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Reactions of transition metal σ-acetylide complexes

X *. Cycloaddition of tetracyanoethene to manganese, iron and nickel complexes, and hydration of a related tungsten complex. X-Ray structures of Fe{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)$_2$(η-C$_5$H$_5$) and Ni{C[=C(CN)$_2$]CPh=C(CN)$_2$}(PPh$_3$)(η-C$_5$H$_5$)

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Abstract

Tetracyanoethene adds to phenylethynyl-metal complexes of manganese, iron or nickel to give the butadienyl derivatives ML$_n${C[=C(CN)$_2$]CPh=C(CN)$_2$} (ML$_n$ = Mn(CO)$_3$(dppe), Fe(CO)$_2$(η-C$_5$H$_5$) or Ni(PPh$_3$)(η-C$_5$H$_5$)). In non-polar solvents, intermediate manganese and iron cyclobutenyl complexes L$_n$M{$\overline{\text{C=CPhC(CN)}_2\text{C}}(CN)_2$} can be isolated, but rapidly isomerise to the butadienyl complexes. Structural assignments of the isomers can be made on the basis of IR ν(CN), ν(CC) absorptions and FAB MS fragmentation pathways. Crystals of Fe{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)$_2$(η-C$_5$H$_5$) are triclinic, space group $P\bar{1}$ with unit cell dimensions a 9.378(2), b 13.874(3), c 7.935(4) Å, α 92.92(3), β 101.57(2), γ 108.78(1)° and $Z = 2$. Crystals of Ni{C[=C(CN)$_2$]CPh=C(CN)$_2$}(PPh$_3$)(η-C$_5$H$_5$) are monoclinic, space group $P2_1/c$, with unit cell parameters a 13.765(6), b 10.89(2), c 20.753(8) Å, β 95.55(2)° and $Z = 4$. Both structures were refined by a full-matrix least-squares procedure to final R 0.038, R_w 0.044 for 2825 reflections with $I \geqslant 2.5\sigma(I)$ (Fe) and R 0.048, R_w 0.054 for 1702 reflections with $I \geqslant 2.5\sigma(I)$ (Ni).

Introduction

The first report of cycloaddition of tetracyanoethene, C$_2$(CN)$_4$ (tcne) to σ-acetylide complexes of iron appeared in 1979 [1], and was followed by our initial

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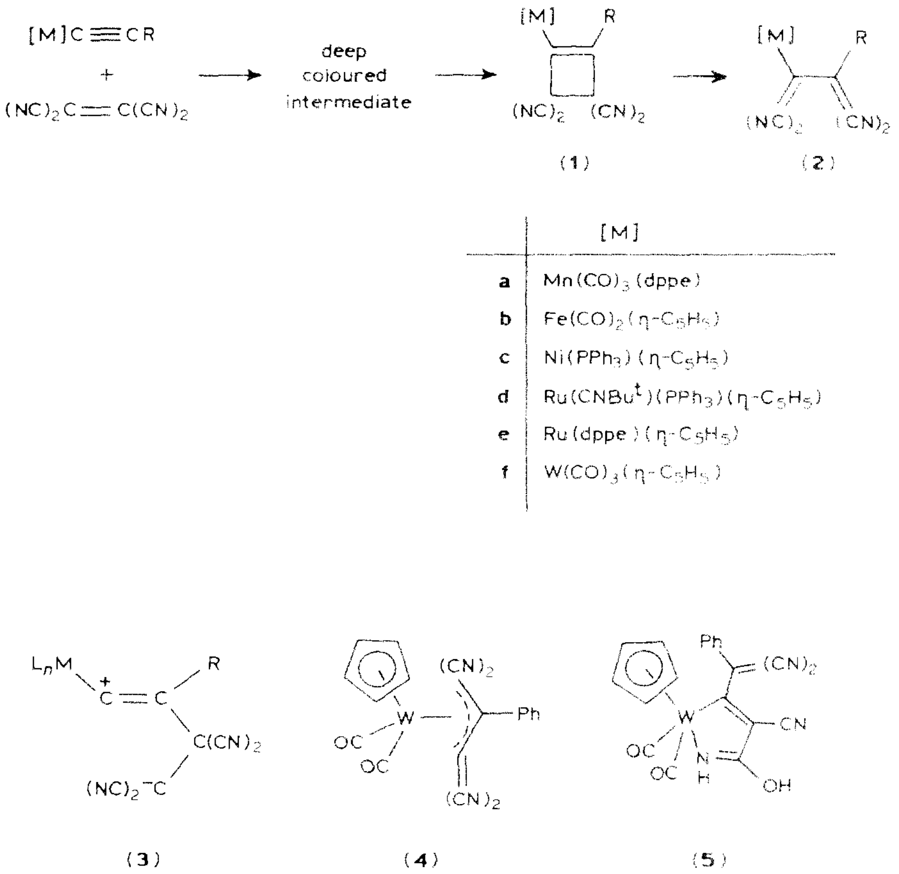
* For Part IX, see Ref. 24.



	[M]
a	$Mn(CO)_3(dppe)$
b	$Fe(CO)_2(\eta\text{-}C_5H_5)$
c	$Ni(PPh_3)(\eta\text{-}C_5H_5)$
d	$Ru(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$
e	$Ru(dppe)(\eta\text{-}C_5H_5)$
f	$W(CO)_3(\eta\text{-}C_5H_5)$

Scheme 1

communication concerning a ruthenium system [2]. These reactions proceed via deep-coloured intermediates which lighten to give σ-cyclobutenyl complexes (**1**); these may not be isolable in all cases, as the organic ligand more-or-less rapidly undergoes a ring-opening reaction to give the isomeric σ-butadienyl complexes (**2**) (Scheme 1). We now report our studies of some manganese, iron and nickel complexes which complement our extended accounts of the tungsten and ruthenium reactions [3,4]. We have determined the crystal structure of the two title butadienyl complexes, which serve to clarify some of the critical observations. Finally we report a further example of the addition of water to the CN group of a coordinated cyanocarbon.

