

Compound (I) was synthesized by refluxing bicyclo[2.2.2]octa-2,5-diene-2,3-dicarbonitrile (III) (Weis, 1962) with pentacarbonyliron in di-*n*-butyl ether for 4–5 h. After dilution with hexane the solution was poured off and evaporated under vacuum. Compound (I) was obtained by flash chromatography on silica gel 60 (solvent: cyclohexane–ethyl acetate 2:1) as orange–yellow prisms.  $^1\text{H NMR}$ :  $\delta$  = 4.05 (2H), 3.8 (2H), 1.3 (2H), 1.65 (2H). IR ( $\text{cm}^{-1}$ ): 2200 (s), 2050/2000 (vs), 1370 (w), 1340 (w), 860 (m). MS (high resolution):  $m/z(\%)$  = 267.995, 240.003, 211.992, 183.977, 156.066, 129.040, 128.034, 101.022, 55.937. Slow crystallization from methanol afforded single crystals of (I) (m.p. 440–442 K).

Compound (II) was synthesized by heating enneacarbonyl iron with dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (IV) in toluene (Nametkine, Tyurine, Nekhaev, Ivanov & Bayaouova, 1976). Single crystals of (II) were obtained by crystallization from methanol (m.p. 387 K).

Structure solution was carried out with *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refinement was performed with a full-matrix least-squares technique. The H atoms were located in difference maps and refined isotropically. Absorption correction was applied. All calculations were carried out with the *SDP* program package (Frenz, 1985).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles involving H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55539 (54 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1001]

## References

- Almenningen, A., Haaland, A. & Wahl, K. (1969). *Acta Chem. Scand.* **23**, 2245–2252.
- Beagley, B., Cruickshank, D. W. J., Pinder, P. M., Robiette, A. G. & Sheldrick, G. M. (1969). *Acta Cryst.* **B25**, 737–744.
- Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
- Irgartinger, H. & Jahn, R. (1991). *Croat. Chem. Acta*, **64**, 289–294.
- Irgartinger, H., Jahn, R., Rodewald, H., Kiers, C. T. & Schenk, H. (1986). *Acta Cryst.* **C42**, 847–849.
- Irgartinger, H., Oeser, T., Jahn, R. & Kallfass, D. (1992). *Chem. Ber.* **125**, 2067–2073.
- Johnson, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Nametkine, N. S., Tyurine, V. D., Nekhaev, A. I., Ivanov, V. I. & Bayaouova, F. S. (1976). *J. Organomet. Chem.* **107**, 377–391.
- Watson, W. H., Nagl, A., Kashyap, R. P., Marchand, A. P. & Dave, P. R. (1990). *Acta Cryst.* **C46**, 24–27.
- Weis, C. D. (1962). *J. Org. Chem.* **28**, 74–78.

*Acta Cryst.* (1993). **C49**, 381–383

## Structure of $[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{ClNO}_4)(\text{CO})_3]$

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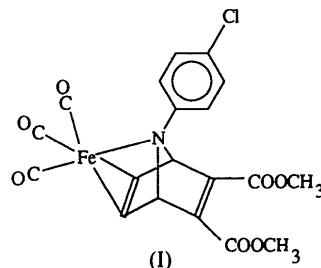
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## Abstract

Tricarbonyl[(5,6- $\eta$ )-dimethyl 7-(*p*-chlorophenyl)-7-azabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate- $\kappa\text{N}$ ]iron(0),  $[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{ClNO}_4)(\text{CO})_3]$ , was synthesized and structurally characterized. The Fe—CO distances are 1.807 (3), 1.800 (3) and 1.741 (3) Å. The Fe—N distance is 2.064 (2) Å. The Fe atom interacts with the unsubstituted olefinic bond. The two Fe—C distances are 2.030 (3) and 2.028 (2) Å. The C—C distances for substituted and unsubstituted double bonds are 1.341 (3) and 1.424 (3) Å, respectively. Two H atoms attached to the coordinated double bond are 0.36 (4) Å away from the least-squares plane of C1C2C3C4.

## Comment

Transition-metal-promoted nitrene-extrusion reactions in 7-azanorbornadiene derivatives (ANB) are of importance in the synthesis of aromatic compounds (Sun & Chow, 1988; Sun, Chow & Liu, 1990). Several complexes of transition metals with ANB have been structurally characterized (Sun, Chow & Liu, 1990; Wang, Sun, Chow & Liu, 1991; Liu, Sun, Yang, Wen, Wu, Shih & Lin, 1992). In this paper we report the crystal structure of  $[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{ClNO}_4)(\text{CO})_3]$  (I). Two CO groups, which are *cis* to each other and *trans* to the double bond, have Fe—CO distances 1.807 (3) and 1.800 (3) Å.



