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1,3-Dipolar cycloaddition to a Fe–N=C fragment

XII †. Reactivity of Fe(2,6-xylyl-isocyanide)$_3$(^{i}Pr-α-diimine) towards heteroallenic C=S bonds

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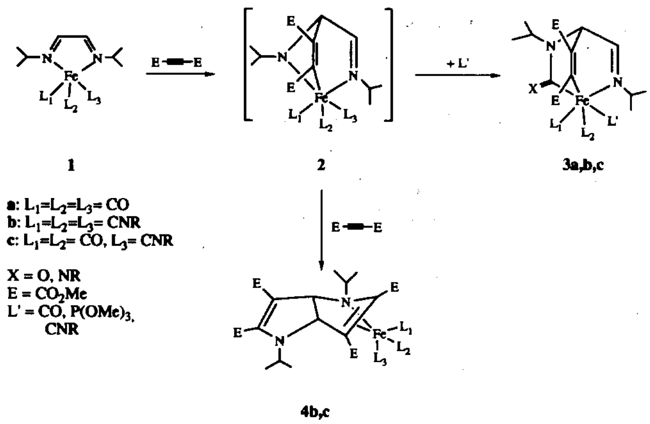
Abstract

The reaction of Fe(2,6-xylylNC)$_3$(^{i}Pr-DAB) (**5**) with carbon disulfide and carbonyl sulfide yields bicyclic structures. The reaction with carbon disulfide proceeds via a 1,3-dipolar cycloaddition of the C=S bond across the Fe–N=C unit, followed by an isocyanide insertion to form the ferra[2.2.2]bicyclic complex (**8**). A single crystal X-ray structure determination on (**8**) showed it to contain three six-membered rings; the carbon disulfide is attached to the central metal atom through a sulphur atom and to the former imine carbon atom through its central carbon atom. In the 1,3-dipolar cycloaddition of carbonyl sulfide the presence of moisture resulted in a protonation of the amido function. This inhibits the isocyanide insertion and stabilizes the initially formed ferra[2.2.1]-bicyclic compound.

Key words: Iron; Isocyanide; Diimine; Heteroallenes; Cycloaddition

1. Introduction

The reactions of unsaturated substrates towards Fe(CO)$_{3-n}$(CNR)$_n$(DAB) [2*] (M = Fe, Ru; n = 0, 1 and 3) complexes (**1**) [3] have been studied intensively in our laboratories. The reactions (see Scheme 1) involve a 1,3-dipolar cycloaddition of the dipolarophile (an electron deficient alkyne) across the Fe–N=C fragment, leading finally to a [2.2.2] bicyclic complex (**3**). Substitution of CO for the better σ-donating/poorer



Scheme 1. Cycloaddition of Fe(CO)$_{3-n}$(CNR)$_n$(DAB) (n = 0, 1, 3) (**1**) to DMADC.

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† For Part 11, see ref. 1.

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

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π-accepting isocyanide ligands [4], resulting in an enhanced electron density on the complex, was found to lead to a greater 1,3-dipolar activity. This was reflected in the formation of pyrrolo[3,2-*b*]pyrrole complexes (**4**) *via* a second cycloaddition of an alkyne across the Fe^{II}–N=C unit in the initially formed ferra[2.2.1]bicyclic intermediate **2** [3a,b]. Cycloaddition reactions also took place with less activated dipolarophiles such as alkenes [1], resulting in the formation of analogous [2.2.2]bicyclic structures (**3**).

In view of the high 1,3-dipolar reactivity of the $Fe(CNR)_3(DAB)$ (**1**) complexes we were prompted to search for other possible dipolarophiles, a great variety of which is known from classical organic chemistry. Dipolarophiles containing heteroatoms were considered to hold particular potential for use in the synthesis of organic heterocycles. Following the observation that C–N multiple bonds in imines and isocyanides are unreactive towards $Fe(CNR)_3(DAB)$ (**1**) [5*], we decided to investigate cycloaddition reactions with C=S bonds.

We describe below the results of a study of the cycloaddition reaction of carbon disulfide, carbonyl sulfide and carbon dioxide across the Fe–N=C unit of $Fe(2,6\text{-xylylNC})_3(^iPr\text{-DAB})$ (**5**). The single crystal X-ray structure of the $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ [2*] (**8**) resulting from CS_2 cycloaddition and subsequent isocyanide insertion is described.

2. Experimental details

2.1. Material and apparatus

^1H- and ^{13}C-NMR spectra were obtained on Bruker AC 100 and AMX 300 spectrometers. IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer. All solvents were dried and distilled under nitrogen prior to use. The experiments were performed under N_2 by use of standard Schlenk techniques. Column chromatography was carried out on silanized silica gel 60 (Merck, 70–230 mesh) dried and activated before use, [6*]. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. $Fe(2,6\text{-xylylNC})_3(^iPr\text{-DAB})$ (**5**) was prepared by known procedures [3b,7]. The 2,6-xylyl isocyanide (Fluka), CS_2 (Merck), COS (Union Carbide) and CO_2 (Hoekloos, The Netherlands) were obtained commercially and used without purification.

2.2. Synthesis of $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (8)

To a freshly-prepared solution of $Fe(2,6\text{-xylylNC})_3(^iPr\text{-DAB})$ (**5**) (1173 mg, 2 mmol) in 20 ml pentane at −20°C a solution of CS_2 (227 mg, 3 mmol) in 10 ml pentane was added during 45 min. The resulting yellow precipitate was washed three times with 20 ml cold pentane and dried *in vacuo*, to give the $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**) in 80% yield. The product was purified by column chromatography; it was dissolved in Et_2O/CH_2Cl_2 (5/2) and the solution transferred to the column. Initial elution with neat Et_2O afforded a small quantity of an unidentified compound. Further elution with Et_2O/THF (1/1) yielded a brown/yellow fraction, containing the $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**). Concentration of the last fraction followed by cooling to −20°C gave crystals suitable for single crystal X-ray structure determination.

