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## Coupling reactions of ynamines. Syntheses, structural characterization and electrochemistry of some *nido* and *closo* ferracyclopentadiene complexes

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### Abstract

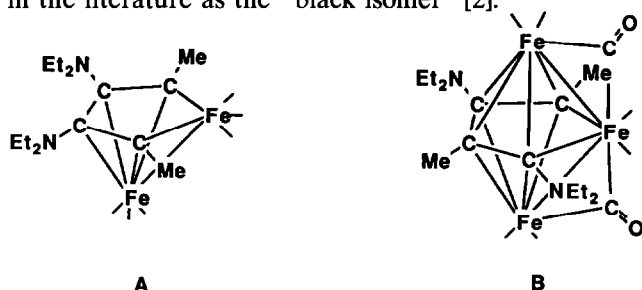
The reaction of  $[\text{Fe}_2(\text{CO})_7\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\}]$  (1) with ynamines  $\text{RC}\equiv\text{CNEt}_2$  ( $\text{R} = \text{Me}$ ,  $\text{C}_3\text{H}_5$ , or  $\text{CH}_2\text{Ph}$ ) at  $20^\circ\text{C}$  yielded dinuclear ferracyclopentadiene complexes  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{R})\}]$  ( $\text{R} = \text{Me}$  (2),  $\text{R} = \text{CH}_2\text{Ph}$  (3),  $\text{R} = \text{C}_3\text{H}_5$  (4)). Complex 5,  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{C}_3\text{H}_5)\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$ , was obtained directly from the reaction of  $\text{C}_3\text{H}_5\text{C}\equiv\text{CNEt}_2$  with  $[\text{Fe}_2(\text{CO})_9]$ . All complexes were characterized by a combination of microanalytical and spectroscopic techniques. The molecular structure of 4 was determined X-ray crystallographically: triclinic,  $P\bar{1}$ ,  $a = 8.820(2)$  Å,  $b = 9.261(2)$  Å,  $c = 18.470(2)$  Å,  $\alpha = 89.40(1)^\circ$ ,  $\beta = 81.81(1)^\circ$ ,  $\gamma = 70.23(2)^\circ$ ,  $R_w = 0.0406$  for 2580 reflections. The *nido* complexes 4 and 5 transformed to the *closo* tripledecker compounds  $[\text{Fe}_3(\text{CO})_8\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{R})\}]$  ( $\text{R} = \text{Ph}$  (6);  $\text{R} = \text{C}_3\text{H}_5$  (7)) by an excess of  $[\text{Fe}_2(\text{CO})_9]$  in refluxing hexane. Both complexes were characterized by IR,  $^1\text{H}$  NMR, mass spectra and chemical analysis. The X-ray structure of 6 was carried out: monoclinic,  $P2_1/c$ ,  $a = 14.900(3)$ ,  $b = 11.149(2)$ ,  $c = 18.453(4)$  Å,  $\beta = 91.14(2)^\circ$ ,  $R_w = 0.0414$  for 2304 reflections. Only one isomer could be isolated for the *nido* compounds. The *nido*–*closo* transformation did not modify the coupling within the butadiene moiety. Electrochemistry of the *nido* and *closo* complexes is reported. The *closo* compounds showed two reversible one-electron reduction waves whereas the *nido* species were completely irreversibly reduced.

### Introduction

In the course of our studies on the chemistry of ynamines,  $\text{RC}\equiv\text{CNEt}_2$ , and iron complexes, we reported the formation of two types of ferracyclopentadiene cluster. The first,  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{Me})\}]$  [1] (A), corresponds to the well known ferrole type structure [2]. The second,  $[\text{Fe}_3(\text{CO})_8\{\text{C}(\text{Me})\text{C}$

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$(\text{NEt}_2)\text{C}(\text{Me})\text{C}(\text{NEt}_2)]$  [3] (**B**), closely resembles the trinuclear complex described in the literature as the "black isomer" [2].



Surprisingly, the butadiene moiety in these two compounds results from different couplings of two ynamines molecules: tail-to-tail in **A** and head-to-tail in **B**.

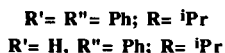
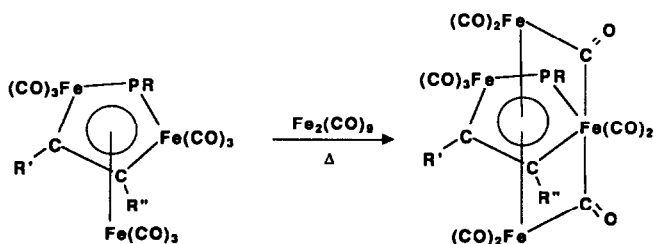
In the polyhedral skeletal electron pair (PSEP) approach [4], both these complexes are expected to assume a pentagonal bipyramidal geometry [S(skeletal electron pairs) = 8]. The ferrole **A** with 6 skeletal atoms is a *nido* species, whereas the trinuclear cluster **B** which contains 7 skeletal atoms is *closo*. The transformation of the *nido* into the *closo* species, as well as the reverse reaction, may be accounted for by addition, or elimination, of an apical  $\text{Fe}(\text{CO})_2$  fragment.

The thermal decomposition of  $[\text{Fe}_3(\text{CO})_8(\text{RC}_2\text{R})_2]$  systems to  $[\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R})_2]$  has been clearly established by Hübel *et al.* [2], and more recently the redox chemistry of these triiron clusters has been investigated [5].

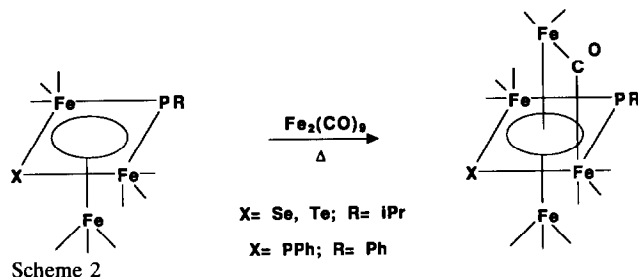
Recently, Huttner *et al.* [6] reported the transformation of *nido* complexes  $[\text{Fe}_3(\text{CO})_9\{\text{P}(\text{R})\text{C}(\text{R}')\text{C}(\text{R}'')\}]$  (isoelectronic with the ferrole structure) into the *closo* so-called tripledecker compounds  $[\text{Fe}_4(\text{CO})_{11}\{\text{P}(\text{R})\text{C}(\text{R}')\text{C}(\text{R}'')\}]$  (Scheme 1).

A closely related transformation has also been observed for complexes with a tetragonal bipyramid structure [7]. In every case, whatever the structure of the metallocycle, it remains unchanged during the transformation (Scheme 2).

With a view to understanding the coupling mechanisms in the chemistry of ynamines, and in order to assess the influence of the electron-releasing  $\text{NEt}_2$  substituents on the chemistry and the electrochemical behaviour of such complexes, we have optimized stepwise syntheses of a series of  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{R})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{R}')\}]$  derivatives and their transformations into the *closo* tripledecker clusters  $[\text{Fe}_3(\text{CO})_8\{\text{C}(\text{R})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{R}')\}]$ ; these have been fully characterized and studied by electrochemistry.



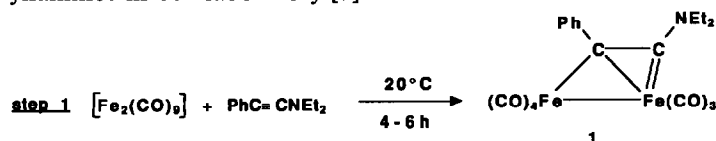
Scheme 1.



