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TRANSITION METAL COMPLEXES OF AZO COMPOUNDS

VI*. CYCLOADDITION OF ALKYNES TO THE COMPLEXED *cis*-AZO GROUP. STEPWISE CYCLODIMERISATION OF DIPHENYLACETYLENE TO TETRAPHENYLCYCLOBUTADIENE TRICARBONYLIRON

ANGELO ALBINI** and HORST KISCH***

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim an der Ruhr (Deutschland)

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Summary

The μ-(*cis*-azo) complexes $LFe_2(CO)_6$ (L = 4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline, 4-isopropyl-3,3-bis(methoxycarbonyl)-1-pyrazoline, 2,3-diazanorbornene, and benzo[*c*]cinnoline) each contain an activated N—N bond which reacts thermally and/or photochemically with the alkynes RC_2R (R = H, CH_3, Ph, $COOCH_3$) by insertion into the Fe—N bond to give the novel cycloadduct $L(RC_2R)Fe_2(CO)_6$. The pyrazoline and diazanorbornene complexes are transformed smoothly into the 1,2,3-diazaferrole derivatives $L(RC_2R)Fe(CO)_4$. These compounds react with a further molecule of the alkyne to give the "double-addition" products $L(RC_2R)_2COFe(CO)_2$, which can be converted into the cyclobutadiene derivative π-$(RC_2R)_2Fe(CO)_3$ if R = Ph; this complex can be synthesized very conveniently in yields of 70% by reaction of diphenylacetylene and the pyrazoline compound $LFe_2(CO)_6$ at 150°C. It is shown that the cyclodimerisation of the alkyne occurs stepwise.

Introduction

The different modes of coordination of N=N double bonds with transition metals are attracting considerable interest [1]. It is well established now that iron carbonyls react with cyclic five- or six-membered azo compounds to give up to five different types of complexes [1c-i]. One of the most stable contains the *cis*-azo group as a six electron donor which bridges two $Fe(CO)_3$ groups

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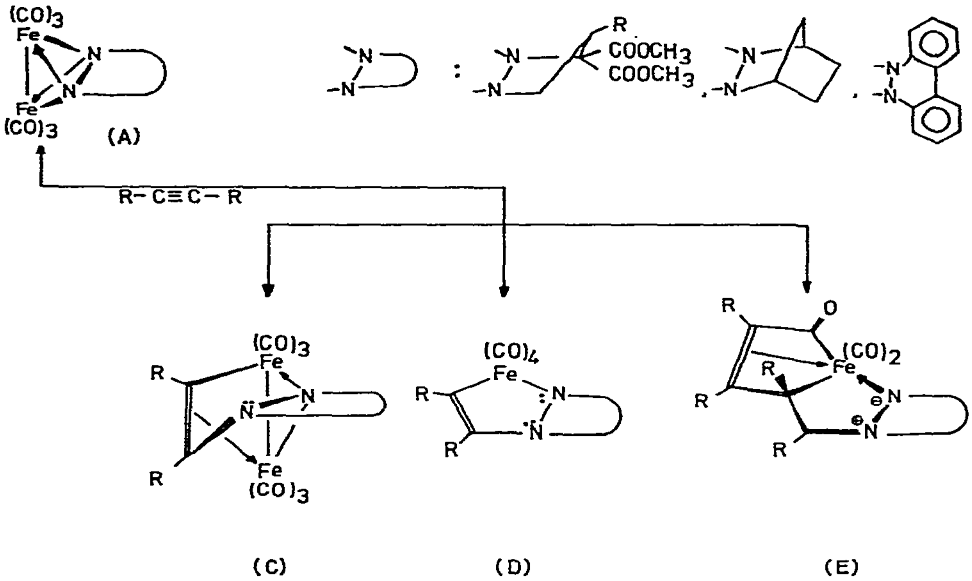
* Part V: ref. 1h.

** Present address: Istituto di Chimica Organica, Università, I-27100 Pavia (Italy).

*** To whom correspondence should be addressed.

SCHEME 1



(A, Scheme 1) [2]. To learn something about the reactivity of the complexed azo group in these binuclear iron compounds, the thermal and photochemical reactions with alkynes were studied. In the present paper we report the results obtained from hexacarbonyldiiron complexes of 3,3-bis(methoxycarbonyl)-4-phenyl-1-pyrazoline (I), 3,3-bis(methoxycarbonyl)-4-isopropyl-1-pyrazoline (II), 2,3-diazanorbornene (VI), benzo[*c*]cinnoline and various alkynes [3] (Scheme 1). When this work was in progress a short note was published on the reaction of μ-(3,6-diphenylpyridazine)hexacarbonyldiiron with maleic anhydride, diphenylacetylene and dimethyl acetylenedicarboxylate; however, no physical data or structural assignments were reported for the products derived from the alkynes [4].

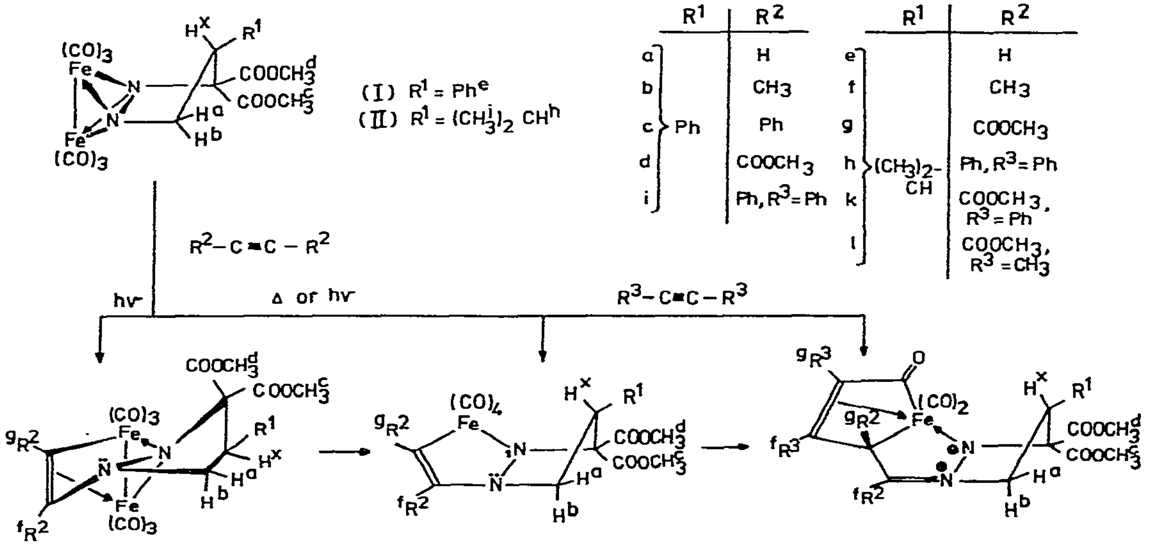
Results and discussion

(A) Reactions of pyrazoline complexes I and II

Irradiation ($\lambda \geqslant 290$ nm) of μ-[3,3-bis(methoxycarbonyl)-4-phenyl-1-pyrazoline]hexacarbonyldiiron (I) in the presence of a twofold excess of diphenylacetylene affords adduct IIIc, metallocycle IVc, "double-addition" product Vi, and the tricarbonylferrol-irontricarbonyl derivative $(PhC_2Ph)_2Fe_2(CO)_6$ [5] in yields of 18, 20, 12, and 37%, respectively (vide experimental). Complex IIIc is obtained in this yield only if the chromatographic separation is conducted at −20°C; otherwise IIIc decomposes into IVc. Recrystallisation from ether/n-hexane at −70°C, affords IIIc as black crystals of composition $(C_{13}H_{14}N_2O_4)$-$(PhC_2Ph)Fe_2(CO)_6$ which can be stored at −20°C without decomposition. The structure has been resolved by X-ray analysis and can be rationalized as the result of an insertion of the alkyne into an iron—nitrogen bond, accompanied by opening of a second Fe—N bond, and coordination of the resulting olefinic moiety to an iron atom [3] (Scheme 2).