Elemental analysis [8]: $FeC_{45}H_{52}N_6S_2$, Observed: C, 68.66; H, 6.95; N, 10.58. Calculated: C, 67.82; H, 6.58; N, 10.54.

2.3. Synthesis of $Fe(2,6\text{-xylylNC})_3([2.2.1]bic)$ (9)

A stream of the COS gas was led through a freshly-prepared solution of $Fe(2,6\text{-xylylNC})_3(^iPr\text{-DAB})$ (**5**) (937 mg, 1.6 mmol) in 20 ml pentane at −20°C until nearly all of the red starting complex Fe(2,6-

TABLE 1. Crystal data and details of the structure determination of $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**)

Crystal data	
Formula	$FeC_{45}H_{52}N_6S_2$
Mol. wt.	796.91
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a, b, c, (Å)	11.162(5), 17.911(6), 21.499(7)
β(°)	94.31(3)
V (Å^3)	4286(3)
Z	4
D_{calc} (g cm^{-3})	1.235
F(000)	1688
μ(cm^{-1})	4.8
Crystal size (mm)	$0.2 \times 0.2 \times 0.7$
Data collection	
Temperature (K)	295
$\theta_{min}, \theta_{max}$	1.0, 26.5
Radiation	Mo Kα(Zr filter) 0.71073 Å
$\Delta\omega$(°)	$1.25 + 0.35 \tan\theta$
Hor. and vert. aperture (mm)	4.56, 5.00
Reference reflections	−235; 223; −312
Data set	−13: 13; −22: 0; −26: 26
Total data	10663
Total unique data, R_{int}	8822, 0.047
Observed data	2956 [$I > 2.5\sigma(I)$]
DIFABS correction range	0.63, 1.34
Refinement	
No. of refined parameters	489
Weighting scheme	$1/[\sigma^2(F) + 0.0013F^2]$
Final R, R_w, S	0.076, 0.086, 3.28
U overall isotr. H atoms	0.097(9), 0.164(15)
$(\Delta/\sigma)_{av}$ in final cycle	0.027
Min. and max. resd. dens. e|Å^3	−0.43, 0.75

xylylNC)$_3$(^{i}Pr-DAB) (**5**) had disappeared. Work-up of the yellow precipitate was as described for **8**. The yield of Fe(2,6-xylylNC)$_3$([2.2.1]bic) (**9**) was 80%.

Elemental analysis [8]: $FeC_{36}H_{45}N_5O_2S$, Observed: C, 66.86; H, 6.67; N, 9.08. Calculated: C, 64.76; H, 6.80; N, 10.49.

TABLE 2. Fractional coordinates of the non hydrogen atoms of Fe(2,6-xylylNC)$_3$([2.2.2]bic) (**8**) (e.s.d. values in parentheses)