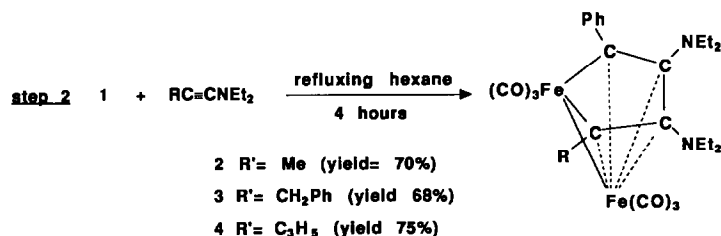
## Results and discussion

*Syntheses of  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{R})\}]$  ( $\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{or } \text{C}_3\text{H}_5$ )*

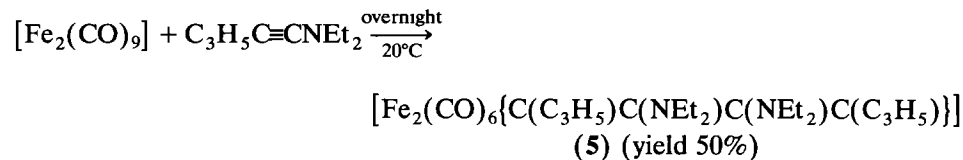
The ynamine  $\text{PhC}\equiv\text{CNEt}_2$  reacts with  $[\text{Fe}_2(\text{CO})_9]$  to yield the dinuclear aminocarbene complex  $[\text{Fe}_2(\text{CO})_7\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\}]$  in 50% yield. The formation of this binuclear complex is in accordance with previous studies on the reactivity of ynamines in our laboratory [3].



This stable species can be isolated and purified by column chromatography, and it reacts further with different ynamines to yield ferracyclopentadiene derivatives. It may be noted that only one isomer is formed by coupling both carbon atoms bearing the amino groups.



In step 1, if the reaction mixture is stirred at room temperature overnight with an excess of the ynamine, formation of the ferrole is observed as well as uncharacterized green products. This procedure was used to synthesize the ferracyclopentadiene  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{C}_3\text{H}_5)\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$ . Complex 1 with a  $\text{C}_3\text{H}_5$  group instead of the Ph group is unstable and could not be isolated.



All four complexes were purified by column chromatography. Yellow crystals of compounds 2–5 were obtained from hexane solutions cooled to  $-20^\circ\text{C}$ .

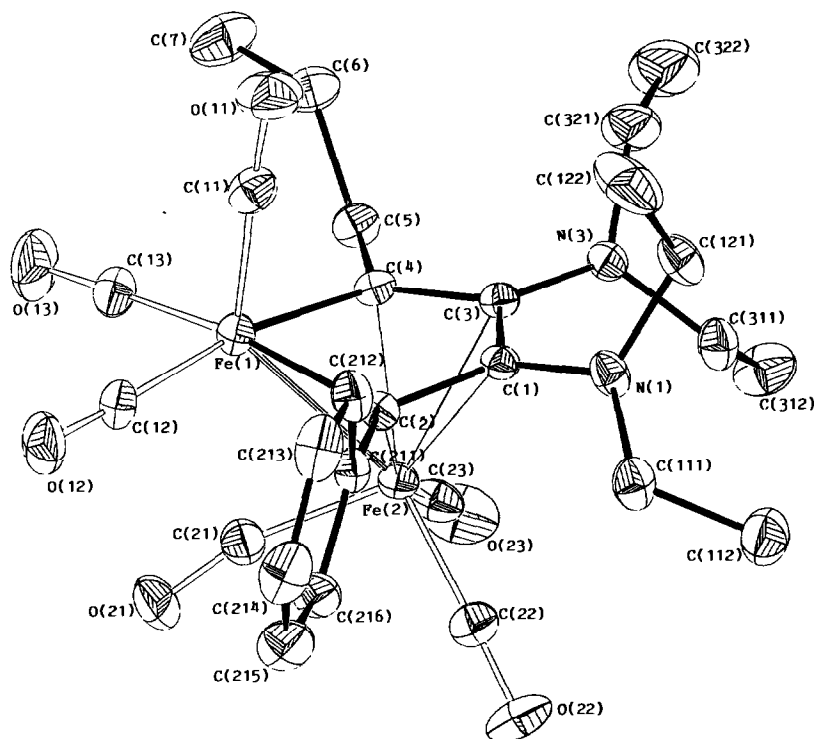


Fig. 1. ORTEP drawing of  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$  (**4**) showing 30% probability thermal ellipsoids.

These four complexes were characterized by a combination of microanalytical and spectroscopic techniques; the molecular structure of **4** was determined by X-ray crystallography.

#### *Structure of $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$ (**4**)*

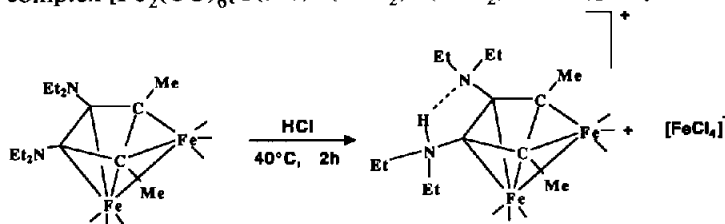
The molecular structure of **4** with the atom-labeling scheme is shown in Fig. 1. Final atomic positional parameters are listed in Table 1. Selected interatomic distances are given in Table 2.

As expected, the molecule corresponds to a ferracyclopentadiene complex. Two  $\text{Fe}(\text{CO})_3$  moieties are linked by a Fe–Fe bond (2.487(1) Å). This bond is bridged by a  $\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)$  ligand, formed by the tail-to-tail coupling of two ynamine molecules. As observed in other ferracyclopentadiene complexes containing aminoalkynes [1,8], the Fe(2)–C bond distances (2.201(5) and 2.276(5) Å) to the amine-substituted carbon atoms are longer than those to the bridging alkyl-substituted carbon atoms (2.057(5) and 2.074(5) Å). This may be explained by partial C–N  $\pi$ -bonding, and hence a weakening of the Fe–C bonding.

Recent papers [9] on the chemistry of ynamines with metal clusters note a strong C–N  $\pi$ -bonding interaction between the nitrogen atom and the amine-substituted carbon atom of the alkynyl group. The formation of a C=N double bond (mean value 1.30 Å) appears to disrupt the expected metal–carbon bonding.

In the case of the ferrole-ynamine system, the Fe–C bond still exists, and the C–N bond length of 1.39 Å (mean value) is indicative of weak C–N  $\pi$ -bonding. It

is worth pointing out that the IR spectra of these ferroles do not show  $\nu(\text{C}=\text{N})$  bands [10] as would be expected if strong C–N  $\pi$ -bonding occurred. Moreover, we recently reported protonation of one of the nitrogen atoms of the related ferrole complex  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{Me})\}]$  to yield the ionic species [8].



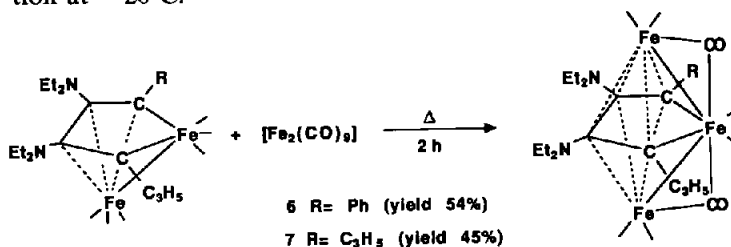
This protonation results in a shortening of the Fe–C bond to 2.181(7) Å from 2.236(9) Å and a lengthening of the C–N bond to 1.468(8) Å from 1.391(9) Å.