The pink metallocycle IVc contains one iron carbonyl group less than IIIc

SCHEME 2



	R^1	R^2
a	Ph	H
b		CH_3
c		Ph
d		$COOCH_3$
i		Ph, R^3 = Ph
e	$(CH_3)_2$-CH	H
f		CH_3
g		$COOCH_3$
h		Ph, R^3 = Ph
k		$COOCH_3$, R^3 = Ph
l		$COOCH_3$, R^3 = CH_3

(IIIc) (IVa, c, d, e, f, g) (Vi, h, k, l)

and can also be prepared thermally from I and diphenylacetylene at 100°C; the structure will be discussed together with the acetylene derivatives IVa, IVe which are formed by irradiation of I or II in the presence of an excess of acetylene. In this case the initial adduct of type C could not be isolated.

Complex IVa (R^2 = H) has composition $(C_{13}H_{14}N_2O_4)(C_2H_2)Fe(CO)_4$ as demonstrated by the mass spectrum which shows a molecular ion and successive loss of four CO groups. The low field part of the ^{1}H NMR spectrum exhibits two doublets at τ 2.95 and 0.78 ppm (J = 6 Hz). By analogy to $(\pi\text{-}C_5H_5)(CO)_2FeCH{=}CH_2$ [6] (see Scheme 5) these signals are assigned to a σ-bonded vinyl group. The high field part of the spectrum closely resembles that of I and thus indicates the presence of a pyrazolidine ring in IVa (Table 1). In the region of terminal CO groups the IR spectrum contains four bands at 2043 vs, 1974 s, 1967 s, and 1957 vs cm^{-1}; the ester carbonyls absorb at 1730 cm^{-1}. On the basis of these physical data and the smooth formation of this type of complex from the initial adduct (e.g. IVc is formed by dissolving IIIc in chloroform), the structure with a bicyclic metallocycle is assigned to complex IVa (Scheme 2). The 1,2,3-diazaferracyclopent-4-ene ring resembles the metallocycle formed by reaction of $Na[(\pi\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) with ethyl diazoacetate and subsequent protonation [7] (Scheme 5). The structure of the 1-π-cyclopentadienyldicarbonyl-4-ethoxycarbonyl-5-hydroxy-1,2,3-diazamolybdole produced has been established by X-ray analysis [8].

Complexes IVd, IVf, IVg are conveniently prepared by heating a mixture of I or II with 2-butyne or dimethyl acetylenedicarboxylate, respectively; their structure follows from comparison of their IR and UV spectra with those of IVa.

The third complex (Vi) obtained by irradiation of I in the presence of PhC_2Ph is more stable than IIIc and IVc and can be crystallized from dichloromethane/methanol to give air-stable, deep red prisms of composition $(C_{13}H_{14}\text{-}N_2O_4)(PhC_2Ph)_2Fe(CO)_3$. Compound Vi is prepared in yields up to 80% by conducting the reaction thermally at 100°C. Complex Vi is formed also in good yield by treatment of IVc thermally with diphenylacetylene. The mass spectrum exhibits no molecular ion but shows a fragmentation pattern very similar to that of tetraphenylcyclobutadienetricarbonyliron. The latter complex is formed in 80% yield by thermolysis of Vi at 150°C/0.01 torr (Scheme 7); the cyclopropane and olefin derivatives formed as by-products are typical decomposition products of the free pyrazoline [9] and thus indicate the presence of an N—N bond in Vi. This is confirmed by the NMR spectrum which exhibits the typical absorption pattern of the ring protons $H^{a,b,x}$ at τ 6.8-5.5 (τ 6.5-5.8 for I in $CDCl_3$) (Table 1). The equal intensities of the two sharp CO stretching bands at 2003 and 1946 cm^{-1} indicate the presence of an $Fe(CO)_2$ group. As expected, two moles of carbon monoxide per mole of Vi are evolved on oxidative degradation of Vi with bromine in glacial acetic acid; however, if ceric ammonium nitrate is used as oxidizing agent, three moles of CO are obtained. These data point to an $Fe(CO)_2$ group and a ketonic carbonyl group hidden under the broad ester carbonyl bands at 1765 and 1730 cm^{-1}. This is verified by the IR spectrum of the 2,3-diazanorbornene derivative IXe which shows a ketonic band at 1720 cm^{-1} (Scheme 3, Table 3). The failure of this keto group to form a 2,4-dinitrophenylhydrazone indicates the presence of a (Ph)C=C(Ph)(Ph)C=C-(Ph)(CO)Fe moiety rather than a (Ph)C=C(Ph)(CO)(Ph)C=C(Ph) skeleton [10]. These data exclude the presence of a coordinated cyclobutadiene or ferrole ring in Vi but suggest an insertion of diphenylacetylene and CO into the Fe—N or Fe—C bond of metallocycle IVc. The deep red color of complex Vi is typical for the presence of an Fe—N—N bond and thus insertion into the Fe—C bond may have occurred. An X-ray structural determination has recently confirmed the main feature of the proposed structure, but the Fe—C bond surprisingly has not been cleaved. The molecular structure can be written as in Scheme 2 and will be discussed in detail elsewhere [11]. The mixed complexes Vk, Vl, ($R^2 \neq R^3$) are prepared thermally or photochemically from the metallocycle IVg and the appropriate alkyne. Structural assignments are based on comparison of the physical properties with those of Vi (Tables 1, 2, 3).

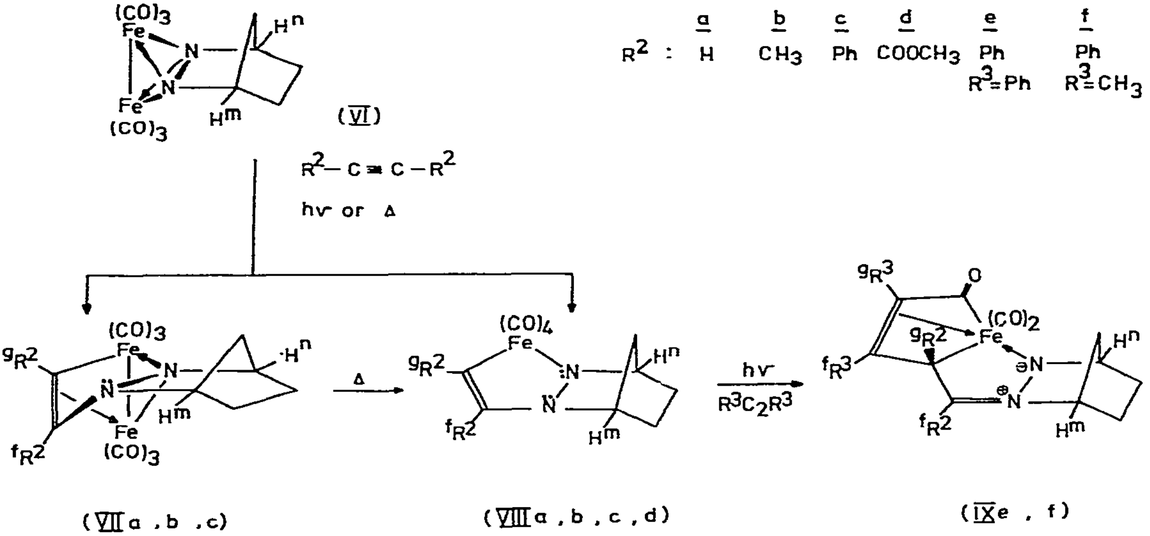
(B) Reactions of μ-(2,3-diazanorbornene)hexacarbonyldiiron (VI)

Irradiation of complex VI in the presence of acetylene or 2-butyne gives the dark green cycloadducts VIIa or VIIb, respectively. The diphenylacetylene derivative VIIc is prepared more conveniently by performing the reaction thermally at 90°C (Scheme 3). The structures of these complexes are obviously of type C as demonstrated by comparison of their physical and chemical properties with those of IIIc (Tables 2, 3).

