Transition Metal–Cyanocarbon Chemistry. Part 8.[1] Cyano-substituted Buta-1,3-dienylidene Bridged Di-iron Complexes from Unprecedented Cyanoalkyne Insertion into the Carbon–Hydrogen Bond of a Bridging Alkenylidene Ligand

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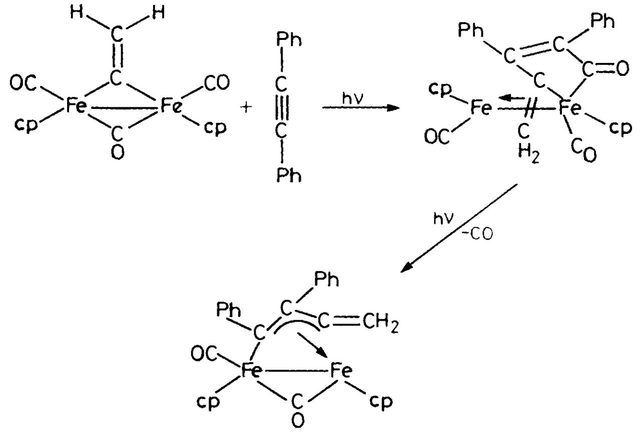
The reactions of [{Fe(cp)(CO)}$_2$(μ-CO)(μ-C=CHR)] [cp = η^5-C$_5$H$_5$; R = H(**1**), CH(CH$_3$)$_2$ (**3**), or CH$_3$ (**4**)] with monocyanoethyne H–C≡C–CN at 340 K lead to the substituted μ-4-cyanobuta-1,3-dienylidene complexes [{Fe(cp)(CO)}$_2$(μ-CO){μ-C=CR–CH=C(CN)H}] [R = H (**2**), CH(CH$_3$)$_2$ (**5**), or CH$_3$ (**6**)] *via* an unprecedented formal insertion of the alkyne into a vinylic carbon–hydrogen bond. The reactions are regio- but not stereo-selective: the nitrile is attached to the C_δ carbon and both *Z* and *E* isomers (with respect to the C_γ=C_δ double bond) are formed. Complex (**1**) reacts at 210 K with dicyanoethyne NC–C≡C–CN to yield the μ-3,4-dicyanobuta-1,3-dienylidene complex [{Fe(cp)(CO)}$_2$(μ-CO){μ-C=CH–C(CN)=C(CN)H}] (**7**) similarly, with *Z* and *E* isomers again being formed. Reaction of (**2**-*Z*) with Ph$_2$PCH$_2$PPh$_2$ (dppm) in refluxing toluene gives the triply bridged complex [{Fe(cp)}$_2$(μ-CO){μ-C=CH–CH=C(CN)H}(μ-dppm)] (**8**) in both *Z* and *E* forms. A possible mechanism of the insertion reaction is discussed.

The reactivity of molecules containing hydrocarbon fragments bridging two or more metal centres is a subject of great significance as a result of the interest in the Fischer–Tropsch synthesis and related reactions.[2] In this connection, the reactions between alkylidene-bridged bimetallic complexes and alkynes have been widely explored: in most cases insertion of the alkyne into a metal–carbon bond of the bridging ligand is observed.[3] This insertion may be accompanied by rearrangements occurring in the bridge, such as hydrogen migration or carbonyl incorporation.[4] In some cases more than one molecule of alkyne reacts, leading to oligomerization and polymerization.[5,6]

In contrast to alkylidene complexes, the reactivity of related alkenylidene (vinylidene) complexes has been little studied.[7,8] However, this reactivity is of special importance since ethenylidene C=CH$_2$ is an isomer of ethyne H–C≡C–H and its generation from ethyne has been observed both on metal surfaces[9] and in transition-metal complexes.[7,10] To the best of our knowledge, in the case of dimetal centres, the photochemical reaction of the μ-ethenylidene di-iron complex[11] [{Fe(cp)(CO)}$_2$(μ-CO)(μ-C=CH$_2$)] (**1**) (cp = η^5-C$_5$H$_5$) with alkynes such as 2-butyne or diphenylethyne represents a unique study.[12] A metallacyclopentenone unit was formed by linking of the alkyne and a carbonyl group, further rearrangement leading to a bridging σ, π unit as shown; the details of the mechanism are unknown.



