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Reaction of Diethylpent-4-en-1-ynylamine with Dodecacarbonyltriiron. Preparation of Three Dinuclear Complexes with Multiple Shifts of Hydrogen within the Bridging Ligand: $[Fe_2(CO)_6(CH_2CHCHCHCNEt_2)]$, $[Fe_2(CO)_6(CH_3CCHCHCNEt_2)]$, and $[Fe_2(CO)_6(CHCHCHCHCHNEt_2)]$

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Diethylpent-4-en-1-ynylamine, $CH_2{=}CHCH_2C{\equiv}CNEt_2$, reacts with $[Fe_3(CO)_{12}]$ to form seven major products. Four of them result from the coupling of two alkyne molecules: $[Fe_2(CO)_6\{C_4(CH_2CHCH_2)_2(NEt_2)_2\}]$ (2); $[Fe_2(CO)_6\{C_5O(CH_2CHCH_2)_2(NEt_2)_2\}]$ (3); $[Fe_3(CO)_8\{C_4(CH_2CHCH_2)_2(NEt_2)_2\}]$ (4); $[Fe_3(CO)_8\{C_4(CHCHCH_3)(CH_2CHCH_2)(NEt_2)_2\}]$ (5). Complexes 2, 3, and 4 are of the classical type: 2 and 4 contain a ferracyclopentadiene fragment capped by one or two $Fe(CO)_3$ groups, respectively; compound 3 is a flyover type complex containing a substituted μ,η-pentadienone fragment as a ligand. Complex 5 contains a triangular iron cluster which supports a butadiene-type ligand resulting from the head to tail coupling of two alkyne molecules. One of the allyl double bonds is coordinated to one iron atom after a 1,3-hydrogen shift. The last three complexes $[Fe_2(CO)_6(CH_2CHCHCHCNEt_2)]$ (6), $[Fe_2(CO)_6(CH_3CCHCHCNEt_2)]$ (7), and $[Fe_2(CO)_6(CHCHCHCHCHNEt_2)]$ (8) have related structures, containing a dinuclear $Fe_2(CO)_6$ unit linked by a bridging organic group which is an isomer of the initial aminoalkyne formed by varius hydrogen shifts that are different in each case. These hydrogen migrations lead to μ-alkylidene-type complexes with either a hydrogen atom or a diethylamino or a methyl group as the bridgehead. Complex 7 also contains an aminocarbene and may be described as a dicarbene complex. A pathway to explain the formation of these three complexes is presented. All complexes have been characterized by IR and mass spectra. Molecular structures of 3, 5, 6, 7, and 8 have been determined by X-ray crystallography. Compound 3: triclinic, $P\bar{1}$; $a = 13.017$ (8), $b = 11.372$ (7), $c = 9.745$ (4) Å; $\alpha = 109.51$ (5), $\beta = 101.86$ (8), $\gamma = 82.59$ (1)°; $Z = 2$; $R = 0.025$, $R_w = 0.031$; 3850 observed reflections. Compound 5: triclinic, $P\bar{1}$; $a = 10.813$ (12), $b = 11.028$ (5), $c = 14.379$ (6) Å; $\alpha = 71.34$ (3), $\beta = 71.43$ (5), $\gamma = 65.09$ (4)°; $Z = 2$; $R = 0.055$, $R_w = 0.046$; 2898 observed reflections. Compound 6: triclinic, $P\bar{1}$, $a = 8.188$ (1), $b = 8.439$ (7), $c = 13.191$ (3) Å; $\alpha = 77.63$ (5), $\beta = 87.85$ (1), $\gamma = 75.80$ (4)°; $Z = 2$; $R = 0.029$, $R_w = 0.035$; 2119 observed reflections. Compound 7: triclinic, $P\bar{1}$; $a = 6.638$ (2), $b = 10.288$ (2), $c = 13.436$ (3) Å; $\alpha = 91.63$ (2), $\beta = 95.56$ (2), $\gamma = 103.13$ (2)°; $Z = 2$; $R = 0.028$, $R_w = 0.031$; 2092 observed reflections. Compound 8: orthorhombic, $P2_12_12_1$; $a = 7.446$ (4), $b = 13.152$ (7), $c = 18.302$ (8) Å; $Z = 4$; $R = 0.044$, $R_w = 0.041$; 1094 observed reflections.

Introduction

The study of the reactivity of organic molecules linked to dinuclear metal complexes has received a great deal of attention during the last 10 years.[1] In a recent publication we have shown that diethylprop-1-ynylamine, $CH_3C{\equiv}CNEt_2$, reacts with $[Fe_3(CO)_{12}]$ or $[Fe_2(CO)_9]$ to give, among other well-known compounds, an unusual dinuclear complex, $[Fe_2(CO)_7(\mu,\eta\text{-}MeCCNEt_2)]$ (1),[2] containing a bridging carbene and a terminal aminocarbene. The $Fe{=}C$ bond in this compound was shown to react with unsaturated molecules such as another molecule of aminoalkyne, diphenylacetylene, and diphenyldiazomethane to give addition products.[3] Compound 1 may also be described as containing a μ-alkylidene bridge. When such a bridge bears an alkenyl group, a bidentate alkene–carbene ligand is occurring and the resulting complex is known to react with alkynes.[4,5] The straightforward way we found to synthesize a μ-alkylidene from an aminoalkyne prompted us to investigate the reaction of iron carbonyl on diethylpent-4-en-1-ynylamine, $CH_2{=}CHCH_2C{\equiv}CNEt_2$, which contains an allyl group attached to the ethynyl core.

The diethylpent-4-en-1-ynylamine reacted with $[Fe_3(CO)_{12}]$ to yield primarily two classical products: a cycloferrapentadiene $[Fe_2(CO)_6\{C_4(CH_2CHCH_2)_2(NEt_2)_2\}]$ (2) and a diferracycloheptadiene $[Fe_2(CO)_6\{C_5O(CH_2CHCH_2)_2(NEt_2)_2]$ (3), which involve the coupling of two molecules of aminoalkyne. As revealed by an X-ray study, the allylic double bonds are not ligated but they could be brought into a position to coordinate to iron atoms. In refluxing toluene, one double bond can ligate and a trinuclear cluster, $[Fe_3(CO)_8\{C_4(CH_2CHCH_2)(CH_3CHCH)(NEt_2)_2\}]$ (5), is formed together with three other dinuclear complexes, $[Fe_2(CO)_6(CH_2CHCHCHCNEt_2)]$ (6), $[Fe_2(CO)_6(CH_3CCHCHCNEt_2)]$ (7), and $[Fe_2(CO)_6(CHCHCHCHCHNEt_2)]$ (8). These three μ-η-type complexes contain only one molecule of ligand which derives from the initial alkyne after various hydrogen migrations. This paper reports the synthesis and the structural determinations of these complexes.

Results and Discussion

Synthesis and X-ray Structures of 3 and 5. Dodecacarbonyltriiron reacted smoothly with $CH_2{=}$

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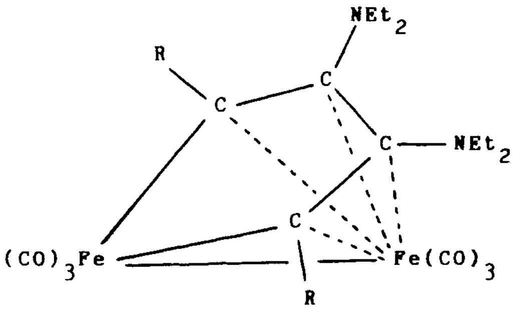
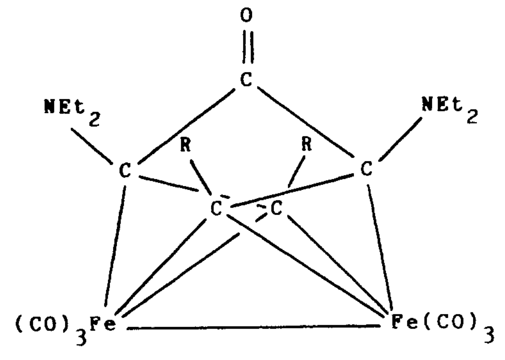
$CHCH_2C{\equiv}CNEt_2$ in hexane at 45 °C (reaction 1); after

$$[Fe_3(CO)_{12}] + CH_2{=}CHCH_2C{\equiv}CNEt_2 \xrightarrow{\text{hexane, 45 °C}} 2 + 3 \quad (1)$$

24 h no starting carbonyl compound is left as shown by thin-layer chromatography. Two major products (yellow and dark green) were isolated by column chromatography. From IR and mass spectra evidence, both compounds appear to have a structure of a type already reported.[6-8] In the yellow complex $[Fe_2(CO)_6\{C_4(CH_2CHCH_2)_2(NEt_2)_2\}]$ (**2**), two aminoalkyne molecules coupled to give a ferracyclopentadiene ring. The green complex $[Fe_2(CO)_6\{C_5O(CH_2CHCH_2)_2(NEt_2)_2\}]$ (**3**) is of "flyover" type in which the two alkynes are bound to one CO group to give a dinuclear complex. Such dinuclear species are usually found in reactions of alkynes with $[M_3(CO)_{12}]$ (M = Fe, Ru, Os).[6-8] To check the coupling type of the (allylamino)alkyne compounds and also the double bond position, the X-ray structure determination of **3** was carried out.



