp$ (**14**) were obtained in 75% yield from the reaction between **2** and tcne. The illustrated structure was determined by an X-ray study and spectral properties were in accord with it. Two ν(CN) bands at 2225 and 2165 cm^{-1}, a ν(C≡C) absorption at 2073 cm^{-1} and two ν(CO) bands at 2026 and 1965 cm^{-1} are present in the IR spectrum, while the singlets for the FeCp and WCp groups occur at δ_H 4.37 and 5.79 and δ_C 72.49 and 92.56, respectively. Other resonances in the ^{13}C-NMR spectrum can be assigned to the CN carbons (at δ ca. 111–114), dienyl carbons (at δ 75.43 and 88.03), acetylenic carbons C(2) and C(6) (δ 147.73 and 170.18) and the $C(CN)_2$ carbons (at δ ca. 31). Positive- and negative-ion ES mass spectra of a solution containing NaOMe contained $[M+Na]^+$ and $[M+OMe]^-$ at m/z 717 and 725, respectively.

2.3.3. With $W\{(C{\equiv}C)_3Fc\}(CO)_3Cp$

The red–brown complex obtained in 48% yield from **3** and tcne is probably $W\{C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}CFc\}(CO)_3Cp$ (**15**). The IR spectrum contains two ν(CN) bands (2225, 2164 cm^{-1}), two ν(C≡C) bands (2130 and 2055 cm^{-1}) and two ν(CO) bands (2025 and 1967 cm^{-1}). In the NMR spectra, singlets are found for the FeCp and WCp groups (δ_H 4.41 and 5.70; δ_C 72.67 and 92.12, respectively); carbon resonances at δ ca. 110–113 (CN), ca. 75 [$C(CN)_2$], and between δ ca. 71 and 76 (diene carbons) are accompanied by signals at δ 148.53 and 169.66 [for C(2) and C(6)] and at δ 209.27 and 222.85 [W(CO)]. The ESMS of a solution containing $[Ag(NCMe)_4]^+$ contained ions at m/z 1544 and 826, corresponding to $[2M+Ag]^+$ and $[M+Ag]^+$, respectively.



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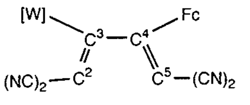

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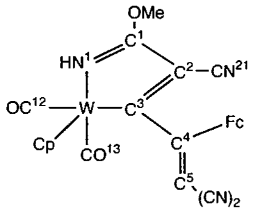
[W] = $W(CO)_3Cp$



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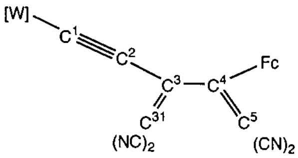

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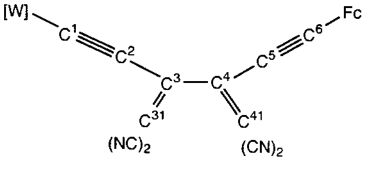

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[W] = $W(CO)_3Cp$

2.4. Molecular structures

The molecular structures of **2**, **5**, **7**, **8** and **10**–**14** have been determined by single-crystal X-ray diffraction studies. A single molecule, devoid of crystallographic symmetry, comprises the asymmetric unit in each case, with the exception of **7**, where two independent molecules are found. A molecule of each is depicted in

Figs. 1–9 and significant structural data are collected in Tables 2–4.

All complexes except **5** and **13** contain W(CO)$_3$-Cp groups, which have the usual piano–stool structure, with CO(12) group being *trans* to the σ-bonded carbon ligand. The structural parameters fall within a narrow range [W–C(Cp) 2.291(7)–2.393(5) Å, W–CO 1.969–2.029(4) Å; angles at W: OC–W–CO(*cis*) 71.3–78.5(3)°, OC–W–CO(*trans*) 108.3–115.0(2)°, C(1)–W–CO(*trans*) 125.8–131.1(2)°]. Similarly, Fe–C(Cp) [2.01(1)–2.063(4) Å] falls within the usual range. Other details worthy of comment follow.

2.4.1. W(C≡CC≡CFc)(CO)$_3$Cp (2)

The W–C [2.12(2) Å] and C–C distances [1.20, 1.37, 1.24(2) Å] confirm the diyne nature of the carbon chain, which is slightly bent (by ca. 4° at each carbon atom).

2.4.2. W{C≡CC$_2$Fc[Co$_2$(CO)$_6$]}(CO)$_3$Cp (7) (values of molecule 1), W{C≡CC$_2$[Co$_2$(CO)$_6$]C$_2$Fc[Co$_2$(CO)$_6$]}-(CO)$_3$Cp (10) and W{C≡CC$_2$Fc[Co$_2$(μ-dppm)(CO)$_4$]}-(CO)$_3$Cp (8)

The W–C(α) distances for these three complexes are similar [2.118(7), 2.128(4), 2.139(3) Å] and the C(α)–C(β) distances [1.222(9), 1.207(6), 1.217(4) Å] confirm the presence of the C≡C triple bond. Complexing to the Co$_2$ unit lengthens the C–C separations to 1.345(8), 1.343(6), 1.360(4) Å and induces bend-back angles of between 141.1(7) and 142.8(4)°. The Co–Co separations are 2.467–2.480(1) Å, the presence of the dppm ligand resulting in little change. The pair of Co$_2$ components in **10** lie *transoid* about C(4)–C(5).

2.4.3. Co$_2$W(μ$_3$-PPhCH$_2$PPh$_2$)(μ$_3$-CCPhFc)(CO)$_5$Cp (5)

The X-ray structure determination (Fig. 5 and Table 5) confirms the molecular arrangement, with the Co$_2$W

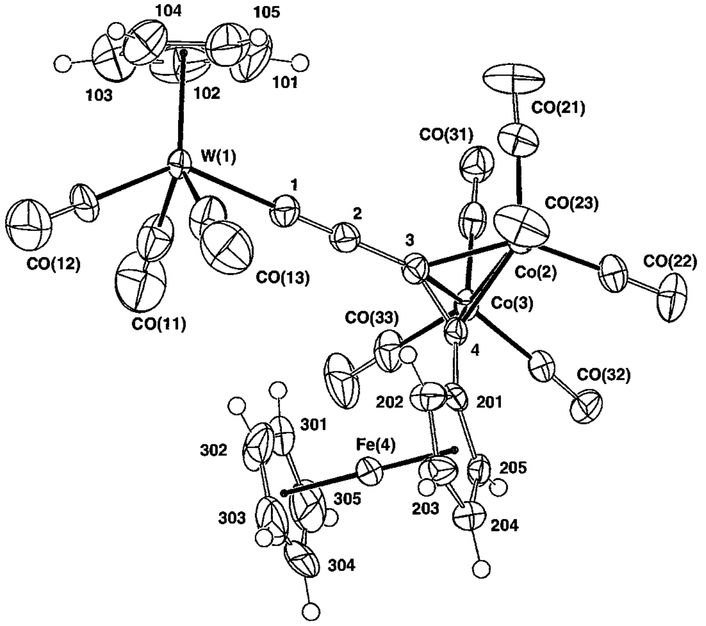

Fig. 2. Plot of a molecule of W{C≡CC$_2$Fc[Co$_2$(CO)$_6$]}(CO)$_3$Cp (7), showing atom numbering scheme.

