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A rare example of three C–H activations of the methyl group: synthesis and crystal structure of $[Fe_3(CO)_9\{\mu_3\text{-}C{=}N(CH_3)_2\}(\mu_3\text{-}CC_2H_5)]$

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Abstract

A di-μ_3-carbyne cluster $[Fe_3(CO)_9\{\mu_3\text{-}C{=}N(CH_3)_2\}(\mu_3\text{-}CC_2H_5)]$ has been synthesized by reaction of $[Fe_2(CO)_9]$ with the alkynylethyl sulphide $C_2H_5SC{\equiv}CCH_3$ and trimethylamine oxide at 69°C. One of the μ_3-carbyne functions resulted from the rare activation of the three C–H bonds of a trimethylamine methyl group.

1. Introduction

Acetylenic compounds exhibit an interesting and versatile reactivity toward metal clusters. Many papers have been published concerning reactions of functionalized acetylenic ligands that have phosphorus or nitrogen attached to the triple bond [1–3]. The C–P bond of phosphinoalkynes is often cleaved [4] whereas the C–N bond of aminoalkynes rarely breaks. This difference in behaviour may be due to the overlap of the alkyne π orbital with the lone pair orbital of the heteroatom. This overlap is stronger in the case of nitrogen than in the case of phosphorus because the two atoms have different dimensions. The comparable sizes of phosphorus and sulphur suggest that similar rupture of the C–S bond should be possible in an alkyne with sulphur as heteroatom. Some work has been reported with symmetrical bisalkylthioacetylenes, and no C–S cleavage was observed [5].

2. Experimental details

2.1. Synthesis

The reaction of ethyl(prop-1-ynyl) sulphide with nonacarbonyldiiron using trimethylamine oxide as a decarbonylating agent was carried out under dry argon using standard Schlenk techniques. All solvents were freshly distilled over appropriate drying agents. The alkyne was prepared by a previously reported method [6]. A solution of $[Fe_2(CO)_9]$ (1.273 g, 3.5 mmol), $CH_3C{\equiv}CSC_2H_5$ (0.2 g, 2 mmol), and $(CH_3)_3NO$ (0.263 g, 3.5 mmol) in hexane (60 ml) was heated under reflux for 2.5 h. After the solvent was evaporated under vacuum, the residue was chromatographed on silica gel. Two compounds were found in the first chromatographed fraction; a clean separation was not possible. This fraction yielded two kinds of crystals. To identify them, their structures were determined by X-ray diffraction; they correspond to *syn* (20%) and *anti* (80%) isomers of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$ (total yield 10%). The ^1H NMR spectrum of the above fraction was recorded on a Bruker 250 MHz in C_6D_6 and is characteristic of a mixture of both isomers: *syn*: 0.9 (t); 1.98 (q); *anti*: 0.79 (t); 0.9 (t); 1.78 (q); 1.98 (q) ppm. Mass spectroscopy by chemical ionization gave a single peak at $M + 1 = 403$. IR (heptane): ν(CO) 1940 weak, 1990, 2000, 2040, 2080 cm^{-1}. The title compound was eluted with hexane in the second fraction and dark red single crystals were obtained with a 5% yield. Mass spectrometry gave a peak at $m/z = 517$ and a peak at 420 which suggested the presence of the $Fe_3(CO)_9$ group. The IR ν(CO) stretching region (1980, 1990, 2010, 2040 cm^{-1}, in heptane) gave evidence only for terminal CO groups. ^1H NMR spectrum in C_6D_6 (250 MHz, with one pulse every 10 s): 0.85 (t, 3H, CH_3–CH_2–); 1.95 (q, 2H, CH_3–CH_2–); 2.93 (s, 6H, $N(CH_3)_2$) ppm.

