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Transition metai-cyanocarbon chemistry

IX *. Reactions of monocyanoacetylene with dicarbonylcydopentadienylmethylthiolatoiron(II). Crystal structures of [FeC(O)C(CN)=CH(SCH 3)(~S-CsH s)(CO) I and of [p-~2-Fe(C=:--C-CN)(T/s-CsHs) (CO) ~][Co(CO) 3]2

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Abstract

The reaction of [Fe(~5-CsHs)(SCHa)(CO)2] with monocyanoacetylene (HC=:-CCN) in THF at room temperature gives the acetylide [Fe(C=-CCNX~/s-Cs H s)(CO) 2] (1), the acylic species [FeC(O)C(CN)--CH(SCH 3)(~S-Cs H s)(CO)] (2), the binuclear complex [Fe(,/5-C5H 5)(CO) 2C(CN)=C(SCH a)Fe(7/5-C5 H~)(CO) 2] (3), and the disubstituted olefin Z-(NC)CH--CH((SCH3) (4). If the HC=:-CCN is condensed on to a frozen solution of the thiolato complex and the mixture then allowed to warm up, the acylic compound 2 is not isolated. Irradiation of I and 3 in the presence of PPh 3 in THF gives the substituted complex [Fe(C~-CCN)(T/S-C sHs)(CO)(PPh 3)] (6) and [Fe(7/5-C5H s)(CO) 2C(CN)=C(SCH 3)Fe(~/~-CsH 5)(CO)-(PPh3)] (10). Cycloaddition of tetracyanoethylene on 1 and 6 gives the corresponding complexes [Fe(C=C(CN)C(CN)2CJ(CN)2(~/~-C~ H~)(CO)(L)] (L = CO (7) or PPh 3 (8)). Under UV irradiation 8 is converted into Fe(~/3-C(CN)2C(CN)(~==C(CN)2)(T/5-CsHs)(PPh3)] by loss of CO. Complex 1 reacts with Co2(CO)8 to form the [p-~/2,Fe(C=-C-CN)(T/5-CsHs)(CO)2][Co(CO)3]2 (5). The structures of 2 and 5 have been determined by X-ray diffraction.

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* **Part VIII: M. Etienne and J.E. Guerchais, submitted.**

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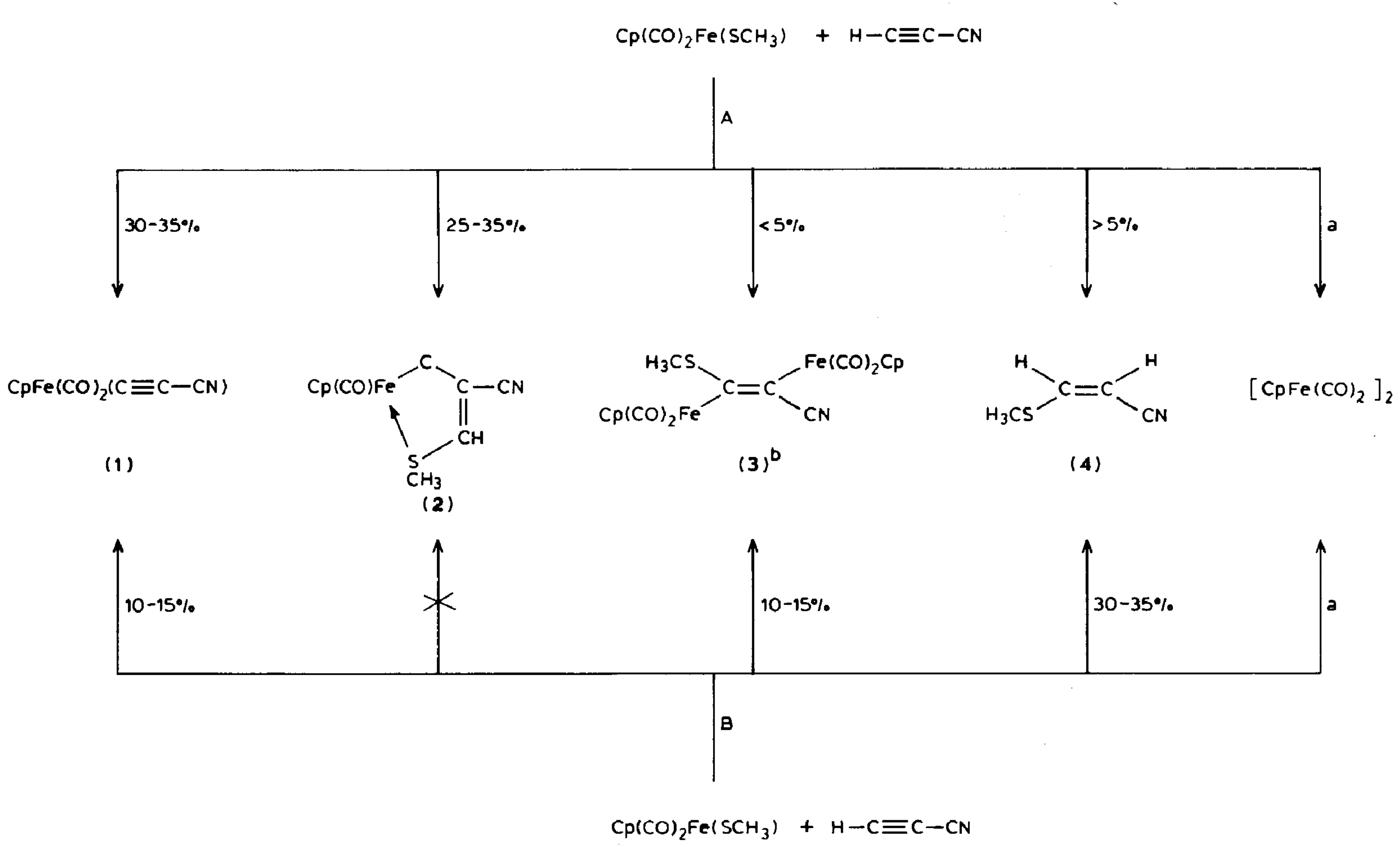


Scheme 1. A: HC≡CCN dissolved in THF then transferred to a THF solution of $Cp(CO)_2Fe(SCH_3)$ at room temperature; B: HC≡CCN trapped in a THF solution of $Cp(CO)_2Fe(SCH_3)$ frozen in liquid nitrogen; Cp: $(\eta^5\text{-}C_5H_5)$; a: yields not calculated (see Experimental); b: see text for the structure of **3**; yields based on $Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2$.

Introduction

Many types of reactions between organometallic thiolato complexes and electron-withdrawing alkynes have been described in literature. Hexafluorobut-2-yne, for instance, inserts into the metal–sulfur bond of $[Fe(\eta^5\text{-}C_5H_5)(SR)(CO)_2]$ to give σ-vinylic compounds [1]. However, this same alkyne reacts by an alternative pathway with $[M(\eta^5\text{-}C_5H_5)(SR)(CO)_3]$ ($M = Mo$ or W, $R = CF_3$; $M = Mo$, $R = C_6F_5$), giving coordinatively unsaturated complexes $[M(\eta^5\text{-}C_5H_5)(SR)(CO)(CF_3C{\equiv}CCF_3)]$ [2]. Various carbonylated metallacyclic species may be also obtained [3,4]. Addition of a second alkyne is possible in some cases, and the resulting products contain either σ-bonded or π-bonded heterocycles [1]. This brief outline is not exhaustive, and many efforts have been undertaken to rationalise the diverse modes of reaction. For some years we have been engaged in a systematic study of the behaviour of cyano-substituted alkynes, involving, for example their regio- and stereo-specific insertion into M–H bonds of organometallic hydride complexes, and we thus decided to study reactions of cyano-substituted alkynes with thiolato complexes. We found that the monocyanoacetylene $HC{\equiv}CCN$ (MCA) inserts into the W–S bond and forms an acylic complex in the presence of $[W(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_3]$, both of the products reacting with PPh_3, to give a phosphorane and a σ-terminal acylic species, respectively [5]. In completion of this study, we describe here the reactions between the thiolato iron complex $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ and MCA.