We report here the thermal behaviour of several bridging alkenylidene di-iron complexes towards activated alkynes such as monocyanoethyne (mca) and dicyanoethyne (dca). Striking differences are observed between the previously observed photochemical activation[12a] and the thermal reaction described here, which leads, without precedent, to cyano-substituted bridging buta-1,3-dienylidene complexes. A preliminary account of part of this work has appeared.[13]

Results and Discussion

The reaction of the μ-ethenylidene complex [{Fe(cp)(CO)}$_2$(μ-CO)(μ-C=CH$_2$)] (**1**) with monocyanoethyne (mca) in toluene occurs quite slowly at ambient temperature. Photochemical and thermal activation was examined. While u.v. irradiation gave large quantities of intractable dark materials, heating the reaction mixture at 340 K overnight (*ca.* 15 h) led to the formation of the μ-4-cyanobuta-1,3-dienylidene di-iron complex [{Fe(cp)(CO)}$_2$(μ-CO){μ-C=CH–CH=C(CN)H}] (**2**) in 65% yield. Small amounts of starting material (**1**) were recovered and separated by column chromatography. The crude chromatographic mixture of (**2**) consists of two isomers (1.4/1 ratio) which can be identified readily by ^{1}H n.m.r. spectroscopy as *E* and *Z* isomers, with respect to the C_γ=C_δ double bond of the bridging ligand. These two isomers were separated by crystallization. The *Z* isomer (**2**-*Z*) was obtained as pure crystals, and the cisoid nature of the bridging butadienylidene ligand ascertained by the magnitude of the $^3J(H_\gamma–H_\delta)$ coupling constant, which is 10.5 Hz. For the *E* isomer (**2**-*E*), $^3J(H_\gamma–H_\delta)$ is 15.6 Hz (see Table 1). The AMX system for the hydrogens in the ^{1}H n.m.r. spectrum, together with the observation in the ^{13}C n.m.r. spectrum (see Table 2) of a bridging carbon resonance at δ 304 p.p.m., establishes unequivocally the nature of (**2**-*Z*). It is noteworthy that this isomer also has a *cis* configuration for the cyclopentadienyl ligands about the Fe–Fe bond as evidenced by the

Table 1. Proton n.m.r. data of new μ-buta-1,3-dienylidene di-iron complexes[a]

Compound	H_β	H_γ	H_δ	C_5H_5	Others
(**2**–*Z*)	8.50	7.39	4.78	5.13	—
	(dd, *J* = 11.1, 0.8)	(dd, *J* = 11.1, 10.5)	(dd, *J* = 10.5, 0.8)	5.11	
(**2**–*E*)	8.31	7.50	*b*	5.16	—
	(d, *J* = 10.8)	(dd, *J* = 10.8, 15.6)		5.07	
(**5**–*Z*)	—	7.54	5.03[c]	5.15	$CH(CH_3)_2$
		(dd, *J* = 13.0, 0.9)	(d, *J* = 13.0)	5.09	CH 3.88 (m)
					CH_3 1.71 (d, *J* = 7.5)
					1.35 (d, *J* = 7.3)
(**5**–*E*)	—	7.65	5.25	5.14[d]	$CH(CH_3)_2$
		(dd, *J* = 17.1, 1.4)	(d, *J* = 17.1)		CH 3.88 (m, *J* 7.4, 1.4)
					CH_3 1.61 (d, *J* = 7.5)
					1.30 (d, *J* = 7.3)
(**6**–*Z*)	—	7.52	4.81	5.16[e]	CH_3 2.93
		(d, *J* = 12.0)	(d, *J* = 12.0)		
(**6**–*E*)	—	7.76	5.01[e]	5.19[e]	CH_3 2.58
		(d, *J* = 16.0)		5.18	
(**7**–*Z*)	8.62	—	5.69	5.20	—
	(d, *J* = 0.4)		(d, *J* = 0.4)	5.17	
(**7**–*E*)	8.54	—	5.85	5.20	—
	(d, *J* = 0.4)		(d, *J* = 0.4)	5.14	
(**8**–*Z*)[f]	8.75	6.70	4.11	4.53	CH_2
				4.42	H_{eq} 2.22 [m, *J*(H–H) = 14.3]
	[dpt, *J*(P–H) *ca.* 3, *J*(H–H) = 11.7]	(dd, *J* = 10.2, 11.7)	(d, *J* = 10.2)	[d, *J*(P–H) *ca.* 1]	H_{ax} 1.64 [m, *J*(H–H) = 14.3]
(**8**–*E*)[f]	8.41	6.76	*c*	4.54	CH_2
				4.43	H_{eq} 2.20 [m, *J*(H–H) = 14.5]
	[dpt, *J*(P–H) *ca.* 3, *J*(H–H) = 11.4]	(dd, *J* = 11.4, 15.3)		[d, *J*(P–H) *ca.* 1]	H_{ax} 1.55 [m, *J*(H–H) = 14.5]

