Carbon–carbon bond formation between a diferra(μ-alkylidene)carbene complex and an isocyanate RNCX (R = Et, Ph; X = O, S). X-ray structure of [Fe₂(CO)₆{ μ,η²-MeCC(NEt)₂CONR}]

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Abstract

The major products from the reaction of $[Fe_2(CO)_7\{\mu,\eta^2\text{-MeCC}(NEt_2)\}]$ (**1**) with isocyanates and isothiocyanate RNCX were the binuclear complexes $[Fe_2(CO)_6\{\mu,\eta^2\text{-MeCC}(NEt_2)CXNR\}]$ containing a ferrapyrrolidone fragment (**2**: X = O, R = Et; **3**: R = Ph; **4**: X = S, R = Ph). Compounds **2** and **3** were characterized by X-ray diffraction studies. Complex **4** was characterized by IR, ^{1}H NMR, and mass spectrometry. Crystal data for **2**: monoclinic, space group $P2_1/a$, a 13.079(2), b 11.436(2), c 13.544(2) Å, β 94.21(1)°, V 2020 Å^3, $Z = 4$, $R_w = 0.0281$ for 2348 reflexions. Crystal data for **3**: triclinic, space group $P\bar{1}$, a 9.326(1), b 10.786(1), c 12.145(2) Å, α 75.39(1)°, β 80.59(1)°, 76.75(1)°, V 1143 Å^3, $Z = 2$, $R_w = 0.0313$ for 2703 reflexions. They contain two $Fe(CO)_3$ fragment linked by a metal–metal bond and bridged by the $MeC=C(NEt_2)CONR$ ligand, which is derived from the combination of the isocyanate ligand with the aminoalkyne $CH_3C\equiv CNEt_2$ in **1**.

The complex $[Fe_2(CO)_7(\mu,\eta^2\text{-MeCCNEt}_2)]$ (**1**) contains an aminoalkyne molecule attached to iron atoms through a bridging carbene and a terminal aminocarbene. We have recently reported on its reactivity with alkynes and diphenyldiazomethane [1], in both cases, addition reaction occurs at the terminal Fe–C carbene bond, leading to C–C bond formation with alkynes and to C–N bond formation with diphenyldiazomethane. When considered in terms of the canonical form $C_6H_5C^+=N=N^-$, the C–N bond formation may be interpreted as the result of the nucleophilic attack of the diazo terminal nitrogen atom on the electrophilic aminocarbene carbon atom. It therefore seemed worthwhile to investigate the reactions of other similarly polarized organic molecules, and we describe here some

reactions with isocyanates and isothiocyanates R–N=C=X (X = O, S; R = Ph, Et). The charge distribution in RNCX molecules, deduced from theoretical calculations [2], is characterized by negative charges on the N and X atoms and a positive charge on the carbon atom, suggesting canonical forms:

$$R–N=C=X \leftrightarrow R–N^- –C^+ =X \leftrightarrow R–N=C^+ –X^-$$

Nucleophilic attack of the oxygen atom on the electrophilic carbene carbon atom of **1** might be considered a possibility. However, the reactions of isocyanate molecules towards transition metal complexes has been much investigated in the last ten years, and it has been shown that reactions mainly involve the C=N double bond. Metatheses of the W≡C triple bond with this C=N bond has been reported recently [3]. Cycloaddition of the C=N bond to terminal metal-oxo linkage has been observed for molybdenum [4] and rhenium [5] complexes. Coupling reactions between alkenes or alkynes with the C=N bond of isocyanates on ligand-nickel(0) system [6], dinuclear rhodium complex [7] and ruthenium [8] or osmium [9] clusters, have also been reported. Imidazolidinylidene complexes [(CO)$_5$W=C{C(Ph)(OEt)-NR'CONR}] are formed via template condensation of isocyanide with carbene-tungsten complex and the C=N bond of isocyanates [10]. Some examples involving reaction at oxygen can also be given. Thus dimolybdenum and ditungsten hexaalkoxides react with isocyanates to form products resulting from the insertion of isocyanates into the metal–alkoxide bond, in this case, the oxygen atom of the isocyanate molecule ligates to one metal center [11]. The oxygen atom is also involved in formation of the complex produced by insertion of PhNCO into the uranium–carbon bond of [Cp$_3$U=CH(PPhRMe)] [12]. Another reaction of iso-cyanates is the cleavage of the N–C bond, which yields CO and a nitrene fragment RN. For example, an imidotungsten compound can be conveniently prepared from [WOCl$_4$] and RNCO [13].

Our results show that isocyanates react with complex **1** through cycloaddition involving C=N bond and Fe=C carbene bonds to give the binuclear complexes: [Fe$_2$(CO)$_6${μ,η^2-MeCC(NEt$_2$)CXNR}] (X = O, S; R = Et, Ph). They have been characterized by X-ray structural analysis, which reveals that one iron atom is incorporated into a ferrapyrrolidone ring.

Results and discussion

Compound 2. The reaction of ethylisocyanate with **1** in refluxing hexane gives complex **2** in 62% yield. Upon chromatography, two green and one red products were observed. The green products were not separated in sufficiently large amounts to be characterized, but air-stable red crystals of **2** were grown from an hexane solution.

