CO Activation in the Reactions of Iron Carbonyls and Alkynes. Syntheses, Crystal Structures,† and Nuclear Magnetic Resonance Studies on Hydroxyferrole and Maleoyliron Derivatives

By **Silvio Aime, Luciano Milone,** and **Enrico Sappa,*** Istituto di Chimica Generale ed Inorganica dell'Università, Corso M. D'Azeglio 48, Torino, Italy
Antonio Tiripicchio and **Anna Maria Manotti Lanfredi,** Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., via M. D'Azeglio 85, Parma, Italy

New syntheses are described for the complexes $[Fe_2(CO)_6\{C_4(OH)_2RR'\}]$ (' sawhorse ' geometry), and $[Fe(CO)_4\{(CO)_2C_2RR'\}]$; the former are obtained in anhydrous hydrocarbon solvents, and the latter in alkaline methanolic solutions. The structures of $[Fe_2(CO)_6\{C_2(OH)Et\}_2]$ and $[Fe(CO)_4\{(CO)_2C_2Et_2\}]$ have been determined by *X*-ray diffraction methods; crystals of the binuclear derivative are monoclinic, space group $P2_1/c$, with $Z = 4$, in a unit cell of dimensions: $a = 13.392(8)$, $b = 16.242(9)$, $c = 7.617(8)$ Å, $\beta = 96.05(8)°$; crystals of the mononuclear derivative are tetragonal, space group $I4_1/a$ with $Z = 16$, in a unit cell of dimensions: $a = 20.819(12)$, $c = 12.950(9)$ Å. The structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.038$ and 0.036 respectively. Both complexes contain a five-membered heterocyclic ring formed upon CO activation. The ^1H and ^{13}C n.m.r. spectra indicate CO fluxionality in the binuclear derivative. Chemical and structural relationships between these complexes are discussed and some comments made on CO activation, in the formation of the heterocyclic rings.

THE reactions of iron carbonyls and alkynes have been studied both in hydrocarbon solvents, and in aqueous alkaline solutions. A large number of tetra-, tri-, bi-, and mononuclear derivatives were obtained, among which were some complexes containing ketonic CO,[1-3] as well as CO groups inserted between the metal and the organic moieties;[1,2,4] thus CO activation is not an uncommon feature of these reactions.

We have recently obtained, in n-heptane solution, a carboxylic derivative, $[Fe_2(CO)_6\{(C_2Et_2)CO_2\}]$,[5] in which CO activation, to give a CO_2 group, is hypothesized. We report now the synthesis, the crystal structure, and the fluxionality of two classes of complexes in which CO activation is achieved: $[Fe_2(CO)_6\{C_2(OH)R\}_2]$ (1), which are hydroxyferrole derivatives,[6] and $[Fe(CO)_4\{(CO)_2C_2RR'\}]$ (2), ' maleoyliron ' derivatives.

Complexes (1) were first obtained by reacting, in aqueous alkaline solution, iron carbonyls and alkynes;[7,8] the *X*-ray structure of $[Fe_2(CO)_6\{C_2(OH)Me\}_2]$,[9] characterized by a tricarbonylferrole–iron tricarbonyl ensemble, has been determined. This ensemble is quite common in iron carbonyl chemistry; it has been established for various complexes obtained from $[Fe_3(CO)_{12}]$ and alkynes, namely $[Fe_2(CO)_6(C_2Ph_2)]$,[10] $[Fe_2(CO)_6(C_{12}H_{16})]$,[11] $[Fe_2(CO)_6(C_4H_4)]$,[12] $[Fe(CO)_3(PhC_2C_6H_4C_2Ph)_2Fe(CO)]$,[13] and $[Fe_2(CO)_5(PPh_3)(C_4Ph_4)]$.[14] Additionally it has been found in the product of the reaction of $SiMe_3I$ and $Na[Fe(CO)_4]$ in tetrahydrofuran, $[Fe_2(CO)_6(COSiMe_3)_4]$,[15] and in one of the products of the reaction of $[Fe_2(CO)_6\{C_4(OMe)_2H_2\}]$ with diphenyldiazomethane under u.v. irradiation, *i.e.* tricarbonyl[π-1,1,1-tricarbonyl-5-(diphenylmethyl)-2,3-dimethoxyferracyclopentadiene]iron.[16]

Two structures were found in the ferrole complexes, the ' non-sawhorse ' and the ' sawhorse '.[6] The former is characterized by the CO groups in staggered position and by a semi-bridging CO group (sb-CO) between the two iron atoms, whereas the latter, which is less common, has eclipsed CO groups without a sb-CO. The sb-CO was considered a stabilizing factor[17] of the structure; indeed, among the above complexes, only the tricarbonyl[π-1,1,1-tricarbonyl-5-(diphenylmethyl)-2,3-dimethoxyferracyclopentadiene]iron[16] has the ' sawhorse ' structure. However this structure has been determined for the osmium derivatives $[Os_2(CO)_6\{C_2(H)Me\}_2]$[18] and $[Os_2(CO)_6(C_8H_{10})]$.[19]

The ferracyclopentadiene moiety is present in complexes (2), which were originally synthesized from $[Fe_3(CO)_{12}]$ and alkynes in hydrocarbon solvents, sometimes under pressure, and were characterized by chemical means.[20,21] Structural evidence was reported only for $[Fe(CO)_4\{(CO)_2C_4Me_2\}]$ (2f)[22] obtained from $[Fe(CO)_5]$ and dimethyldiacetylene in thf under u.v. irradiation. These derivatives can also be obtained upon acidic oxidation of hydroxyferrole derivatives (1);[7] thus complexes (1) and (2) are both structurally and chemically related.

We now report new syntheses for complexes (1) and (2); complexes (1) have been obtained in non-polar media, by reacting $[Fe_3(CO)_{12}]$ and alkynes in anhydrous n-heptane, together with minor quantities of (2). Both (1) and (2) were obtained in a very fast reaction by treating $[Fe(CO)_5]$ and solid NaOH with alkynes in refluxing methanol; this method avoids the preparation of $[Fe_3(CO)_{12}]$, the long reaction times required when aqueous alkaline solutions were reacted, and, finally, avoids u.v. irradiation. A comparable procedure has been recently reported for the synthesis of $[HFe(CO)_4]^-$.[23]

The *X*-ray structure of the hydroxy-derivative $[Fe_2(CO)_6\{C_2(OH)Et\}_2]$ (1a) shows that this complex belongs to the ' sawhorse ' geometry and lacks the sb-CO, and thus is different from the only other hydroxy-derivative known, $[Fe_2(CO)_6\{C_2(OH)Me\}_2]$,[9] although their stabilities are comparable.