Results and discussion

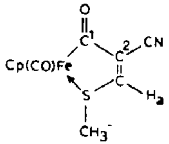
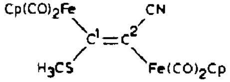
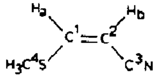
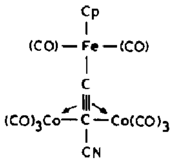
Reaction of $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ with $HC{\equiv}CCN$

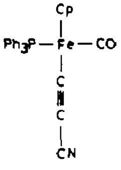
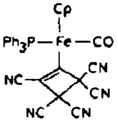
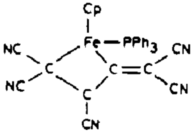
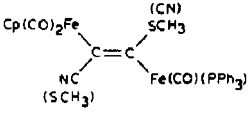
The outcome of the reaction between $HC{\equiv}CCN$ and $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ depends upon the experimental conditions. When a solution of the alkyne in THF was added to a THF solution of the thiolato iron complex at room temperature (way A), in addition to the dimer $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, four products containing cyano groups were separated by chromatography: the acetylide $[Fe(C{\equiv}CCN)(\eta^5\text{-}C_5H_5)(CO)_2]$ (**1**), an acylic species $[\overline{FeC(O)C(CN){=}CH(S}CH_3)(\eta^5\text{-}C_5H_5)(CO)]$ (**2**), a binuclear compound $[Fe(\eta^5\text{-}C_5H_5)(CO)_2C(CN){=}C(SCH_3)Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ (**3**) and the disubstituted olefin *Z*-$(NC)CH{=}CH(SCH_3)$ (**4**). When the $HC{\equiv}CCN$ was condensed into a solution of the iron complex frozen in liquid nitrogen (way B), the acylic compound **2** was not formed (Scheme 1).

Infrared data for compounds **1**, **2** and **3** are given in the Experimental section. The $\nu(C{\equiv}N)$ stretching vibrations appear in the expected 2200–2300 cm^{-1} range. For complex **1** the $\nu(C{\equiv}C)$ acetylide vibration is given as 2080 cm^{-1}, but this assignment was not obvious because for other iron acetylides of the type $[Fe(C{\equiv}CR)(\eta^5\text{-}C_5H_5)(CO)_2]$ containing weaker electron-withdrawing R groups ($R = CH_3$, C_4H_9, C_6H_5) the $\nu(C{\equiv}C)$ vibration was observed in the 2105–2140 cm^{-1} range, i.e. at higher frequencies but with lower intensities than the $\nu(C{\equiv}O)$ vibrations [6,7]. The presence of the CN group may account for the observed shift of the $\nu(C{\equiv}C)$ vibration to a lower frequency, either by the interaction of conjugated bonds, such as was suggested for the platinum complex $[Pt(CN)(C{\equiv}CCN)(PPh_3)_2]$ (vide infra) [8], or simply by the removal of electron density from the triple $C{\equiv}C$ bond.

Table 1

NMR data (δ (ppm), J(Hz)) ($CDCl_3$ solutions)

	^1H				^{13}C					
	(H)	(C_5H_5)	(CH_3)	(C_6H_5)	(CN)	(C≡O)	(C_5H_5)	(CH_3)	C(1)	C(2)
$Cp(CO)_2FeC^1{\equiv}C^2CN$ (1)		5.09(s)			113.2	209.7	85.8		105.6	86.1
 (2)	8.26(s)	4.73(s)	2.59(s)		113.7	215.7	84.1	27.0	255.4	136.1
 (3)		4.66(s) 4.86(s)	2.63(s)		118.0	209.3 213.2 213.4 217.5	84.7 86.6	30.4	^{a}	^{a}
 (4)*	7.33(H_a,d) 5.36(H_b,d) ($J(H_aH_b)$ 10.0)		2.56(s)		115.9(d) (^2J(C3-H_b) 14.5)			16.8(qd) (^1J(C4H) 141.1) (^3J(C4H_a) 5.3)	154.2(dq) (^1J(C1H_1) 174.3 (^3J(C1H) 5.3)	91.9(d) (^3J(C2H_b) 180.0)
 (5)		5.09(s)			115.2	212.2 198.9	86.9			

 (6)	4.53(s)		7.42(m)	116.0	217.3(d) (*J*(CP) 28.5)	85.0	
 (8)	4.82(s)		7.36(m)	110.4 110.6 111.9 115.9	216.7	90.6	
 (9)	4.97(s)		7.43(m)	110.5–119.1		93.2	
 (10)	4.13(s) 4.40(s)	2.46(s)	7.33(m)		217.5 219.8 221.0	84.1 84.4	29.9

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[a] Not observed; s: singulet; d; doublet; q: quadruplet; m: multiplet.

*: ^{1}H NMR data for the *trans* (*E*) isomer (δ (ppm), *J* (Hz)): H_a: 7.45(d); H_b: 5.11(d); $J(H_aH_b)$: 16.0; CH_3: 2.36.

The acylic structure of **2** is consistent with the presence of a single $\nu(C\equiv O)$ band at 1960 cm^{-1} and of a $\nu(C=O)$ band at 1590 cm^{-1}. The $\nu(C=C)$ vibration bands are identified at 1575 and 1600 cm^{-1} for complexes **2** and **3**, respectively.

^1H and ^{13}C NMR data of the different compounds are listed in Table 1. The strong electron withdrawing effect of the CN group, and its magnetic anisotropy, together with deshielding due to the metal, gives rise to a substantial polarization of the acetylide $C\equiv C$ bond in complex **1** in the sense $-Fe-C_\alpha^{\delta+}\equiv C_\beta^{\delta-}-CN$ ($\delta(C_\alpha)$ 105.6 ppm; $\delta(C_\beta)$ 86.1 ppm), and to a greater deshielding of the H_a metallacyclic proton in complex **2** than in the corresponding complex $[\overline{FeC(O)C(CF_3)=CH_a(S}CH_3)(\eta^5\text{-}C_5H_5)(CO)]$ (8.26 and 7.80 ppm, respectively) which was formed together with the acetylide $[Fe(C\equiv C\text{-}CF_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ in the reaction between trifluoropropyne and $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ [4].

The ^{13}C resonances of the terminal and the acylic carbonyl groups are at 210 and 255.4 ppm, respectively, for complex **2**.

Two peaks of equal intensity are observed for the (^1H) (4.66 and 4.86 ppm) and for the (^{13}C) (84.7 and 86.6 ppm) $\eta^5\text{-}C_5H_5$ resonances of the dinuclear complex **3**, revealing the non-equivalency of the two cyclopentadienyl ligands, but the poor stability of this product in solution prevented recording of the complex ^{13}C carbon NMR spectrum.