The orange metallocycles VIIIa-VIIIc are obtained by simple heating of the corresponding cycloadducts VIIa-VIIc, respectively. In the case of dimethyl acetylenedicarboxylate the initial cycloadduct VIId seems to be very unstable and the thermal reaction affords VIIId only. Structural assignments again are straightforward by comparison with the pyrazoline complexes IV.

The red-brown "double-addition" products IXe, IXf can only be prepared in considerable yields photochemically from the metallocycle VIIIc and diphe-

SCHEME 3



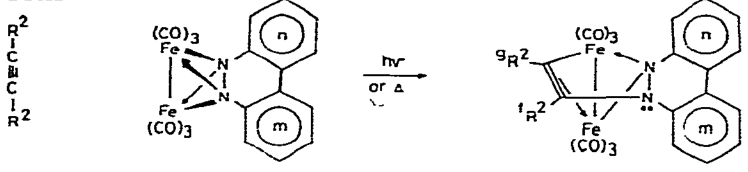
nylacetylene or 2-butyne. The more direct route to IXe, from diphenylacetylene and complex VI, yields at 90°C large amounts of tetraphenylcyclopentadienone together with complexes VIIc, VIIIc, and small quantities of the tricarbonylferroleiron tricarbonyl complex (PhC$_2$Ph)$_2$Fe$_2$(CO)$_6$. At 140°C, however, tetraphenylcyclobutadiene tricarbonyliron and hexaphenylbenzene are formed as the major products.

(C) Reactions of μ-(benzo[c]cinnoline)hexacarbonyldiiron (X)

In contrast to the behaviour of the pyrazoline and diazanorbornene complexes I, II and VI, the benzo[*c*]cinnoline derivative X reacts with alkynes to give only the initial cycloadducts of type C and no complexes of types D or E. These red complexes are conveniently prepared by irradiation (XIb) or heating (XIc, XId) of X in the presence of 2-butyne, diphenylacetylene, and dimethyl acetylenedicarboxylate, respectively. The molecular formulae of these complexes are derived from elemental analysis and mass spectra which contain the corresponding molecular ions. The IR spectra closely resemble that of the starting complex X and indicate the presence of an Fe$_2$(CO)$_6$ group. The failure of compounds XI to yield the metallocycles of type D upon heating to 180°C, and the different UV spectra compared to complexes of type C point to another structure. The possibility of a π-complex of the alkyne or a symmetrically bridging alkyne is discarded on the basis of the NMR spectrum of XIb which shows two singlets due to the methyl protons at τ 7.96 and 7.6 ppm.

This absorption at relatively low field points to the presence of a CH$_3$C=C-CH$_3$ moiety not coordinated to iron; in complex VIIb this group is coordinated to iron and accordingly the methyl protons appear at τ 9.27 and 8.67 ppm. The same conclusion is drawn from comparison of the ^{13}C NMR spectra of VIIc and XIc [12] and from the absorptions of the aromatic protons. In complex X the latter give rise to two multiplets of intensity ratio 2/6 while for XId three multiplets (2/4/2) are observed; that indicates a more unsymmetrical structure for

SCHEME 4



X

XI b, c, d

R^2 CH3, Ph, COOCH3

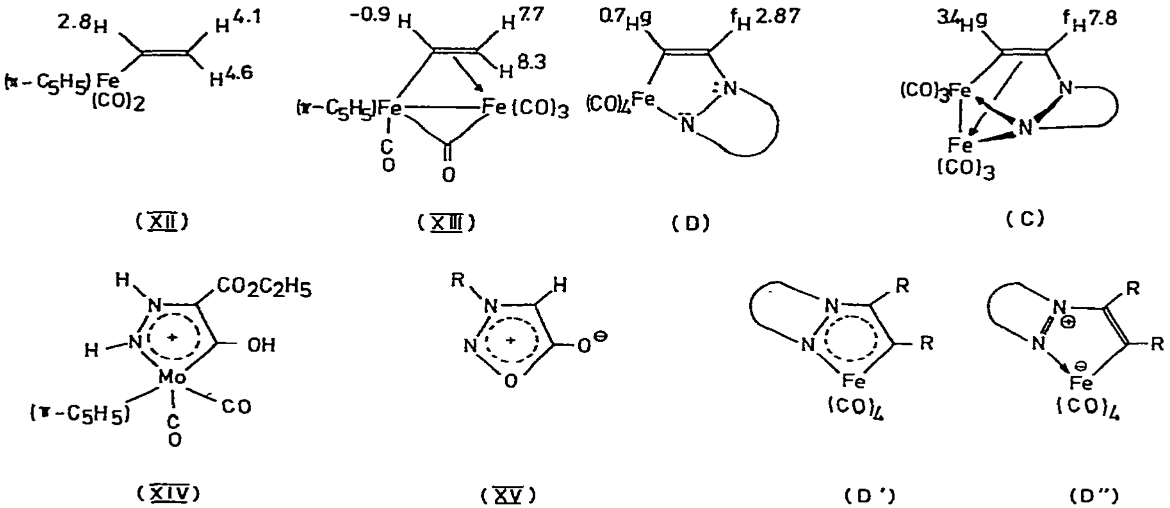
XId compared to X. Despite the fact that chemical and spectral evidence suggests a structure different to type C, preliminary X-ray results reveal that complexes XI belong to the same structural type [11].

(D) ¹H NMR spectra

The discussion will be restricted to complexes derived from diazanorbornene because the spectra are simpler than those of compounds obtained from the pyrazoline complexes I and II. The spectra of the latter (Table 1) obviously exhibit the same trends as observed in the case of complexes VI-IX. The unsymmetrical structure of metallocycles of type D is nicely reflected by the spectrum of e.g. VIIIa (R^2 = H). The bridgehead protons give rise to two apparent singlets at τ 6.17 and 5.33 ppm, compared to one signal at τ 7.2 and 5.34 ppm for starting complex VI and free 2,3-diazanorbornene, respectively (Table 2). This indicates that the diamagnetic shielding of the bridgehead protons by the N—N bond is approximately the same as in free diazanorbornene; the same effect is observed in the corresponding ^{13}C NMR spectra [12]. That implies that the N—N bond of VIIIa has some double-bond character. The absorptions of the σ-vinyl group appear as two doublets at τ 0.75 and 2.87 ppm, J = 5 Hz. The latter signal is split into a further doublet, $J \sim$ 1 Hz, by long range coupling probably to H^n or H^m. By analogy with the σ-vinyl iron complex XII we assign this signal to H^f and the doublet at lower field to H^g (Scheme 5). Both signals, however, absorb about 1.3-2 ppm downfield from those of XII. The most likely explanation is that the five-membered metallocycle has some degree of aromaticity which should give rise to a stronger deshielding of the protons in VIIIa compared to XII. Thus the structure of complexes of type D may be better described by the non-classical formulation D′ indicating a certain amount of electron delocalisation within the 1,2,3-diazaferrole ring. The observed bond lengths of the 1,2,3-diazamolybdole XIV support this formulation. The five-membered metallocycles may be formally derived from the well known sydnones XV by replacing oxygen by a transition metal group [8].