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TABLE 1. Crystallographic data collections and structure refinements

Formula	Title compound	$[Fe_2(CO)_6(\mu\text{-}SC_2H_5)]$	
		anti	*syn*
Crystal colour	Dark red	Orange	Orange
Mol. Weight (g)	517	402	402
Crystal size (mm^3)	0.34 × 0.2 × 0.06	0.2 × 0.1 × 0.3	0.4 × 0.3 × 0.2
ρ_{calc} ($g\ cm^{-3}$)	1.80	1.69	1.72
μ (Mo Kα) (cm^{-1})	23.02	21.03	21.399
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	8.155(1)	15.631(1)	8.231(5)
b (Å)	8.914(1)	11.685(2)	9.732(4)
c (Å)	13.711(1)	9.015(2)	10.721(3)
α (°)	96.123(9)		107.75(5)
β (°)	94.13(1)	106.05(1)	93.58(4)
γ (°)	104.96(1)		105.66(1)
V (Å^3)	952	1582	784
$F(000)$	504	808	404
Z	2	4	2
Diffractometer	Enraf-Nonius CAD4	Philips PW1100	Philips PW1100
Radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
Scan type	θ–2θ	θ–2θ	θ–2θ
Scan range (°)	0.8 + 0.34 tg θ	1.2 + 0.345 tg θ	1 + 0.345 tg θ
2θ range (°)	2–42	4–50	4–50
Reflections measured	hkl, $\bar{h}\bar{k}l$	hkl, $\bar{h}kl$	hkl, $\bar{h}\bar{k}l$
No. of reflections collected	4423	3150	2862
No. of independent reflections merged	4166	2780	2680
No. of reflections kept for refinement	2798 ($I > 3\sigma(I)$)	1596 ($I > 3\sigma(I)$)	1470 ($I > 3\sigma(I)$)
Computing programs	SHELXS and CRYSTALS [a]		
Diffusion factors	b	b	b
Minimized function	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
Weighting scheme	$w = 1$	$w = 1$	$w = 1$
Secondary extinction parameter	29×10^{-6}		
Absorption corrections	DIFABS [c]	DIFABS [c]	DIFABS [c]
Average shift/e.s.d. (last cycle)	0.09	0.13	0.06
$N_{ref.}/N_{var.par.}$	9.71	7.5	6.9
Max. height in final difference Fourier synthesis (e Å^{-3})	0.4	0.5	0.5
R	0.0275	0.052	0.0385
R_w	0.0288	0.0578	0.041

[a] J. R. Carruthers and D. J. Watkin, *Crystals and Advanced Crystallographic Computer Program*, University of Oxford, 1986. [b] *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, Vol. IV. [c] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, (1983) 3156.

2.2. X-Ray structure determinations

Crystallographic data collection and refinement conditions for the three compounds are given in Table 1. Structures were solved using direct methods (SHELXS [7]) and CRYSTALS programs [8]. The refinement was carried out including anisotropic temperature factors for all atoms but hydrogen. Hydrogen atoms were found on the Fourier difference map and included as fixed contributions in refinement, with an overall variable isotropic thermal parameter. Tables 2–7 give atomic parameters, selected interatomic distances, and bond angles for the three compounds. Supplementary material provides atomic and thermal parameters for all atoms, structure factors and all bond distances and angles and is available from the authors.

3. Results and discussion

The asymmetric unit of the title compound is a trigonal bipyramid with three iron atoms in the basal plane (Fig. 1). Each iron is bound to three carbonyl ligands. Apical positions are occupied by two triply bridging ligands. One is μ_3-CC_2H_5 (C1–C2 in Fig. 1) and the other is μ_3-$C{=}N(CH_3)_2$ (C4–N1 in Fig. 1). Although no labelling study was carried out to support a mechanism, it is assumed that $CH_3C{\equiv}CSC_2H_5$ is

TABLE 2. Fractional coordinates for the *anti* form of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)]$

Atom	*x*	*y*	*z*
Fe(1)	0.2821(1)	0.2876(1)	0.1287(2)
Fe(2)	0.22904(9)	0.1730(1)	−0.1168(2)
S(1)	0.3007(2)	0.0974(2)	0.1126(3)
S(2)	0.1382(2)	0.2343(2)	0.0234(3)
C(1)	0.4162(7)	0.052(1)	0.131(1)
C(2)	0.4630(9)	0.037(1)	0.301(1)
C(3)	0.1007(9)	0.119(1)	0.130(2)
C(4)	0.075(2)	0.167(2)	0.266(3)
C(11)	0.2484(8)	0.429(1)	0.059(1)
C(12)	0.3950(8)	0.320(1)	0.134(1)
C(13)	0.2899(8)	0.304(1)	0.333(1)
C(21)	0.3261(8)	0.169(1)	−0.184(1)
C(22)	0.1727(7)	0.049(1)	−0.217(1)
C(23)	0.1790(8)	0.281(1)	−0.256(1)
O(11)	0.2275(6)	0.5182(7)	0.009(1)
O(12)	0.4660(6)	0.3396(9)	0.135(1)
O(13)	0.2985(8)	0.3135(9)	0.459(1)
O(21)	0.3899(6)	0.1688(8)	−0.222(1)
O(22)	0.1359(6)	−0.0289(8)	−0.280(1)
O(23)	0.1475(6)	0.3499(8)	−0.342(1)

