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## Two Iron–Tricarbonyl Complexes with Substituted Bicyclo[2.2.2]octadienes

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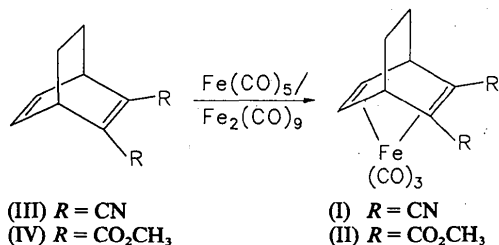
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### Abstract

The iron–tricarbonyl complexes { $\eta^4$ -(bicyclo[2.2.2]octa-2,5-diene-2,3-dicarbonitrile)}tricarbonyliron(0) (I) and tricarbonyl{ $\eta^4$ -(dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate)}iron(0) (II) of the bicyclo[2.2.2]octadiene systems (III) and (IV) have distorted trigonal bipyramidal structures. The C=C double bonds in axial positions (long Fe–C distances) are shorter [(I) 1.372 (3), (II) 1.373 (3) Å] than the corresponding bonds in equatorial positions [(I) 1.447 (3), (II) 1.433 (2) Å]. The pyramidalization of the olefinic C atoms of the bicyclo[2.2.2]octadiene system is considerably increased by complexation with the Fe(CO)<sub>3</sub> group.

### Comment

In the course of stereochemical studies of norbornadienes and related systems, we investigated the structure of quadricyclanes (Irgartinger & Jahn, 1991; Irgartinger, Jahn, Rodewald, Kiers & Schenk, 1986) and compared the structures of 1,4-bridged 2,5-cyclohexadienes with respect to varying bridge length (Irgartinger, Oeser, Jahn & Kallfass, 1992). Within the scope of these studies we investigated the complexing behaviour of bicyclo[2.2.2]octadiene derivatives and we determined the structure of complexes (I) and (II) (Figs. 1 and 2).



Like pentacarbonyliron (Beagley, Cruickshank, Pinder, Robiette & Sheldrick, 1969; Almennigen, Haaland & Wahl, 1969), the iron complexes (I) and

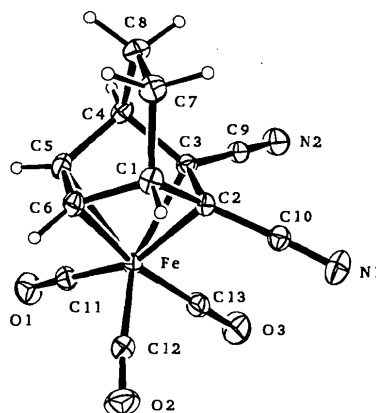


Fig. 1. ORTEP (Johnson, 1971) plot of (I) with thermal ellipsoids drawn at the 30% probability level.

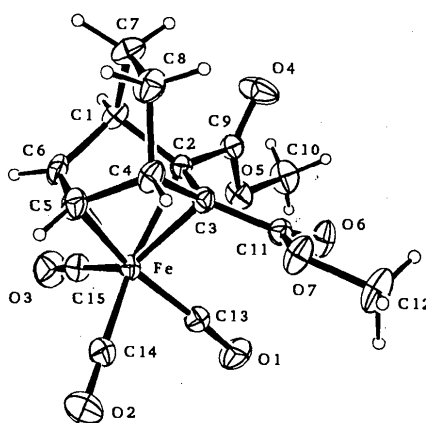


Fig. 2. ORTEP plot of (II) with thermal ellipsoids drawn at the 30% probability level.

(II) have a trigonal bipyramidal structure which is distorted in these complexes. The centres  $M23$  and  $M56$  of the double bonds  $\text{C}2=\text{C}3$  and  $\text{C}5=\text{C}6$  and the carbonyl groups occupy equatorial and axial positions as shown in Fig. 3. As a consequence of the molecular structure of the organic ligands the angles  $M23\text{—Fe—}M56$  of complexes (I) and (II) deviate strongly from the geometry of a trigonal bipyramid structure by the order of  $20^\circ$  (Table 2, Fig. 3).

