suggest that III is an adequate description for the present dithiocarbimate structure as well.

The mechanism of formation of the present complex, especially the abstraction of the "extra S atom" from the medium, remains unaccounted for. The compound can be formed by reaction of excess EtOCONCS with the initially formed Pd(SCNCOOEt)$(PPh_3)_2$. Whether the organic fragment, EtOOCNC, is trapped by PPh_3 is a possibility that is now under study.

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Registry No. Pd(S_2CNCOOEt)$(PPh_3)_2$, 61202-76-4; Pd(SCNCOOEt)$(PPh_3)_2$, 61202-77-5; $Pd_2(dba)_3$, 52409-22-0.

Supplementary Material Available: Table IV, the root-mean-square amplitudes of vibration, and Table V, the structure amplitudes (41 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of 1,1'-(Tetraphenyl-*o*-phenylene)ferrocene

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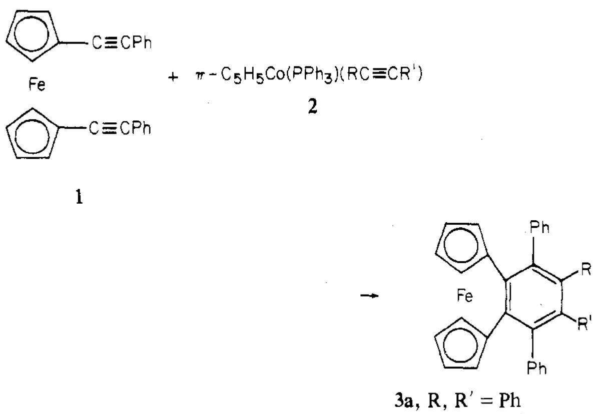
1,1'-(Tetraphenyl-*o*-phenylene)ferrocene, $C_{40}H_{28}Fe$, crystallizes in the monoclinic of space group $P2_{1/a}$, and four molecules in the unit cell with $a = 24.342$ (7), $b = 10.959$ (5), $c = 11.397$ (5) Å, and $\beta = 112.69$ (3)°. A single-crystal x-ray structural analysis has been completed. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located, the final discrepancy indices being $R_1 = 5.40$ % and $R_2 = 6.25$ % for 2939 independent reflections. The cyclopentadienyl rings in the ferrocene moiety are eclipsed and tilted by 23.7°.

Introduction

Reaction of 1,1'-bis(phenylethynyl)ferrocene (**1**) with acetylene–cobalt complexes (**2**) yielded 1,1'-(*o*-phenylene)ferrocene, (*o*-phenylene)-[2]ferrocenophane, derivatives (**3**).



3a, R, R' = Ph
b, R = Ph; R' = CO_2CH_3
c, R, R' = CO_2CH_3

The structures **3** have been presented on the basis of their microanalyses and spectral properties.[1] In particular, the ^1H NMR spectra exhibited a set of A_2B_2 patterns associated with the ferrocenyl rings for **3a** and **3c** and two broad signals attributable to the overlap of two sets of A_2B_2 patterns for **3b**.

It has been known that the splitting of the A_2B_2 signals of the ferrocenyl protons[2] and the electronic spectra, especially the band corresponding to λ_{max} 440 nm of $(C_5H_5)_2Fe$, correlate to ring-tilt distortion angle in [*m*]ferrocenophane.[3] Structural features of the ferrocene and benzene moiety of **3a**, a new [2]ferrocenophane with the shortest bridging group, e.g., two sp^2 carbons, are of great interest in connection with the large splitting ($\Delta\delta = 0.87$) of the A_2B_2 signals and λ_{max} 466 nm ($\epsilon = 470$) of this compound. We now report the crystal structure of **3a**.