This weakening of C–N  $\pi$ -bonding in ferrole clusters could be explained by a recent theoretical study of binuclear  $[\text{Me}_2(\text{CO})_6(\text{C}_4\text{H}_4)]$  [11] complexes, which points out that the butadiene moiety is negatively charged, thus having a repulsive effect on the nitrogen lone pair.

In 4, as observed in the structure of  $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Me})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{Me})\}]$  previously reported, the butadiene moiety results from tail-to-tail coupling of the ynamines. On the basis of  $^1\text{H}$  NMR spectroscopy (Table 3), a similar coupling mode may be assumed for compounds 2, 3 and 5. Other isomers, if formed, do not separate upon chromatographic work-up.

*Syntheses of the closo tripledecker complexes:  $[\text{Fe}_3(\text{CO})_8\{\text{C}(\text{R})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$  ( $\text{R} = \text{Ph}$  (6);  $\text{R} = \text{C}_3\text{H}_5$  (7))*

When a large excess of  $[\text{Fe}_2(\text{CO})_9]$  is added to ferrole complexes 4 or 5 in refluxing hexane, a rapid change from yellow to dark green is observed. Besides unreacted starting ferrole compound and  $[\text{Fe}_3(\text{CO})_{12}]$ , chromatographic separation with a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane (2:10) as eluant afforded pure fractions containing complexes 6 and 7. Dark green crystals were obtained by recrystallization at  $-20^\circ\text{C}$ .



Each complex was characterized by IR,  $^1\text{H}$  NMR, mass spectra and chemical analysis.

In the terminal CO stretching region, both compounds show six infrared active bands, and in the bridging carbonyl stretching region two main bands. Proton NMR spectroscopy shows that the organic moieties contain two diethylamino-groups. However a new signal (doublet of doublet) around 1.50 ppm in both complexes indicates that the allylic fragments have been modified during the reaction, through double bond isomerization associated with hydrogen migration.

$$-\text{CH}_2-\text{CH}=\text{CH}_2 \longrightarrow -\text{CH}=\text{CH}-\text{CH}_3$$

Table 1

Fractional atomic coordinates with e.s.d.s in parentheses, and equivalent isotropic thermal parameter  $U_{\text{eq}}$  for compound **4**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Fe(1)	0.09858(9)	0.40785(9)	0.77748(4)	0.0464
Fe(2)	0.38195(9)	0.39108(9)	0.78808(4)	0.0422
C(1)	0.4076(6)	0.1830(5)	0.7166(3)	0.0391
C(2)	0.2947(6)	0.3253(6)	0.7011(3)	0.0413
C(3)	0.3884(6)	0.1517(6)	0.7947(3)	0.0401
C(4)	0.2458(6)	0.2609(6)	0.8346(3)	0.0409
C(5)	0.2053(7)	0.2458(7)	0.9164(3)	0.0522
C(6)	0.0738(8)	0.1755(8)	0.9356(3)	0.0675
C(7)	-0.047(1)	0.225(1)	0.9867(4)	0.0915
N(1)	0.5310(6)	0.0829(5)	0.6681(2)	0.0496
C(111)	0.6114(7)	0.1363(7)	0.6035(3)	0.0568
C(112)	0.7945(9)	0.0642(9)	0.5942(4)	0.0845
C(121)	0.5404(8)	-0.0774(6)	0.6636(3)	0.0600
C(122)	0.420(1)	-0.1070(9)	0.6217(5)	0.1035
N(3)	0.4972(5)	0.0313(5)	0.8269(2)	0.0459
C(311)	0.6730(7)	-0.0005(7)	0.8085(3)	0.0594
C(312)	0.7596(9)	-0.0033(9)	0.8717(4)	0.0844
C(321)	0.4480(9)	-0.0960(9)	0.8539(5)	0.0823
C(322)	0.468(1)	-0.157(1)	0.9207(6)	0.1206
C(211)	0.2803(6)	0.3800(6)	0.6261(3)	0.0452
C(212)	0.2216(7)	0.3049(7)	0.5777(3)	0.0576
C(213)	0.1983(8)	0.3600(9)	0.5084(3)	0.0721
C(214)	0.2325(8)	0.488(1)	0.4863(4)	0.0753
C(215)	0.2898(9)	-0.5622(9)	0.5332(4)	0.0731
C(216)	0.3118(7)	0.5111(7)	0.6026(3)	0.0597
C(11)	0.0219(7)	0.2641(8)	0.7553(3)	0.0602
O(11)	-0.0208(6)	0.1662(6)	0.7416(3)	0.0927
C(12)	-0.0090(7)	0.5551(7)	0.7195(3)	0.0556
O(12)	-0.0806(5)	0.6442(5)	0.6833(3)	0.0790
C(13)	-0.0491(7)	0.4992(7)	0.8560(4)	0.0662
O(13)	-0.1470(6)	0.5596(6)	0.9034(3)	0.0954
C(21)	0.2423(7)	0.5831(7)	0.7988(3)	0.0612
O(21)	0.1822(6)	0.7131(5)	0.8076(3)	0.0852
C(22)	0.5472(7)	0.4330(7)	0.7371(3)	0.0618
O(22)	0.6508(6)	0.4641(6)	0.7057(3)	0.0868
C(23)	0.4598(8)	0.3962(7)	0.8715(3)	0.0624
O(23)	0.5087(7)	0.4011(6)	0.9248(3)	0.0897

$$^a U_{\text{eq}} = [U(11) \times U(22) \times U(33)]^{1/3}$$

We recently reported such a rearrangement of a  $\text{C}_3\text{H}_5$  fragment [12].

The mass spectra show parent ions at  $m/e$  702 and  $m/e$  666 for **6** and **7**, respectively, with fragments due to the successive loss of eight molecules of carbon monoxide. These results, together with the IR and NMR spectroscopic data, strongly suggest that **6** and **7** correspond to the expected tripledecker system. To confirm this, the X-ray crystal structure of **6** has been determined.

#### Structure of $[\text{Fe}_3(\text{CO})_8\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$ (**6**)

An ORTEP drawing of the molecular structure of **6** is shown in Fig. 2. Final atomic positional parameters are listed in Table 4. Selected interatomic distances

Table 2

Interatomic distances (Å) and bond angles (°) for  $[\text{Fe}_2(\text{CO})_6(\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5))] (4)$ 