In the cycloadducts of type C the σ-vinyl moiety becomes bonded to a second iron carbonyl group. The corresponding coordination shifts of the protons H^g and H^f when going from VIIIa to VIIa ($\Delta\tau(H^g) = 2.7$, $\Delta\tau(H^f) = 4.93$) are different from those of the pair XII→XIII ($\Delta\tau(H^g) = -3.7$, $\Delta\tau(H^f) = 3.6$). The large negative shift observed in this case may be rationalized by the assumption that the σ-bonded iron atom in XIII has a considerable positive charge; the paramagnetic shielding of the more positive metal [13] may then overcome the diamagnetic shift caused by the π-bonded $Fe(CO)_3$ group. In the case of VIIIa→VIIa

SCHEME 5



this charge decreases* and the expected positive coordination shifts are observed. The very large value for $\Delta\tau(H^f)$ (4.93!) can be taken as further argument for the "aromatic character" of the metallocycles of the type D. Complexation of the double bond of VIIIa prevents the possibility of a paramagnetic ring current and thus the corresponding protons of VIIa absorb at remarkably high field [13]. The bridgehead protons of VIIa appear about 0.6 ppm upfield from those of the starting complex VI. This indicates the presence of an N—N bond with less "double-bond" character than that of VI. X-ray analysis of the pyrazoline derivative IIIc has indeed revealed a rather long N—N bond of 1.49 Å [3].

The spectra of the "double-addition" products of type E are more complicated due to the presence of less informative phenyl and methyl groups. These complexes in solution probably form geometrical and/or conformational isomers as demonstrated by the appearence of four signals due to the bridgehead protons of IXe. As in the case of metallocycles of type D, the absorption at relatively low field (τ 5-6 ppm) indicates some degree of double bond character of the N—N bond. In accordance with this explanation the preliminary X-ray structural investigation of the pyrazoline derivative Ve reveals an N—N bond length of 1.35 compared to 1.49 Å for the cycloadduct IIIc [3,11].

(E) IR and electronic absorption spectra (Table 3)

The electronic spectra of the starting complexes of type A exhibit three absorption bands between 20 000 and 35 000 wavenumbers. The transition of lowest energy (21 000-25 000 cm^{-1}) seems to be a function of the cyclic azo ligand. No assignment, however, can be made at present.

The spectra of the cycloadducts III and VII show a characteristic low energy absorption of medium intensity ($\epsilon \sim 700$) at 16 000-17 000 cm^{-1}. We presume that the lone pair at one nitrogen is involved in this transition; a detailed assign-

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* This is supported by the Mössbauer parameters of VIIId and VIIa [14].

TABLE 1

^{1}H NMR SPECTRA OF COMPLEXES I-V[a]

	$H^{c,d}$	$H^{f,g}$	H^e	$H^{a,b}$	H^x	H^i	H^h
I[b]	7.33s, 6.68s		3.1m	6.97q (J_{ab} 12) 6.74q (J_{ax} 6.9)	5.1q (J_{bx} 12.1)		
II[b]	6.82s, 6.55s			7.3-6.3m		9.5d, 9.08d	8.65m (J_{ih} 6)
IIIc[c,d]	7.4s, 6.7s	3.1-3.4m		6.85m	5.75m		
IVa[b]	7.06s, 6.68s	2.95d 0.78d (J_{fg} 6)	3-3.4m	6.45q (J_{ab} 12.6) 6.1q (J_{ax} 1.8)	5.75q (J_{bx} 7.2) (J_{bx} 7.2)		
IVe	6.65s, 6.6s	3.03d 0.7d (J_{fg} 6)		6.5-7m		9.6d, 9.3d	8.5m (J_{ih} 6.5)
IVf	6.55s, 6.5s	8.2s, 7.17s		6-7m		9.5d, 9.3d	8m (J_{ih} 6.5)
IVc	6.95s, 6.5s	3.2-2.5m		6.35q (J_{ab} 12.5) 5.95q (J_{ax} 1.8)	5.52q (J_{bx} 6.5)		
IVd[b]	6.68s, 6.58s, 7.15s, 6.2s		3.1-3.4m	5.75q (J_{ab} ~ 12) 5.25q (J_{ax} ~ 0)	5.45d (J_{bx} ~ 7)		
IVg	6.5s, 6.47s, 6.37s, 6.02s			5.6q, 5.8-6.5m	6.4-6.8m	9.38d, 9.1d	8.15m (J_{ih} 6.5)
Vi[e]	6.5s, 6.2s	3.1-2.6m		6.8q (J_{ab} 12) 5.5q (J_{ax} 6)	6.2-6.3m (J_{bx} 7)		
Vh[e]	5.6s, 5.7s	2.1-2.9m		6.2-6.6m	7.2-7.4m	8.9d, 8.7d	7.8m (J_{ih} 6.7)
Vk[e]	6.4s, 6.3s, 6.2s, 6.1s		3-2.4m	6-6.5m, 5.5q	7.5q	9.2t	8.3 (J_{ih} 7)
Vl	6.4s, 6.45s, 6.7s[f]	8.12s, 8.46s		4.7q 6.1q	7.05q	9.25d, 9.45d	8.5m

[a] C_6D_6 solution, 60 MHz, τ-values, internal standard TMS, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; J(Hz): coupling constants from first order analysis. [b] 100 MHz spectrum. [c] C_7D_8 solution. [d] —70°C. [e] $CDCl_3$ solution, 90 MHz, TMS external standard. [f] Relative intensities 2/1/1.

ment is deferred. In contrast to that, the spectra of the cycloadducts XI do not contain a comparable low energy band.

The metallocycles of type D exhibit two well-separated absorption maxima at about 20 000 and 29 000 cm^{-1}. The energy of both transitions depends on the substituent present at the olefinic double bond and on the cyclic azo ligand. Presumably, these bands arise from charge-transfer transitions between the $Fe(CO)_4$ group and the N—NC(R)=C(R) moiety and from "*d—d*" type transitions [15].

The IR absorptions of the terminal CO groups of the starting complexes I, II and VI are shifted to slightly smaller wavenumbers when one alkyne is intro-

TABLE 2

^1H NMR SPECTRA OF COMPLEXES VI-XI[a]

	$H^{f,g}$	$H^{n,m}$ (broad signal)	CH_2-protons
VI		7.2	7.7m, 7.86m, 8.3-9.4m
VIIa	7.78d (J_{fg} 5) 3.47dd (J_{fm} ~ 1)	7.82, 7.63	8.2-10m
VIIb	9.27s, 8.67s	7.78, 7.45	8.4-9.7m
VIIc	3.38-2.92m	7.58, 7.23	8-9.8m
VIIIa	2.87dd (J_{fm} ~ 1) 0.75 (J_{fg} 5)	6.17, 5.33	8.4-9.2m
VIIIb[b]	8.1s, 7.13s	6.08, 5.38	8.3-9.3m
VIIIc[b]	3.1-2.5m	5.72, 5.26	8.2-9.3m
VIIId	6.5s, 6.17s	5.55, 4.63	8.3-9.3m
IXe[b,c]	3.2-2.8m	6.3, 6.05, 5.6, 5.05	7.7-8.4m
IXf[b,c]	7.75s, 8.18s, 3.2m	4.55, 5.95	7.6-8.6m
		$H^{n,m}$	
X[c]		2.15m,1.5m	
XIb	7.96s, 7.6s	3.75-2.9m	
XIc[c]	2-3.4m, 2.9s		
XId[c]	6.08s, 6.12s	2.4m, 2.75m, 3.25m	

[a] See a in Table 1, dd, double doublet. [b] TMS external standard. [c] $CDCl_3$ solution.

duced to yield the complexes of type C. If any shift is seen it is in the opposite direction from that observed for the benzo[*c*]cinnoline derivatives of type C (X→XI). The metallocycles of type D presumably have the $Fe(CO)_4$ group in an octahedral coordination sphere of C_{2v} local symmetry as demonstrated by the presence of four CO stretching bands in the spectra of IVa-IVf. Distortions from this idealized geometry seem to occur if R is very large, as in IVg (R = $COOCH_3$), and if the azo ligand is the very rigid 2,3-diazanorbornene, as in VIIIa-VIIId. The observation of only three ν(CO) bands for these complexes can be accounted for by a distortion towards a tetragonal pyramid. "Back-bonding" from Fe into the heterocyclic ring seems to be more effective in the case of pyrazoline derivatives (IV) than for the diazanorbornene complexes (VIII). As one might expect, electron-withdrawing substituents facilitate back-donation as demonstrated by the increasing wavenumbers on going from IVa, VIIIa (R = H) to IVd, IVg, VIIId (R = $COOCH_3$); the opposite effect is observed if R = CH_3 (IVf, VIIIb). This influence of both the azo ligand and the olefinic part of the metallocycle on the values of the CO stretching frequencies indicates that the acceptor orbital for back-donation is composed of both these parts and delocalized over the –N–N–C–C-moiety. As mentioned above, ^1H NMR and ^{13}C NMR spectra point to considerable double-bond character of the N–N group. That is in accord with the relative low CO stretching frequencies of the metallocycles (D) and