Experimental Section

Recrystallization of air-stable **3a**, $C_{40}H_{28}Fe$, from hexane/methylene chloride gave well-formed columnar crystals suitable for x-ray studies. Precession and Weissenberg photography indicated that the crystals were monoclinic with the systematic absence of *h*0*l*, $h = 2n + 1$, and 0*k*0, $k = 2n + 1$, consistent with space group $P2_{1/a}$. Cell constants of $a = 24.342$ (7) Å, $b = 10.959$ (5) Å, $c = 11.397$ (5) Å, and $\beta = 112.69$ (3)° were determined from high-order reflections on a Rigaku four-circle automated diffractometer. The unit cell volume is 2805.0 Å^3, yielding a calculated density of 1.337 g cm^{-3} for $M = 564.5$ and $Z = 4$. [The experimental density is 1.38 (10) g cm^{-3} by flotation

Table I. Final Atomic Parameters and Their Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.1096 (0)	0.2144 (1)	0.2096 (1)	0.0009 (0)	0.0054 (1)	0.0045 (1)	−0.0000 (0)	0.0006 (0)	0.0002 (1)
C(1)	0.0041 (2)	0.2469 (5)	−0.0161 (5)	0.0008 (1)	0.0049 (5)	0.0046 (5)	−0.0001 (2)	0.0005 (2)	−0.0001 (4)
C(2)	−0.0169 (2)	0.2065 (5)	0.0744 (5)	0.0009 (1)	0.0059 (5)	0.0055 (5)	0.0000 (2)	0.0008 (2)	−0.0002 (5)
C(3)	−0.0780 (2)	0.1988 (5)	0.0479 (5)	0.0010 (1)	0.0053 (5)	0.0059 (5)	−0.0002 (2)	0.0011 (2)	−0.0003 (4)
C(4)	−0.1183 (2)	0.2334 (5)	−0.0759 (5)	0.0008 (1)	0.0050 (5)	0.0071 (6)	−0.0003 (2)	0.0007 (2)	−0.0001 (4)
C(5)	−0.0974 (2)	0.2685 (5)	−0.1693 (5)	0.0009 (1)	0.0053 (5)	0.0060 (6)	−0.0000 (2)	0.0006 (2)	−0.0002 (4)
C(6)	−0.0352 (2)	0.2780 (5)	−0.1396 (5)	0.0012 (1)	0.0052 (5)	0.0052 (5)	−0.0003 (2)	0.0009 (2)	−0.0011 (5)
C(11)	0.0709 (2)	0.2612 (5)	0.0287 (5)	0.0013 (1)	0.0057 (5)	0.0047 (5)	−0.0005 (2)	0.0013 (2)	−0.0007 (4)
C(12)	0.1031 (2)	0.3648 (5)	0.1003 (5)	0.0013 (1)	0.0062 (6)	0.0051 (6)	−0.0006 (2)	0.0007 (2)	0.0002 (5)
C(13)	0.1645 (3)	0.3303 (6)	0.1588 (5)	0.0014 (1)	0.0088 (7)	0.0056 (6)	−0.0009 (2)	0.0009 (2)	0.0002 (5)
C(14)	0.1704 (2)	0.2096 (7)	0.1220 (5)	0.0012 (1)	0.0108 (7)	0.0061 (6)	0.0001 (3)	0.0011 (2)	0.0005 (6)
C(15)	0.1128 (2)	0.1647 (6)	0.0403 (5)	0.0012 (1)	0.0075 (6)	0.0058 (6)	0.0005 (2)	0.0009 (2)	−0.0001 (5)
C(21)	0.0293 (2)	0.1755 (5)	0.2037 (5)	0.0011 (1)	0.0067 (6)	0.0048 (5)	−0.0002 (2)	0.0011 (2)	0.0010 (4)
C(22)	0.0564 (2)	0.2642 (6)	0.3029 (5)	0.0014 (1)	0.0087 (7)	0.0045 (5)	0.0002 (2)	0.0009 (2)	0.0004 (5)
C(23)	0.1096 (3)	0.2096 (7)	0.3920 (5)	0.0014 (1)	0.0108 (7)	0.0053 (6)	−0.0005 (3)	0.0006 (2)	0.0008 (6)
C(24)	0.1143 (3)	0.0908 (6)	0.3515 (6)	0.0014 (1)	0.0080 (7)	0.0085 (7)	0.0006 (2)	0.0009 (3)	0.0034 (5)
C(25)	0.0649 (3)	0.0673 (6)	0.2347 (6)	0.0015 (1)	0.0058 (6)	0.0080 (7)	0.0001 (2)	0.0014 (2)	0.0013 (5)