The C02O02 group approximately *trans* to the N atom has a shorter Fe—CO distance [1.741 (3) Å] owing to the poor  $\pi$ -acceptor property of the N atom. The Fe—N distance is 2.064 (2) Å. The unsubstituted double bond interacts in a  $\pi$  fashion with the Fe atom. The two Fe—C distances are 2.030 (3) and 2.028 (2) Å. The C—C distance for the unsubstituted double bond, 1.424 (3) Å, is significantly longer than the C—C distance for the substituted double bond, 1.341 (3) Å. Two H atoms attached to the coordinated double bond are 0.36 (4) Å above the C1C2C3C4 least-squares plane and the Fe atom lies 1.900 (1) Å below this same plane.

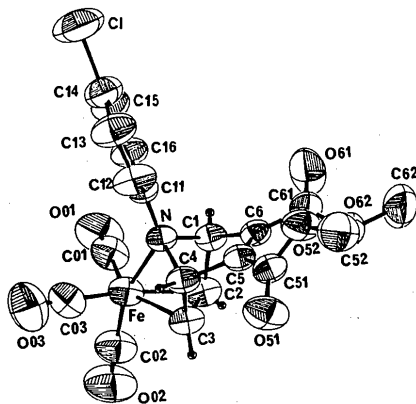


Fig. 1. ORTEP (Johnson, 1970) drawing of the title compound with 50% probability ellipsoids for non-H atoms and with an arbitrary size for H atoms.

## Experimental

### Crystal data

[Fe(C<sub>16</sub>H<sub>14</sub>ClNO<sub>4</sub>)(CO)<sub>3</sub>]

$M_r = 459.63$

Triclinic

$P\bar{1}$

$a = 7.959 (1) \text{ \AA}$

$b = 11.488 (4) \text{ \AA}$

$c = 11.559 (2) \text{ \AA}$

$\alpha = 91.58 (2)^\circ$

$\beta = 101.69 (1)^\circ$

$\gamma = 91.62 (2)^\circ$

$V = 1033.3 (4) \text{ \AA}^3$

$Z = 2$

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega$ - $2\theta$  scans

Absorption correction: empirical

$T_{\min} = 0.925$ ,  $T_{\max} = 1.00$

4730 measured reflections

4730 independent reflections

2872 observed reflections

$[I \geq 3\sigma(I)]$

$D_x = 1.477 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10$ – $12^\circ$

$\mu = 0.90 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Irregular fragment

$0.58 \times 0.50 \times 0.30 \text{ mm}$

Dark red

$\theta_{\max} = 55^\circ$

$h = 0 \rightarrow 10$

$k = -14 \rightarrow 14$

$l = -14 \rightarrow 14$

3 standard reflections (300, 030, 005)

frequency: 10000 s

intensity variation:  $< 4\%$

## Refinement

Refinement on  $F$

Final  $R = 0.049$

$wR = 0.056$

$S = 2.649$

2872 reflections

310 parameters

$4F_o/[\sigma^2(I) + (0.02F_o)^2]$

$(\Delta/\sigma)_{\max} = 0.06$

$\Delta\rho_{\max} = 0.306 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.260 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