Atom	x	y	z	U_{eq} (Å^2) [a]
Fe	0.078077(13)	0.20563(9)	0.13035(6)	0.0359(5)
S_1	0.5733(3)	0.3386(2)	0.28277(14)	0.0679(15)
S_2	0.7655(3)	0.30135(18)	0.20139(12)	0.0505(10)
N_1	0.6710(9)	0.1426(5)	0.1760(3)	0.042(3)
N_2	0.5380(8)	0.2638(5)	0.1118(3)	0.043(3)
N_3	0.6382(7)	0.2466(5)	0.0196(3)	0.040(5)
N_4	0.9282(9)	0.3089(5)	0.0584(4)	0.048(4)
N_5	0.8069(7)	0.0889(5)	0.0328(4)	0.042(3)
N_6	1.0043(8)	0.1619(5)	0.2107(4)	0.044(3)
C_1	0.7149(13)	0.0536(8)	0.2648(5)	0.085(6)
C_2	0.6055(14)	0.0110(7)	0.1628(7)	0.101(7)
C_3	0.7000(10)	0.0634(6)	0.1943(5)	0.051(4)
C_4	0.5739(11)	0.1693(7)	0.1941(5)	0.046(4)
C_5	0.5368(10)	0.2477(6)	0.1796(4)	0.043(4)
C_6	0.6251(10)	0.2969(7)	0.2219(5)	0.054(4)
C_7	0.4439(10)	0.3169(6)	0.0878(5)	0.055(4)
C_8	0.3191(12)	0.2847(11)	0.0900(7)	0.124(8)
C_9	0.4568(17)	0.3904(8)	0.1189(7)	0.125(8)
C_{10}	0.6345(10)	0.2426(6)	0.0793(5)	0.040(4)
C_{11}	0.5418(10)	0.2540(7)	−0.0265(4)	0.045(4)
C_{12}	0.4604(10)	0.1962(7)	−0.0386(5)	0.055(4)
C_{13}	0.4657(11)	0.1284(7)	0.0000(6)	0.072(5)
C_{14}	0.3790(11)	0.2023(9)	−0.0918(6)	0.074(5)
C_{15}	0.3760(12)	0.2648(10)	−0.1280(6)	0.080(6)
C_{16}	0.4581(12)	0.3212(8)	−0.1164(5)	0.012(9)
C_{17}	0.5437(11)	0.3170(7)	−0.0656(5)	0.011(7)
C_{18}	0.6317(12)	0.3786(7)	−0.0525(6)	0.078(6)
C_{19}	0.8689(10)	0.2691(6)	0.0871(4)	0.043(4)
C_{20}	1.0064(11)	0.3534(7)	0.0296(6)	0.057(5)
C_{21}	1.0477(12)	0.4195(8)	0.0638(7)	0.071(6)
C_{22}	0.9955(16)	0.4413(8)	0.1224(7)	0.111(8)
C_{23}	1.1280(16)	0.4628(11)	0.0364(11)	0.122(9)
C_{24}	1.1717(19)	0.4387(18)	−0.0165(12)	0.141(16)
C_{25}	1.137(2)	0.3805(13)	−0.0519(10)	0.110(10)
C_{26}	1.0484(14)	0.3337(10)	−0.0243(7)	0.082(7)
C_{27}	1.001(2)	0.2664(10)	−0.0563(7)	0.151(12)
C_{28}	0.7963(8)	0.1332(5)	0.0715(4)	0.032(3)
C_{29}	0.8066(9)	0.0315(6)	−0.0112(4)	0.038(4)
C_{30}	0.7621(10)	0.0462(7)	−0.0730(5)	0.057(5)
C_{31}	0.7247(12)	0.1218(8)	−0.0943(5)	0.085(6)
C_{32}	0.7593(11)	−0.0140(8)	−0.1150(5)	0.063(5)
C_{33}	0.8049(12)	−0.0826(8)	−0.0958(6)	0.072(6)
C_{34}	0.8487(13)	−0.0946(7)	−0.0367(6)	0.070(6)
C_{35}	0.8511(10)	−0.0382(6)	0.0079(5)	0.046(4)
C_{36}	0.9011(11)	−0.0504(7)	0.0748(5)	0.068(5)
C_{37}	0.9162(10)	0.1755(6)	0.1796(5)	0.043(4)
C_{38}	1.1163(9)	0.1513(7)	0.2438(4)	0.041(4)
C_{39}	1.1851(10)	0.2133(7)	0.2597(4)	0.049(4)
C_{40}	1.1409(12)	0.2895(8)	0.2428(6)	0.080(6)
C_{41}	1.2967(10)	0.2021(9)	0.2914(5)	0.064(5)
C_{42}	1.3317(12)	0.1295(9)	0.3061(6)	0.077(6)
C_{43}	1.2618(11)	0.0684(8)	0.2910(5)	0.062(5)
C_{44}	1.1490(10)	0.0786(7)	0.2607(4)	0.050(4)
C_{45}	1.0677(12)	0.0144(7)	0.2438(6)	0.074(6)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

2.4. *Crystal structure determination of Fe(2,6-xylylNC)$_3$([2.2.2]bic) (8)*

Crystal data and numerical details of the structure determination are given in Table 1. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

A red, rod shaped crystal was mounted in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Lattice parameters were determined by least-squares fitting of the SET4 setting angles of 25 reflections with $7.4° < \theta < 15.9°$. The unit-cell parameters were checked for the presence of higher lattice symmetry [9]. All data were collected with $\omega/2\theta$ scan mode. Data were corrected for L_p and for the observed linear decay (< 4%) of the reference reflections during 151 h of X-ray exposure time. Absorption correction was applied using the DIFABS procedure [10]. Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.056I)^2$ [11]. The structure was solved by automated direct methods [12]. Refinement on F was carried out by full-matrix least-squares techniques [13]. The hydrogen atoms were included in the refinement on calculated positions (C–H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with two common isotropic thermal parameters, one for the methyl group of ^{i}Pr fragments and the hydrogens of the 2,6-xylylNC group containing N4 and one for the other hydrogen atoms. Weights were introduced in the final refinement cycles. Atomic scattering factors were taken from Cromer and Mann [14]; anomalous-dispersion corrections from Cromer and Liberman [15]. Geometric calculations and illustrations were performed with PLATON [16]. Calculations were carried out on a DEC station 5000. Supplementary data have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

The ligands and complexes employed in this article are shown in Scheme 2. Both carbon disulfide and

TABLE 3. Bond lengths (Å) of the non hydrogen atoms of $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**). e.s.d. values in parentheses)

$Fe-S_2$	2.311(3)	$Fe-N_1$	1.980(9)	$Fe-C_{10}$	2.010(11)
$Fe-C_{19}$	1.806(11)	$Fe-C_{28}$	1.829(9)	$Fe-C_{37}$	1.859(11)
S_1-C_6	1.649(12)	S_2-C_6	1.662(12)	N_1-C_3	1.501(14)
N_1-C_4	1.272(16)	N_2-C_5	1.487(11)	N_2-C_7	1.481(14)
N_2-C_{10}	1.380(14)	N_3-C_{10}	1.289(13)	N_3-C_{11}	1.413(12)
N_4-C_{19}	1.178(14)	N_4-C_{20}	1.364(16)	N_5-C_{28}	1.162(12)
N_5-C_{29}	1.397(13)	N_6-C_{37}	1.172(14)	N_6-C_{38}	1.404(13)
C_1-C_3	1.522(15)	C_2-C_3	1.531(18)	C_4-C_5	1.490(16)
C_5-C_6	1.562(15)	C_7-C_8	1.512(18)	C_7-C_9	1.479(18)
$C_{11}-C_{12}$	1.389(17)	$C_{11}-C_{17}$	1.408(16)	$C_{12}-C_{13}$	1.470(17)
$C_{12}-C_{14}$	1.410(17)	$C_{14}-C_{15}$	1.36(2)	$C_{15}-C_{16}$	1.37(2)
$C_{16}-C_{17}$	1.398(16)	$C_{17}-C_{18}$	1.490(18)	$C_{20}-C_{21}$	1.450(19)
$C_{20}-C_{26}$	1.33(2)	$C_{21}-C_{22}$	1.48(2)	$C_{21}-C_{23}$	1.35(2)
$C_{23}-C_{24}$	1.34(3)	$C_{24}-C_{25}$	1.33(4)	$C_{25}-C_{26}$	1.46(3)
$C_{26}-C_{27}$	1.47(2)	$C_{29}-C_{30}$	1.408(14)	$C_{29}-C_{35}$	1.394(15)
$C_{30}-C_{31}$	1.479(19)	$C_{30}-C_{32}$	1.405(18)	$C_{32}-C_{33}$	1.38(2)
$C_{33}-C_{34}$	1.344(18)	$C_{34}-C_{35}$	1.392(17)	$C_{35}-C_{36}$	1.519(15)
$C_{38}-C_{39}$	1.379(17)	$C_{38}-C_{44}$	1.393(17)	$C_{39}-C_{40}$	1.487(19)
$C_{39}-C_{41}$	1.389(15)	$C_{41}-C_{42}$	1.39(2)	$C_{42}-C_{43}$	1.37(2)
$C_{43}-C_{44}$	1.386(16)	$C_{44}-C_{45}$	1.493(18)		

