Program(s) used to refine structure: *CRYM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CRYM*.

WPS thanks Harry B. Gray for insightful comments on the structure. This work was supported by the Gas Research Institute, Chicago, IL, and the US Department of Energy, Morgantown Energy Technology Center, Morgantown, WV.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2255–2258

3,4-Bis(*tert*-butoxy)-2,4-cyclopentadien-1-one and its *fac*-Tricarbonyliron(0) Complex

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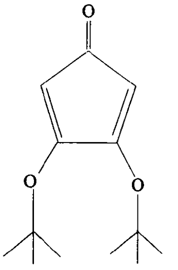
(*Received* 7 *December* 1994; *accepted* 1 *March* 1995)

Abstract

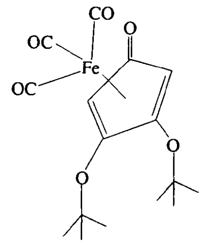
The crystal structures of 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one, $C_{13}H_{20}O_3$, and *fac*-[η^5-3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one]tricarbonyliron(0), $[Fe(C_{13}H_{20}O_3)(CO)_3]$, have been determined. The organic compound is planar with the positions of the double bonds well defined. The inclusion of an $Fe(CO)_3$ moiety induces a loss of planarity, producing an envelope form and delocalization of the double bonds.

Comment

The ring of the 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one molecule, (II), is planar; the largest deviation of an atom from the mean plane is 0.001 (5) Å. The double bonds are well defined with C(2)═C(3) and C(4)═C(5) of average length 1.321 (6) Å, and C(3)—C(4) of length 1.530 (5) Å.



(I)



(II)

The Fe atom of the iron complex, (I), is octahedrally coordinated to three carbonyl ligands in *fac* positions and the 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one moiety on the opposite face of the octahedron. The Fe—CO bond lengths [average value 1.807 (9) Å] are similar to those observed in other iron complexes with C_{sp^2} atoms *trans* to the carbonyl ligands (average value 1.790 Å) (Ros, Viñas, Mathieu, Solans & Font-Bardia, 1988; Yañez, Ros, Mathieu, Solans & Font-Bardia, 1990; Yañez, Ros, Solans, Font-Bardia & Mathieu, 1990; Yañez, Ros, Salans, Font-Altaba & Mathieu, 1990). The distance between the centroid of the five-membered ring and the Fe atom is 1.777 (4) Å, similar to that observed in ferrocenyl (1.64 Å) (Bosque, Font-Bardia, López, Sales, Silver & Solans, 1994; López, Solans & Tramuns, 1994).

The greatest π-donor character of C(1) in the five-membered ring produces a C(8)—Fe—Cp—C(1) torsion angle of −6.3 (2)° (Cp is the centroid of the cyclopentadienyl ring), thus avoiding a carbonyl group in the *trans* position. It also results in a lengthening of the Fe—C(1) bond [2.368 (4) Å] in comparison to the average of 2.106 (26) Å for the remaining Fe—C(ring) bond lengths, as well as the loss of planarity of the five-membered ring [envelope form, with C(1) −0.298 (4) Å out of the mean plane defined by the remaining four atoms]. This is associated with an electronic delocalization of the C(3)—C(4) bond, which has a length of 1.444 (5) Å, similar to the average value of C(2)—C(3) and C(4)—C(5) [1.436 (5) Å]. Thus, the geometry values of the five-membered ring in the Fe complex are intermediate between those obtained for the free molecule and those found in 3α-epoxypumilin (Seaman, Malcolm, Fronczek, Lee & Fischer, 1984) and in 4-(2′-aminoethyl)-1,8,8-trimethoxy-2,6-dioxobicyclo-[3.2.1]oct-3-ene (Yonemitsu, Nakai, Kanaoka, Karle & Witkop, 1970).

