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Two Iron(0) Tricarbonyl Complexes with Substituted Norbornadienes

By William H. Watson,[*] Ante Nagl[†] and Ram P. Kashyap

Department of Chemistry, Materials Research Laboratory, Texas Christian University, Fort Worth, Texas 76129, *USA*

and Alan P. Marchand[*] and Paritosh R. Dave

Department of Chemistry, University of North Texas, Box 5068, *Denton, Texas, USA*

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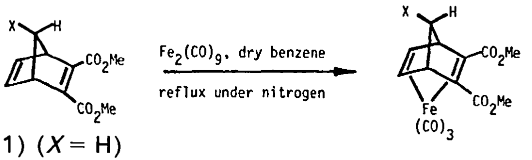
Abstract. Tricarbony[2–3:5–6-η-(dimethyl 8,9,10-trinorborna-2,5-diene-2,3-dicarboxylate)]iron(0) (3), $[Fe(C_{11}H_{12}O_4)(CO)_3]$, M_r = 348·10, monoclinic, $P2_1/c$, a = 8·274 (1), b = 7·876 (1), c = 22·021 (2) Å, β = 92·23 (1)°, V = 1433·8 (3) Å^3, Z = 4, D_x = 1·612 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 10·8 cm^{-1}, F(000) = 712, T = 295 K, R = 0·0417 for 2624 reflections. Tricarbonyl[2–3:5–6-η-(dimethyl 7-trimethylsilyl-8,9,10-trinorborna-2,5-diene-2,3-dicarboxylate]iron(0) (4), $[Fe(C_{14}H_{20}O_4Si)(CO)_3]$, M_r = 420·28, orthorhombic, $P2_12_12_1$, a = 10·738 (2), b = 12·875 (2), c = 14·316 (2) Å, V = 1979·2 (4) Å^3, Z = 4, D_x = 1·410 g cm^{-3}, λ(Mo $K\alpha$), μ = 8·51 cm^{-1}, F(000) = 872, T = 295 K, R = 0·0441 for 1648 reflections. The Fe atoms in each structure are coordinated to both norbornadiene double bonds, and the geometries involving the two double-bond midpoints and the three carbonyl groups can be described as distorted trigonal bipyramidal. The two double bonds within each norbornadiene moiety are statistically inequivalent with average values of 1·442 (3) and 1·359 (4) Å. The longest bond in each structure is conjugated with the ester groups and occupies an equatorial site. The average distance between Fe(0) and the midpoint of the axial double bond is 2·100 (6) Å, which is significantly longer than the distance to the midpoint of the equatorial double bond of 1·928 (6) Å. The C atoms associated with the longest double bond in each structure are more pyramidalized than those of the short bond.

Introduction. As part of an ongoing study of the thermal reactions of iron carbonyls with 7-substituted norbornadienes (Marchand, Earlywine & Heeg, 1986; Marchand, Goodin, Hossain & van der Helm, 1984; Marchand & Hayes, 1977), the thermal reactions of $[Fe(CO)_5]$ with dimethyl 8,9,10-trinorborna-2,5-diene-2,3-dicarboxylate (1) and with dimethyl 7-trimethylsilyl-8,9,10-trinorborna-2,5-diene-2,3-dicarboxylate (2) were investigated. The structures of the two iron(0) tricarbonyl compounds (3) and (4) are described.



(1) (X = H)
(2) (X = SiMe$_3$)

(3) (X = H, 50%)
(4) (X = SiMe$_3$, 60%)

Experimental. Compounds (1) and (2) were synthesized *via* Diels–Alder cycloadditions of dimethyl acetylenedicarboxylate to cyclopentadiene and to 5-(trimethylsilyl)cyclopentadiene, respectively. Thermal reaction of (1) with $[Fe_2(CO)_9]$ was carried out by refluxing a solution of the two reactants in dry benzene overnight under nitrogen. Compound (3) was obtained as yellow platelets in 50% yield. A good-quality single crystal of (3), m.p. 365–366 K (uncorr.), was obtained by slow recrystallization from hexane (lit. m.p. 358·1–358·6 K; Nametkine, Tyurine, Nekhaev, Ivanov & Bayaouova, 1976). Similarly, thermal reaction of (2) with $[Fe_2(CO)_9]$ was carried out by refluxing a solution of the two reactants in dry benzene under nitrogen for three days. Compound (4) was obtained as yellow needles in 60% yield. A single crystal of (4), m.p. 420–421 K (uncorr.), was obtained by slow recrystallization from ethanol.