Compound **2** has been crystallographically characterized (Fig. 1). It contains an acrylamide ligand bridging two irons atoms; one of them is σ-bonded to C and N atoms to form a ferrapyrrolidone ring. The reaction may be described as a (2 + 2) cycloaddition between the C=N double bond and the Fe=C carbene as shown in Scheme 2. A metallacycle similar to intermediate **b** (Scheme 2) has been postulated as intermediate in the reaction between alkylidyne tungsten complex with cyclohexyl isocyanate [3]. Then, this intermediate could rearrange to form the stable ferrapyrrolidone ring.
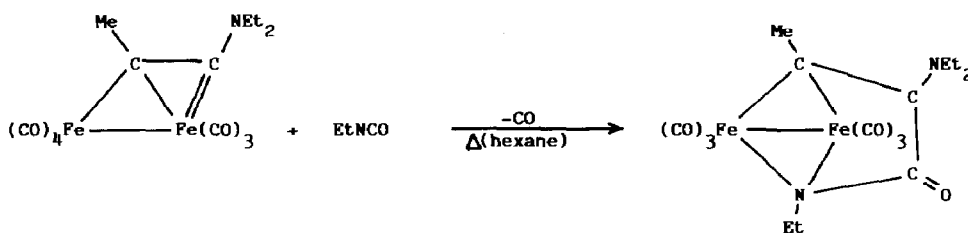
Scheme 1

Carbon–carbon bond formation between the central carbon atom of cumulene molecules and one of the triple bond carbon atoms of coordinated alkyne ligand seems to be a logical first step in the known catalytic cooligomerization reaction of alkynes with alkylisocyanates [14]. Adams has recently reported examples of carbon–carbon bond formation between the alkyne ligand in the osmium cluster $[Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)]$ and methyl isocyanate to give $[Os_3(CO)_9(\mu_3,\eta^3\text{-}HCCCO_2MeCONMe)(\mu_4\text{-}S)]$; this complex contains a derivative of acrylamide which bridges three osmium atoms [9]. Another example of the coupling of an isocyanate molecule to the coordinated alkyne ligand has been reported by Dickson for the complex $[(C_5H_5)_2Rh_2(CO)(CF_3CCCF_3)]$, the product being $[(C_5H_5)_2Rh_2\text{-}\{CF_3CC(CF_3)CONR\}]$, which contains also an acrylamide ligand bridging both metal centers [7].
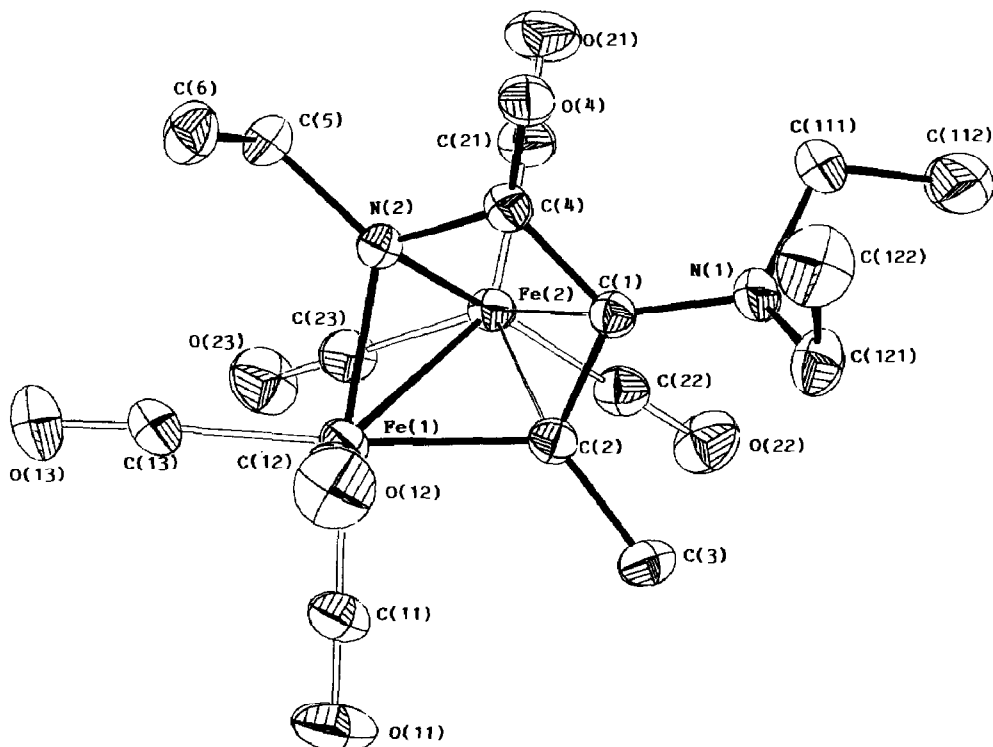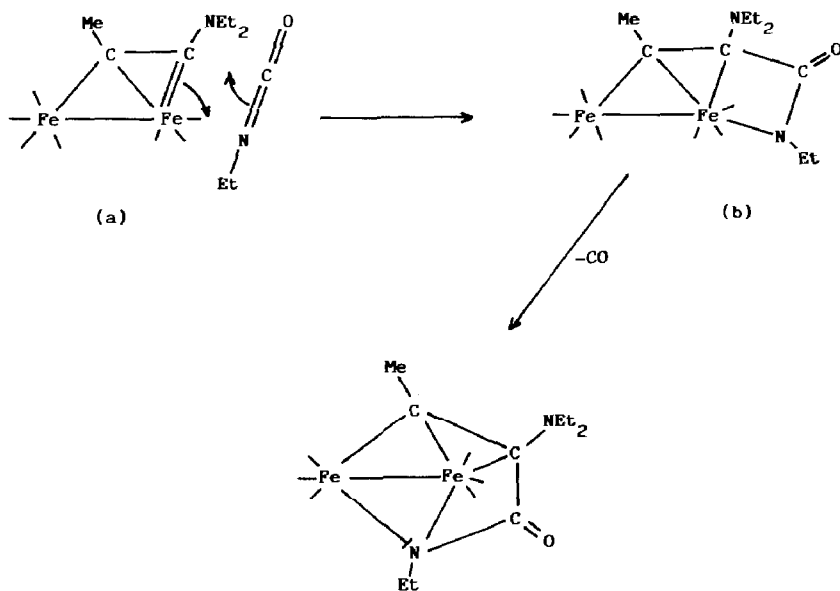