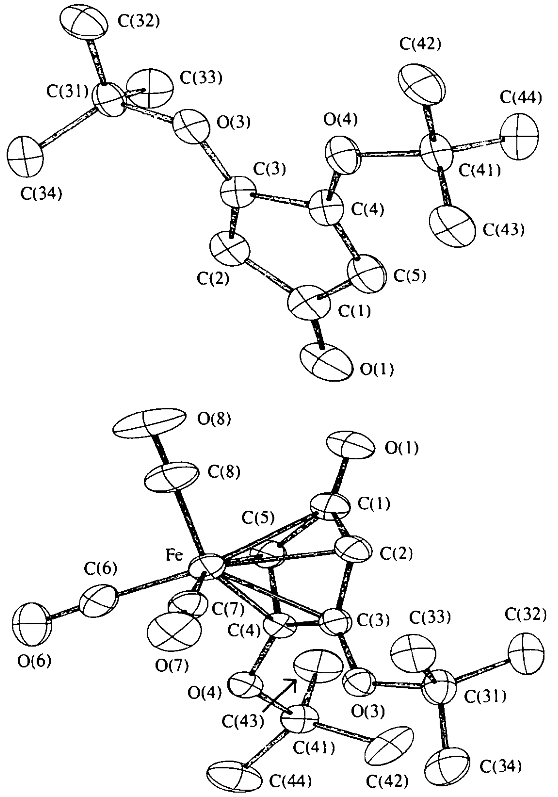


Fig. 1. *ORTEP*II (Johnson, 1976) views of 3,4-bis(*tert*-butoxy)-2,4-cyclopentadien-1-one and its iron complex. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Compound (I)

Crystal data

$[Fe(C_{13}H_{20}O_3)(CO)_3]$
$M_r = 364.17$
Monoclinic
$P2_1/a$
$a = 13.363\ (3)$ Å
$b = 12.802\ (2)$ Å
$c = 10.828\ (2)$ Å
$\beta = 107.04\ (2)°$
$V = 1771.1\ (6)$ Å^3
$Z = 4$
$D_x = 1.366$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–$12°$
$\mu = 0.877$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Philips PW1100 four-circle diffractometer
ω scans
Absorption correction: none
2307 measured reflections
2197 independent reflections
2147 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 25°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.124$
$S = 0.972$
2147 reflections
270 parameters
All H atoms from difference synthesis and refined isotropically with an overall $U_{\rm iso}$
$w = 1/[\sigma^2(I) + (0.0965P)^2 + 0.7763P]$
where $P = (|F_o|^2 + 2|F_c|^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.3$
$\Delta\rho_{\rm max} = 0.67$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.67$ e Å^{-3}
Extinction correction: *SHELXL*93 (Shledrick, 1993)
Extinction coefficient: 0.031 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Compound (II)

