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Reaction of heterocumulenes $R-N=C=N-R$ and $R-P=C=P-R$ with a di-iron aminocarbene complex

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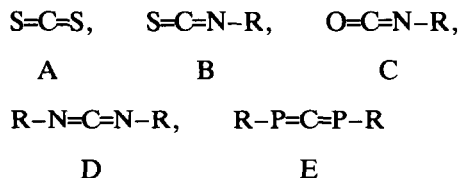
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Abstract

Reaction of $R-N=C=N-R$ ($R=p\text{-Me-C}_6\text{H}_4$) and $R-P=C=P-R$ ($R=2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$) with the di-iron aminocarbene complex $[\text{Fe}_2(\text{CO})_7(\mu\text{-C}(\text{Ph})\text{C}(\text{NEt}_2))] (1c)$ gave corresponding complexes $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{NC}_6\text{H}_4\text{Me})\text{N}(\text{C}_6\text{H}_4\text{Me})\}] (2)$ and $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{PC}_6\text{H}_2^i\text{Bu}_3)\text{P}(\text{C}_6\text{H}_2^i\text{Bu}_3)\}] (4)$, resulting from a coupling reaction with carbon–carbon bond formation. $[\text{Fe}_2(\text{CO})_5(\text{CNC}_6\text{H}_4\text{Me})\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{N}(\text{C}_6\text{H}_4\text{Me})]$, complex 3, obtained in the reaction with $R-N=C=N-R$, resulted from C=N bond rupture and insertion of a nitrene fragment into the Fe=C bond. Complexes 2–4 were characterized by X-ray diffraction. The different geometries of complexes 2 and 4 are discussed. The formation of these complexes may be explained by cycloaddition on the Fe=C metal–carbene bond.

1. Introduction

Dinuclear aminocarbene complexes $[\text{Fe}_2(\text{CO})_7(\mu\text{-C}(\text{R})\text{C}(\text{NEt}_2))] (1)$, obtained by the action of $[\text{Fe}_2(\text{CO})_9]$ on aminoalkynes $R-C\equiv C-NEt_2$ [1a–c], have a bridging carbene and a terminal aminocarbene group (Scheme 1). Because the insertion of an organic molecule or of an inorganic functional group into a metal–carbon bond represents a basic step for the metal-promoted functionalization of an organic group, previous work in our group has focussed on the study of the reactivity of these complexes with various heterocumulenes (A–C). In all cases reactions occur at the terminal Fe=C carbene bond. We have observed C=S bond rupture and insertion of an S atom into the Fe=C double bond for A [1b], insertion of an S atom into the Fe=C double bond and cycloaddition between N=C and Fe=C for B [2], and cycloaddition between N=C and Fe=C for C [2]. A preliminary report on the reaction with the heterocumulene *p*-tolylcarbodiimide [3] (type D) shows that both cycloaddition and insertion reactions occur, as for B.



The more recently synthesized diphosphaallene $R-P=C=P-R$ [4], the phosphorus analogue of carbodiimide, provides opportunities for comparative studies. The chemistry of diphosphaallene is much less developed than that of carbodiimide. The first reports have described diphosphaallene η_1 and η_2 transition metal complexes [5]. Interesting examples have recently appeared of facile hydrogen migration reactions in ligated diphosphaallene metal carbonyl complexes [6].

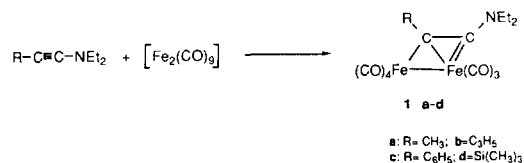
This paper describes (i) the full results of our studies of the reactions of the di-iron aminocarbene complex 1c with heterocumulenes of type D and E, (ii) a comparison of the structures of the resultant complexes and (iii) a possible mechanism of their formation.

2. Results and discussion

2.1. Reaction of carbodiimide with complex 1c

Di-*p*-tolylcarbodiimide reacted with complex 1c in hexane at 70°C to yield two dinuclear complexes, 2 and

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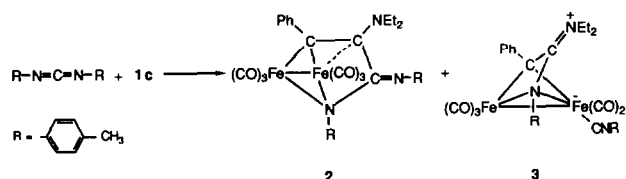


Scheme 1.

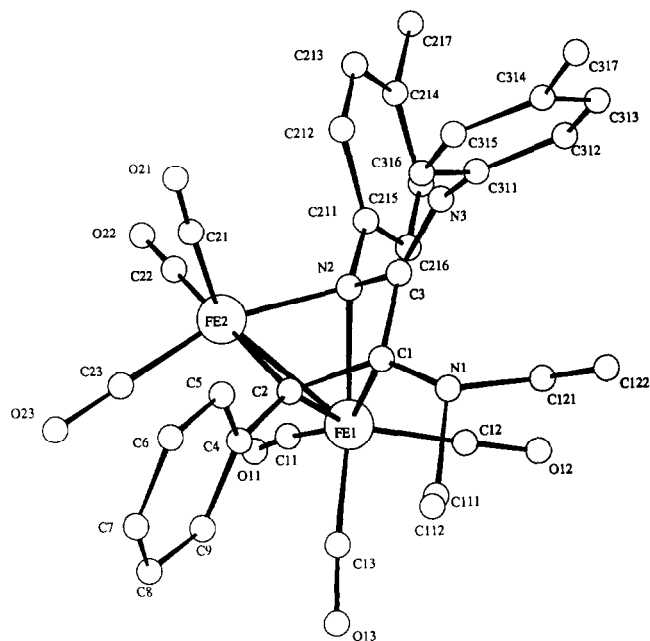
3, as major products after 4 h [3] (Scheme 2). These two compounds, separated by column chromatography, were characterized by IR and ¹H NMR spectroscopy, mass spectrometry, and single crystal X-ray diffraction analysis. The structures are shown in Figs. 1 and 2. Selected interatomic bond distances and angles are listed in Tables 1 and 2.

Compound 2 is dinuclear with an Fe–Fe bond length of 2.46 Å. This complex results from C–C bond formation between the central carbon of the carbodiimide and the carbon atom of 1c bearing the diethylamino-group. The C(Ph)–C(NEt₂)–C(NC₆H₄Me)–N(C₆H₄Me) ligand bridges the two iron atoms through C₁, C₂ and N₂, to form a ferrapyrrolidone ring. The C₁ and C₂ atoms are asymmetrically π-bonded to Fe₁ (C₁–Fe₁ = 2.30 Å, C₂–Fe₁ = 2.13 Å). The [Fe₁–C₁–C₂] and [Fe₂–C₁–C₂] planes make a dihedral angle of 117.8°, similar to that of 1c (110.3°). In contrast, the nitrogen atom N₂ is symmetrically bound to both iron atoms (N₂–Fe₁ = 2.00 Å, N₂–Fe₂ = 1.99 Å). The non-planar arrangement around N₁ and the C₁–N₁ distance (1.38 Å) are consistent with a C₁–N₁ single bond. In solution, the equivalence of the two N-ethyl groups observed by ¹H NMR spectroscopy indicates free rotation about the C₁–N₁ bond, consistent with a single bond. The carbon C₃ of the imine group is not bonded to Fe₁, as indicated by the C₃–Fe₁ distance (2.64 Å). The C₃–N₃ bond length (1.26 Å) is consistent with a C=N double bond (IR band at 1640 cm⁻¹). Similar metal-pyrrolidone complexes have been obtained by cycloaddition of isocyanate to the di-iron aminocarbene complex 1 [2].