Fig. 1. ORTEP view of complex 2 showing the atom numbering scheme used in tables; ellipsoids represent 25% probability.
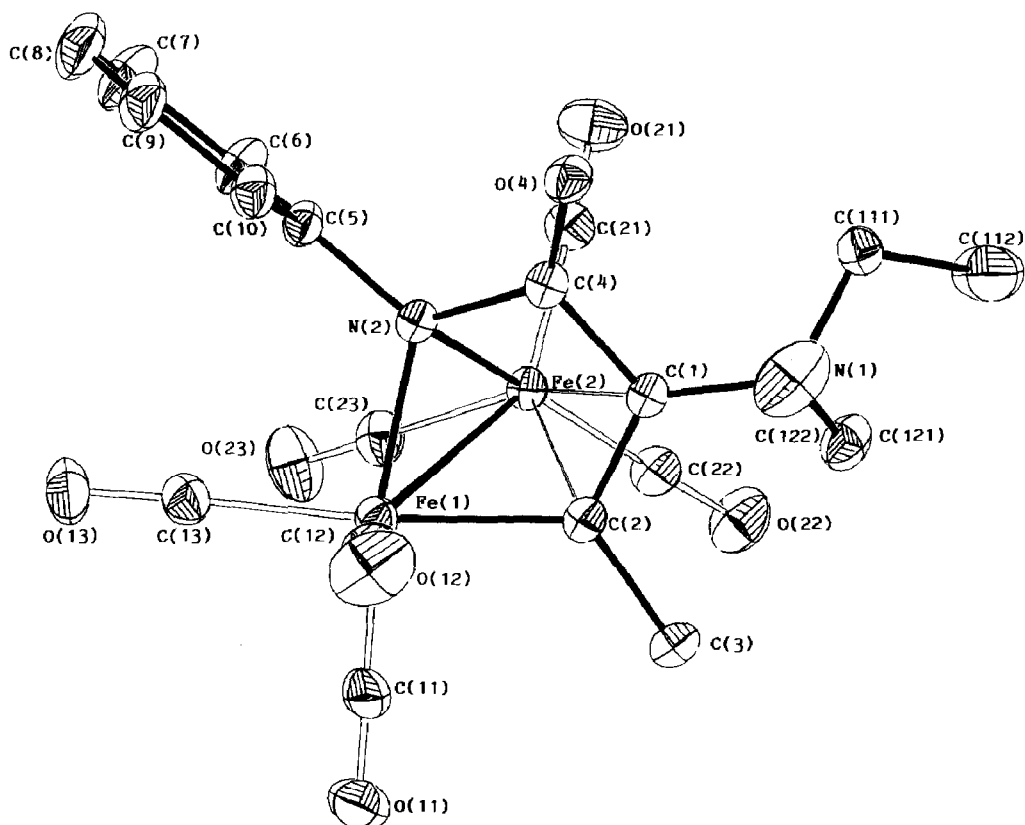
Scheme 2

Fig. 2. ORTEP view of complex **3** showing the atom numbering scheme used in tables; ellipsoids represent 20% probability.

Compound 3. The reaction of phenylisocyanate with **1** in refluxing hexane gave a whitish precipitate and a red brown supernatant. The supernatant liquor was syringed off, concentrated, and cooled to $-20°C$ to give dark red crystals of **3** (63% yield). The precipitate was washed and recrystallized from CH_2Cl_2 to give colorless crystals, which were shown to be triphenylbiuret $(C_6H_5NHCO)_2NC_6H_5$ from IR, ^1H NMR and mass spectrometry. This organic compound probably results from the presence of a small amount of water in the phenylisocyanate.

Complex **3** has a similar structure to **2**; it contains a bridging acrylamide ligand as part of a ferrapyrrolidone ring (Fig. 2).

Compound 4. As mentioned above, complexes **2** and **3** may be formed by a (2 + 2) cycloaddition between the isocyanate C=N double bond and the Fe=C carbene bond of **1**. However there is another way of considering the formation of **2** and **3**, arising from the knowledge that cleavage of isocyanate N=C bonds can yield CO and RN fragments [13]. If such a bond rupture occurred, the nitrene fragment RN could react with **1**; a subsequent rearrangment involving one CO molecule would give complex **2** or **3**. The formation of metallapyrrolidone rings from nitrene and CO has, in fact, been observed in the case of $[(C_5H_5)_2Rh_2\{CF_3CC(CF_3)CONR\}]$ [7] and in $[Ru_2(CO)_6\{PhCC(Ph)CONPh\}]$ [15]. To check this possibility we treated **1** with phenyl isothiocyanate in refluxing hexane. Upon chromatography, four bands were observed, and the major band yielded small dark red crystals of **4**. These crystals were much too small for an X-ray study, but **4** was identified by IR, ^1H NMR and mass spectrometry.