[a] Solvent $(CD_3)_2CO$, δ, *J* in Hz is $J(^1H-^1H)$ unless otherwise stated. [b] Obscured by C_5H_5; in C_6D_6 δ 4.83 (d, *J* = 15.4), see ref. 13. [c] Obscured or partly obscured by C_5H_5. [d] Two peaks separated by 0.4 Hz. [e] Partly obscured by C_5H_5 impurities. [f] $^{31}P-\{^1H\}$ [δ relative to external H_3PO_4, toluene–$(CD_3)_2CO$]: 89.7 (d, *J* = 81), 88.5 (s), and 86.8 (d, *J* = 81 Hz).

Table 2. ^{13}C N.m.r. data for new μ-buta-1,3-dienylidene di-iron complexes[a]

Compound	C_α	C_β	C_γ	C_δ	μ-CO	CO	C_5H_5	CN	Others
(**2**–*Z*)	303.3	150.4	140.8	*b*	266.0	208.8	87.7	*b*	—
						208.4	87.0		
(**2**–*Z*)[c]	304.6	151.4	141.7	83.9	266.8	210.6	88.9	118.8	—
						210.2	82.2		
(**5**–*E*)	300.2	153.1	154.1	*b*	266.4	208.8	87.3	*b*	CH 40.0
							87.1		CH_3 21.2, 19.6
(**7**–*Z*)	307.7	136.4	128.5	93.4	263.4	208.0	88.0	116.8	—
						207.7	87.9	115.2	
(**8**–*Z*)[d]	329.8	152.0	141.6	72.6	290.5	—	87.3 [d, *J*(P–C) *ca.* 4]	*b*	CH_2 24.6
+									
(**8**–*E*)	[pt, *J*(P–C) = 20]	150.6	141.4		[pt, *J*(P–C) *ca.* 15]		86.3 [d, *J*(P–C) *ca.* 4]		[t, *J*(P–C) = 25]

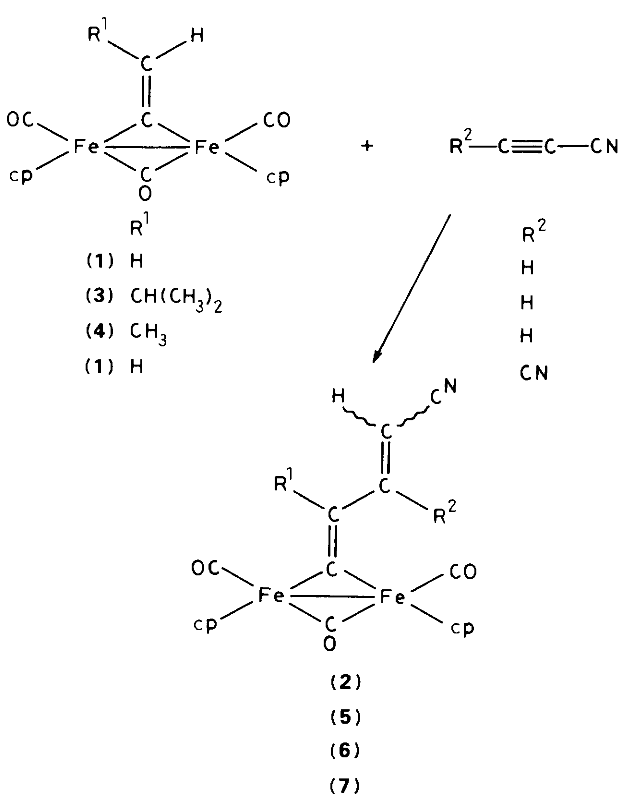
[a] Solvent $CDCl_3$ containing 0.075 mol dm^{-3} $[Cr(acac)_3]$ (acac = acetylacetonate), δ in p.p.m., *J* in Hz. [b] Not observed. [c] In CD_2Cl_2 containing 0.075 mol dm^{-3} $[Cr(acac)_3]$. [d] Without $[Cr(acac)_3]$; phenyl resonances not quoted.

observation[11b] of three i.r. carbonyl bands at 1 998s, 1 960w–m, and 1 806m–s cm^{-1}. Similar behaviour has been observed[14] for the related μ-pentadienylidene complex $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)(\mu\text{-}C{=}CH{-}CH{=}CHCH_3]$. No new n.m.r. signals were observed when a variable-temperature (193—371 K, $[^2H_8]$toluene) experiment was carried out on pure (**2**–*Z*), indicating no easy *cis–trans* isomerization about the Fe–Fe bond. The nitrile is identified by its characteristic i.r. stretching absorption at 2 200 cm^{-1}, enhanced because of conjugation. We have recently reported[15] the formation of a related μ-3,4,4-tricyanobuta-1,3-dienylidene di-iron complex $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}C{=}CH{-}C(CN){=}C(CN)_2\}]$ from the reaction of (**1**) with tetracyanoethylene (tcne). Its *X*-ray structure has been determined, and comparison of its spectroscopic data with those of the compounds reported here further supports their proposed structure.