2: R = CH_2CHCH_2



3: R = CH_2CHCH_2

The molecular structure of **3** is shown on Figure 1. Intramolecular distances and angles are indicated in Table I. The coupling is identical with that obtained with diethylpropynylamine.[2] Both allylic double bonds, C(72)–C(73) and C(75)–C(76), remain free. However, it can be seen from Figure 1 that these allylic groups might be brought close to a coordinative position after rotation around the C(71)–C(72) and C(74)–C(75) bonds. Note that one allyl group is disordered; it can be described as a statistical distribution of the double bond on two sites related by a pseudo mirror plane containing C(4), C(74), and H(76) (Figure 2). The hydrogen atoms H(6) and H(7) do not seem to be affected by the disorder, as seen on a Fourier map.

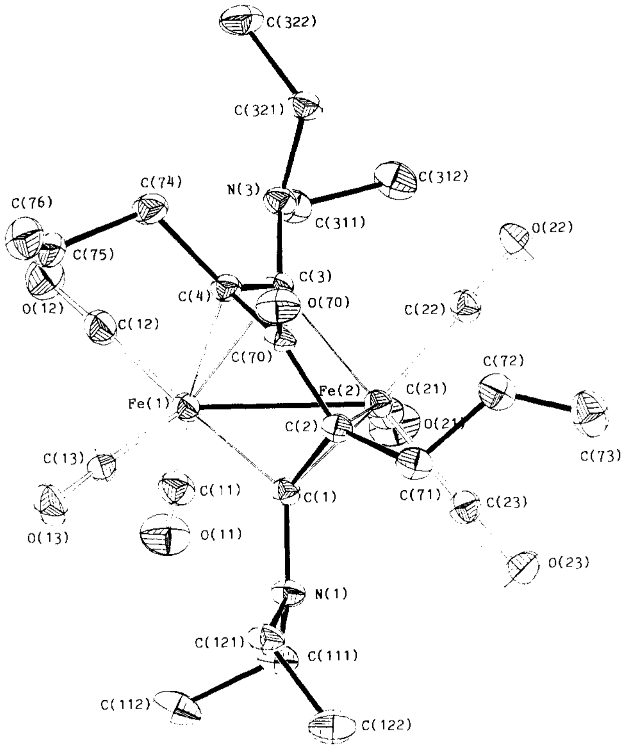


Figure 1. ORTEP view of complex **3** giving the atom numbering scheme used in tables; ellipsoids represent 20% probability.

Table I. Interatomic Distances (Å) and Bond Angles (deg) for Compound 3[a]

Bond Distances			
Fe(2)-Fe(1)	2.5856 (3)		
Fe(1)-C(1)	2.091 (2)	C(71)-C(72)	1.496 (3)
Fe(1)-C(3)	2.063 (2)	C(72)-C(73)	1.296 (4)
Fe(1)-C(4)	2.148 (2)	C(74)-C(75)	1.542 (4)
Fe(2)-C(1)	2.048 (2)	C(74)-C(751)	1.521 (7)
Fe(2)-C(2)	2.152 (2)	C(75)-C(76)	1.306 (5)
Fe(2)-C(3)	2.072 (2)	C(751)-C(762)	1.23 (1)
C(1)-C(2)	1.427 (2)	N(1)-C(111)	1.470 (2)
C(1)-N(1)	1.373 (2)	N(1)-C(121)	1.473 (2)
C(2)-C(70)	1.484 (2)	C(111)-C(112)	1.521 (4)
C(2)-C(71)	1.529 (3)	C(121)-C(122)	1.506 (3)
C(3)-C(4)	1.429 (2)	N(3)-C(311)	1.467 (2)
C(3)-N(3)	1.370 (2)	N(3)-C(321)	1.475 (2)
C(4)-C(70)	1.484 (3)	C(311)-C(312)	1.508 (3)
C(4)-C(74)	1.529 (3)	C(321)-C(322)	1.518 (3)
C(70)-O(70)	1.220 (2)		

Bond Angles			
N(1)-C(1)-C(2)	121.2 (2)	C(751)-C(74)-C(4)	111.6 (3)
C(70)-C(2)-C(1)	114.1 (2)	C(76)-C(75)-C(74)	120.6 (3)
C(71)-C(2)-C(1)	124.6 (2)	C(762)-C(751)-C(74)	119.8 (8)
C(71)-C(2)-C(70)	115.7 (2)	C(111)-N(1)-C(1)	120.9 (2)
N(3)-C(3)-C(4)	120.6 (2)	C(121)-N(1)-C(1)	120.3 (1)
C(70)-C(4)-C(3)	114.0 (1)	C(121)-N(1)-C(111)	115.5 (1)
C(74)-C(4)-C(3)	123.5 (2)	C(112)-C(111)-N(1)	114.8 (2)
C(74)-C(4)-C(70)	116.2 (2)	C(122)-C(121)-N(1)	113.4 (2)
C(4)-C(70)-C(2)	115.2 (1)	C(311)-N(3)-C(3)	119.2 (1)
O(70)-C(70)-C(2)	122.0 (2)	C(321)-N(3)-C(3)	121.5 (1)
O(70)-C(70)-C(4)	122.8 (2)	C(321)-N(3)-C(311)	115.8 (1)
C(72)-C(71)-C(2)	113.9 (2)	C(312)-C(311)-N(3)	114.5 (2)
C(73)-C(72)-C(71)	124.4 (2)	C(322)-C(321)-N(3)	115.5 (2)
C(75)-C(74)-C(4)	115.0 (2)		

[a] Esd's in parentheses refer to the last significant digit.

The possibility of coordinating the lateral allyl groups to iron atoms prompted us to carry out the reaction in refluxing toluene. After 12 h under dry nitrogen, no starting $[Fe_3(CO)_{12}]$ remained (reaction 2). Seven products were separated by chromatography; among them, complexes **2** and **3** were characterized by their IR spectra.

$$[Fe_3(CO)_{12}] + CH_2{=}CHCH_2C{\equiv}CNEt_2 \xrightarrow{\text{refluxing toluene}} 2 + 3 + 4 + 5 + 6 + 7 + 8$$

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(6) Aime, S.; Osella, D.; Arce, A. J.; Deeming, A. J.; Hursthouse, M. B.; Calas, A. M. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1981.

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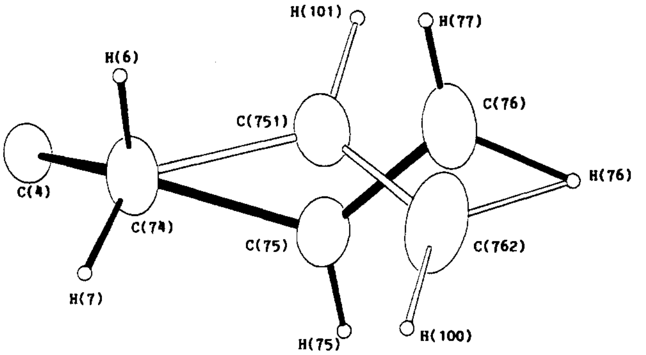
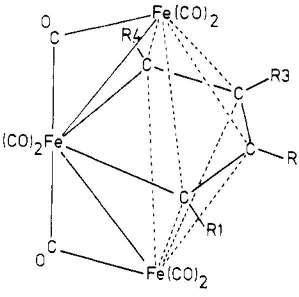


Figure 2. Statistical distribution of one of the allyl chains observed in 3.

Spectroscopic data for all new complexes are given in the Experimental Section. From mass spectrometry, compounds 4 and 5 were identified as isomers with formula $[Fe_3(CO)_8L_2]$. Their IR spectra suggested they are structurally different. The spectrum of 4 showed a strong band at 1845 cm^{-1} and a shoulder at 1855 cm^{-1} which may be attributed to CO-bridging stretching frequencies. Therefore, complex 4 could have the known pentagonal-bipyramidal structure which contains a ferracyclopentadiene group capped on each side by one iron atom.[2,9,10] The formula of complex 5 derived from mass spectrometry suggested the known structure shown in reaction 2.[9] However, the IR spectrum displayed a strong band at 1785 cm^{-1} which is typical of a CO capping a metal triangle and which therefore suggested a different structure, for example, with the two double bonds involved in ligation. To elucidate the structure of complex 5, an X-ray structure was undertaken.



4

R1 = R3 = Me, R2 = R4 = NEt_2[2]
R1 = R2 = R3 = R4 = C_6H_5[9]
R1 = R_2 = $SiMe_3$, C_6H_5; R3 = OC_2H_5, R4 = Me[10]

The ORTEP drawing of 5 is shown in Figure 3. Important bond distances and bond angles are given in Table II. The molecular structure consists of a triangular metal framework which supports an organic moiety resulting from a head to tail coupling of two aminoalkyne molecules. The formed butadiene C(1),C(2),C(3),C(4) fragment is a part of a ferracyclopentadiene ring containing Fe(3) and π-bonded to Fe(1); one of the allyl groups, C(70), C(71), C(72), is coordinated to Fe(2) after isomerization due to a 1,3-hydrogen shift. This structure is similar to that of $[Fe_3(CO)_8\{MeCC(NEt_2)C(Me)CNEt_2\}]$[2] in which the two alkynes coupled in the head to tail manner and one of the two nitrogen atoms is attached to one iron atom.