The mass spectrum showed a peak at m/e 526 which corresponds to the addition of one C_6H_5NCS molecule to complex **1** and loss of one CO group. Two possible structures can be considered as shown in Scheme 3. It has been shown that the insertion of PhNCX into the platinum–nitrogen bond of $[Pt(PPh_3)_2(PhNO)]$ [16] gives two different types of product depending on whether X is an O or a S atom (Scheme 3, II). The IR spectrum of **4** shows the presence of a strong absorption band at 1120 cm^{-1} which can be attributed to $\nu(C=S)$ stretching vibration; this value is consistent with an uncoordinated C=S double bond [17], and thus favours structure **a** (Scheme 3, I). No absorption is observed in the $\nu(C=N)$ region (1650–1750 cm^{-1}), ruling out structure **b**. Moreover, it is noteworthy that the IR spectra in the $\nu(C\equiv O)$ region for compounds **3** and **4** are closely similar suggesting similar structures for the two complexes.

Crystal and molecular structures of 2 and 3. ORTEP drawings of the molecules are shown in Fig. 1 and 2; important bond distances and angles are given in Table 1. Complexes **2** and **3** have virtually identical frameworks, differing only in the identities of the substituents on the nitrogen atom of the ferrapyrrolidone rings (**2**, R = Et; **3**, R = Ph). Both Fe atoms are joined by a single metal–metal bond (**2**, 2.4686(4) Å; **3**, 2.4701(5) Å), and are bridged by the μ,η-MeC=C(NEt_2)CONR ligand which is derived from a combination of the isocyanate ligand with the aminoalkyne $CH_3C\equiv CNEt_2$ attached to complex **1**. Each Fe atom is further coordinated by three CO ligands.

Bond lengths within ferrapyrrolidone rings are identical to those observed for other molecules with similar structures, as shown in Table 2. The values of the torsion angles (Table 3) in the ferrapyrrolidone ring (Fe(1) to N(2)) indicate a conformation intermediate between a half-chair and an envelope [20], with a maximum puckering at C(4). As observed for other metallapyrrolidone complexes,

(a)

(b)

I

II
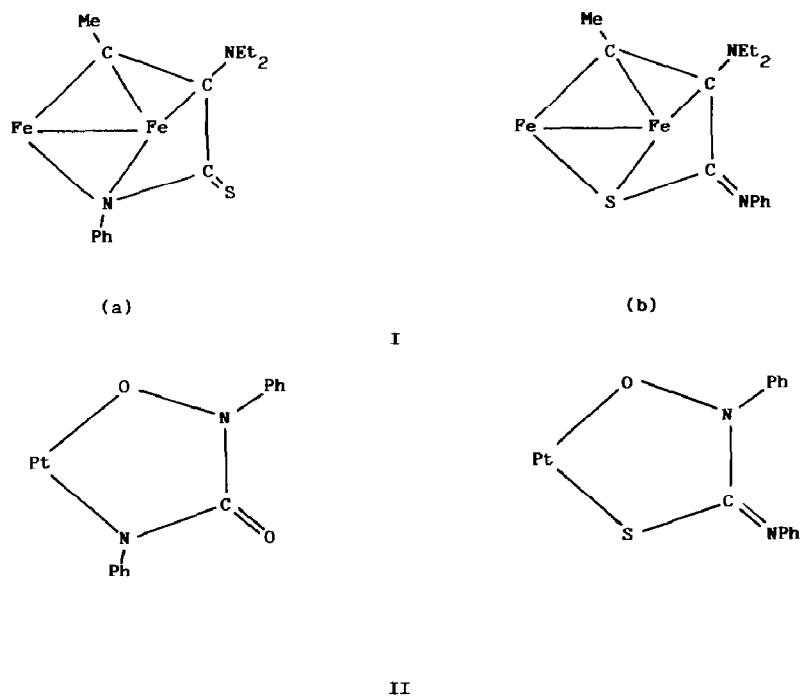
Scheme 3

the carbon of the ketone group is not bonded to iron, but the nitrogen atom of the isocyanate symmetrically bridges both iron atoms. The triple bond carbons are bonded to the binuclear unit as a σ,π-vinyl ligand. C(1)–C(2) distances are 1.409(3) and 1.393(4) Å for **2** and **3**, respectivly, typical of π-bonded olefin ligands.
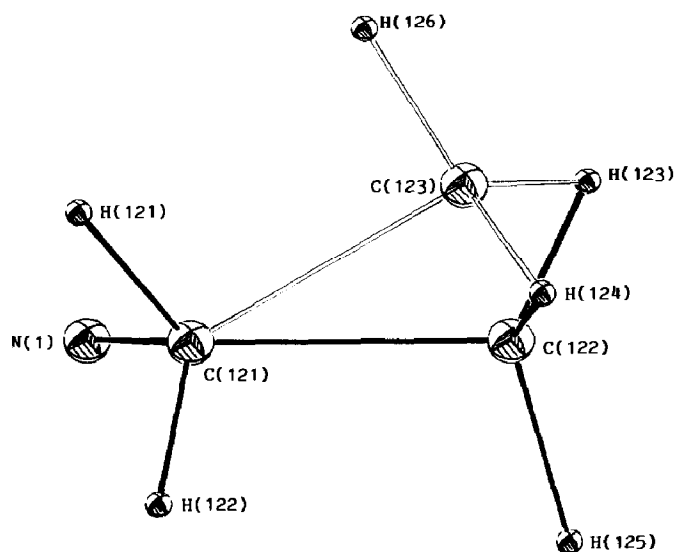

Fig. 3. Statistical distribution of one of the ethyl of the amino group observed in **2**.