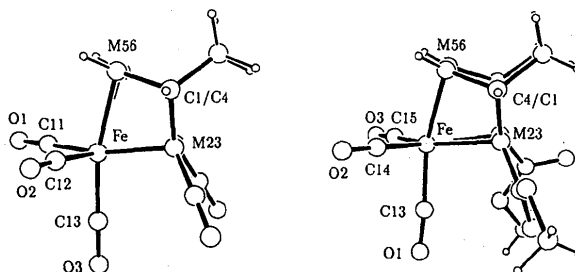


Fig. 3. Ball and stick drawing of (I) and (II).  $M23$  and  $M56$  are the centres of the corresponding double bonds.

The present structures show pseudo-staggered conformations between the nitrile or ester substituents and the axial CO ligands. Further steric interactions would take place in the case of axial C2=C3 bonds, with their substituents standing nearly in eclipsed positions to the equatorial CO ligands. Like comparable norbornadiene Fe<sup>0</sup> complexes (Watson, Nagl, Kashyap, Marchand & Dave, 1990), the axial Fe—C<sub>sp<sup>2</sup></sub> distances are longer than the corresponding equatorial bonds (Table 2). As a result the axial C5=C6 double bonds are shorter than the equatorial C2=C3 double bonds with stronger Fe— $\pi$ -system complexation. In comparison, the double-bond lengths of the uncomplexed ligand (III) are 1.346 (1) and 1.325 (2) Å (Iringtinger, Oeser, Jahn & Kallfass, 1992). The axial Fe—CO distances are shorter than the equatorial ones (Table 2).

The four C atoms of the iron complexes (I) and (II) associated with these double bonds are much more pyramidalized than in the non-complexed compound (III). The dihedral angles of (I) between the C1, C2, C3, C4 plane and the C9, C3, C2 and C10, C2, C3 planes are 27.1 (2) and 21.6 (2)°. The corresponding interplanar angles of (II) between C1, C2, C3, C4 and C9, C2, C3 and C11, C3, C2 are 33.3 (2) and 20.1 (2)°, respectively. In (III) the corresponding deviation is only 1.2 (1)° (Iringtinger, Oeser, Jahn & Kallfass, 1992). The interplanar angles between C1, C6, C5, C4 and H6, C6, C5 and H5, C5, C6 are 6 (1) and 12 (1)° in (I), 7 (2) and 11 (2)° in (II) and only 3 (1)° in (III). All reported deviations are *exo* (in the direction of the bismethylene bridge). In the complexes (I) and (II), the non-bonding distances between the double bonds of the organic ligands [C2...C6 and C3...C5 are 2.336 (2) and 2.324 (2) Å for (I), and 2.328 (2) and 2.330 (2) Å for (II)] are shorter than the corresponding distance [2.444 (2) Å] between the double bonds of the uncomplexed ligand (III). Consequently, the distances between the bridgehead atoms alter in the opposite sense: C1...C4 is 2.589 (3) Å for (I), 2.583 (2) Å for (II) compared to 2.558 (2) Å for (III).

## Experimental

### Compound (I)

#### Crystal data

[Fe(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(CO)<sub>3</sub>]  
*M<sub>r</sub>* = 296.07  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 6.525 (2) Å  
*b* = 13.183 (4) Å  
*c* = 14.031 (6) Å  
 $\beta$  = 99.16 (4)°  
*V* = 1191 (1) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.65 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71071 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 10–17°  
 $\mu$  = 1.27 mm<sup>-1</sup>  
*T* = 293 K  
 Prism  
 0.5 × 0.3 × 0.3 mm  
 Orange–yellow

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: numerical  
 $T_{\min} = 0.684$ ,  $T_{\max} = 0.744$   
 3235 measured reflections  
 2853 independent reflections

#### Refinement

Refinement on *F*<sup>2</sup>  
 Final *R* = 0.028  
 $wR = 0.036$   
 $S = 1.64$   
 2270 reflections  
 204 parameters  
 All H-atom parameters refined

### Compound (II)

#### Crystal data

[Fe(C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>)(CO)<sub>3</sub>]  
*M<sub>r</sub>* = 361.96  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 8.180 (1) Å  
*b* = 8.097 (1) Å  
*c* = 23.059 (4) Å  
 $\beta$  = 91.03 (1)°  
*V* = 1527.0 (7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.58 Mg m<sup>-3</sup>

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: numerical  
 $T_{\min} = 0.744$ ,  $T_{\max} = 0.770$   
 4035 measured reflections  
 3652 independent reflections

#### Refinement

Refinement on *F*<sup>2</sup>  
 Final *R* = 0.029  
 $wR = 0.038$   
 $S = 1.80$   
 2849 reflections  
 264 parameters  
 All H-atom parameters refined