The olefin **4** was obtained exclusively as the *Z* isomer, as indicated by the value of the coupling constants ^3J(Ha–Hb) of 10 Hz, which is typical of "*cis*" vinylic protons [9–12], and those of ^1J(C–H) 174.4 and 180.0 Hz (Table 1).

In considering the nature of the various compounds obtained we note that the presence of the CN group increases the acidic character of the proton of MCA and this may favour the formation of an acetylide (like **1**) from this alkyne. As suggested by Davidson [13] for reactions of iron and tungsten mercapto complexes with symmetric electrophilic acetylenes ($CF_3C\equiv CCF_3$ and $CH_3CO_2C\equiv CCO_2CH_3$), a nucleophilic attack of the sulfur atom bearing the proton in MCA, favoured by polarization of the $C\equiv C$ bond [14*], can account for the formation of the acylic complex **2** and the relative positions of the substituents on the metallacycle formed.

Because the complex **2** is the first example of a metallacycle formed from MCA, and because its behaviour is different from that of $[\overline{FeC(O)C(CF_3)=CH(S}CH_3)(\eta^5\text{-}C_5H_5)]$ (which rearranges giving a σ-vinylic complex $[FeC(CF_3)=CH(SCH_3)(\eta^5\text{-}C_5H_5)(CO)_2]$, whereas no reaction of **2** is observed under similar conditions), we decided to carry out an X-ray diffraction study of **2**.

The molecular structure of **2** (Fig. 1) is typical of other acylic complexes derived from symmetrical or true alkynes and organometallic thiolates of Mo, W and Fe [3,13,15]. The average value (90.6°) of three angles around the iron atom (Table 2) indicates that the coordination polyhedron of iron is an octahedron in which the three other sites are occupied by the ($\eta^5\text{-}C_5H_5$) ring, as suggested by Davis [16]. The Fe–C(1) bond length of 1.929(5) Å is shorter than the Fe–C (sp^2) bond length in σ-vinylic (1.99(2) Å [17]) and in σ-acylic (1.97–2.02 Å [18]) complexes, but lies in the range 1.88–2.00 Å observed for carbeneiron complexes [19]. This contraction of the Fe–C(1) bond in **2** may be due to geometrical constraints within the metallacycle or to the drift of electrons from the metal (there is an electron donor ligand SCH_3 in

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* Reference number with asterisk indicates a note in the list of references.

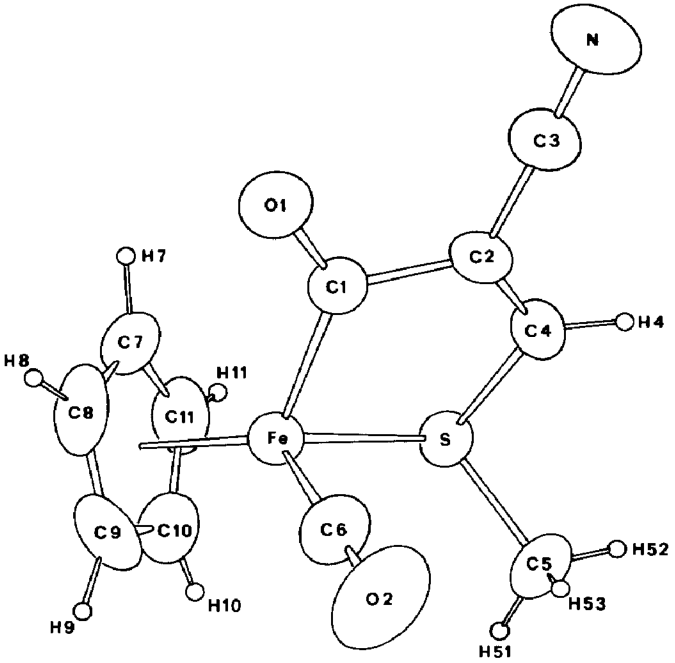
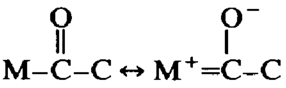


Fig. 1. ORTEP drawing of 2.

its coordination sphere) into the acetyl–carbonyl group reflected in the following resonance:



$$\mathrm{M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C} \leftrightarrow \mathrm{M^{+}{=}\overset{\overset{\displaystyle O^{-}}{|}}{C}{-}C}$$

Such a drift of electrons may be favoured by the presence of electron-withdrawing substituents on the metallacycle in 2.

Table 2

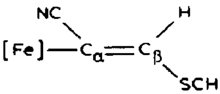
Significant interatomic distances (Å) and angles (°) for 2; data in brackets are those for [FeC(O)C(CF$_3$)=CH(SCH$_3$)(η^5-C$_5$H$_5$)(CO)] (ref. 21)

Fe–S	2.195(1) [2.19]	S–Fe–C(1)	86.7(2)
Fe–C(1)	1.929(5) [1.95]	C(1)–Fe–C(6)	89.9(3)
Fe–C(6)	1.733(6)	S–Fe–C(6)	95.2(2)
Fe–CP [a]	1.720	Fe–C(1)–O(1)	128.3(4)
C(1)–O(1)	1.221(6)	Fe–C(1)–C(2)	115.4(4)
C(1)–C(2)	1.525(7) [1.52]	O(1)–C(1)–C(2)	116.3(5)
C(2)–C(3)	1.440(7) [1.50]	C(1)–C(2)–C(3)	117.8(5)
C(3)–N	1.133(6)	C(1)–C(2)–C(4)	119.7(5)
C(2)–C(4)	1.321(7) [1.32]	C(2)–C(3)–N	178.5(6)
S–C(4)	1.758(5) [1.75]	S–C(4)–C(2)	115.0(4)
S–C(5)	1.810(6)	Fe–S–C(4)	101.3(2)
C(6)–O(2)	1.152(7)	Fe–S–C(5)	114.7(3)
		C(4)–S–C(5)	100.5(3)

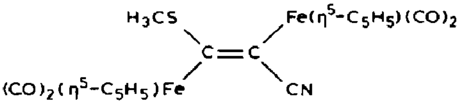
[a] CP is the center of gravity of the C(7)–C(11) ring.

Except for the C(2)–C(3) bond length, which is considerably shorter in **2** than in its CF_3 analogue (1.44 vs. 1.50 Å) [20,21], but being a normal consequence of different radii of *sp* and sp^3 hybridized carbon atoms, the geometrical parameters are similar in the CN and CF_3 structures. However it is possible that the slight shortening of the Fe–C(1) bond in **2** (1.929(5) Å compared with 1.95 Å in the CF_3 complex, for which the standard deviations are not reported) is significant. Electron delocalization over the iron, carbonyl carbon, and C(2) carbon atoms induced by the presence of the CN substituent on the metallacycle may reinforce the Fe–C(1)–C(2) bonding, thus preventing a rearrangement to a σ-alkenyl structure upon UV irradiation. This last type of structure, which could arise in another way, from a direct insertion of MCA into the Fe–S bond, has not been detected in our work. Moreover we have encountered a similar problem during the studies on the reactions of MCA with iron hydrides. Relatively stable σ-vinylic insertion products could be isolated only when the $[FeH(\eta^5\text{-}C_5H_5)(CO)L]$ complexes were stabilized by phosphines [22]. This suggests that the iron–carbon Fe–C(CN)= or the Fe–C(H)=C(CN) bonds are less stable than the Fe–C(O) and Fe–C(CF_3) linkages.