The *X*-ray structure of $[Fe(CO)_4\{(CO)_2C_2Et_2\}]$ (2a) is

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† Of the compounds μ-(1-4-η-2,3-diethyl-1,4-dihydroxybutadiene-1,4-diyl $C^1C^4(Fe^1)$:$\eta^4(Fe^2)$-bis(tricarbonyliron) and tetracarbonyl(2,3-diethyl-1,4-dioxobut-2-ene-1,4-diyl)iron.

comparable with that of $[Fe(CO)_4\{(CO)_2C_4Me_2\}]$ (2f).[22] Structural relationships between (1a) and (2a) are discussed later.

Homologues of (1a) and (2a) with other alkynes have also been prepared, which were characterized by instrumental and mass spectral analyses; thus the new synthetic methods reported are shown to be of general application to C_2R_2 and RC_2R' alkynes.

EXPERIMENTAL

Synthesis in n-Heptane Solutions.—Refluxing $[Fe_3(CO)_{12}]$ with a two-fold molar excess of hex-3-yne in distilled n-heptane, under dry nitrogen for 45 min, yielded the orange-yellow complex (1a) (5% with respect to the iron carbonyl); the alkyne was purchased from K & K, and the iron carbonyl, prepared by literature methods,[24] contained trace amounts of moisture. The reaction mixture was filtered, the solvent removed under reduced pressure and the residue, dissolved in $CHCl_3$, purified on preparative t.l.c. plates (Kieselgel PF, eluant ether–light petroleum). The other major reaction products have already been reported; [5] significant is the presence, among them, of the orange $[Fe_2(CO)_6(C_2Et_2)_2]$ ferrole, ' non-sawhorse ' derivative (3), and of the black $[Fe_3(CO)_9(C_2Et_2)]$, (4).

The fraction containing (1a) was further purified by t.l.c.; from these runs, small quantities of yellow (2a) were recovered. The purified platelets (1a) were dissolved in $CHCl_3$–n-heptane (1 : 1), and set aside for several days at -5 °C. Well formed crystals were deposited, but partial decomposition also occurred; storage of the crystals at -20 °C partly prevents superficial decomposition.

Similar reaction conditions afforded hydroxyferrole derivatives of but-2-yne (Fluka), (1b), but-1-yne (Matheson Gas Products), (1c), pent-1-yne (Fluka), (1d), and isopropenylacetylene (Fluka), (1e) [Found: C, 40.15; H, 2.95; Fe, 26.4; O, 30.5 Calc. for $C_{14}H_{12}Fe_2O_8$ (1a): C, 40.05; H, 2.90; Fe, 26.6; O, 30.5. Found: C, 36.9; H, 2.15; Fe, 28.55; O, 32.4. Calc. for $C_{12}H_8Fe_2O_8$ (1b): C, 36.8; H, 2.05; Fe, 28.5; O, 32.65. Found: C, 36.8; H, 2.15; Fe, 28.65; O, 32.4. Calc. for (1c): see (1b). Found: C, 39.0; H, 2.55; Fe, 27.4; O, 31.05. Calc. for $C_{13}H_{10}Fe_2O_8$ (1d): C, 38.45; H, 2.50; Fe, 27.55; O, 31.5. Found: C, 38.85; H, 2.10; Fe, 27.75; O, 31.25. Calc. for $C_{13}H_8Fe_2O_8$ (1e): C, 38.65; H, 2.00; Fe, 27.65; O, 31.7%].

Reactions of $[Fe(CO)_5]$ *in Alkaline Methanol Solution.*—A solution of $[Fe(CO)_5]$ (2 ml, *ca.* 10 mM) (Fluka) in methanol (200 ml) was saturated with dry nitrogen, then solid NaOH (drops) (1 g, 25 mmol) was added, and the solution vigorously stirred for 15 min; but-2-yne, hex-3-yne, pent-1-yne, or isopropenylacetylene (1 ml) was then added, or gaseous but-1-yne was bubbled into the solution, which was refluxed for 30 min. After cooling, the brown residue was filtered off and the solvent removed *in vacuo*; the residue was dissolved in $CHCl_3$ and subjected to preparative t.l.c. Seven to ten products were usually obtained, including complexes (1) (probably in more than one isomeric form) and (2), both in *ca.* 5% yields with respect to the iron carbonyl. Investigations as to whether the isomerism of the complexes (1) is due to the substitution of the organic moiety, or to the ' non-sawhorse '–' sawhorse ' geometry, are in progress.

All complexes (2) are crystalline, yellow solids; (2a) was obtained as crystals suitable for *X*-ray analysis by allowing a saturated n-heptane–$CHCl_3$ solution to cool at -10 °C [Found: C, 47.1; H, 3.45; Fe, 18.65; O, 30.75. Calc. for $C_{12}H_{10}FeO_6$ (2a) (obtained from hex-3-yne): C, 47.1; H, 3.30; Fe, 18.25; O, 31.35. Found: C, 43.5; H, 2.25; Fe, 20.0; O, 34.3. Calc. for $C_{10}H_6FeO_6$ (2b) (obtained from but-2-yne): C, 43.2; H, 2.15; Fe, 20.1; O, 34.55. Found: C, 43.5; H, 2.35; Fe, 20.2; O, 34.0. Calc. for (2c) (obtained from but-1-yne): see (2b). Found: C, 47.2; H, 3.35; Fe, 18.05; O, 31.4. Calc. for (2d) (obtained from pent-1-yne): see (2a). Found: C, 45.7; H, 2.15; Fe, 19.4; O, 32.75. Calc. for $C_{11}H_6FeO_6$ (2e) (obtained from isopropenylacetylene): C, 45.55; H, 2.10; Fe, 19.25; O, 33.1%].

Other Reactions.—*Thermal decomposition of* (4) *in the presence of* N_2, CO, H_2O, *and* H_2. Refluxing (4) in n-heptane under dry nitrogen (40 min) yielded small quantities of (1a), whereas under CO flow (same conditions) this product is not obtained. Refluxing (4) (n-heptane, 60 min) under flowing H_2 led to considerable decomposition. When (4) was refluxed in the presence of distilled water (2 ml) (light petroleum, 120 min, dry nitrogen atmosphere) (1a) was not obtained.

Thermal decomposition of (1a) *under* N_2 *and* CO. Refluxing (1a) (n-heptane, 60 min) under dry nitrogen yielded *ca.* 15% of (2a), with extensive decomposition. To obtain ^{13}CO-enriched (1a), (1a) was set aside in sealed vials for 4 d at 40 °C under 15 mmHg * of ^{13}CO, in n-heptane; this yielded $>40\%$ of (2a) selectively enriched in ^{13}CO (see later), with some decomposition.