All data were collected on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer. Unit-cell parameters were obtained by a least-squares refinement of 25 reflections. Intensity data were collected in the ω mode with a variable scan rate of 4 to 29·3° min^{-1} using graphite-monochromated Mo $K\alpha$ radiation. Lorentz and polarization corrections were made, and ψ-scan-based empirical absorption corrections were applied. The intensities of standard reflections varied

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[*] Authors to whom correspondence should be addressed.

[†] On leave from the Faculty of Technology, University of Zagreb, Zagreb, Yugoslavia.

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Table 1. *Crystal and refinement data*

	(3)	(4)
Color	Light yellow	Yellow
Crystal size (mm)	0·43 × 0·30 × 0·30	0·25 × 0·38 × 0·38
2θ range for data collection (°)	3–55	3–50
2θ range for lattice parameters (°)	23·73–29·96	37·04–44·19
Systematic extinction	$h0l$, $l = 2n + 1$ $0k0$, $k = 2n + 1$	$h00$, $h = 2n + 1$ $0k0$, $k = 2n + 1$
Monitored reflections	$133,\bar{2}02$	$\bar{2}37,\bar{6}44$
h,k,l, range	− 10,10;0,10;0,28	0,12;0,15;0,16
Number of reflections measured	3876	2137
Number of unique reflections	3299	1997
R_{int}	0·010	0·008
Number with $I \geq 3\sigma(I)$	2624	1648
Transmission factors	0·607–0·692	0·838–0·886
Number of parameters	248	238
R	0·0417	0·0441
wR	0·0425	0·0530
R (all data)	0·0582	0·0589
wR (all data)	0·0551	0·0620
S	1·470	1·209
$(\Delta/\sigma)_{\text{max}}$	0·013	0·010
Max. electron density (e Å^{-3})	0·27	0·33
Min. electron density (e Å^{-3})	−0·30	−0·29
g (weight)	0·00025	0·00091
x (isotropic extinction parameter)*	0·0056 (2)	—

$*F = F_c/[1{\cdot}0 + (x)0{\cdot}002F_c^2/\sin(2\theta)]$.

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$) *for* (3)

	x	y	z	U_{eq}*
Fe	1735 (1)	3205 (1)	4024 (1)	37 (1)
C(1)	1567 (3)	630 (3)	3880 (1)	38 (1)
C(2)	− 216 (3)	358 (4)	4016 (1)	47 (1)
C(3)	− 714 (3)	2168 (4)	4148 (1)	48 (1)
C(4)	− 730 (3)	3019 (4)	3612 (1)	45 (1)
C(5)	− 244 (3)	1746 (4)	3130 (1)	45 (1)
C(6)	1560 (3)	1535 (3)	3312 (1)	36 (1)
C(7)	− 968 (3)	111 (4)	3376 (1)	56 (1)
C(8)	2778 (3)	− 471 (3)	4188 (1)	42 (1)
O(8)	2537 (3)	− 1246 (3)	4640 (1)	67 (1)
O(9)	4172 (2)	− 528 (2)	3908 (1)	51 (1)
C(9)	5406 (3)	− 1566 (4)	4213 (1)	67 (1)
C(10)	2694 (3)	1413 (3)	2811 (1)	43 (1)
O(10)	2307 (3)	867 (4)	2330 (1)	100 (1)
O(11)	4153 (2)	2012 (3)	2931 (1)	63 (1)
C(11)	5311 (4)	1861 (5)	2462 (2)	72 (1)
C(12)	1663 (3)	5245 (4)	3661 (1)	46 (1)
O(12)	1668 (3)	6517 (3)	3419 (1)	69 (1)
C(13)	1641 (3)	3634 (4)	4823 (1)	49 (1)
O(13)	1611 (3)	3894 (3)	5329 (1)	76 (1)
C(14)	3892 (3)	3263 (4)	4092 (1)	52 (1)
O(14)	5251 (2)	3398 (3)	4157 (1)	82 (1)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$) *for* (4)