Table 1

Interatomic distances (Å) and bond angles (°) for **2** and **3**; esd's in parentheses refer to the last significant digit.

Compound **2**		Compound **3**	
Fe(2)–Fe(1)	2.4686(4)	Fe(2)–Fe(1)	2.4701(5)
Fe(2)–C(1)	2.231(2)	Fe(2)–C(1)	2.215(2)
Fe(2)–C(2)	2.105(2)	Fe(2)–C(2)	2.101(2)
Fe(2)–C(4)	2.422(2)	Fe(2)–C(4)	2.438(2)
Fe(2)–N(2)	1.988(2)	Fe(2)–N(2)	1.993(2)
Fe(1)–C(2)	1.970(2)	Fe(1)–C(2)	1.964(3)
Fe(1)–N(2)	1.966(2)	Fe(1)–N(2)	1.976(2)
C(1)–N(1)	1.394(3)	C(1)–N(1)	1.405(3)
C(1)–C(2)	1.409(3)	C(1)–C(2)	1.394(4)
C(1)–C(4)	1.471(3)	C(1)–C(4)	1.475(4)
N(1)–C(111)	1.465(4)	N(1)–C(111)	1.464(4)
N(1)–C(121)	1.464(4)	N(1)–C(121)	1.460(4)
C(2)–C(3)	1.501(3)	C(2)–C(3)	1.501(4)
C(4)–O(4)	1.210(3)	C(4)–O(4)	1.207(3)
C(4)–N(2)	1.416(3)	C(4)–N(2)	1.426(3)
N(2)–C(5)	1.477(3)	N(2)–C(5)	1.445(3)
C(2)–C(1)–N(1)	123.7(2)	C(2)–C(1)–N(1)	123.5(2)
C(4)–C(1)–N(1)	121.6(2)	C(4)–C(1)–N(1)	120.7(2)
C(4)–C(1)–C(2)	115.1(2)	C(4)–C(1)–C(2)	114.3(2)
C(111)–N(1)–C(1)	118.5(2)	C(111)–N(1)–C(1)	117.9(2)
C(121)–N(1)–C(1)	116.9(2)	C(121)–N(1)–C(1)	115.5(2)
C(121)–N(1)–C(111)	116.4(2)	C(121)–N(1)–C(111)	116.9(2)
C(1)–C(2)–Fe(1)	114.2(2)	C(1)–C(2)–Fe(1)	114.6(2)
C(3)–C(2)–Fe(1)	125.4(2)	C(3)–C(2)–Fe(1)	124.7(2)
C(3)–C(2)–C(1)	119.8(2)	C(3)–C(2)–C(1)	120.1(2)
O(4)–C(4)–C(1)	128.1(2)	O(4)–C(4)–C(1)	128.7(2)
N(2)–C(4)–C(1)	107.1(2)	N(2)–C(4)–C(1)	106.0(2)
N(2)–C(4)–O(4)	124.5(2)	N(2)–C(4)–O(4)	125.1(2)
Fe(2)–N(2)–Fe(1)	77.27(7)	Fe(2)–N(2)–Fe(1)	76.97(7)
C(4)–N(2)–Fe(1)	114.3(1)	C(4)–N(2)–Fe(1)	114.2(2)
C(5)–N(2)–FE(1)	124.7(1)	C(5)–N(2)–Fe(1)	120.6(2)
C(5)–N(2)–C(4)	114.6(2)	C(5)–N(2)–C(4)	115.6(2)
N(2)–Fe(1)–C(2)	79.47(8)	N(2)–Fe(1)–C(2)	79.2(1)

Table 2

Interatomic distances (Å) in some metallapyrrolidone rings

	C(1)–C(2)	C(2)–C(4)	C(4)–O(4)	C(4)–N(2)	
[Fe$_2$(CO)$_6${MeCC(NEt$_2$)CONEt}]	1.409(3)	1.471(3)	1.210(3)	1.416(3)	this work
[Fe$_2$(CO)$_6${MeCC(NEt$_2$)CONPh}]	1.393(4)	1.475(4)	1.207(3)	1.426(3)	this work
[Fe$_2$(CO)$_6${(OEt)CCMeCONNCPh$_2$}]	1.410(6)	1.486(6)	–	1.409(5)	(18)
[Ru$_2$(CO)$_6${PhCCPhCONPh}]	1.425(5)	1.494(5)	1.211(5)	1.437(5)	(15)
[Ru$_2$(CO)$_6${PhCCMeCONPh}]	1.423(8)	1.481(8)	1.212(8)	1.427(8)	(15)
[Rh$_2$(Cp)$_2${CF$_3$CCCF$_3$CONPh}]	1.45(1)	1.48(1)	1.20(1)	1.41(1)	(7)
[Os$_3$(CO)$_9${HCC(CO$_2$Me)CONMe}(μ_3-S)]	1.40(2)	1.49(2)	1.21(2)	1.44(2)	(9)

Table 3

Torsion angles ($^\circ$) in the metallapyrrolidone ring: a positive rotation is anti-clockwise from atom 1, when viewed from atom 3 to atom 2.