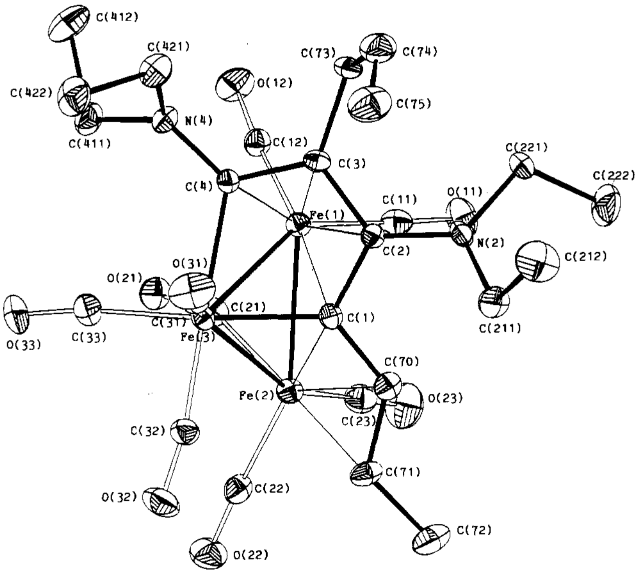


Figure 3. ORTEP view of complex 5 projected onto the cycloferrapentadiene plane; ellipsoids represent 20% probability.

Table II. Interatomic Distances (Å) and Bond Angles (deg) for Compound 5[a]

Bond Distances			
Fe(1)-Fe(2)	2.590 (1)	C(2)-C(3)	1.453 (7)
Fe(1)-Fe(3)	2.5566 (9)	C(2)-N(2)	1.390 (6)
Fe(1)-C(21)	2.200 (5)	C(3)-C(4)	1.453 (7)
Fe(1)-C(1)	2.136 (4)	C(3)-C(73)	1.516 (7)
Fe(1)-C(2)	2.249 (4)	C(4)-N(4)	1.361 (6)
Fe(1)-C(3)	2.146 (5)	C(70)-C(71)	1.373 (7)
Fe(1)-C(4)	1.995 (5)	C(71)-C(72)	1.492 (9)
Fe(2)-Fe(3)	2.642 (1)	C(73)-C(74)	1.493 (9)
Fe(2)-C(32)	2.688 (6)	C(74)-C(75)	1.32 (1)
Fe(2)-C(1)	2.381 (5)	N(2)-C(211)	1.468 (7)
Fe(2)-C(70)	2.139 (5)	N(2)-C(221)	1.463 (7)
Fe(2)-C(71)	2.266 (5)	C(211)-C(212)	1.508 (9)
Fe(3)-C(21)	2.710 (5)	C(221)-C(222)	1.50 (1)
Fe(3)-C(1)	1.965 (5)	N(4)-C(411)	1.466 (7)
Fe(3)-C(4)	2.136 (5)	N(4)-C(421)	1.481 (7)
C(21)-O(21)	1.182 (6)	C(411)-C(412)	1.517 (9)
C(1)-C(2)	1.444 (6)	C(421)-C(422)	1.521 (9)
C(1)-C(70)	1.452 (7)		
Bond Angles			
Fe(3)-Fe(1)-Fe(2)	61.78 (3)	N(4)-C(4)-C(3)	119.9 (4)
Fe(3)-Fe(2)-Fe(1)	58.49 (3)	C(71)-C(70)-C(1)	127.5 (5)
Fe(2)-Fe(3)-Fe(1)	59.73 (3)	C(72)-C(71)-C(70)	122.2 (6)
Fe(2)-C(21)-Fe(1)	79.8 (2)	C(74)-C(73)-C(3)	116.9 (5)
Fe(3)-C(21)-Fe(1)	61.7 (1)	C(75)-C(74)-C(73)	125.4 (6)
Fe(3)-C(21)-Fe(2)	68.2 (2)	C(211)-N(2)-C(2)	117.0 (4)
C(70)-C(1)-C(2)	116.7 (4)	C(221)-N(2)-C(2)	124.6 (4)
C(3)-C(2)-C(1)	113.9 (4)	C(221)-N(2)-C(211)	118.1 (4)
N(2)-C(2)-C(1)	120.9 (4)	C(212)-C(211)-N(2)	114.4 (5)
N(2)-C(2)-C(3)	125.0 (4)	C(222)-C(221)-N(2)	112.6 (5)
C(4)-C(3)-C(2)	113.3 (4)	C(411)-N(4)-C(4)	120.8 (4)
C(73)-C(3)-C(2)	123.5 (4)	C(421)-N(4)-C(4)	120.3 (4)
C(73)-C(3)-C(4)	123.1 (4)	C(421)-N(4)-C(411)	116.3 (4)
C(3)-C(4)-Fe(3)	112.4 (3)	C(412)-C(411)-N(4)	111.5 (5)
N(4)-C(4)-Fe(3)	123.7 (3)	C(422)-C(421)-N(4)	113.7 (5)

[a] Esd's in parentheses refer to the last significant digit.

The butadiene fragment and the ligated CH=CH—CH_3 group are roughly coplanar with the largest deviation from this plane being 0.215 Å at C(71). However, if this butadiene and this C(70), C(71), C(72) chain are considered separately, they make a dihedral angle of 34.2°. The structure might be then described as the fusion of a ferracyclopentadiene group, Fe(3),C(1),C(2),C(3),C(4), and a μ,η^3-fragment, Fe(3),Fe(2),C(1),C(70),C(71).

Although butadiene fragment C–C distances are identical within experimental errors, this butadiene moiety is not symmetrically bound to Fe(1) and Fe(3). The Fe(1)–C π-bonds range from 1.995 (5) to 2.249 (5) Å whereas the

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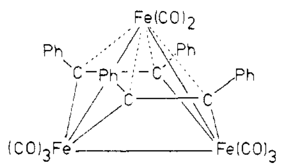
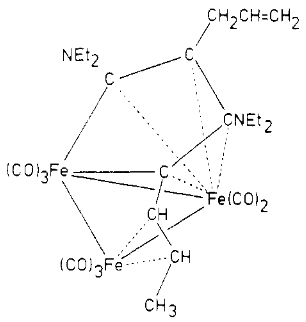
Fe(3)–C(1) σ-bond, 1.965 (5) Å, is much shorter than the Fe(3)–C(4) bond of 2.136 (5) Å. Such distorsions are attributed to the spacial situation of C(1) which may be described as a μ_3-alkylidene (C(1)–Fe(1) = 2.136 (4), C(1)–Fe(2) = 2.381 (5), and C(1)–Fe(3) = 1.965 (5) Å), and consequently the propenyl C(1)–C(70)–C(71) is unsymmetrically bound to Fe(2), with Fe(2)–C(70) = 2.139 (5) and Fe(2)–C(71) = 2.266 (5) Å. As quoted above a similar capping situation was found in [$Fe_3(CO)_8${MeCC($NEt)_2$C(Me)C(NEt_2)}][2] in which one nitrogen atom donates its lone pair to an iron atom and in [$Fe_3(CO)_9${C(COMeCH_2)NHC_6H_{11}}] in which nitrogen also donates its lone pair.[11]

Examination of the structure reveals another interesting feature. The C(21)–O(21) carbonyl group is semibridging since Fe(1)–C(21) = 2.200 (5) Å, Fe(2)–C(21) = 1.813 (5) Å, and Fe(2)–C(21)–O(21) = 152.4 (4)°. The Fe(3)–C(21) distance is 2.710 (5) Å. Although this last bond has a small formal bond order, it is sufficient to characterize this peculiar bonding mode as *semi-triply bridging*.[12] The angle between the C(21)–O(21) vector and the Fe(1),Fe(2),Fe(3) plane is 84°. This particular CO group is identified in the IR spectrum by a characteristic absorption band at 1785 cm^{-1}. There is another semibridging CO along the Fe(2)–Fe(3) edge (Fe(2)–C(32) = 2.688 (6) Å, Fe(3)–C(32)–O(32) = 167.1 (5)°, α = 0.509).

Complexes 6, 7, and 8 [$Fe_2(CO)_6L$]. Three other complexes obtained in refluxing toluene are isomers with the formula [$Fe_2(CO)_6L$] (see reaction 2). However, IR spectra suggest they are structurally different from each other and from preceding compounds since the ν(C=C) band has disappeared in each case. Suitable crystals for an X-ray structure were obtained for 6, 7, and 8.



5a: ref 9



5b: this work (X-ray)

6,7,8: isomers [$Fe_2(CO)_6L$]

6: L = $CH_2CHCHCHCNEt_2$
7: L = $CH_3CCHCHCNEt_2$
8: L = $CHCHCHCHCHNEt_2$

ORTEP views of the three structures with atom-labeling schemes are shown on Figures 4, 5 and 6. Selected bond lengths and most relevant bond angles are given in Table III. These three complexes have related structures, containing a dinuclear $Fe_2(CO)_6$ unit linked by a bridging organic group which is an isomer of the initial aminoalkyne; various hydrogen shifts occurred and they are different in each case. All hydrogen atoms could be found on difference Fourier maps; complex 6 contains $CH_2CHCHCHCNEt_2$, complex 7 contains

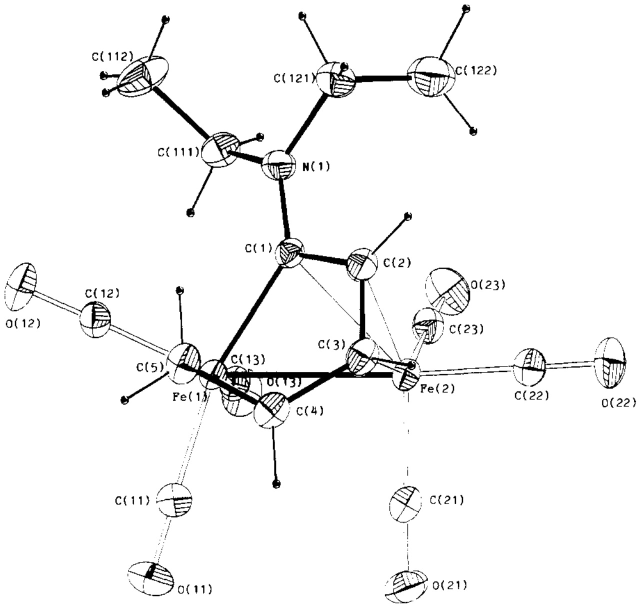


Figure 4. ORTEP view of complex 6 with hydrogen atoms artificially reduced, B(H) = 0.25 Å^2; ellipsoids represent 20% probability.