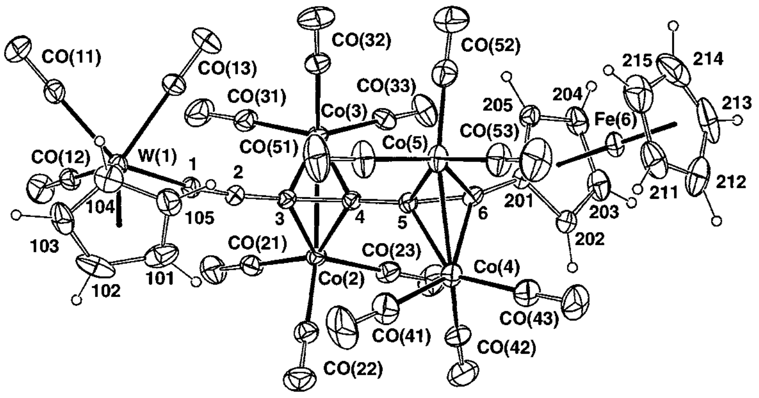

Fig. 3. Plot of a molecule of W{C≡CC$_2$[Co$_2$(CO)$_6$]Fc[Co$_2$(CO)$_6$]}(CO)$_3$Cp (10), showing atom numbering scheme.

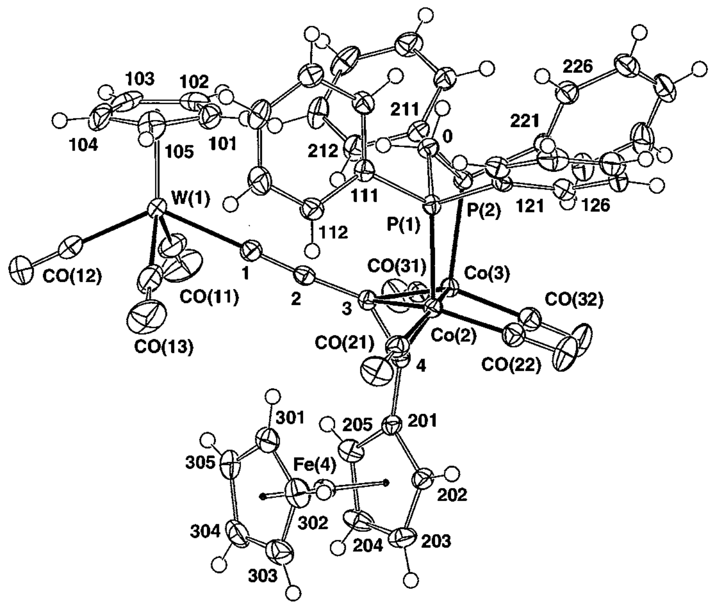

Fig. 4. Plot of a molecule of $W\{C{\equiv}CC_2Fc[Co_2(\mu\text{-dppm})CO)_4]\}(CO)_3Cp$ (**8**), showing atom numbering scheme.

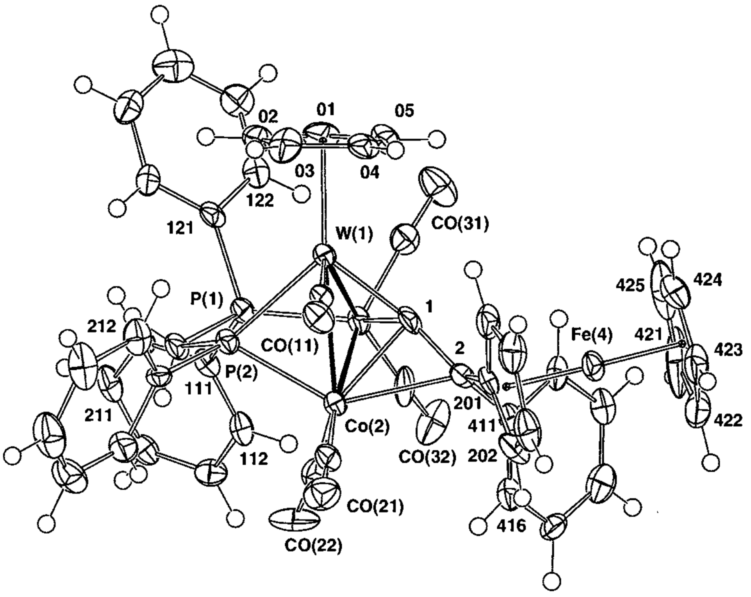

Fig. 5. Plot of a molecule of $Co_2W(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}CCPhFc)(CO)_5Cp$ (**5**), showing atom numbering scheme.

cluster [Co–Co 2.500(2) Å, Co(2,3)–W 2.660, 2.717(1) Å] supporting the vinylidene ligand, in which the C–C distance is lengthened to 1.41(1) Å as a result of interaction with Co(2). The difference in Co–W distances results from π attachment of both C(1) and C(2) to Co(2), increasing the electron density at this centre and thus shortening the Co(2)–W bond compared with Co(1)–W. Structural parameters for the $PhCH_2PPh_2$ ligand are similar to those found in numerous other examples.

2.4.4. W{C=CFcC(CN)$_2$C(CN)$_2$}(CO)$_3$Cp (**11**), *W{C[=C(CN)$_2$]CFc=C(CN)$_2$}(CO)$_3$Cp* (**12**) *and W{C≡CC[=C(CN)$_2$]CFc=C(CN)$_2$}(CO)$_3$Cp* (**14**)

The first two structures enable a direct comparison to be made between the cyclobutenyl and butadienyl ligands. In **11**, the C(3)–C(4) bond is relatively long [1.596(5) Å] and the torsion angle about this bond is − 1.8(2)°, suggesting that the conrotatory ring-opening which eventually leads to **12** is beginning in this complex. In the butadienyl, a *transoid* conformation is

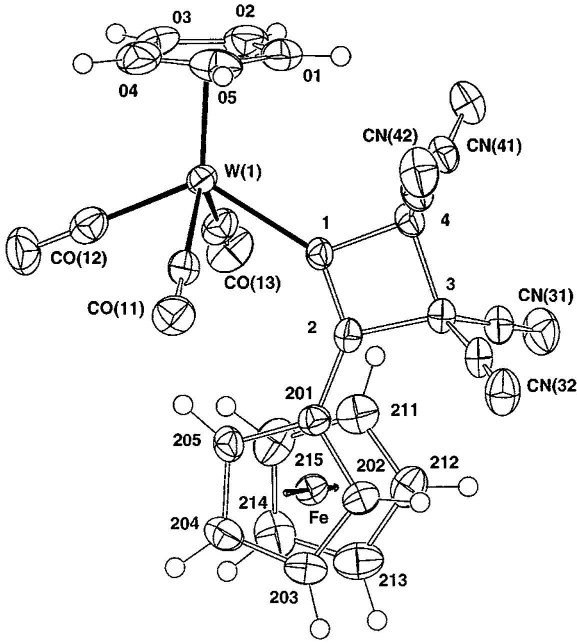

Fig. 6. Plot of a molecule of $W\{C{=}CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (**11**), showing atom numbering scheme.

adopted, the C(1)–C(4) and C(2)–C(3) separations clearly showing the presence of C=C double bonds. The W–C(1) distances [2.198(3), 2.228(3) Å for **11** and **12**, respectively] are ca. 0.09, 0.12 Å longer than found for the W–C(sp) bond in **14** [2.107(3) Å], and are consistent with the usual lengthening found on going from sp to sp^2 hybridised carbons. The structural determination of **14** confirms the site of addition of the cyano-olefin as the Fc–C≡C triple bond of precursor **2**, bond parameters being similar to those of **12**.

2.4.5. $W\{C[{=}C(CN)C(OMe){=}NH]CFc{=}C(CN)_2\}(CO)_2Cp$ (**13**)

The structure determination (Fig. 9, Table 6) confirms the site of addition of the MeOH molecule to one of the dicyanomethylene CN groups adjacent to the tungsten, thus allowing chelation of the resulting imine group. Structural data are consistent with the formulation, with W–C and W–N distances of 2.140(4) and 2.149(5) Å, respectively; the various C–C and C–N separations in the ligand are consistent with the formulation shown in structure **13**.