	x	y	z	U_{eq}*
Fe	1635 (1)	2467 (1)	2201 (1)	41 (1)
C(1)	− 16 (6)	1997 (4)	1616 (4)	32 (2)
C(2)	− 756 (5)	1744 (4)	2482 (4)	44 (2)
C(3)	188 (7)	2037 (5)	3224 (4)	49 (2)
C(4)	299 (6)	3090 (4)	3229 (4)	41 (2)
C(5)	− 632 (5)	3464 (4)	2496 (4)	40 (2)
C(6)	62 (6)	3116 (4)	1591 (4)	38 (2)
C(7)	− 1679 (4)	2677 (4)	2575 (3)	43 (2)
C(8)	− 17 (7)	1215 (4)	829 (4)	47 (2)
C(9)	618 (10)	7801 (6)	− 663 (5)	108 (4)
C(10)	198 (7)	3866 (4)	836 (4)	41 (2)
C(11)	1088 (9)	4250 (5)	− 663 (7)	90 (3)
C(12)	2494 (7)	3598 (5)	2503 (5)	65 (3)
C(13)	2479 (7)	1411 (5)	2724 (6)	68 (3)
C(14)	2530 (5)	2316 (5)	1151 (5)	61 (2)
C(15)	− 2970 (15)	3997 (10)	3947 (11)	256 (9)
C(16)	− 2149 (14)	2088 (15)	4632 (8)	340 (13)
C(17)	− 4127 (12)	2058 (17)	3358 (10)	430 (16)
O(8)	− 554 (6)	400 (4)	918 (4)	82 (2)
O(9)	531 (5)	1514 (3)	84 (3)	74 (2)
O(10)	− 278 (6)	4689 (4)	850 (4)	88 (2)
O(11)	945 (5)	3578 (4)	152 (3)	77 (2)
O(12)	3053 (6)	4331 (4)	2678 (5)	114 (3)
O(13)	3010 (6)	735 (4)	2990 (5)	116 (3)
O(14)	3144 (4)	2173 (5)	520 (4)	100 (2)
Si	− 2727 (2)	2712 (2)	3632 (1)	65 (1)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

by less than ±2% for (3) and ±3% for (4). The structures were solved by direct methods and refined by a block-cascade least-squares technique. The H atoms in (3) were located in a difference map and were refined with isotropic thermal parameters. Because of the large thermal motion in (4), the H atoms were allowed to ride on the attached atoms and three separate groups of isotropic thermal parameters were refined, *i.e.* one parameter for the trimethylsilyl group, one for the two methyl esters and one for the remaining H atoms; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + g\,F_o^2]^{-1}$. Crystal and refinement data are presented in Table 1. All computer programs supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30 Microeclipse and Nova 4/C configurations; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Tables 2 and 3 give the atomic positional parameters for (3) and (4) while Tables 4 and 5 list selected interatomic distances and valence angles. Figs. 1 and 2 are drawings of the two compounds.*

Discussion. The Fe atoms in (3) and (4) are bound to three carbonyl groups and to the two double bonds of the substituted norbornadiene moieties. The geometries can be described as distorted trigonal bipyramids with the carbonyl C(14) atom and the midpoint of the C(3)—C(4) double bond occupying the approximate axial sites. In each compound, the Fe(0) atom is not equidistant from the two double bonds. The distances from Fe(0) to the midpoint of the longest double bond, $M(1,6)$, average 1·928 (6) Å for (3) and (4) while the distances to the midpoint of the

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52137 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Selected bond distances* (Å)

	(3)	(4)		(3)	(4)
Fe—C(1)	2·056 (3)	2·052 (6)	C(4)—C(5)	1·525 (4)	1·529 (9)
Fe—C(3)	2·212 (2)	2·206 (7)	C(5)—C(6)	1·540 (3)	1·560 (9)
Fe—C(4)	2·204 (2)	2·206 (6)	C(5)—C(7)	1·528 (4)	1·517 (7)
Fe—C(6)	2·047 (2)	2·076 (6)	C(6)—C(10)	1·479 (3)	1·456 (8)
Fe—*M*(1,6)*	1·922 (3)	1·934 (6)	C(8)—O(8)	1·190 (3)	1·203 (8)
Fe—*M*(3,4)*	2·101 (3)	2·099 (7)	C(8)—O(9)	1·331 (3)	1·278 (8)
Fe—C(12)	1·794 (3)	1·777 (7)	O(9)—C(9)	1·452 (3)	1·430 (9)
Fe—C(13)	1·797 (3)	1·798 (7)	C(10)—O(10)	1·175 (3)	1·177 (7)
Fe—C(14)	1·786 (3)	1·795 (7)	C(10)—O(11)	1·313 (3)	1·320 (8)
C(1)—C(2)	1·531 (3)	1·509 (8)	O(11)—C(11)	1·442 (4)	1·461 (10)
C(1)—C(6)	1·439 (3)	1·444 (7)	C(12)—O(12)	1·135 (3)	1·147 (9)
C(1)—C(8)	1·471 (3)	1·511 (8)	C(13)—O(13)	1·133 (3)	1·108 (10)
C(2)—C(3)	1·516 (4)	1·515 (9)	C(14)—O(14)	1·133 (3)	1·133 (8)
C(2)—C(7)	1·530 (4)	1·563 (7)	Si—C(7)	—	1·887 (5)
C(3)—C(4)	1·358 (4)	1·361 (8)			

* *M*(1,6) and *M*(3,4) are the midpoints of bonds C(1)—C(6) and C(3)—C(4).