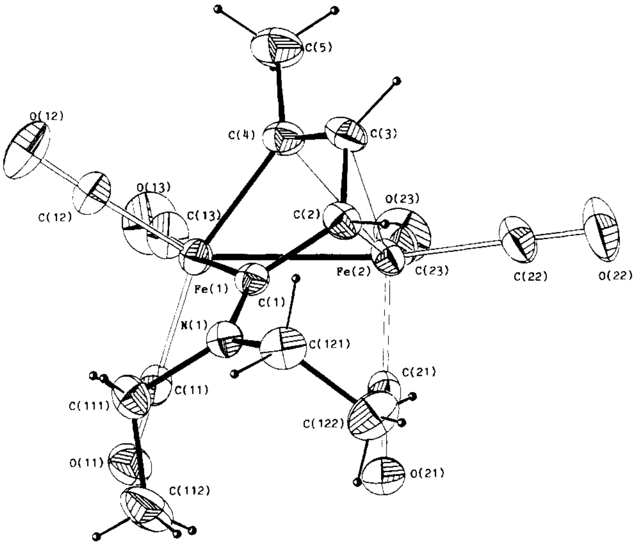


Figure 5. ORTEP view of complex 7 with hydrogen atoms artificially reduced, B(H) = 0.25 Å^2; ellipsoids represent 20% probability.

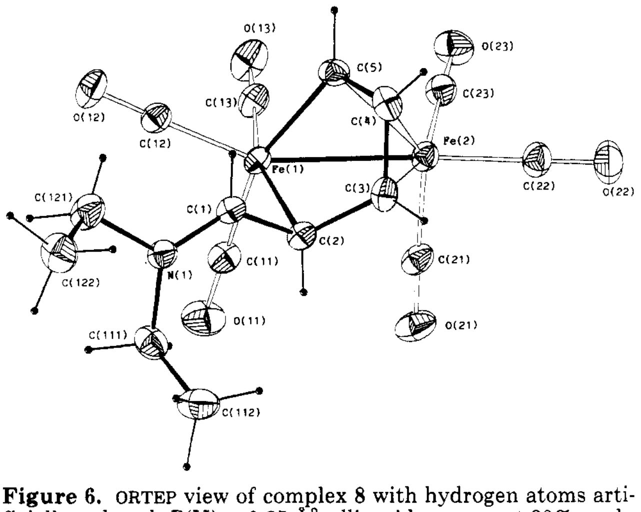


Figure 6. ORTEP view of complex 8 with hydrogen atoms artificially reduced, B(H) = 0.25 Å^2; ellipsoids represent 20% probability.

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[12] Yeh, W. Y.; Shapley, J. R.; Li, Y. J.; Churchill, M. R. *Organometallics* **1985**, *4*, 767. In considerations of "semibridging" carbonyl groups, it is customary to calculate the α value, defined as $(d_2 - d_1)/d_1$ (where d_1 and d_2 are the shorter and longer M–CO distances). Values with $0.1 < \alpha < 0.6$ are considered "semibridging". The comparison of Fe(1)–C(21) and Fe(3)–C(21) with Fe(2)–C(21) distances in the present molecule yields values of 0.21 and 0.49, respectively.

Table III. Interatomic Distances (Å) and Bond Angles (deg)[a]

Compound 6			
Bond Distances			
Fe(1)–Fe(2)	2.6669 (6)	C(1)–N(1)	1.344 (4)
Fe(1)–C(1)	1.997 (3)	C(2)–C(3)	1.421 (5)
Fe(1)–C(4)	2.197 (3)	C(3)–C(4)	1.447 (5)
Fe(1)–C(5)	2.182 (3)	C(4)–C(5)	1.383 (5)
Fe(2)–C(1)	2.333 (3)	N(1)–C(111)	1.476 (4)
Fe(2)–C(2)	2.060 (3)	N(1)–C(121)	1.492 (5)
Fe(2)–C(3)	2.033 (3)	C(111)–C(112)	1.489 (6)
C(1)–C(2)	1.434 (4)	C(121)–C(122)	1.457 (7)
Bond Angles			
N(1)–C(1)–C(2)	119.3 (3)	C(121)–N(1)–C(1)	120.9 (3)
C(3)–C(2)–C(1)	115.8 (3)	C(121)–N(1)–C(111)	115.6 (3)
C(4)–C(3)–C(2)	117.7 (3)	C(112)–C(111)–N(1)	114.2 (3)
C(122)–C(121)–N(1)	111.6 (4)	C(5)–C(4)–C(3)	122.2 (3)
C(111)–N(1)–C(1)	123.1 (3)		
Compound 7			
Bond Distances			
Fe(1)–Fe(2)	2.5682 (6)		
Fe(1)–C(4)	1.966 (3)	C(3)–C(2)	1.415 (5)
Fe(1)–C(1)	1.977 (3)	C(2)–C(1)	1.440 (4)
Fe(2)–C(4)	2.096 (3)	C(1)–N(1)	1.324 (4)
Fe(2)–C(3)	2.051 (3)	N(1)–C(111)	1.470 (4)
Fe(2)–C(2)	2.096 (3)	N(1)–C(121)	1.487 (4)
Fe(2)–C(1)	2.573 (3)	C(111)–C(112)	1.499 (7)
C(5)–C(4)	1.505 (5)	C(121)–C(122)	1.498 (6)
C(4)–C(3)	1.398 (5)		
Bond Angles			
C(3)–C(4)–C(5)	118.8 (4)	C(121)–N(1)–C(1)	122.1 (3)
C(2)–C(3)–C(4)	114.3 (3)	C(121)–N(1)–C(111)	114.6 (3)
C(1)–C(2)–C(3)	114.3 (3)	C(112)–C(111)–N(1)	113.5 (4)
N(1)–C(1)–C(2)	118.9 (3)	C(122)–C(121)–N(1)	113.4 (3)
C(111)–N(1)–C(1)	123.1 (3)		
Compound 8			
Bond Distances			
Fe(1)–Fe(2)	2.601 (1)		
Fe(1)–C(5)	1.991 (8)	C(4)–C(3)	1.40 (1)
Fe(1)–C(2)	2.207 (7)	C(3)–C(2)	1.45 (1)
Fe(1)–C(1)	2.721 (7)	C(2)–C(1)	1.40 (1)
Fe(2)–C(5)	2.060 (8)	C(1)–N(1)	1.31 (1)
Fe(2)–C(4)	2.052 (8)	N(1)–C(111)	1.45 (1)
Fe(2)–C(3)	2.095 (7)	N(1)–C(121)	1.48 (1)
Fe(2)–C(2)	2.869 (7)	C(111)–C(112)	1.45 (1)
C(5)–C(4)	1.41 (1)	C(121)–C(122)	1.38 (2)
Bond Angles			
C(2)–C(3)–C(4)	117.8 (7)	C(121)–N(1)–C(1)	121.0 (7)
C(1)–C(2)–C(3)	117.6 (7)	C(121)–N(1)–C(111)	116.2 (8)
N(1)–C(1)–C(2)	129.9 (7)	C(112)–C(111)–N(1)	114.8 (9)
C(3)–C(4)–C(5)	113.7 (7)	C(122)–C(121)–N(1)	115.0 (13)
C(111)–N(1)–C(1)	122.4 (7)		

[a] Esd's in parentheses refer to the last significant digit.

$CH_3CCHCHCNEt_2$, and complex 8 contains $CHCHCHCHCHNEt_2$.