2.5. Electrochemistry

Interest in the conduction of electronic effects along the unsaturated carbon chains led us to examine the CVs of these complexes, although as described previously, the tungsten end-cap is not generally redox active in similar compounds. Consequently, the single reversible oxidation wave found for each compound [E° + 0.50 (**1**), + 0.56 (**2**), + 0.62 (**3**), + 0.65 V (**4**); referenced to $FcH/[FcH]^+ = +0.46$ V] (Table 5) is assigned to the usual Fc/Fc^+ oxidation, which moves to higher potentials as the chain is lengthened. This is consistent with partial electron transfer from the ferrocene nucleus on to the carbon chain. Irreversible oxidations between + 1.04 and + 1.11 V are assigned to processes occurring at the tungsten centre: there is no obvious correlation between these potentials and chain length.

Addition of the $Co_2(CO)_6$ fragment to **2** to give **7** resulted in a decrease in oxidation potential to + 0.49 V, with an irreversible oxidation at + 1.03 V. More dramatic changes in oxidation potential were found with the adducts **6** and **8**, which showed two reversible 1-e oxidations at + 0.29 and 0.63 V, and + 0.32 and 0.71 V, respectively. Only **8** showed an irreversible oxidation at higher potential (+ 1.11 V). The reduction in oxidation potential of $Co_2(\mu\text{-dppm})(CO)_4$ adducts of poly-ynyl complexes has been noted before and is ascribed to the increased electron density in the Co_2C_2 core [10].

Alteration of the carbon chain by cycloaddition and subsequent ring-opening reactions to give tetra-

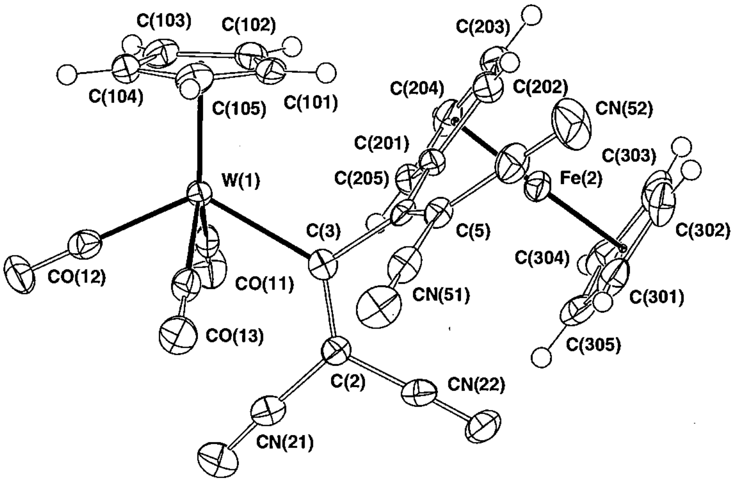

Fig. 7. Plot of a molecule of $W\{C[{=}C(CN)_2]CFc{=}C(CN)_2\}(CO)_3Cp$ (**12**), showing atom numbering scheme.

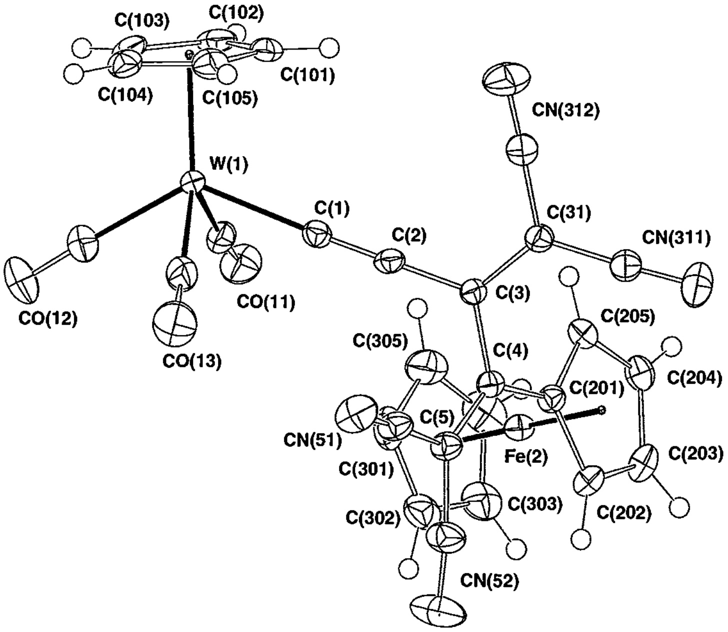

Fig. 8. Plot of a molecule of $W\{C\equiv CC[{=}C(CN)_2]CFc{=}C(CN)_2\}(CO)_3Cp$ (**14**), showing atom numbering scheme.

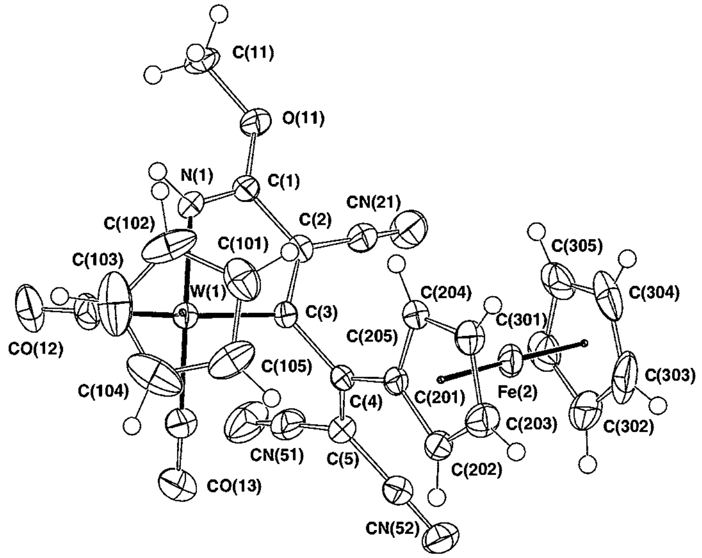

Fig. 9. Plot of a molecule of $W\{C[{=}C(CN)C(OMe){=}NH]CFc{=}C(CN)_2\}(CO)_2Cp$ (**13**), showing atom numbering scheme.

cyanobutadienyl derivatives results in an increase in the first oxidation potentials to $+0.73$, 0.76 and 0.89 V for **11**, **12** and **14**, respectively. The first two showed irreversible oxidations at $+1.44$ and $+1.42$ V, respectively, while for **14**, this second oxidation was found at $+1.18$ V. Unusually, the latter complex also showed two reduction waves at -0.59 and -0.80 V, which are likely to involve the cyanocarbon groups. These observations are all consistent with the addition of strongly electron-withdrawing groups to the chain, although we have not yet carried out any further characterisation of the oxidation or reduction products.

3. Discussion

Application of Sonogashira, Hay and oxidative coupling reactions has enabled us to prepare a series of alkynyl and poly-ynyl complexes of tungsten which additionally contain redox-active ferrocenyl groups. Thus, copper(I)-catalysed reactions of ethynyl- and butadiynyl-ferrocenes with $WCl(CO)_3Cp$ gave $W\{(C\equiv C)_n\}(CO)_3Cp$ ($n = 1$ and 2, respectively), while Hay coupling of $FcC\equiv CI$ with the first of these gave the derivative with $n = 3$. The heterometallic tetrayne was obtained with the two homometallic complexes by oxidative coupling of $FcC\equiv CC\equiv CH$ with $W(C\equiv CC\equiv$

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **2**, **7**, **8**, **10–12** and **14**