H atoms were refined with fixed  $B_{\text{iso}}$  values. For other atoms  $B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
Fe	0.34200 (6)	0.2353 (5)	0.07667 (4)	5.72 (1)
Cl	0.2806 (2)	-0.1079 (1)	-0.4865 (1)	10.69 (4)
O01	0.7111 (4)	0.2204 (4)	0.0792 (3)	11.1 (1)
O02	0.3960 (5)	0.3028 (4)	0.3243 (3)	11.8 (1)
O03	0.2201 (5)	0.0006 (3)	0.1210 (3)	10.7 (1)
O51	-0.2944 (3)	0.3494 (3)	-0.1775 (2)	6.84 (6)
O52	-0.2117 (3)	0.3724 (2)	-0.3476 (2)	5.98 (6)
O61	0.2668 (4)	0.5078 (3)	-0.3314 (3)	12.42 (9)
O62	0.0288 (3)	0.5709 (2)	-0.2944 (2)	7.44 (7)
N	0.2353 (3)	0.2341 (2)	-0.1017 (2)	4.23 (5)
C1	0.2911 (4)	0.3602 (3)	-0.1152 (3)	4.64 (7)
C01	0.5671 (5)	0.2248 (4)	0.0735 (3)	7.4 (1)
C2	0.2828 (4)	0.3947 (3)	0.0115 (3)	5.48 (8)
C02	0.3793 (5)	0.2745 (4)	0.2265 (4)	8.0 (1)
C3	0.1337 (4)	0.3351 (3)	0.0335 (3)	5.19 (8)
C03	0.2672 (5)	0.0909 (4)	0.1029 (3)	7.2 (1)
C4	0.0598 (3)	0.2656 (3)	-0.0806 (3)	4.42 (7)
C5	-0.0009 (3)	0.3465 (3)	-0.1806 (3)	4.20 (6)
C6	0.1379 (4)	0.4055 (3)	-0.2002 (3)	4.44 (7)
C11	0.2444 (4)	0.1515 (3)	-0.1958 (3)	4.61 (7)
C12	0.1001 (6)	0.0868 (4)	-0.2531 (4)	6.1 (1)
C13	0.1142 (6)	0.0058 (5)	-0.3416 (5)	7.0 (1)
C14	0.2667 (5)	-0.0077 (3)	-0.3725 (3)	6.8 (1)
C15	0.4098 (6)	0.0513 (4)	-0.3126 (4)	6.6 (1)
C16	0.3977 (6)	0.1304 (4)	-0.2244 (4)	5.9 (1)
C22	0.192 (2)	0.049 (1)	-0.192 (1)	7.2 (4)
C23	0.196 (2)	-0.033 (1)	-0.283 (1)	8.0 (5)
C25	0.325 (2)	0.111 (2)	-0.382 (1)	8.2 (4)
C26	0.316 (2)	0.189 (1)	-0.296 (1)	6.5 (4)
C51	-0.1844 (4)	0.3568 (3)	-0.2339 (3)	4.44 (7)
C52	-0.3867 (5)	0.3891 (4)	-0.4069 (3)	7.3 (1)
C61	0.1520 (4)	0.4988 (3)	-0.2818 (3)	5.57 (8)
C62	0.0252 (6)	0.6592 (4)	-0.3790 (4)	10.4 (1)
H1	0.399 (5)	0.369 (3)	-0.138 (3)	6.50
H2	0.330 (5)	0.467 (3)	0.048 (3)	6.50
H3	0.062 (5)	0.356 (3)	0.082 (3)	6.50
H4	-0.011 (5)	0.200 (3)	-0.073 (3)	6.50

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Fe—N	2.064 (2)	N—C1	1.524 (3)
Fe—C01	1.807 (3)	N—C4	1.518 (2)
Fe—C2	2.030 (3)	N—C11	1.438 (3)
Fe—C02	1.741 (3)	C1—C2	1.522 (3)
Fe—C3	2.028 (2)	C1—C6	1.517 (3)
Fe—C03	1.800 (3)	C1—H1	0.95 (3)
Cl—C14	1.747 (2)	C2—C3	1.424 (3)
O01—C01	1.138 (3)	C2—H2	0.95 (3)
O02—C02	1.147 (3)	C3—C4	1.525 (3)
O03—C03	1.132 (3)	C3—H3	0.91 (3)
O51—C51	1.195 (2)	C4—C5	1.513 (3)
O52—C51	1.305 (2)	C4—H4	0.94 (3)
O52—C52	1.443 (2)	C5—C6	1.341 (3)
O61—C61	1.175 (3)	C5—C51	1.476 (3)
O62—C61	1.289 (3)	C6—C61	1.464 (3)
O62—C62	1.426 (3)		

N—Fe—C01	101.00 (9)	C1—C2—H2	122 (2)
N—Fe—C2	65.36 (8)	C3—C2—H2	125 (2)
N—Fe—C02	159.7 (1)	Fe—C02—O02	176.6 (3)
N—Fe—C3	65.54 (7)	Fe—C3—C2	69.5 (1)
N—Fe—C03	96.6 (1)	Fe—C3—C4	94.2 (1)
C01—Fe—C2	103.6 (1)	Fe—C3—H3	126 (2)
C01—Fe—C02	94.2 (1)	C2—C3—C4	105.1 (2)
C01—Fe—C3	144.6 (1)	C2—C3—H3	129 (2)
C01—Fe—C03	106.3 (1)	C4—C3—H3	119 (2)
C2—Fe—C02	98.1 (1)	Fe—C03—O03	179.0 (3)
C2—Fe—C3	41.10 (9)	N—C4—C3	93.4 (1)
C2—Fe—C03	147.6 (1)	N—C4—C5	101.9 (1)
C02—Fe—C3	94.3 (1)	N—C4—H4	114 (2)
C02—Fe—C03	92.0 (1)	C3—C4—H4	116 (2)
C3—Fe—C03	107.7 (1)	C5—C4—H4	118 (2)
C3—C4—C5	110.6 (2)	C4—C5—C6	107.2 (2)
Fe—N—C1	93.6 (1)	C4—C5—C51	122.1 (2)
Fe—N—C4	93.0 (1)	C6—C5—C51	130.5 (2)
Fe—N—C11	131.3 (1)	C1—C6—C5	106.6 (2)
C1—N—C4	93.9 (1)	C1—C6—C61	123.1 (2)
C1—N—C11	117.9 (2)	C5—C6—C61	130.3 (2)
C4—N—C11	118.5 (1)	N—C1—H1	114 (2)
N—C1—C2	93.1 (2)	C2—C1—H1	118 (2)
N—C1—C6	102.5 (1)	C6—C1—H1	116 (2)
C2—C1—C6	110.2 (2)	Fe—C2—C1	95.0 (1)
Fe—C2—H2	125 (2)	Fe—C01—O01	175.4 (2)
C1—C2—C3	105.3 (2)	Fe—C2—C3	69.4 (1)