Complex 6 contains a ligand derived from the initial alkyne by an hydrogen shift from the allylic internal CH_2 group onto the adjacent alkyne carbon atom. The five carbon atoms are ligated on the iron frame. C(1), C(2), and C(3) are bound on Fe(2), while C(1), C(4), and C(5) are bound on Fe(1). The nitrogen atom has a planar environment. In order to achieve the 18-electron bookkeeping around each iron, the electron distribution along the free ligand may be described as follows. The hydrogen shift made C(2)–C(3) a double bond while C(4)–C(5) remains a double bond. Consequently C(1) may be regarded as a carbene which is bonded to Fe(1) and the C(4)–C(5) double bond is π-bonded to Fe(1) while C(2)–C(3) is π-bonded to Fe(2). Thus Fe(1) has 18 electrons and Fe(2) 16 electrons which are raised to 18 by a electron pair from Fe(1). Although this discussion is quite formal since electron delocalization occurs all along N(1)–C(1)–C(2)–C(3)–C(4)–C(5) with the sequence of distances 1.345 (4), 1.435 (4), 1.423 (5), 1.452 (5), and 1.386 (5) Å, the Fe(1)–Fe(2) distance is the longest (Fe(1)–Fe(2) = 2.669 (6) Å) in the series of complexes 6, 7, and 8 and is slightly above the usual range (2.602–2.642 Å) found in related iron dinuclear complexes.[13-16]

It is worthwhile to point out that the C(4)–C(5) vector is perpendicular to the Fe(1)–C(1) vector (93.9°). This situation is identical with the one observed in other chelated alkenylcarbene complexes,[17] and it is believed to be the most stable geometry.[18]

C(1) is the point of coordination of the aminocarbene ligand. The Fe(1)–C(1) distance, 1.997 (3) Å, is within the range of iron carbene bond;[19,20] the Fe(1)–C(1)–N(1)–C(2) atoms are nearly in the same plane, the largest deviation from the plane being 0.06 Å; the C(1)–N(1) bond length of 1.345 (4) Å indicates substantial double-bond character (>C=N< bonds in iminium salts lie within the range 1.28–1.38 Å[21]) and agrees with values found in some other aminocarbene complexes: 1.316 (7) Å in $[W(CO)_4\{C(C_4H_7)(NHC_3H_5)_5\}]$[17] and 1.327 (9) Å in $[Fe_2(CO)_7(MeC{\equiv}CNEt_2)]$.[2]

When compared with 6, it appears that in 7 one hydrogen atom has migrated from C(4) to C(5) to become a methyl group. The three central atoms C(2), C(3), and C(4) are symmetrically bound to Fe(2) making this three-carbon group a substituted allyl ligand; on one side C(4) is connected to CH_3 and Fe(1) while C(2) is connected to $CNEt_2$, so that C(4) is bridging Fe(1) and Fe(2). C(1) is again the point of coordination of the aminocarbene as demonstrated by the same three features as above: Fe(1)–C(1) = 1.977 (3) and C(1)–N(1) = 1.324 (4) Å and the Fe(1),C(1),C(2),N(1) atoms make a plane. The Fe(1)–C(1) distance is shorter than in 6; indeed C(1) is not any longer a μ-alkylidene since C(1)–Fe(2) = 2.574 (3) Å. If the ligand is assumed to be a *free* organic entity, it may be described as $CH_3{-}C{-}CH{=}CH{-}C{-}NEt_2$ in which the carbons without hydrogens attached are carbenes respectively bound to Fe(1) and bridging Fe(1) and Fe(2); indeed Fe(1)–C(1) and Fe(1)–C(4) = 1.966 (3) Å have both of them a bond order higher than 1.

Complex 8 is the most surprising compound, in which the bridging group corresponds to a uniform distribution of hydrogen atoms with the resulting sequence $CHCHCHCHCHN(C_2H_5)_2$. It may be described as being derived from 6 by hydrogen shift from C(1) to C(5), very likely through an intermediate Fe hydride. A simplified way to describe the isolated ligand is to consider the terminal C(5) as a methylene, one hydrogen of which is substituted by a chain containing two double bonds, C(4)=C(3) and C(2)=C(1), and a terminal diethylamino group of the enamine type. When ligated, the C(5) carbene behaves as a bridging carbene; the first C(3)=C(4) bond is π-bonded on Fe(2) and the second C(1)=C(2) bond is π-bonded on

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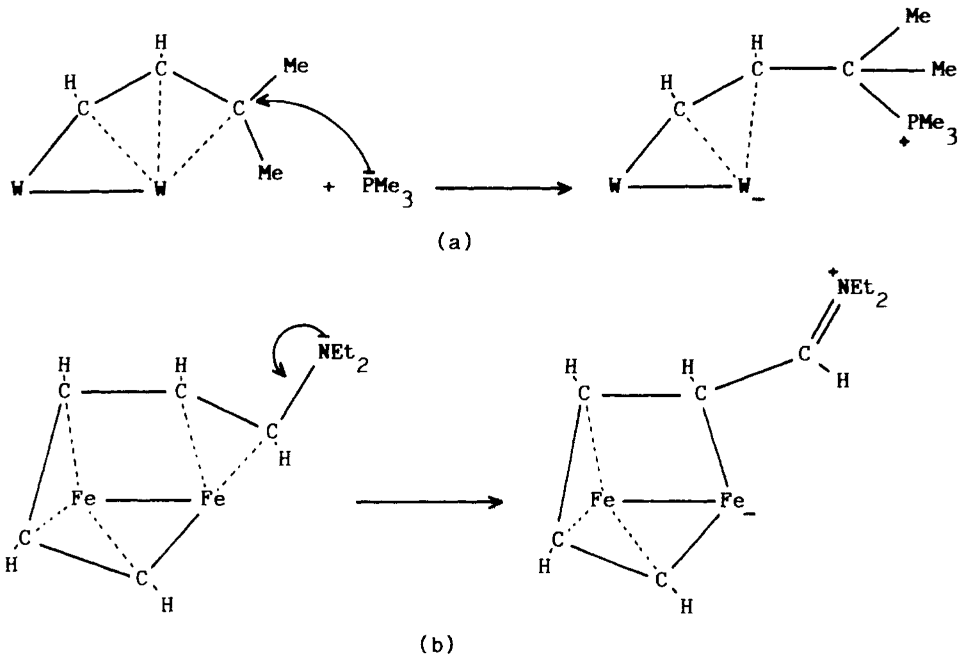
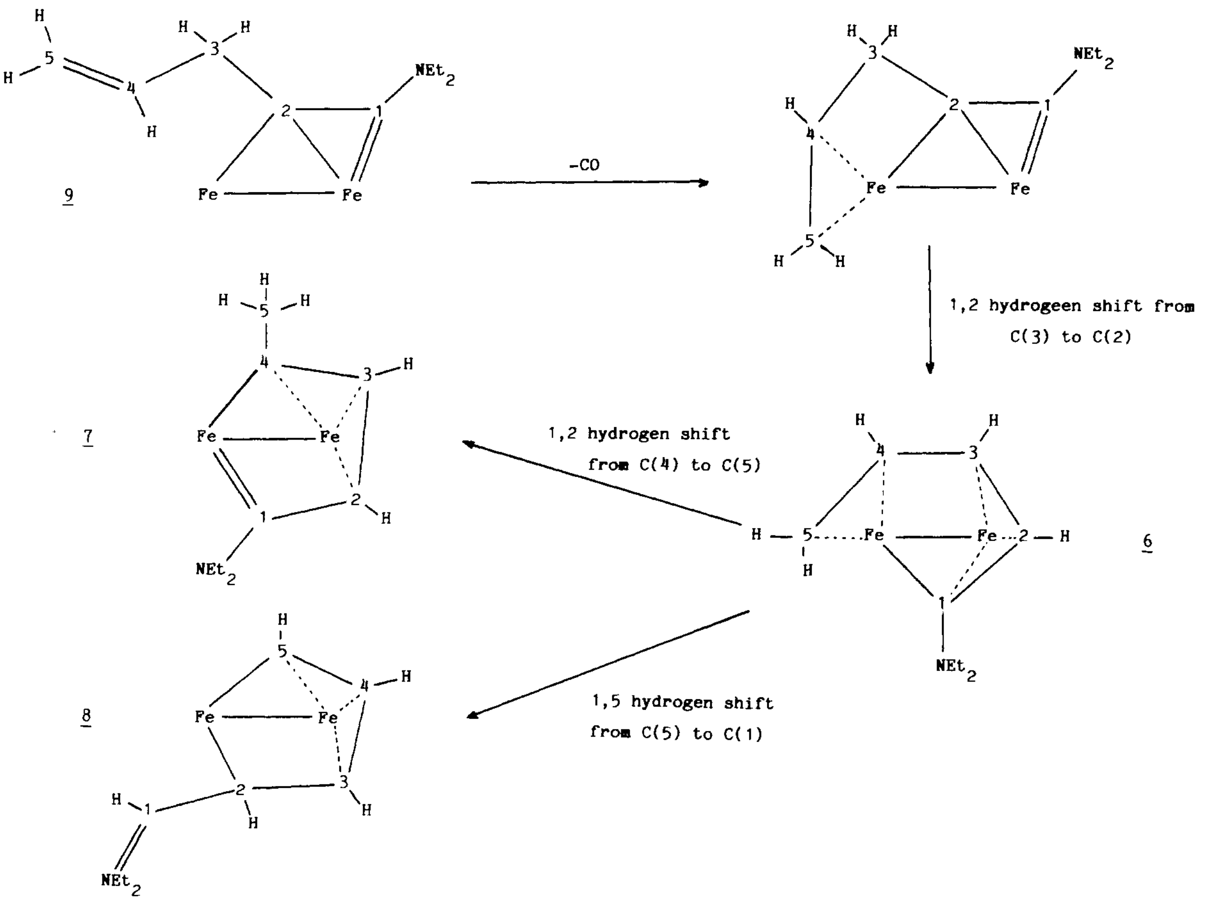
Scheme I



(a)

(b)