Analysis of the Products.—The elementary analyses were performed by means of an F & M 185 C, H, N Analyzer and a model 303 Perkin-Elmer Atomic Absorption Spectrophotometer. The i.r. spectra were recorded on a Beckman IR-12 spectrometer (KBr optics) in n-heptane solutions. The mass spectra of complexes (1) have been discussed, together with those of $[Fe_2(CO)_6\{(C_2Et_2)CO_2\}]$ and (4); [25] these, and the ones of complexes (2) were registered on a Varian CH-5 single-focusing instrument operating with an electron-impact ion source and direct inlet system, at 70 eV. The ^1H n.m.r. spectra were recorded on a JEOL C 60 HL instrument in $CDCl_3$ solutions; the ^{13}C n.m.r. spectra were recorded on a JEOL PS 100 FT instrument in the Fourier-transform mode at 25.1 MHz, using $CDCl_3$ as solvent, and in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate) as a shift-relaxation reagent.

Crystal Data.—(1a). $C_{14}H_{12}Fe_2O_8$, $M = 419.94$, Monoclinic, $a = 13.392(8)$, $b = 16.242(9)$, $c = 7.617(8)$ Å, $\beta = 96.05(8)°$, $U = 1\,648(2)$ Å^3, $D_c = 1.693$ g cm^{-3}, $Z = 4$, $F(000) = 848$, Mo-K_α radiation, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 17.97 cm^{-1}, space group $P2_1/c$ from systematic absences.

(2a). $C_{12}H_{10}FeO_6$, $M = 306.05$, Tetragonal, $a = 20.819(12)$, $c = 12.950(9)$ Å, $U = 5\,613(5)$ Å^3, $D_c = 1.449$ g cm^{-3}, $Z = 16$, $F(000) = 2\,496$, Mo-K_α radiation, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 10.88 cm^{-1}, space group $I4_1/a$ from systematic absences.

Preliminary unit-cell parameters, determined from rotation and Weissenberg photographs, were refined by a least-squares procedure minimizing the differences between the observed and calculated θ values for 16 (1a) and 14 (2a) reflections carefully measured on a Siemens AED single-crystal diffractometer.

Intensity data. Intensity data were collected on the same diffractometer by using Zr-filtered Mo-K_α radiation

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* Through this paper 1 mmHg $\approx 13.6 \times 9.8$ Pa.

and the ω—2θ scan technique. A flattened prismatic crystal of (1a) (of dimensions *ca.* 0.15 × 0.30 × 0.40 mm) and a prismatic crystal of (2a) (of dimensions 0.20 × 0.25 × 0.50 mm) were aligned with their c axis parallel to the ϕ axis of the diffractometer and all the reflections in the range of $3 < \theta < 29°$ for (1a) and $2.7 < \theta < 26°$ for (2a) were measured. Of 4 394 (1a) and 2 756 (2a) independent reflections, 3 288 (1a) and 1 616 (2a) were considered observed, having $I > 2\sigma(I)$, and used in the final analysis. The intensity data were corrected for Lorentz and polarization factors, but no absorption correction was applied because of the low value of μR. The absolute scale and the mean temperature factor were determined by Wilson's method.

Structure determination and refinement. The structures were solved by Patterson and Fourier methods and the refinements were carried out by means of the SHELX system of computer programs.[26] Some cycles of full-matrix least squares using anisotropic thermal parameters for all the non-hydrogen atoms were computed for both structures. The subsequent ΔF maps revealed clearly the positions of all the hydrogen atoms. Further least-squares cycles were then computed, including the hydrogen atoms with isotropic thermal parameters. Unit weights were used at each stage of the refinement by analyzing the variation of $|\Delta F|$ as a function of $|F_o|$.

Atomic scattering factors (corrected for the anomalous dispersion of Fe) were taken from ref. 27. The final R was 0.038 for (1a) and 0.036 for (2a) (observed reflections only). Final atomic co-ordinates for (1a) and (2a) are given in Tables 1 and 2 respectively. Thermal parameters of the atoms and a list of calculated and observed structure factors for (1a) and (2a) are available from the authors on request, and are also deposited as Supplementary Publication No. SUP 22536 (34 pp.).*

All the calculations were carried out on a CYBER 76 computer at Centro di Calcolo Elettronic Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna).

RESULTS

I.r. Spectra.—For complexes (1), the following absorptions in the CO stretching region were observed: (1a), 2 064m, 2 024vs, 1 995s(sh), 1 990s, and 1 970m(sh) cm^{-1}; (1b), 2 074m—s, 2 042s, 2 018vs, and 1 987vs(br) cm^{-1}; (1c), 2 065m, 2 047m, 2 025vs, and 1 990vs(br) cm^{-1}; (1d), 2 064s, 2 047s, 2 023vs, and 1 990vs(br) cm^{-1}; (1e), 2 064s, 2 048s, 2 025vs, and 1 992vs(br) cm^{-1}. For all these complexes a broad absorption in the 3 400—3 300 cm^{-1} range due to the OH groups was also observed; this band does not sharpen when CCl$_4$ is used as solvent instead of n-heptane.

For complexes (2) the following absorptions in the CO stretching region were observed: (2a), 2 106s, 2 043vs, 2 018vs, 1 968w, and 1 644m cm^{-1}; (2b), 2 109s, 2 046vs, 2 021vs, 1 990w, and 1 636m cm^{-1}; (2c), 2 105s, 2 041vs, 2 020vs, 1 988w, and 1 640m cm^{-1}; (2d), 2 110s, 2 047vs, 2 023vs, 1 986w, and 1 658m cm^{-1}; (2e), 2 109s, 2 048vs, 2 024vs, 2 000w, and 1 654m cm^{-1}; (2f), 2 116m, 2 058s, 2 037s, and 1 668s cm^{-1}.[22]

Mass Spectra.—The mass spectra of complexes (1) have been discussed in detail elsewhere.[25] In the mass spectrum of (2a) the following ions were observed: m/e 304 (10%), $[\mathrm{Fe(CO)_6(C_6H_8)}]^+$; 276 (114), $[\mathrm{Fe(CO)_5(C_6H_8)}]^+$; 248 (18),