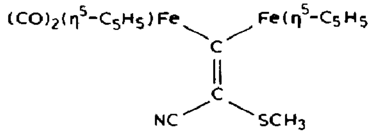
Although, as indicated above, no insertion products were recovered from the reaction between $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ and HC≡CCN, their formation cannot be ruled out. The prior nucleophilic attack of the sulfur atom proposed for the formation of the acylic complex **2** may lead to a σ-vinylic compound of the type via



a "*cis*" insertion of the alkyne, with the CN group attached to the C_α carbon (α-with respect to the metal). On the other hand, a β-metallated σ-alkenyl product such as $[Fe]\text{–}CH{=}C(CN)(SCH_3)$, comparable with that obtained in the reaction of $[W(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_3]$ with HC≡CCN [5], may be envisaged. A subsequent reaction of these two, presumably unstable, σ-vinylic intermediates, could by reaction with another molecule of $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ and elimination of $HSCH_3$, lead to the "*trans*", **a**, or to the vinylidene, **b**.



(a)

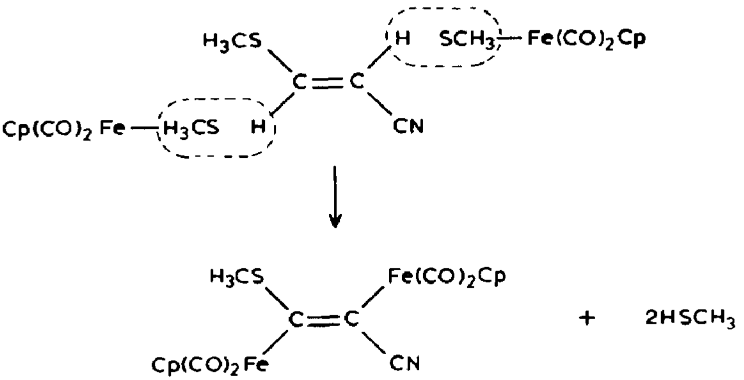


(b)

Unfortunately decomposition of the dinuclear complex **3** in solution occurred before all the (^{13}C) peaks could be recorded, and suitable crystals for a structural determination could not be obtained. However, the reaction of **3** with PPh_3 gives rise to the substitution of only one (CO) group in the compound **10** (Table 1), favouring the less symmetrical form (**a**).

Another mechanism which does not involve the formation of σ-vinylic intermediates (which were not detected) could account for the "*trans*" dinuclear form (**a**). Methanethiol results from the reaction of formation of the acetylide (eq. 2):

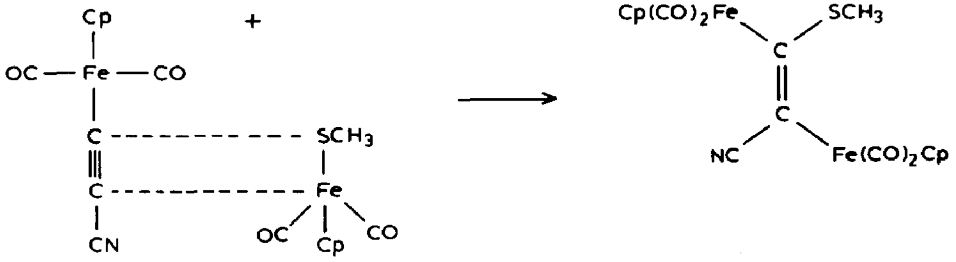
$$\left[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2\right] + HC{\equiv}CCN \rightarrow \left[Fe(C{\equiv}C\text{-}CN)(\eta^5\text{-}C_5H_5)(CO)_2\right] + HSCH_3 \quad (2)$$



(3)

A subsequent reaction with MCA present in the solution could lead to the formation of the olefin (4) in the (*E*) and (*Z*) configurations, as was observed in the direct reaction between $HSCH_3$ and MCA ((NC)CH=CH(SCH_3): *E*/*Z* 1/3), and the (*E*) isomer ((^1H) NMR data: Table 1 footnote) could be consumed in the formation of the "*trans*" dinuclear complex **3** (eq. 3).

On the other hand, the insertion of the acetylide complex **1**, regarded as an activated alkyne, into the Fe–S bond of the thiolato complex as shown in eq. 4.

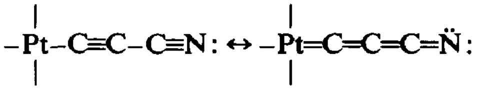


(4)

must be ruled out. This is because when the compound **1** and the starting thiolato iron complex were mixed under the same experimental conditions as those used for the reactions in Scheme 1, no reaction occured.

Reactions of [Fe(C≡CCN)(η⁵-C₅H₅)(CO)₂] (1)

[Fe(C≡CCN)(η^5-C_5H_5)$(CO)_2$] (**1**) is the first transition metal acetylide made from monocyanoacetylene, so we were interested in its behaviour as an alkyne. Another known cyanoacetylide [Pt(CN)(C≡CCN)$(PPh_3)_2$] was formed by isomerisation of a π-dicyanoacetylene adduct. It has been suggested that electron delocalization over the cyanoacetylide moiety arises from calculations by the canonical form **B**.



$$-\overset{|}{\underset{|}{Pt}}-C{\equiv}C-C{\equiv}N: \leftrightarrow -\overset{|}{\underset{|}{Pt}}{=}C{=}C{=}C{=}\ddot{N}:$$

(A) **(B)**

Such a delocalization may alter the acetylenic behaviour of cyanoacetylides. Thus in order to examine the reactions of [Fe(C≡CCN)(η^5-C_5H_5)$(CO)_2$] which could be

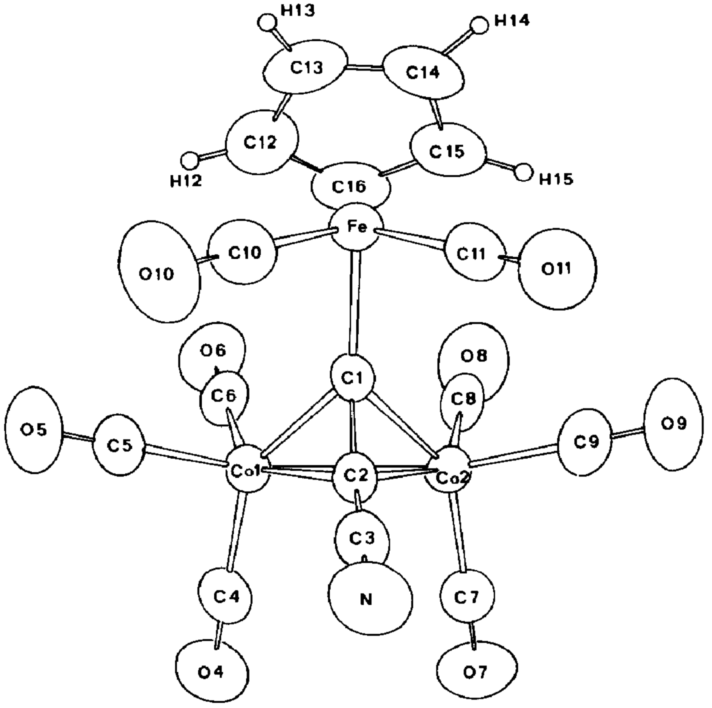


Fig. 2. ORTEP drawing of 5.

related to both the localized and delocalized canonical forms, we carried out reactions of **1** with various reagents such as $Co_2(CO)_8$, PPh_3 and $(CN)_2C{=}C(CN)_2$ (Scheme 2). Compounds **5**, **6**, **7**, **8** and **9** were obtained, and their spectroscopic data are listed in Table 1.