Table 5. *Selected valence angles* (°)

	(3)	(4)
M(1,6)—Fe—*M*(3,4)*	71·0 (1)	70·7 (2)
M(1,6)—Fe—C(12)	124·0 (1)	121·6 (2)
M(1,6)—Fe—C(13)	129·7 (1)	132·9 (2)
M(1,6)—Fe—C(14)	96·8 (1)	96·6 (2)
M(3,4)—Fe—C(12)	97·1 (1)	98·7 (2)
M(3,4)—Fe—C(13)	96·5 (1)	96·5 (2)
M(3,4)—Fe—C(14)	167·5 (1)	166·8 (2)
C(12)—Fe—C(13)	105·4 (1)	104·8 (3)
C(12)—Fe—C(14)	91·7 (1)	90·8 (3)
C(13)—Fe—C(14)	89·7 (1)	89·8 (3)
C(2)—C(1)—C(6)	105·5 (2)	105·4 (5)
C(2)—C(1)—C(8)	118·1 (2)	117·9 (5)
C(6)—C(1)—C(8)	132·3 (2)	130·3 (5)
C(1)—C(2)—C(3)	100·2 (2)	99·8 (5)
C(1)—C(2)—C(7)	101·4 (2)	103·8 (4)
C(3)—C(2)—C(7)	101·1 (2)	100·0 (4)
C(2)—C(3)—C(4)	106·9 (2)	108·1 (5)
C(3)—C(4)—C(5)	106·6 (2)	104·6 (5)
C(4)—C(5)—C(6)	99·7 (2)	99·6 (5)
C(4)—C(5)—C(7)	100·9 (2)	102·9 (4)
C(6)—C(5)—C(7)	101·9 (2)	103·0 (4)
C(1)—C(6)—C(5)	104·5 (2)	103·8 (5)
C(1)—C(6)—C(10)	129·4 (2)	133·2 (5)
C(5)—C(6)—C(10)	116·7 (2)	118·3 (5)
C(2)—C(7)—C(5)	93·9 (2)	92·1 (4)

* *M*(1,6) and *M*(3,4) are the midpoints of bonds C(1)—C(6) and C(3)—C(4).

shortest double bond average 2·100 (6) Å. This discrepancy in lengths may be related to the axial position of *M*(3,4) and to the shorter C(3)—C(4) double bonds of 1·359 (2) Å (average) compared to the average C(1)—C(6) distance of 1·442 (3) Å. The four C atoms associated with these double bonds are significantly pyramidalized. The interplanar angles between C(2)C(1)C(6)C(5) and C(8)C(1)C(6)C(10) are 30·1 (4) and 27·6 (9)° for (3) and (4), respectively. In (3) the interplanar angle between C(2)C(3)-C(4)C(5) and H(3)C(3)C(4)H(4) is 13 (1)°, which is consistent with the shorter C(3)—C(4) double bond and less pyramidalization. The H atoms in (4) were not refined.

The Fe—C(O) distances in (3) and (4) average 1·792 (6) and 1·790 (11) Å, respectively, which compare well with the normal range of 1·78–1·79 Å (Cotton, Day, Frenz, Hardcastle & Troup, 1973). In (3) the thermal motion is considerably smaller than in (4) and all chemically equivalent bonds in the norbornadiene moiety are statistically equivalent. In both compounds the two ester side chains are planar (0·02 r.m.s.d.) with interplanar angles of 62·9 (8) and 47 (1)°, respectively. No structural reports of Fe(0) bound simultaneously to the two endocyclic double bonds of norbornadiene could be found; however, structures with metals such as rhodium and palladium have been reported (Chizhevsky, Koridze, Bakhmutov, Kolobova, Andrianov & Struchkov, 1981; Allen, Lock, Turner & Powell, 1975; Baenziger, Richards & Doyle, 1965).