Compound 2			
ψ_0	N(2)–Fe(1)–C(2)–C(1)	16.00	
ψ_1	C(4)–N(2)–Fe(1)–C(2)	-29.38	
ψ_2	C(1)–C(4)–N(2)–Fe(1)	35.15	$\Delta = 479.7$
ψ_3	C(2)–C(1)–C(1)–N(2)	-21.26	
ψ_4	Fe(1)–C(2)–C(1)–C(4)	-1.08	
Compound 3			
ψ_0	N(2)–Fe(1)–C(2)–C(1)	-15.40	
ψ_1	C(4)–N(2)–Fe(1)–C(2)	29.55	
ψ_2	C(1)–C(4)–N(2)–Fe(1)	-35.72	$\Delta = 483.5$
ψ_3	C(2)–C(1)–C(4)–N(2)	22.62	
ψ_4	Fe(1)–C(2)–C(1)–C(4)	-0.31	

Conformation parameter (phase angle of pseudorotation)

$$\tan \Delta /2 = (\psi_2 + \psi_4) - (\psi_1 + \psi_3)/2\psi_0 (\sin 36^\circ + \sin 72^\circ) \text{ (ref. 19)}$$

Moreover, the C(2) carbon in each molecule is 0.14 Å closer to the Fe atom to which it is σ-bonded than to the other Fe atom.

It is noteworthy that in complex **2** one of the ethyl groups of the aminoalkyne ligand is disordered: the methyl fragment is statistically distributed between two sites related by a pseudo mirror plane containing N(1), C(122) and bissecting the H(121)–C(121)–H(122) angle (Fig. 3).

In complex **3**, the phenyl ring (C(5) to C(10)) and the Fe(1), C(2), C(1), N(2) plane make a dihedral angle of 86.6°.

Experimental

All reactions were carried out under dry nitrogen by standard Schlenk or vacuum line techniques. Preparative column chromatography was performed on 70–230 mesh Merck silica gel. For thin-layer analytical chromatography (TLC) aluminium sheets coated with silica gel $60F_{254}$ were used. Infrared absorption spectra were recorded on a Perkin–Elmer 597 spectrometer. A Nermag R10-10 spectrometer was used for recording of the mass spectrum. The NMR spectra were recorded on a Brucker WM 200 with tetramethylsilane as reference. Hexane and dichloromethane were purified by standard procedures and stored over molecular sieves. Complex **1** was prepared as described in ref. 1. The reagents C_6H_5NCO, C_2H_5NCO and C_6H_5-NCS were purchased from Aldrich.

Synthesis of [Fe$_2$(CO)$_6${CH$_3$CC(NEt$_2$)CONEt}] (2)

A mixture of [Fe$_2$(CO)$_7${C(CH$_3$)C(NEt$_2$)}] (1) (20 mg, 0.048 mmol), C_2H_5NCO (4.4 mg, 0.0624 mmol), and dry hexane (20 ml) was refluxed under nitrogen for 2 h, during which the solution changed from orange to dark red. Thin layer chromatography showed the presence of three products. The dark red solution was concentrated to a volume of 10 ml, and chromatographed over a silica column. Elution with hexane gave very small amount of two green products which were not

characterized. Elution with CH_2Cl_2 yielded 14 mg of complex **2** (yield: 62%; 0.029 mmol) as a dark red powder. Recrystallization from hexane at $-20°C$ gave dark red crystals of **2**.

MS: m/e 463 (M^+); IR (KBr pellets) $\nu(C\equiv O)$ 2080(s), 2040(s), 2005(s), 1995(s) cm^{-1}; $\nu(C=O)$ 1680(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.25 (q, 4H, $N(CH_2CH_3)_2$, 2.8 (q, 2H, NCH_2CH_3), 2.5 (s, 3H, CH_3 bridgehead), 2.0 (t, 3H, NCH_2CH_3), 1.25 (t,6H, $N(CH_2CH_3)_2$). Anal. Found: C, 41.72; H, 4.15; N, 6.18. $C_{16}H_{18}N_2O_7Fe_2$ calcd.: C, 41.59; H, 3.93; N, 6.06%.

Synthesis of 3

A solution of **1** (20 mg, 0.048 mmol) and C_6H_5NCO (7.4 mg, 0.0624 mmol) in dry hexane (20 ml) was refluxed under nitrogen for 2 h during which the orange solution became burgundy red and a whitish precipitate separated. The dark red supernatant liquid was syringed off, and thin layer chromatography showed only one band. The solution was concentrated and cooled to $-20°C$, to give dark red crystals of **3** (yield: 63%; 15.4 mg). The whitish precipitate was dissolved in warm

Table 4

Crystal Data

Empirical formula	$C_{16}H_{18}N_2O_7Fe_2$	$C_{20}H_{18}N_2O_7Fe_2$
f_w	462	510
Crystal system	monoclinic	triclinic
Space group	$P2_1/a$	$P\bar{1}$
a, Å	13.079(2)	9.326(1)
b, Å	11.436(2)	10.786(1)
c, Å	13.544(2)	12.145(2)
α, °	90.0	75.39(1)
β, °	94.21(1)	80.59(1)
γ, °	90.0	76.75(1)
V, Å^3	2020	1143
Z	4	2
$\mu(Mo\text{-}K_\alpha)$, cm^{-1}	14.71	13.08
p(calcd), g cm^{-3}	1.509	1.481
Temperature, °C	20	20
Radiation	Mo-K_α	Mo-K_α
Scan range θ, deg	1.0 + 0.345 tan θ ^{a}	1.0 + 0.345 tan θ ^{a}
2θ range, deg	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$
Absorption	Empirical cor. [23]	Difabs. [24]
Speed range, deg min^{-1}	$1.5 \le sp \le 5.5$	$1.8 \le sp \le 6.7$
$F(000)$	944	520
Std. reflect.	11,1,2; 8,0,7	5,3,3; 8,1,5
Reflect. collect	3924	4224
Reflect. merged (R_m)	3553(0.021)	4018(0.019)
Reflect. used	2348	2703
Criteria	$I \ge 3\sigma(I)$	$I \ge 3\sigma(I)$
R ^{b}	0.0219	0.0280
R_w	0.0281	0.0313
rms (shift/esd)	0.25	0.30
Ar coefficients for w ^{c}	10.57, −4.20, 8.42	4.38, −2.11, 3.36
Ratio of obs. to param.	7.5	8