TABLE 1

Fractional atomic co-ordinates (× 10^4 for Fe, O, C; × 10^3 for H) for the compound (1a) with estimated standard deviations in parentheses

	x/a	y/b	z/c
Fe(1)	−1 318(1)	1 541(1)	908(1)
Fe(2)	290(1)	2 346(1)	653(1)
O(1)	−1 116(4)	73(2)	−1 274(6)
O(2)	−1 061(4)	636(2)	4 282(5)
O(3)	−3 466(4)	1 691(3)	567(7)
O(4)	1 096(4)	1 234(3)	−1 878(6)
O(5)	1 142(4)	1 550(3)	3 927(5)
O(6)	1 828(3)	3 612(3)	587(9)
O(7)	−1 184(3)	1 987(2)	−2 862(4)
O(8)	−1 052(3)	2 778(2)	3 832(4)
C(1)	−1 205(4)	626(3)	−378(7)
C(2)	−1 161(4)	977(3)	2 966(6)
C(3)	−2 616(4)	1 626(3)	705(7)
C(4)	789(4)	1 667(4)	−864(7)
C(5)	808(4)	1 855(3)	2 647(7)
C(6)	1 228(4)	3 109(4)	610(8)
C(7)	−1 081(3)	2 220(3)	−1 094(5)
C(8)	−818(3)	3 053(2)	−793(5)
C(9)	−780(3)	3 254(2)	1 048(5)
C(10)	−1 026(3)	2 576(3)	2 096(5)
C(11)	−660(4)	3 663(3)	−2 335(6)
C(12)	−1 631(5)	4 064(4)	−2 987(9)
C(13)	−611(4)	4 106(3)	1 817(7)
C(14)	−1 610(6)	4 544(4)	1 954(9)
H(7)	−143(4)	144(3)	−283(7)
H(8)	−122(4)	237(3)	449(7)
H(111)	−32(4)	344(3)	−326(7)
H(112)	−18(4)	408(3)	−189(7)
H(121)	−208(4)	431(3)	−228(7)
H(122)	−224(4)	366(3)	−355(7)
H(123)	−163(4)	439(3)	−377(7)
H(131)	−20(4)	408(3)	306(7)
H(132)	−22(4)	439(3)	122(7)
H(141)	−217(4)	418(3)	269(7)
H(142)	−221(4)	460(3)	73(7)
H(143)	−160(4)	492(3)	244(7)

TABLE 2

Fractional atomic co-ordinates (× 10^4 for Fe, O, C; × 10^3 for H) for the compound (2a), with estimated standard deviations in parentheses

Fe	4 238(1)	5 080(1)	3 159(1)
O(1)	4 181(2)	5 837(2)	5 096(3)
O(2)	4 391(2)	6 245(2)	1 929(4)
O(3)	2 849(2)	4 862(2)	2 845(4)
O(4)	4 429(2)	3 812(2)	4 094(3)
O(5)	5 522(2)	5 403(2)	3 774(3)
O(6)	3 987(2)	4 425(2)	1 242(3)
C(1)	4 194(3)	5 535(3)	4 372(5)
C(2)	4 307(3)	5 795(3)	2 403(4)
C(3)	3 376(3)	4 968(3)	2 984(4)
C(4)	4 352(3)	4 307(3)	3 756(4)
C(5)	5 199(2)	5 127(3)	3 142(4)
C(6)	5 496(2)	4 787(3)	2 250(4)
C(7)	5 093(2)	4 521(2)	1 585(4)
C(8)	4 402(2)	4 609(2)	1 826(4)
C(9)	6 216(3)	4 824(3)	2 149(6)
C(10)	6 394(4)	5 454(4)	1 623(7)
C(11)	5 265(4)	4 145(3)	634(5)
C(12)	5 294(5)	3 429(4)	865(7)
H(91)	636(2)	446(2)	177(4)
H(92)	638(2)	479(2)	288(4)
H(101)	681(2)	548(2)	156(4)
H(102)	622(2)	582(2)	212(4)
H(103)	623(2)	537(2)	87(4)
H(111)	495(2)	419(2)	16(4)
H(112)	573(2)	425(2)	45(4)
H(121)	490(2)	328(2)	111(4)
H(122)	534(2)	324(2)	27(4)
H(123)	570(2)	338(2)	135(4)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

$[Fe(CO)_4(C_6H_8)]^+$; 220 (212), $[Fe(CO)_3(C_6H_8)]^+$; 208 (35); $[Fe(CO_2(O)(C_6H_8)]^+$; 196 (44), $[Fe(CO)_5]^+$; 192 (100), $[Fe(CO)_2(C_6H_8)]^+$; 164 (66), $[Fe(CO)(C_6H_8)]^+$; 152 (98), $[Fe(O)(C_6H_8)]^+$; 140 (99), $[Fe(CO)_3]^+$; 136 (125), $[FeC_6H_8]^+$; 110 (102), $[C_6H_{10}(CO)]^+$; 84 (175), $[Fe(CO)]^+$; 82 (106), $[C_6H_{10}]^+$; and 56 (144), Fe^+. In the mass spectrum of (2b), the following ions were observed; *m/e* 278 (29%), $[Fe(CO)_6(C_4H_6)]^+$; 250 (114), $[Fe(CO)_6(C_4H_4)]^+$; 248 (10), $[Fe(CO)_5(C_4H_6)]^+$; 222 (29), $[Fe(CO)_4(C_4H_6)]^+$; 194 (64), $[Fe(CO)_3(C_4H_6)]^+$; 166 (100), $[Fe(CO)_2(C_4H_6)]^+$; 164 (12), $[Fe(CO)_2(C_4H_4)]^+$; 140 (86), $[Fe(CO)_3]^+$; 138 (429), $[Fe(CO)(C_4H_6)]^+$; 112 (50), $[Fe(CO)_2]^+$; 110 (214), $[C_4H_6(CO)_2]^+$; 84 (101); $[Fe(CO)]^+$; and 56 (114), Fe^+. In the mass spectrum of (2d) the following ions were observed; *m/e* 282 (7%), $[Fe(CO)_6(C_5H_8)]^+$; 254 (187), $[Fe(CO)_5(C_5H_8)]^+$; 226 (31), $[Fe(CO)_4(C_5H_8)]^+$; 198 (203), $[Fe(CO)_3(C_5H_8)]^+$; 170 (100), $[Fe(CO)_2(C_5H_8)]^+$; 168 (20), $[Fe(CO)_4]^+$; 142 (117), $[Fe(CO)(C_5H_8)]^+$; 140 (42), $[Fe(CO)_3]^+$; 114 (365), $[FeC_5H_8]^+$; 112 (171), $[Fe(CO)_2]^+$; 84 (283), $[Fe(CO)]^+$; and 56 (240), Fe^+. The metastable ions support the proposed fragmentation.