Results and discussion

The reaction between $Mn(C_2Ph)(CO)_3(dppe)$ and tetracyanoethane in dichloromethane afforded a yellow crystalline material, shown to be the butadienyl complex **2a** from its spectroscopic properties. Thus, the IR spectrum contained two ν(CN) bands at 2208 and 2222 cm^{-1}. In previous papers we have shown that the ν(CN) bands of the butadienyl isomer are much stronger than those for the cyclobutenyl isomer; the intensities of the two ν(C=C) bands found at 1573 and 1533 cm^{-1} are also consistent with this formulation. The ν(CO) spectrum contains three strong bands between 1944–2018 cm^{-1}, and resembles that of the phenylacetylide precursor.

If the reaction is performed in benzene, a short-lived (minutes) pale green intermediate is formed, which on standing is converted into the white cyclobutenyl complex **1a**. This material is characterised by very weak, single ν(CN) and ν(C=C) bands at 2234 and 1573 cm^{-1}, respectively. While **1a** is relatively insoluble in hydrocarbon solvents, solutions in more polar media rapidly deepen in colour to yellow, and afford complex **2a** upon evaporation. This further example of isomerisation provides additional evidence for the identities of **1a** and **2a**, and further substantiates the IR ν(CN) and ν(C=C) correlations with structure that were reported earlier [5].

Similarly, dichloromethane solutions of $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ and $C_2(CN)_4$ gave a yellow-green solution when mixed, from which yellow crystals of butadienyl **2b** can be isolated. In diethyl ether, on the other hand, the mixture is initially a dark green colour, but changes to pale yellow after 15 min, depositing a yellow precipitate of the cyclobutenyl derivative **1b**. These two complexes show different IR and NMR spectra, the weak ν(CN) band moving to lower frequency as **1b** changes to **2b**, while the ν(CO) bands move to higher wavenumbers. The major change in the ^1H NMR spectra is found in the C_5H_5 resonance (at δ 5.18 in **1b**, 5.30 in **2b**); in the ^{13}C NMR spectra the C_5H_5 resonance hardly changes (from δ 87.0 in **1b** to 86.9 in **2b**), while two CO resonances are found in **2b**, but only one in **1b**.

In the original report of this reaction, the same colour changes were reported [1]; the deep green compound was assumed to be a charge-transfer complex, the derived yellow compound a dipolar adduct formulated as **3**, and the yellow-brown compound was assigned the cyclobutenyl structure **1b**. Our results above, combined with a single-crystal X-ray study of **2b** (see below) show that these assignments must be modified, and although we have no further evidence for the identity of the deep green intermediate, we suggest that it has a geometry similar to that of the proposed dipolar complex, but with a diradical formulation (it has not proved possible to obtain NMR spectra, and ESR measurements of similar solutions obtained from tungsten- or ruthenium-containing precursors to show the presence of unpaired electrons).

We have also studied the reaction between $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ and tetracyanoethane, which occurs rapidly in toluene to give a brown complex identified as the butadienyl derivative **2c**. Final structural assignment was also achieved via a single-crystal study, but the single medium intensity ν(CN) and ν(C=C) bands at ca. 2200 and 1550 cm^{-1} provided strong evidence for the ring-opened formulation.

The present results complement those reported earlier for some tungsten- and ruthenium-containing systems [2–4], and confirm the course of the reaction as proceeding via an initial paramagnetic adduct formed by attack of the electron-rich β-carbon of the acetylide ligand at an olefinic carbon atom (Scheme 1). The adduct quickly forms the cyclobutenyl complex, isolated here from the reactions of the manganese and iron complexes on account of their limited solubilities. In more polar solvents, the final (and often only) isolated product is the butadienyl complex, of which examples containing tungsten, iron, ruthenium and nickel have now been fully characterised by X-ray structural studies.

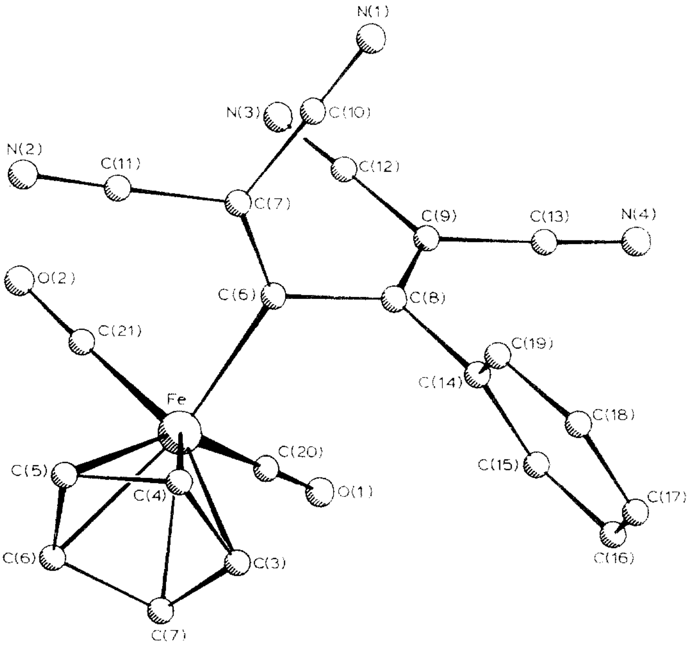


Fig. 1. The molecular structure of Fe{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)$_2$(η-C$_5$H$_5$) (**2b**) showing the numbering scheme employed.