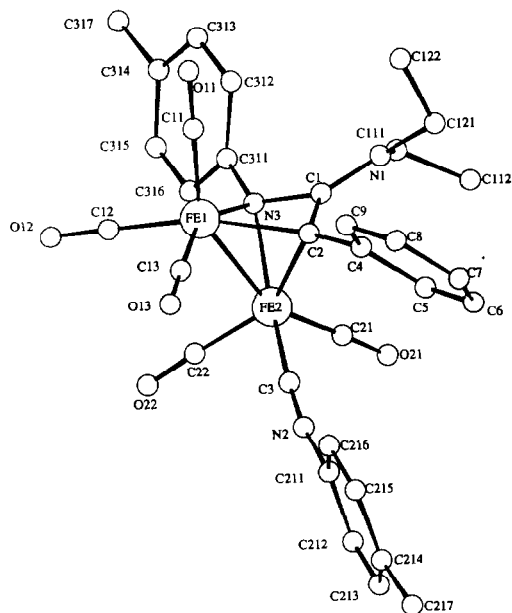
Compound 3 is also dinuclear with an Fe–Fe bond length of 2.44 Å. It contains a nitrene bridging the two iron atoms to form two fused ferrazeterings Fe₁–C₂–



Scheme 2.

Fig. 1. View of molecule 2, [Fe₂(CO)₆(C(Ph)C(NEt₂)C(NC₆H₄Me)N(C₆H₄Me))].

C₁–N₃ and Fe₂–C₂–C₁–N₃, sharing N₃–C₁ and C₂–C₁ edges. The N₃ and C₂ atoms symmetrically bridge both iron atoms (N₃–Fe₁ = 2.01 Å, N₃–Fe₂ = 1.97 Å, C₂–Fe₁ = 1.98 Å, C₂–Fe₂ = 2.08 Å). In contrast, the observed distances C₁–Fe₁ = 2.47 Å and C₁–Fe₂ = 2.26

Fig. 2. View of molecule 3, [Fe₂(CO)₅(CNC₆H₄Me)(C(Ph)C(NEt₂)N(C₆H₄Me))].

Å show that the carbon atom C₁ is asymmetrical with respect to Fe₁ and Fe₂ atoms. The C₁-N₁ bond is short (1.36 Å), the N₁ atom is planar (sum of angles close to 359.7°), and the N-ethyl groups are non-equivalent, as shown by ¹H NMR spectroscopy, due to hindered rotation about the C₁-N₁ bond. All these factors are indicative of a partial multiple-bonding interaction formed by donation of the lone pair of N₁ to C₁. This suggests a zwitterionic character for the molecule that would place a positive charge on N₁ and a negative charge on Fe₁. Complex 3 results from cleavage of one C=N bond of the carbodiimide and insertion of the nitrene fragment into the Fe=C bond of 1c. The fragmentation of the carbodiimide gives an isonitrile which replaces a CO at the Fe₂ atom. The C₃-N₂ bond length (1.15 Å) indicates a C≡N triple bond (IR band at 2130 cm⁻¹). The structure of 3 may be described as a basket-like structure with the two Fe₁-C₂-Fe₂ and Fe₁-N₃-Fe₂ triangles forming the basket and the C-NEt₂ representing the handle. A similar structure, in which the nitrene fragment is replaced by sulphur, was obtained from reaction of

other heterocumulenes such as CS₂ and R-N=C=S with 1 [1b,2].

2.2. Reaction of diphosphaallene with complex 1c

1,3-Diphosphaallene reacted with complex 1c in refluxing hexane to yield complex 4 as the major product (Scheme 3). Contrary to the reaction with carbodiimide to give 2 and 3, the phosphorus analogue of complex 3 was not isolated. Compound 4 was characterized by IR, ¹H NMR and ³¹P NMR spectroscopy and mass spectrometry. The structure of 4 was established by X-ray diffraction analysis (Fig. 3). Selected bond distances and angles are given in Table 3. As in complex 2, 4 results from C-C bond formation between the central carbon of the diphosphaallene and the carbon atom carrying the NEt₂ group of 1c. This complex is dinuclear with a metal-metal bond of 2.49 Å. The C(Ph)-C(NEt₂)-C(PC₆H₅¹Bu₃)-P(C₆H₅¹Bu₃) ligand bridges the two iron atoms through the C₂ and P₁ atoms. P₁ and C₂ are symmetrical with respect to each iron atom within experimental error (P₁-Fe₁ = 2.23(2) Å, P₁-Fe₂ = 2.20(2) Å, C₂-Fe₁ = 2.25(4) Å, C₂-Fe₂ = 1.99(4) Å). The distances C₁-Fe₁ = 2.63 Å, C₁-Fe₂ = 2.98 Å, C₃-Fe₁ = 3.06 Å and C₃-Fe₂ = 3.26 Å show that the C₁ and C₃ atoms are bonded neither to Fe₁ nor to Fe₂. Although the N₁ atom has a planar geometry (sum of angles equal to 358.6°), the C₁-N₁ bond length (1.33(5) Å) is marginally longer than a C=N bond when estimated standard deviation is taken into account. The carbon-nitrogen double bond in iminium salts lies within the range 1.28–1.38 Å. The C₁-N₁ double bond character in 4 is probably weak, because hindered rotation about the C₁-N₁ bond is not evident at 25°C. Both ethyl groups are equivalent, as judged by ¹H NMR spectroscopy. The shortest C-P bond length (C₃-P₂ = 1.66(5) Å) suggests a P=C double bond. Although the N₁, C₁, C₃ and P₂ atoms are in the same plane, the NEt₂ group is twisted out of this plane (47.9°). Compound 4 can be considered to be a basket-like structure with the two Fe₁-C₂-Fe₂ and Fe₁-P₁-Fe₂ triangles forming the basket and the fragment C₁(NEt₂)C₃(PR') providing the handle.

2.3. Structural comparison of complexes 2 and 4

The formation of 2 and 4 may be considered to be the result of analogous coupling reactions between the heterocumulenes D or E and the aminocarbene complex 1c. However, X-ray structure determinations show two different geometries for these compounds, depending on the presence or absence of a C₁-Fe₁ bond. For 2, the value of 2.30 Å is indicative of such a C₁-Fe₁ bond, but the C₁-Fe₁ distance of 2.63 Å observed for 4 shows that C₁ and Fe₁ atoms are not bonded. There is a consequent modification of orientation of the ligand with respect to the Fe₁-Fe₂ bond as indicated by the

TABLE 1. Selected interatomic distances (Å) and bond angles (deg.) for compound (2), [Fe₂(CO)₆{C(Ph)C(NEt₂)C(NC₆H₄Me)N(C₆H₄Me)}]

Fe(1)-Fe(2)	2.459(2)	Fe(2)-C(2)	2.01(1)
Fe(2)-N(2)	1.988(8)	Fe(2)-C(21)	1.79(1)
Fe(2)-C(22)	1.80(1)	Fe(2)-C(23)	1.77(1)
Fe(1)-C(1)	2.30(1)	Fe(1)-C(2)	2.13(1)
Fe(1)-N(2)	2.000(8)	Fe(1)-C(11)	1.83(2)
Fe(1)-C(12)	1.79(1)	Fe(1)-C(13)	1.77(1)
C(1)-C(2)	1.44(1)	N(3)-C(311)	1.43(1)
C(1)-C(3)	1.48(1)	C(1)-N(1)	1.38(1)
C(2)-C(4)	1.46(1)	C(3)-N(2)	1.45(1)
C(3)-N(3)	1.26(1)	N(2)-C(211)	1.44(1)
N(1)-C(121)	1.43(1)	N(1)-C(111)	1.59(2)
O-C(av)	1.13(1)		
C(11)-Fe(1)-N(2)	95.8(5)	C(12)-Fe(1)-N(2)	97.7(4)
C(12)-Fe(1)-C(11)	104.0(6)	C(13)-Fe(1)-C(11)	91.2(8)
C(13)-Fe(1)-N(2)	167.6(5)	C(13)-Fe(1)-C(12)	90.4(6)
N(2)-Fe(2)-C(2)	79.8(4)	C(21)-Fe(2)-C(2)	91.8(4)
C(21)-Fe(2)-N(2)	102.9(4)	C(22)-Fe(2)-C(2)	167.8(5)
C(22)-Fe(2)-N(2)	93.5(5)	C(22)-Fe(2)-C(21)	99.7(5)
C(23)-Fe(2)-C(2)	93.6(5)	C(23)-Fe(2)-N(2)	159.4(5)
C(23)-Fe(2)-C(21)	96.7(5)	C(23)-Fe(2)-C(22)	89.1(6)
C(3)-C(1)-C(2)	112.4(8)	N(1)-C(1)-C(2)	128.5(9)
N(1)-C(1)-C(3)	118.3(9)	C(1)-C(2)-Fe(2)	111.4(7)
C(4)-C(2)-Fe(2)	119.4(7)	C(4)-C(2)-C(1)	124.3(9)
N(2)-C(3)-C(1)	104.4(8)	N(3)-C(3)-C(1)	135.3(9)
N(3)-C(3)-N(2)	120.3(8)	C(111)-N(1)-C(1)	109.8(21)
C(121)-N(1)-C(1)	120.7(9)	C(121)-N(1)-C(111)	104.1(9)
Fe(2)-N(2)-Fe(1)	76.1(3)	C(3)-N(2)-Fe(1)	98.6(6)
C(3)-N(2)-Fe(2)	107.1(6)	C(211)-N(2)-Fe(1)	131.1(5)
C(211)-N(2)-Fe(2)	119.6(6)	C(211)-N(2)-C(3)	116.5(7)
C(311)-N(3)-C(3)	124.5(8)	O-C-Fe(av)	175.4(21)