^{a} Scan extended by 25% on either side for background determination. ^{b} $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$. $R_w = \{\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2\}^{1/2}$. ^{c} $w = 1/\Sigma_{r=1}Ar.Tr(x)[1 - (\Sigma\Delta F/6\sigma(F_0))^2]^2$ (ref 25)

dichloromethane; slow cooling of the CH_2Cl_2 solution at $0\,^\circ C$ yielded colorless crystals of triphenylbiuret $(C_6H_5NHCO)_2NC_6H_5$.

Complex 3: IR (KBr pellets) $\nu(C\equiv O)$ 2080(s), 2045(s), 2020(s), 2005(s), 1990(s), 1975(s) cm^{-1}, $\nu(C=O)$ 1685(s)cm^{-1}. MS: m/e 511 (M^+). ^1H NMR (CDCl$_3$): δ 7.2–7.4 (br, 5H, C_6H_5), 3.4 (m, 4H, CH_2CH_3), 2.6 (s, 3H, CH_3 bridgehead), 1.2 (m, 6H, CH$_2$CH_3). Anal. Found: C, 47.65; H, 3.88; N, 5.80. $C_{20}H_{18}N_2O_7Fe_2$ calcd.: C, 47.10; H, 3.56; N, 5.49%.

Triphenylbiuret: IR (KBr pellets) $\nu(C=O)$ 1720(s) cm^{-1}; $\nu(C=C)$ 1600(s), 1520 (m), 1450(m) cm^{-1}; $\nu(N-H)$ 3400(br) cm^{-1}. ^1H NMR (CDCl$_3$) δ 7–7.5 (m, 15H, C_6H_5). MS: m/e 332 (M^+), 212 ($M^+ - C_6H_5NCO$), 119 (C_6H_5NCO), 93 ($C_6H_5NH_2$), 77 (C_6H_5), 65 (C_5H_5). Anal. Found: C, 73.11; H, 6.1; N, 13.02. $C_{20}H_{17}N_3O_2$ calcd.: C, 72.48; H, 5.17; N, 12.67%.

Synthesis of [Fe$_2$(CO)$_6${CH$_3$CC(NEt$_2$)CSNPh}] (4)

A solution of 1 (20 mg, 0.048 mmol) and C_6H_5NCS (8.42 mg, 0.062 mmol) in dry hexane (20 ml) was refluxed under nitrogen for 2 h during which the orange solution became burgundy red. Thin layer chromatography gave four bands. The solution was concentrated to a volume of ca. 10 ml and chromatographed on a silica column.

Table 5

Fractional atomic coordinates for 2. $U_{eq} = [U_{11} \times U_{22} \times U_{33}]^{1/3}$

Atom	x	y	z	U_{eq}
Fe(1)	0.29818(2)	0.01234(3)	0.15167(2)	0.0447
Fe(2)	0.13095(2)	0.08377(3)	0.20017(2)	0.0406
C(1)	0.2252(2)	0.0538(2)	0.3420(2)	0.0433
N(1)	0.2146(2)	0.1007(2)	0.4357(1)	0.0576
C(111)	0.1191(3)	0.0792(3)	0.4828(2)	0.0675
C(121)	0.3079(3)	0.1104(3)	0.5018(2)	0.0709
C(112)	0.0802(3)	0.1848(3)	0.5300(3)	0.0938
C(122)	0.3188(8)	0.0030(8)	0.5662(7)	0.1054
C(123)	0.3660(8)	−0.003(1)	0.5267(8)	0.1105
C(2)	0.2788(2)	0.1098(2)	0.2687(2)	0.0424
C(3)	0.3286(2)	0.2262(2)	0.2903(2)	0.0576
C(4)	0.1921(2)	−0.0660(2)	0.3165(2)	0.0442
O(4)	0.1627(2)	−0.1408(1)	0.3709(1)	0.0582
N(2)	0.1900(1)	−0.0762(2)	0.2121(1)	0.0419
C(5)	0.1438(2)	−0.1856(2)	0.1717(2)	0.0550
C(6)	0.2177(3)	−0.2878(2)	0.1828(2)	0.0696
C(11)	0.2866(2)	−0.0668(3)	0.0347(2)	0.0651
O(11)	0.2832(2)	−0.1145(3)	−0.0388(2)	0.0962
C(12)	0.4088(2)	−0.0585(3)	0.2096(2)	0.0628
O(12)	0.4768(2)	−0.1015(2)	0.2493(2)	0.0942
C(13)	0.3670(2)	0.1252(3)	0.0942(2)	0.0595
O(13)	0.4118(2)	0.1958(2)	0.0579(2)	0.0818
C(21)	0.0034(2)	0.0407(2)	0.2289(2)	0.0540
O(21)	−0.0755(1)	0.0094(2)	0.2449(2)	0.0747
C(22)	0.1105(2)	0.0905(2)	0.0682(2)	0.0561
O(22)	0.0905(2)	0.1009(2)	−0.0143(1)	0.0779
C(23)	0.1082(2)	0.2363(2)	0.2157(2)	0.0518
O(23)	0.0948(2)	0.3329(2)	0.2280(2)	0.0727