We also found that the isopropyl- and methyl-substituted μ-alkenylidene di-iron complexes[16] $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)(\mu\text{-}C{=}CHR)]$ [R = $CH(CH_3)_2$ (**3**) or CH_3 (**4**)] react with mca in a similar manner, but the yields and rates of the reactions are lower than those of (**1**) (see Experimental section). The new complexes (**5**) and (**6**), isolated after chromatography as above, were found to be 1:1 adducts between mca and (**3**) or (**4**) respectively, on the basis of analytical data. Their μ-buta-1,3-dienylidene nature was deduced from spectroscopic data and comparison with (**2**).

The i.r. spectrum of $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}C{=}CCH(CH_3)_2{-}CH{=}C(CN)H\}]$ (**5**) shows a nitrile band at 2 190m cm^{-1} and three carbonyl bands at 1 995vs, 1 960m, and 1 793s cm^{-1}. As in the case of (**2**), two isomers are observed and separated by crystallization. A typical *E* isomer (**5**–*E*) is characterized by its ^1H n.m.r. spectrum (see Table 1), which shows two vinylic hydrogen resonances for H_γ and H_δ with a coupling constant of 17.1 Hz. The μ-alkenylidene nature of (**5**–*E*) was ascertained by the observation of a deshielded ^{13}C resonance at δ 300 p.p.m. (see Table 2). The ^1H n.m.r. spectrum of the *Z* isomer (**5**–*Z*) displays doublet splittings of 13.0 Hz (see Table 1).

The i.r. spectrum of the new complex (**6**), derived from the



methyl-substituted μ-alkenylidene (**4**), exhibits the usual nitrile and carbonyl features, and the ^{1}H n.m.r. spectrum establishes the presence of vinylic hydrogens, confirming the μ-4-cyanobuta-1,3-dienylidene di-iron nature, [{Fe(cp)(CO)}$_2$(μ-CO){μ-C=CCH$_3$–CH=C(CN)H}]. Again, a mixture of two isomers (not separated) can be characterized as (**6**–*Z*) and (**6**–*E*) with, respectively, $^3J(H_\gamma-H_\delta)$ of 12.0 and 16.0 Hz (see Table 1).

The new μ-4-cyanobuta-1,3-dienylidene complexes (**2**), (**5**), and (**6**) formally result from the insertion of an alkyne into a vinylic carbon–hydrogen bond. This contrasts sharply with the results previously obtained upon irradiation of (**1**) and 2-butyne or diphenylethyne,[12a] when the more frequently encountered insertion into a metal–carbon bond was observed. The nitrile group of (**2**), (**5**), and (**6**) is always attached to the δ carbon of the new buta-1,3-dienylidene ligand. This regioselectivity is suggested to result from the creation of a carbon–carbon bond between the electron-rich β-carbon of a μ-alkenylidene ligand[7,17] and the electron-poor protonated carbon of the activated alkyne mca.