Crystal structures of complexes 2b and 2c

The molecular structures of the iron and nickel complexes are shown in Figs. 1 and 2, respectively, while Table 1 summarises pertinent bond parameters of the

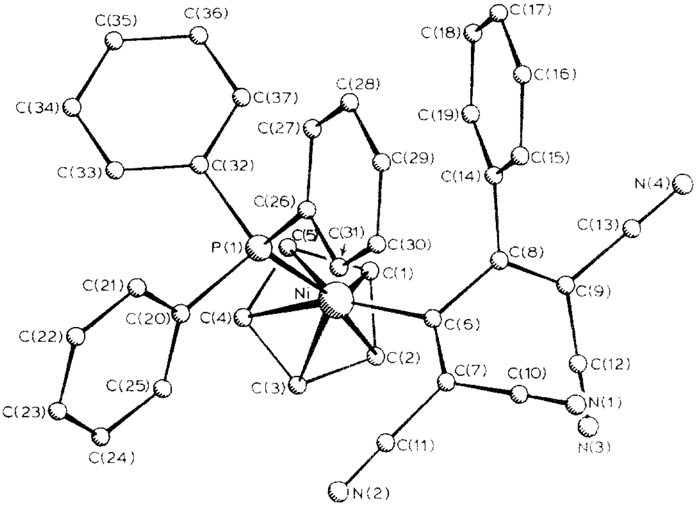
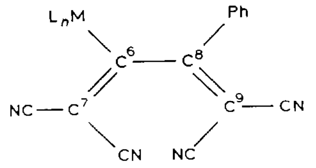


Fig. 2. The molecular structure of Ni{C[=C(CN)$_2$]CPh=C(CN)$_2$}(PPh$_3$)(η-C$_5$H$_5$) (**2c**) showing the numbering scheme employed.

Table 1

Structural parameters for tetracyanobutadienyl ligands in four metal complexes



	$Fe(CO)_2$ $(\eta\text{-}C_5H_5)$ [a]	$Ru(CNBu^t)(PPh_3)$ $(\eta\text{-}C_5H_5)$ [b]	$Ru(dppe)$ $(\eta\text{-}C_5H_5)$ [b]	$Ni(PPh_3)$ $(\eta\text{-}C_5H_5)$ [a]
Bond distances (Å)				
M–C(6)	1.972(2)	2.074(3)	2.068(4)	1.895(6)
C(7)–C(6)	1.347(4)	1.382(5)	1.370(6)	1.338(8)
C(6)–C(8)	1.476(3)	1.478(4)	1.484(6)	1.483(6)
C(8)–C(9)	1.356(3)	1.362(4)	1.346(6)	1.356(6)
C(8)–Ph	1.485(3)	1.479(5)	1.497(6)	1.474(8)
C–CN (av.)	1.441	1.439	1.433	1.439
C–N (av.)	1.131	1.142	1.134	1.141
Bond angles (°)				
M–C(6)–C(7)	126.8(2)	122.5(3)	124.4(3)	125.0(6)
M–C(6)–C(8)	114.8(2)	124.7(2)	119.5(3)	114.8(6)
C(7)–C(6)–C(8)	118.4(2)	122.8(3)	114.4(4)	120.0(8)
C(6)–C(8)–C(9)	120.2(2)	117.9(3)	124.3(4)	120.1(8)
C(6)–C(7)–CN	122.8(2), 123.3(2)	123.7(4), 124.2(4)	122.3(4), 122.7(4)	122.3(8), 124.4(8)
C(8)–C(9)–CN	121.1(2), 122.5(2)	121.4(3), 126.3(4)	122.7(4), 124.3(4)	121.1(8), 125.2(8)
NC–C(7)–CN	113.9(2)	112.0(4)	114.8(4)	113.2(8)
NC–C(9)–CN	116.5(2)	112.1(3)	112.7(4)	113.7(8)
Torsion angles (°)				
M–C(6)–C(8)–Ph	76.6	70.0	70.2	70.3
M–C(6)–C(8)–C(9)	99.2	111.7	112.9	108.7
C(7)–C(6)–C(8)–C(9)	81.7	81.5	80.6	67.2
C(7)–C(6)–C(8)–Ph	102.6	106.4	95.4	113.9

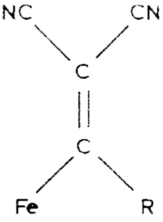
[a] This work. [b] Ref. 4.

metal-substituted butadienyl moiety in **2b**, **2c** and the related ruthenium complexes $Ru\{C[=C(CN)_2]CPh=C(CN)_2\}(L)(L')(\eta\text{-}C_5H_5)$ (**2d**, L = CNBu^t, L = PPh$_3$; **2e**, LL′ = dppe).

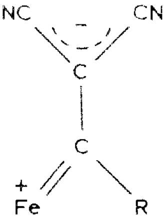
In **2b**, the iron atom is coordinated by the η-cyclopentadienyl group (Fe–C(cp) 2.075–2.093(3), av. 2.086 Å), two CO groups (Fe–CO, 1.775(3), 1.785(3) Å) and the cyanocarbon ligand (Fe–C(6) 1.972(2) Å). As is usually found, the angles subtended at the iron by the CO groups and C(6) (C(20)–Fe–C(21) 93.8(1), C(20)–Fe–C(6), 94.9(1), C(21)–Fe–C(6) 90.3(1)°) are all close to 90°, further substantiating the assignment of distorted octahedral stereochemistry to the iron coordination [6].

In the nickel complex **2c**, the central atom is coordinated by the η-cyclopentadienyl group (Ni–C(cp) 2.111(6)–2.146(6), av. 2.130 Å), the PPh$_3$ ligand (Ni–P 2.128(4) Å) and the cyanocarbon ligand (Ni–C(6) 1.895(6) Å). The angles subtended at the nickel atom by the P(1), C(6) atoms and C(pt) (where C(pt) is the point at the centre of the cp group) are P(1)–Ni–C(6) 101.2(3), P(1)–Ni–C(pt) 129.3(3), and C(6)–Ni–C(pt) 129.3(3)°.