C(31)	−0.0980 (2)	0.1676 (5)	0.1524 (5)	0.0010 (1)	0.0070 (6)	0.0054 (6)	−0.0009 (2)	0.0008 (2)	−0.0007 (5)
C(32)	−0.1333 (3)	0.2495 (6)	0.1861 (6)	0.0015 (1)	0.0094 (7)	0.0081 (7)	−0.0002 (2)	0.0020 (2)	−0.0011 (5)
C(33)	−0.1494 (3)	0.2211 (8)	0.2885 (7)	0.0022 (2)	0.0159 (10)	0.0114 (9)	−0.0001 (4)	0.0029 (3)	−0.0035 (9)
C(34)	−0.1312 (3)	0.1143 (8)	0.3546 (7)	0.0022 (2)	0.0144 (10)	0.0080 (8)	−0.0012 (3)	0.0018 (3)	0.0008 (7)
C(35)	−0.0967 (3)	0.0347 (7)	0.3230 (6)	0.0022 (2)	0.0101 (8)	0.0084 (8)	−0.0012 (2)	0.0011 (3)	0.0020 (6)
C(36)	−0.0805 (3)	0.0598 (6)	0.2208 (6)	0.0017 (1)	0.0076 (7)	0.0062 (6)	−0.0006 (2)	0.0011 (2)	0.0002 (5)
C(41)	−0.1841 (2)	0.2302 (6)	−0.1054 (5)	0.0009 (1)	0.0080 (6)	0.0060 (6)	0.0002 (2)	0.0009 (2)	0.0001 (5)
C(42)	−0.2156 (3)	0.3395 (7)	−0.1306 (6)	0.0014 (1)	0.0096 (7)	0.0095 (8)	0.0007 (3)	0.0012 (3)	0.0014 (6)
C(43)	−0.2768 (3)	0.3399 (8)	−0.1556 (8)	0.0017 (2)	0.0141 (10)	0.0136 (10)	0.0017 (3)	0.0016 (3)	0.0029 (8)
C(44)	−0.3051 (3)	0.2305 (9)	−0.1581 (7)	0.0011 (1)	0.0216 (13)	0.0132 (9)	0.0004 (4)	0.0011 (3)	0.0004 (10)
C(45)	−0.2736 (3)	0.1192 (8)	−0.1312 (8)	0.0018 (2)	0.0140 (10)	0.0175 (12)	−0.0021 (3)	0.0021 (4)	−0.0028 (9)
C(46)	−0.2133 (3)	0.1219 (6)	−0.1050 (7)	0.0013 (1)	0.0081 (7)	0.0139 (9)	−0.0007 (2)	0.0014 (3)	−0.0009 (6)
C(51)	−0.1402 (2)	0.3038 (5)	−0.2998 (5)	0.0010 (1)	0.0070 (6)	0.0045 (5)	0.0003 (2)	0.0005 (2)	−0.0010 (4)
C(52)	−0.1380 (3)	0.4168 (6)	−0.3516 (6)	0.0017 (1)	0.0060 (6)	0.0062 (6)	0.0005 (2)	0.0008 (2)	−0.0007 (5)
C(53)	−0.1794 (3)	0.4507 (6)	−0.4691 (6)	0.0022 (2)	0.0081 (7)	0.0062 (7)	0.0013 (3)	0.0011 (3)	0.0005 (5)
C(54)	−0.2246 (3)	0.3716 (7)	−0.5376 (6)	0.0013 (1)	0.0150 (10)	0.0065 (7)	0.0015 (3)	0.0007 (2)	−0.0011 (6)
C(55)	−0.2272 (3)	0.2569 (7)	−0.4887 (6)	0.0012 (1)	0.0149 (10)	0.0063 (6)	−0.0004 (3)	0.0004 (2)	−0.0046 (6)
C(56)	−0.1854 (3)	0.2204 (7)	−0.3697 (5)	0.0014 (1)	0.0103 (7)	0.0065 (6)	−0.0006 (3)	0.0011 (2)	−0.0023 (6)
C(61)	−0.0102 (2)	0.3146 (5)	−0.2344 (5)	0.0010 (1)	0.0061 (6)	0.0055 (6)	0.0001 (2)	0.0007 (2)	0.0009 (4)
C(62)	0.0232 (3)	0.4216 (6)	−0.2173 (6)	0.0015 (1)	0.0062 (6)	0.0066 (6)	0.0000 (2)	0.0011 (2)	−0.0004 (5)
C(63)	0.0473 (3)	0.4537 (6)	−0.3049 (6)	0.0016 (1)	0.0079 (7)	0.0084 (7)	−0.0007 (2)	0.0013 (3)	0.0015 (5)
C(64)	0.0398 (3)	0.3819 (7)	−0.4070 (6)	0.0021 (2)	0.0104 (8)	0.0076 (7)	−0.0000 (3)	0.0023 (3)	0.0014 (6)
C(65)	0.0071 (3)	0.2753 (7)	−0.4254 (6)	0.0025 (2)	0.0103 (7)	0.0072 (7)	0.0008 (3)	0.0020 (3)	−0.0002 (6)
C(66)	−0.0181 (3)	0.2422 (6)	−0.3394 (5)	0.0017 (1)	0.0073 (6)	0.0056 (6)	0.0000 (2)	0.0010 (2)	−0.0006 (5)