carbonyl sulfide react with $Fe(2,6\text{-xylylNC})_3(^iPr\text{-DAB})$ (**5**) to give bicyclic species, whereas carbon dioxide does not react. Addition of CS_2 across the Fe–N=C unit of **5**, followed by an isocyanide insertion gives the [2.2.2]bicyclic complex (**8**). The structure of **8** revealed by an X-ray study is discussed below. In the reaction

TABLE 4. Bond angles (°) of the non hydrogen atoms of $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**) (e.s.d. values in parentheses)

S_2-Fe-N_1	90.9(3)	S_2-Fe-C_{10}	91.1(3)	S_2-Fe-C_{19}	86.8(3)
S_2-Fe-C_{28}	177.1(3)	S_2-Fe-C_{37}	86.3(3)	N_1-Fe-C_{10}	87.2(4)
N_1-Fe-C_{19}	174.5(5)	N_1-Fe-C_{28}	91.9(4)	N_1-Fe-C_{37}	93.4(4)
$C_{10}-Fe-C_{19}$	87.9(5)	$C_{10}-Fe-C_{28}$	88.4(4)	$C_{10}-Fe-C_{37}$	177.4(5)
$C_{19}-Fe-C_{28}$	90.4(4)	$C_{19}-Fe-C_{37}$	91.4(5)	$C_{28}-Fe-C_{37}$	94.2(4)
$Fe-S_2-C_6$	104.9(4)	$Fe-N_1-C_3$	122.7(7)	$Fe-N_1-C_4$	120.7(8)
$C_3-N_1-C_4$	116.6(9)	$C_5-N_2-C_7$	114.1(8)	$C_5-N_2-C_{10}$	120.5(9)
$C_7-N_2-C_{10}$	124.1(8)	$C_{10}-N_3-C_{11}$	128.6(9)	$C_{19}-N_4-C_{20}$	174.1(11)
$C_{28}-N_5-C_{29}$	172.8(9)	$C_{37}-N_6-C_{38}$	173.6(10)	$N_1-C_3-C_1$	112.0(9)
$N_1-C_3-C_2$	109.6(9)	$C_1-C_3-C_2$	112.9(10)	$N_1-C_4-C_5$	121.3(10)
$N_2-C_5-C_4$	111.4(8)	$N_2-C_5-C_6$	114.2(9)	$C_4-C_5-C_6$	104.9(9)
$S_1-C_6-S_2$	125.7(7)	$S_1-C_6-C_5$	118.3(8)	$S_2-C_6-C_5$	116.0(8)
$N_2-C_7-C_8$	112.0(10)	$N_2-C_7-C_9$	111.8(10)	$C_8-C_7-C_9$	112.6(12)
$Fe-C_{10}-N_2$	116.5(7)	$Fe-C_{10}-N_3$	118.5(8)	$N_2-C_{10}-N_3$	125.0(10)
$N_3-C_{11}-C_{12}$	120.9(10)	$N_3-C_{11}-C_{17}$	116.7(10)	$C_{12}-C_{11}-C_{17}$	121.6(10)
$C_{11}-C_{12}-C_{13}$	120.8(10)	$C_{11}-C_{12}-C_{14}$	117.8(11)	$C_{13}-C_{12}-C_{14}$	121.2(12)
$C_{12}-C_{14}-C_{15}$	120.9(13)	$C_{14}-C_{15}-C_{16}$	120.9(12)	$C_{15}-C_{16}-C_{17}$	120.6(12)
$C_{11}-C_{17}-C_{16}$	118.0(11)	$C_{11}-C_{17}-C_{18}$	121.3(10)	$C_{16}-C_{17}-C_{18}$	120.7(1)
$Fe-C_{19}-N_4$	178.2(10)	$N_4-C_{20}C_{21}$	115.9(11)	$N_4-C_{20}-C_{26}$	121.3(13)
$C_{21}-C_{20}-C_{26}$	122.6(13)	$C_{20}-C_{21}-C_{22}$	121.1(12)	$C_{20}-C_{21}-C_{23}$	116.3(15)
$C_{22}-C_{21}-C_{23}$	122.4(15)	$C_{21}-C_{23}-C_{24}$	119(2)	$C_{23}-C_{24}-C_{25}$	129(2)
$C_{24}-C_{25}-C_{26}$	113.3(19)	$C_{20}-C_{26}-C_{25}$	119.8(16)	$C_{20}-C_{26}-C_{27}$	119.2(15)
$C_{25}-C_{26}-C_{27}$	120.9(15)	$Fe-C_{28}-N_5$	177.9(8)	$N_5-C_{29}-C_{30}$	119.0(10)
$N_5-C_{29}-C_{35}$	118.5(8)	$C_{30}-C_{29}-C_{35}$	122.6(10)	$C_{29}-C_{30}C_{31}$	122.3(10)
$C_{29}-C_{30}-C_{32}$	116.9(11)	$C_{31}-C_{30}-C_{32}$	120.7(10)	$C_{30}-C_{32}-C_{33}$	120.0(11)
$C_{32}-C_{33}-C_{34}$	121.6(12)	$C_{33}-C_{34}-C_{35}$	121.5(12)	$C_{29}-C_{35}-C_{34}$	117.3(10)
$C_{29}-C_{35}-C_{36}$	120.3(9)	$C_{34}-C_{35}-C_{36}$	122.3(10)	$Fe-C_{37}-N_6$	175.0(10)
$N_6-C_{38}-C_{39}$	118.4(10)	$N_6-C_{38}-C_{44}$	117.7(10)	$C_{39}-C_{38}-C_{44}$	123.9(10)
$C_{38}-C_{38}-C_{40}$	120.7(10)	$C_{38}-C_{39}-C_{41}$	117.9(12)	$C_{40}-C_{39}-C_{41}$	121.4(12)
$C_{39}-C_{41}-C_{42}$	118.3(13)	$C_{41}-C_{42}-C_{43}$	123.3(12)	$C_{42}-C_{43}-C_{44}$	119.2(13)
$C_{38}-C_{44}-C_{43}$	117.2(11)	$C_{38}-C_{44}-C_{45}$	120.9(10)	$C_{43}-C_{44}-C_{45}$	121.8(12)