Complex **5** (Fig. 2) formed in the reaction of the acetylide with $Co_2(CO)_8$ was shown by an X-ray structural determination to be a further example of a well-known type of μ-alkyne hexacarbonyldicobalt complex, $[Co_2(\mu\text{-}C_2RR')(CO)_6]$ [23], thus indicating the acetylenic nature of the parent $[Fe(C{\equiv}CCN)(\eta^5\text{-}C_5H_5)(CO)_2]$ complex.

There are only two X-ray structures reported for this type of compound derived from $Co_2(CO)_8$ and metal phenylacetylides, $[Mn(C{\equiv}CPh)(CO)_4\{P(C_6H_{11})_3\}]$ [24] and $[Fe(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_2]$ [25]. The bond lengths in **5** (Table 3) are similar to those found in previous examples: the Co(1)–Co(2) of 2.478(1) Å, Co–C (alkyne) of 1.937 to 2.021 Å and C(1)–C(2) of 1.335(7) Å distances are within the normal values found earlier. However, the Fe–C(1) bond length of 1.954(5) Å merits comment. It is distinctly longer than those in the phenylacetylide iron complex $[Fe(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_2]$, 1.920(6) Å [26], and in its CuCl adduct, 1.906(10) Å [27]. In this last compound, the coordination of the copper atom to the C≡C triple bond lowers the enegy of its π^* antibonding orbital and thus weakens the bond. In consequence, the Fe–C bond becomes stonger and shorter than that in the parent pure acetylide, as observed. The metallated carbon atom remains roughly *sp* hybridized in the adduct, the Fe–C–C angle being 162(2)° [27]. The electronic features are different in the acetylides coordinated to $Co_2(CO)_6$. There is an increasing degree of back-bonding into the C≡C π^* orbitals and the metallated

Table 3

Significant interatomic distances (Å) and angles (°) for **5**

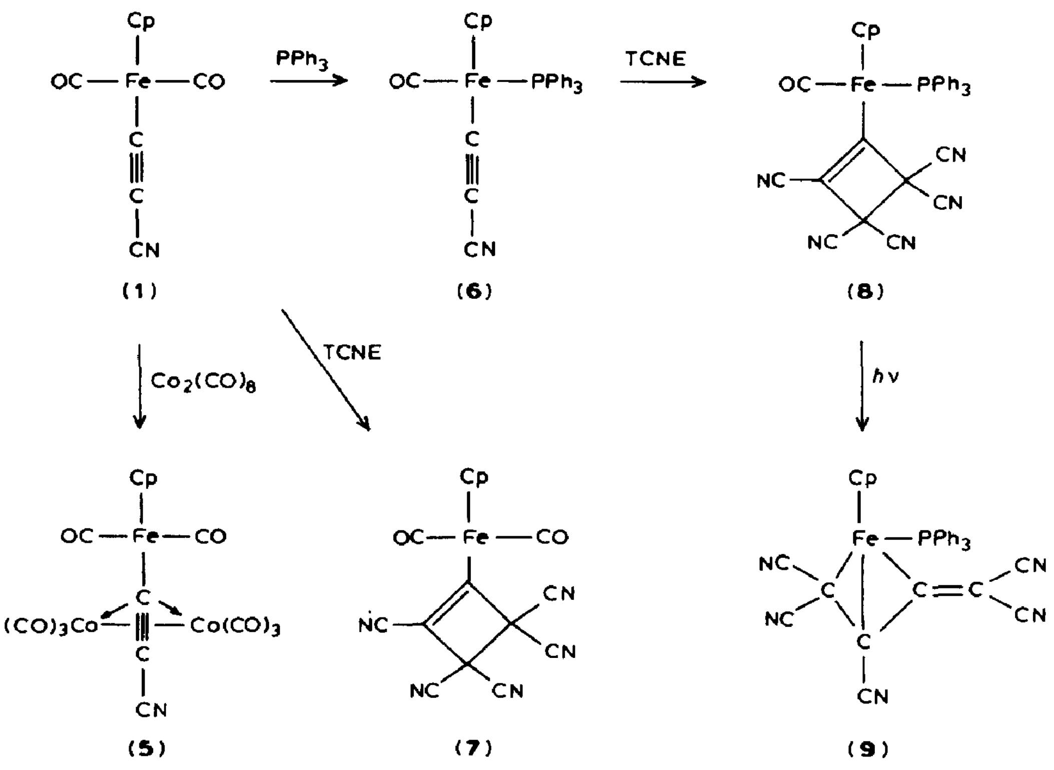
Co(1)-Co(2)	2.478(1)	Co(1)-C(1)-Co(2)	75.9(1)
Co(1)-C(1)	2.006(5)	Co(1)-C(2)-Co(2)	79.4(1)
Co(1)-C(2)	1.944(5)	Fe-C(1)-Co(1)	136.4(2)
Co(2)-C(1)	2.021(4)	Fe-C(1)-Co(2)	135.7(2)
Co(2)-C(2)	1.937(5)	Fe-C(1)-C(2)	143.3(3)
Co(1)-C(4)	1.820(6)	Co(1)-C(1)-C(2)	67.7(2)
Co(1)-C(5)	1.783(6)	Co(2)-C(1)-C(2)	66.9(2)
Co(1)-C(6)	1.813(6)	Co(1)-C(2)-C(1)	72.8(2)
Co(2)-C(7)	1.827(6)	Co(2)-C(2)-C(1)	73.7(2)
Co(2)-C(8)	1.798(6)	C(1)-C(2)-C(3)	138.9(5)
Co(2)-C(9)	1.795(6)	C(2)-C(3)-N	178.4(6)
C(4)-O(4)	1.121(7)	Co(1)-C(2)-C(3)	134.0(2)
C(5)-O(5)	1.130(7)	Co(2)-C(2)-C(3)	132.7(2)
C(6)-O(6)	1.121(7)	C(1)-Co(1)-C(2)	39.5(2)
C(7)-O(7)	1.122(7)	C(1)-Co(1)-Co(2)	52.3(1)
C(8)-O(8)	1.126(7)	C(2)-Co(1)-Co(2)	50.2(1)
C(9)-O(9)	1.121(7)	C(1)-Co(2)-C(2)	39.3(2)
C(1)-C(2)	1.335(7)	C(1)-Co(2)-Co(1)	51.8(1)
C(2)-C(3)	1.408(7)	C(2)-Co(2)-Co(1)	50.4(1)
C(3)-N	1.149(7)	C(1)-Fe-C(10)	87.6(3)
Fe-C(1)	1.954(5)	C(1)-Fe-C(11)	88.7(2)
Fe-C(10)	1.732(7)	C(10)-Fe-C(11)	93.5(3)
Fe-C(11)	1.773(6)		
C(10)-O(10)	1.161(8)		
C(11)-O(11)	1.122(7)		

carbon atom approaches sp^2 hybridization. The Fe–C(1)–C(2) angle is 143.3° in **5**. The Fe–C(1) distance is however, shorter than that, viz. 1.99(1) Å, in the phenyl analogue of **5** [25], and we think that this is due to the presence of the strongly electron-withdrawing C≡N group in **5**.