Scheme II



Fe(1). Then for each iron the 18-electron count is achieved by employing one electron from the bridging carbene, two electrons from the π-bond, three lone pairs from the carbonyl ligands, and one electron from the metal bond. This simplified description allows easy electron bookkeeping but does not fully describe the actual structure. First of all C(3)–C(4)–C(5) looks like an allyl group symmetrically bound on Fe(2) with Fe–C bond lengths of 2.060 (8), 2.052 (8), and 2.095 (7) Å. Secondly, a salient feature of 8 is the bonding mode of the C(1)–C(2) initial triple bond, especially the long Fe(1)–C(1) distance, 2.721 (7) Å, well outside the usual range of typical Fe–C bonds; the Fe(1)–C(2) bond length is 2.207 (7) Å while the C(1)–C(2) bond length, 1.40 (1) Å, indicates that this fragment retains some olefinic character. The angles around C(2) are nearly those of a sp^2 carbon, and the N(1),C(1),C(2),H(1),H(2) atoms are roughly in the same plane. The same situation was encountered in $[Fe_2(CO)_6\{C(Ph)C(Ph)C(CF_3)CHC(OEt)_2\}]$

Table IV. Crystal Data

	3	5	6	7	8
formula	$C_{25}H_{30}N_2O_7Fe_2$	$C_{26}H_{30}N_2O_8Fe_3$	$C_{15}H_{15}NO_6Fe_2$	$C_{15}H_{15}NO_6Fe_2$	$C_{15}H_{15}NO_6Fe_2$
fw	582	666	417	417	417
cryst system	triclinic	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a, Å	13.017 (8)	10.813 (12)	8.188 (1)	6.638 (2)	7.446 (4)
b, Å	11.372 (7)	11.028 (5)	8.439 (7)	10.288 (2)	13.152 (7)
c, Å	9.745 (4)	14.379 (6)	13.191 (3)	13.436 (3)	18.302 (8)
α, deg	109.51 (5)	71.34 (3)	77.63 (5)	91.63 (2)	90
β, deg	101.86 (8)	71.43 (5)	87.85 (1)	95.96 (2)	90
γ, deg	82.59 (1)	65.09 (4)	75.80 (4)	103.13 (2)	90
V, Å^3	1327	1439	863	888	1792
Z	2	2	2	2	4
cryst size, mm	0.35 × 0.3 × 0.25	0.4 × 0.35 × 0.28	0.4 × 0.4 × 0.12	0.5 × 0.26 × 0.26	0.4 × 0.14 × 0.09
μ(Mo Kα), cm^{-1}	11.36	15.39	17.08	16.60	16.45
ρ(calcd), g·cm^{-3}	1.457	1.537	1.605	1.559	1.545
diffractometer	PW1100	PW1100	CAD4	CAD4	PW1100
radiatn	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temp, °C	20	20	20	20	20
scan range θ, deg	$0.9 + 0.34 \tan \theta$	$0.9 + 0.34 \tan \theta$	$1.0 + 0.34 \tan \theta$	$1.1 + 0.34 \tan \theta$	$0.9 + 0.34 \tan \theta$
2θ range, deg	4–50	4–46	3–50	3–50	3–46
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
reflctn collected	4391	3814	3162	3250	1383
reflctn merged (R_m)	4095 (0.007)	3642 (0.023)	3019 (0.019)	3107 (0.013)	1372
reflctn used	3850	2898	2119	2092	1094
criteria	$I > 3\sigma(I)$	$\lvert F_o\rvert > 8$ (scaled on F_c)	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R	0.0256	0.0547	0.0295	0.0279	0.0437
R_w	0.0314	0.0460	0.0351	0.0307	0.0409
rms (shift/esd)	0.21	0.28	0.18	0.20	0.18
coeff (Ar)	2.71, 0.03, 2.12	4.91, −2.70, 3.84	5.95, −2.48, 4.60	4.39, −1.93, 3.17	2.09, 0.03, 1.83
least-squares parameters	436	354	264	264	219
degrees of freedom	3414	2544	1855	1828	875
GOF	1.14	1.041	0.96	1.18	1.5

(2.86 (1) and 2.15 (1) Å, respectively).[22] It was suggested that this dissymmetry was the consequence of the presence of the two ethoxy groups. In complex **8**, the amino group with a heteroatom may play a similar role; as a matter of fact it may be noted that the CN distance in **8** is the shortest in the **6**, **7**, **8** series. This situation might be described as a tendency of C(1) to become a cation due to a transfer of electron density on Fe(2); then the charge deficiency on C(2) is compensated by the nitrogen lone pair and carbon is lost from iron. The molecule would therefore behave as a zwitterion. Such a situation has already been described in a somewhat different compound of tungsten containing an ylide group.[23] The starting dinuclear tungsten complex contains a $W_2(\mu,\eta\text{-}CHCHCMe_2)$ fragment. The terminal CMe_2 ligated to tungsten is part of the C_4 ligand which underwent a nucleophilic attack by a phosphine and subsequently was displaced to yield an ylide system (Scheme Ia). In the title compound N is part of the ligand already bonded to the metal but a similar intramolecular nucleophilic attack may be considered (Scheme Ib). In complexes **6** and **7**, the nitrogen lone pair is also contributing to the π-system which is delocalized all along the ligand but to a smaller extent so that the carbon atom bearing the amine group is not lost from the metal.

The unusual feature of these three complexes is the formation of various ligands via multiple hydrogen shifts. Iron carbonyl promoted hydrogen migration is not a new reaction, and considerable effort has been devoted to better understand the driving force of such a reaction.[24] However, the fact that this (allylamino)alkyne undergoes a multiple hydrogen redistribution is exceptional.

A diiron complex (**1**) containing one molecule of diethylprop-1-ynylamine was described.[2] The same compound with an allyl group instead of a methyl group has not yet been fully characterized. However, such a nonisolated dinuclear μ-alkylidene carbon complex, **9**, is postulated as a precursor for these three complexes, **6**, **7**, and **8**. Complex **1** reacts with an excess of aminoalkyne to yield the ferracyclopentadiene and the flyover complexes. Since those last two complexes were also isolated when methyl is replaced by allyl, the assumed occurrence of **9** seems realistic.

Possible pathways consistent with those results are presented in Scheme II. Starting from **9**, the first step would be the coordination of the allylic double bond on Fe(2) with the loss of one CO ligand. Metal hydride addition–elimination reaction[25] would account for the different hydrogen shifts leading to complexes **6**, **7**, and **8**.

Experimental Section

All reactions were carried out under dry nitrogen using standard Schlenk or vacuum line techniques. Preparative column chromatography was performed by using 70–230 mesh Merck silica gel. For thin-layer analytical chromatography (TLC) aluminium sheets (silica gel $60F_{254}$) were used. Infrared absorption spectra were measured with a Perkin-Elmer 597 spectrometer. A Nermag R10-10 spectrometer was used for molecular mass determination. The NMR spectra of **6** and **8** were recorded on a Brucker WM 200 spectrometer with tetramethylsilane as a reference. Hexane and dichloromethane were purified by standard procedures and stored over molecular sieves. Literature procedure was used to prepare $CH_2CHCH_2C{\equiv}CNEt_2$.[26]

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Table V. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters (U(eq), Å^2)[a]