TABLE 3

IR AND UV SPECTRA OF COMPLEXES I-XI[a]

	ν(C≡O) (cm^{-1})	ν(C=O) (cm^{-1})	UV ($\epsilon \cdot 10^{-3}$) ($cm^{-1} \cdot 10^{-3}$)
I	2074m, 2033s, 1993s, 1985(sh), 1971m	1748s, 1765m	24.0(sh)(1.7), 29.0(sh)(3.5), 34.0(24)
II	2073m, 2031s, 1992s, 1983(sh), 1971m	1742s, 1757m	24.0(sh)(1.7), 29(sh)(3.0), 33.7(25.7)
VI[b]	2068m, 2022s, 1991s, 1970s, 1959m		25.0(sh)(1.8), 29.0(sh)(2.4), 33.6(30.0)
X[c]	2069m, 2039s, 1989s, 1985s, 1972m		22.0(sh)(1.3), 29.0(sh)(11), 31(26.3), 34.5(22.7)
IIIc[d]	2067m, 2053m, 2020(sh), 2013s, 1966m	1730m	16.5(0.7), 22.5(sh)(2.9), 29.2 (7.7)
VIIa	2054s, 2010vs, 1975vs, 1954vs, 1942w		17.0(0.74), 24.5(sh)(2.56), 29.6(9.2)
VIIb	2047, 2001, 1968, 1947 all vs, 1936s		17.0(0.58), 24.0(sh)(2.2), 29.3(9.3)
VIIc	2050s, 2008vs, 1976vs, 1956w, 1948vs, 1937w		16.3(0.6), 24.7(sh)(2.5), 29.4 (7.9)
XIb	2065s, 2032vs, 1990vs, 1976m, 1964w		22.3(3.9), 31.1(sh)(9)
XIc	2066s, 2040vs, 1999vs, 1992vs, 1985m, 1952w		22.1(3.6)
XId	2082s, 2054vs, 2029s, 2005vs, 1976w	1710s	21.4(3.5), 33.4(sh)(15)[e]
IVa	2043vs, 1978s, 1972s, 1958vs	1730m	20.2(4.2), 28.3(6.7)
IVe	2041vs, 1974s, 1967s, 1957vs	1730m	20.4(4.4), 28.9(7)[e]
IVf	2032vs, 1965s, 1959s, 1946vs	1730vs	19.6(4.8), 29.1(7)[e]
IVc	2042vs, 1980(sh), 1975s, 1957vs	1730m	19.5(3.8), 29.0(6.1)[e]
IVd	2054vs, 1995s, 1988s, 1982vs	1730, 1710m	20.2(5.0), 28.3(4.3)[e]
IVg	2057vs, 1992s, 1980vs(br)	1740m, 1710s	20.3(5.0), 28.5(4.3)[e]
VIIIa	2034vs, 1955vs(br), 1921m		21.9(4.1), 29.8(7.41), 33.5(sh) (6.33)[e]
VIIIb	2028vs, 1950vs, 1945vs		20.9(4.6), 30.3(9.5)[e]
VIIIc	2035vs, 1965vs, 1950vs		20.8(5.5), 29.5(8.2)[e]
VIIId	2052vs, 1982vs, 1974vs	1710m	21.7(4.5), 29.3(4.6)[e]
Vi[f]	2003vs, 1946vs	1765s, 1730s	22.0(sh)(5.2), 28.5(sh)(10)
Vh[g]	1998vs, 1940vs	1730(sh), 1690m	24.0(sh)(5.2), 28.5(sh)(9.5), 33.5(42)
Vk[g]	2025vs, 1968vs	1730s, 1690s	20.1(sh)(2), 22.1(2.56), 25.6 (3.1)[e]
Vl[g]	2021vs, 1960vs	1725s, 1685s	20.9(sh)(2.2), 22.2(2.4)30.3(8)[e]
Vm[h]	1918vs	1720s, 1680s	19.0(1.9), 27(18.0)[e]
IXe[e]	1997vs, 1940vs	1720	18.5(sh)(0.69), 24.4(5.6), 27.8(sh) (7.9), 35(20)[h]
IXf[g]	1995vs, 1933vs	1710	

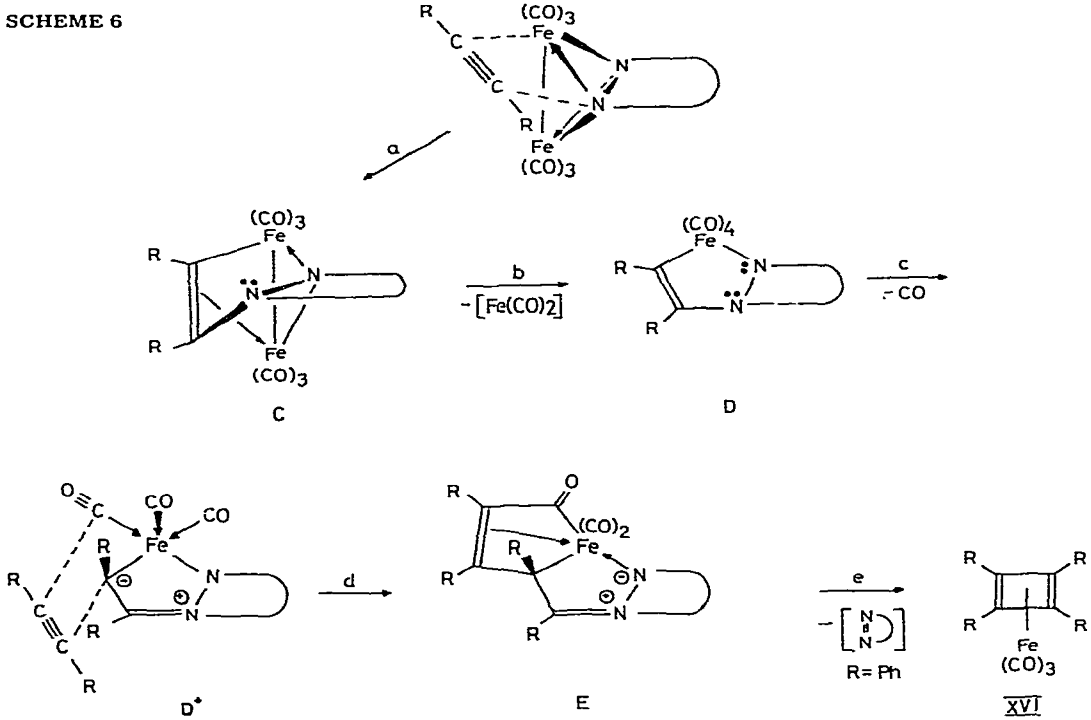
[a] n-Hexane solution. [b] See ref. 1e. [c] See ref. 1i. [d] Chloroform solution, —25°C. [e] Benzene solution. [f] KBr pellet. [g] Dichlormethane solution. [n] Toluene solution.

points to a predominant contribution of valence structures like D″ to the ground state of the 1,2,3-diazaferrole system (D′, Scheme 5). The "double-addition" products E show two strong ν(CO) bands of equal intensity and a third band of medium intensity at 1710-1720 cm^{-1}; the latter arises from the acyl ν(CO) vibration and is shifted by 120 cm^{-1} to lower energy compared to a similar *trihapto*-acryloylcobalt complex [16].