TABLE 4. Fractional coordinates for the *syn* form of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$

Atom	*x*	*y*	*z*
Fe(1)	0.1132(1)	0.7193(1)	0.7936(1)
Fe(2)	0.4014(1)	0.7837(1)	0.7195(1)
S(1)	0.3657(2)	0.7982(2)	0.9308(2)
S(2)	0.2505(2)	0.9509(2)	0.7840(2)
C(1)	0.411(1)	0.650(1)	0.9845(9)
C(2)	0.313(2)	0.630(1)	1.096(1)
C(3)	0.157(1)	0.997(1)	0.649(1)
C(4)	0.286(2)	1.121(1)	0.620(1)
C(11)	0.084(1)	0.525(1)	0.7718(8)
C(12)	−0.022(1)	0.763(1)	0.917(1)
C(13)	−0.035(1)	0.6707(9)	0.6494(9)
C(21)	0.455(1)	0.610(1)	0.6846(8)
C(22)	0.615(1)	0.911(1)	0.7434(8)
C(23)	0.332(1)	0.7453(9)	0.5486(8)
O(11)	0.0688(8)	0.4006(7)	0.7577(7)
O(12)	−0.111(1)	0.7839(9)	0.9926(9)
O(13)	−0.1313(9)	0.6398(8)	0.5551(7)
O(21)	0.4890(9)	0.5011(7)	0.6605(7)
O(22)	0.7515(8)	0.9859(8)	0.7556(8)
O(23)	0.2868(8)	0.7205(8)	0.4386(6)

cleaved to yield $CH_3C{\equiv}C$ and SC_2H_5 fragments. The $CH_3C{\equiv}C$ acetylide would be transformed into a C_2H_5C fragment by asymmetric hydrogenation of the triple bond, the two hydrogen atoms coming from one methyl group of trimethylamine; the third hydrogen of this methyl group would serve to give C_2H_5SH with the SC_2H_5 fragment.

$$3[Fe_2(CO)_9]+2(CH_3)_3NO+2CH_3C{\equiv}CSC_2H_5$$
$$\downarrow$$
$$2[Fe_3(CO)_9\{C{=}N(CH_3)_2\}(CC_2H_5)]+2CO_2+2C_2H_5SH+7CO$$

This proposal is supported by the following facts:

(i) A two C–H activation was described by Rosenberg *et al.* [9] who reported the reaction of tertiary amines with $[Ru_3(CO)_{12}]$ promoted by $[Fe_2(CO)_4(PPh_3)_2(\mu\text{-}SC_2H_5)_2]$; the tertiary amine was transformed into a $\mu_3\text{-}\eta_2\text{-}CH_3C{=}NC_2H_5$ ligand and a hydride bridge Ru–H–Ru was formed.

(ii) A three-C–H activation of a methyl group has been observed previously by Choo Ying and Deeming [10]. They prepared $[HOs_3\{\mu_2\text{-}C{=}N(CH_3)_2\}(CO)_{10}]$ by reaction of $[Os_3(CO)_{12}]$ with $N(CH_3)_3$ at 150°C in nonane for 7 h, or at 170°C under vacuum for 2 h. Elimination of one molecule of gaseous hydrogen and transfer of one hydrogen atom to osmium led to the bridging $\mu_2\text{-}C{=}N(CH_3)_2$ group.

(iii) Kölle has recently observed the activation of the three C–H bonds of a methanolate bound to ruthenium which was transformed into a carbonyl [11].