The Fe–C(sp^2) distance in **2b** is considerably shorter than those in Fe{(Z)-CMe=C(Ph)Me}(CO){P(OPh)$_3$}(η-C$_5$H$_5$) (2.031(8) Å) [7] and Fe{C(CO$_2$Et)=CMe$_2$}(CO)(PPh$_3$)(η-C$_5$H$_5$) (2.030(2) Å) [8], although it is close to the Fe–C(O) distances in (R,S)-Fe{(Z)-C(O)CH=CHMe}(CO)(PPh$_3$)(η-C$_5$H$_5$) (1.962(6) Å) [9] and Fe{(Z)-C(O)CMe=C(Ph)Me}(CO){P(OPh)$_3$}(η-C$_5$H$_5$) (1.966(3) Å) [10]. In this respect, it would appear that the dicyanomethylene group has a similar structural effect to oxygen; the chemical similarities have been noted earlier, both in organometallic complexes [11] and in organic chemistry [12]. The short Fe–C(sp^2) distance found here, indicating a degree of multiple bond order, probably results from a contribution from the polar form **B**:



(A)



(B)

In contrast, the Ni–C(sp^2) bond distance of 1.895(6) Å is equal, within experimental error, to the comparable bonds in related systems, which possess a wide variety of donor atoms, i.e. 1.909(3) Å in *trans*-Ni($\overline{\mathrm{C{=}CHCH_2CH_2O}}$)(C$_6Cl_5$)(PMe$_3$)$_2$ [13]; 1.902(3) Å in [Ni{C(CF$_3$)=C(CF$_3$)CH$_2$C$_6$H$_4$NMe$_2$}(PEt$_3$)(μ-Cl)]$_2$ [14]; 1.897 Å in (Z)-Ni{CPh=C(Me)Ph}(acac)(Ph$_3$P) [15]; and 1.896(7) Å in Ni[C(Ph)=C(H)(COCH$_2$SiMe$_3$)]Cl(PMe$_3$)$_2$ [16].

Within the butadienyl ligand, we note that the mutual dispositions of the four groups in the two dicyanomethylene fragments are such as to prevent the *cisoid* diene from achieving planarity. The torsion angles C(7)–C(6)–C(8)–C(9) for the iron and nickel complexes are 81.7 and 67.2° respectively. This results in the presence of localised C–C single (C(6)–C(8) 1.476(3) (Fe), 1.483(6) Å (Ni)) and C=C double bonds (C(6)–C(7) 1.347(4) (Fe), 1.338(8) (Ni); C(8)–C(9) 1.356(3) (Fe), 1.356(6) Å (Ni)) in these ligands. Comparison of the four structures shows that the degree of twisting about the central C–C bond of the diene is essentially independent of the size of the ML$_n$ fragment, and is a reflection of the interaction between the overlapping CN groups. In other complexes containing non-polar *cisoid* 1,3-dienes, the torsion angles range from 80.6° (in Ru{C[=(CN)$_2$]CMe=C(CF$_3$)$_2$}-(CO)(PPh$_3$)(η-C$_5$H$_5$) [17]) to 82.4° (in Ru{C[=C(CN)$_2$]CPh=CH(C$_6$H$_4$NO$_2$-4)}-(PPh$_3$)$_2$(η-C$_5$H$_5$) [5]). It is also of interest that we have not yet found any examples of reactions affording *transoid* dienes.

FAB mass spectra

The positive ion FAB mass spectra of **1a**, **1b**, **2a** and **2b** show features common to conventional electron impact mass spectra of similar complexes. Thus ready stepwise loss of the CO groups is followed by loss of CN or Ph groups. The base peaks for **1a** and **2a** are [Mn(CN)(dppe)]$^+$, formed by CN transfer to the metal, and reminiscent of similar F-atom transfer reactions found for fluorocarbon complexes. In addition, cleavage of the cyanocarbon ligand affords $[Mn(CO)_3(dppe)]^+$, which apparently loses the three CO groups simultaneously to give $[Mn(dppe)]^+$. With both iron complexes, loss of $C_2(CN)_4$ from $[M - 2CO]^+$ is an important process, but this fragmentation is only found in the Mn-cyclobutenyl complex. Fragmentation of coordinated dppe involves loss of $C_2H_4PPh_2$, generating a diphenylphosphido ligand.

The negative ion spectra are characterised by ready loss of CO and dppe for **1a** and **2a**; ions of the type $[MnC_2PhC_2(CN)_4]^-$ and their fragmentation products are particularly stable, as is $[Mn(PPh_2)]^-$.

Addition of water to the cyanocarbon ligand

In earlier accounts [2,3] we described UV irradiation of $W\{C[=C(CN)_2]CPh=C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**2f**), which afforded the allylic complex $W\{\eta^3\text{-}C(CN)_2CPhC=C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**4**). We have attempted to achieve this transformation by chemical means, removing the CO using trimethylamine oxide. A rapid change in colour to orange was observed when $Me_3NO \cdot 2H_2O$ was employed in this reaction, and a 70% yield of a new dicarbonyl complex (**5**) was obtained. Microanalytical and spectroscopic data were consistent with the loss of one CO ligand and addition of one H_2O to the cyanocarbon. Thus, the IR $\nu(CO)$ spectrum contained only two equal intensity strong bands, and absorptions assigned to $\nu(OH)$ and $\nu(NH)$ were found between 2800–3350 cm^{-1}. We have observed a similar reaction with the compound $W\{C[=C(CN)_2]CPh=C(CF_3)_2\}(CO)_3(\eta\text{-}C_5H_5)$ whereby the chelate complex, containing a W–N–C–C–C ring was formed [18]. In the present case, we suggest similar addition of water to one of the CN groups has occurred to give the chelating 1,1,4-tricyano-2-phenyl-5-hydroxy-5-imidopenta-1,3-dien-3-yl ligand. Similar molybdenum and tungsten complexes have been described by King and Saran [19] and were obtained from σ-chlorodicyanovinyl complexes during chromatography on alumina which contained adsorbed water.

Experimental

General conditions

All reactions and work-up of solutions were performed under nitrogen. Solvents were dried and distilled (dme and thf from sodium diphenylketyl) before use. All reactions were carried out in the dark, using foil-covered flasks.

Instruments

Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^1H NMR at 80 MHz, ^{13} C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials

Literature methods were used to prepare $Mn(C_2Ph)(CO)_3(dppe)$ [20], $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ [21], $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ [21] and $W\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ [3]. Tetracyanoethylene (Fluka) and $Me_3NO \cdot 2H_2O$ (Aldrich) were used as received.