Fe(1)–Fe(2)	2.487(1)	C(6)–C(7)	1.275(9)
Fe(1)–C(2)	1.999(5)	C(11)–O(11)	1.136(7)
Fe(1)–C(4)	1.954(5)	C(12)–O(12)	1.132(6)
Fe(1)–C(11)	1.760(7)	C(13)–O(13)	1.138(7)
Fe(1)–C(12)	1.814(6)	C(21)–O(21)	1.142(7)
Fe(1)–C(13)	1.804(6)	C(22)–O(22)	1.130(7)
Fe(2)–C(1)	2.276(5)	C(23)–O(23)	1.138(7)
Fe(2)–C(2)	2.057(5)	C(111)–C(112)	1.510(9)
Fe(2)–C(3)	2.201(5)	C(111)–N(1)	1.468(7)
Fe(2)–C(4)	2.074(5)	C(121)–C(122)	1.49(1)
Fe(2)–C(21)	1.781(6)	C(121)–N(1)	1.460(7)
Fe(2)–C(22)	1.773(6)	C(211)–C(212)	1.391(8)
Fe(2)–C(23)	1.780(6)	C(211)–C(216)	1.386(8)
C(1)–C(2)	1.414(7)	C(212)–C(213)	1.389(8)
C(1)–C(3)	1.466(7)	C(213)–C(214)	1.37(1)
C(1)–N(1)	1.380(6)	C(214)–C(215)	1.36(1)
C(2)–C(211)	1.479(7)	C(215)–C(216)	1.379(8)
C(3)–C(4)	1.429(7)	C(311)–C(312)	1.478(9)
C(3)–N(3)	1.394(6)	C(311)–N(3)	1.466(7)
C(4)–C(5)	1.518(7)	C(321)–C(322)	1.37(1)
C(5)–C(6)	1.512(8)	C(321)–N(3)	1.449(8)
C(4)–Fe(1)–C(2)	80.0(2)	C(4)–C(3)–C(1)	112.1(4)
C(11)–Fe(1)–C(2)	92.0(3)	N(3)–C(3)–C(1)	124.3(5)
C(11)–Fe(1)–C(4)	89.3(2)	N(3)–C(3)–C(4)	123.6(5)
C(12)–Fe(1)–C(2)	93.4(2)	C(3)–C(4)–Fe(1)	116.8(4)
C(12)–Fe(1)–C(4)	170.3(2)	C(5)–C(4)–Fe(1)	123.3(4)
C(12)–Fe(1)–C(11)	98.1(3)	C(5)–C(4)–C(3)	119.4(5)
C(13)–Fe(1)–C(2)	167.1(3)	C(6)–C(5)–C(4)	113.0(5)
C(13)–Fe(1)–C(4)	94.5(3)	C(7)–C(6)–C(5)	125.4(7)
C(13)–Fe(1)–C(11)	99.7(3)	O(11)–C(11)–Fe(1)	176.7(6)
C(13)–Fe(1)–C(12)	90.4(3)	O(12)–C(12)–Fe(1)	177.4(6)
C(21)–Fe(2)–C(1)	134.0(2)	O(13)–C(13)–Fe(1)	177.0(6)
C(21)–Fe(2)–C(2)	96.8(2)	O(21)–C(21)–Fe(2)	165.2(6)
C(21)–Fe(2)–C(3)	141.1(2)	O(22)–C(22)–Fe(2)	178.0(6)
C(21)–Fe(2)–C(4)	103.8(3)	O(23)–C(23)–Fe(2)	179.4(6)
C(22)–Fe(2)–C(1)	95.5(2)	N(1)–C(111)–C(112)	112.4(5)
C(22)–Fe(2)–C(2)	97.6(2)	N(1)–C(121)–C(122)	115.1(5)
C(22)–Fe(2)–C(3)	119.8(2)	C(212)–C(211)–C(2)	119.6(5)
C(22)–Fe(2)–C(4)	158.7(3)	C(216)–C(211)–C(2)	122.8(5)
C(22)–Fe(2)–C(21)	97.0(3)	C(216)–C(211)–C(212)	117.5(5)
C(23)–Fe(2)–C(1)	128.6(2)	C(213)–C(212)–C(211)	120.5(6)
C(23)–Fe(2)–C(3)	95.9(2)	C(214)–C(213)–C(212)	120.8(7)
C(23)–Fe(2)–C(4)	90.9(2)	C(215)–C(214)–C(213)	119.2(6)
C(23)–Fe(2)–C(21)	95.1(3)	C(216)–C(215)–C(214)	121.0(7)
C(23)–Fe(2)–C(22)	91.5(3)	C(215)–C(216)–C(211)	121.0(6)
C(3)–C(1)–C(2)	112.1(5)	N(3)–C(311)–C(312)	115.2(5)
N(1)–C(1)–C(2)	127.3(5)	N(3)–C(321)–C(322)	124.9(8)
N(1)–C(1)–C(3)	120.6(4)	C(111)–N(1)–C(1)	121.9(4)
C(1)–C(2)–Fe(1)	114.9(4)	C(121)–N(1)–C(1)	118.4(5)
C(211)–C(2)–Fe(1)	117.5(4)	C(121)–N(1)–C(111)	115.6(4)
C(211)–C(2)–C(1)	123.1(5)	C(311)–N(3)–C(3)	120.0(4)
C(321)–N(3)–C(311)	116.2(5)	C(321)–N(3)–C(3)	119.4(5)

Table 3

IR,  $^1\text{H}$  NMR, and mass spectra and chemical analyses

Compd	IR $\nu(\text{C}\equiv\text{O})$ ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR	MS, $m/e$ ( $\text{M}^+$ )	Anal.	
				Calc.	Found
1	2090m	0.9 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )	481	C 47.21	47.44
	2020sh	2.7 (q(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		H 3.23	3.14
	1990vs	7.2 (m(5),C <sub>6</sub> H <sub>5</sub> )		N 2.89	2.91
	1950s				
	1930vs				
2	2080m	1.01 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )	564	C 53.22	53.35
	2020vs	1.21 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		H 5.00	4.98
	1980sh	4.24 (s(3),CH <sub>3</sub> )		N 4.97	4.88
	1975vs	2.85 (qe(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )			
	1935sh	3.30 (q(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ) 7.21 (m(5),C <sub>6</sub> H <sub>5</sub> )			
3	2055m	1.11 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )	640	C 58.15	58.40
	2010s	1.13 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		H 5.04	5.00
	1970vs	2.90 (qe(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		N 4.38	4.28
	1910s	3.30 (q(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ) 4.24 (se(2),CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) 7.26 (m(5),C <sub>6</sub> H <sub>5</sub> )			
4	2080m	1.03 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )	590	C 54.95	54.94
	2060s	1.25 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		H 5.12	5.10
	2020vs	2.85 (qe(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		N 4.75	4.72
	1980vs	3.34 (q(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )			
	1975vs	3.48 (d(2),CH <sub>2</sub> CH=CH <sub>2</sub> )			
	1955vs	5.17 (mc(2),CH <sub>2</sub> CH=CH <sub>2</sub> )			
	1905s	5.80 (m(1),CH <sub>2</sub> CH=CH <sub>2</sub> ) 7.21 (m(5),C <sub>6</sub> H <sub>5</sub> )			
6	2050m	1.21 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )	702	C 49.61	49.66
	1995vs	1.38 (t(6),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		H 4.30	4.21
	1985vs	1.44 (dd(3),H <sub>3</sub> C-CH=CH)		N 3.99	3.97
	1970s	3.17 (q(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )			
	1955vs	3.71 (q(4),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )			
	1920s	4.72 (m(1),H <sub>3</sub> C-CH=CH)			
	1860s	5.34 (d(1),H <sub>3</sub> C-CH=CH)			
	1845m	6.52 (d(2),C <sub>6</sub> H <sub>5</sub> )			
	1825s	7.00 (d(3),C <sub>6</sub> H <sub>5</sub> )			
7	2060m	1.34 (t(12),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )	666	C 46.88	46.98
	2030s	1.44 (d(6),H <sub>3</sub> C-CH=CH)		H 4.54	4.49
	2000s	3.65 (q(8),N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )		N 4.20	4.05
	1980s	4.63 (m(2),H <sub>3</sub> C-CH=CH)			
	1970s	5.10 (d(2),H <sub>3</sub> C-CH=CH)			
	1960s				
	1855sh				
	1845m				

are given in Table 5. This structure has the *closo* structure expected for a tripledecker system.