angle between the $[N_1-C_1-C_2-C_3]$ plane and the Fe_1Fe_2 vector: 50.2° for **2** and 61.4° for **4** (Fig. 4). Thus, this plane is less inclined towards Fe_2 for **4** than for **2**. The distortion of the ligand is reflected by torsional angles $[C_2-C_1-C_3-X]$ ($X = N_2$ or P_1): 39° for **2** and 20° for **4**. The distortion in **4** may be related to the involvement of the N_1 nitrogen lone pair. Due to the very small crystal size and the low quality of data for **4**, it is difficult to compare the C_1-N_1 bond lengths in **2** and **4**; however, the sum of angles around N_1 (**4**: 358.6° , **2**: 334.6°) shows that N_1 is planar in compound **4**. This is consistent with a delocalization of the nitrogen lone pair and a C_1-N_1 multiple-bonding interaction. In organometallic clusters containing ynamine ligands [7], short C–N distances and planar geometries of the amino-groups imply significant interactions between the lone pair of electrons of the nitrogen atom and the adjacent alkyne carbon atom. This is supported by recent molecular orbital calculations [8]. In the complex $[Ru_2(CO)_6(\mu-S(CNEt_2)CMe)]$, obtained by reaction of $[Ru_3(CO)_{10}(\mu_3-S)]$ with $Me-C\equiv C-NEt_2$, lone pair donation causes a weakening of the Ru–CNEt₂ metal–carbon bond, $Ru-C = 2.419 \text{ \AA}$ [9]. In **4**, the

donation of the nitrogen lone pair is even stronger and breaks the Fe_1-C_1 bond, $C_1-Fe_1 = 2.63 \text{ \AA}$.

Complexes **2** and **4** may be discussed using the Polyhedral Skeletal Electron Pair approach [10]. A skeletal electron count for **2** leads to 18 electrons: 4 electrons for the two $Fe(CO)_3$ groups, 6 electrons for the two CR groups, 4 electrons for the NR group and 4 electrons for the CNR group. Considering the geometry around the N_1 atom (Σ angles = 334.6°) which excludes the donation of the nitrogen lone pair, the C–NEt₂ group is taken as a C–R group (3-electron donor). Thus, **2** has 9 skeletal electron pairs and appears to have an *arachno* structure based on the 8-vertex polyhedron shown on Fig. 5a. For **4**, the N_1 nitrogen lone pair is involved and it is considered that two additional electrons are given to the cluster cage. Therefore, a 9-vertex polyhedron is expected. Thus, complex **4** may be described as a *hypho* structure (Fig. 5b).

A similar phenomenon was observed in a series of clusters obtained by addition of isocyanate to the aminocarbene complex **1** [2a,11]. In these clusters, the formal *arachno* \rightarrow *hypho* transformation is related to

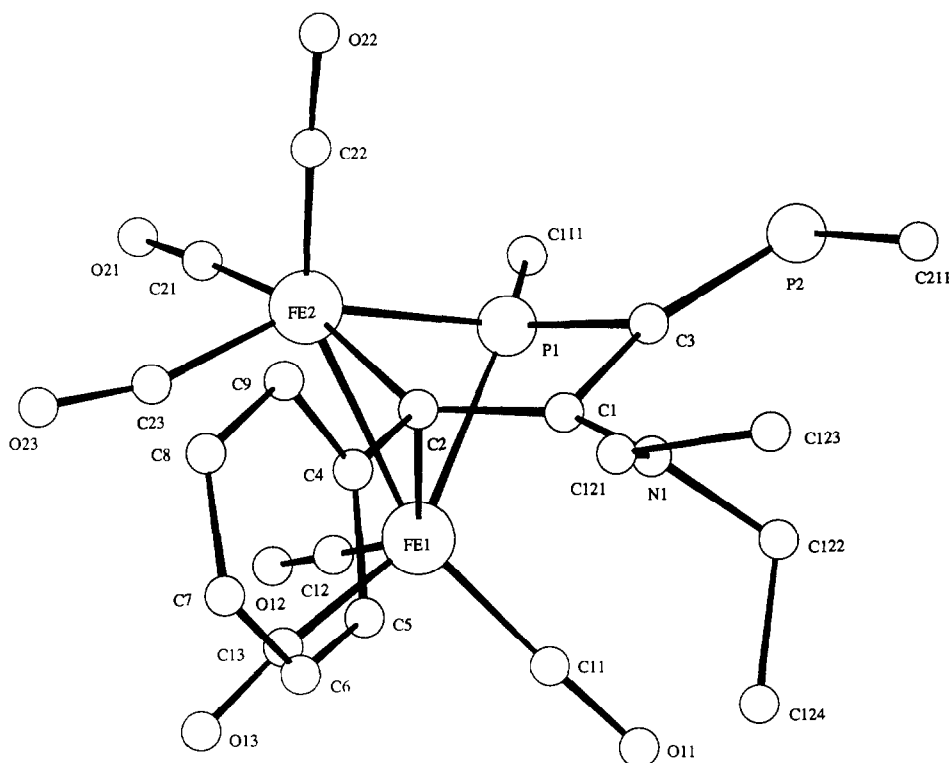


Fig. 3. View of molecule **4**, $[Fe_2(CO)_6(C(Ph)C(NEt_2)C(PC_6H_5Bu_3)P(C_6H_5Bu_3))]$.

TABLE 2. Selected interatomic distances (Å) and bond angles (deg.) for compound 3, $[\text{Fe}_2(\text{CO})_5(\text{CNC}_6\text{H}_4\text{Me})\{\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{N}(\text{C}_6\text{H}_4\text{Me})\}]$