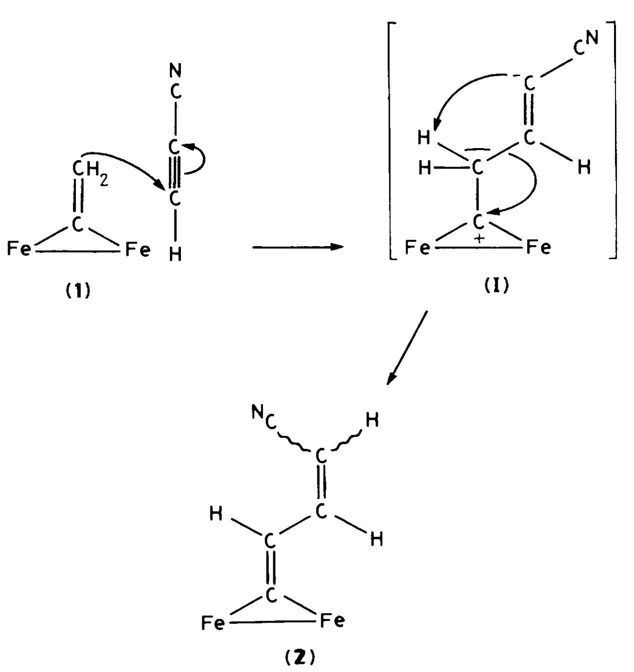
Whereas the reaction between the μ-ethenylidene complex (**1**) and mca was slow at ambient temperature, that with dicyanoethyne (dca) readily occurred at 210 K. A deep red-violet colour developed as soon as (**1**) and dca were mixed in dichloromethane at 210 K. The reaction mixture was maintained in the dark at low temperature for 1 h. Products were then separated by column chromatography in the dark. In addition to a small amount of starting material (**1**), an orange band was eluted which yielded bright orange-red crystals upon recrystallization. These were found to be a 1:1 adduct of (**1**) and dca. The i.r. spectrum of this new complex (**7**) shows nitrile bands at 2 225w and 2 200m cm^{-1} and carbonyl bands at 2 000vs, 1 973m, and 1 810s cm^{-1}. Intense absorption at 1 525 cm^{-1} indicates the presence of double carbon–carbon bonds, presumably enhanced because of conjugation. The ^{1}H n.m.r. spectrum is quite simple, showing two finely split doublets at δ 8.62 and 5.69 for vinylic hydrogens, with a coupling constant of 0.4 Hz. The ^{13}C n.m.r. spectrum (see Table 2) establishes the μ-buta-1,3-dienylidene nature of the complex (**7**); the resonance of the bridgehead carbon of the ligand is found at δ 308 p.p.m. and moving away stepwise from the bridgehead gives carbon resonances at δ 136.4, 128.5, and 93.4 p.p.m. The resonance at δ 136.4 and 93.4 p.p.m. disappear upon low-noise decoupling, indicating the location of the vinylic hydrogens.

This new μ-3,4-dicyanobuta-1,3-dienylidene di-iron complex [{Fe(cp)(CO)}$_2$(μ-CO){μ-C=CH–C(CN)=C(CN)H}] (**7**) also results from the insertion of a highly activated alkyne, dca, into a vinylic carbon–hydrogen bond. As in the mca case, the reaction is not stereoselective and another isomer can be identified by ^{1}H n.m.r. spectroscopy (see Table 1). The main difference between the reactions of the two alkynes mca and dca is the very rapid reaction of dca compared with that of mca. The observation of highly coloured species even at low temperature led us to suspect the generation of radicals at the early stage of the reaction. This is indeed the case; when a frozen solution of the reaction mixture was analysed by e.s.r. spectroscopy (*X*-band frequency) at 140 K a strong single signal was observed with $g = 2.004 \pm 0.001$ and $\Delta H_{pp} = 9.5$ G (9.5×10^{-4} T). No fine structure was apparent and neither were there any signs of a triplet state arising from a biradical. Raising the temperature caused the signal to decay rapidly in such a way that a spectrum at ambient temperature could hardly be recorded ($g = 2.005 \pm 0.001$), indicating fast reaction (or decomposition) of the radical. The observed signal is so transient that it cannot be attributed to polymeric dicyanoethyne.[18]