^1H *N.M.R. Spectra*.—Complex (1a) shows the following spectrum: τ 7.55 and 7.58 (4 H, CH_2), 8.82 and 8.84 (6 H, Me), and a broad band centred at 5.43 (2 H, OH). Complex (2a) shows the following spectrum: τ 7.75 q (4 H, q, CH_2) and 9.10 (6 H, t, Me). Complex (2d), which is asymmetrically substituted, shows the following spectrum: τ 260(s, 1 H), 7.50(q, 2 H, CH_2), and 7.80(q) and 8.95(t) (τ 5 H, CH_2 and CH_3). Noteworthy is the low-field chemical shift of the acetylenic hydrogen.

^{13}C *N.M.R. Spectra*.—*Complex* (1a). The spectrum, recorded at room temperature, shows six resonances at 211.5, 210.6, 206.1, 106.1, 18.7, and 13.5 p.p.m. The two high-field resonances are assigned to the ethyl group from the off-resonance spectrum; the peak centred at 106.1 p.p.m. (broad singlet in the ^1H-coupled spectrum) is attributed to the carbon atom bearing the ethyl group. According to the ^{13}C data reported for the carbonyl region of various ferrole derivatives,[28-30] three resonances are expected, with integrated intensities 3 : 1 : 2 from low to high field. These resonances are, from low to high field, due to the rapidly scrambling carbonyl bound to the iron which is π-bonded to the organic moiety, to the unique carbonyl, and to the two equivalent carbonyls attached to the iron of the ferrole moiety. The three downfield resonances observed for (1a) are in the ratio 3 : 3.4 : 2. The signal at 210.6 p.p.m. is then due to the fortuitous superposition of the unique carbonyl in the $Fe_2(CO)_6$ core and of the carbons σ-bonded to one metal and π-bonded to the other. Similar low-field shifts have been reported elsewhere for such carbon atoms.[14,28,29]

Complex (2a). The room-temperature spectrum of (2a) shows six resonances, centred at 243.4, 202.6, 199.9, 174.3, 19.3, and 12.5 p.p.m. The two high-field resonances are assigned to the methylene (19.3) and methyl (12.5) groups. The ^1H-coupled spectrum allows the assignment of the Fe(CO) resonances to the two unaffected peaks at 202.6 and 199.9 p.p.m., with integrated intensities of 1 : 1. Of the two remaining resonances, the peak at 174.3 p.p.m. shows broadening due to the C–H residual coupling in the ^1H coupled spectrum, and is thus assigned to the sp^2 carbons bearing the ethyl groups. The lowest-field signal is then attributed to the ketonic carbons.

Structures of the Complexes.—*Complex* (1a). The structure of (1a) is represented in Figure 1; the bond distances and angles not involving the hydrogen atoms are given in Table 3. As in other ferrole derivatives, this complex is formed by two different iron atoms, one of which, through two σ bonds, is bound to the organic moiety forming a tricarbonylferracyclopentadiene ring, whereas the other is π-bonded to this ring (Figure 2). The structural parameters in the ferrole moiety are comparable with those

TABLE 3

Bond distances (Å) and angles (°) not involving hydrogen atoms for (1a) with estimated standard deviations in parentheses

(*a*) In the co-ordination sphere of the iron atoms

Fe(1)–Fe(2)	2.544(3)	Fe(2)–C(5)	1.789(6)
Fe(1)–C(1)	1.795(5)	Fe(2)–C(6)	1.767(6)
Fe(1)–C(2)	1.809(5)	Fe(2)–C(7)	2.161(4)
Fe(1)–C(3)	1.734(6)	Fe(2)–C(8)	2.095(4)
Fe(1)–C(7)	1.935(5)	Fe(2)–C(9)	2.100(4)
Fe(1)–C(10)	1.930(5)	Fe(2)–C(10)	2.205(5)
Fe(2)–C(4)	1.778(6)		
Fe(2)–Fe(1)–C(1)	105.3(2)	C(4)–Fe(2)–C(5)	97.9(3)
Fe(2)–Fe(1)–C(2)	107.7(2)	C(4)–Fe(2)–C(6)	96.1(3)
Fe(2)–Fe(1)–C(3)	143.2(2)	C(4)–Fe(2)–C(7)	83.9(2)
Fe(2)–Fe(1)–C(7)	55.7(2)	C(4)–Fe(2)–C(8)	107.0(2)
Fe(2)–Fe(1)–C(10)	57.1(2)	C(4)–Fe(2)–C(9)	146.9(2)
C(1)–Fe(1)–C(2)	92.6(2)	C(4)–Fe(2)–C(10)	143.5(2)
C(1)–Fe(1)–C(3)	99.1(2)	C(5)–Fe(2)–C(6)	96.6(3)
C(1)–Fe(1)–C(7)	90.7(2)	C(5)–Fe(2)–C(7)	135.1(2)
C(1)–Fe(1)–C(10)	162.3(2)	C(5)–Fe(2)–C(8)	151.7(2)
C(2)–Fe(1)–C(3)	98.1(2)	C(5)–Fe(2)–C(9)	113.6(2)
C(2)–Fe(1)–C(7)	163.3(2)	C(5)–Fe(2)–C(10)	84.9(2)
C(2)–Fe(1)–C(10)	92.0(2)	C(6)–Fe(2)–C(7)	127.9(2)
C(3)–Fe(1)–C(7)	97.5(2)	C(6)–Fe(2)–C(8)	94.1(2)
C(3)–Fe(1)–C(10)	97.1(2)	C(6)–Fe(2)–C(9)	90.4(2)
C(7)–Fe(1)–C(10)	30.3(2)	C(6)–Fe(2)–C(10)	119.8(2)
Fe(1)–Fe(2)–C(4)	96.3(2)	C(7)–Fe(2)–C(8)	38.7(2)
Fe(1)–Fe(2)–C(5)	87.8(2)	C(7)–Fe(2)–C(9)	66.8(2)
Fe(1)–Fe(2)–C(6)	166.1(2)	C(7)–Fe(2)–C(10)	69.6(2)
Fe(1)–Fe(2)–C(7)	47.7(2)	C(8)–Fe(2)–C(9)	40.0(2)
Fe(1)–Fe(2)–C(8)	76.3(2)	C(8)–Fe(2)–C(10)	67.1(2)
Fe(1)–Fe(2)–C(9)	75.8(2)	C(9)–Fe(2)–C(10)	38.4(2)
Fe(1)–Fe(2)–C(10)	47.3(2)		