(a) With $Mn(C_2Ph)(CO)_3(dppe)$ in dichloromethane

$Mn(C_2Ph)(CO)_3(dppe)$ (140 mg, 0.22 mmol) was dissolved in dichloromethane (30 ml) and tcne (31 mg, 0.24 mmol) was added. After 24 h stirring, with monitoring by IR, the mixture had become deeper yellow in colour. The solvent was then removed and the residue chromatographed (Florisil column). A yellow band was eluted (3/2 petroleum spirit/acetone), and after solvent removal and recrystallization (dichloromethane/ethanol) gave yellow plates of $Mn\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3(dppe) \cdot 0.25CH_2Cl_2$ (**2a**) (121 mg, 72%), m.p. 140–145 °C (dec.) (Found: C, 66.05; H, 3.85; N, 7.14; *M* (FAB/MS), 766. $C_{43}H_{29}MnN_4O_3P_2 \cdot 0.25CH_2Cl_2$ calc: C, 65.94; H, 3.77; N, 7.11%; *M* 766). IR (CH_2Cl_2): ν(CN) 2222w, 2208w; ν(CO) 2018s, 1957s, 1944s; (Nujol) (ν(C=C) 1573w, 1533m; other peaks at 1487w, 1438m, 1158w, 1103w, 1097w, 880w, 842w, 818m, 761w, 749m, 742m, 720w, 705(sh), 698s, 662m, 620w, 607w cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 7.63–7.36 (m, 25H, Ph); 3.16 (m, 4H, CH_2).

(b) With $Mn(C_2Ph)(CO)_3(dppe)$ in benzene

$Mn(C_2Ph)(CO)_3(dppe)$ (200 mg, 0.31 mmol) was dissolved in benzene (5 ml) and a solution of tcne (48 mg, 0.37 mmol) in benzene (15 ml) was added. After an initial green colour formed the solution became progressively paler and a white precipitate was deposited. After 4 h this was filtered off, washed with petroleum spirit (10 ml), dried, and then recrystallized quickly at −30 °C from CH_2Cl_2/Et_2O to give $Mn[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2](CO)_3(dppe) \cdot 0.5CH_2Cl_2$ (**1a**) (160 mg, 67%, m.p. 120–125 °C (dec.). (Found: C, 64.26; H, 4.08; N, 6.67%; *M* (FAB/MS) 766. $C_{43}H_{29}MnN_4O_3P_2 \cdot 0.5CH_2Cl_2$ calc: C, 64.58; H, 3.73; N, 6.92%; *M* 766). IR (CH_2Cl_2): ν(CN) 2234vw, ν(CO) 2017s, 1942s,br; (Nujol) ν(C=C) 1573vw; other bands at 1481w, 1440m, 1098w, 1000w, 795w, 710m, 698(sh), 690m, 688w, 667w, 650w, 628w cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 7.65–7.39 (m, 25H, Ph) 3.30 (m, 4H, CH_2).

(c) With $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ in dichloromethane

$Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ (165 mg, 0.59 mmol) and tcne (150 mg, 1.18 mmol) were dissolved in dichloromethane (10 ml). After 1.5 h stirring the yellow-brown solution was filtered, ethanol (10 ml) added and the volume reduced to 5 ml. Cooling to −50 °C resulted in formation of a yellow precipitate, which was collected by filtration and washed with cold ethanol (2 × 5 ml) and petroleum spirit (10 ml). Recrystallization (dichloromethane/pentane) gave yellow crystalline $Fe\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5) \cdot 0.125CH_2Cl_2$ (**2b**) (185 mg, 77%) m.p. > 202 °C (dec.). (Found: C, 60.79; H, 2.57; N, 13.46%; *M* (EI/MS) 406. $C_{21}H_{10}N_4O_2Fe \cdot 0.125CH_2Cl_2$ calc: C, 60.80; H, 2.45; N, 13.43%; *M* 406). IR (CH_2Cl_2): ν(CN) 2226w, ν(CO) 2050s, 2005s; (Nujol) ν(C=C) 1540w; other bands at 1494w, 865w, 826w, 772w, 741w, 695w, 662w cm^{-1} (lit. [1] ν(CO) 2050, 2005

cm^{-1}). ^1H NMR: $\delta(CDCl_3)$ 7.60 (m, 5H, Ph), 5.30 (s, 0.25H, CH_2Cl_2), 4.95 (s, 5H, C_5H_5). ^{13}C NMR: $\delta(CD_2Cl_2/CH_2Cl_2)$ 211.0, 209 (s, CO); 130.7 (m, Ph); 115.6, 112.3, 110.5 (s, CN); 86.9 (s, C_5H_5).

(d) With $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ *in diethyl ether*

$Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ (150 mg, 0.54 mmol) was dissolved in diethyl ether (10 ml) and tcne (77 mg, 0.60 mmol) was added. The solution immediately went dark green then lightened to pale yellow over 15 min with deposition of a yellow precipitate. This was filtered off, washed with diethyl ether (10 ml), dried, and shown to be $Fe[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ (**1b**) (110 mg, 50%), m.p. 78–79 °C. (Found: C, 61.22; H, 2.65; N, 13.68%; *M* (EI/MS) 406. $C_{21}H_{10}N_4O_2Fe$ calc: C, 62.10; H, 2.48; N, 13.79%; *M*, 406]. The complex is unstable in the solid state, even under nitrogen. IR (CH_2Cl_2): ν(CN) 2229vw; ν(CO) 2045s, 2001s; (Nujol) ν(C=C) 1599w, 1582w, 1555w; other bands at 1447w, 1435w, 1422w, 1340w, 1257m, 1187w, 1160w, 1075w, 1018m, 1005w, 915m, 885m, 861m, 840w, 781w, 772s, 721w, 692 s cm^{-1} (lit. [1] ν(CO) 2040, 1990 cm^{-1}). ^1H NMR: $\delta(CDCl_3)$ 7.55 (m, 5H, Ph), 5.18 (s, 5H, C_5H_5). ^{13}C NMR: δ (acetone-d^6/acetone; at -73 °C) 212.5 (s, CO), 130.0 (m, Ph), 112.3, 111.4 (s, CN); 87.0 (s, C_5H_5).