The metallic framework consists of an open triangle in which two edges are asymmetrically bridged by CO groups and the ferracyclopentadiene plane perpen-



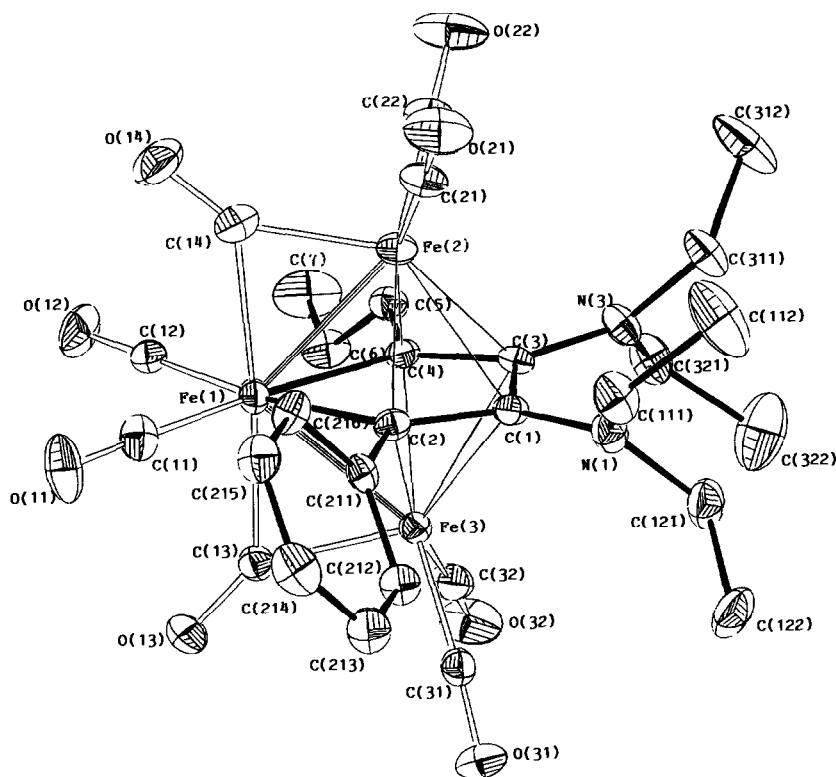


Fig. 2. ORTEP drawing of  $[\text{Fe}_3(\text{CO})_8\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NEt}_2)\text{C}(\text{C}_3\text{H}_5)\}]$  (6) showing 30% probability thermal ellipsoids.

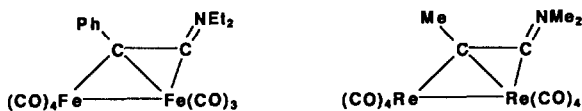
dicularly intersects the Fe3 plane. The overall geometry is very similar to that already reported for  $[\text{Fe}_3(\text{CO})_8(\text{C}_4\text{R}_4)]$  [13].

The Fe(1)–C(2)–C(1)–C(3)–C(4) atoms form a plane, the largest deviation being 0.044 Å at C(1). Atoms attached to this ring are tilted out from the plane by a maximum of 0.146 Å.

As suggested by the  $^1\text{H}$  NMR spectrum, double bond isomerization has occurred in the allylic fragment. The C=C bond is now between C(5) and C(6) (1.328(9) Å) whereas C(7) belongs to a methyl group.

The most important feature revealed by the structure is that the tail-to-tail coupling of the butadiene fragment is still tail-to-tail, as in the equivalent *nido* system. Thus the previously characterized *closo* complex **B** in Scheme 1 with head-to-tail coupling suggests that the equivalent *nido* complex may also exist.

Recently, Adams *et al.* [14] reported the formation and characterization of a di-rhenium aminocarbene complex analogous to **1**.



On addition of an excess of ynamine, this Re complex yields all three possible isomers, tail-to-tail, head-to-tail and head-to-head. The three possible coupling

Table 4

Fractional atomic coordinates with e.s.d.s in parentheses, and equivalent isotropic thermal parameter  $U_{eq}$  for compounds **6**

Atom	x	y	z	$U_{eq}^a$
Fe(1)	0.28534(6)	0.18684(8)	0.74378(5)	0.0376
Fe(2)	0.36203(5)	0.00115(9)	0.71486(5)	0.0388
Fe(3)	0.16594(5)	0.12967(8)	0.65993(4)	0.0347
C(1)	0.2216(4)	-0.0517(6)	0.6803(3)	0.0364
C(2)	0.2268(4)	0.0179(5)	0.7454(3)	0.0370
C(3)	0.2713(3)	0.0047(6)	0.6208(3)	0.0346
C(4)	0.3018(3)	0.1237(6)	0.6391(3)	0.0366
C(5)	0.3544(4)	0.1940(6)	0.5874(3)	0.0431
C(6)	0.3419(4)	0.3089(7)	0.5708(4)	0.0538
C(7)	0.3990(5)	0.3813(8)	0.5217(5)	0.0732
N(1)	0.1801(4)	-0.1636(5)	0.6743(3)	0.0495
C(111)	0.1903(6)	-0.2548(7)	0.7300(4)	0.0586
C(112)	0.2271(9)	-0.3715(9)	0.7018(6)	0.0956
C(121)	0.1167(5)	-0.1853(7)	0.6133(4)	0.0614
C(122)	0.0243(5)	-0.2194(9)	0.6365(5)	0.0707
N(3)	0.2846(4)	-0.0527(5)	0.5546(3)	0.0450
C(311)	0.3150(5)	-0.1764(7)	0.5515(4)	0.0600
C(312)	0.3950(7)	-0.1961(9)	0.5052(6)	0.0868
C(321)	0.2681(5)	0.0108(7)	0.4853(3)	0.0566
C(322)	0.1966(9)	-0.047(1)	0.4389(5)	0.1057
C(211)	0.1828(4)	-0.0203(5)	0.8137(3)	0.0347
C(212)	0.0910(4)	-0.0400(6)	0.8162(3)	0.0484
C(213)	0.0503(5)	-0.0714(7)	0.8805(4)	0.0565
C(214)	0.0991(6)	-0.0794(7)	0.9434(4)	0.0620
C(215)	0.1903(5)	-0.0618(7)	0.9420(3)	0.0563
C(216)	0.2310(4)	-0.0313(6)	0.8777(3)	0.0476
C(11)	0.2632(5)	0.2251(6)	0.8353(4)	0.0529
O(11)	0.2474(5)	0.2548(6)	0.8921(3)	0.0755
C(12)	0.3453(4)	0.3249(6)	0.7319(3)	0.0450
O(12)	0.3841(3)	0.4115(4)	0.7272(3)	0.0621
C(13)	0.1689(4)	0.2669(6)	0.7167(3)	0.0409
O(13)	0.1318(3)	0.3546(4)	0.7328(3)	0.0591
C(14)	0.4082(4)	0.1146(7)	0.7778(4)	0.0535
O(14)	0.4647(3)	0.1438(6)	0.8181(3)	0.0764
C(21)	0.3921(4)	-0.1251(7)	0.7696(4)	0.0513
O(21)	0.4153(4)	-0.2029(5)	0.8047(3)	0.0758
C(22)	0.4609(4)	-0.0147(7)	0.6659(4)	0.0559
O(22)	0.5254(3)	-0.0229(7)	0.6333(3)	0.0809
C(31)	0.0502(4)	0.1024(6)	0.6692(3)	0.0446
O(31)	-0.0262(3)	0.0959(5)	0.6729(3)	0.0695
C(32)	0.1363(4)	0.2057(7)	0.5785(4)	0.0532
O(32)	0.1139(4)	0.2577(6)	0.5288(3)	0.0719

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

modes have also been observed during the reaction of  $[\text{Os}_4(\text{CO})_{12}(\mu^3\text{-S})]$  with  $\text{MeC}\equiv\text{NMe}_2$  [15].