2270 observed reflections  
 $[F > 3.0\sigma(F)]$   
 $R_{\text{int}} = 0.02$   
 $\theta_{\text{max}} = 28^\circ$   
 $h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 17$   
 $l = -18 \rightarrow 18$   
 3 standard reflections  
 frequency: 60 min  
 intensity variation: 3.7%

$w = 1/[\sigma(F_o)^2]$   
 $= 4 \times (F_o^2)/[\sigma(F_o^2)^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.01$   
 $\Delta\rho_{\text{max}} = 0.533 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.315 \text{ e } \text{Å}^{-3}$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Mo *K*α radiation  
 $\lambda$  = 0.71071 Å  
 Cell parameters from 70 reflections  
 $\theta$  = 9–26°  
 $\mu$  = 1.02 mm<sup>-1</sup>  
*T* = 293 K  
 Prism  
 0.4 × 0.3 × 0.3 mm  
 Orange

2849 observed reflections  
 $[F > 2.5\sigma(F)]$   
 $R_{\text{int}} = 0.02$   
 $\theta_{\text{max}} = 28^\circ$   
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 10$   
 $l = -30 \rightarrow 30$   
 3 standard reflections  
 frequency: 60 min  
 intensity variation: 0.9%

$w = 1/[\sigma(F_o)^2]$   
 $= 4 \times (F_o^2)/[\sigma(F_o^2)^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.01$   
 $\Delta\rho_{\text{max}} = 0.246 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.382 \text{ e } \text{Å}^{-3}$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