Parameter	**2**	**7** (2 molecules)	**8**	**10**	**11**	**12**	**14**
W–C(Cp)	2.30–2.35(1)	2.29–2.40(1)	2.308–2.369(3)	2.302–2.355(5)	2.306–2.393(5)	2.314–2.373(4)	2.306–2.359(7)
(Avg.)	2.32(2)	2.34(4)	2.34(3)	2.33(2)	2.34(4)	2.34(3)	2.33(2)
W–CO(a) [a]	2.00(1)	2.005(7), 2.006(9)	2.002(4)	2.001(5)	1.987(4)	1.992(4)	2.007(6)
W–CO(b,c) [a]	2.01,2.00(1)	1.981–2.006(7)	1.996, 2.005(4)	1.969, 1.987(5)	2.001, 1.988(4)	1.994, 2.029(4)	1.995, 2.007(6)
C(a)–W–C(b,c)	77.8, 77.4(5)	77.3(3)–82.9(4)	78.2(2), 78.1(1)	76.5, 77.3(2)	78.5, 76.7(2)	74.4(1), 77.0(2)	77.9(2), 76.3(1)
C(b)–W–C(c)	113.8(5)	108.3(3), 108.9(4)	110.4(1)	107.7(2)	115.0(2)	114.2(1)	110.0(2)
Fe–C(Cp)	2.01–2.06(1)	2.018–2.055(6)	2.030–2.055(3)	2.00(1)–2.057(5)	2.035–2.052(4)	2.026–2.059(4)	2.034–2.063(4)
(Avg.)	2.04(1)	2.05(1)	2.041(9)	2.03(1)	2.042(6)	2.04(1)	2.05(1)
W–C(1)	2.12(2)	2.118(7)	2.139(3)	2.128(4)	2.198(3)	2.228(3)	2.107(3)
C(1)–W–C(a)	128.2(5)	130.6(3)	131.1(1)	128.9(2)	126.0(1)	125.8(1)	129.4(2)
C(1)–W–C(b,c)	75.6, 73.9(5)	77.5, 71.3(3)	74.2, 75.0(1)	75.7, 71.7(2)	73.8, 74.6(1)	75.6, 75.8(1)	74.2(1), 74.9(2)
C(1)–C(2)	1.20(2)	1.222(9)	1.217(4)	1.207(6)	1.360(5)	1.496(5)	1.211(5)
C(2)–C(3)	1.37(2)	1.406(9)	1.404(4)	1.405(6)	1.531(4)	1.366(5)	1.404(5)
C(3)–C(4)	1.24(2)	1.345(8)	1.360(4)	1.343(6)	1.596(5)	1.496(5)	1.508(8)
C(n)–C(201)	1.39(2) ($n = 4$)	1.441(8) ($n = 4$)	1.453(4) ($n = 4$)	1.458(6) ($n = 6$)	1.448(5) ($n = 2$)	1.454(4) ($n = 2$)	1.439(5) ($n = 4$)
W–C(1)–C(2)	176(1)	176.5(5)	178.9(3)	173.9(4)	140.6(3)	[117.1(2)]	177.6(4)
C(1)–C(2)–C(3)	176(1)	177.5(7)	176.1(3)	175.2(5)	97.0(3)	[118.8(3)]	178.8(4)
C(2)–C(3)–C(4)	176(2)	141.1(7)	141.2(3)	142.8(4)	84.5(2)	114.8(3)	118.2(4)
C($n-1$)–C(n)–C(201)	177(1) ($n = 4$)	140.3 ($n = 4$)	141.3(3) ($n = 4$)	136.5(3) ($n = 6$)	138.5(3) ($n = 2$)	[115.5(2)]	117.3(4) ($n = 4$)

[a] The three W–CO carbons are designated a, b, c; a is *trans* to c.

In **7**, Co(n)–C(3,4) are 1.962, 1.988(6) ($n = 2$); 1.986, 1.954(6) ($n = 3$); Co(2)–Co(3) 2.469(1) Å. In **8**, Co(n)–C(3,4) are 1.981, 1.937(3) ($n = 2$); 1.987, 1.967(3) ($n = 3$); Co(2)–Co(3) 2.4745(6); Co–P 2.2118, 2.2245(8); P–C(0) 1.842, 1.834(3) Å. In **10**, Co(n)–C(3,4) are 1.976, 1.953(4) ($n = 2$); 1.976, 1.976(4) ($n = 3$); Co(2)–Co(3) 2.4672(9), Co(4)–Co(5) 2.480(1); Co(n)–C(5,6) 1.975, 1.944(4) ($n = 4$); 1.962, 1.983(4) ($n = 5$); C(5)–C(4,6) 1.433(6), 1.350(6) Å; C(3)–C(4)–C(5), C(4)–C(5)–C(6) are 142.3, 142.4(4)°. In **11**, C(1)–C(4) is 1.563(5) Å. In **12**, C(4)–C(5) is 1.366(5); C(2)–C(3)–C(4) is 114.8(3)°. In **14**, C(4)–C(5), C(3)–C(31) are 1.367(6), 1.379(7) Å; C(3)–C(4)–C(5) is 116.1(4)°. In **11**, **12**, **14**, C–CN range between 1.461 and 1.481(5), 1.435 and 1.453(6), 1.427 and 1.449(9) Å, respectively.

CH)(CO)$_3$Cp, all three coupling products being obtained in approximately equal amounts. All complexes **1**–**4** were obtained pure as crystalline solids and characterised spectroscopically. Unfortunately, it has not been possible to assign the resonances for the carbon chains unequivocally as couplings to tungsten were not resolved. The possibility of using tertiary phosphine-substituted tungsten groups was not explored. X-ray crystal structure determinations of **1**, **3** and **4** were dogged by difficulties in refinement so that only the structure of **2** was satisfactorily obtained.

Subsequent chemistry associated with the poly-yne system was carried out with the dicobalt carbonyl and tcne adducts. With $Co_2(CO)_8$, **2** gave a mono-adduct, shown crystallographically to be the expected isomer with the $Co_2(CO)_6$ unit attached to the C_2 group adjacent to the Fc group, i.e. the least sterically hindered site. No evidence for the formation of the other isomer with the Co_2 group attached to the W–C≡C triple bond was obtained. With **3**, two adducts were obtained, one bearing a $Co_2(CO)_6$ fragment attached to the central C_2 unit and the other being the bis-adduct, where the second dicobalt fragment is attached to the C_2 unit next to the Fc group. The formation of mono-adducts in which the Co_2 unit is attached to either the W–C≡C or the Fc–C≡C triple bond was not observed, nor were any complexes containing a complexed W–C≡C triple bond obtained.

Reactions of $Co_2(\mu\text{-dppm})(CO)_6$ with **1** afforded the expected simple adduct **4**, together with a rearranged product which was identified crystallographically as the Co_2W cluster **5**. Although the latter was obtained from a reaction carried out in refluxing benzene for 16 h,

Table 3
Selected bond lengths (Å) and bond angles (°) in **5**

Bond lengths			
Co(2)–Co(3)	2.500(2)	W(1)–C(1)	2.021(8)
Co(2)–W(1)	2.660(1)	Co(2)–C(1)	2.004(8)
Co(3)–W(1)	2.717(1)	Co(2)–C(2)	2.336(8)
Co(2)–P(2)	2.219(2)	Co(3)–C(1)	1.973(8)
Co(3)–P(1)	2.266(2)	W(1)–C(Cp)	2.315–2.385(9)
W(1)–P(2)	2.341(2)	(Avg.)	2.35(3)
W–CO	1.959(8)	Fe–C(Cp)	2.002–2.080(7)
Co(2)–CO	1.800, 1.761(8)	(Avg.)	2.04(2)
Co(3)–CO	1.752, 1.799(9)		
P–C(0)	1.841, 1.847(8)	C(1)–C(2)	1.41(1)
Bond angles			
Co(2)–P(2)–W(1)	71.29(6)	W(1)–C(1)–C(2)	145.5(6)
P(1)–C(0)–P(2)	105.2(4)	C(1)–C(2)–C(201)	120.3(7)
Co(3)–C(1)–C(2)	122.5(6)	C(1)–C(2)–C(411)	122.4(7)