(*b*) In the carbonyl groups

O(1)–C(1)	1.142(6)	O(4)–C(4)	1.152(8)
O(2)–C(2)	1.141(6)	O(5)–C(5)	1.142(7)
O(3)–C(3)	1.137(8)	O(6)–C(6)	1.147(8)
Fe(1)–C(1)–O(1)	175.9(5)	Fe(2)–C(4)–O(4)	178.4(5)
Fe(1)–C(2)–O(2)	178.6(4)	Fe(2)–C(5)–O(5)	179.2(5)
Fe(1)–C(3)–O(3)	179.2(5)	Fe(2)–C(6)–O(6)	179.1(6)

(*c*) In the organic ligand

C(7)–O(7)	1.392(5)	C(9)–C(10)	1.419(6)
C(10)–O(8)	1.366(5)	C(9)–C(13)	1.510(6)
C(7)–C(8)	1.411(6)	C(11)–C(12)	1.512(8)
C(8)–C(9)	1.436(6)	C(13)–C(14)	1.529(9)
C(8)–C(11)	1.511(6)		
C(8)–C(7)–Fe(1)	118.5(3)	C(10)–C(9)–Fe(2)	74.8(2)
C(8)–C(7)–Fe(2)	68.1(2)	C(10)–C(9)–C(8)	112.7(3)
C(8)–C(7)–O(7)	114.6(4)	C(13)–C(9)–Fe(2)	128.5(3)
Fe(1)–C(7)–Fe(2)	76.6(2)	C(13)–C(9)–C(8)	125.1(3)
Fe(1)–C(7)–O(7)	126.9(3)	Fe(2)–C(9)–C(8)	69.8(2)
Fe(2)–C(7)–O(7)	127.8(3)	Fe(1)–C(10)–Fe(2)	75.6(2)
C(9)–C(8)–C(11)	124.6(3)	Fe(1)–C(10)–O(8)	129.7(3)
C(9)–C(8)–Fe(2)	70.2(2)	Fe(1)–C(10)–C(9)	117.4(3)
C(9)–C(8)–C(7)	111.1(3)	Fe(2)–C(10)–O(8)	128.8(3)
C(11)–C(8)–Fe(2)	126.6(3)	Fe(2)–C(10)–C(9)	66.8(2)
C(11)–C(8)–C(7)	124.2(4)	O(8)–C(10)–C(9)	112.9(4)
Fe(2)–C(8)–C(7)	73.2(2)	C(12)–C(11)–C(8)	112.2(5)
C(10)–C(9)–C(13)	121.8(4)	C(14)–C(13)–C(9)	110.9(5)

(*d*) Hydrogen bond

O(8) · · · O(7) (x, y, $1 + z$)	2.849(5)	O(8)–H(8)–O(7) (x, y, $1 + z$)	143(4)
H(8) · · · O(7) (x, y, $1 + z$)	2.10(3)	H(8)–O(8)–O(7) (x, y, $1 + z$)	26(3)

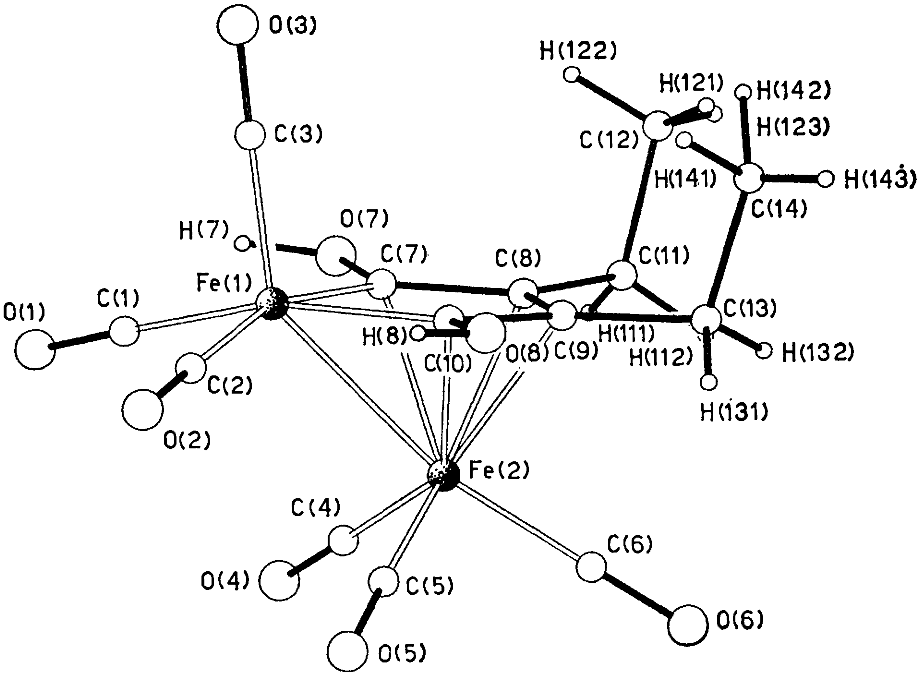


FIGURE 1 Perspective view showing the molecular shape and the atomic numbering of the compound $[Fe_2(CO)_6\{C_2(OH)Et\}_2]$

found in the other derivatives containing this structure.[11-14] The double bond is delocalized over the three C–C bonds as shown by the equal distances (1.411, 1.419, and 1.436 Å).

The carbonyls are eclipsed and all terminal (the Fe–C–O angles being in the range 175.9—179.2°). The whole heterocycle Fe(1)–C(7)–C(8)–C(9)–C(10) is nearly planar, with the carbon atoms perfectly coplanar and the iron atom a little out of the plane. The equation of the mean plane passing through the carbon atoms C(7)–C(8)–C(9)–C(10) is $-0.956\,8X + 0.258\,6Y - 0.132\,3Z = 2.345\,6$, where X, Y, and Z are orthogonal co-ordinates, obtained from the fractional ones by applying the matrix $||a, 0, c\cos\beta|0, b, 0|0, 0\ c\sin\beta||$. The displacements of C(7), C(8), C(9), C(10), Fe(1), O(7), O(8), C(11), and C(13) are −0.002, 0.004, −0.004, 0.002, −0.031, 0.073, 0.080, 0.091, and 0.120 Å respectively.