Fe(1)–Fe(2)	2.4471(9)	Fe(1)–C(2)	1.985(4)
Fe(1)–N(3)	2.011(3)	Fe(1)–C(11)	1.786(5)
Fe(1)–C(13)	1.773(5)	Fe(1)–C(12)	1.805(5)
Fe(2)–C(1)	2.260(4)	N(3)–C(311)	1.429(5)
Fe(2)–C(2)	2.078(4)	Fe(2)–C(3)	1.846(5)
Fe(2)–N(3)	1.970(3)	Fe(2)–C(21)	1.772(6)
Fe(2)–C(22)	1.796(5)	C(1)–C(2)	1.413(6)
C(1)–N(3)	1.393(5)	C(1)–N(1)	1.357(6)
C(2)–C(4)	1.483(6)	N(1)–C(111)	1.489(7)
N(1)–C(121)	1.482(6)	N(2)–C(211)	1.392(6)
N(2)–C(3)	1.150(6)	O–C(av)	1.14(6)
N(3)–Fe(1)–C(2)	66.2(2)	C(11)–Fe(1)–C(2)	99.3(2)
C(13)–Fe(1)–C(2)	93.8(2)	C(11)–Fe(1)–N(3)	104.4(2)
C(13)–Fe(1)–N(3)	152.0(2)	C(13)–Fe(1)–C(11)	97.9(2)
C(12)–Fe(1)–C(2)	156.3(2)	C(12)–Fe(1)–N(3)	97.2(2)
C(12)–Fe(1)–C(11)	101.2(3)	C(12)–Fe(1)–C(13)	94.9(2)
C(3)–Fe(2)–C(2)	88.2(2)	N(3)–Fe(2)–C(2)	65.2(2)
N(3)–Fe(2)–C(3)	151.5(2)	C(21)–Fe(2)–C(2)	113.2(2)
C(21)–Fe(2)–C(3)	94.3(2)	C(21)–Fe(2)–N(3)	105.1(2)
C(22)–Fe(2)–C(2)	148.2(2)	C(22)–Fe(2)–C(3)	94.1(2)
C(22)–Fe(2)–N(3)	103.3(2)	C(22)–Fe(2)–C(21)	98.2(3)
N(2)–C(3)–Fe(2)	175.2(4)	N(3)–C(1)–C(2)	102.1(4)
N(1)–C(1)–C(2)	132.3(4)	N(1)–C(1)–N(3)	125.6(4)
Fe(2)–C(2)–Fe(1)	74.0(1)	C(1)–C(2)–Fe(1)	91.8(3)
C(1)–C(2)–Fe(2)	78.1(2)	C(4)–C(2)–Fe(1)	135.1(3)
C(4)–C(2)–Fe(2)	127.3(3)	C(4)–C(2)–C(1)	128.4(4)
C(111)–N(1)–C(1)	121.0(4)	C(121)–N(1)–C(1)	119.8(4)
C(121)–N(1)–C(111)	118.9(4)	C(3)–N(2)–C(211)	171.0(5)
Fe(2)–N(3)–Fe(1)	75.8(1)	C(1)–N(3)–Fe(1)	91.3(2)
C(1)–N(3)–Fe(2)	82.5(2)	C(311)–N(3)–Fe(1)	123.7(3)
C(311)–N(3)–Fe(2)	139.6(3)	C(311)–N(3)–C(1)	126.8(4)
O–C–Fe(av)	178.3(5)		

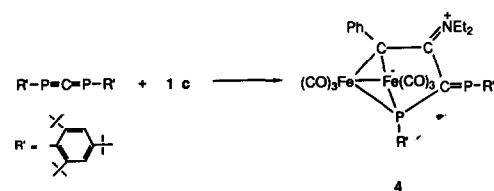
TABLE 3. Selected interatomic distances (Å) and bond angles (deg.) for compound 4, $[\text{Fe}_2(\text{CO})_6(\text{C}(\text{Ph})\text{C}(\text{NEt}_2)\text{C}(\text{PC}_6\text{H}_2^1\text{Bu}_3)\text{P}(\text{C}_6\text{H}_2^1\text{Bu}_3))]$

Fe(1)–Fe(2)	2.49(1)	Fe(1)–C(1)	2.63(5)
Fe(1)–C(3)	3.06(5)	Fe(1)–P(1)	2.23(2)
Fe(1)–C(11)	1.75(2)	Fe(1)–C(12)	1.74(1)
Fe(1)–C(13)	1.75(5)	Fe(1)–C(2)	2.25(4)
Fe(2)–P(1)	2.20(2)	Fe(2)–C(21)	1.75(2)
Fe(2)–C(22)	1.75(2)	Fe(2)–C(23)	1.75(2)
Fe(2)–C(3)	3.26(5)	Fe(2)–C(2)	1.99(4)
Fe(2)–C(1)	2.98(5)	P(1)–C(3)	1.88(4)
P(1)–C(111)	1.80(5)	P(2)–C(3)	1.66(5)
P(2)–C(211)	1.87(5)	N(1)–C(1)	1.33(5)
N(1)–C(121)	1.48(5)	N(1)–C(122)	1.50(6)
C(1)–C(2)	1.38(6)	C(1)–C(3)	1.61(6)
C(2)–C(4)	1.46(6)	O–C(av)	1.16(2)
C(11)–Fe(1)–P(1)	109.5(10)	C(12)–Fe(1)–P(1)	92.2(20)
C(12)–Fe(1)–C(11)	102.4(23)	C(13)–Fe(1)–P(1)	152.6(26)
C(13)–Fe(1)–C(11)	97.7(27)	C(13)–Fe(1)–C(12)	84.8(19)
C(2)–Fe(1)–P(1)	74.1(12)	C(2)–Fe(1)–C(11)	115.5(23)
C(2)–Fe(1)–C(12)	142.1(17)	C(2)–Fe(1)–C(13)	91.7(21)
C(21)–Fe(2)–P(1)	96.5(9)	C(22)–Fe(2)–P(1)	107.5(11)
C(22)–Fe(2)–C(21)	102.2(23)	C(23)–Fe(2)–P(1)	149.9(21)
C(23)–Fe(2)–C(21)	87.1(17)	C(23)–Fe(2)–C(22)	100.9(21)
C(2)–Fe(2)–P(1)	80.1(14)	C(2)–Fe(2)–C(21)	164.9(21)
C(2)–Fe(2)–C(22)	92.8(20)	C(2)–Fe(2)–C(23)	88.7(23)
Fe(2)–P(1)–Fe(1)	68.3(5)	C(3)–P(1)–Fe(1)	95.9(18)
C(3)–P(1)–Fe(2)	106.0(16)	C(111)–P(1)–Fe(1)	126.4(20)
C(111)–P(1)–Fe(2)	120.4(20)	C(111)–P(1)–C(3)	125.1(26)
C(211)–P(2)–C(3)	113.2(23)	C(121)–N(1)–C(1)	123.3(50)
C(122)–N(1)–C(1)	117.0(43)	C(122)–N(1)–C(121)	118.3(42)
C(2)–C(1)–N(1)	129.4(49)	C(3)–C(1)–N(1)	110.5(47)
C(3)–C(1)–C(2)	118.7(43)	Fe(2)–C(2)–Fe(1)	71.4(12)
C(1)–C(2)–Fe(1)	89.2(30)	C(1)–C(2)–Fe(2)	123.3(36)
C(4)–C(2)–Fe(1)	119.1(34)	C(4)–C(2)–Fe(2)	122.0(37)
C(4)–C(2)–C(1)	114.1(41)	P(2)–C(3)–P(1)	120.8(26)
C(1)–C(3)–P(1)	97.8(32)	C(1)–C(3)–P(2)	141.1(33)
O–C–Fe(av)	173.2(50)		

the shortening of the $\text{C}_1\text{--N}_1$ bond and the lengthening of the $\text{C}_1\text{--Fe}_1$ distances (Table 4). Furthermore, an increase of the $\text{C}_3\text{--Fe}_1$ non-bonded distance is observed. The same variations of distance are found on comparing structural parameters of 2 and 4 (Table 4).

2.4. A possible mechanism

With these results, we propose a reaction mechanism to explain the formation of complexes 2–4 (Scheme 4). We have recently observed that nucleophilic attack of PPh_3 resulted in the substitution of one CO ligand on the “ $\text{Fe}(\text{CO})_4$ ” fragment of 1c [12]. Considering this reaction site, the first step of the reaction would be the fixation of the heterocumulene



Scheme 3.

at the iron atom with elimination of CO (intermediate 1'). This reaction would be followed by a (2 + 2) cycloaddition between the $\text{X}=\text{C}$ ($\text{X} = \text{N}, \text{P}$) and $\text{Fe}=\text{C}$ bonds with a C–C coupling leading to the formation of a compound with structure type (a), observed for 2 (Scheme 4). A subsequent donation of the nitrogen lone pair would then rupture $\text{C}_1\text{--Fe}_1$ and form a compound with structure type (b), observed for 4 (Scheme 4). The fact that the phosphorus complex is unstable in a type (a) structure and stable in a type (b) structure is probably the consequence of the bulk of the phosphorus atom.

Complex 3 does not form by thermal rearrangement of complex 2 [13*], but probably arises from a competitive (2 + 2) cycloaddition. The proposed intermediate 1' can undergo two (2 + 2) cycloadditions as shown in Scheme 4. The compound resulting from C–N bond

* Reference number with asterisk indicates a note in the list of references.