(e) With $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$

A mixture of $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ (370 mg, 0.75 mmol) and tcne (97 mg, 0.75 mmol) in toluene (10 ml) was stirred at room temperature (1 h). Solvent was removed (rotary evaporator) and the complex product mixture separated by preparative TLC (silica gel, 1/1 acetone/light petroleum). Of the nine varicoloured bands that developed, the material in band 1 (R_f 0.88, green) was identified (IR) as recovered $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ (15 mg, 4%). The product in band 2 (R_f 0.81, brown) was extracted with dichloromethane and recrystallised (CH_2Cl_2/heptane) to give brown $Ni\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (**2c**) (185 mg, 40%). (Found: C, 71.42; H, 3.99; N, 8.86. $C_{37}H_{25}N_4NiP$ calc: C, 72.22; H, 4.09; N, 9.10%). IR (Nujol): ν(CN) 2230(sh), 2222m; ν(C=C) 1575w, 1532m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 5.3 (s, 5H, C_5H_5), 7.05–7.58 (m, 20H, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 96.1 (C_5H_5), 110.4, 110.8, 112.7, 116.7 (CN), 128.5–134.6 (m, Ph).

Preparation of $\overline{W\{NH{=}C(OH)C(CN){=}C}CPh{=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ *(5)*

$W\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (100 mg, 0.18 mmol) was stirred with $Me_3NO\cdot 2H_2O$ (65 mg, 0.58 mmol) in acetone (15 ml). After 15 min the solution had become orange and thin layer chromatography indicated completion of reaction. The mixture was filtered and the solvent removed. Thin layer chromatography of the residue (2/1/1, petroleum spirit/acetone/dichloromethane) developed 7 bands; the major band (bright orange, R_f 0.68) was collected and recrystallised (diffusion of benzene/petroleum spirit into a dichloromethane/methanol solution) to yield $\overline{W\{NH{=}C(OH)C(CN){=}C}C(Ph){=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)\cdot 0.125(CH_2Cl_2)$ (**5**) (70 mg, 70%). (Found: C, 45.05; H, 2.16; N, 9.97%; *M* (FAB/MS), 552. $C_{21}H_{12}N_4O_3W\cdot 0.125CH_2Cl_2$ calc: C, 45.08; H, 2.17; N, 9.95%; *M*, 552]. IR (CH_2Cl_2): ν(CN) 2230vw, 2208w, ν(CO) 1976s, 1903s; (Fluorolube A): ν(OH) 3342s, 3240s; 3200s, 3118(sh); ν(NH) 2960w, 2934w, 2865w; (Nujol): ν(C=C) 1716w, 1675s, 1550s, 1540s; other peaks at 1262w, 1090(sh), 1072m, 1062(sh), 1009w, 1002w, 853m, 840w, 828m, 781w, 762m, 724w, 697m, 657w cm^{-1}. ^1H NMR:

δ(acetone-d^6) 7.67 (m, 5H, Ph), 5.30 (s, 5.125H, C_5H_5 + CH_2Cl_2). The OH and NH resonances were not located.

FAB MS (m/z for ^{56}Fe, ^{184}W, as appropriate), assignment, relative intensity). Peaks marked with * indicate overlapping isotopic envelopes of which the principal ion has the indicated m/z.

Mn{$\overline{C{=}CPhC(CN)_2}C(CN)_2$}(CO)$_3$(dppe) **(1a)**. *Positive ions*: 767*, $[M + H]^+$, 8; 737*, $[M - H - CO]^+$, 1; 711*, $[M + H - 2CO]^+$, 2; 682, $[M - 3CO]^+$, 30; 656, $[M - 3CO - CN]^+$, 5; 630, $[M - 3CO - 2CN]^+$, 1; 605*, $[M - 3CO - Ph]^+$, 3; 581, $[M - 3CO - C_2Ph]^+$, 9; 554 $[Mn(C_2Ph)(dppe)]^+$, 19; 537, $[Mn(CO)_3(dppe)]^+$, 14; 479, $[Mn(CN)(dppe)]^+$, 100; 453* $[Mn(dppe)]^+$, 28; 425, $[Mn(PPh_2)_2]^+$, 9; 321, $[dppe - Ph]^+$, 6; 293, $[P_2Ph_3]^+$, 28; 185, $[PPh_2]^+$, 41; 183, $[C_{12}H_8P]^+$, 35. Weak ($\leqslant$ 1%) ions were observed above $[M]^+$ at m/z 1135, 966, 905, 903 and 838.

Negative ions: 765, $[M - H]^-$, 2; 738, $[M - CO]^-$, 3; 710, $[M - 2CO]^-$, 3; 682, $[M - 3CO]^-$, 1; 612, $[M - 2Ph]^-$, 3; 553, $[Mn(C_2Ph)(dppe) - H]^-$, 11; 459, ?, 18; 368, $[M - dppe]^-$, 21; 306, ?, 100; 284, $[M - 3CO - dppe]^-$, 19; 240, $[Mn(PPh_2)]^-$, 43; 203, $[C_2PhC_2(CN)_3]^-$, 14; 199, ?, 64.