Infrared (see Experimental section) and NMR spectral data (Table 1) are consistent with this structure, and show that all the carbonyl ligands present in the molecule are in terminal positions. The coordination of the $Co_2(CO)_6$ entity at the C≡C bond gives rise to a lowering of the ν(C≡N) frequency from 2220 cm^{-1} in complex **1** to 2180 cm^{-1} in **5**, and corresponds to a decrease in the π-electron density of the CN group.

Triphenylphosphine is well known to react with alkynes. In the case of dicyanoacetylene for instance it forms a stable adduct, an alkylidene-1,6-diphosphorane [28]. In the case of **1** only the substituted $[Fe(C{\equiv}CCN)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ (**6**) was formed even upon photolysis (18 h), and none of the possible phosphorane product was detected [27a*]. An analogous substitution occurred in the reaction of PPh_3 with $[Mo(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_3]$ [29]. Attachment of PPh_3 to the iron atom in **6** was confirmed by the presence of one (^{31}P) peak at 72.9 ppm and of a doublet (^{13}C) for the carbonyl group (^2J(CP) 28.5 Hz). Decreases in the ν(C≡O) and ν(C≡C) frequencies are consistent with the presence of a π-back bonding between the iron atom and the carbonyl and acetylide ligands.

On the other hand, the C≡C triple bond of metal acetylide complexes is susceptible to attack by electrophiles [30], and cycloaddition to the C≡C bond in



Scheme 2.

such complexes have been described by several authors [31–34]. The yellow complexes **1** and **6** were thus treated with $(NC)_2C{\equiv}C(CN)_2$ (TCNE) in benzene, to give the green compounds $[Fe(C{=}C(CN)C(CN)_2C(CN)_2)(\eta^5\text{-}C_5H_5)(CO)_2]$ (**7**) and $[Fe(C{=}C(CN)C(CN)_2C(CN)_2)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ (**8**), respectively. The mass spectrum of **7** and microanalysis of **8** indicate that these compounds are 1/1 adducts of **1** and **6** with TCNE. Their infrared spectra showed no band assignable to a $\nu(C{\equiv}C)$ vibration, but a $\nu(C{=}C)$ one appeared at 1600 cm^{-1} for **7** and at 1590 cm^{-1} for **8**. The other characteristic bands are at 2220 cm^{-1} ($\nu(C{\equiv}N)$), 2015 and 2040 cm^{-1} ($\nu(C{\equiv}O)$) for **7**, and at 2220 cm^{-1} ($\nu(C{\equiv}N)$) and 1970 cm^{-1} ($\nu(C{\equiv}O)$) for **8**. Unfortunately because these complexes seem to react or decompose in all common solvents (an amorphous precipitate was formed after a few hours, more quickly in the case of the dicarbonyl compound) their (^{13}C) NMR spectra are not well resolved and, so are not very informative.

UV irradiation of **8** for 6 h in THF at room temperature results in the loss of the CO group, the colour of the solution changing from green to red-violet. Analytical, infrared and ^1H NMR data have been obtained for the product **9**. Decomposition of **9** occurred before the complete ^{13}C NMR spectrum could be accumulated, and only ^{13}C (CN), (C_6H_5) and ($\eta^5\text{-}C_5H_5$) resonances were detected (Table 1). However by analogy with information for tungsten and ruthenium complexes [33,34] it seems reasonable to suggest the following scheme for the reactions of acetylide **1** with TCNE (Scheme 2). It is noteworthy that no butadienyl intermediate, such as was proposed in ref. 33 and 34, was detected in our case.

We note finally that whereas the cyclic acylic complex $[W(C(O)C(CN)=CH(SCH_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ was transformed into the terminal one $[W(C(O)C(CN)=CH(SCH_3)(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)]$ in the presence of triphenylphosphine [5], there is no reaction between **2** and PPh_3, and moreover there is no enlargement of the cycle in **2** analogous to that observed for $[Fe(C(O)C(CF_3)=CH(SCH_3)(\eta^5\text{-}C_5H_5)(CO)]$ in the presence of alkyne [4].

Experimental

The reactions were performed under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and purged with nitrogen before use. $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ was prepared from commercial $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ and CH_3SSCH_3 [35]. Monocyanoacetylene was obtained in 70% yield by a published method from the corresponding amide $HC{\equiv}CCONH_2$ [36]. Commercial triphenylphosphine, tetracyanoethylene, and octacarbonyldicobalt were used.

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JNM-FX 100 spectrometer. Chemical shifts (δ values) are relative to internal TMS (^1H, ^{13}C) or external aqueous H_3PO_4 (^{31}P).

Infrared spectra of samples examined as Nujol mulls on CsI plates or CH_2Cl_2 solutions were recorded on a Perkin–Elmer 1430 spectrophotometer.

Mass spectra were recorded at 70 eV on a Varian MAT 8*M* spectrometer at the Faculté des Sciences of Rennes.

Microanalysis were performed at the Centre de Microanalyses of the CNRS.

Reaction of $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ with $(HC{\equiv}CCN)$

Freshly prepared monocyanoacetylene (~ 30 mmol) was condensed on to a THF solution of $[Fe(\eta^5\text{-}C_5H_5)(SCH_3)(CO)_2]$ (6.3 g, 28 mmol) frozen in liquid nitrogen. The mixture was stirred as the temperature was slowly (6 h) allowed to rise to room temperature, and then filtered. The solvent was evaporated, and the solid residue was dissolved in CH_2Cl_2 and chromatographed on a Florisil column. Elution with dichloromethane/hexane (2/1 in volume) gave the (*Z*) olefin $(NC)CH=CH(SCH_3)$ (**4**) as a red-orange liquid. Further bands were contaminated with the dimer $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, so the bands eluted with CH_2Cl_2 (containing the complex $[Fe(C{\equiv}C\text{-}CN)(\eta^5\text{-}C_5H_5)(CO)_2]$ (**1**)) and with 95/5 CH_2Cl_2/THF (containing the complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2C(CN)=C(SCH_3)Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ (**3**)) were rechromatographed separately to give **1** as a yellow powder and **3** as an orange solid.

Complex **1**. Analysis: Found: C, 53.6; H, 2.4; Fe, 24.0; N, 5.9. $C_{10}H_5FeNO_2$ calc.: C, 52.91; H, 2.22; Fe, 24.60; N, 6.17%. Infrared (cm^{-1}), Nujol suspension: 2220(s) ν (C≡N); 2010(s), 2025(sh), 2040(m) ν (C≡O); 2080(s) ν (C≡C).

Complex **3**. Analysis: Found: C, 48.5; H, 3.3; Fe, 23.5; N, 3.0. $C_{18}H_{13}Fe_2NO_4S$ calc.: C, 47.93; H, 2.91; Fe, 24.76; N, 3.11%. Infrared (cm^{-1}), CH_2Cl_2 solution: 2200(s) ν (C≡N); 1930(s), 1985(s), 2040(s) ν (C≡O); 1600(s) ν (C=C). *M* (*m/z* 451, calc. 451); other peaks at 423 $(M-CO)^+$ and 274 $[Fe(C(CN)=C(SCH_3)(\eta^5\text{-}C_5H_5)(CO)_2]^+$.