with COS, protonation of the amido lone pair resulted in stabilization and consequent isolation of a [2.2.1]bicyclic compound (**9**).

Reactions with CS_2 were also carried out with $Fe(CNR)_3(DAB)$ complexes containing aliphatic isocyanide. The products are different from the bicyclic species formed from the complexes containing the aromatic isocyanides, and their structure and properties are still under investigation. A difference between the behaviour of DAB-complexes containing aliphatic and aromatic isocyanide ligands has been encountered before [3a–c].

3.1. Molecular structure of Fe(2,6-xylylNC)₃([2.2.2]bic) (8)

The bond lengths and angles for $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**) are listed in Tables 3 and 4. The molecular structure, together with the atomic numbering, is shown in Fig. 1.

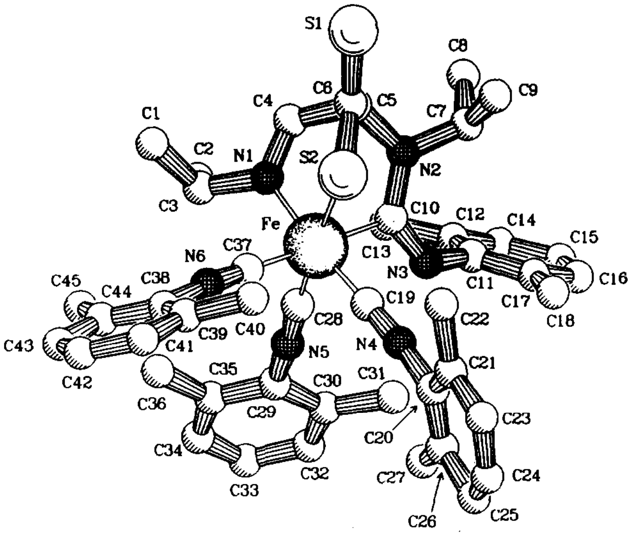


Fig. 1. PLUTO drawing of $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**). The hydrogen atoms are omitted for clarity.

Complex **8** possesses a bicyclo[2.2.2] framework, in which the bridgehead positions are occupied by the iron atom and the former imine carbon atom (C5). The plane of Fe–C10–N2–C5 (0.05(3) Å) makes an angle of 61.0(5)° with the Fe–S2–C6–C5 (0.10(5) Å) plane, and an angle of 57.1(5)° with the Fe–N1–C4–C5 plane (0.01(3) Å). These last two planes make an angle of 61.9(5)°. The geometry around the central metal atom is slightly distorted octahedral. The configuration index of the complex is [OC-6-44]. The trans positions of the

TABLE 5. ^{13}C-NMR [a], ^{1}H-NMR [b] and IR data [c] of $Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**) and $Fe(2,6\text{-xylylNC})_3([2.2.1]bic)$ (**9**)