atom	x/a	y/b	z/c	U(eq)	atom	x/a	y/b	z/c	U(eq)
Compound **3**									
Fe(1)	0.27863 (2)	0.19907 (2)	0.11956 (2)	0.0344	O(70)	0.4222 (1)	0.3728 (1)	0.5361 (2)	0.0567
C(11)	0.2011 (2)	0.1849 (2)	−0.0589 (2)	0.0484	C(71)	0.4036 (2)	0.1130 (2)	0.3937 (2)	0.0477
O(11)	0.1511 (2)	0.1669 (2)	−0.1743 (2)	0.0698	C(72)	0.5096 (2)	0.1041 (2)	0.3527 (3)	0.0567
C(12)	0.4083 (2)	0.2106 (2)	0.0889 (2)	0.0456	C(73)	0.5533 (2)	0.0030 (3)	0.2714 (3)	0.0755
O(12)	0.4886 (1)	0.2219 (2)	0.0685 (2)	0.0641	C(74)	0.3091 (2)	0.5740 (2)	0.4454 (2)	0.0537
C(13)	0.2829 (2)	0.0302 (2)	0.0677 (2)	0.0476	C(75)	0.2406 (3)	0.6243 (3)	0.5674 (4)	0.0517
O(13)	0.2868 (2)	−0.0755 (1)	0.0332 (2)	0.0695	C(751)	0.2944 (7)	0.5987 (7)	0.6034 (8)	0.0567
Fe(2)	0.14656 (2)	0.36413 (2)	0.25594 (3)	0.0390	C(76)	0.2840 (4)	0.6572 (4)	0.7068 (4)	0.0708
C(21)	0.1059 (2)	0.3862 (2)	0.4283 (2)	0.0487	C(762)	0.241 (1)	0.692 (1)	0.665 (1)	0.0855
O(21)	0.0807 (1)	0.3954 (2)	0.5372 (2)	0.0643	N(1)	0.1670 (1)	0.1070 (1)	0.3119 (2)	0.0418
C(22)	0.0946 (2)	0.5120 (2)	0.2291 (3)	0.0560	C(111)	0.0722 (2)	0.0572 (2)	0.2074 (2)	0.0544
O(22)	0.0609 (2)	0.6053 (2)	0.2154 (3)	0.0794	C(112)	−0.0303 (2)	0.1022 (3)	0.2661 (3)	0.0730
C(23)	0.0324 (2)	0.3004 (2)	0.1267 (3)	0.0550	C(121)	0.1829 (2)	0.0843 (2)	0.4553 (2)	0.0500
O(23)	−0.0431 (1)	0.2693 (2)	0.0434 (2)	0.0777	C(122)	0.1931 (2)	−0.0524 (3)	0.4421 (3)	0.0712
C(1)	0.2167 (1)	0.2004 (2)	0.2972 (2)	0.0359	N(3)	0.2968 (1)	0.4674 (1)	0.1183 (2)	0.0413
C(2)	0.3268 (1)	0.2129 (2)	0.3491 (2)	0.0370	C(311)	0.2386 (2)	0.4526 (2)	−0.0328 (2)	0.0511
C(3)	0.2823 (1)	0.3920 (2)	0.1960 (2)	0.0364	C(312)	0.3002 (2)	0.3858 (3)	−0.1565 (2)	0.0624
C(4)	0.2984 (1)	0.4364 (2)	0.3539 (2)	0.0393	C(321)	0.3946 (2)	0.5315 (2)	0.1587 (2)	0.0485
C(70)	0.3557 (1)	0.3440 (2)	0.4244 (2)	0.0390	C(322)	0.3804 (2)	0.6649 (2)	0.1573 (3)	0.0711
Compound **5**									
Fe(1)	0.29327 (7)	0.15645 (7)	0.34597 (5)	0.0331	C(1)	0.3312 (5)	0.1405 (5)	0.1944 (3)	0.0321
Fe(2)	0.52321 (7)	−0.01841 (7)	0.26870 (5)	0.0368	C(2)	0.1816 (5)	0.2036 (5)	0.2236 (3)	0.0310
Fe(3)	0.44522 (7)	0.24552 (7)	0.18424 (5)	0.0333	C(3)	0.1371 (5)	0.3182 (5)	0.2706 (3)	0.0342
C(11)	0.2319 (6)	0.0189 (6)	0.4125 (4)	0.0483	C(4)	0.2521 (5)	0.3517 (5)	0.2732 (3)	0.0334
O(11)	0.1899 (5)	−0.0676 (5)	0.4560 (3)	0.0667	C(70)	0.3849 (5)	0.0003 (5)	0.1825 (4)	0.0377
C(12)	0.2585 (6)	0.2024 (5)	0.4617 (4)	0.0426	C(71)	0.5139 (6)	−0.0687 (6)	0.1307 (4)	0.0437
O(12)	0.2279 (5)	0.2308 (5)	0.5377 (3)	0.0597	C(72)	0.5574 (7)	−0.2148 (7)	0.1264 (5)	0.0628
C(21)	0.5132 (5)	0.0722 (5)	0.3576 (4)	0.0412	C(73)	−0.0143 (5)	0.3946 (6)	0.3138 (4)	0.0449
O(21)	0.5629 (4)	0.0961 (4)	0.4089 (3)	0.0520	C(74)	−0.1078 (7)	0.4756 (8)	0.2410 (6)	0.0674
C(22)	0.7069 (6)	−0.0957 (6)	0.2314 (4)	0.0450	C(75)	−0.0669 (8)	0.4967 (8)	0.1419 (7)	0.0839
O(22)	0.8242 (4)	−0.1504 (5)	0.2090 (4)	0.0688	N(2)	0.0931 (4)	0.1493 (5)	0.2131 (3)	0.0394
C(23)	0.5148 (6)	−0.1712 (6)	0.3560 (5)	0.0565	C(211)	0.1178 (6)	0.1194 (6)	0.1150 (4)	0.0494
O(23)	0.5161 (6)	−0.2726 (5)	0.4107 (4)	0.0841	C(212)	−0.0041 (9)	0.196 (1)	0.0638 (6)	0.0835
C(31)	0.3736 (6)	0.3785 (6)	0.0853 (4)	0.0471	C(221)	−0.0302 (6)	0.1335 (7)	0.2888 (4)	0.0511
O(31)	0.3293 (5)	0.4591 (5)	0.0206 (3)	0.0683	C(222)	−0.038 (1)	−0.0047 (9)	0.3065 (6)	0.0849
C(32)	0.6033 (6)	0.1588 (6)	0.1066 (4)	0.0479	N(4)	0.2259 (4)	0.4704 (4)	0.2985 (3)	0.413
O(32)	0.7044 (4)	0.1272 (5)	0.0468 (3)	0.0652	C(411)	0.3171 (7)	0.4789 (6)	0.3508 (4)	0.0520
C(33)	0.5494 (6)	0.3217 (6)	0.2087 (4)	0.0515	C(412)	0.2339 (9)	0.5518 (8)	0.4367 (5)	0.0747
O(33)	0.6256 (5)	0.3630 (5)	0.2157 (4)	0.0725	C(421)	0.1338 (6)	0.6022 (6)	0.2484 (5)	0.0542
					C(422)	0.2106 (8)	0.6961 (7)	0.1773 (5)	0.0697
Compound **6**									
Fe(1)	0.19564 (5)	0.47841 (6)	0.21658 (3)	0.0413	C(23)	0.2722 (5)	0.8604 (5)	0.2257 (3)	0.0549
Fe(2)	0.30259 (5)	0.66980 (5)	0.32317 (3)	0.0432	O(23)	0.2486 (4)	0.9872 (3)	0.1707 (2)	0.0806
C(11)	0.3778 (5)	0.3217 (5)	0.1915 (3)	0.0618	C(1)	0.0362 (4)	0.6550 (4)	0.2752 (2)	0.0423
O(11)	0.4938 (4)	0.2281 (4)	0.1733 (3)	0.0881	C(2)	0.0736 (4)	0.6390 (4)	0.3827 (2)	0.0483
C(12)	0.0431 (5)	0.4196 (4)	0.1475 (3)	0.0545	C(3)	0.2072 (4)	0.5014 (4)	0.4268 (2)	0.0503
O(12)	−0.0504 (4)	0.3795 (4)	0.1041 (2)	0.0747	C(4)	0.2417 (5)	0.3556 (4)	0.3810 (3)	0.0538
C(13)	0.2599 (4)	0.6200 (5)	0.1128 (3)	0.0511	C(5)	0.1149 (5)	0.3017 (4)	0.3425 (3)	0.0572
O(13)	0.3034 (4)	0.7017 (4)	0.0415 (2)	0.0723	N(1)	−0.0986 (3)	0.7723 (4)	0.2306 (2)	0.0530
C(21)	0.5153 (4)	0.5551 (4)	0.3116 (3)	0.0537	C(111)	−0.1293 (5)	0.8199 (5)	0.01173 (3)	0.0591
O(21)	0.6501 (3)	0.4798 (4)	0.3078 (2)	0.0747	C(112)	−0.2953 (6)	0.8039 (8)	0.0843 (3)	0.0816
C(22)	0.3506 (5)	0.7696 (5)	0.4188 (3)	0.0621	C(121)	−0.2158 (6)	0.8774 (6)	0.2932 (4)	0.0771
O(22)	0.3829 (5)	0.8372 (5)	0.4786 (3)	0.0903	C(122)	−0.1547 (7)	1.0208 (7)	0.3051 (5)	0.0989
Compound **7**									
Fe(1)	0.22401 (7)	0.26768 (4)	0.33036 (3)	0.0519	C(23)	0.1116 (6)	0.4171 (4)	0.1324 (3)	0.0736
Fe(2)	0.22857 (7)	0.27923 (5)	0.13986 (3)	0.0537	O(23)	0.0366 (5)	0.5069 (3)	0.1283 (3)	0.1020
C(11)	−0.0231 (6)	0.1635 (4)	0.3527 (2)	0.0606	C(5)	0.5241 (9)	0.5303 (4)	0.2778 (5)	0.0909
O(11)	−0.1841 (4)	0.1057 (3)	0.3673 (2)	0.0851	C(4)	0.4358 (5)	0.3826 (3)	0.2589 (3)	0.0625
C(12)	0.3875 (6)	0.2729 (4)	0.4421 (3)	0.0715	C(3)	0.5343 (5)	0.3103 (4)	0.1974 (3)	0.0644
O(12)	0.5000 (5)	0.2759 (4)	0.5125 (2)	0.1047	C(2)	0.4476 (5)	0.1709 (3)	0.1898 (3)	0.0572
C(13)	0.1229 (7)	0.4100 (4)	0.3611 (3)	0.0785	C(1)	0.3302 (4)	0.1217 (3)	0.2711 (2)	0.0476
O(13)	0.0564 (6)	0.4985 (3)	0.3806 (3)	0.1085	N(1)	0.3014 (4)	−0.0064 (2)	0.2899 (2)	0.0540
C(21)	0.0025 (5)	0.1456 (4)	0.1249 (2)	0.0575	C(111)	0.1957 (7)	−0.0648 (4)	0.3749 (3)	0.0708
O(21)	−0.1389 (4)	0.0578 (3)	0.1144 (2)	0.0789	C(112)	−0.002 (1)	−0.1674 (5)	0.3442 (5)	0.1005
C(22)	0.2859 (6)	0.2826 (5)	0.0127 (3)	0.0773	C(121)	0.3880 (6)	−0.1009 (4)	0.2304 (3)	0.0706
O(22)	0.3206 (6)	0.2842 (5)	−0.0683 (2)	0.1125	C(122)	0.2609 (9)	−0.1487 (5)	0.1324 (4)	0.0922
Compound 8									
Fe(1)	0.2158 (1)	0.28587 (8)	0.32126 (6)	0.0540	C(23)	0.396 (1)	0.1912 (6)	0.1603 (5)	0.0692
Fe(2)	0.4716 (1)	0.28556 (8)	0.22445 (5)	0.0531	O(23)	0.347 (1)	0.1337 (5)	0.1184 (4)	0.0808
C(11)	0.287 (2)	0.2160 (8)	0.4003 (5)	0.0887	C(5)	0.223 (1)	0.3547 (7)	0.2244 (4)	0.0601
O(11)	0.336 (1)	0.1715 (6)	0.4501 (5)	0.1229	C(4)	0.361 (1)	0.4285 (6)	0.2210 (5)	0.0629
C(12)	0.003 (1)	0.3364 (8)	0.3507 (5)	0.0764	C(3)	0.481 (1)	0.4245 (6)	0.2803 (4)	0.0600
O(12)	−0.1300 (9)	0.3661 (7)	0.3689 (5)	0.1036	C(2)	0.406 (1)	0.4072 (5)	0.3526 (4)	0.0499
C(13)	0.117 (1)	0.1777 (7)	0.2802 (5)	0.0763	C(1)	0.272 (1)	0.4745 (5)	0.3770 (4)	0.0563
O(13)	0.053 (1)	0.1085 (6)	0.2524 (5)	0.1017	N(1)	0.217 (1)	0.4945 (6)	0.4438 (3)	0.0652
C(21)	0.583 (1)	0.2116 (6)	0.2928 (4)	0.0630	C(111)	0.296 (2)	0.4465 (7)	0.5075 (4)	0.0742
O(21)	0.664 (1)	0.1675 (5)	0.3339 (4)	0.0896	C(112)	0.454 (2)	0.497 (1)	0.5364 (6)	0.1115
C(22)	0.664 (1)	0.3156 (8)	0.1725 (5)	0.0823	C(121)	0.058 (2)	0.5589 (8)	0.4570 (6)	0.0930
O(22)	0.791 (1)	0.3370 (8)	0.1391 (5)	0.1251	C(122)	0.092 (3)	0.650 (1)	0.4914 (9)	0.1484