Table 4
Selected bond lengths (Å) and bond angles (°) for **13**

Bond length		*Bond angles*	
W–C(Cp)	2.291–2.369(7)	C(3)–W–C(12)	115.5(2)
(Avg.)	2.33(3)	C(3)–W–C(13)	80.4(2)
W–C(CO)	1.979(4), 1.989(5)	C(12)–W–C(13)	79.8(2)
Fe–C(Cp)	2.032–2.062(7)	N(1)–W–C(3)	72.8(2)
(Avg.)	2.05(1)	N(1)–W–C(12)	77.4(2)
W–N(1)	2.149(5)	N(1)–W–C(13)	132.4(2)
W–C(3)	2.140(4)	W–N(1)–C(1)	120.3(3)
		W–C(3)–C(2)	117.4(3)
N(1)–C(1)	1.288(6)	W–C(3)–C(4)	124.5(4)
C(1)–C(2)	1.425(6)	C(1)–C(2)–C(3)	113.9(4)
C(2)–C(3)	1.388(8)	C(2)–C(3)–C(4)	118.0(4)
C(3)–C(4)	1.479(6)	C(3)–C(4)–C(5)	120.3(4)
C(4)–C(5)	1.365(6)	C(3)–C(4)–C(201)	115.8(3)
C(4)–C(201)	1.457(6)	N(1)–C(1)–C(2)	115.5(5)
C–CN	1.434, 1.432, 1.447(7)		

Table 5
Selected electrochemical data (V)

Complex	E^1	E^2
1	0.50	1.06 (irr)
2	0.56	1.05 (irr)
3	0.62	1.04 (irr)
4	0.65	1.11 (irr)
6	0.29	0.63
7	0.49	1.03 (irr)
8 [a]	0.32	0.71
11	0.73	1.44 (irr)
12	0.76	1.42 (irr)
14 [b]	0.89	1.18 (irr)

0.1 mg ml^{-1} in CH_2Cl_2, 0.1 M $[NBu_4]BF_4$, r.t., Pt electrodes (FcH/$[FcH]^+ = 0.46$ V).

[a] Also shows third, irreversible oxidation wave at +1.11 V.

[b] Also shows two reversible reduction waves at −0.59, −0.80 V.

similar treatment of **4** did not result in any transformation to **5**. The cluster contains a dephenylated dppm ligand together with a vinylidene bearing both phenyl and ferrocenyl groups, which bridges all three metal atoms.

As found previously [10], the vinylidene is π-bonded to the most electronegative metal centre. It is reasonable to suggest that thermal cleavage of a P–Ph bond liberates a Ph group which is trapped by the ferrocenylethynyl ligand, effectively an electrophilic attack by the phenyl group. Under the reaction conditions, decarbonylation also occurs with concomitant cluster formation, no doubt assisted by the cluster-capping requirements of the two non-carbonyl ligands. It is not possible to say whether any other intermediates are formed, for example, by oxidative addition of the P–Ph bond to either W or Co_2 centres. Coordination of a $Co_2(\mu\text{-dppm})(CO)_4$ fragment to the Fc–C≡C triple bond of **2** gives as the only isolated product **8**, from the reaction between **2** and $Co_2(\mu\text{-dppm})(CO)_6$.

Many reactions of tcne with σ-alkynyl-metal complexes have been described [9]. The generally accepted course of these reactions is via a radical (or diradical) intermediate to give a σ-cyclobutenyl complex, which then more or less rapidly undergoes ring-opening to form the corresponding σ-buta-1,3-dien-2-yl derivative. The butadienyl ligand in these complexes may chelate the metal centre if the latter contains an easily displaced ligand to give an η^3-allylic system.

The present study has examined reactions of tcne with **1**, **2** and **3**. Only with **1** has the cyclobutenyl complex (**11**) been isolated; thermolysis of **11** afforded butadienyl **12**. Both complexes were crystallographically characterised as was an unusual product obtained when **12** was extracted from TLC silica gel with methanol. We have subsequently found that this reaction between **12** and MeOH occurs only in the presence of the solid support. The product **13** is formed by addition of MeOH across one of the CN groups of the tetracyano-dienyl ligand to give the methoxy-imine which chelates the tungsten via the NH group with displacement of CO. We have earlier described a similar product, serendipitously isolated from the reaction between $W\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_3Cp$ and $Me_3NO{\cdot}2H_2O$, again the result of hydrolysis of a CN group, this time with water [9e].

The product **14** obtained from tcne and **2** results from addition of the cyano-olefin to the Fc–C≡C triple bond, whereas that from **3** is formed by addition to the central C≡C triple bond. In all cases, the reactions apparently occur under steric control. We have no evidence for the formation of complexes containing more than one molecule of tcne.

4. Conclusions

This paper has described the preparation of a series of poly-ynyl complexes containing ferrocenyl and $W(CO)_3Cp$ end-groups. The redox properties of the ferrocenyl nucleus show a moderate increase in oxidation potential which can be correlated with increasing chain length. The tungsten centre is oxidised at higher and relatively constant potentials. Conventional addition reactions occur between the complexes and dicobalt carbonyls or tcne, an unexpected product in one case being formed by dephenylation of a dppm ligand and trapping of the released phenyl group by the ferrocenylethynyl group to form a vinylidene ligand. Reaction of the tcne adduct **12** with MeOH in the presence of silica gel resulted in addition of MeOH to one CN group to form an imine ligand which chelates the tungsten atom.

Table 6
Crystal data and refinement details for **2**, **5**, **7**, **8**, **10–14**

Compound	**2**	**5**	**7**	**8**	**10**	**11**	**12**	**13**	**14**
Formula	$C_{22}H_{14}FeO_3W$	$C_{47}H_{36}Co_2FeO_5$-$P_2W \cdot CH_2Cl_2$	$C_{28}H_{14}Co_2$-FeO_9W	$C_{51}H_{36}Co_2FeO_7$-P_2W	$C_{36}H_{14}Co_4$-$FeO_{15}W$	$C_{26}H_{14}FeN_4O_3W$	$C_{26}H_{14}FeN_4O_3W$	$C_{26}H_{18}FeN_4O_3W \cdot 2H_2O$	$C_{28}H_{14}FeN_4O_3W \cdot CHCl_3$
MW	566.05	1185.24	851.97	1180.35	1161.92	670.12	670.12	710.18	813.52
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/c$	Cc
Unit cell dimensions									
a (Å)	7.736(1)	13.253(1)	7.913(1)	10.663(1)	10.924(1)	14.882(1)	10.221(2)	29.891(4)	22.494(3)
b (Å)	19.733(3)	21.245(2)	18.232(3)	11.325(1)	11.712(1)	10.7525(9)	16.352(3)	9.934(2)	10.788(1)
c (Å)	12.151(2)	15.819(l)	19.536(3)	19.278(2)	15.251(2)	16.035(1)	14.894(3)	20.798(3)	14.325(2)
α (°)			83.536(3)	87.803(2)	94.031(2)				
β (°)	104.235(2)	97.949(1)	84.374(3)	83.388(2)	94.762(2)	112.890(1)	109.272(3)	123.506(2)	123.201(1)
γ (°)			88.395(3)	77.602(2)	96.853(2)				
V (Å^3)	1821	4411	2786	2258	1924	2364	2350	5149	2908
Z	4	4	4	2	2	4	4	4	4
D_{calc} (g cm^{-3})	2.064	1.784	2.031	1.736	2.005	1.883	1.894	1.832	1.858
Crystal size (mm)	0.24 × 0.20 × 0.15	0.24 × 0.20 × 0.05	0.25 × 0.15 × 0.05	0.15 × 0.06 × 0.05	0.22 × 0.14 × 0.11	0.35 × 0.30 × 0.20	0.12 × 0.12 × 0.05	0.40 × 0.35 × 0.12	0.35 × 0.28 × 0.16
Max/min transmission	0.55, 0.89	0.73, 0.93	0.57, 0.91	0.57, 0.77	0.72, 0.91	0.60, 0.89	0.64, 0.89	0.45, 0.75	0.52,0.72
μ (cm^{-1})	71	39	58	37	51	55	55	51	48
$2\theta_{max}$ (°)	50	58	58	58	58	58	58	58	58
N_{tot}	19470	52183	32361	22625	22428	27437	23094	25095	14052
N_r (R_{int})	3194 (0.070)	11294 (0.04)	13593 (0.045)	11129(0.025)	9364 (0.026)	5969 (0.030)	5953 (0.042)	6453 (0.031)	3454 (0.024)
N_o	2616	8757	10438	9236	6321	5243	4724	5456	3385
R	0.055	0.062	0.043	0.027	0.031	0.026	0.025	0.030	0.015
R_w	0.059	0.074	0.049	0.027	0.030	0.035	0.023	0.041	0.022