As noted above, only the tail-to-tail coupled *nido* structures for the ferrole-nyamine complexes were isolated. It may be that the other two isomers were formed in low yield, and not isolated during the chromatographic work-up. Indeed,

Table 5

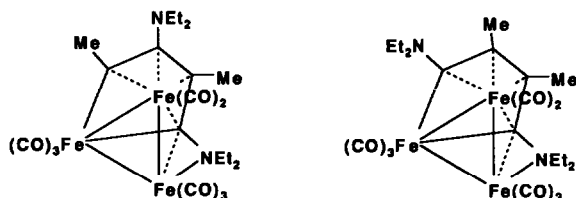
Interatomic distances (Å) and bond angles (°) for [Fe<sub>3</sub>(CO)<sub>8</sub>{C(Ph)C(C(NEt<sub>2</sub>))C(NEt<sub>2</sub>)(C<sub>3</sub>H<sub>5</sub>)}]

Fe(1)–Fe(2)	2.429(1)	C(3)–N(3)	1.397(7)
Fe(1)–Fe(3)	2.420(1)	C(4)–C(5)	1.473(8)
Fe(1)–C(2)	2.076(6)	C(5)–C(6)	1.328(9)
Fe(1)–C(4)	2.075(6)	C(6)–C(7)	1.49(1)
Fe(1)–C(11)	1.779(7)	N(1)–C(111)	1.453(9)
Fe(1)–C(12)	1.796(7)	N(1)–C(121)	1.475(9)
Fe(1)–C(13)	2.005(6)	C(111)–C(112)	1.51(1)
Fe(1)–C(14)	2.086(6)	C(121)–C(122)	1.50(1)
Fe(2)–C(1)	2.253(6)	N(3)–C(311)	1.453(9)
Fe(2)–C(2)	2.111(5)	N(3)–C(321)	1.477(8)
Fe(2)–C(3)	2.180(5)	C(311)–C(312)	1.50(1)
Fe(2)–C(4)	2.139(6)	C(321)–C(322)	1.50(1)
Fe(2)–C(14)	1.842(7)	C(211)–C(212)	1.387(8)
Fe(2)–C(21)	1.785(7)	C(211)–C(216)	1.375(8)
Fe(2)–C(22)	1.752(6)	C(212)–C(213)	1.388(9)
Fe(3)–C(1)	2.215(6)	C(213)–C(214)	1.36(1)
Fe(3)–C(2)	2.192(6)	C(214)–C(215)	1.37(1)
Fe(3)–C(3)	2.229(5)	C(215)–C(216)	1.385(9)
Fe(3)–C(4)	2.069(5)	C(11)–O(11)	1.128(7)
Fe(3)–C(13)	1.854(6)	C(12)–O(12)	1.129(7)
Fe(3)–C(31)	1.763(6)	C(13)–O(13)	1.164(7)
Fe(3)–C(32)	1.774(7)	C(14)–O(14)	1.158(7)
C(1)–C(2)	1.430(8)	C(21)–O(21)	1.133(8)
C(1)–C(3)	1.477(8)	C(22)–O(22)	1.148(7)
C(1)–N(1)	1.396(8)	C(31)–O(31)	1.144(7)
C(2)–C(211)	1.496(8)	C(32)–O(32)	1.129(8)
C(3)–C(4)	1.440(8)		
Fe(3)–Fe(1)–Fe(2)	88.74(4)	C(3)–C(4)–Fe(1)	119.2(4)
C(4)–Fe(1)–C(2)	76.3(2)	C(5)–C(4)–Fe(1)	119.8(4)
C(11)–Fe(1)–C(2)	96.8(3)	C(5)–C(4)–C(3)	120.5(5)
C(11)–Fe(1)–C(4)	173.0(3)	C(6)–C(5)–C(4)	126.1(6)
C(12)–Fe(1)–C(2)	171.8(3)	C(7)–C(6)–C(5)	125.6(7)
C(12)–Fe(1)–C(4)	96.2(3)	C(111)–N(1)–C(1)	122.0(6)
C(12)–Fe(1)–C(11)	90.7(3)	C(121)–N(1)–C(1)	118.9(5)
C(13)–Fe(1)–C(2)	92.6(2)	C(121)–N(1)–C(111)	118.8(6)
C(13)–Fe(1)–C(4)	92.1(2)	C(112)–C(111)–N(1)	113.1(7)
C(13)–Fe(1)–C(11)	87.4(3)	C(122)–C(121)–N(1)	113.7(6)
C(13)–Fe(1)–C(12)	91.1(3)	C(311)–N(3)–C(3)	121.2(5)
C(14)–Fe(1)–C(2)	90.7(2)	C(321)–N(3)–C(3)	120.9(5)
C(14)–Fe(1)–C(4)	91.7(3)	C(321)–N(3)–C(311)	117.9(5)
C(14)–Fe(1)–C(11)	89.1(3)	C(312)–C(311)–N(3)	114.4(7)
C(14)–Fe(1)–C(12)	86.1(3)	C(322)–C(321)–N(3)	113.1(7)
C(14)–Fe(1)–C(13)	175.5(3)	C(212)–C(211)–C(2)	121.4(5)
C(21)–Fe(2)–C(14)	95.6(3)	C(216)–C(211)–C(2)	121.3(5)
C(22)–Fe(2)–C(14)	95.0(3)	C(216)–C(211)–C(212)	117.2(5)
C(22)–Fe(2)–C(21)	90.5(3)	C(213)–C(212)–C(211)	121.0(6)
C(31)–Fe(3)–C(13)	95.7(3)	C(214)–C(213)–C(212)	120.7(6)
C(32)–Fe(3)–C(13)	95.0(3)	C(215)–C(214)–C(213)	119.2(6)
C(32)–Fe(3)–C(31)	86.4(3)	C(216)–C(215)–C(214)	120.1(6)
Fe(3)–C(1)–Fe(2)	98.7(2)	C(215)–C(216)–C(211)	121.8(6)
C(3)–C(1)–C(2)	111.9(5)	O(11)–C(11)–Fe(1)	176.4(7)
N(1)–C(1)–C(2)	124.6(5)	O(12)–C(12)–Fe(1)	177.3(6)
N(1)–C(1)–C(3)	123.3(5)	Fe(3)–C(13)–Fe(1)	77.6(2)
Fe(3)–C(2)–Fe(2)	104.0(2)	O(13)–C(13)–Fe(1)	136.3(5)

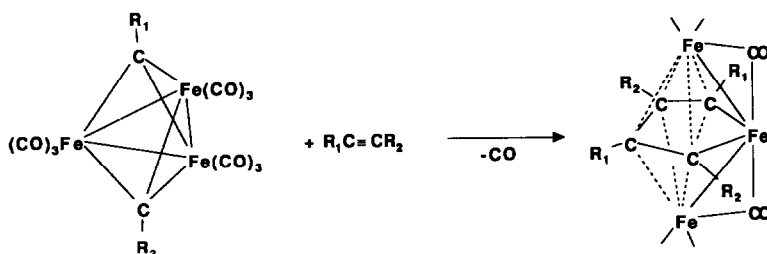
Table 5 (continued)