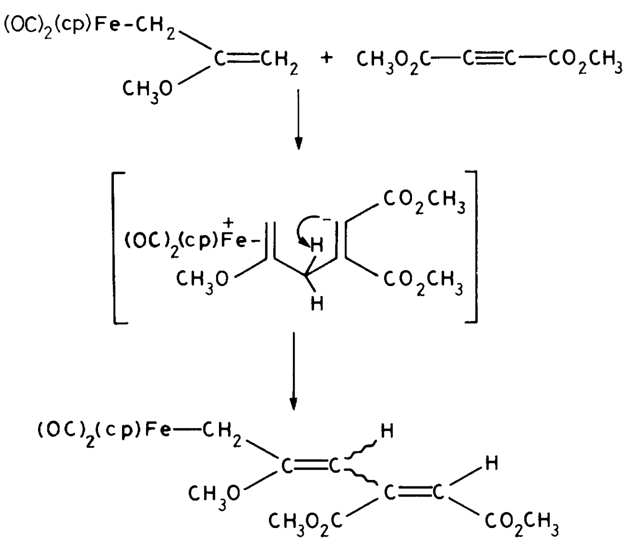
Refluxing the pure isomer (**2**–*Z*) with bis(diphenylphosphino)methane $PPh_2CH_2PPh_2$ (dppm) in toluene for 48 h leads to carbonyl substitution and isolation of the green triply bridged di-iron complex [{Fe(cp)}$_2$(μ-CO){μ-C=CH–CH=C-(CN)H}(μ-dppm)] (**8**). The i.r. spectrum displays a bridging carbonyl band at 1 725m–br cm^{-1} with a shoulder at 1 710 cm^{-1} and a nitrile stretching absorption at 2 175m cm^{-1}. The ^{31}P n.m.r. spectrum shows two signals: a singlet at δ 88.5 p.p.m. and an AB type system whose doublets are centred at 89.7 and 86.8 p.p.m. with ^2J(P–P) = 81 Hz. This indicates that two closely related isomers coexist, the two terminal carbonyl ligands being replaced by the diphosphine. The ^{1}H n.m.r. spectrum has been fully assigned by means of hetero-(^{31}P broad-band) and homo-(selective irradiation) decoupling experiments at 250 MHz. The results are compiled in Table 1. The main conclusion is that the substitution of the two terminal carbonyl groups by dppm is accompanied by isomerization of the $C_\gamma=C_\delta$ double bond of the buta-1,3-dienylidene ligand. The ratio (**8**–*Z*)/(**8**–*E*) is *ca.* 1.5:1, the same as for (**2**–*Z*)/(**2**–*E*) observed previously. We believe that the observed isomerization is the result of prolonged heating.

Mechanism of the Reactions.—We have previously proposed[13] that the 'insertion' reaction of mca could proceed *via* an intermediate such as (**I**) (see Scheme 1), the subsequent [1,3] migration of a proton leading to complex (**2**). This type of mechanism, based on nucleophilic attack by the β-carbon of the μ-ethenylidene complex (**1**), is quite natural since it is well known that this carbon is electron rich and is the site of protonation of several μ-alkenylidene complexes.[7,11b,17]

The reaction of the deuteriated analogue[19] of (**1**) [{Fe(cp)-(CO)}$_2$(μ-CO)(μ-C=CD$_2$)] ([$^2H_2$]**1**) with mca was carried out. If the above mechanism is correct we would expect to observe the formation of [{Fe(cp)(CO)}$_2$(μ-CO){μ-C=CD–CH=C(CN)-D}] ([$^2H_2$]**2**), with the β and δ positions occupied by deuterium instead of hydrogen as in (**2**). Unfortunately, we observed (^{1}H n.m.r.) H/D scrambling over the three vinylic sites of the bridging ligand. Whatever the mechanism of this exchange



Scheme 1.



Scheme 2.

process, we cannot conclude whether or not the proposed mechanism is correct. However, simple experimental considerations provide support for it: (*i*) the low yields for the isopropyl-(**5**) and methyl-(**6**) substituted butadienylidene complexes are most probably related to steric congestion at the β site of the starting μ-alkenylidene complexes (**3**) and (**4**), and (*ii*) the more electrophilic the alkyne, the faster is the reaction (dca *versus* mca). Moreover, such a rearrangement, *i.e.* the [1,3] shift of a proton in a zwitterionic intermediate, has been observed in mononuclear organometallic chemistry; the monoiron σ-allyl complexes $[Fe(cp)(CO)_2(\sigma\text{-}CH_2\text{–}CR\text{=}CH_2)]$ react[20] with dimethyl acetylenedicarboxylate $CH_3O_2C\text{–}C\equiv C\text{–}CO_2CH_3$ to afford different types of products depending on the nature of R (see Scheme 2). When the intermediate is stabilized by an electron-donating methoxy group ($R = OCH_3$), the complex resulting from the [1,3] proton shift is the major product of the reaction.[20b] In our case, the positive charge is stabilized by the electron-rich Fe(cp)(CO) moieties and the negative charge by the nitrile group. The alternative ring closure in intermediate (**I**) is highly improbable due to both severe steric hindrance and probable low stability of the resulting bridging cyclobutenylidene complex.

The formation of *Z* and *E* isomers cannot be attributed as a direct consequence of the [1,3] proton shift since the dppm experiment indicates that prolonged heating [which is common to the formation of (**2**), (**5**), (**6**), and (**8**)] results in such an isomerization. Although a unified base-catalysed isomerization [dppm for (**8**) and column chromatography for the mca and dca reactions] cannot be rejected, it must be kept in mind that complex (**7**) is synthesized at temperatures far below that required for *E*/*Z* isomerization and, as suggested by the e.s.r. experiment, a radical process could be involved. Cyanoalkynes have low-lying π^* orbitals and can act as electron acceptors; we have shown recently[15] that such a process could be involved in the reaction of tcne with complex (**1**). The initial formation of a radical does not, however, rule out the overall scheme of the mechanism.