	$Fe(2,6\text{-xylylNC})_3([2.2.2]bic)$ (**8**) [d]	$Fe(2,6\text{-xylylNC})_3([2.2.1]bic)$ (**9**)
^{13}C-NMR	250.1 (C_6), 187.0 (C_{10}), 178.0, 174.7, 173.4 (C_{19}, C_{28}, C_{37}), 168.0 (C_4), 134.6, 134.5, 134.2, 126.8, 128.7, 127.9, 127.8, 127.7, 127.5, 127.2, 127.1, 126.9, 126.6, 126.4 (C_{11}, C_{12}, C_{14}, C_{16}, C_{17}, C_{20}, C_{21}, C_{23}, C_{24}, C_{25}, C_{26}, C_{29}, C_{30}, C_{32}, C_{33}, C_{34}, C_{35}, C_{38}, C_{39}, C_{41}, C_{42}, C_{43}, C_{44}), 117.8 (C_{15}), 77.3 (C_5), 64.0, 48.2 (C_7, C_{13}), 24.1, 24.0, 22.5, 21.1 (C_1, C_2, C_8, C_9), 19.2, 19.0, 18.9 (C_{22}, C_{27}, C_{31}, C_{36}, C_{40}, C_{45}), 19.3, 19.1 (C_{13}, C_{18})	245.5 (*C*OS), 171.5, 170.2, 166.7 (*C*≡Naryl), 169.1 (imine *C*=N), 136.2, 135.5, 135.4 (ipso aryl *C*), 129.8, 129.7, 129.6 (*p*-aryl *C*), 129.0, 128.9, 128.8 (*m*-aryl *C*), 128.3, 128.2, 128.1 (*o*-aryl *C*), 89.4 (amido *C*–N), 62.6, 53.0 ($\mathit{C}H(CH_3)_2$), 24.5, 23.7, 21.4, 20.2, ($CH(\mathit{C}H_3)_2$), 26.2, 19.8, 19.7 (C≡Naryl $\mathit{C}H_3$)
^{1}H-NMR	8.48 (1H, d, 6 Hz; *H*C=N), 7.14–6.94 (9H, m; aryl*H*), 6.64, 6.61 (2 × 1H, 2 × d, 8 Hz; *m*-aryl*H*), 6.40 (1H; dd, 8 Hz, 8 Hz; *p*-aryl*H*), 5.78 (1H, d, 6 Hz; N=CC*H*), 4.52, 4.39 (2 × 1H 2 × sept, 7 Hz; $C\mathit{H}(CH_3)_2$), 2.42, 2.38, 2.27 (3 × 6H, s; terminal aryl $C\mathit{H}_3$), 1.92, 1.90 (2 × 3H, s; ring C=N aryl$C\mathit{H}_3$), 1.41, 1.26, 1.08, 0.98 (4 × 3H, 4 × d, 7 Hz; $CH(C\mathit{H}_3)_2$	8.26 (1H, d, 3 Hz; *H*C=N), 7.47 (1H, d, 10 Hz; N*H*), 7.20–7.08 (9H, m; aryl*H*), 5.69 (1H, d, 3 Hz; N=CC*H*), 4.43 (1H, m; $C\mathit{H}(CH_3)_2$), 3.29 (1H, m; $C\mathit{H}(CH_3)_2$), 2.65, 2.41, 2.40 (3 × 6H, s; terminal aryl $C\mathit{H}_3$), 1.56, 1.48, 1.42, 1.34 (4 × 3H, 4 × d, 6 Hz; $CH(C\mathit{H}_3)_2$
IR	2142, 2112 ($\nu_{C\equiv N}$) [e], 1535 ($\nu_{C=O}$) [f], 1169 ($\nu_{C=S}$) [f]	2152, 2115 ($\nu_{C\equiv N}$) [e], 1082 ($\nu_{C=S}$) [f]

[a] The chemical shift values, in ppm relative to Me_4Si, measured in $CDCl_3$ at 243 K and 75.47 MHz. [b] The chemical shift values, in ppm relative to Me_4Si, measured n $CDCl_3$ at 293 K and 300.15 MHz. [c] Stretching vibrations (cm^{-1}). [d] See Figure 1 for atomic numbering. [e] Measured in $CHCl_3$. [f] Recorded in KBr.

octahedron are taken by S2 and C28, N1 and C19 and by C10 and C37. The strong interaction between the atoms in mutual *trans* positions results in characteristic differences in the bond distances to the central iron atom. The C28–Fe and C37–Fe bonds are substantially longer (1.829(9) Å and 1.859(9) Å respectively) than the bond Fe–C19 (1.806(10) Å), owing to the presence of the good donor N1 atom in the *trans* position. As a result of the insertion, the former triple bond between C10 and N3 is replaced by a double bond, reflected by the bond length of 1.289(13) Å. Furthermore the bond angle at N3 of 128.6(9)° is indicative of sp^2 hybridisation.

The mean angles around C6 (120°) indicate sp^2 hybridisation. The lengths of the formal single bond C6–S2 and the formal double bond C6–S1 are comparable (1.662(12) and 1.649(12), respectively), indicating a large degree of delocalization in the S1–C6–S2 unit. The lengths of both C–S bonds are intermediate between that of a double bond in the linear free CS_2 molecule (1.554 Å) [17] and that of the single bond in $(CH_3)_2S$ (1.81 Å) [18]. Comparable bond lengths have been found in the $M(\eta^2\text{-}CS_2)$ complexes, and were accounted for in terms of delocalization in the CS_2 unit [19].

The mean distances in the terminal isocyanides of the C≡N and N–C fragments are 1.171 Å and 1.388 Å, respectively, *i.e.* in keeping with a triple and a single bond, respectively. The angles at N4, N5, and N6 are 174.1(4), 172.8(9) and 173.6(11) respectively, *i.e.* close to linear. Such values are commonly encountered for terminally-coordinated isocyanide [4c,d,20].

3.2. Spectroscopic properties

The spectroscopic data [21*] (^{1}H- ^{13}C-NMR and IR) for the Fe(2,6-xylylNC)$_3$([2.2.2]bic) (**8**) and Fe(2,6-xylylNC)$_3$([2.2.1]bic) (**9**) are listed in Table 5.