(I)	x	y	z	$U_{\text{eq}}$				
Fe	-0.02400 (4)	0.14982 (2)	0.15223 (2)	0.0247 (1)	Fe—C2	2.065 (2)	C1—C6	1.515 (3)
O1	0.2677 (3)	0.0607 (1)	0.0353 (1)	0.0528 (8)	Fe—C6	2.227 (2)	C1—C7	1.547 (3)
O2	-0.3167 (3)	-0.0159 (1)	0.1740 (1)	0.0553 (8)	Fe—C3	2.083 (2)	C2—C3	1.433 (2)
O3	0.2651 (3)	0.0923 (2)	0.3247 (1)	0.0630 (9)	Fe—C5	2.216 (2)	C2—C9	1.502 (2)
N1	-0.2266 (3)	0.2289 (2)	0.3901 (1)	0.0476 (9)	O1—C13	1.139 (2)	C3—C4	1.520 (2)
N2	0.3067 (3)	0.3697 (1)	0.3105 (2)	0.0448 (9)	O2—C14	1.142 (2)	C3—C11	1.473 (2)
C1	-0.3701 (3)	0.2722 (1)	0.1320 (1)	0.0287 (7)	O3—C15	1.135 (3)	C4—C5	1.511 (3)
C2	-0.1837 (3)	0.2598 (1)	0.2127 (1)	0.0248 (7)	O4—C9	1.193 (2)	C4—C8	1.542 (3)
C3	0.0039 (3)	0.3018 (1)	0.1857 (1)	0.0253 (7)	O5—C9	1.320 (2)	C5—C6	1.373 (3)
C4	-0.0340 (3)	0.3472 (1)	0.0844 (1)	0.0297 (7)	O5—C10	1.454 (2)	C7—C8	1.539 (3)
C5	-0.1131 (3)	0.2542 (2)	0.0269 (1)	0.0311 (8)	O6—C11	1.208 (2)		
C6	-0.2914 (3)	0.2141 (2)	0.0517 (1)	0.0303 (8)				
C7	-0.4054 (3)	0.3841 (2)	0.1024 (2)	0.0374 (9)	M23*—Fe	1.947 (2)	M56*—Fe	2.113 (2)
C8	-0.2030 (3)	0.4297 (2)	0.0761 (2)	0.0373 (9)	(I)			
C9	0.1706 (3)	0.3390 (1)	0.2559 (1)	0.0286 (7)	Fe—C11—O1	177.9 (2)	C2—C3—C9	122.2 (2)
C10	-0.2088 (3)	0.2444 (2)	0.3114 (1)	0.0301 (7)	Fe—C12—O2	175.1 (2)	C3—Fe—C2	41.3 (1)
C11	0.1541 (3)	0.0963 (2)	0.0789 (1)	0.0342 (8)	Fe—C13—O3	178.3 (2)	C3—Fe—C5	65.4 (1)
C12	-0.2039 (3)	0.0459 (2)	0.1618 (1)	0.0344 (8)	Fe—C2—C1	99.5 (1)	C3—Fe—C6	78.8 (1)
C13	0.1504 (3)	0.1137 (2)	0.2579 (2)	0.0366 (9)	Fe—C6—C1	92.6 (1)	C3—Fe—C11	117.8 (1)
					Fe—C2—C3	69.8 (1)	C3—Fe—C12	138.5 (1)
(II)					Fe—C2—C10	116.3 (1)	C2—Fe—C13	92.8 (1)
Fe	0.83091 (3)	0.17953 (3)	0.60361 (1)	0.0341 (1)	Fe—C3—C4	100.0 (1)	C3—C2—C10	122.5 (1)
O1	0.4761 (2)	0.1551 (2)	0.6113 (1)	0.0703 (9)	Fe—C3—C9	121.3 (1)	C3—C4—C5	99.7 (1)
O2	0.8039 (2)	0.0972 (2)	0.4795 (1)	0.0786 (10)	Fe—C5—C4	93.2 (1)	C3—C4—C8	110.8 (2)
O3	0.8506 (2)	-0.1370 (2)	0.6659 (1)	0.0714 (10)	Fe—C6—C5	72.4 (1)	C4—C3—C9	119.9 (2)
O4	0.7967 (2)	0.4807 (2)	0.7561 (1)	0.0757 (9)	N1—C10—C2	177.7 (2)	C4—C5—C6	114.1 (2)
O5	0.6401 (2)	0.2745 (2)	0.7252 (1)	0.0456 (6)	N2—C9—C3	178.3 (2)	C4—C8—C7	109.6 (2)
O6	0.5801 (2)	0.5327 (2)	0.6301 (1)	0.0510 (7)	C1—C2—C3	111.8 (1)	C5—Fe—C6	35.8 (1)
O7	0.7165 (2)	0.6198 (2)	0.5528 (1)	0.0517 (7)	C1—C2—C10	121.9 (2)	C5—Fe—C11	84.4 (1)
C1	1.0508 (2)	0.3123 (2)	0.6832 (1)	0.0397 (8)	C1—C6—C5	113.3 (2)	C5—Fe—C12	115.5 (1)
C2	0.8711 (2)	0.3487 (2)	0.6694 (1)	0.0312 (7)	C1—C7—C8	109.8 (2)	C5—Fe—C13	150.4 (1)
C3	0.8507 (2)	0.4340 (2)	0.6153 (1)	0.0325 (7)	C2—C3—Fe	68.9 (1)	C5—C4—C8	110.7 (1)
C4	1.0118 (2)	0.4611 (2)	0.5849 (1)	0.0411 (8)	C2—Fe—C5	78.7 (1)	C6—C5—Fe	71.9 (1)
C5	1.0700 (2)	0.2849 (3)	0.5791 (1)	0.0450 (9)	C6—Fe—C6	66.1 (1)	C6—Fe—C11	107.3 (1)
C6	1.0917 (2)	0.2059 (2)	0.6314 (1)	0.0435 (9)	C2—Fe—C11	157.7 (1)	C6—Fe—C12	83.4 (1)
C7	1.1549 (2)	0.4718 (3)	0.6825 (1)	0.0520 (10)	C2—Fe—C12	97.3 (1)	C6—Fe—C13	163.5 (1)