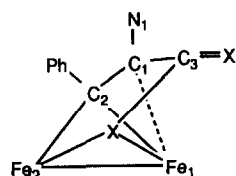


Fig. 4.

formation, less stable than **2**, would rearrange and lose a second CO to give compound **3**. It is worth pointing out that the phosphorus compound analogous to **3** has not been isolated. The presence of a bulky substituent on the phosphorus atom probably prevents it from attacking the carbon atom bearing the NEt_2 group.

In the field of carbodiimide and diphosphaallene organometallic chemistry, the complexes **2** and **4** are rare examples of addition to a metal-carbene bond. Further studies of the reactivity of these complexes are in progress.

3. Experimental section

All reactions were carried out under dinitrogen or argon. Hexane and dichloromethane were purified by standard procedures and stored over molecular sieves. Preparative column chromatography was performed on 70–230 mesh Merck silica gel. The complex **1c** [$\text{Fe}_2(\text{CO})_7\{\mu - \text{C}(\text{Ph})\text{C}(\text{NEt}_2)\}$] was prepared as described in ref. 2. Di-*p*-tolylcarbodiimide was purchased from Aldrich Chemical Co. 1,3-Diphosphaallene was synthesized according to the previously described pro-

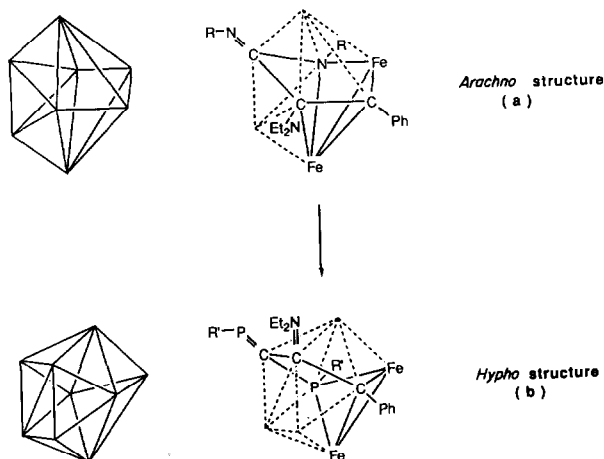


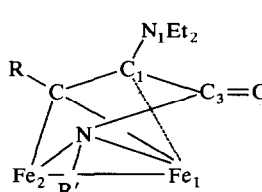
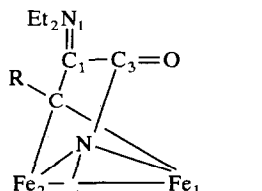
Fig. 5.

cedure [14]. IR spectra (KBr pellet) were recorded on a Perkin-Elmer 597 spectrophotometer. Mass spectra were obtained on a Nermag R10-10 instrument. NMR spectra (^1H and ^{31}P) were recorded on a Bruker AC 300 spectrometer.

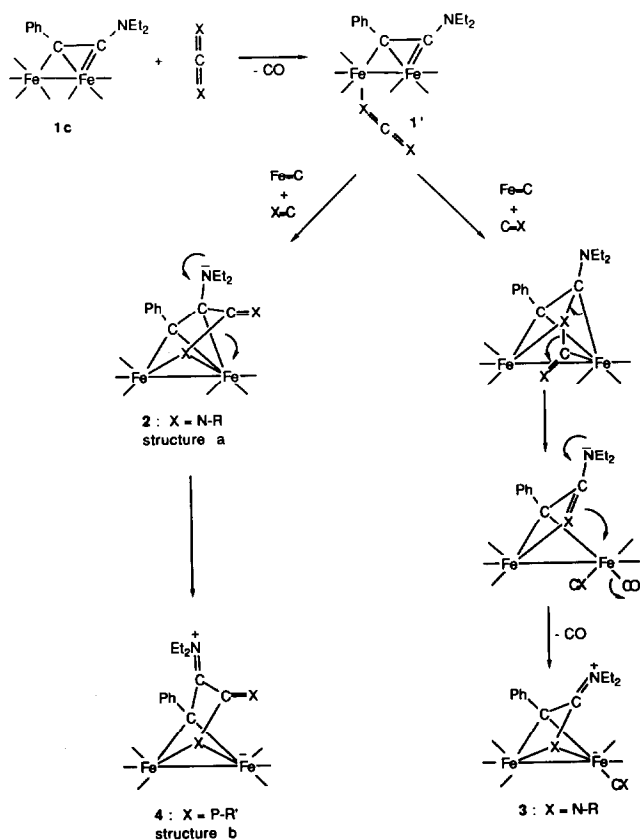
3.1. Reaction of complex **1c** with carbodiimide

Di-*p*-tolylcarbodiimide (60 mg, 0.27 mmol) was added to a solution of complex **1c** (120 mg, 0.25 mmol) in dry hexane (20 ml). The reaction mixture was heated under reflux for 4 h, then concentrated and chro-

TABLE 4. Comparison of structural parameters of selected complexes ^a

Complex	$\text{Fe}_1\text{-C}_1$	$\text{C}_1\text{-N}_1$	$\text{Fe}_1\text{-Fe}_2$	$\text{Fe}_1\text{-C}_3$
	2.29	1.40	2.46	2.53
2	2.30	1.38	2.46	2.63
	2.42	1.35	2.42	2.64
4	2.63	1.33	2.49	3.09

^a Interatomic distances are in Å.



Scheme 4.

matographed on a silica column. Complexes 2 and 3 were separated and purified using dichloromethane/hexane (10/90) as eluent.

2: red crystals (59 mg, 35%), mp = 125°C, IR: $\nu(\text{C}\equiv\text{O})$ 2070s, 2020s, 2000s, 1970s, 1950s, $\nu(\text{C}=\text{N})$ 1640m cm^{-1} ; ^1H NMR (300.13 MHz, C_6D_6) δ : 0.35 (t, 6H, $\text{CH}_3\text{-CH}_2$), 1.92 (s, 3H, $p\text{-CH}_3$), 2.02 (s, 3H, $p\text{-CH}_3$), 2.59 (q, 4H, $\text{CH}_3\text{-CH}_2$); MS (m/e): 675 (M^+), 647 ($\text{M}^+ - \text{CO}$), 619 ($\text{M}^+ - 2\text{CO}$), 591 ($\text{M}^+ - 3\text{CO}$), 563 ($\text{M}^+ - 4\text{CO}$), 535 ($\text{M}^+ - 5\text{CO}$), 507 ($\text{M}^+ - 6\text{CO}$).

3: red crystals (88 mg, 55%), mp = 101°C, IR: $\nu(\text{C}\equiv\text{O})$ 2030s, 1970s, 1950s, 1935s, 1925s, $\nu(\text{C}=\text{N})$ 2130s cm^{-1} ; ^1H NMR (300.13 MHz, C_6D_6) δ : 0.61 (m, 6H, $\text{CH}_3\text{-CH}_2$), 1.81 (s, 3H, $p\text{-CH}_3$), 1.96 (s, 3H, $p\text{-CH}_3$), 2.42 (m, 2H, $\text{CH}_3\text{-CH}_2$), 2.55 (m, 2H, $\text{CH}_3\text{-CH}_2$); MS (m/e): 647 (M^+), 619 ($\text{M}^+ - \text{CO}$), 591 ($\text{M}^+ - 2\text{CO}$), 563 ($\text{M}^+ - 3\text{CO}$), 535 ($\text{M}^+ - 4\text{CO}$), 507 ($\text{M}^+ - 5\text{CO}$).