(F) Discussion

The reaction of μ-(*cis*-azo)hexacarbonyldiiron complexes of type A with alkynes is summarized in Scheme 6. The formation of the cycloadducts can

SCHEME 6



be explained formally as the result of a [4 + 4] cycloaddition. By analogy with the well-known cyclo-oligomerisation reactions of acetylenes in the presence of transition metals, it seems most probable that both reactions occur stepwise and are started by formation of a π-complex of the alkyne [17]. The vacant coordination site necessary for that process might be formed by loss of carbon monoxide or opening of an Fe—N bond; preliminary kinetic investigations do not reveal an inhibitory influence of carbon monoxide and thus favour the latter or a direct attack of the alkyne at the Fe—N bond in the kind of a concerted cycloaddition. The failure of complexes XI to give the corresponding type D derivatives on heating or irradiation may be due to the much stronger π-bond of the olefinic moiety in XI compared to IIIc [11]. However, the different electronic and steric situation of the N—N bond in the benzo[*c*]cinnoline complexes, compared to the pyrazoline and diazanorbornene compounds, may be also responsible for this distinct difference in chemical reactivity. Further work is in progress to clarify these questions.

Complexes of type C are more stable in the case of the diazanorbornene derivatives (VIIa-VIIc) than with the pyrazoline compounds; in the latter case only one adduct (IIIc) could be isolated. The most characteristic reaction of these cycloadducts is their smooth conversion into the metallocycles of type D by simple heating. The fact that this process (e.g. VIIa-VIIIa) can easily be monitored by NMR spectroscopy indicates that no paramagnetic species is created and that the leaving iron carbonyl fragment is converted into a diamagnetic complex of unknown composition.

In contrast to the addition of the first alkyne (reactions a), the introduction of the second one is initiated by loss of carbon monoxide, as can easily be demonstrated by inhibition experiments with CO. The alkyne then occupies the vacant coordination site and finally forms the stable endproduct E by a process which most likely can be formulated as a [4 + 2] cycloaddition. This final step resembles the 1,3-dipolar cycloaddition between alkynes and 2,3-dipoles; the latter are defined as organic compounds containing four π-electrons distributed among three atoms as in an allyl anion system [18]. The corresponding transition state of this reaction step is depicted in Scheme 6 (D^+). This mechanism is corroborated by the successful observation of a short-lived species, probably $LFe(CO)_3$ (or solvated), by flash photolysis of IVg [19], and by low temperature experiments. If IVg is irradiated at —53°C in the presence of diphenylacetylene, simultaneous recording of the IR spectrum shows the gradual appearance of a new peak at 2067 cm^{-1}, which probably belongs to the spectrum of a π-complex of the alkyne.

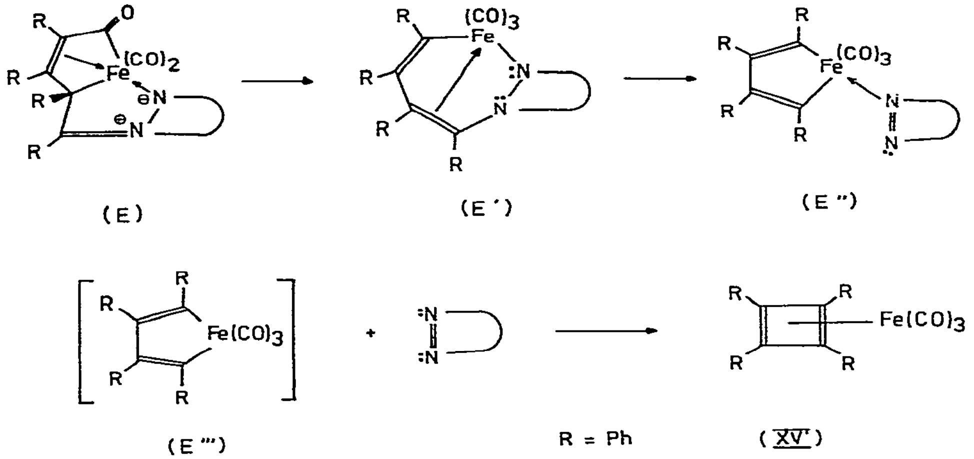
When the irradiation is interrupted and the solution warmed up to room temperature, the new band disappears and the spectrum corresponds to a mixture of IVg and Vk, the stable endproduct. The reaction can also be accomplished by prolonged irradiation at —53°C.

These new metallocycles of type E form a class of compounds with interesting chemical properties. We observed e.g. a photochemical Diels—Alder reaction of IVg with 2,3-dimethyl-1,3-butadiene and formation of new complexes by reaction with $Fe_2(CO)_9$ [19].

The "double-addition" products of type E are surprisingly stable. Complex Vi, e.g., can be crystallized from CH_2Cl_2/CH_3OH in the presence of hydrochloric acid without substantial decomposition. Boiling with glacial acetic acid yields unchanged Vi and a new complex of hitherto unknown structure, which apparently contains only one terminal CO group. The most striking property of Vi or Vh ($R^2 = R^3 = Ph$) is the smooth formation of tetraphenylcyclobutadienetricarbonyliron XVI upon heating in a vacuum to 150° C. Cyclopropane and olefin derivatives which appear as by-products of this reaction are also produced by thermolysis of the free azo ligand [9]. The diazanorbornene complex IXe gives the same reaction although XVI is formed in much lower yield. A possible mechanism of this process (e, Scheme 6) is formulated in Scheme 7. Rearrangement of rather strained tricyclic complex of type E yields the eight-membered ferracycle E′; cleavage of the C—N bond should give the relatively stable ferrole E″. The conversion of the latter into the cyclobutadiene complex parallels the formation of π-tetraphenylcyclobutadiene-π-cyclopentadienylcobalt from the cobaltocyclopentadiene complex $(\pi\text{-}C_5H_5)Co(PPh_3)(PhC_2Ph)_2$ [20]. Complex Vm, the trimethyl phosphite derivative of Vi, produces on heating a mixture of the cyclobutadiene complexes $(\pi\text{-}PhC_2Ph)_2Fe(CO)_2P(OCH_3)_3$ and XVI.

As previously reported [3] the cyclobutadiene complex XVI is prepared more conveniently by heating a mixture of I or II and diphenylacetylene to

SCHEME 7



150°C. If the alkyne is used in an six-fold excess, yields up to 70% can be obtained (based on the reasonable assumption, that one mol of XVI is formed from one mol of I). The by-products of this reaction are the same as the decomposition products found in the pyrolysis of Vi. In addition small amounts of tetracyclone, hexaphenylbenzene, and the ferrole $(PhC_2Ph)_2Fe_2(CO)_6$ are formed. The observation that in this reaction the latter complex is converted into the cyclobutadiene complex XVI is currently being investigated in more detail. Obviously, complexes of type C-E are intermediates in the formation of XVI as demonstrated by IR analysis of the reaction of VI with PhC_2Ph at 150°C and the stepwise synthesis of XVI (reactions a-e, Scheme 6). However, we have not succeeded in the cyclo-dimerisation of alkynes other than diphenylacetylene. Further work on the critical reaction steps (c-e, Scheme 6) as well on the use of other transition metals in these reactions, is in progress.

Experimental

Microanalysis and molecular weight determinations were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr. Melting points are uncorrected and determined on a Kofler melting point apparatus. Spectra were taken as follows: NMR: Varian A56/60, A60A and HA-100, Bruker WH 90; IR: Perkin—Elmer 621; UV: SEM Brückl HRS 4001C; mass spectra: MAT CH5. Acetylene (aceton free), 2-butyne, diphenylacetylene, and dimethyl acetylenedicarboxylate were commercial products; the latter was redistilled before use. Solvents were dried over alumina and saturated with argon before use. Photolysis were performed with a Philips HPK 125 W lamp using pyrex filter ($\lambda \geqslant 290$ nm). All reactions and manipulations with organometallic compounds were carried out in an argon atmosphere. If not otherwise indicated, silica gel Merck (0.063-0.2 mm) was used in column chromatographic separations. Complexes I, II, VI and X were prepared according to literature [21,1i]. Analytical data, melting points, and solvents are summarized in Table 4.