C8	1.1334 (2)	0.5589 (3)	0.6235 (1)	0.0514 (10)	C2—Fe—C13	98.3 (1)	C6—C1—C7	109.7 (2)
C9	0.7646 (2)	0.3773 (2)	0.7209 (1)	0.0361 (7)	C2—C1—C6	99.9 (1)	C11—Fe—C12	103.1 (1)
C10	0.5340 (3)	0.3034 (3)	0.7741 (1)	0.0592 (11)	C2—C1—C7	111.6 (1)	C11—Fe—C13	89.2 (1)
C11	0.7025 (2)	0.5307 (2)	0.6016 (1)	0.0352 (7)	C2—C3—C4	112.0 (1)	C12—Fe—C13	94.1 (1)
C12	0.5749 (3)	0.7165 (3)	0.5364 (1)	0.0675 (12)				
C13	0.6144 (2)	0.1697 (2)	0.6095 (1)	0.0442 (9)	M23*—Fe—M56*	70.1 (1)		
C14	0.8168 (2)	0.1307 (3)	0.5275 (1)	0.0483 (9)	(II)			
C15	0.8488 (2)	-0.0152 (2)	0.6416 (1)	0.0454 (9)	Fe—C13—O1	175.9 (2)	C2—C3—C4	112.5 (1)
					Fe—C14—O2	178.0 (2)	C2—C3—C11	121.7 (1)
					Fe—C15—O3	176.0 (2)	C3—Fe—C2	40.4 (1)
					Fe—C2—C1	99.5 (1)	C3—Fe—C5	65.5 (1)
					Fe—C6—C1	93.3 (1)	C3—Fe—C6	78.3 (1)
					Fe—C2—C3	70.5 (1)	C3—Fe—C13	96.3 (1)
					Fe—C2—C9	126.5 (1)	C3—Fe—C14	110.3 (1)
					Fe—C3—C4	98.6 (1)	C3—Fe—C15	142.6 (1)
					Fe—C3—C11	115.9 (1)	C3—C2—C9	123.6 (1)
					Fe—C5—C4	93.4 (1)	C3—C4—C5	100.4 (1)
					Fe—C5—C6	72.4 (1)	C3—C4—C8	111.3 (1)
					O4—C9—O5	123.5 (2)	C4—C3—C11	122.8 (1)
					O4—C9—C2	121.5 (2)	C4—C5—C6	113.5 (2)
					O5—C9—C2	115.0 (1)	C4—C8—C7	109.7 (2)
					O6—C11—O7	122.2 (2)	C5—C6—Fe	71.6 (1)
					O6—C11—C3	125.2 (2)	C5—Fe—C13	157.0 (1)
					O7—C11—C3	112.5 (1)	C5—Fe—C14	83.0 (1)
					C1—C2—C3	111.8 (1)	C5—Fe—C15	113.2 (1)
					C1—C2—C9	115.8 (1)	C5—C4—C8	109.5 (1)
					C1—C6—C5	113.6 (2)	C6—Fe—C5	36.0 (1)
					C1—C7—C8	109.7 (2)	C6—Fe—C13	158.7 (1)
					C2—C3—Fe	69.1 (1)	C6—Fe—C14	110.2 (1)
					C2—Fe—C5	78.6 (1)	C6—Fe—C15	82.8 (1)
					C2—Fe—C6	65.6 (1)	C6—C1—C7	109.7 (1)
					C2—Fe—C13	96.8 (1)	C9—O5—C10	115.5 (1)
					C2—Fe—C14	150.2 (1)	C11—O7—C12	115.5 (2)
					C2—Fe—C15	102.3 (1)	C13—Fe—C14	91.1 (1)
					C2—C1—C6	99.8 (1)	C13—Fe—C15	89.8 (1)
					C2—C1—C7	111.4 (1)	C14—Fe—C15	106.5 (1)
					M23*—Fe—M56*	69.9 (1)		
(I)								
Fe—C11	1.813 (2)	C1—C2	1.533 (2)					
Fe—C12	1.823 (2)	C1—C6	1.518 (3)					
Fe—C13	1.784 (2)	C1—C7	1.540 (3)					
Fe—C2	2.047 (2)	C2—C3	1.447 (3)					
Fe—C6	2.229 (2)	C2—C10	1.435 (3)					
Fe—C3	2.059 (2)	C3—C4	1.527 (3)					
Fe—C5	2.235 (2)	C3—C9	1.433 (2)					
O1—C11	1.136 (3)	C4—C5	1.513 (3)					
O2—C12	1.128 (3)	C4—C8	1.540 (3)					
O3—C13	1.138 (3)	C5—C6	1.372 (3)					
N1—C10	1.146 (3)	C7—C8	1.549 (3)					
N2—C9	1.150 (3)							
M23*—Fe	1.921 (2)	M56*—Fe	2.124 (2)					
(II)								
Fe—C13	1.780 (2)	O7—C11	1.344 (2)					
Fe—C14	1.802 (2)	O7—C12	1.443 (3)					
Fe—C15	1.808 (2)	C1—C2	1.528 (2)					

\*M23 and M56 are the centres of the C2=C3 and C5=C6 double bonds.

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 (Nemetkine, 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]

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

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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.