Elution with hexane gave very small amount of two green and one red products, which were not characterized. Elution with CH_2Cl_2 yielded 10 mg of complex **4** (yield: 40%; 0.019 mmol). Attempts to grow crystals of a size suitable for an X-ray study failed. IR (KBr pellets) $\nu(C\equiv O)$ 2085(s), 2040(s), 2020(s), 2010(s), 1995(s), 1975(s) cm^{-1}, $\nu(C=S)$ 1150(s) cm^{-1}. ^1H NMR (CDCl$_3$) δ 7.25 (m, 5H, C$_6$H$_5$), 3.25 (q, 4H, CH_2CH$_3$), 2.2 (s, 3H, CH_3 bridgehead), 1.25 (t, 6H, CH$_2$CH_3). MS m/e 526 (M^+). Anal. Found: C, 45.95; H, 4.05; N, 5.72. C$_{20}$H$_{18}$N$_2$O$_6$SFe$_2$ calcd.: C, 45.67; H, 3.45; N, 5.33%.

Crystal data for complexes 2 and 3

For both compounds, preliminary unit-cell dimensions and symmetry informations were derived from precession photographs; the selected crystals were mounted on a Nonius CAD4 automatic diffractometer. Cell dimensions and orientation matrices were obtained from least-squares refinements of the setting angles of 25 reflections.

Table 6

Fractional atomic coordinates for **3**. $U_{eq} = [U_{11} \times U_{22} \times U_{33}]^{1/3}$

Atom	x	y	z	U_{eq}
Fe(1)	0.29755(4)	0.26894(4)	0.11468(3)	0.0436
Fe(2)	0.04251(4)	0.27752(3)	0.21220(3)	0.0375
C(1)	0.1361(3)	0.0677(2)	0.2197(2)	0.0392
N(1)	0.0646(3)	−0.0378(2)	0.2346(2)	0.0494
C(111)	−0.0369(4)	−0.0665(3)	0.3390(3)	0.0593
C(121)	0.1516(4)	−0.1492(3)	0.1902(3)	0.0624
C(112)	−0.1864(5)	−0.0723(7)	0.3143(4)	0.1038
C(122)	0.2839(6)	−0.2225(4)	0.2530(5)	0.0955
C(2)	0.1694(3)	0.1481(2)	0.1134(2)	0.0397
C(3)	0.1252(3)	0.1265(3)	0.0074(2)	0.0519
C(4)	0.2030(3)	0.0863(2)	0.3148(2)	0.0405
O(4)	0.2194(2)	0.0143(2)	0.4076(2)	0.0527
N(2)	0.2340(2)	0.2149(2)	0.2801(2)	0.0384
C(5)	0.2960(3)	0.2564(3)	0.3631(2)	0.0451
C(6)	0.2272(4)	0.3651(3)	0.4037(3)	0.0621
C(7)	0.2957(5)	0.4040(4)	0.4791(4)	0.0813
C(8)	0.4271(5)	0.3342(4)	0.5149(3)	0.0783
C(9)	0.4960(4)	0.2251(4)	0.4757(3)	0.0653
C(10)	0.4315(3)	0.1863(3)	0.3989(3)	0.0566
C(11)	0.2973(3)	0.3372(3)	−0.0355(3)	0.0601
O(11)	0.2985(3)	0.3799(3)	−0.1311(2)	0.0843
C(12)	0.4596(3)	0.1485(4)	0.1019(3)	0.0626
O(12)	0.5591(3)	0.0671(4)	0.0940(3)	0.0981
C(13)	0.3839(4)	0.4003(3)	0.1297(3)	0.0614
O(13)	0.4388(3)	0.4804(3)	0.1356(3)	0.0837
C(21)	−0.0794(3)	0.2818(3)	0.3429(3)	0.0513
O(21)	−0.1565(3)	0.2895(3)	0.4239(2)	0.0786
C(22)	−0.1100(3)	0.2919(3)	0.1353(3)	0.0532
O(22)	−0.2082(3)	0.2979(3)	0.0892(2)	0.0750
C(23)	0.0542(3)	0.4456(3)	0.1642(3)	0.0558
O(23)	0.0459(3)	0.5558(2)	0.1375(3)	0.0787

Crystal data and data collection parameters are listed in Table 4. Intensities of two standard reflections were monitored every hour, and showed no change during data collection. Corrections were made for Lorentz and polarization effects.

Computations were performed with the CRYSTALS [21] program adapted for a MicroVAX II. Atomic form factors for neutral Fe, C, N, O and H were taken from ref. 22; anomalous dispersion was taken into account for Fe. In both compounds Fe atom positions were determined by Harker vector analysis of three dimensional Patterson maps. All remaining non-hydrogen atoms were found by successive electron density map calculations. All non-hydrogen were refined anisotropically. For both compounds hydrogen atoms were located from difference electron density maps. Hydrogen atomic coordinates were refined together with a variable overall isotropic thermal parameter. Both structures were refined by least-squares with a four block approximation to the normal matrix.

The criterion for a satisfactory complete analysis was a shift to error ratio of a less than 0.3, and no significant features in the final difference maps. Main refinement features appear in Table 4; fractional atomic coordinates are given in Tables 5 and 6.

Supplementary material available. Tables of anisotropic temperature factors, important least-squares planes, hydrogen coordinates, distances and angles for CO ligands, and observed and calculated structure factors, are available from the authors.

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