When a THF solution of monocyanoacetylene was added to the solution of thiolato iron at room temperature, in addition to the dimer $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ four other products were recovered after 6 h of stirring, namely complex **1**, complexes **3** and **4** in small amounts, and an additional acylic red product

$[\overline{\mathrm{FeC(O)C(CN){=}CH(S}}\mathrm{CH_3)(\eta^5\text{-}C_5H_5)(CO)]}$ (**2**) which was eluted with a (95/5) CH_2Cl_2/THF mixture.

Complex **2**. Analysis: Found: C, 47.6; H, 3.4; Fe, 20.1; N, 5.3. $C_{11}H_9FeNO_2S$ calc.: C, 48.02; H, 3.30; Fe, 20.3; N, 5.09%. Infrared (cm^{-1}), Nujol suspension: 2220(m) ν (C≡N); 1960(s) ν (C≡O); 1575(m) ν (C=C); 1590(m) ν (C=O). Monocrystals of **2** were obtained by slow evaporation of a benzene solution.

Formation of $[\mu\text{-}\eta^2Fe(C{\equiv}C\text{-}CN)(\eta^5\text{-}C_5H_5)(CO)_2][Co(CO)_3]_2$ *(5)*

A solution of equimolar amounts of **1** (0.8 g, 3.5 mmol) and $Co_2(CO)_8$ (1.2 g, 3.5 mmol) in 60 ml of THF was stirred for 6 days at room temperature. The solvent was evaporated off and the residual solid was redissolved in a minimum of CH_2Cl_2 and chromatographed (Florisil). Elution with CH_2Cl_2 gave the green complex **5** (yield 60–65%). Good single crystals were obtained by recrystallization from toluene.

Complex **5**. Analysis: Found: C, 37.8; H, 0.9; Co, 22.9; Fe, 10.9; N, 2.5. $C_{16}H_5Co_2FeNO_8$ calc.: C, 37.47; H, 0.98; Co, 22.98; Fe, 10.89; N, 2.73%. Infrared (cm^{-1}), CH_2Cl_2 solution: 2180(s) ν (C≡N); 2092(w), 2042(s), 2028(s), 1998(s) ν (C≡O).

Formation of $[Fe(C{\equiv}C\text{-}CN)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ *(6)*

A THF solution of $P(C_6H_5)_3$ (0.8 g, 3.0 mmol) was added to one of **1** (0.6 g, 2.6 mmol) in THF (50 ml). The mixture was irradiated for 17 h, filtered and the solvent then evaporated off. Elution from a Florisil column (CH_2Cl_2), followed by solvent evaporation, yielded complex **6** as a yellow powder (yield 65–70%).

Analysis: Found: C, 69.9; H, 4.5; Fe, 11.6; N, 3.1; P, 6.6. $C_{27}H_{20}FeNOP$ calc.: C, 70.30; H, 4.37; Fe, 12.11; N, 3.04; P, 6.71%. (^{31}P) NMR: δ 72.9ppm. Infrared, Nujol suspension: 2200(s) ν (C≡N); 1970(s) ν (C≡O); 2030(s) ν (C≡C).

Formation of 1/1 $[Fe(C{\equiv}C\text{-}CN)(\eta^5\text{-}C_5H_5)(CO)_2]/(NC)_2C{=}C(CN)_2$ *adduct:* $[\overline{Fe(C{=}C(CN)C(CN)_2C}(CN)_2(\eta^5\text{-}C_5H_5)(CO)_2]$ *(7)*

Equimolar amounts of complex **1** and TCNE were dissolved in toluene and the solution was stirred for 10 h, during which the colour changed from yellow to green. Elution from a Florisil column (CH_2Cl_2) yielded a green solid (yield 40%). *M* (*m/z* 355, calc. 355).

Formation of 1/1 $[Fe(C{\equiv}C\text{-}CN)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]/(NC)_2C{=}C(CN)_2$ *adduct:* $[\overline{Fe(C{=}C(CN)C(CN)_2C}(CN)_2(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ *(8)*

Reaction of equimolar amounts of **6** and TCNE in benzene for 15 h gave rise to a colour change from yellow to green. The solven was evaporated off and the residual solid was dissolved in CH_2Cl_2 and chromatographed on a Florisil column. Elution with CH_2Cl_2 yielded the complex **8** in 80–85% yield. Analysis: found: C, 66.5; H, 3.4; N, 11.6; P, 4.9. $C_{33}H_{20}FeN_5OP$ calc.: C, 67.25; H, 3.42; N, 11.18; P, 5.26%. ^{31}P NMR: δ 62.0 ppm. Infrared (cm^{-1}), Nujol suspension, 2220(m) ν (C≡N); 1970(s) ν (C≡O); 1590(w) ν (C=C).

Photolysis of 8: formation of $[\overline{Fe(\eta^3\text{-}C(CN)_2C(CN)C}{=}C(CN)_2)(\eta^5\text{-}C_5H_5)(PPh_3)]$ *(9)*

When a THF solution of the complex **8** (0.45 g, 0.76 mmol) was irradiated for 6 h at room temperature the colour changed from green to red-violet. The product **9** was eluted from a Florisil column (CH_2Cl_2/THF, 90/10) and was recrystallized from dichloromethane/hexane (yield 55–60%). Analysis: Found: C, 67.9; H, 3.5; Fe, 9.2; P, 5.3. $C_{32}H_{20}FeN_5P$ calc.: C, 68.47; H, 3.59; Fe, 9.95; P, 5.52%. Infrared (cm^{-1}), Nujol suspension: 2220(m) ν (C≡N), 1610(w) ν (C=C).

Formation of [Fe(η^5-C_5H_5)(CO)$_2$C(CN)=C(SCH$_3$)Fe(η^5-C_5H_5)(CO)(PPh$_3$)] (10)

A solution of 0.5 g (1.9 mmol) of PPh_3 in THF was added to a THF solution of **3** (0.5 g, 1.11 mmol). The stirred mixture was irradiated for 17 h, then the solvent was removed and the residual solid dissolved in CH_2Cl_2. Chromatography on a Florisil column (CH_2Cl_2/hexane 3/1) gave the red-orange complex **10** (yield 80–85%). Analysis: Found: C, 60.2; H, 4.0; Fe, 15.5; N, 2.0; P, 4.5; S, 4.5. $C_{35}H_{28}Fe_2NO_3PS$ calc.: C, 61.34; H, 4.12; Fe, 16.30; N, 2.04; P, 4.52; S, 4.68%. Infrared, Nujol suspension, 2200(m) ν (C≡N); 1930(s), 1960(s) ν (C≡O), 1615(w) ν (C=C). ^{31}P NMR: δ 71.4 ppm. Spectroscopic data are not sufficient to know on which iron atom PPh_3 is fixed.