^{1}H-NMR: complex **8** shows the familiar pattern for a bicyclo[2.2.2] complex, such as was observed for the analogous products **3** [1,3]. After cycloaddition of CS_2 to the Fe–N=C fragment in Fe(2,6-xylylNC)$_3$(^{i}Pr-DAB) (**5**), the reacting imine carbon atom (C_5) is sp^3 hybridized, as this is reflected in an upfield shift of *ca.* 3 ppm of the signal from the former imine proton to 5.78 ppm. The proton of the intact imine function still resonates at low field (8.48 ppm) and is seen as a doublet. The diastereotopic i-propyl methyl groups give rise to a set of four doublets. As described for the bicyclo [2.2.2] products of from reaction of **5** with other dipolarophiles [1,3a,b], the 2,6-xylyl group of the inserted isocyanide in **8** cannot rotate freely around the bond to N3. This results in an inequivalence of the two sides of the aryl groups: the two methyl groups resonate at 1.90 and 1.92 ppm; the inequivalent *meta* protons give two doublets at 6.64 and 6.61 ppm; and the *para* proton couples with both *meta* protons, resulting in a double doublet at 6.40 ppm. Because of the identical coupling constants ($^3J_{HH}$ = 8 Hz) the signal is seen as a triplet. The aromatic signals of the inserted isocyanide are slightly shifted upfield from those for the terminal isocyanides.

In the ^{1}H-NMR spectrum of the [2.2.1]bicyclo adduct of COS (**9**), the protons of the intact imine group and the rehybridised imine function give two doublets, at 8.26 and 5.69 ppm, respectively. The newly introduced proton at the amine nitrogen atom appears as a broad doublet at 7.47 ppm. The methyne proton of the isopropyl group is split into a rather broad double septet at 3.29 ppm, owing to coupling with the two methyl groups and the nitrogen proton. This coupling unequivocally indicates that the hydrogen is located on the nitrogen atom.

^{13}C-NMR: the signal from the carbon atom (C6) of the CS_2 unit of the [2.2.2]bicyclic complex (**8**) is found at 250.1 ppm, within the 150 to 290 ppm range usual for CS_2-containing complexes. The values at higher field are encountered in complexes in which the CS_2 fragment is part of a cyclic structure and bonded to the metal through either the carbon or the sulphur atom [22]. The values at lower field are typical for $\eta^2\text{-}CS_2$ complexes [23]. The cycloaddition of CS_2 to the imine fragment results in a change of hybridization for C5 from sp^2 to sp^3, leading to a shift in the signal upfield to 77.3 ppm. Carbon C4 of the remaining imine unit resonates at 168.0 ppm. The signal from carbon C10 of the inserted isocyanide molecule appears at 187.0 ppm. The rotational rigidity of the 2,6-xylyl group of the inserted isocyanide is reflected by the appearance of two signals for the methyl groups (C13, C18), at 19.3 and 19.1 ppm. The three terminal carbon nuclei (C19, C28, C37) of the terminal isocyanides give rise to three signals near 175 ppm. The three pairs of methyl groups appear give a set of three signals around 19.0 ppm; this indicates that the three terminal isocyanide ligands can rotate freely, but do not scramble on the NMR time scale.

The central carbon atom of the COS fragment in the [2.2.1]bicyclic complex **9** resonates at 245.5 ppm. The ^{13}C-NMR spectra of **8** and **9** are very similar. The most salient feature in the spectrum of **9** is the absence of the signals belonging to an inserted isocyanide. The terminal carbon atoms of the three isocyanide ligands appear as three separate signals around 170 ppm. The six methyl groups give three distinct signals, indicating that also in this case the three terminal isocyanides do not undergo interchange on the NMR time scale.

IR: the IR spectra of both complexes show two intense C≡N stretching bands. Although the structures are slightly different, the complexes give rise to $\nu_{C\equiv N}$ stretching vibrations in the same region. This indicates that there is comparable back donation to the terminal isocyanide ligands in both complexes owing to the fact that the central iron atom in both is in the formal oxidation state (II).

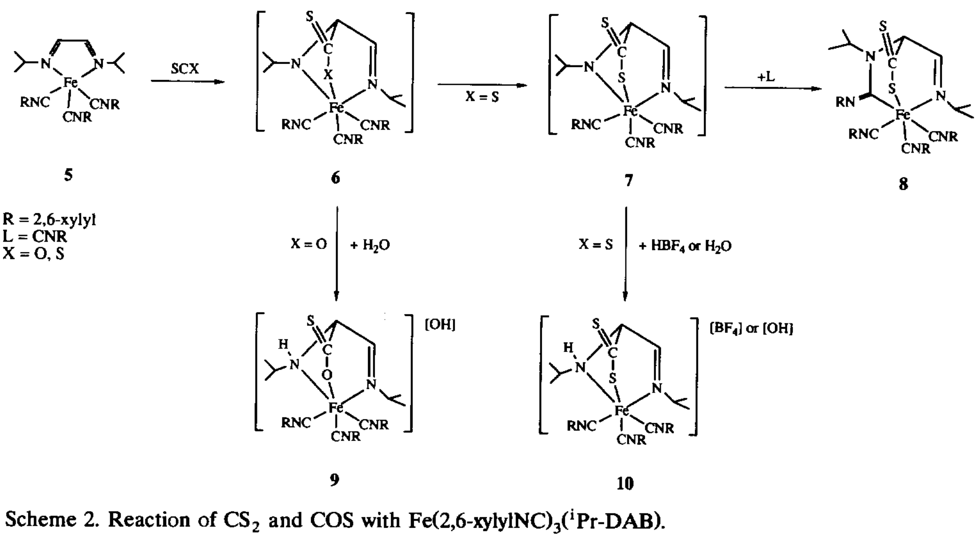
The C=N stretching vibration of the inserted isocyanide in the ferra[2.2.2]bicyclic complex (**8**) appears as a (broad) band at 1535 cm^{-1} in the solid state, while the $\nu_{C=S}$ band of the exocyclic C=S unit is found at 1169 cm^{-1}, which is normal for CS bonds [22,23,24]. In the [2.2.1]bicyclic compound (**9**) the corresponding band is observed at a comparable frequency (1082 cm^{-1}), pointing to the presence of an exocyclic C=S fragment. The shift of *ca.* 80 cm^{-1} is the result of replacing an oxygen by a sulphur atom on going from the CS$_2$ to the COS cycloadduct. No band around 1600 cm^{-1}, indicative of a C=O function, was found.