5. Experimental

5.1. General experimental conditions

All reactions were carried out under dry, high purity N_2 unless otherwise stated, using standard Schlenk techniques. Common solvents were dried, distilled under N_2 and degassed before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, BC, Canada. Preparative TLC was carried out on glass plates (20×20 cm^2) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

5.2. Instrumentation

Infrared spectra were obtained on a Perkin–Elmer 1720X FTIR spectrometer. Spectra in cyclohexane were obtained using a 0.5 mm path length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Bruker ACP 300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^{1}H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Samples, dissolved in $CDCl_3$, were contained in 5 mm sample tubes. ESMS were measured using MeOH solutions (unless otherwise stated) which were injected into a Finnigan LCQ mass spectrometer via slow infusion using a syringe pump (250 μl) at a flow rate of 15 μl min^{-1}. Nitrogen was used as the drying and nebulising gas. A capillary voltage of 27 V was used and the spray voltage was 5.4 V. Aids to ionisation were used as indicated in Ref. [11]. Electrochemistry was carried out as described previously [4].

5.3. Reagents

CuI (Fluka), $Co_2(CO)_8$ (Strem), CuCl (Ajax), tmed (Merck) and tcne (Fluka) were used as received. The compounds $FcC{\equiv}CH$ [12], $WCl(CO)_3Cp$ [13], $FcC{\equiv}CC{\equiv}CH$ [6b], $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ [14], $Pd(PPh_3)_4$ [15], $Co_2(\mu\text{-dppm})(CO)_6$ [16] and $FcC{\equiv}CI$ [17] were prepared using the cited methods.

5.4. Preparation of Hay's catalyst

To a suspension of freshly purified CuCl (50 mg, 0.51 mmol) in acetone (5 ml) was added tmeda (75 μl, 59 mg, 0.51 mmol). The solution turned blue immediately and was stirred for a further 30 min.

5.5. Preparation of *W{(C≡C)$_n$Fc}(Co)$_3$Cp* ($n = 1$–4)

5.5.1. *W(C≡CFc)(CO)$_3$Cp* (**1**)

To a stirred solution of $WCl(CO)_3Cp$ (750 mg, 2.04 mmol) in THF (15 ml)–$NHEt_2$ (30 ml) was added CuI (40 mg) followed by $FcC{\equiv}CH$ (428 mg, 2.04 mmol). After 30 min, the solution was then filtered to remove $[NH_2Et_2]Cl$ and the solvent removed. The residue was taken up in CH_2Cl_2 and passed down an alumina column. Elution with hexane produced an orange fraction which yielded orange $W(C{\equiv}CFc)(CO)_3Cp$ (**1**) (604 mg, 55%). Anal. Found: C, 43.89; H, 2.60. Calc. for $C_{20}H_{14}FeO_3W$: C, 44.32; H, 2.60%. M, 542. IR : $\nu(C{\equiv}C)$ 2099w; $\nu(CO)$ 2036s, 1951s (br). ^{1}H-NMR: $\delta = 4.04, 4.25$ ($2 \times$ m, FeC_5H_4), 4.14 (s, FeCp), 5.60 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion): 542 $[M]^+$, 514 $[M-CO]^+$, 458 $[M-2CO]^+$.

5.5.2. *W(C≡CC≡CFc)(CO)$_3$Cp* (**2**)

To a stirred solution of $WCl(CO)_3Cp$ (150 mg, 0.41 mmol) in THF (5 ml)–$NHEt_2$ (10 ml) was added CuI (ca. 10 mg) followed by $FcC \equiv CC \equiv CH$ (95 mg, 0.41 mmol). After 15 min the solution was then filtered to remove $[NH_2Et_2]Cl$ and the solvent removed. The residue was taken up in CH_2Cl_2 and passed down an alumina column. Elution with hexane produced a red–orange fraction which yielded red $W(C \equiv CC \equiv CFc)(CO)_3Cp$ (**2**) (184 mg, 79%). Crystals suitable for the X-ray study were grown from CH_2Cl_2–pentane. Anal. Found: C, 46.04; H, 2.55. Calc. for $C_{22}H_{14}FeO_3W$: C, 46.68; H, 2.49%; M, 566. IR (cm^{-1}): $\nu(C \equiv C)$ 2186w, 2054 (sh); $\nu(CO)$ 2036s, 1955s (br). ^{1}H-NMR: $\delta = 4.15, 4.25$ ($2 \times$ m, FeC_5H_4), 4.20 (s, FeCp), 5.62 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion): 566 $[M]^+$, 538 $[M-CO]^+$.

5.5.3. *W{(C≡C)$_3$Fc}(CO)$_3$Cp* (**3**)

$NHPr^i_2$ (15 ml) in a flame-dried Schlenk tube was rigorously deoxygenated using the freeze–pump–thaw method. $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (200 mg, 0.52 mmol), $FcC{\equiv}CI$ (176 mg, 0.52 mmol), $Pd(PPh_3)_4$ (40 mg, 0.034 mmol) and CuI (ca. 10 mg) were added in that order and the resulting orange–red solution was stirred in the dark for 3 h. After this time the orange precipitate which had formed was collected and dissolved in a minimum amount of CH_2Cl_2. This solution was then passed down an alumina column, eluting with hexane to yield bright orange $W\{(C{\equiv}C)_3Fc\}(CO)_3Cp$ (**3**) (220 mg, 72%). Anal. Found: C, 48.04; H, 2.46. Calc. for $C_{24}H_{14}FeO_3W$: C, 48.85; H, 2.39%. M, 590. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2178w, 2138m, 2023m; $\nu(CO)$ 2047s, 1959s (br). ^{1}H-NMR: $\delta = 4.20, 4.45$ ($2 \times$ m, FeC_5H_4), 4.20 (s, FeCp), 5.62 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion): 590 $[M]^+$, 562 $[M-CO]^+$.

5.5.4. *W(C≡CC≡CC≡CC≡CFc)(CO)$_3$Cp* (**4**)

$W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (150 mg, 0.39 mmol) and $Fc(C{\equiv}CC{\equiv}CH)$ (92 mg, 0.39 mmol) were dissolved in acetone (20 ml) and a vigorous stream of oxygen was passed through the orange–red solution. The Hay catalyst was added in portions until the reaction was adjudged complete (TLC). The solvent was removed in vacuo and the residue extracted with CH_2Cl_2. Preparative TLC (hexane–acetone, 7:3) gave three compounds. The first (R_f 0.7) contained $Fc_2(C\equiv C)_4$ (40 mg, 22%). The second (R_f 0.5) afforded $W\{(C\equiv C)_4Fc\}(CO)_3Cp$ (**4**) (57 mg, 24%). The third band contained $\{W(CO)_3Cp\}(C\equiv C)_4$ (70 mg, 24%). The two known compounds were characterised from their IR and ^{1}H-NMR spectra. Data for $W\{(C\equiv C)_4Fc\}(CO)_3Cp$: Anal. Found: C, 49.92; H, 2.63. Calc. for $C_{26}H_{14}FeO_3W$: C, 50.85; H, 2.30%. M, 614. IR (cm^{-1}): $\nu(C\equiv C)$ 2184m, 2131w, 2099w, 2011m; $\nu(CO)$ 2047s, 1961s (br). ^{1}H-NMR: $\delta = 4.25$, 4.49 ($2\times m$, FeC_5H_4), 4.23 (s, FeCp), 5.63 (s, WCp). ESMS; m/z (MeCN, positive ion, with $[Ag(NCMe)_4]BF_4$): 1336 $[2M+Ag]^+$, 655 $[M+NCMe]^+$.