C(1)–C(2)–Fe(1)	119.7(4)	O(13)–C(13)–Fe(3)	146.2(5)
C(211)–C(2)–Fe(1)	117.5(4)	Fe(2)–C(14)–Fe(1)	76.1(2)
C(211)–C(2)–C(1)	122.5(5)	O(14)–C(14)–Fe(1)	135.0(6)
Fe(3)–C(3)–Fe(2)	100.5(2)	O(14)–C(14)–Fe(2)	148.8(6)
C(4)–C(3)–C(1)	112.2(5)	O(21)–C(21)–Fe(2)	176.6(6)
N(3)–C(3)–C(1)	122.5(5)	O(22)–C(22)–Fe(2)	178.6(7)
N(3)–C(3)–C(4)	125.3(5)	O(31)–C(31)–Fe(3)	173.4(6)
Fe(3)–C(4)–Fe(2)	107.4(3)	O(32)–C(32)–Fe(3)	176.1(6)

Adams *et al.* [15] note a lower yield for the head-to-tail and head-to-head coupling than for the tail-to-tail mode. They also might be less stable owing to the presence of the amino substituent on the C atom  $\sigma$ -bonded to iron. It was noted that formation of a C=N double bond may disrupt the expected Fe–C bond. These two couplings have indeed been observed in trinuclear clusters where the nitrogen lone pair is engaged in bonding interaction with the third iron atom [3,16].



Alternative formation of the head-to-tail *closo* tripledecker compound may not require formation of the *nido* complex as an intermediate. Mathieu *et al.* [13b] reported the formation of tripledecker complexes from reaction of alkynes with the trinuclear bis(carbyne)iron cluster  $[\text{Fe}_3(\text{CO})_9(\mu^3\text{COEt})(\mu^3\text{CCH}_3)]$ .



During our investigations on the reactivity of ynamines with iron clusters, we isolated a trinuclear bis(carbyne) iron cluster  $[\text{Fe}_3(\text{CO})_9(\mu^3\text{CNEt}_2)(\mu^3\text{CCH}_3)]$  [17] which could also be an intermediate in the formation of the *closo* system. The chemistry of this bis(carbyne) system, which formed in presence of diphenylketyl anion, has not yet been investigated.

## Electrochemistry

The electrochemical behaviour of the newly prepared compounds was of interest for two reasons. Comparison with the redox behaviour reported for “innocently” substituted ferrole derivatives might give additional insight into the

Table 6

Cyclovoltammetric data of selected compounds

Compound	Oxidation		Reduction			
	$E_{1/2}$ (V)	$\Delta E$ (V) <sup>a</sup>	$E_{1/2}$ (V)	$\Delta E$ (V) <sup>a</sup>	$E_{1/2}$ (V)	$\Delta E$ (V) <sup>a</sup>
<b>2</b> <sup>b</sup>	0.840	0.280	-2.125			
<b>4</b> <sup>b</sup>	0.930	0.140	-2.150			
<b>6</b>	1.200		-0.968	0.135	-1.298	0.130
<b>7</b>	1.133		-1.019	0.138	-1.351	0.138

<sup>a</sup>  $\Delta E = E_{pa} - E_{pc}$ ;  $E_{pa}$ ,  $E_{pc}$ ; anodic and cathodic potentials, respectively. <sup>b</sup> Measured at  $-30^\circ\text{C}$

electron-donating behaviour of the amino-substituents in those clusters. Additionally, a simple model [7b] predicting the relative ease of reducibility of *nido* vs. *closo* cluster compounds could be checked independently.

For these reasons a pair of *nido* compounds (**2,4**) and a pair of *closo* species (**6,7**) were examined by cyclovoltammetry. The data are shown in Table 6. The *closo* compounds show two reversible one-electron reduction waves. This behaviour is generally shown by ferrole-derived *closo* clusters [5]. It is also characteristic of other *closo* compounds which may be derived conceptually from an organometallic  $\pi$ -cycle by adding two capping groups [7b,18]. The first reduction potential is qualitatively related to the energy of the LUMO; comparison with the appropriate potentials reported for ferrole-type *closo* compounds reveals that the  $\text{NR}_2$ -substituted derivatives **6** and **7** are more difficult to reduce (by about 0.3 to 0.4 V) than compounds derived from "innocently" substituted ferroles [5]. This may be correlated to the mesomerically induced transfer of negative charge to the cluster framework by the  $\text{NR}_2$ -substituents (see also structure).

Whereas ferrole-derived *nido* clusters normally show reversible reductions at around  $-1.4$  V [5], compounds **2** and **4** are only reduced at below  $-2$  V, the reduction being completely irreversible. Again, mesomeric charge transfer from the amino-groups to the cluster framework is a plausible explanation for the observed behaviour. Even though reduction of the *nido* clusters is irreversible, a comparison of the relative ease with which the *closo* species **6** and **7** are reduced relative to the stability to reduction of the *nido* compounds **2** and **4**, is rewarding. A simple model [7b] in which both *nido* and *closo* species are considered as derivatives of the corresponding organometallic  $\pi$ -cycles predicts just this behaviour. In this model, *closo* compounds should have a set of essentially non-bonding molecular orbitals which are absent for the *nido* species [7b].

Oxidation of both the *closo* compounds **6** and **7** occurs only above 1 V and is irreversible. At least two compounds [5] are observed for the oxidation wave with the peak maximum as given in Table 6.

For the *nido* species **2** and **4**, quasi-reversible oxidations are observed. Reversibility increases on cooling the solution to  $-30^\circ\text{C}$  (see Table 6). No reversible oxidation processes appear to be reported for ferrole-derived *nido* clusters, the reversibility observed for **2** and **4** obviously being a consequence of the conjugatively active amino-groups.

## Experimental part

Reactions were carried out under dry dinitrogen 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<sub>254</sub> were used. Infrared absorption spectra were measured with a Perkin–Elmer 597 spectrometer. A Nermag R10-10 spectrometer was used for molecular mass determination. NMR spectra were recorded on a Bruker WM 200. Hexane and dichloromethane were purified by standard procedures and stored over molecular sieves. Literature procedures were used to prepare ynamines [19] (MeC≡CNEt<sub>2</sub>, C<sub>3</sub>H<sub>5</sub>C≡CNEt<sub>2</sub>, PhC≡CNEt<sub>2</sub> and PhCH<sub>2</sub>C≡CNEt<sub>2</sub>). [Fe<sub>2</sub>(CO)<sub>9</sub>] was formed by irradiation of [Fe(CO)<sub>5</sub>] [20].

### Preparation of [Fe<sub>2</sub>(CO)<sub>7</sub>{C(Ph)C(NEt<sub>2</sub>)}] (1)

*N,N*-Diethylphenyl-2-ethynyl-1-amine (0.48 g, 2.74 mmol) was added to a suspension of [Fe<sub>2</sub>(CO)<sub>9</sub>] (1 g, 2.74 mmol) in 60 mL of dried dichloromethane. The reaction mixture was stirred overnight at room temperature causing the colour to change from yellow to dark orange. Solvent was removed under reduced pressure, and the residue was chromatographed with a dichloromethane/hexane mixture (1:10) as eluant giving a main dark orange band. Evaporation of the solvent containing the dark-orange product followed by recrystallization from *n*-hexane at –20°C afforded red-orange crystals of **1** (0.53 g, 1.10 mmol; 40% yield) identified from infrared. <sup>1</sup>H NMR and mass spectra (Table 3).