A shortening of the Fe–C distance for the CO bonded to Fe(1) and nearly perpendicular to the heterocycle is observed [Fe(1)–C(3) = 1.734 Å]. This feature has been observed in the other ferrole derivatives, regardless of

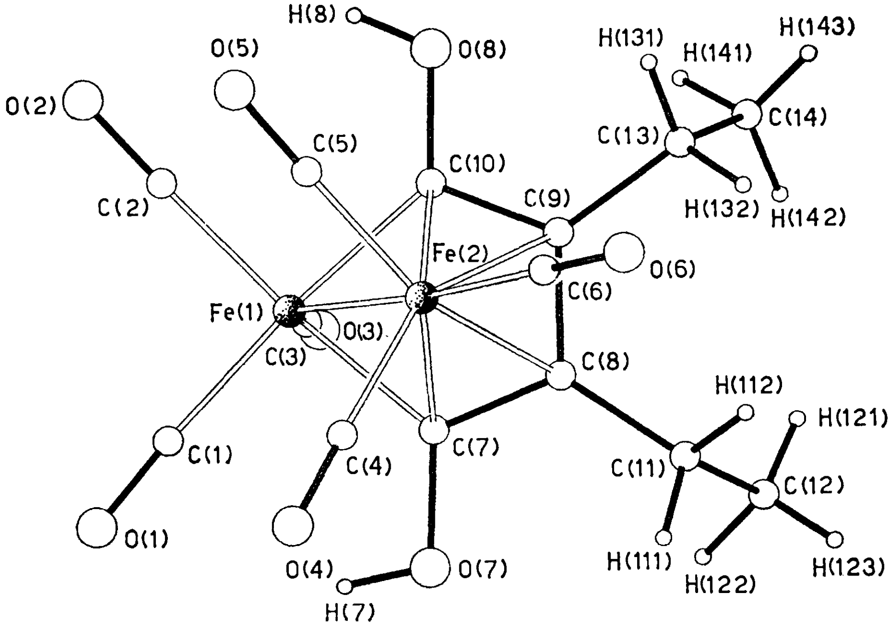


FIGURE 2 Bonding of the organic ligand to the two iron atoms, with formation of a five-membered heterocycle, in the compound $[Fe_2(CO)_6\{C_2(OH)Et\}_2]$

whether they have the ' sawhorse ' or ' non-sawhorse ' structures. We consider that this effect is electronic; indeed it does not depend on the Fe–Fe distance, whether the carbonyls are staggered or eclipsed, or on the existence of a sb-CO. However, the presence of a heteroatom in the organic ring,[30] or the presence of π-bonded nickel instead of iron,[31] influence considerably the Fe(σ)–C distance. As it has been shown that PPh_3 will replace this carbonyl,[14] and considering that PPh_3 is a better σ-donor but a weaker π-acceptor than CO, we believe that the shortening is due to an increased electron donation from CO to Fe, in order to balance the electron deficiency of the metal.

The $Fe(CO)_3$ moiety, which is π-bonded to the ferrole ring, is disposed as reported for tricarbonyl[π-1,1,1-tricarbonyl-5-(diphenylmethyl)-2,3-dimethoxyferracyclopentadiene]-iron,[16] that is with the carbonyl groups eclipsed with respect to the carbonyl of the heterocyclic iron. The eclipsed configuration is not due to the Fe–Fe bond length or the C–C bond lengths in the ring; the latter have been shown to be comparable (with few exceptions) in all these derivatives, and the Fe–Fe distances all fall close to 2.50 Å, which is in the middle of the Fe–Fe bond lengths found in binuclear iron derivatives. Theoretical calculations,[6] on the other hand, also showed that very little energy differences exist between the ' sawhorse ' and ' non-sawhorse ' geometries. In the ' sawhorse ' derivatives, *e.g.* (1a), no sb-CO is expected for steric reasons; however, no large variation in either the Fe–Fe bond length or other structural parameters is observed (in trinuclear complexes Fe–Fe bond lengths considerably longer have been reported when sb-CO were present [32–34]) with respect to complexes containing the sb-CO. This is particularly evident when considering the other hydroxyferrole $[Fe_2(CO)_6\{C_2(OH)Me\}_2]$ [9] which has one sb-CO. Thus, this feature is not essential for the stabilization of these derivatives.

TABLE 4

Bond distances (Å) and angles (°) not involving hydrogen atoms for (2a) with estimated standard deviations in parentheses

(*a*) In the co-ordination sphere of the iron atom			
Fe–C(1)	1.837(7)	Fe–C(4)	1.801(6)
Fe–C(2)	1.787(6)	Fe–C(5)	2.003(5)
Fe–C(3)	1.824(7)	Fe–C(8)	2.014(5)
C(1)–Fe–C(2)	92.5(3)	C(2)–Fe–C(8)	85.6(2)
C(1)–Fe–C(3)	97.1(3)	C(3)–Fe–C(4)	93.9(3)
C(1)–Fe–C(4)	95.8(3)	C(3)–Fe–C(5)	171.0(3)
C(1)–Fe–C(5)	92.0(3)	C(3)–Fe–C(8)	89.9(2)
C(1)–Fe–C(8)	172.9(3)	C(4)–Fe–C(5)	85.2(3)
C(2)–Fe–C(3)	96.8(3)	C(4)–Fe–C(8)	84.9(2)
C(2)–Fe–C(4)	165.6(3)	C(5)–Fe–C(8)	81.1(2)
C(2)–Fe–C(5)	82.7(3)		
(*b*) In the carbonyl groups			
O(1)–C(1)	1.129(8)	O(3)–C(3)	1.134(8)
O(2)–C(2)	1.134(8)	O(4)–C(4)	1.131(7)
Fe–C(1)–O(1)	176.9(6)	Fe–C(3)–O(3)	175.6(6)
Fe–C(2)–O(2)	175.7(6)	Fe–C(4)–O(4)	177.3(5)
(*c*) In the organic ligand			
C(5)–O(5)	1.205(7)	C(8)–O(6)	1.210(6)
C(5)–C(6)	1.489(8)	C(7)–C(8)	1.483(6)
C(6)–C(7)	1.324(7)	C(7)–C(11)	1.503(8)
C(6)–C(9)	1.507(8)	C(11)–C(12)	1.522(10)
C(9)–C(10)	1.524(11)		
Fe–C(5)–O(5)	125.0(4)	Fe–C(8)–O(6)	124.6(4)
Fe–C(5)–C(6)	113.6(3)	Fe–C(8)–C(7)	113.9(3)
O(5)–C(5)–C(6)	121.5(4)	O(6)–C(8)–C(7)	121.4(5)
C(5)–C(6)–C(7)	116.1(4)	C(8)–C(7)–C(11)	117.9(5)
C(5)–C(6)–C(9)	117.1(5)	C(8)–C(7)–C(6)	115.2(4)
C(7)–C(6)–C(9)	126.6(5)	C(6)–C(7)–C(11)	126.9(5)
C(6)–C(9)–C(10)	109.0(6)	C(7)–C(11)–C(12)	111.0(6)

Complex (2a). The structure of (2a) is shown in Figure 3; the bond distances and angles not involving the hydrogen atoms are given in Table 4. The complex consists of one iron atom co-ordinated to four terminal CO groups, and to two CO groups inserted between the metal and the alkyne molecule, forming a five-membered heterocyclic ring. The iron is in a slightly distorted octahedral environment.