In conclusion, we note that the reactivity of the μ-alkenylidene di-iron complexes is governed by the bridging alkenylidene ligand, *i.e.* the complexes behave like 1,1-dimetallated electron-rich olefins. This is in agreement with a recent theoretical analysis[17] which shows that the μ-ethylidene ligand is energetically and spatially exposed. Moreover, any reaction involving the π orbital of the ethenylidene will hardly affect the stability of the complex. Thus, the μ-ethenylidene complex (**1**) reacts with diazoalkanes[21] to give μ-cyclopropylidene complexes which readily rearrange to μ-allene complexes upon photolysis.[22] The former reaction involves the olefin-like behaviour of (**1**), and the latter is organometallic in character. We propose that the novel reaction described in this paper, leading to an overall insertion of a cyanoalkyne into a vinylic carbon–hydrogen bond of μ-alkenylidene di-iron complexes, is the result of such co-operative effects.

Experimental

Reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over an appropriate agent and degassed before use: toluene and thf over sodium–benzophenone; diethyl ether over sodium–benzophenone then $LiAlH_4$; CH_2Cl_2, hexane, and pentane over CaH_2. Light petroleum (b.p. 100—110 °C) was dried over molecular sieves. Chromatography was on silica gel columns except where indicated. Deuteriated solvents for n.m.r. spectroscopy were dried over molecular sieves and degassed before use.

Infrared spectra were run on a Perkin-Elmer 1 430 spectrophotometer, n.m.r. spectra on a JEOL FX 100 spectrometer operating at 99.60 MHz for ^1H, 40.32 MHz for ^{31}P, and 25.05 MHz for ^{13}C, except for compound (**8**) for which the ^1H spectrum was obtained on a Bruker WM250 instrument. E.s.r. spectra were recorded on a JEOL ME3X spectrometer. Analytical data were obtained from the Service Central de Microanalyse du CNRS, Villeurbanne.

The complexes $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)(\mu\text{-}C\text{=}CH_2)]$ (**1**),[11b] $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)(\mu\text{-}C\text{=}CD_2)]$ ([$^2H_2$]**1**),[18] and $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)(\mu\text{-}C\text{=}CHCH_3)]$ (**4**)[16] were prepared according to published procedures. The synthesis of $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}C\text{=}CH\text{–}CH(CH_3)_2\}]$ (**3**) was derived from published procedures for related complexes,[14] and involved treatment of $[\{Fe(cp)(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}C\text{–}CH\text{=}C(CH_3)_2\}]BF_4$[23] with $Li(BEt_3H)$ followed by salt elimination on a short alumina column (yield 95%). Mono- and di-cyanoethyne were prepared by dehydration of the corresponding amides[24] and condensed in a liquid-nitrogen-cooled tube under vacuum; *ca.* 2—4 fold excesses of the cyanoalkyne *vs.* the metal complexes were used.

$[\{\mathrm{Fe(cp)(CO)}\}_2(\mu\text{-CO})\{\mu\text{-C=CH-CH=C(CN)H}\}]$ (**2**).—In a glass tube fitted with a Teflon stopcock, a mixture of complex (**1**) (0.700 g, 2 mmol) and mca in toluene was heated at 340 K in the dark under a slight vacuum for 16 h. The solution turned from red to dark red-purple. It was then filtered through a Celite pad and evaporated to dryness before chromatography. Elution with CH_2Cl_2–hexane (1:1, v/v) gave unreacted (**1**). Further elution with CH_2Cl_2 gave a red-purple band. The solvent was evaporated and precipitation from CH_2Cl_2–hexane gave complex (**2**) (0.520 g, 1.3 mmol, 65%). Recrystallization from thf-light petroleum (b.p. 100—110 °C) gave pure (**2**–*Z*) which was washed with pentane and dried under vacuum (Found: C, 53.9; H, 3.4; Fe 27.7; N, 3.5. $C_{18}H_{13}Fe_2NO_3$ requires C, 53.6; H, 3.2; Fe, 27.7; N, 3.5%). I.r.(CH_2Cl_2) ν(CN) 2 200m; ν(CO) 1 995s, 1 960m, and 1 806s; ν(C=C) 1 565m and 1 535w cm^{-1}.