### Preparation of [Fe<sub>2</sub>(CO)<sub>6</sub>{C(Ph)C(NEt<sub>2</sub>)C(NEt<sub>2</sub>)CR}] (R = Me (2); PhCH<sub>2</sub> (3); C<sub>3</sub>H<sub>5</sub> (4))

Synthetic procedures were similar for the three complexes. The relevant ynamine (MeC≡CNEt<sub>2</sub>, PhCH<sub>2</sub>C≡CNEt<sub>2</sub>, or C<sub>3</sub>H<sub>5</sub>C≡CNEt<sub>2</sub>; 0.1 mmol) was added to a *n*-hexane solution (20 mL) of compound **1** (0.048 g, 0.1 mmol). After stirring for 6 h at 40°C, the solution was concentrated and chromatographed, giving a main yellow band with *n*-hexane as eluant. Evaporation of the yellow solution followed by recrystallization from *n*-hexane at –20°C afforded yellow crystals of **2**, **3** and **4**, respectively (see Table 3).

### Preparation of [Fe<sub>2</sub>(CO)<sub>6</sub>{C(C<sub>3</sub>H<sub>5</sub>)C(NEt<sub>2</sub>)C(NEt<sub>2</sub>)C(C<sub>3</sub>H<sub>5</sub>)}] (5)

*N,N*-Diethylpentene-4-ynyl-1-amine (0.089 g, 0.65 mmol) was added to a suspension of [Fe<sub>2</sub>(CO)<sub>9</sub>] (0.25 g, 0.65 mmol) in 40 mL of hexane. The mixture was stirred at 0°C for 2 h and at room temperature overnight. The solution was concentrated and chromatographed, giving a main yellow band with *n*-hexane as eluant. Recrystallization from *n*-hexane at –15°C gave yellow crystals of complex **5** identified from its infrared and mass spectra [12].

[Fe<sub>2</sub>(CO)<sub>6</sub>{C(C<sub>3</sub>H<sub>5</sub>)C(NEt<sub>2</sub>)C(NEt<sub>2</sub>)C(C<sub>3</sub>H<sub>5</sub>)}]: IR: ν(CO) 1900m, 1965sh, 1975s, 2020s, 2060s cm<sup>-1</sup>. MS: *m/e* 554(*M*<sup>+</sup>).

### Preparation of [Fe<sub>3</sub>(CO)<sub>8</sub>{C(R)C(NEt<sub>2</sub>)C(NEt<sub>2</sub>)C(C<sub>3</sub>H<sub>5</sub>)}] (R = C<sub>3</sub>H<sub>5</sub> (5); Ph (6))

[Fe<sub>2</sub>(CO)<sub>9</sub>] was added slowly to a refluxing hexane solution (20 mL) of [Fe<sub>2</sub>(CO)<sub>6</sub>{C(R)C(NEt<sub>2</sub>)C(NEt<sub>2</sub>)C(C<sub>3</sub>H<sub>5</sub>)}] (0.1 mmol) until all the dinuclear complex was consumed. The solution was then concentrated, and the residue was

Table 7

## Crystal data

Compound	4	6
Formula	C <sub>27</sub> H <sub>30</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	C <sub>29</sub> H <sub>30</sub> Fe <sub>3</sub> N <sub>2</sub> O <sub>8</sub>
FW	590.2	702.1
System	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	8.820(2)	14.900(3)
<i>b</i> (Å)	9.261(2)	11.149(2)
<i>c</i> (Å)	18.470(2)	18.453(4)
$\alpha$ (°)	89.40(1)	90.0
$\beta$ (°)	81.81(1)	91.14(2)
$\gamma$ (°)	70.23(2)	90.0
<i>V</i> (Å <sup>3</sup> )	1404	3065
<i>Z</i>	2	4
$\mu$ (Mo- <i>K</i> $\alpha$ ) (cm <sup>-1</sup> )	10.72	14.50
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.39	1.52
2 $\theta$ range (°)	3 < 2 $\theta$ < 50	3 < 2 $\theta$ < 50
Scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
Scan width (°)	1.0 + 0.34 tg $\theta$	1.0 + 0.34 tg $\theta$
Scan speed (° min <sup>-1</sup> )	1.8–5.5	1.8–8.2
Diffractometer	CAD4F	CAD4F
No. of reflections collected	5095	5876
No. of unique reflections	4927	5379
Merging <i>R</i> factor	0.022	0.065
No. of reflections with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	2580	2304
Abs. correction	DIFABS	DIFABS [25]
<i>R</i>	0.0388	0.0397
<i>R</i> <sub>w</sub>	0.0406	0.0414
Weighting scheme	1	Chebyshev
Coefficient for the Chebyshev series		6.68; -4.79; 5.40
No. of variables	335	380

chromatographed giving two main green bands. The first was [Fe<sub>3</sub>(CO)<sub>12</sub>]. The second green band was eluted with a dichloromethane/hexane mixture (2:10). Crystals of complexes **5** and **6** were obtained from the concentrated eluant solution at -20°C. They were characterized by infrared, <sup>1</sup>H NMR and mass spectra, and by chemical analyses (Table 3).

#### Crystal data for complexes 4 and 6

For both compounds, selected crystals were set up on an automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table 7. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections were applied.

Computations were performed by using CRYSTALS [21] adapted on a MicroVax II. Atomic form factors for neutral Fe, C, N, O and H were taken from [22]. Anomalous dispersion was taken into account. All structures were solved by direct

methods using the SHELX86 program [23]. Hydrogen atoms were found on difference electron density maps but they were introduced in the refinement as fixed contributors in calculated position. Their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbons to which they were attached. 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. Unit weight was used for compound 4 whereas for 6, the weighting scheme used in the last refinement cycle was  $w = w'[1 - (\Delta F/6\sigma(F_o))^2]^2$  where  $w' = 1/\sum_i^3 A_i T_i(x)$  with three coefficients  $A_i$  for the Chebyshev polynomial  $A_i T_i(x)$  where  $x$  was  $F_c/F_o(\max)$  [24]. Models reached convergence with  $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$  and  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$  having values listed in Table 7. Criteria for a satisfactory complete analysis were ratios of rms shift to standard deviation less than 0.1 and no significant features in final difference maps. Atomic coordinates are given in Tables 1 and 4.

### *Electrochemistry*

Cyclic voltammograms were measured using a Princeton Applied Research Potentiostat 273 equipped with a BBC/Servogor (XY 733) plotter as the recording instrument. Electrochemistry was done in a gas-tight thermostatted Universal Mess- and Titriergefäß apparatus (Metrohm). A platinum wire (diameter 0.3 mm) was used as the counter electrode; the reference electrode consisted of a Radiometer K 401 saturated calomel electrode. The working electrode consisted of a circular glassy carbon electrode (diameter 3 mm) fitted to a Metrohm RDE 628 building block. The supporting electrolyte was  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $\text{Bu}_4\text{NPF}_6$ . The concentration of the electroactive organometallic species was typically 0.001 M. The voltammograms were registered with a scan rate of 200 mV/s.

*Supplementary material available from the authors:* Tables of anisotropic temperature factors, hydrogen coordinates and observed and calculated structure factors (20 pages).

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