3.2. Reaction of complex 1c with 1,3-diphosphaallene

Diphosphaallene (130 mg, 0.230 mmol) was added to a solution of complex 1c (110 mg, 0.228 mmol) in dry hexane (20 ml). The reaction mixture was heated under reflux for 12 h, during which time it slowly changed from red to dark brown. After removing the solvent

under vacuum, the residue was dissolved in hexane and was chromatographed on a silica column. A red band was eluted with a dichloromethane/hexane (20/80) solution and afforded dark red crystals of 4 (100 mg, 43%). IR $\nu(\text{C}\equiv\text{O})$: 2050s, 2010s, 1980s, 1970m, 1960s, 1940m cm^{-1} ; ^1H NMR (300.13 MHz, C_6D_6) δ : 0.53 (m, 6H, $\text{CH}_3\text{-CH}_2$), 1.28 (s, 9H, $p\text{-}^i\text{Bu}$), 1.37 (s, 9H, $p\text{-}^i\text{Bu}$), 1.71 (s, 18H, $o\text{-}^i\text{Bu}$), 2.11 (s, 18H, $o\text{-}^i\text{Bu}$), 2.40 (m, 4H, $\text{CH}_3\text{-CH}_2$); ^{31}P NMR (121.5 MHz, C_6D_6) δ : 139.9 (d, $^2J_{\text{PP}} = 83$ Hz), 250.7 (d, $^2J_{\text{PP}} = 83$ Hz); MS (m/e): 961 ($\text{M}^+ - 2\text{CO}$), 933 ($\text{M}^+ - 3\text{CO}$), 905 ($\text{M}^+ - 4\text{CO}$), 877 ($\text{M}^+ - 5\text{CO}$), 849 base peak ($\text{M}^+ - 6\text{CO}$).

3.3. Crystal data for complexes 2, 3 and 4

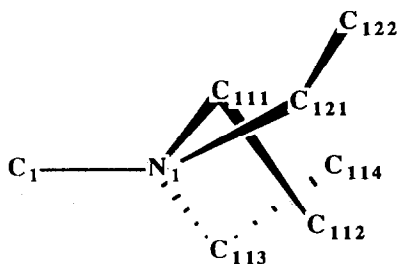
For each complex a selected crystal was set up on an automatic diffractometer (Nonius-CAD4 and Philips PW1100). Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 centred reflections well dispersed in reciprocal space. Two standard reflections were monitored periodically; they showed no change during data collection carried out at room temperature. Crystallographic data and other pertinent information are summarized in Table 5. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (DIFABS) [15] were applied.

Computations were performed by using CRYSTALS [16] adapted for MicroVax II. Atomic form factors for neutral Fe, P, O, N, C and H atoms were taken from ref. 17. Anomalous dispersion was provided by CRYSTALS. The three structures were solved by direct methods using the SHELX86 [18] program. 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. The weighting scheme used in the last refinement cycle was $w = w'[1 - (\Delta F/6\sigma(F_o))^2]^2$ where $w' = 1/\sum_1^3 A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was $F_c/F_o(\text{max})$ [19]. 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 values listed in Table 5. For analysis of compounds 2 and 3, the positions of all hydrogen atoms except those attached to disordered carbon atoms, were calculated assuming idealized geometries. Their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they were attached. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in final difference maps. Atomic coordinates are given in Tables 6–8. Tables 1–3 contain interatomic distances and bond angles.

TABLE 5. Crystallographic data

<i>Crystal parameters</i>			
Compound	C ₃₃ H ₂₉ N ₃ O ₆ Fe ₂	C ₃₃ H ₂₉ N ₃ O ₅ Fe ₂ , 1/2C ₆ H ₁₂	C ₅₅ H ₆₈ NO ₆ P ₂ Fe ₂
fw	675.1	690.4	1012.8
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> , Å	14.761(6)	15.002(8)	19.037(6)
<i>b</i> , Å	20.094(7)	15.674(2)	13.828(3)
<i>c</i> , Å	11.380(3)	30.255(6)	21.253(4)
β, deg	106.95(2)	93.85(2)	100.47(2)
<i>V</i> , Å ³	3229(16)	7098(28)	5501(21)
<i>Z</i>	4	8	4
ρ (calcd), g. cm ⁻³	1.34	1.29	1.22
μ (Mo Kα) cm ⁻¹	9.4	8.57	6.28
<i>Data collection</i>			
diffractometer	Philips PW1100	Philips PW 1100	CAD 4F
monochromator	graphite	graphite	graphite
radiation	Mo Kα (0.71070)	Mo Kα (0.71070)	Mo Kα (0.71070)
scan type	ω/2θ	ω/2θ	ω/2θ
scan range θ, deg	0.9 + 0.345 tg θ	0.9 + 0.345 tg θ	0.8 + 0.345 tg θ
2θ range, deg	4 < 2θ < 40	4 < 2θ < 50	3 < 2θ < 36
reflectn collected	2931	4417	4165
reflectn merged (R _m)	2691 (0.038)	4317 (0.031)	3925 (0.068)
reflectn used (<i>I</i> > 3σ(<i>I</i>))	1491	3293	917
<i>Refinement</i>			
<i>R</i>	0.067	0.045	0.100
<i>R</i> _w *	0.075	0.055	0.115
abs. corr. **	DIFABS	DIFABS	DIFABS
min./max. abs	0.927/1.068	0.964/1.028	0.804/1.029
second. extinct. param.	no	no	no
weighting scheme	Chebyshev	Chebyshev	Chebyshev
Coeff.Ar	1.27; 0.514; 09.39	1.11; 0.696; 0.632	4.68; -0.95; 3.19
I.s. parameters	296	396	222

Crystals of compound **2** are monoclinic. The space group *P*2₁/*a* was identified on the basis of systematic absences observed during data collection. Of the two ethyl of the amino group NEt₂, one appeared to be disordered, since the thermal parameters of its carbon atoms had large values and several peaks were found in the difference Fourier map in the immediate vicinity of these atoms. Several attempts at modelling this disorder resulted in the one shown below, where the disordered group corresponds to C₁₁₁–C₁₁₂ and C₁₁₃–C₁₁₄.



In view of the rather low ratio of data to parameters (5), the three phenyl groups were refined isotropically and they were constrained to chemically reasonable values (C–C = 1.40 Å, C–C–C = 120°). Anisotropic temperature factors were introduced for all other non-hydrogen atoms.

Compound **3** crystallized in a C centred monoclinic unit cell. The centrosymmetric space group *C*2/*c* was assumed and confirmed by successful refinement of the structure. Each methyl of the two amino groups was disordered and distributed on two sites with occupation factors of 0.7 and 0.3 respectively. In the final stage of the analysis, a molecule of hexane was located around a centre of symmetry. It was included in calculations and refined using constrained geometry to fit chemically reasonable values (C–C = 1.54 Å, C–C–C = 109°). Anisotropic refinements were used for all non-hydrogen atoms but the disordered C atoms of the methyl groups and the solvent molecule.

Compound **4** was difficult to crystallize. Only tiny crystals were obtained. The space group *P*2₁/*a* was

TABLE 6. Fractional atomic coordinates with e.s.d.s in parentheses, and equivalent isotropic thermal parameters U_{eq} for compound 2