Mn{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)$_3$(dppe) **(2a)**. *Positive ions*: 767*, $[M + H]^+$, 3; 737, $[M - H - CO]^+$, 1; 711, $[M - H - 2CO]^+$, 0.5; 682*, $[M - 3CO]^+$, 27; 656*, $[M - 3CO - CN]^+$, 2; 605*, $[M - 3CO - Ph]^+$, 2; 537, $[Mn(CO)_3(dppe)]^+$,

Table 2

Crystal data and refinement details for complexes **2b** and **2c**

	2b	**2c**
Formula	$C_{21}H_{10}FeN_4O_2$	$C_{37}H_{25}N_4NiP$
MW	406.2	615.3
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
	(C_i^1, No. 2)	(C_{2h}^5, No. 14)
a (Å)	9.378(2)	13.765(6)
b (Å)	13.874(3)	10.89(2)
c (Å)	7.935(4)	20.753(8)
α (°)	92.92(3)	90
β (°)	101.57(2)	95.55(2)
γ (°)	108.78(1)	90
U (Å^3)	950.1	3096.3
Z	2	4
D_c (g cm^{-3})	1.420	1.320
$F(000)$	411	1264
μ (cm^{-1})	7.85	6.79
2θ limits (°)	1–25	1–20
No. of data collected	4174	3007
No. of unique data	3342	2408
No. of unique data used (with $I \geqslant 2.5\sigma(I)$)	2825	1702
R	0.038	0.048
k	1.2	2.4
g	0.0010	0.0008
R_w	0.044	0.054
ρ_{max} (e Å^{-3})	0.44	0.40

18; 479, $[\mathrm{Mn(CN)(dppe)}]^+$, 100; 453★, $[\mathrm{Mn(dppe)}]^+$, 52; 425, $[\mathrm{Mn(PPh_2)_2}]^+$, 9; 321, $[\mathrm{dppe-Ph}]^+$, 16; 293, $[\mathrm{P_2Ph_3}]^+$, 14; 185, $[\mathrm{PPh_2}]^+$, 54; 183, $[\mathrm{C_{12}H_8P}]^+$, 46. Weak ($\leqslant 1\%$) ions were observed above $[M]^+$ at m/z 1161, 1151, 1135, 966 and 800.

Negative ions: 765, $[M-\mathrm{H}]^-$, 3; 737, $[M-\mathrm{H}-\mathrm{CO}]^-$, 5; 710, $[M-2\mathrm{CO}]^-$, 4; 682★, $[M-3\mathrm{CO}]^-$, 3; 605, $[M-3\mathrm{CO}-\mathrm{Ph}]^-$, 1; 553, $[\mathrm{Mn(C_2Ph)(dppe)}-\mathrm{H}]^-$, 8; 368, $[M-\mathrm{dppe}]^-$, 23; 305★, ?, 17; 284, $[M-3\mathrm{CO}-\mathrm{dppe}]^-$, 32; 229, $[\mathrm{C_2PhC_2(CN)_4}]^-$, 100; 203, $[\mathrm{C_2PhC_2(CN)_3}]^-$, 25; 199, ?, 12; 168, ?, 14.

Fe{C=CPhC(CN)₂C(CN)₂}(CO)₂(η-C₅H₅) (**1b**). *Positive ions*: 407, $[M+\mathrm{H}]^+$, 18; 406, $[M]^+$, 20; 380, $[M-\mathrm{CN}]^+$, 8; 350★, $[M-2\mathrm{CO}]^+$, 66; 324, $[M-2\mathrm{CO}-\mathrm{CN}]^+$, 46; 279, $[M+\mathrm{H}-\mathrm{C_2(CN)_4}]^+$, 100; 274, $[M+\mathrm{H}-2\mathrm{CO}-\mathrm{Ph}]^+$, 26; 268, ?, 17; 259, $[\mathrm{FeC_2PhC_2(CN)_3}]^+$, 11.

Fe{C[=C(CN)₂]CPh=C(CN)₂}(CO)₂(η-C₅H₅) (**2b**). *Positive ions*: 407, $[M+\mathrm{H}]^+$, 45; 406, $[M]^+$, 38; 379★, $[M+\mathrm{H}-\mathrm{CO}]^+$, 9; 363★, ?, 9; 350★, $[M-2\mathrm{CO}]^+$, 100; 324, $[M-2\mathrm{CO}-\mathrm{CN}]^+$, 48; 279, $[M+\mathrm{H}-\mathrm{C_2(CN)_4}]^+$, 90; 274, $[M+\mathrm{H}-2\mathrm{CO}-\mathrm{Ph}]^+$, 48; 268, ?, 26; 259 $[\mathrm{FeC_2PhC_2(CN)_4}]^+$, 24.

W{NH=C(OH)C(CN)=CCPh=C(CN)₂}(CO)₂(η-C₅H₅) (**5**). *Positive ions*: 552, $[M]^+$ 69; 512, ?, 23; 496, $[M-2\mathrm{CO}]^+$, 100; 470, $[M-2\mathrm{CO}-\mathrm{CN}]^+$, 15.

Table 3

Fractional atomic coordinates for $\mathrm{Fe\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)}$ (**2b**)

Atom	x	y	z
Fe	0.12175(4)	0.22575(2)	0.23234(5)
O(1)	−0.1117(3)	0.0244(2)	0.1095(3)
O(2)	0.2723(3)	0.1597(2)	0.5406(4)
N(1)	−0.1214(4)	0.4168(2)	0.6563(4)
N(2)	0.3434(4)	0.4380(2)	0.6420(4)
N(3)	−0.0994(4)	0.0868(3)	0.6513(5)
N(4)	−0.5389(3)	0.0499(3)	0.2956(5)
C(1)	0.0967(5)	0.2946(3)	0.0072(5)
C(2)	0.1825(7)	0.3685(3)	0.1446(7)
C(3)	0.3151(6)	0.3494(4)	0.2140(6)
C(4)	0.3095(5)	0.2593(4)	0.1142(6)
C(5)	0.1766(5)	0.2284(3)	−0.0107(5)
C(6)	−0.0016(3)	0.2736(2)	0.3695(3)
C(7)	0.0528(3)	0.3472(2)	0.5065(3)
C(8)	−0.1706(3)	0.2227(2)	0.3103(3)
C(9)	−0.2462(3)	0.1451(2)	0.3916(3)
C(10)	−0.0463(3)	0.3841(2)	0.5914(4)
C(11)	0.2154(3)	0.3974(2)	0.5803(4)
C(12)	−0.1651(3)	0.1124(2)	0.5380(4)
C(13)	−0.4107(3)	0.0911(2)	0.3365(4)
C(14)	−0.2521(3)	0.2538(2)	0.1534(3)
C(15)	−0.3349(3)	0.1837(2)	0.0073(4)
C(16)	−0.4079(4)	0.2160(3)	−0.1377(4)
C(17)	−0.4054(4)	0.3147(3)	−0.1352(5)
C(18)	−0.3263(4)	0.3839(3)	0.0077(5)
C(19)	−0.2463(3)	0.3550(2)	0.1521(4)
C(20)	−0.0213(3)	0.1021(2)	0.1588(4)
C(21)	0.2139(3)	0.1852(2)	0.4194(4)