TABLE 4

ANALYTICAL DATA OF COMPLEXES III-V, VII-IX, AND XI

	Crystal appearance	M.p. (°C)	Re-cryst. solv.^{a}	Analysis found (calcd.) (%)				Mol. wt. found^{b} (calcd.)
				C	H	N	Fe	
IIIc	black	132-134	e/h	55.7 (55.0)	3.35 (3.33)	3.85 (3.89)	15.19 (15.55)	496 (720)
IVa	deep red plates	88-90	e/h	49.65 (50.0)	4.18 (3.51)	6.11 (6.13)	12.19 (12.3)	456 (456)
IVc	deep red plates	51^{c}	e/h	61.1 (61.2)	4.3 (3.95)	4.75 (4.6)	8.7 (9.2)	552 (608)
IVd	deep red plates	142-144	e/h	49.66 (48.9)	3.55 (3.5)	5.00 (4.9)	10.15 (9.8)	516 (572)
IVe	deep red plates	73.5-74.5	e/h	45.67 (45.5)	4.76 (4.26)	6.89 (6.74)	13.75 (13.48)	422 (422)
IVf	deep red plates	89.5-91	e/p	48.37 (48.0)	5.12 (5.0)	6.57 (6.2)	13.24 (12.6)	395 (450)
IVg	deep red plates	111-112	e/h	44.76 (44.6)	4.35 (4.1)	5.44 (5.2)	11.01 (10.4)	482 (538)
Vi	red prism	183^{c}	d/m	69.05 (68.65)	4.72 (4.48)	3.75 (3.69)	7.38 (7.39)	496 725 (758)
Vh	red prism	167-169^{c}	d/m	68.53 (67.95)	5.05 (4.97)	4.12 (3.87)	8.13 (7.79)	724 (724)
Vk	red prism	156-159	d/m	56.87 (57.5)	4.70 (4.65)	3.92 (3.92)	7.71 (8.14)	627 (688)
Vl	red prism	223^{c}	d/m	49.35 (48.93)	5.30 (4.96)	5.25 (4.96)	10.40 (9.93)	508 (564)
Vm	red prism	165^{c}	t/h	62.92 (63.38)	5.52 (5.65)	3.41 (3.35)	6.80 (6.65)	(820)
VIIa	olive-green needles	90.5-91.5^{d}	e/h	38.70 (38.8)	2.97 (2.48)	7.02 (6.96)	27.79 (27.85)	376 262 (402)
VIIb	dark green needles	130^{d}	e/h	41.95 (41.8)	3.25 (3.25)	6.41 (6.6)	25.92 (26.05)	430 (430)
VIIc	dark green needles	154^{d}	e/h	54.2 (54.1)	3.21 (3.25)	5.08 (5.05)	20.12 (20.2)	554 (554)
VIIIa	orange powder	68-69	e/h	43.89 (44.5)	3.70 (3.45)	9.99 (9.76)	22.42 (21.32)	262 (290)
VIIIb	orange needles	72-75	d/h	49.31 (49.1)	4.32 (4.4)	8.90 (8.8)	17.36 (17.6)	318 402 (318)
VIIIc	orange needles	157.5-159	d/h	62.40 (62.4)	4.10 (4.06)	6.33 (6.32)	12.71 (12.65)	442 526 (442)
VIIId	orange plates	133-134	a/h	44.40 (44.35)	3.77 (3.45)	7.29 (6.9)	14.70 (13.8)	406 (406)
IXe	dark brown red plates	191-195	d/m	71.29 (72.8)	4.40 (4.74)	4.43 (4.47)	9.20 (9.47)	564 637 (592)
IXf	red brown plates	166-172	d/m	65.12 (66.6)	5.37 (5.12)	5.51 (5.97)	11.31 (11.95)	468 (468)
XIb	orange plates	190^{c}	e/h	51.28 (51.4)	3.05 (2.72)	5.38 (5.45)	21.57 (21.8)	514 (514)
XIc	red plates	203^{c}	e/h	59.92 (60.1)	3.12 (2.82)	4.34 (4.5)	17.41 (17.55)	638 (638)
XId	dark red plates	168.5-170.5	e/h	48.0 (47.85)	2.31 (2.3)	4.65 (4.65)	18.61 (18.6)	602 (602)

^{a}e, ether; h, n-hexane; p, n-pentane; d, dichloromethane; m, methanol; a, acetone; t, toluene. ^{b}Highest peak in mass spectrum. ^{c}Dec. and gas evolution. ^{d}Melts with partial conversion into the corresponding complex VIII.

Reaction of complexes I and II

Irradiation of I in the presence of PhC_2Ph. A solution of 3 g (5.5 mmol) of I and 2 g (11.2 mmol) of PhC_2Ph in 150 ml of toluene is irradiated for 20 h. The solvent is evaporated and the remaining dark oil chromatographed at —20°C. Elution with the solvents indicated yields the following products: n-hexane: unreacted PhC_2Ph, some hexaphenylbenzene, and 0.73 g (37%) of the ferrole $(PhC_2Ph)_2Fe_2(CO)_6$; toluene: 0.4 g (13%) of starting complex I, 0.7 g (18%) of IIIc and 0.7 g (20%) of IVc; Et_2O/n-hexane (3/2): 0.5 g (12%) of Vi. Complexes IIIc and IVc are crystallized from Et_2O/n-hexane mixtures at —70°C.

Synthesis of IVa, IVe. A solution of 0.55 g (1 mmol) of I in 150 ml of toluene is cooled to —40°C and 300 ml of acetylene are allowed to dissolve. The mixture is irradiated for 2 h, concentrated and chromatographed at room temperature. Elution with ether/benzene (1/1) affords 100 mg (22%) of IVa. Complex IVe is prepared analogously from II in a yield of 45%.

Synthesis of IVf. A mixture of 0.5 g (1 mmol) of II and 1 g (18 mmol) of 2-butyne is refluxed for 8 h. Chromatographic separation affords 250 mg (50%) of IVf by elution with toluene.

Synthesis of IVg, IVd. A mixture of 0.5 g (1 mmol) of II, 0.7 g (5 mmol) of dimethyl acetylenedicarboxylate, and 2 ml of toluene is heated to 90°C. A vigorous exothermic reaction occurs accompanied by gas evolution. Evaporation of the solvent and crystallization of the residue from Et_2O/n-hexane yields 0.43 g (80%) of IVg. Complex IVd is prepared analogously.

Synthesis of IVc. A mixture of 0.6 g (1.1 mmol) of I, 0.4 g (2.2 mmol) of PhC_2Ph, and 10 ml of toluene is heated to 70°C for 12 h. The resulting pink coloured solution is chromatographed on florisil. Unreacted PhC_2Ph is eluted with toluene; further elution with toluene/Et_2O (5/1) affords 0.29 g (48%) of IVc which is crystallized from Et_2O/n-hexane at —70°C. This complex is relatively unstable compared to the other compounds IV.

Synthesis of Vi from IVc. Complex IVc (0.1 g, 0.16 mmol) and 0.15 g (0.8 mmol) of PhC_2Ph are heated in 6 ml of toluene for 3 h at 100°C. Chromatographic work up (eluting agent toluene/acetone (10/1)) affords 0.7 g (56%) of Vi.

Synthesis of Vi, Vh. Complex I (2 g, 4 mmol) and 3.1 g (17.4 mmol) of PhC_2Ph are dissolved in 30 ml of toluene and heated to 100°C for 8 h. The deep red solution is concentrated and chromatographed on neutral Al_2O_3. Elution with toluene/Et_2O (10/1) yields small amounts of the ferrole $(PhC_2Ph)_2Fe_2(CO)_6$ and of tetracyclone. A dark red band appears, which is eluted with ethyl acetate to give 2.22 g (70%) of Vi. Vh is prepared analogously.