(iv) It is known [12] that the reaction of C_2H_5SH with $[Fe_2(CO)_9]$ leads to $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$. The formation of C_2H_5SH in our reaction is likely because both *syn* and *anti* isomers of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$ have been synthesized and identified by X-ray diffraction (Fig. 2). The structure of the *anti* isomer was described previously [13] with $R = 11.6\%$ but our structure is more accurate. The *syn* isomer was identified by

TABLE 3. Selected interatomic distances (Å) and bond angles (°) for the *anti* form of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$

Fe(1)–Fe(2)	2.523(2)	Fe(1)–S(1)	2.251(3)
Fe(1)–S(2)	2.273(3)	Fe(2)–S(1)	2.243(3)
Fe(2)–S(2)	2.263(3)		
S(1)–Fe(1)–Fe(2)	55.70(8)	S(2)–Fe(1)–Fe(2)	56.01(8)
S(2)–Fe(1)–S(1)	80.4(1)	S(1)–Fe(2)–Fe(1)	56.01(8)
S(2)–Fe(2)–Fe(1)	56.39(8)	S(2)–Fe(2)–S(1)	80.8(1)
Fe(2)–S(1)–Fe(1)	68.30(9)	C(1)–S(1)–Fe(1)	114.8(4)
C(1)–S(1)–Fe(2)	115.0(4)	Fe(2)–S(2)–Fe(1)	114.8(4)
C(3)–S(2)–Fe(1)	113.8(5)	C(3)–S(2)–Fe(2)	113.6(5)

TABLE 5. Selected interatomic distances (Å) and bond angles (°) for the *syn* form of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$

Fe(1)–Fe(2)	2.527(1)	Fe(1)–S(1)	2.267(2)
Fe(1)–S(2)	2.269(2)	Fe(2)–S(1)	2.269(2)
Fe(2)–S(2)	2.277(2)		
S(1)–Fe(1)–Fe(2)	56.19(6)	S(2)–Fe(1)–Fe(2)	56.37(6)
S(2)–Fe(1)–S(1)	74.76(8)	S(1)–Fe(2)–Fe(1)	56.09(6)
S(2)–Fe(2)–Fe(1)	56.06(6)	S(2)–Fe(2)–S(1)	74.56(8)
Fe(2)–S(1)–Fe(1)	67.72(7)	C(1)–S(1)–Fe(1)	113.5(3)
C(1)–S(1)–Fe(2)	115.7(3)	Fe(2)–S(2)–Fe(1)	67.57(6)
C(3)–S(2)–Fe(1)	114.6(3)	C(3)–S(2)–Fe(2)	114.6(3)

TABLE 6. Fractional coordinates for $[Fe_3(CO)_9\{\mu_3\text{-}C{=}N(CH_3)_2\}(\mu_3\text{-}CC_2H_5)]$

Atom	x	y	z
Fe(1)	0.19069(6)	0.39013(6)	0.80487(4)
Fe(2)	0.45335(6)	0.29598(6)	0.75859(4)
Fe(3)	0.16866(7)	0.18960(6)	0.65892(4)
C(1)	0.3246(4)	0.4138(4)	0.6952(2)
C(2)	0.3731(6)	0.5426(5)	0.6316(3)
C(3)	0.5069(8)	0.6849(6)	0.6810(4)
C(4)	0.2205(4)	0.1712(4)	0.7933(2)
C(5)	0.0932(9)	−0.1000(6)	0.8159(4)
C(6)	0.2466(7)	0.0869(6)	0.9557(3)
N(1)	0.1820(4)	0.0595(3)	0.8513(2)
C(11)	0.3079(5)	0.5599(5)	0.8864(3)
C(12)	0.0508(5)	0.4810(4)	0.7434(3)
C(13)	0.0435(5)	0.3218(5)	0.8939(3)
C(21)	0.6086(5)	0.4479(5)	0.8359(3)
C(22)	0.5703(5)	0.2994(5)	0.6536(3)
C(23)	0.5287(5)	0.1418(5)	0.8095(3)
C(31)	0.2366(6)	0.0252(5)	0.6099(3)
C(32)	−0.0542(5)	0.1033(5)	0.6615(3)
C(33)	0.1393(6)	0.2542(5)	0.5406(3)
O(11)	0.3793(4)	0.6702(4)	0.9375(3)
O(12)	−0.0370(4)	0.5393(4)	0.7029(3)
O(13)	−0.0514(4)	0.2813(4)	0.9484(3)
O(21)	0.7092(4)	0.5460(4)	0.8833(3)
O(22)	0.6378(4)	0.3032(4)	0.5841(2)
O(23)	0.5762(4)	0.0453(4)	0.8391(3)
O(31)	0.2807(5)	−0.0810(5)	0.5809(3)
O(32)	−0.1947(4)	0.0476(4)	0.6653(3)
O(33)	0.1173(6)	0.2899(5)	0.4651(3)