$[\{\mathrm{Fe(cp)(CO)}\}_2(\mu\text{-CO})\{\mu\text{-C=CCH(CH}_3)_2\text{-CH=C(CN)H}\}]$ (**5**).—Complex (**3**) (0.394 g, 1 mmol) and mca were mixed in toluene, as for the synthesis of (**2**), but heating was prolonged for 40 h. Chromatography yielded unreacted (**3**), eluted with CH_2Cl_2–hexane (1:1) (0.120 g, 30%). Elution with CH_2Cl_2 gave a red-purple band from which complex (**5**) was obtained as a purple solid after precipitation from CH_2Cl_2–hexane (0.087 g, 20%). In separate experiments (**5**–*Z*) and (**5**–*E*) were separated *via* careful recrystallization from CH_2Cl_2–hexane mixtures (Found: C, 56.1; H, 4.3; N, 3.15. $C_{21}H_{19}Fe_2NO_3$ requires C, 56.7; H, 4.3; N, 3.15%). I.r.(CH_2Cl_2) ν(CN) 2 190m; ν(CO) 1 995vs, 1 960m, and 1 793s cm^{-1}.

$[\{\mathrm{Fe(cp)(CO)}\}_2(\mu\text{-CO})\{\mu\text{-C=CCH}_3\text{-CH=C(CN)H}\}]$ (**6**).—Reaction and work-up were exactly as for complex (**5**). Starting with complex (**4**) (0.700 g, 1.9 mmol) led to 23% recovery and to 0.161 g of the new complex (**6**) (0.4 mmol, 21%), after reprecipitation from large amounts of CH_2Cl_2-hexane mixtures in order to avoid the formation of oils (Found: C, 55.0; H, 3.7; N, 3.3. $C_{19}H_{15}Fe_2NO_3$ requires C, 54.7, H, 3.6; N, 3.4%). I.r.(CH_2Cl_2): ν(CN) 2 195m-w; ν(CO) 1 998vs, 1 962m-w, and 1 800s; ν(C=C) 1 530w-br cm^{-1}.

$[\{\mathrm{Fe(cp)(CO)}\}_2(\mu\text{-CO})\{\mu\text{-C=CH-C(CN)=C(CN)H}\}]$ (**7**).—A solution of dca in CH_2Cl_2 (*ca.* 15 cm^3) was added to a solution of complex (**1**) (0.700 g, 2 mmol) in CH_2Cl_2 (20 cm^3) at 190 K (ethanol, liquid nitrogen) in a vessel protected from light. As the temperature rose slowly to 210 K, the colour of the solution turned from red to dark red-violet. Stirring was maintained at 210 K for 10 min, then over 60 min the temperature was allowed to reach 273 K. The solvent was evaporated and chromatography performed in the dark. Unreacted (**1**) (0.190 g, 27%) was eluted with CH_2Cl_2–hexane (1:1) and elution with CH_2Cl_2–hexane (1:1) yielded an orange band. Evaporation of the solvent gave an orange powder which was recrystallized from CH_2Cl_2–hexane mixtures to yield crystals of (**7**) (0.308 g, 0.72 mmol, 36%). Solutions of (**7**) exposed to laboratory light decomposed readily to leave black residues and complex mixtures of unidentified products (Found: C, 53.1; H, 2.8; N, 6.40. $C_{19}H_{12}Fe_2N_2O_3$ requires C, 53.3; H, 2.8; N, 6.55%). I.r.(CH_2Cl_2): ν(CN) 2 225w and 2 200m; ν(CO) 2 000vs, 1 973m, and 1 810s; ν(C=C) 1 525s cm^{-1}.

$[\{\mathrm{Fe(cp)}\}_2(\mu\text{-CO})\{\mu\text{-C=CH-CH=C(CN)H}\}(\mu\text{-dppm})]$ (**8**).—Pure complex (**2**—*Z*) (0.400 g, 1 mmol) was refluxed with dppm (0.410 g, 1.1 mmol) in toluene (50 cm^3) for 72 h, during which time the initial red solution slowly turned to brown-red then to green. The solution was filtered through Celite and concentrated. Hexane was added to precipitate a green powder, which was further purified by recrystallization from CH_2Cl_2–hexane. Microcrystals of (**8**) were washed with pentane and dried under vacuum (0.490 g, 67%) (Found: C, 67.1; H, 4.7; N, 1.8. $C_{41}H_{35}Fe_2NOP_2$ requires C, 67.3; H, 4.8; N, 1.9%). I.r.(CH_2Cl_2): ν(CN) 2 175m; ν(CO) 1 725m–br and 1 710 (sh) cm^{-1}.

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