Crystal data

$C_{13}H_{20}O_3$
$M_r = 224.29$
Monoclinic
$P2_1/c$
$a = 11.679\ (3)$ Å
$b = 9.741\ (2)$ Å
$c = 11.740\ (3)$ Å
$\beta = 95.50\ (3)°$
$V = 1329.5\ (6)$ Å^3
$Z = 4$
$D_x = 1.121$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–$12°$
$\mu = 0.078$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Philips PW1100 four-circle diffractometer
ω scans
Absorption correction: none
1432 measured reflections
1021 independent reflections
971 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.037$
$\theta_{\rm max} = 25°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.052$
$wR(F^2) = 0.126$
$S = 0.930$
971 reflections
153 parameters
All H atoms calculated and refined isotropically using a riding model and an overall $U_{\rm iso}$
$w = 1/[\sigma^2(I) + (0.1058P)^2 + 0.2110P]$
where $P = (|F_o|^2 + 2|F_c|^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.007 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (I)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe	0.8353 (1)	0.0382 (1)	0.1686 (1)	0.045 (1)
C(1)	0.8960 (3)	−0.0867 (3)	0.3351 (4)	0.051 (1)
O(1)	0.9800 (2)	−0.1279 (3)	0.3903 (3)	0.067 (1)
C(2)	0.8522 (3)	0.0123 (3)	0.3677 (4)	0.047 (1)
C(3)	0.7432 (3)	0.0161 (3)	0.2983 (3)	0.041 (1)
O(3)	0.6640 (2)	0.0770 (2)	0.3091 (2)	0.048 (1)
C(31)	0.6662 (4)	0.1344 (4)	0.4285 (4)	0.059 (1)
C(32)	0.6990 (6)	0.0626 (6)	0.5450 (5)	0.083 (2)
C(33)	0.7384 (5)	0.2302 (4)	0.4435 (6)	0.074 (2)
C(34)	0.5536 (5)	0.1687 (6)	0.3994 (7)	0.086 (2)
C(4)	0.7230 (3)	−0.0629 (3)	0.1988 (3)	0.039 (1)
O(4)	0.6300 (2)	−0.0813 (2)	0.1092 (2)	0.042 (1)
C(41)	0.5601 (3)	−0.1623 (3)	0.1370 (4)	0.047 (1)
C(42)	0.5236 (6)	−0.1285 (5)	0.2490 (7)	0.084 (2)
C(43)	0.6171 (5)	−0.2660 (4)	0.1654 (6)	0.070 (1)
C(44)	0.4731 (5)	−0.1679 (5)	0.0109 (6)	0.080 (2)
C(5)	0.8198 (3)	−0.1178 (3)	0.2133 (4)	0.047 (1)
C(6)	0.7829 (4)	0.0190 (4)	−0.0035 (5)	0.060 (1)
C(7)	0.8063 (3)	0.1756 (4)	0.1577 (4)	0.056 (1)
O(7)	0.7861 (3)	0.2621 (3)	0.1484 (4)	0.088 (1)
O(6)	0.7468 (3)	0.0066 (3)	−0.1114 (3)	0.086 (1)
C(8)	0.9738 (4)	0.0487 (4)	0.1816 (6)	0.077 (2)
O(8)	1.0592 (3)	0.0564 (4)	0.1894 (6)	0.123 (2)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (II)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.1487 (3)	0.1588 (4)	0.0298 (4)	0.056 (1)
O(1)	0.0949 (3)	0.1782 (3)	−0.0639 (3)	0.080 (1)
C(2)	0.1263 (3)	0.0525 (4)	0.1128 (4)	0.052 (1)
C(3)	0.2017 (3)	0.0689 (4)	0.2026 (3)	0.042 (1)
O(3)	0.2233 (2)	0.0088 (2)	0.3034 (2)	0.048 (1)
C(31)	0.1469 (3)	−0.1027 (4)	0.3407 (3)	0.045 (1)
C(32)	0.2001 (4)	−0.1323 (5)	0.4603 (3)	0.069 (1)
C(33)	0.0259 (3)	−0.0459 (5)	0.3427 (4)	0.064 (1)
C(34)	0.1525 (4)	−0.2252 (4)	0.2628 (4)	0.065 (1)
C(4)	0.2796 (3)	0.1907 (4)	0.1810 (4)	0.046 (1)
O(4)	0.3610 (2)	0.2189 (2)	0.2648 (2)	0.054 (1)
C(41)	0.4251 (3)	0.3497 (4)	0.2689 (3)	0.051 (1)
C(42)	0.5040 (4)	0.3347 (5)	0.3767 (4)	0.075 (1)
C(43)	0.4923 (3)	0.3660 (5)	0.1662 (4)	0.070 (1)
C(44)	0.3402 (4)	0.4663 (5)	0.2793 (4)	0.078 (2)
C(5)	0.2464 (3)	0.2419 (4)	0.0787 (4)	0.057 (1)

Table 3. *Selected bond lengths* (Å) *and bond angles* (°) *for* (I) *and* (II)