$$U_{eq} = [U_{11} \cdot U_{22} \cdot U_{33}]^{1/3}$$

Atom	x	y	z	U_{eq}	U_{iso}
Fe(1)	0.1596(1)	0.35452(8)	0.8807(2)	0.0635	
Fe(2)	0.3190(1)	0.36224(8)	0.8554(1)	0.0494	
C(1)	0.2563(6)	0.3954(5)	1.063(1)	0.0461	
C(2)	0.2934(7)	0.3393(5)	1.0143(9)	0.0495	
C(4)	0.3447(5)	0.2843(4)	1.0882(8)		0.041(3)
C(5)	0.4286(7)	0.2968(4)	1.179(1)		0.074(4)
C(6)	0.4817(7)	0.2456(5)	1.2501(9)		0.078(4)
C(7)	0.4507(7)	0.1801(4)	1.2293(9)		0.065(3)
C(8)	0.3687(7)	0.1666(4)	1.1353(9)		0.066(3)
C(9)	0.3144(6)	0.2181(4)	1.0670(9)		0.066(3)
C(3)	0.2586(7)	0.4574(5)	0.9937(9)	0.0388	
N(1)	0.2335(7)	0.4000(4)	1.1725(9)	0.0506	
C(111)	0.197(1)	0.330(1)	1.205(2)		0.064(6)
C(112)	0.255(2)	0.312(2)	1.334(3)		0.090(8)
C(113)	0.283(2)	0.359(1)	1.294(2)		0.060(7)
C(114)	0.220(2)	0.300(2)	1.292(4)		0.09(1)
C(121)	0.1634(8)	0.4461(5)	1.186(1)	0.0491	
C(122)	0.1741(9)	0.4715(6)	1.313(1)	0.0750	
N(2)	0.2326(5)	0.4364(4)	0.8663(7)	0.0478	
C(211)	0.2134(5)	0.4882(4)	0.7756(8)		0.049(3)
C(212)	0.2848(6)	0.5320(5)	0.7693(9)		0.067(3)
C(213)	0.2674(6)	0.5809(5)	0.678(1)		0.077(4)
C(214)	0.1772(6)	0.5871(4)	0.5949(8)		0.062(3)
C(215)	0.1057(6)	0.5447(5)	0.6028(9)		0.064(3)
C(216)	0.1231(6)	0.4957(4)	0.6936(8)		0.055(3)
C(217)	0.1571(8)	0.6410(6)	0.495(1)		0.097(4)
N(3)	0.2783(5)	0.5173(4)	1.0214(7)	0.0468	
C(311)	0.3209(6)	0.5410(4)	1.1438(8)		0.050(3)
C(312)	0.2843(6)	0.5983(5)	1.1832(8)		0.068(3)
C(313)	0.3305(7)	0.6253(5)	1.2981(8)		0.071(3)
C(314)	0.4143(6)	0.5979(5)	1.3706(8)		0.075(4)
C(315)	0.4511(7)	0.5413(5)	1.3313(9)		0.082(4)
C(316)	0.4035(6)	0.5120(4)	1.2191(8)		0.055(3)
C(317)	0.4685(9)	0.6320(7)	1.491(1)		0.111(5)
C(11)	0.1312(9)	0.3309(7)	0.719(1)	0.0833	
O(11)	0.1041(7)	0.3147(5)	0.621(1)	0.1122	
C(12)	0.0542(8)	0.3948(5)	0.892(1)	0.0649	
O(12)	-0.0120(6)	0.4212(5)	0.8960(9)	0.0918	
C(13)	0.1175(9)	0.2771(7)	0.918(2)	0.0928	
O(13)	0.0841(7)	0.2287(5)	0.941(1)	0.1200	
C(21)	0.4336(8)	0.3949(5)	0.9342(9)	0.0428	
O(21)	0.5045(5)	0.4165(4)	0.9874(7)	0.0719	
C(22)	0.3150(9)	0.3817(7)	0.699(1)	0.0658	
O(22)	0.3168(8)	0.3931(6)	0.6028(8)	0.0962	
C(23)	0.3570(8)	0.2807(6)	0.834(1)	0.0695	
O(23)	0.3795(6)	0.2285(4)	0.8113(8)	0.0898	

identified on the basis of the systematic absences observed during the data collection which was of low quality. No reflections were measured above $\theta = 18^\circ$. Thus, only isotropic refinements were carried out.

4. Supplementary material available

Tables of anisotropic temperature factors, hydrogen coordinates, and bond lengths and angles may be ob-

TABLE 7. Fractional atomic coordinates with e.s.d.s in parentheses, and equivalent isotropic thermal parameters U_{eq} for compound 3

$$U_{eq} = [U_{11} \cdot U_{22} \cdot U_{33}]^{1/3}$$

Atom	x	y	z	U_{eq}	U_{iso}
Fe(1)	0.19730(4)	0.60304(4)	0.34899(2)	0.0555	
Fe(2)	0.15508(4)	0.62540(4)	0.42486(2)	0.0570	
C(1)	0.0587(3)	0.5502(3)	0.3794(1)	0.0539	
C(2)	0.1451(3)	0.5150(2)	0.3868(1)	0.0515	
C(4)	0.1702(3)	0.4272(3)	0.4009(2)	0.0577	
C(5)	0.1471(3)	0.3949(3)	0.4411(2)	0.0665	
C(6)	0.1715(4)	0.3146(3)	0.4549(2)	0.0772	
C(7)	0.2198(4)	0.2636(3)	0.4289(2)	0.0832	
C(8)	0.2444(4)	0.2938(3)	0.3896(2)	0.0814	
C(9)	0.2201(4)	0.3756(3)	0.3753(2)	0.0727	
N(2)	0.3018(3)	0.5370(3)	0.4790(1)	0.0717	
C(211)	0.3614(3)	0.4805(3)	0.5008(2)	0.0677	
C(212)	0.3804(4)	0.4906(4)	0.5459(2)	0.0780	
C(213)	0.4373(4)	0.4328(4)	0.5677(2)	0.0822	
C(214)	0.4755(3)	0.3664(3)	0.5455(2)	0.0731	
C(215)	0.4568(4)	0.3599(3)	0.5002(2)	0.0879	
C(216)	0.3995(4)	0.4169(3)	0.4776(2)	0.0805	
C(217)	0.5374(5)	0.3021(4)	0.5690(3)	0.1042	
C(3)	0.2472(3)	0.5742(3)	0.4587(2)	0.0653	
N(3)	0.0774(2)	0.6351(2)	0.3700(1)	0.0542	
C(311)	0.0184(3)	0.6951(3)	0.3477(1)	0.0552	
C(312)	-0.0331(3)	0.6722(3)	0.3102(2)	0.0681	
C(313)	-0.0830(4)	0.7335(3)	0.2861(2)	0.0716	
C(314)	-0.0827(3)	0.8175(3)	0.2989(2)	0.0662	
C(315)	-0.0329(4)	0.8389(3)	0.3369(2)	0.0763	
C(316)	0.0173(3)	0.7786(3)	0.3618(2)	0.0674	
C(317)	-0.1337(5)	0.8834(4)	0.2708(2)	0.0905	
C(11)	0.1722(3)	0.5557(3)	0.2959(2)	0.0676	
O(11)	0.1581(3)	0.5250(3)	0.2622(1)	0.1047	
C(13)	0.3078(3)	0.5636(3)	0.3584(2)	0.0670	
O(13)	0.3779(2)	0.5369(3)	0.3651(2)	0.0878	
C(12)	0.2312(4)	0.7088(3)	0.3336(2)	0.0802	
C(21)	0.0814(4)	0.6265(3)	0.4682(2)	0.0795	
O(21)	0.0349(4)	0.6278(4)	0.4971(2)	0.1169	
O(12)	0.2544(3)	0.7752(3)	0.3242(2)	0.1193	
C(22)	0.1997(4)	0.7311(3)	0.4324(2)	0.0755	
O(22)	0.2300(3)	0.7974(3)	0.4381(2)	0.1085	
N(1)	-0.0241(3)	0.5157(2)	0.3804(1)	0.0685	
C(111)	-0.1008(4)	0.5676(4)	0.3939(2)	0.0817	
C(121)	-0.0369(4)	0.4231(3)	0.3727(2)	0.0843	
C(112)	-0.1400(7)	0.5304(6)	0.4328(3)		0.116(3)
C(113)	-0.181(2)	0.560(2)	0.3665(9)		0.083(7)
C(122)	-0.022(1)	0.3981(9)	0.3243(5)		0.123(4)
C(123)	-0.082(2)	0.408(2)	0.3271(9)		0.130(7)
C(200)	0.0000	0.179(2)	0.2500		0.33(1)
C(201)	0.134(1)	0.138(1)	0.2980(8)		0.38(1)
C(202)	0.1027(6)	0.176(2)	0.2532(6)		0.30(1)
C(203)	0.036(1)	0.115(2)	0.285(1)		0.30(2)
C(204)	0.178(2)	0.060(2)	0.322(1)		0.34(2)

tained from the Cambridge Crystallographic Data Centre.