3.3. Complex formation

The reactions of Fe(CO)$_{3-n}$(CNR)$_n$(^{i}Pr-DAB) (n = 0, 1, 3) complexes with alkenes and alkynes have been described as oxidative 1,3-dipolar [3 + 2] cycloadditions [3], the Fe–N=C fragment being regarded as an isolobal [25] analogue of an azomethyne ylide (R$_2$C=N$^+$C$^-$R$_2$) [3j], a classical 1,3-dipole. Likewise the first step in the present reaction sequence (see Scheme 2) can be regarded as a 1,3-dipolar [3 + 2] cycloaddition of the heteroallene across the Fe–N=C fragment, to form a ferra[2.2.1]bicyclic intermediate **6**. In the reaction with CS$_2$, this is followed by an isocyanide insertion, involving nucleophilic attack by the amido lone pair. The resulting coordinatively- and electronically-unsaturated [2.2.2] bicyclic intermediate **7** readily accepts an additional isocyanide ligand [26*] to give the [2.2.2] bicyclic complex **8**.

In the ground state of the symmetrical CS$_2$, the HOMO (π_g) has a node at the central carbon atom [27], making orbital overlap of the C=S unit with the Fe–N=C dipole impossible. Consequently the 1,3-dipolar cycloaddition reaction of CS$_2$ is governed by HOMO(dipole)–LUMO(dipolarophile) interactions. This agrees with the conclusions drawn in earlier papers [1,3a,b] that this type of cycloaddition is, in terms of the Sustmann classification [28], HOMO(dipole) controlled. This type of cycloaddition is characterized by a dominant interaction of the HOMO of the dipole with the LUMO of the dipolarophile. Since at present the orbital energies of the starting compound, Fe(2,6-xylylNC)$_3$(^{i}Pr-DAB) (**5**), are unknown, a more quantitative description of the reaction is impossible.

The reaction sequence in the case of carbonyl sulfide is at present not completely clear, and needs to be further investigated. The first step in the reaction of Fe(2,6-xylylNC$_3$)^{i}Pr-DAB) (**5**) can also be described as a 1,3-dipolar cycloaddition to the Fe–N=C fragment, to yield the ferra[2.2.1]bicyclic complex (**6**), but it is not clear whether the carbonyl sulfide molecule has reacted across the C=S or the C=O bond. The IR data (the comparable frequencies around 1100 cm^{-1} and the absence of a C=O absorption) indicate that the C=O bond of the COS molecule was involved in the cycloaddition. However, such a preference for reaction at the C=O bond is in conflict with both the higher reactivity of C=S bonds compared to C=O bonds, encountered in organic cycloadditions [29], and with the observation that Fe(2,6-xylylNC)$_3$(^{i}Pr-DAB) (**5**) does not react with the C=O bond in carbon dioxide. Also in one of the few cycloaddition reactions in which both



Scheme 2. Reaction of CS$_2$ and COS with Fe(2,6-xylylNC)$_3$(^{i}Pr-DAB).

CS_2 and COS have been used, only the C=S bond reacted [30]. In order to establish which bond has reacted, more research, especially a solid state structure determination of complex **9**, is required.

The presence of moisture, in the COS-gas or the solvents, results in a protonation of the amido lone pair. Consequently the route to an isocyanide insertion *via* a nucleophilic attack by the amido lone pair becomes blocked, and the [2.2.1]bicyclic complex **9** is isolated. Protonation of the amido nitrogen and consequently stabilization of the [2.2.1]bicyclic structure has been observed in comparable reactions of $M(CO)_3$-(DAB) (M = Fe, Ru) and $Mn(CO)_3(DAB)$ radicals with alkynes [3c,e,j], and allowed isolation of the [2.2.1]bicyclic complexes and their characterization by crystal structure determinations.

In view of their similar structures, the two [2.2.1]bicyclic intermediates formed from CS_2 and COS respectively are expected to exhibit comparable reactivities. Consequently the difference in the course of the reaction, CS_2 forming a [2.2.2]bicyclic complex and COS a [2.2.1]bicyclic product, must be the result of an external factor, namely the presence of a protonating agent. This is confirmed by the observation that in the reaction with CS_2 also, the corresponding bicyclo[2.2.1]cationic complex **10** is isolated when water or HBF_4 is added to the reaction mixture [31*].

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31 ^{1}H-NMR data of the [2.2.1]bicyclic product **10** from the reaction of $Fe(2,6\text{-xylylNC})_3(DAB)$ with CS_2 in the presence of HBF_4: 8.17 (1H, d, 3 Hz; $HC{=}N$), 7.30–6.95 (9H, m; aryl$H$), 5.67 (1H, d, 3Hz; $N{=}CCH$), 4.66 (1H, d, 10Hz; NH), 4.04 (1H, sept, 6 Hz, $CH(CH_3)_2$), 3.27 (1H, m; $CH(CH_3)_2$), 2.73, 2.41, 2.39 (3 × 6H, s; terminal aryl CH_3), 1.52, 1.46, 1.44, 1.33 (4 × 3H, 4 × d, 6 Hz; $CH(CH_3)_2$).