X-Ray structure analysis of [$\overline{\text{FeC(O)C(CN)=CH(S}}CH_3$)($\eta^5$-$C_5H_5$)(CO)] (2) and [$\mu$-$\eta^2$-Fe(C≡C(CN)($\eta^5$-$C_5H_5$)(CO)$_2$][Co(CO)$_3$]$_2$ (5)

Crystals suitable for an X-ray analysis were grown from benzene (**2**) or toluene (**5**). They were mounted on an Enraf–Nonius CAD4 diffractometer for measure-

Table 4

Positional parameters and their estimated standard deviations for **2**

Atom	x	y	z	B (Å^2)
Fe	0.28347(8)	0.14949(4)	0.19960(9)	2.69(1)
S	0.4251(1)	0.08074(7)	0.0974(2)	3.03(3)
O1	−0.0876(4)	0.1350(2)	−0.0653(5)	4.6(1)
O2	0.3113(6)	0.2592(2)	−0.0239(6)	7.1(1)
N	0.8148(6)	0.0538(3)	0.4981(7)	5.0(1)
C1	0.0673(6)	0.1228(3)	−0.0275(6)	3.0(1)
C2	0.0949(6)	0.0818(3)	−0.1795(7)	3.1(1)
C3	−0.0606(6)	0.0659(3)	−0.3609(7)	3.5(1)
C4	0.2576(6)	0.0620(3)	−0.1411(6)	3.2(1)
C5	0.5912(6)	0.1178(3)	0.0382(8)	4.7(1)
C6	0.3022(7)	0.2156(3)	0.0672(7)	4.2(1)
C7	0.1764(7)	0.1150(3)	0.3828(7)	4.7(1)
C8	0.1682(7)	0.1822(3)	0.3732(7)	5.1(1)
C9	0.3485(9)	0.2054(3)	0.4523(8)	5.4(2)
C10	0.4614(7)	0.1512(4)	0.5055(7)	5.0(1)
C11	0.3544(8)	0.0962(3)	0.4607(7)	4.7(1)
H4	0.289(6)	0.038(2)	−0.235(6)	*
H51	0.6972	0.1312	0.1630	*
H52	0.6297	0.0854	−0.0340	*
H53	0.5385	0.1570	−0.0471	*
H7	0.0714	0.0848	0.3405	*
H8	0.0572	0.2095	0.3208	*
H9	0.3867	0.2521	0.4668	*
H10	0.5951	0.1520	0.5651	*
H11	0.3984	0.0500	0.4813	*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$\tfrac{4}{3}\left[a^2B_{1,1}+b^2B_{2,2}+c^2B_{3,3}+ab(\cos\gamma)\times B_{1,2}+ac(\cos\beta)\times B_{1,3}+bc(\cos\alpha)\times B_{2,3}\right].$$

Table 5

Positional parameters and their estimated standard deviations for **5**

Atom	x	y	z	B (Å^2)
Co1	0.12757(9)	0.48390(8)	0.80122(4)	2.91(1)
Co2	0.38190(8)	0.22860(8)	0.86258(4)	2.78(1)
Fe	0.31119(9)	0.20311(9)	0.64115(4)	3.09(2)
O4	0.0883(7)	0.6954(6)	0.9269(3)	7.5(1)
O5	−0.0225(7)	0.7549(6)	0.6465(3)	7.3(2)
O6	−0.1779(5)	0.3433(6)	0.8709(3)	6.1(1)
O7	0.4322(7)	0.3436(6)	1.0133(3)	7.4(1)
O8	0.1843(6)	−0.0152(6)	0.9617(4)	7.6(2)
O9	0.7405(6)	−0.0222(7)	0.8285(4)	7.3(2)
O10	0.2575(9)	0.5382(6)	0.5153(3)	8.7(2)
O11	0.7075(6)	0.1071(6)	0.6086(3)	6.5(1)
N	0.6197(7)	0.5724(6)	0.6789(4)	5.6(1)
C1	0.3117(6)	0.3120(5)	0.7350(3)	2.6(1)
C2	0.3866(6)	0.4125(6)	0.7538(3)	2.8(1)
C3	0.5141(7)	0.5011(6)	0.7115(3)	3.5(1)
C4	0.1041(8)	0.6154(7)	0.8786(4)	4.4(1)
C5	0.0331(8)	0.6492(7)	0.7069(4)	4.2(1)
C6	−0.0629(7)	0.3994(7)	0.8448(4)	3.9(1)
C7	0.4174(7)	0.3003(7)	0.9548(4)	4.2(1)
C8	0.2573(7)	0.0812(7)	0.9236(4)	4.0(1)
C9	0.6027(7)	0.0733(7)	0.8429(4)	4.1(1)
C10	0.2799(9)	0.4028(8)	0.5650(4)	5.0(2)
C11	0.5538(7)	0.1459(6)	0.6213(4)	3.8(1)
C12	0.0521(8)	0.1864(9)	0.6457(5)	6.3(2)
C13	0.1733(9)	0.1198(8)	0.5723(4)	6.2(2)
C14	0.3150(9)	−0.0179(7)	0.6086(4)	5.6(2)
C15	0.2836(8)	−0.0424(7)	0.7047(4)	5.0(1)
C16	0.1216(8)	0.0815(7)	0.7259(4)	5.3(1)
H12	−0.051(7)	0.284(6)	0.643(3)	*
H13	0.175(7)	0.163(6)	0.511(3)	*
H14	0.412(7)	−0.088(6)	0.576(3)	*
H15	0.368(7)	−0.129(6)	0.749(3)	*
H16	0.076(7)	0.092(6)	0.786(4)	*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$\tfrac{4}{3}\left[a^2B_{1,1}+b^2B_{2,2}+c^2B_{3,3}+ab(\cos\gamma)\times B_{1,2}+ac(\cos\beta)\times B_{1,3}+bc(\cos\alpha)\times B_{2,3}\right]$$

ments of the cell parameters (25 randomly selected reflections) and diffraction intensities in an ω–2θ scan (θ min 2°, θ max 28°). 1606 independent planes were recorded for **2** and 2611 ones for **5**.

Crystal data for **2**: $C_{11}H_9FeNO_2S$, FM 275.11. Monoclinic, a 8.372(1), b 20.462(3), c 7.582(1) Å, β 116.9(2)°, U 1158.4 Å^3, space group $P2_1/n$, $Z = 4$, D_c 1.577g cm^{-3}, μ (Mo-K_α) 14.55 cm^{-1}, λ (Mo-K_α) 0.71073 Å.

Crystal data for **5**: $C_{16}H_5Co_2FeNO_8$, FM 512.93. Triclinic, a 7.893(3), b 8.589(1), c 15.506(2) Å, α 72.47(1), β 76.99(2), λ 68.63(2)°, U 925.6 Å^3. Space group $P\bar{1}$, $Z = 2$, D_c 1.840 g cm^{-3}, μ (Mo-K_α) 25.85 cm^{-1}, λ (Mo-K_α) 0.71073 Å.

Both structures were solved and refined by conventional three dimensional Patterson, difference Fourier and full-matrix least squares methods. Reflections with

$I > 3\sigma(I)$ (1149 for **2** and 2247 for **5**, for 173 and 269 variables for **2** and **5**, respectively) were used in calculations carried out with the Enraf–Nonius SDP package [37]. Neutral atom scattering factors and anòmalous dispersion corrections used for all non-hydrogen atoms were those given by Cromer and Waber [38]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms in both structures were calculated by the "Hydro" program of SDP with B_{iso} fixed at 5.0 Å^2. The final residuals were: **2**, $R = 0.036$, $R_w = 0.044$, GOF = 1.077; **5**, $R = 0.034$, $R_w = 0.048$, GOF = 1.047. The weighting scheme employed was $w^{-1} = \sigma^2(F) = 1/4[\sigma(I)/I + 0.06^2(I)]$. The final atomic coordinates are listed in Table 4 and 5. Lists of thermal parameters and structure factors are available from the authors.

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