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TABLE 8. Fractional atomic coordinates with e.s.d.s in parentheses, and isotropic thermal parameters U_{iso} for compound 4

Atom	x	y	z	U_{iso}
Fe(1)	-0.7938(4)	-0.1906(7)	-0.7637(4)	0.059(2)
Fe(2)	-0.6834(4)	-0.2400(6)	-0.6892(4)	0.053(2)
P(1)	-0.7313(7)	-0.095(1)	-0.6893(6)	0.032(4)
P(2)	-0.6638(7)	0.092(1)	-0.7285(6)	0.035(4)
C(11)	-0.851(2)	-0.120(2)	-0.819(2)	0.10(2)
O(11)	-0.890(2)	-0.071(3)	-0.853(2)	0.15(2)
C(12)	-0.850(2)	-0.228(3)	-0.712(2)	0.09(2)
O(12)	-0.886(2)	-0.255(3)	-0.679(2)	0.12(1)
C(13)	-0.814(3)	-0.303(4)	-0.800(3)	0.14(3)
O(13)	-0.835(3)	-0.373(4)	-0.827(2)	0.14(2)
C(21)	-0.710(3)	-0.281(2)	-0.619(2)	0.06(2)
O(21)	-0.733(2)	-0.307(2)	-0.574(1)	0.06(1)
C(22)	-0.591(1)	-0.227(2)	-0.665(2)	0.09(2)
O(22)	-0.532(1)	-0.212(3)	-0.642(2)	0.11(1)
C(23)	-0.689(2)	-0.360(2)	-0.715(3)	0.10(2)
O(23)	-0.681(3)	-0.444(2)	-0.721(3)	0.19(2)
N(1)	-0.671(2)	-0.065(3)	-0.852(2)	0.05(1)
C(1)	-0.864(3)	-0.104(4)	-0.798(2)	0.05(2)
C(2)	-0.680(2)	-0.199(4)	-0.778(2)	0.03(1)
C(3)	-0.689(3)	-0.021(4)	-0.746(2)	0.05(1)
C(4)	-0.662(3)	-0.267(4)	-0.826(3)	0.065(2)
C(5)	-0.710(3)	-0.284(4)	-0.885(3)	0.065(2)
C(6)	-0.689(3)	-0.351(4)	-0.932(3)	0.065(2)
C(7)	-0.632(3)	-0.400(4)	-0.919(3)	0.065(2)
C(8)	-0.586(3)	-0.389(4)	-0.861(3)	0.065(2)
C(9)	-0.595(3)	-0.313(5)	-0.815(2)	0.065(2)
C(111)	-0.760(3)	-0.049(4)	-0.619(3)	0.065(2)
C(112)	-0.725(3)	-0.068(4)	-0.555(3)	0.065(2)
C(113)	-0.759(3)	-0.095(4)	-0.507(3)	0.065(2)
C(114)	-0.833(3)	-0.108(4)	-0.516(3)	0.065(2)
C(115)	-0.872(3)	-0.062(4)	-0.568(3)	0.065(2)
C(116)	-0.838(3)	-0.034(5)	-0.623(3)	0.065(2)
C(121)	-0.621(3)	-0.109(4)	-0.890(3)	0.065(2)
C(122)	-0.721(3)	0.012(4)	-0.883(3)	0.065(2)
C(123)	-0.586(3)	-0.016(4)	-0.928(3)	0.065(2)
C(124)	-0.772(3)	-0.029(4)	-0.947(3)	0.065(2)
C(131)	-0.640(3)	-0.058(4)	-0.531(3)	0.065(2)
C(132)	-0.603(3)	-0.148(4)	-0.506(2)	0.065(2)
C(133)	-0.601(3)	-0.007(4)	-0.584(3)	0.065(2)
C(134)	-0.635(3)	0.026(4)	-0.475(3)	0.065(2)
C(141)	-0.873(3)	-0.132(4)	-0.462(3)	0.065(2)
C(142)	-0.939(3)	-0.189(4)	-0.490(2)	0.065(2)
C(143)	-0.824(3)	-0.210(4)	-0.424(2)	0.065(2)
C(144)	-0.886(3)	-0.045(4)	-0.423(3)	0.065(2)
C(151)	-0.890(3)	0.038(5)	-0.672(3)	0.065(2)
C(152)	-0.954(3)	-0.018(4)	-0.707(3)	0.065(2)
C(153)	-0.907(3)	0.125(4)	-0.631(3)	0.065(2)
C(154)	-0.846(3)	0.081(4)	-0.720(3)	0.065(2)
C(211)	-0.620(3)	0.151(4)	-0.791(3)	0.065(2)
C(212)	-0.541(3)	0.134(4)	-0.787(3)	0.065(2)
C(213)	-0.512(3)	0.170(4)	-0.841(3)	0.065(2)
C(214)	-0.548(3)	0.229(4)	-0.887(2)	0.065(2)
C(215)	-0.618(3)	0.254(4)	-0.880(2)	0.065(2)
C(216)	-0.653(3)	0.222(4)	-0.830(3)	0.065(2)
C(231)	-0.492(3)	0.075(5)	-0.736(3)	0.065(2)
C(232)	-0.500(3)	0.121(4)	-0.668(3)	0.065(2)
C(233)	-0.411(3)	0.090(4)	-0.746(3)	0.065(2)
C(234)	-0.508(3)	-0.035(5)	-0.744(2)	0.065(2)
C(241)	-0.519(3)	0.258(5)	-0.946(2)	0.065(2)
C(242)	-0.574(3)	0.269(4)	-1.001(2)	0.065(2)

TABLE 8 (Continued)

Atom	x	y	z	U_{iso}
C(243)	-0.455(3)	0.203(4)	-0.958(2)	0.065(2)
C(244)	-0.499(3)	0.365(4)	-0.930(2)	0.065(2)
C(251)	-0.726(3)	0.282(4)	-0.823(2)	0.065(2)
C(252)	-0.793(3)	0.215(4)	-0.830(2)	0.065(2)
C(253)	-0.709(3)	0.315(4)	-0.748(2)	0.065(2)
C(254)	-0.741(3)	0.366(4)	-0.864(3)	0.065(2)

References and notes

- (a) E. Cabrera, O. Kristianson, J-C. Daran and Y. Jeannin, *J. Organomet. Chem.*, 310 (1986) 367; (b) V. Crocq, J-C. Daran, Y. Jeannin, B. Eber and G. Huttner, *Organometallics*, 10, (1991) 448; (c) V. Crocq, unpublished results.
- (a) V. Crocq, J-C. Daran and Y. Jeannin, *J. Organomet. Chem.*, 373 (1989) 85; (b) B. Heim, personal communication.
- J-C. Daran, B. Heim and Y. Jeannin, *C.R. Acad. Sci. Paris*, 312 *Serie II* (1991) 1117.
- (a) H-H. Karsch, H-U. Reisacher and G. Müller, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 618; (b) R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 619; (c) M. Yoshifuji, K. Toyota and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, (1984) 689.
- J.F. Nixon, *Chem. Rev.*, 88 (1988) 1327.
- C.A. Akpan, P.B. Hitchcock, J.F. Nixon, M. Yoshifuji, T. Niitsu and N. Inamoto, *J. Organomet. Chem.*, 338 (1988) C35.
- R.D. Adams, J-C. Daran and Y. Jeannin, *J. Cluster Science*, 3 (1992) 1.
- (a) Z. Nomikou, J-F. Halet, R. Hoffmann, J.T. Tanner and R.D. Adams, *Organometallics*, 9 (1990) 588; (b) R.D. Adams, G. Chen, L. Chen, J. Yin and J-F. Halet, *J. Cluster Sci.*, 2 (1991) 83.
- R.D. Adams, G. Chen, J.T. Tanner and J. Yin, *Organometallics*, 9 (1990) 595.
- (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, 18 (1976) 1; (b) D.M.P. Mingos and R.L. Johnston, *Structure and Bonding*, Springer Verlag, Berlin and Heidelberg, 1987.
- V. Crocq, Thesis, University of Paris VI, 1989.
- B. Heim, Thesis, University of Paris VI, 1992.
- A solution of 2 in hexane, heated for 4 h at 80°C, does not afford 3.
- M. Gouygou, C. Tachon, R. El Ouathib, O. Ramarajoana, G. Etamad-Moghadam and M. Koenig, *Tetrahedron Lett.*, 30 (1989) 177.
- N. Walker and D. Stuart, *Acta Crystallogr.*, 39 (1983) 158.
- D.J. Watkin, J.R. Carruthers and P.W. Betteridge, *CRYSTALS, an Advanced Crystallographic Program System*, Chemical Crystallography Laboratory, University of Oxford, 1988.
- International Tables for X-ray Crystallography, Vol. IV*, Kynoch Press, Birmingham, U.K., 1974.
- G.M. Sheldrick, *SHELXS 86, Program for Crystal Structure Solution*, University of Göttingen, 1986.
- E. Prince, *Mathematical Techniques in Crystallography*, Springer-Verlag, Berlin, 1982.