TABLE 7. Selected interatomic distances (Å) and bond angles (°) for $[Fe_3(CO)_9\{\mu_3\text{-}C{=}N(CH_3)_2\}(\mu_3\text{-}CC_2H_5)]$

Fe(1)–Fe(2)	2.5896(7)	Fe(1)–Fe(3)	2.5003(7)
Fe(2)–Fe(3)	2.5073(7)	Fe(1)–C(1)	1.920(3)
Fe(1)–C(4)	2.019(3)	Fe(2)–C(1)	1.896(4)
Fe(2)–C(4)	2.055(3)	Fe(3)–C(1)	2.060(3)
Fe(3)–C(4)	1.895(3)	C(4)–N(1)	1.329(4)
Fe(3)–Fe(1)–Fe(2)	58.99(2)	Fe(3)–Fe(2)–Fe(1)	58.73(2)
Fe(2)–Fe(3)–Fe(1)	62.28(2)	C(1)–Fe(1)–Fe(2)	46.9(1)
C(1)–Fe(1)–Fe(3)	53.6(1)	C(4)–Fe(1)–Fe(2)	51.1(1)
C(4)–Fe(1)–Fe(3)	48.1(1)	C(4)–Fe(1)–C(1)	84.7(1)
C(1)–Fe(2)–Fe(1)	47.7(1)	C(1)–Fe(2)–Fe(3)	53.6(1)
C(4)–Fe(2)–Fe(1)	49.9(1)	C(4)–Fe(2)–Fe(3)	47.83(9)
C(4)–Fe(2)–C(1)	84.3(1)	C(1)–Fe(3)–Fe(1)	48.6(1)
C(1)–Fe(3)–Fe(2)	47.8(1)	C(4)–Fe(3)–Fe(1)	52.5(1)
C(4)–Fe(3)–Fe(2)	53.5(1)	C(4)–Fe(3)–C(1)	84.2(1)
Fe(3)–C(1)–Fe(1)	77.8(1)	Fe(3)–C(1)–Fe(2)	78.6(1)
Fe(3)–C(1)–Fe(2)	78.6(1)	C(2)–C(1)–Fe(1)	132.6(3)
C(2)–C(1)–Fe(2)	132.2(3)	C(2)–C(1)–Fe(3)	129.6(3)
C(3)–C(2)–C(1)	114.3(4)	Fe(2)–C(4)–Fe(1)	78.9(1)
Fe(3)–C(4)–Fe(1)	79.3(1)	Fe(3)–C(4)–Fe(2)	78.7(1)
N(1)–C(4)–Fe(1)	131.5(3)	N(1)–C(4)–Fe(2)	130.4(3)
N(1)–C(4)–Fe(3)	136.2(3)	C(5)–N(1)–C(4)	123.7(4)
C(6)–N(1)–C(4)	121.6(3)	C(6)–N(1)–C(5)	114.3(4)

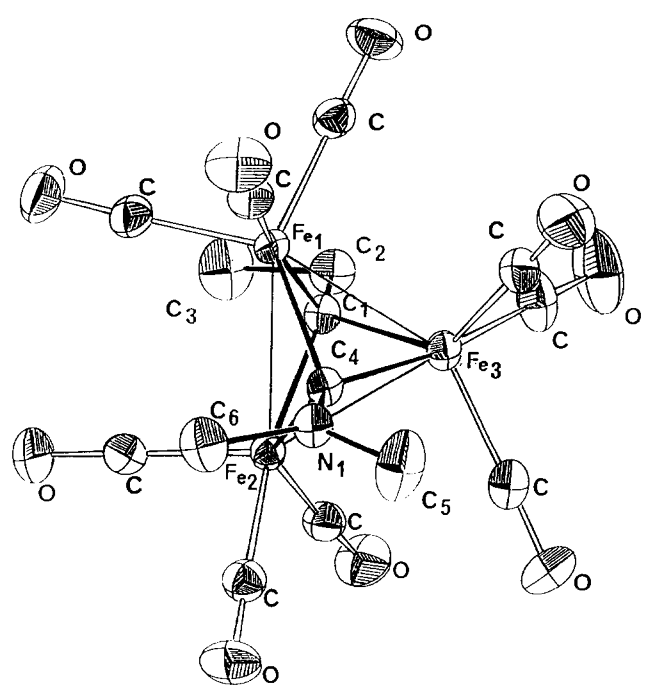


Fig. 1. ORTEP drawing of $[Fe_3(CO)_9\{\mu_3\text{-}C{=}N(CH_3)_2\}(\mu_3\text{-}CC_2H_5)]$ with 50% probability ellipsoids.