Synthesis of Vk. Complex IVg (0.5 g, 1 mmol) and 0.7 g (4 mmol) of PhC_2Ph are heated in 20 ml of toluene at 100°C for 8 h. On cooling to room temperature Vk precipitates as a red powder, which is washed with Et_2O (0.5 g, 75% yield). Complex Vk may also be prepared photochemically as described below for Vl.

Synthesis of Vl. A degassed solution of 0.54 g (1 mmol) of IVg and 1 g (18 mmol) of 2-butyne in 100 ml of benzene is irradiated for 6 h. Chromatographic work up, eluting with benzene/ether (1/1), affords 0.4 g (65%) of Vl.

Thermolysis of Vi, Vh. Complex Vi (0.1 g, 0.13 mmol) is heated in a horizontal vacuum sublimer (0.01 torr) to 160-180°C. After 4 h 0.524 g (80%) of tetraphenylcyclobutadienetricarbonyliron (XVI) [22] are sublimed. The liquid cyclopropane and olefin derivatives deposited in the colder part of the sublimer are identical with the decomposition products of the free pyrazoline [9]. Complex Vh is thermolyzed analogously.

Synthesis of Vm. Complex Vh (0.4 g, 0.55 mmol) and 0.1 g (0.8 mmol) of $(CH_3O)_3P$ are dissolved in 10 ml of toluene and heated to 120°C for 2 h. Chromatographic separation (neutral Al_2O_3, $C_6H_6/CH_3COOC_2H_5$ (5/1)) affords a red brown oil which is crystallized from toluene/n-hexane at —70°C to give 0.32 g (71%) of Vm.

Thermolysis of Vm. Analogous to that of Vi, the mass and IR spectra of the yellow sublimate reveal the presence of a mixture of XVI and π-$(PhC_2Ph)_2$-$Fe(CO)_2(CH_3O)_3P$; ν(CO): 2038 m, 1980 vs, 1925 vs ($CHCl_3$); mass spectrum: *m/e* 592, 496 (molecular ions) and peaks of lower *m/e* values.

Synthesis of XVI. Complex I (0.271 g, 0.5 mmol) and 0.534 g (3 mmol) of PhC_2Ph are heated in a vial for 30 min to 150°C. The residue is dissolved in CH_2Cl_2 and chromatographed on neutral Al_2O_3. Elution with n-hexane and toluene, and crystallization of this yellow fraction (CH_2Cl_2/MeOH) affords 172 mg (70%) of XVI.

IR-spectroscopic experiment. Complex VI (0.1 g, 0.266 mmol) and 0.2 g (1.13 mmol) of PhC_2Ph are heated in a vial to 150°C. Aliquots are withdrawn at various intervals, dissolved in 0.5 ml of benzene and the spectrum is recorded in the range between 2250 and 1800 cm^{-1}. The first spectrum (after 2 min) shows the presence of VIIc, VIIIc, Vk, and $(PhC_2Ph)_2Fe_2(CO)_6$ as demonstrated by the well separated bands at 2050, 2035, 2025, and 2068 cm^{-1} respectively. The bands of VIIc and VIIIc disappear faster than those of Vk and of the ferrole complex; after 30 min only bands due to XVI are observed.

Reactions of complex VI

Synthesis of VIIa. A degassed solution of 0.37 g (1 mmol) of VI in 100 ml of toluene is cooled to —20°C and 300 ml of acetylene are allowed to dissolve. The mixture is irradiated for 6 h, solvent is removed at 0°C and the residue is dissolved in Et_2O; addition of n-hexane and cooling to —70°C affords 0.15 g (37%) of VIIa.

Caution. Complex VIIa is volatile and has toxic action similar to iron pentacarbonyl! All manipulations should be performed under a good hood!

Synthesis of VIIb. A degassed solution of 0.74 g (2 mmol) of VI and of 2 g (36 mmol) of 2-butyne in 150 ml of toluene is irradiated for 3 h. Evaporation and crystallisation of the residue from Et_2O/n-hexane yields 0.65 g (80%) of VIIb.

Synthesis of VIIc. Complex VI (0.37 g, 1 mmol) and 0.35 g (2 mmol) of PhC_2Ph are heated in 4 ml of toluene of 6 h to 90°C. Chromatographic work up, eluting with hexane/toluene mixture, affords 0.27 g (50%) of VIIc and 0.06 g (15%) of VIIIc. Complex VIIc can also be synthesized in good yield by a photochemical reaction analogous to the synthesis of VIIb.

Synthesis of VIIIa. Complex VIIa (0.2 g, 0.5 mmol) is dissolved in 5 ml of benzene and the solution is refluxed for 4 h. Crystallization from Et_2O/n-hexane yields 0.06 g (40%) of VIIIa. Complex VIIIa is also formed from solutions of VIIa on prolonged standing at room temperature.

Synthesis of VIIIb. Complex VIIb (0.21 g, 0.5 mmol) is heated in 10 ml of *p*-xylene to 130°C for 2 h. Evaporation of the solvent and crystallisation from Et_2O/n-hexane yields 0.08 g (50%) of VIIIb.

Synthesis of VIIIc. Complex VI (0.37 g, 1 mmol) and 2 g (11 mmol) of PhC_2Ph are heated to 80°C of 3 h. The solidified mixture is dissolved in toluene and chromatographed with toluene as eluant to give 0.18 g (40%) of VIIIc.

Synthesis of VIIId. Complex VI (0.74 g, 2 mmol) and 1 g (7 mmol) of dimethyl acetylenedicarboxylate are heated in 6 ml of toluene to 70°C (8 h). Chromatographic work up, eluting with benzene/Et_2O, affords 0.17 g (21%) of VIIId, about 0.1 g of unreacted VI, and 0.3 g of the ferrole $(CH_3COOC_2COOCH_3)_2Fe_2(CO)_6$ [23].

Synthesis of IXe. A degassed solution of 0.45 g (1 mmol) of VIIIc and 0.55 g (3 mmol) of PhC_2Ph in 120 ml of benzene is irradiated for 6 h. The solvent is evaporated and the residue chromatographed. Elution with toluene/Et_2O affords 0.4 g (68%) of IXe.

Synthesis of IXf. A degassed solution of 0.45 g (1 mmol) VIIIc and 1.5 g (27 mmol) of 2-butyne in 120 ml benzene is irradiated for 3 h. Chromatographic separation as described above yields 0.2 g (40%) of IXf.

Reactions of complex X

Synthesis of XIb. A degassed solution of 0.46 g (1 mmol) of X and 2 g (36 mmol) of 2-butyne in 150 ml of toluene is irradiated for 24 h. The solution is filtered, evaporated and the residue chromatographed. Elution with toluene/n-hexane affords 0.12 g (20%) of XIb, unreacted X (0.1 g), and 0.05 g of the ferrole $(CH_3C_2CH_3)_2Fe_2(CO)_6$ [23].

Synthesis of XIc. A mixture of 0.46 g (1 mmol) of X and 1 g (5.6 mmol) diphenylacetylene is heated in 8 ml of toluene of 20 h at 90°C. On cooling to room temperature XIc precipitates; recrystallisation from Et_2O/n-hexane yields 0.32 g (50%) of XIc.

Synthesis of XId. Complex X (0.4 g, 1 mmol) and 0.5 g (3.5 mmol) of dimethyl acetylenedicarboxylate are heated in 6 ml of toluene for 8 h at 70°C. Chromatographic work up (eluting agent toluene/Et_2O) affords 0.12 g (20%) of XId and 0.1 g of the ferrole $(CH_3OOCC_2COOCH_3)_2Fe_2(CO)_6$ [23].

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