	(I)	(II)
Fe–C(7)	1.798 (5)	–
Fe–C(6)	1.805 (5)	–
Fe–C(8)	1.820 (6)	–
Fe–C(4)	2.079 (4)	–
Fe–C(5)	2.080 (4)	–
Fe–C(2)	2.127 (4)	–
Fe–C(3)	2.140 (4)	–
Fe–C(1)	2.368 (4)	–
C(1)—O(1)	1.226 (5)	1.227 (5)
C(1)—C(5)	1.466 (6)	1.471 (6)
C(1)—C(2)	1.481 (6)	1.463 (6)
C(2)—C(3)	1.431 (5)	1.317 (5)
C(3)—O(3)	1.347 (4)	1.323 (4)
C(3)—C(4)	1.444 (5)	1.530 (5)
O(3)—C(31)	1.480 (5)	1.497 (4)
C(31)—C(34)	1.509 (7)	1.508 (5)
C(31)—C(32)	1.518 (8)	1.508 (5)
C(31)—C(33)	1.539 (7)	1.520 (5)
C(4)—O(4)	1.354 (4)	1.329 (4)
C(4)—C(5)	1.440 (5)	1.325 (6)
O(4)—C(41)	1.485 (4)	1.476 (4)
C(41)—C(42)	1.498 (7)	1.500 (5)
C(41)—C(43)	1.516 (6)	1.508 (5)
C(41)—C(44)	1.514 (7)	1.521 (6)
C(6)—O(6)	1.137 (6)	–
C(7)—O(7)	1.138 (6)	–
C(8)—O(8)	1.123 (6)	–
C(7)–Fe–C(6)	93.1 (2)	–
C(7)–Fe–C(8)	97.3 (2)	–
C(6)–Fe–C(8)	99.7 (3)	–
O(1)—C(1)—C(5)	128.1 (4)	125.2 (4)
O(1)—C(1)—C(2)	128.4 (4)	126.6 (4)
C(5)—C(1)—C(2)	103.2 (3)	108.2 (4)
O(1)—C(1)–Fe	136.2 (3)	–
C(3)—C(2)—C(1)	108.4 (3)	107.4 (4)
O(3)—C(3)—C(2)	132.7 (3)	135.9 (3)
O(3)—C(3)—C(4)	119.4 (3)	115.1 (3)
C(2)—C(3)—C(4)	107.9 (3)	108.9 (3)
C(4)—C(3)–Fe	67.7 (2)	–
C(3)—O(3)—C(31)	123.3 (3)	120.9 (3)
O(3)—C(31)—C(34)	101.5 (4)	109.6 (3)
O(3)—C(31)—C(32)	110.6 (4)	102.0 (3)
C(34)—C(31)—C(32)	112.2 (5)	112.0 (3)
O(3)—C(31)—C(33)	109.8 (4)	108.8 (3)
C(34)—C(31)—C(33)	110.3 (5)	113.0 (3)
C(32)—C(31)—C(33)	112.1 (5)	110.8 (3)
O(4)—C(4)—C(3)	126.0 (3)	115.6 (3)
O(4)—C(4)—C(5)	126.8 (3)	136.0 (3)
C(3)—C(4)—C(5)	107.1 (3)	108.4 (3)
O(4)—C(4)–Fe	123.3 (2)	–
C(4)—O(4)—C(41)	118.4 (3)	121.8 (3)
O(4)—C(41)—C(42)	109.6 (3)	102.3 (3)
O(4)—C(41)—C(43)	110.2 (4)	111.4 (3)
C(42)—C(41)—C(43)	110.6 (5)	111.1 (3)
O(4)—C(41)—C(44)	102.3 (3)	108.4 (3)
C(42)—C(41)—C(44)	113.4 (5)	110.9 (4)
C(43)—C(41)—C(44)	110.4 (4)	112.3 (4)
C(4)—C(5)—C(1)	109.3 (3)	107.1 (4)
O(6)—C(6)–Fe	177.9 (4)	–
O(7)—C(7)–Fe	178.4 (5)	–
O(8)—C(8)–Fe	179.2 (5)	–

The structures was solved by direct methods and refined by full-matrix least squares.