[a] $U(\mathrm{eq}) = [U(11)U(22)U(33)]^{1/3}$.

Reaction in Hexane Solution at 45 °C. Diethylpent-4-en-1-ynylamine (300 mg, 2.2 mmol) was added to a solution of [$Fe_3(CO)_{12}$] (1011 mg, 2 mmol) in 80 mL of hexane. The solution was stirred at 45 °C for 24 h under dry nitrogen. The reaction mixture was evaporated. The residue was separated by chromatography giving two main bands with a *n*-hexane/CH_2Cl_2 mixture as eluant: a yellow one and a dark green-blue one. Evaporation followed by recrystallization from *n*-hexane at −15 °C afforded yellow crystals of **2** (300 mg; yield with respect to [$Fe_3(CO)_{12}$], 0.27) and green-blue crystals of **3** (200 mg; 0.17).

Complex 2: IR ν(CO) 1900 (m), 1965 (sh), 1975 (s), 2020 (s), 2060 (s) cm^{-1}, ν(C=C) 1640 (w) cm^{-1}; MS *m/z* 554 (M^+).

Complex 3: IR ν(CO) 1910 (w), 1945 (s), 1965 (s), 1985 (s), 2000 (s), 2030 (s), 2060 (s) cm^{-1}, ν(C=C) 1640 (sh) cm^{-1}, ν(C=O) 1650 (s) cm^{-1}; MS *m/z* 582 (M^+).

Reaction in Refluxing Toluene. A solution of [$Fe_3(CO)_{12}$] (1285 mg, 2.55 mmol) and the aminoalkyne (350 mg, 2.55 mmol) in 80 mL of toluene was refluxed under dry nitrogen for 12 h. The reaction mixture was evaporated under vacuum. The residue was separated by chromatography with *n*-hexane/CH_2Cl_2 mixture, starting with pure *n*-hexane eluant and increasing slowly the proportion of dichloromethane to separate five major bands. Evaporation followed by recrystallization from *n*-hexane at −15 °C afforded seven complexes. Compounds **2** (200 mg; 0.14) and **3** (149 mg; 0.10) were obtained from fractions 1 and 5, respectively, and characterized by their infrared spectra. Fraction 2 gave red crystals of **6** (61 mg; 0.06) and yellow crystals of **7** (61 mg; 0.06). Green crystals of complex **4** (60 mg; 0.04) were separated from fraction 3. Green crystals of **5** (121 mg; 0.07) and orange crystals of **8** (125 mg; 0.12) were isolated from fraction 4.

Complex 4: IR ν(CO) 1960 (s), 1970 (s), 1980 (s), 2000 (s), 2060 (m) cm^{-1}, ν(CO bridging) 1845 (s), 1855 (sh) cm^{-1}, ν(C=C) 1635 (w) cm^{-1}; MS *m/z* 666 (M^+).

Complex 5: IR ν(CO) 1920 (m), 1945 (m), 1960 (s), 1975 (s), 2000 (s), 2010 (sh), 2050 (m) cm^{-1}, ν(CO bridging) 1795 (m) cm^{-1}; MS *m/z* 666 (M^+).

Complex 6: IR ν(CO) 1895 (w), 1930 (s), 1940 (sh), 1980 (s), 2000 (s), 2060 (s) cm^{-1}; MS *m/z* 417 (M^+); ^1H NMR (200 MHz, $CDCl_3$) δ 4.77 (m, 1 H, C*H*=CH_2), 4.72 (s, 1 H, C*H*—CH), 3.40 (d, 2 H, CH_2CH_3), 3.07 (d, 1 H, C*H*—NEt_2), 1.56 (t, 2 H, CH_2=CH), 1.16 (t, 3 H, CH_3CH_2). Anal. Calcd for $C_{15}H_{15}NO_6Fe_2$: C, 43.2; H, 3.62; N, 3.36. Found: C, 43.33; H, 3.60; N, 3.43.

Complex 7: IR ν(CO) 1930 (s), 1945 (s), 1965 (s), 1980 (s), 2020 (s), 2060 (s) cm^{-1}; MS *m/z* 417 (M^+). Anal. Calcd for $C_{15}H_{15}NO_6Fe_2$: C, 43.2; H, 3.62; N, 3.36. Found: C, 43.32; H, 3.68; N, 3.41.

Complex 8: IR ν(CO) 1925 (s), 1935 (sh), 1950 (s), 1965 (s), 1990 (s), 2020 (s), 2070 (s) cm^{-1}; MS *m/z* 417 (M^+); ^1H NMR (200 MHz, $CDCl_3$) δ 8.20 (q, 1 H, C*H* bridgehead), 5.82 (d, 1 H, C*H*-NEt_2), 5.00 (t, 1 H, C*H*-CHCHNEt_2), 3.64 (d, 1 H, FeCH-C*H*), 3.00 (dd, 1 H, C*H*-CHNEt_2), 3.15 (m, 2 H, CH_2CH_3), 1.17 (q, 3 H, CH_2CH_3). Anal. Calcd for $C_{15}H_{15}NO_6Fe_2$: C, 43.2; H, 3.62; N, 3.36. Found: C, 43.43; H, 3.30; N, 3.46.

Crystal Data. For all compounds, preliminary unit-cell dimensions and symmetry informations were derived from precession photographs; selected crystals were then set up on an automatic four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Three standard reflections were monitored periodically; they showed no change during data collections. Crystallographic data and other pertinent informations are summarized in Table IV. Corrections were made for Lorentz and polarization effects. No absorption corrections were applied.

Computations were performed by using CRYSTALS[27] adapted on a VAX 11/725. Atomic form factors for neutral Fe, C, N, O, and H were taken from ref 28; anomalous dispersion was taken into account. All structures were solved by interpretation of the Patterson maps which clearly indicated iron atom positions. All remaining non-hydrogen atoms were found by successive electron density map calculations. Hydrogen atoms were located on difference electron density maps. In complexes **5** and **8**, hydrogen atoms were given calculated positions (C–H = 0.96 Å) with a fixed overall isotropic thermal parameter ($U = 0.08$ Å^2); coordinates of these atoms were not refined but were recalculated after each cycle. In the three other complexes, hydrogen atomic coordinates were refined with an overall isotropic thermal parameter. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Absolute configuration was determined for **8**. The weighting scheme used in the last refinement cycles was $w = w'[1 - (\Delta F/6\sigma(F_o))^2]^2$ where $w' = 1/\sum_1{}^3 \mathrm{ArTr}(x)$ with three coefficients Ar for the Chebyshev polynomial ArTr(x) where x was F_o/F_o(max).[29] The models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ having the values listed in Table I. The criteria for a satisfactory complete analysis were the ratios of the rms shift to standard deviation being less than 0.3 and no significant features in the final difference maps. Atomic coordinates are given in Table V.

Registry No. **2**, 120883-22-9; **3**, 120883-23-0; **4**, 120883-26-3; **5**, 120905-02-4; **6**, 120905-03-5; **7**, 120883-24-1; **8**, 120883-25-2; CH_2=$CHCH_2C$≡$CNEt_2$, 120883-21-8; [$Fe_3(CO)_{12}$], 17685-52-8.

Supplementary Material Available: Tables of anisotropic temperature factors, important least-squares planes, hydrogen coordinates, and distances and angles for CO ligands (10 pages); listings of observed and calculated structure factors (78 pages). Ordering information is given on any current masthead page.

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