5.6. Reactions with dicobalt carbonyl complexes

5.6.1. $W(C\equiv CFc)(CO)_3Cp$ and $Co_2(\mu\text{-}dppm)(CO)_6$

$W(C\equiv CFc)(CO)_3Cp$ (70 mg, 0.13 mmol) and $Co_2(\mu\text{-}dppm)(CO)_6$ (100 mg, 0.15 mmol) were dissolved in C_6H_6 (15 ml) and warmed to 80 °C. Stirring was continued for 16 h after which the solvent was removed. Preparative TLC (hexane–CH_2Cl_2, 7:3) gave two major bands. The dark red–brown band (R_f 0.5) contained dark red $Co_2W(\mu_3\text{-}CCPhFc)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_5Cp$ (**5**) (20 mg, 14%). Crystals suitable for the structure determination were grown from CH_2Cl_2–pentane. Anal. Found: C, 48.55; H, 3.38. Calc. for $C_{47}H_{36}Co_2FeO_5P_2W\cdot CH_2Cl_2$: C, 48.64; H, 3.23%. M, 1100. IR (cm^{-1}): $\nu(CO)$ 2014m, 1991s, 1956s (br), 1899m (br). ^{1}H-NMR: $\delta = 3.66$ (s, FeCp), 4.21, 4.41($2\times m$, FeC_5H_4), 5.11 (s, WCp), 7.2–7.8 (m, Ph). ESMS; m/z (MeOH, positive ion, NaOMe added): 1123 $[M+Na]^+$, 1016 $[M-3CO]^+$, 988 $[M-5CO]^{\cdot +}$, 960 $[M-4CO-Ph]^+$.

The black band (R_f 0.35) yielded black $W\{\eta^1{:}\eta^2\text{-}C_2Fc[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_3Cp$ (**6**) (30 mg, 20%). Anal. Found: C, 49.84; H, 3.74. Calc. for $C_{49}H_{36}Co_2FeO_7P_2W$: C, 50.90; H, 3.14%. M, 1156. IR (cm^{-1}): $\nu(CO)$ 1986s, 1954s, 1928 (sh), 1812m (br). ^{1}H-NMR: $\delta = 3.91$ (m, PCH_2), 4.20 (s, FeCp), 4.49, 4.90 ($2\times m$, FeC_5H_4), 4.72 (s, WCp), 7.15–7.62 (PPh_2). ESMS; m/z (CH_2Cl_2–MeOH, positive ion): 1016 $[M-5CO]^+$, 988 $[M-6CO]^+$, 960 $[M-7CO]^+$.

5.6.2. Preparation of $W\{\eta^1{:}\eta^2\text{-}C\equiv CC_2Fc[Co_2(CO)_6]\}(CO)_3Cp$ (7)

$W(C\equiv CC\equiv CFc)(CO)_3Cp$ (50 mg, 0.09 mmol) and $Co_2(CO)_8$ (41 mg, 0.12 mmol) were dissolved in benzene (10 ml) and stirred for 16 h. The black solution was evaporated and the residue purified by preparative TLC (hexane–CH_2Cl_2, 3:1). The black band (R_f 0.4) contained $W\{\eta^1{:}\eta^2\text{-}C\equiv CC_2Fc[Co_2(CO)_6]\}(CO)_3Cp$ (**7**) (46 mg, 60%). Crystals suitable for the X-ray determination were grown from CH_2Cl_2–pentane. Anal. Found: C, 38.54; H, 1.82. Calc. for $C_{28}H_{14}Co_2FeO_9W\cdot 0.5CH_2Cl_2$: C, 38.27; H, 1.69%. M, 852. IR (cm^{-1}): $\nu(C\equiv C)$ 2085m; $\nu(CO)$ 2048s, 2033s, 2021s, 1953s (br). ^{1}H-NMR: $\delta = 4.29$, 4.42 ($2\times m$, FeC_5H_4), 4.29 (s, FeCp), 5.68 (s, WCp). ESMS; m/z (MeOH, negative ion, NaOMe added): 883 $[M+OMe]^-$, 799–631 $[M+OMe-nCO]^-$ ($n = 3$–9).

5.6.3. $W\{\eta^1{:}\eta^2\text{-}C\equiv CC_2Fc[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_3Cp$ (8)

$W(C\equiv CC\equiv CFc)$ (68 mg, 0.12 mmol) and $Co_2(\mu\text{-}dppm)(CO)_6$ (100 mg, 0.15 mmol) were heated in refluxing C_6H_6 (10 ml) for 1 h. The solvent was removed in vacuo and the black residue extracted with CH_2Cl_2. Preparative TLC (hexane–CH_2Cl_2, 7:3) produced a dark–red band (R_f 0.35) from which dark–red $W\{\eta^1{:}\eta^2\text{-}C\equiv CC_2Fc[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_3Cp$ (**8**) (60 mg, 42%) was obtained. X-ray quality crystals were grown from CH_2Cl_2–pentane. Anal. Found: C, 52.84; H, 3.54. Calc. for $C_{51}H_{36}Co_2FeO_7P_2W$: C, 51.90; H, 3.07%. M, 1180. IR (cm^{-1}): $\nu(C\equiv C)$ 2033m; $\nu(CO)$ 2016m, 1992s (br), 1962 (sh), 1951s (br). ^{1}H-NMR: $\delta = 3.25$, 3.80 ($2\times m$, PCH_2), 4.26, 4.50 ($2\times m$, FeC_5H_4), 4.33 (s, FeCp), 5.59 (s, WCp). ESMS; m/z (MeOH, positive ion): 1124–984 $[M-nCO]^+$ ($n=2$–7).

5.6.4. $W\{(C\equiv C)_3Fc\}(CO)_3Cp + Co_2(CO)_8$

$W\{(C\equiv C)_3Fc\}(CO)_3Cp$ (150 mg, 0.25 mmol) and $Co_2(CO)_8$ (87 mg, 0.25 mmol) were dissolved in benzene (30 ml) and stirred in the dark for 16 h. The solvent was then removed in vacuo. The resulting oil was dissolved in CH_2Cl_2. Preparative TLC (hexane–CH_2Cl_2, 3:1) gave two black bands. The first (R_f 0.3) gave $W\{C\equiv CC_2[Co_2(CO)_6]C\equiv CFc\}(CO)_3Cp$ (**9**) (85 mg, 38%). Anal. Found: C, 41.63; H, 2.20. Calc. for $C_{30}H_{14}Co_2FeO_9W$: C, 41.13; H, 1.61%. M, 876. IR (cm^{-1}): $\nu(C\equiv C)$ 2134m, 2089w; $\nu(CO)$ 2054s, 2030s, 1956s (br). ^{1}H-NMR: $\delta = 4.34$, 4.45 ($2\times m$, FeC_5H_4), 4.28 (s, FeCp), 5.69 (s, WCp). ESMS; m/z (MeOH, positive ion): 876 $[M]^+$; 848–764 $[M-nCO]^+$ ($n =$ 1–4).