For both compounds, data collection: Philips diffractometer software; cell refinement: Philips diffractometer software; data reduction: *CFEO* (Solans, 1978); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXS*86 *CIFTAB*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2258–2259

trans-Bis(*O*,*O*′-diethyl dithiophosphato-*S*,*S*′)bis(4-methylpyridine)nickel(II)

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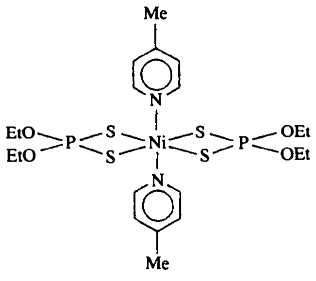
(*Received* 11 *January* 1995; *accepted* 11 *April* 1995)

Abstract

The Ni atom in *trans*-bis(*O*,*O*′-diethyl dithiophosphato-*S*,*S*′)bis(4-methylpyridine)nickel(II), [$Ni\{(C_2H_5O)_2PS_2\}_2(C_6H_7N)_2$], has slightly distorted octahedral coordination. It lies in the plane formed by the four S atoms of the two chelating diethyl dithiophosphates; the two 4-methylpyridine ligands occupy axial sites. The Ni—S bond lengths are 2.488 (1) and 2.498 (1) Å and the Ni—N2 bond lengths are 114 (4) Å.

Comment

Dialkyl dithiophosphate complexes of transition metals have received increasing attention in recent years owing to their extensive applications in lubrication engineering and in the plastics industry (So, Lin, Huang Gibbs & Chang Terny, 1993; Mikhailov, Kokhanov, Kazaryan, Matreeva & Kozodoi, 1970). In addition to their syntheses and various physicochemical investigations, the crystal structures of many of these complexes and their adducts with nitrogen bases have been reported (McConnell & Kastalsky, 1967; Ooi & Fernando, 1970; Huang, Xiong, Dong & You, 1995). In a continuation of our investigation of the reaction of (diethyl dithiophosphate)nickel(II) with neutral nitrogen bases we determined the crystal structure of *trans*-[$Ni\{(C_2H_5O)_2PS_2\}_2(C_6H_7N)_2$], (I).



(I)

The Ni atom in (I) is coordinated to four S atoms and two *trans* N atoms. The dihedral angle between the plane of Ni, C(1), C(2), C(3), C(4), C(5), N and C(6) and that of Ni, S(1), S(2) and P is 88.66 (7)°. In agreement with the data for [$Ni\{(C_2H_5O)_2PS_2\}_2(C_5H_5N)_2$] (Ooi & Fernando, 1970), the Ni—S bond distances are 2.488 (1) and 2.498 (1) Å, the Ni—N bond distances are 2.114 (4) Å, and the S(1)—Ni—S(2) and S(1)—Ni—N bond angles are 81.30 (5) and 90.5 (1)°, respectively.

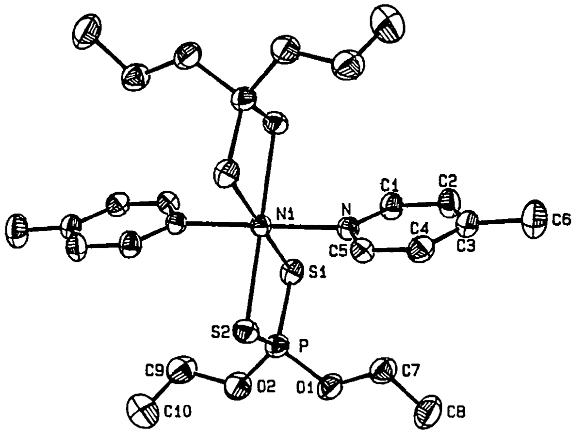


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Bis(*O*,*O*′-diethyl dithiophosphato)nickel(II) was dissolved in ethanol and 4-methylpyridine in $CHCl_3$ solution was added