Dabard *et al.* [14] by its ^1H NMR spectrum in $CDCl_3$ solution of a *syn–anti* mixture, but no single crystal was obtained.

The title compound is the second example of a structure showing a μ_3-C=NR$_2$ triply bonded group which has been fully characterized by X-ray analysis. The first example was obtained from an ynamine by a completely different reaction which did not involve the activation of C–H bonds [15]. Indeed, an unusual cleavage of a C≡C triple bond at room temperature appears to be involved

$$\tfrac{3}{2}[Fe_2(CO)_9] + CH_3C{\equiv}CN(C_2H_5)_2 \longrightarrow [Fe_3(CO)_9\{C{=}N(C_2H_5)_2\}(CCH_3)] + \tfrac{9}{2}CO$$

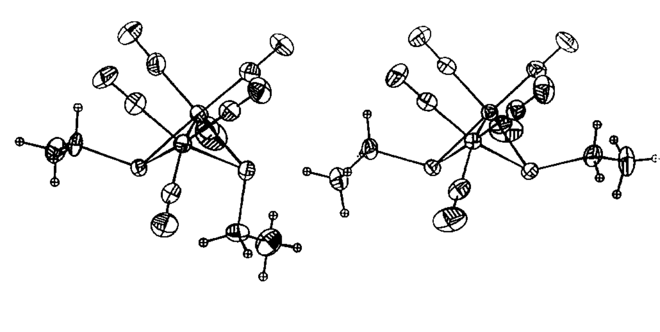
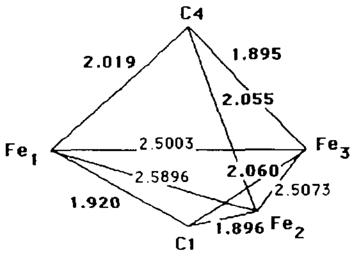
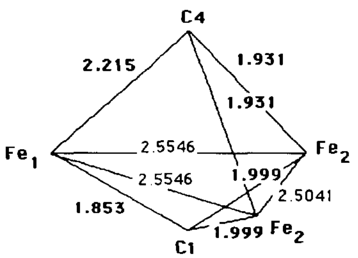


Fig. 2. ORTEP drawing of *syn* and *anti* forms of $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2]$ with 30% probability ellipsoids.



compound 1



compound 2

Fig. 3. Comparison of the trinuclear complexes. Compound **1**, $=N(CH_3)_2$ on C4, $-C_2H_5$ on C1; compound **2**, $-N(C_2H_5)_2$ on C4, $-CH_3$ on C1.

A similar fragment, μ_3-C=NR_2, was observed from the reaction of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with $[C_5H_5M(CO)_2]$ (M = Co and M = Rh) in refluxing trimethylhexane and refluxing octane, respectively [16], leading to $[(C_5H_5)_3M_3\{\mu_3\text{-}C{=}N(C_2H_5)_2\}]$, the structure of which was inferred from an NMR study. The cleavage of the C≡C triple bond has not yet been observed in reactions of $CH_3SC{\equiv}CSCH_3$ [5] with iron carbonyls.

Figure 3 shows both bipyramidal structures (title compound and compound **2** of ref. 15). In each compound, a slight dissymmetry exists between the three metal–metal bonds and the bridging metal–carbon bonds. In the title compound, there are two shorter and one longer Fe–Fe distances. Among the three Fe–C4 bonds, two are longer and one is shorter. The Fe–C1 shows the opposite behaviour and there are two shorter and one longer Fe–C1 bonds (Fig. 3). The situation in compound **2** is the converse. For example, there are two longer and one shorter Fe–Fe bonds (Fig. 3), and so on.

Our experimental conditions are mild compared to those used by Deeming. In the case of the title compound, we suggest that the C–H activation is very likely assisted by the two ligand fragments, $CH_3C{\equiv}C$ and SC_2H_5, which are both hydrogen acceptors and which have both accepted hydrogen.

References

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