The title compound was synthesized by reacting  $\text{Fe}_2(\text{CO})_9$  with 7-azanorbomadiene in thf under  $\text{N}_2$  overnight. During the reaction, three types of stable metal complex were isolated, *i.e.*  $[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{ClNO}_4)(\text{CO})_4]$  and two structural isomers of  $[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{ClNO}_4)(\text{CO})_3]$  (Sun, Wang & Yang, to be published). A similar reaction was observed during the study of other typical reactions of ANB derivatives with  $\text{Fe}_2(\text{CO})_9$  (Sun, Chow & Lui, 1990). Dark-red crystals of  $[\text{Fe}(\text{C}_{16}\text{H}_{14}\text{ClNO}_4)(\text{CO})_3]$  were grown from ethyl acetate/*n*-hexane mixed solvent. The structure was solved by direct methods using *Personal SDP* (Frenz, 1989). H atoms on the fused ring were located on difference maps and refined as normal atoms with fixed isotropic displacement parameters. Other H atoms were placed at idealized positions and included in the structure-factor calculations but not in the least-squares calculations. Four out of six phenyl-ring C atoms are disordered. The site occupancy for one ring is fixed at 0.75 and for the other is fixed at 0.25. The dihedral angle for these two rings is  $54.8(4)^\circ$ . Fig. 1 shows only the larger site occupancy for clarity. All calculations were carried out on an 80386-based IBM-compatible PC.

These studies are supported by the National Science Council (NSC81-0208-M031-03) of Taiwan.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55556 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1009]

## References

- Frenz, B. A. (1989). *Personal SDP – A Real-Time System for Solving, Refining and Displaying Crystal Structures*. B. A. Frenz & Associates, Inc., College Station, Texas, USA.
- Johnson, C. K. (1970). *ORTEP*. Report ORNL-3794, second revision. Oak Ridge National Laboratory, Tennessee, USA.
- Liu, L.-K., Sun, C.-H., Yang, G.-Z., Wen, Y.-S., Wu, C.-F., Shih, S.-Y. & Lin, K.-S. (1992). *Organometallics*, **11**, 972–976.
- Sun, C.-H. & Chow, T. J. (1988). *J. Chem. Soc. Chem. Commun.* pp. 535–536.
- Sun, C.-H., Chow, T. J. & Liu, L.-K. (1990). *Organometallics*, **9**, 560–565.
- Wang, J.-C., Sun, C.-H., Chow, T. J. & Liu, L.-K. (1991). *Acta Cryst.* **C47**, 2459–2461.
- Acta Cryst.* (1993). **C49**, 383–385

## *mer*-Trichlorotris(2,3-dihydrobenzo[*b*]thiophene-*S*)rhodium(III)

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## Abstract

The Rh atom has a distorted octahedral geometry. Two of the benzothiophenyl ligands occupy *trans* equatorial positions with Rh—S distances [2.351 (1) and 2.369 (1) Å] which are significantly longer than the third [2.330 (1) Å] distance. The Rh—Cl distances are in the range 2.333 (2)–2.359 (1) Å. The benzothiophenyl ligand at the axial position is inclined at almost right angles [mean-planes angles 89.6 (2) and 79.5 (2)°] to the other two ligands which lie almost parallel to each other [mean-planes angle 10.4 (2)°].

## Comment

Organosulfur compounds coordinated to transition-metal species are of general interest as models for interactions which occur during the catalytic hydrodesulfurization of hydrocarbons (Dong, Duckett, Ohman & Jones, 1992). Industrially, this process is carried out on a large scale to produce sulfur-free transportation fuels. The title compound (I) is an example of a complex which may model species formed during the hydrodesulfurization of benzo[*b*]thiophene. Partial hydrogenation of benzothiophene is known to produce the 2,3-dihydro derivative, a compound which should readily coordinate to metal species. The rhodium complex of 2,3-dihydrobenzo[*b*]thiophene was prepared by heating