Crystallography

Intensity data were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-K_α (graphite monochromatized) radiation, λ 0.71073 Å, with the use of the $\omega:2\theta$ (for **2b**) or $\omega:\theta$ scan technique for **2c**. The intensities of three standard reflections were measured after every 7200 s (4000 s for **2c**) X-ray

Table 4

Fractional atomic coordinates for Ni{C[=C(CN)$_2$]CPh=C(CN)$_2$}(PPh$_3$)(η-C$_5$H$_5$) (**2c**)

Atom	x	y	z
Ni	0.36696(7)	−0.02472(8)	0.12438(5)
P(1)	0.2316(1)	0.0584(2)	0.1498(1)
N(1)	0.2099(6)	−0.3554(7)	−0.0460(4)
N(2)	0.2621(5)	0.0329(7)	−0.0525(3)
N(3)	0.5086(7)	−0.3365(7)	0.0031(4)
N(4)	0.4309(6)	−0.5707(6)	0.1580(4)
C(1)	0.5072(4)	−0.0722(6)	0.1719(4)
C(2)	0.5144(4)	−0.0489(6)	0.1052(4)
C(3)	0.4849(4)	0.0742(6)	0.0921(4)
C(4)	0.4595(4)	0.1271(6)	0.1507(4)
C(5)	0.4733(4)	0.0366(6)	0.2000(4)
C(6)	0.3188(5)	−0.1651(6)	0.0777(3)
C(7)	0.2797(5)	−0.1647(6)	0.0161(4)
C(8)	0.3338(5)	−0.2829(7)	0.1131(4)
C(9)	0.4001(6)	−0.3652(7)	0.0952(4)
C(10)	0.2416(6)	−0.2719(8)	−0.0184(4)
C(11)	0.2696(6)	−0.0541(7)	−0.0219(4)
C(12)	0.4592(7)	−0.3491(8)	0.0436(5)
C(13)	0.4173(6)	−0.4808(8)	0.1299(4)
C(14)	0.2784(4)	−0.3111(6)	0.1686(2)
C(15)	0.1862(4)	−0.3647(6)	0.1579(2)
C(16)	0.1371(4)	−0.4019(6)	0.2103(2)
C(17)	0.1801(4)	−0.3854(6)	0.2734(2)
C(18)	0.2723(4)	−0.3317(6)	0.2840(2)
C(19)	0.3214(4)	−0.2946(6)	0.2317(2)
C(20)	0.1863(3)	0.1923(5)	0.1035(2)
C(21)	0.0935(3)	0.2375(5)	0.1115(2)
C(22)	0.0588(3)	0.3418(5)	0.0777(2)
C(23)	0.1171(3)	0.4008(5)	0.0358(2)
C(24)	0.2099(3)	0.3555(5)	0.0277(2)
C(25)	0.2446(3)	0.2513(5)	0.0616(2)
C(26)	0.1219(4)	−0.0360(5)	0.1449(2)
C(27)	0.0783(4)	−0.0777(5)	0.1988(2)
C(28)	−0.0060(4)	−0.1493(5)	0.1905(2)
C(29)	−0.0467(4)	−0.1793(5)	0.1283(2)
C(30)	−0.0031(4)	−0.1376(5)	0.0744(2)
C(31)	0.0812(4)	−0.0659(5)	0.0828(2)
C(32)	0.2510(4)	0.1158(4)	0.2330(2)
C(33)	0.2497(4)	0.2413(4)	0.2463(2)
C(34)	0.2728(4)	0.2831(4)	0.3095(2)
C(35)	0.2973(4)	0.1994(4)	0.3593(2)
C(36)	0.2987(4)	0.0739(4)	0.3460(2)
C(37)	0.2755(4)	0.0321(4)	0.2828(2)

exposure time and these indicated that no significant decomposition of either crystal occurred during their respective data collections. Routine corrections were made for Lorentz and polarization effects [22*] and for absorption employing an analytical procedure [22*]. Relevant crystal data are summarised in Table 2.

The structure of **2b** was solved by normal heavy atom methods, while the positions of the Ni and P atoms in **2c** were obtained from the EEES direct methods routine of SHELX [22*]. The structures were refined by a full-matrix least-squares procedure based on F [22*]. The phenyl and cyclopentadienyl groups in **2c** were refined as hexagonal and pentagonal rigid groups, respectively. Non-hydrogen atoms in **2b** were refined anisotropically; for **2c**, the Ni, P, N and C atoms (of the C_5H_5 group only) were refined with anisotropic thermal parameters, the remaining atoms being refined isotropically. Hydrogen atoms were included in both of the models at their calculated positions, a weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ included, and the refinements continued until convergence for both **2b** and **2c**. Refinement details are listed in Table 2.

Scattering factors for neutral Fe and Ni (corrected for $\Delta f'$ and $\Delta f''$) were from ref. 23 and values for the remaining atoms were those incorporated in SHELX [22*]. Data solution and refinement were performed with the SHELX program system on the University of Adelaide's VAX11/785 for **2b** and CYBER for **2c**.

Fractional atomic coordinates are listed in Tables 3 and 4, the numbering schemes used are shown in Figs. 1 and 2. Selected interatomic bond distances and angles are given in Table 1 and listings of thermal parameters, hydrogen atom parameters, all bond distances and angles, and of the observed and calculated structure factors for both compounds are available from the authors.

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