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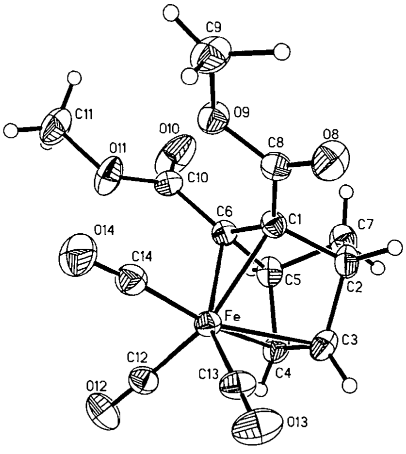

Fig. 1. Drawing of (3) with thermal ellipsoids drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

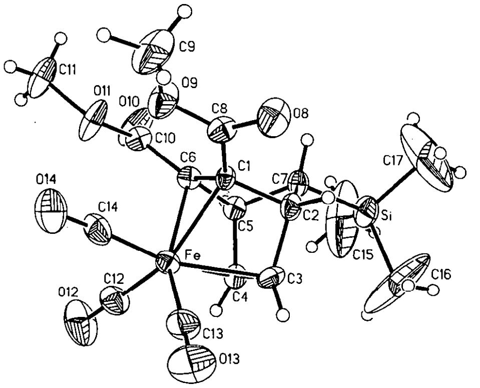

Fig 2. Drawing of (4) with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

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Structure of μ-1,2-Phenylene-bis(trifluoroacetato)dimercury(II)

By Suzanne Deguire and André L. Beauchamp*

Département de Chimie, Université de Montréal, CP 6128, *Succ. A, Montréal, Québec, Canada H*3*C* 3*J*7

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Abstract. $[Hg_2(C_2F_3O_2)_2(C_6H_4)]$, M_r = 703·31, monoclinic, $P2/n$, a = 5·071 (4), b = 11·174 (9), c = 12·750 (5) Å, β = 94·10 (5)°, V = 720·6 Å^3, Z = 2, D_x = 3·241 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 21·36 mm^{-1}, F(000) = 620, T = 175 K, final R = 0·045 for 989 unique observed reflections. One O atom of each CF_3CO_2 group forms a short Hg—O bond of 2·053 (12) Å, whereas the other takes part in bidentate Hg···O interactions [2·844 (11), 2·878 (13) Å] with both Hg atoms in a neighboring molecule.

Introduction. Bidentate Lewis acids containing the 1,2-phenylenedimercury unit can recognize and bind donor atoms in various organic molecules. For instance, dimethylformamide is bound in a cooperative manner by the adjacent Hg atoms of phenylenedimercury dichloride (Beauchamp, Olivier, Wuest & Zacharie, 1987). Tetrahydrofuran is similarly bound to pairs of Hg atoms in a tetradentate organomercury–perfluoroglutarate macrocycle (Wuest & Zacharie, 1987). The title trifluoroacetate compound attracted our attention because of its ability to activate thiocarbonyl groups towards nucleophilic attack (Wuest & Zacharie, 1985). This compound was expected to contain, like phenylmercury trifluoroacetate (Kamenar, Penavic & Hergold-Brundic, 1984), linear two-coordinate Hg atoms forming primary bonds with an aromatic C atom and one of the CF_3CO_2 O atoms. In order to determine how the residual Lewis acidity of the pair of Hg atoms would be expressed in this compound, its crystal structure was determined.

Experimental. Compound prepared by Wuest & Zacharie (1985), who kindly provided a sample of colorless crystals grown by recrystallization from acetonitrile. Plate, 0·33 × 0·27 × 0·019 mm. Enraf–Nonius CAD-4 diffractometer, reduced cell obtained from 25 centered reflections ($11 < \theta < 17°$) found by the automatic search procedure, primitive monoclinic lattice deduced from the Niggli matrix, cell dimensions and monoclinic Laue symmetry checked with axial photographs, systematic absences determined from full data set ($h0l$, $h + l = 2n + 1$), consistent with space groups Pn and $P2/n$ (alternative definitions of Pc, No. 7, and $P2/c$, No. 13, respectively). Accurate cell dimensions by least-squares fit on the setting angles for the 25 reflections. Detailed procedure for data collection described elsewhere (Bélanger-Gariépy & Beauchamp, 1980), graphite-monochromatized Mo $K\bar{\alpha}$ radiation, $2\theta_{\max}$ = 50°, $0 \le h \le 6$, $0 \le k \le 13$, $-15 \le l \le 15$, orientation checked every 100 measurements, intensity of three standards checked every hour, max. fluctuation 3·7%, 1264 independent reflections measured, 989 with $I > 3·0\sigma(I)$. Data corrected for Lp and absorption, transmission range 0·088–0·667.

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* To whom correspondence should be addressed.

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