The Fe–CO (ketonic) bond lengths, 2.003 and 2.014 Å, are in the range of values found for the Fe–C(sp^2) bonds, although slightly shorter than the mean values; this could indicate some π-interaction between these carbons and the metal, and thus explain the low-field resonance in the ^{13}C spectra. Comparable Fe–C distances are observed in $[Fe(CO)_4\{(CO)_2C_4Me_2\}]$.[22]

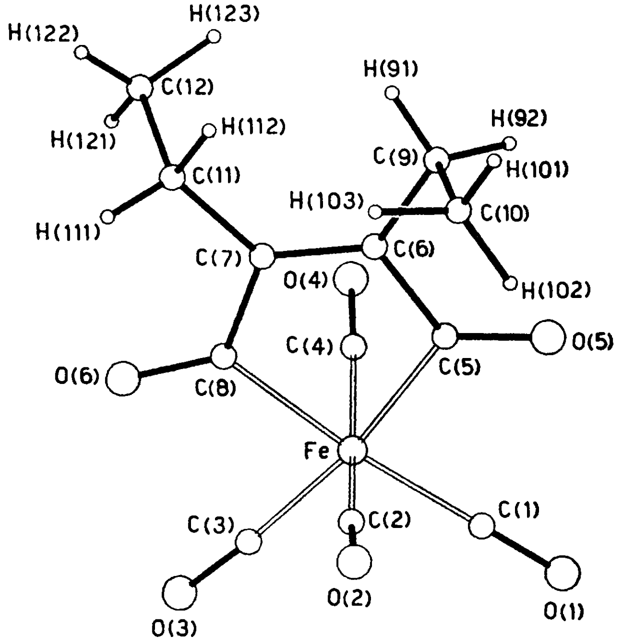
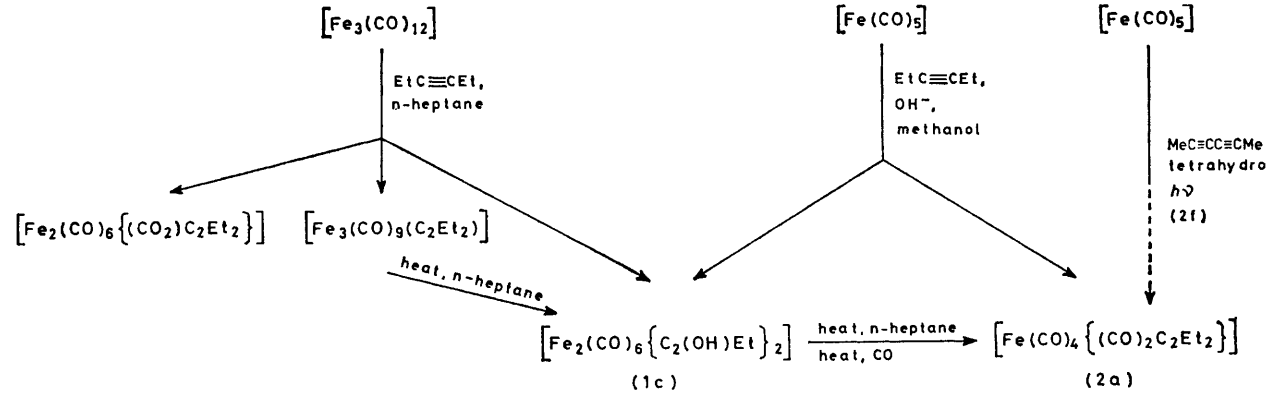


FIGURE 3 Perspective view showing the molecular shape and the atomic numbering of the compound $[Fe(CO)_4\{(CO)_2C_2Et_2\}]$

No delocalization is found in the heterocyclic ring, which thus differs from that in (1a). In this ring of (2a) the carbon atoms C(5), C(6), C(7), and C(8) are perfectly coplanar, with the iron atom slightly out of the plane. The equation of the plane passing through the carbon atoms is $-0.009\,2\,X + 0.848\,2\,Y - 0.529\,7\,Z = 6.801\,2$, where X, Y, and Z are co-ordinates in Å; the displacements of C(5), C(6), C(7), C(8), Fe, O(5), O(6), C(9), and C(11) are -0.002, 0.004, -0.002, 0.001, -0.079, 0.046, 0.085, 0.125, and -0.017 Å, respectively.

DISCUSSION

The different reaction patterns of complexes (1) and (2) and the relations between them are shown in the Scheme. In all these reactions CO activation is achieved, although in different ways; indeed, in hydrocarbon solutions the formation of hydroxyferroles is strongly indicative of CO activation and of hydrogen transfer, probably from excess of alkyne or from the solvent, as it has been shown than considerable amounts of water and of hydrogen



SCHEME

are ineffective in enhancing the yields of complexes (1). It has also been shown, both from chemical evidence and by mass spectrometry,[25] that (1a) can be obtained from the thermal decomposition of (4), probably by loss of the $Fe(CO)_3$ unit σ-bonded to the carbon of the alkyne, to leave an $Fe_2(CO)_6(C_2Et_2)$ fragment which is capable of further reaction.

The heterolysis and dehydrogenation of (1a), in hydrocarbon solvents, yields (2a). It has been shown that CO is effective in this reaction, replacing the π-bonded $Fe(CO)_3$ unit. When this reaction was repeated with ^{13}CO the product (2a) was selectively ^{13}C-enriched in one of the two carbonyl sets. We suggest that the set enriched is the axial one. The two types of carbonyl are not exchanging on the n.m.r. time scale; however, spectra run after some days show signals of equal intensity, indicating that intramolecular carbonyl exchange is occurring.

Thus Fe–Fe bond breaking is caused by an excess of CO following the equation:

$$[Fe_2(CO)_6\{C_2(OH)Et\}_2] + 2\,CO \longrightarrow [Fe(CO)_4\{(CO)_2C_2Et_2\}] + H_2[Fe(CO)_4]$$

In alkaline solution, however, other mechanisms are also operative; *i.e.* the formation of (2) from $[HFe(CO)_4]^-$, which has been synthesized under similar conditions,[23] or from $[Fe(CO)_4]^{2-}$. For the formation of (1) in alkaline solution, the formation of $[Fe_2(CO)_8]^{n-}$ anions [6] must also be taken into account.

Thus, the same products, and corresponding CO activation, can occur under very different reaction conditions, indicating that these processes are non-selective.

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