The second band (R_f 0.4) contained $W\{C\equiv CC_2[Co_2(CO)_6]C_2Fc[Co_2(CO)_6]\}(CO)_3Cp$ (**10**) (31 mg, 21%). Crystals suitable for the X-ray structure determination were grown from CH_2Cl_2–MeOH. Anal. Found: C, 36.90; H, 1.86. Calc. for $C_{36}H_{14}Co_4FeO_{15}W$: C, 37.21; H, 1.21%. M, 1162. IR (cm^{-1}): $\nu(C\equiv C)$ 2095m; $\nu(CO)$ 2076s, 2057vs, 2031s, 2020s, 1954s (br). ^{1}H-NMR: $\delta = 4.24$ (s, FeCp), 4.33, 4.56 ($2\times m$, FeC_5H_4), 5.60 (s, WCp). ESMS; m/z (MeOH, negative ion, NaOMe added): 1192 $[M+OMe]^-$, 1108–742 $[M+OMe-nCO]^-$ ($n = 3$–15).

5.7. Reactions with tetracyanoethene

*5.7.1. Preparation of $W\{C{=}CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (**11**)*

$W(C{\equiv}CFc)(CO)_3Cp$ (200 mg, 0.37 mmol) and tcne (51 mg, 0.40 mmol) were dissolved in CH_2Cl_2 (20 ml). The initial orange solution turned red after a few minutes. After 1 h the volume was reduced to ca. 1–2 ml and dropped into rapidly stirred hexane. The light orange–brown precipitate was purified by preparative TLC (hexane–CH_2Cl_2, 1:1) to give orange $W\{C{=}CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (**11**) (183 mg, 74%). Crystals were grown from CH_2Cl_2–pentane. Anal. Found: C, 46.90; H, 2.20; N, 8.36. Calc. for $C_{26}H_{14}FeN_4O_3W$: C, 46.60; H, 2.11; N, 8.27%. M, 670. IR (cm^{-1}): ν(CN) 2390w, 2338w; ν(CO) 2042s, 1963s, 1944 (sh)cm^{-1}. ^{1}H-NMR: $\delta = 4.29$ (s, FeCp), 4.46, 4.52 ($2 \times$ m, FeC_5H_4), 5.83 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion, NaOMe added): 693 $[M + Na]^+$.

*5.7.2. Pyrolysis of $W\{C{=}CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (**11**)*

$W\{C{=}CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (100 mg, 0.15 mmol) was heated in refluxing THF (15 ml) for 6 h. Solvent was removed and the residue chromatographed on preparative TLC plates developing with CH_2Cl_2. The blue band (R_f 0.6) contained $W\{C[{=}C(CN)_2]{=}CFc{=}C(CN)_2\}(CO)_3Cp$ (**12**) (33 mg, 33%) (from CH_2Cl_2–hexane). Anal. Found: C, 46.31; H, 2.48; N, 7.89. Calc. for $C_{26}H_{14}FeN_4O_3W$: C, 46.60; H, 2.11; N, 8.36%. M, 670. IR (cm^{-1}): ν(CN) 2222w; ν(CO) 2049s, 1960s, (br). ^{1}H-NMR: $\delta = 4.45$ (s, FeCp), 4.73, 4.92 ($2 \times$ m, FeC_5H_4), 5.51 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion): 670, $[M]^+$.

When the blue compound is extracted from silica gel with MeOH, a new red product is formed. Purification (TLC, $CHCl_3$) gave a red band (R_f 0.3). Extraction and precipitation from CH_2Cl_2–hexane gave $W\{C[{=}C(CN)C(OMe){=}NH]CFc{=}C(CN)_2\}(CO)_2Cp$ (**13**). Crystals suitable for X-ray analysis were grown from CH_2Cl_2–MeOH. Anal. Found: C, 45.69; H, 2.33; N, 8.31. Calc. for $C_{26}H_{14}FeN_4O_3W$: C, 46.32; H, 2.69; N, 8.31%. M, 674. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2220w, ν(CO) 2046w, 2033w, 1969s, 1897s. ^{1}H-NMR: $\delta = 5.08$ (s, 5H, WCp), 4.83 (m, 2H, FeC_5H_4), 4.73 (m, 2H, FeC_5H_4), 4.52 (s, 5H, FeCp), 4.05 (s, 3H, OMe). ESMS; *m*/*z* (MeOH, positive ion): 674, $[M]^+$.

*5.7.3. $W\{C{\equiv}CC[{=}C(CN)_2]CFc{=}C(CN)_2\}(CO)_3Cp$ (**14**)*

$W(C{\equiv}CC{\equiv}CFc)(CO)_3Cp$ (50 mg, 0.09 mmol) and tcne (13 mg, 0.10 mmol) were dissolved in CH_2Cl_2 (10 ml). The orange solution turned dark green after 5 min. Stirring was continued for a further 1 h. The solvent was removed in vacuo and the residue extracted with CH_2Cl_2. Preparative TLC (hexane–CH_2Cl_2, 2:3) gave a dark green band which was crystallised (CH_2Cl_2–pentane) to give dark green $W\{C{\equiv}CC[{=}C(CN)_2]CFc{=}C(CN)_2\}(CO)_3Cp$ (**14**) (47 mg, 75%). Crystals suitable for X-ray analysis were grown from $CHCl_3$–MeOH. Anal. Found: C, 48.45; H, 2.03; N, 8.07. Calc. for $C_{28}H_{14}FeN_4O_3W$: C, 48.73; H, 2.54; N, 7.79%. M, 694. IR (cm^{-1}): ν(CN) 2225w, 2166w; ν(C≡C) 2073w; ν(CO) 2026s, 1965s (br). ^{1}H-NMR: $\delta = 4.37$ (s, FeCp), 4.90, 4.96, 5.35 ($3 \times$ m, FeC_5H_4), 5.79 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion, NaOMe added): 717, $[M + Na]^+$, (negative ion): 725, $[M + OMe]^-$, 697, $[M + OMe - CO]^-$, 669, $[M + OMe - 2CO]^-$, 641, $[M + OMe - 3CO]^-$, 615 $[M + OMe - 3CO - CN]^-$.

*5.7.4. $W\{C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C \equiv CFc\}$-$(CO)_3Cp$ (**15**)*

$W\{(C{\equiv}C)_3Fc\}(CO)_3Cp$ (45 mg, 0.08 mmol) and tcne (11 mg, 0.09 mmol) were stirred in CH_2Cl_2 (10 ml) for 1 h. Solvent was removed and the residue extracted with CH_2Cl_2. Preparative TLC (hexane–CH_2Cl_2, 1:3) gave one major red–brown band which yielded $W\{C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}CFc\}(CO)_3Cp$ (**15**) (26 mg, 48%). Anal. Found: C, 49.90; H, 2.07; N, 7.73%. Calc. for $C_{30}H_{14}FeN_4O_3W$: C, 50.17; H, 1.96; N, 7.80%. M, 718. IR (cm^{-1}): ν(CN) 2225w, 2164w; ν(C≡C) 2130s, 2055m; ν(CO) 2025s, 1967s (br). ^{1}H-NMR: $\delta = 4.41$ (s, FeCp), 4.89, 4.97, 5.32 ($2 \times$ m, FeC_5H_4), 5.70 (s, WCp). ESMS; *m*/*z* (MeOH, positive ion, $[Ag(NCMe)_4]BF_4$ added): 1544 $[2M + Ag]^+$, 826 $[M + Ag]^+$, 798 $[M + Ag - CO]^+$.

5.8. Structure determinations

Full spheres of data were obtained with a Bruker CCD AXS instrument (monochromatic Mo–Kα radiation, λ 0.71073 Å, *T* was ca. 153 K (**10** excepted: ca. 300 K)); N_{tot} reflections were measured and reduced to N_r independent (R_{int} given), after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were refined for all hydrogen atoms for **8**, **12** only, otherwise constrained at estimates. Conventional residuals R, R' on $|F|$ are given [weights: $(\sigma^2(F) + 0.0004F^4)^{-1}$]. Computation used the XTAL 3.4 program system [18] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in Figs. 1–9 and Tables 2–4 and 6. In **14**, 'Friedel pair' data were retained distinct and χ_{abs} refined [value: 0.021(5)].

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 157500–157508 for compounds **2**, **5**, **7**, **8** and **10**–**14**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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