Atom	x	y	z	β_{11}	Atom	x	y	z	β_{11}
H(12)	0.084 (2)	0.448 (4)	0.114 (4)	1.8 (10)	H(43)	−0.296 (3)	0.442 (7)	−0.187 (7)	7.8 (21)
H(13)	0.196 (3)	0.397 (6)	0.225 (6)	5.5 (17)	H(44)	−0.347 (3)	0.221 (7)	−0.176 (6)	6.8 (18)
H(14)	0.209 (3)	0.143 (6)	0.147 (6)	4.7 (15)	H(45)	−0.296 (3)	0.037 (6)	−0.150 (6)	6.2 (18)
H(15)	0.102 (3)	0.071 (6)	0.001 (6)	4.9 (15)	H(46)	−0.196 (3)	0.044 (6)	−0.085 (6)	6.1 (18)
H(22)	0.039 (3)	0.369 (7)	0.305 (7)	7.8 (20)	H(52)	−0.108 (3)	0.476 (6)	−0.309 (6)	4.2 (14)
H(23)	0.136 (3)	0.247 (6)	0.477 (6)	5.4 (16)	H(53)	−0.175 (2)	0.518 (5)	−0.513 (5)	2.9 (12)
H(24)	0.149 (3)	0.024 (5)	0.388 (5)	4.1 (14)	H(54)	−0.254 (3)	0.411 (7)	−0.627 (7)	7.5 (20)
H(25)	0.059 (2)	0.001 (4)	0.177 (4)	2.1 (11)	H(55)	−0.255 (4)	0.191 (8)	−0.538 (7)	8.8 (23)
H(32)	−0.153 (3)	0.333 (6)	0.128 (6)	4.8 (15)	H(56)	−0.189 (3)	0.127 (6)	−0.328 (6)	4.7 (15)
H(33)	−0.171 (3)	0.286 (6)	0.302 (6)	5.1 (15)	H(62)	0.030 (2)	0.484 (5)	−0.144 (5)	2.4 (11)
H(34)	−0.140 (3)	0.072 (6)	0.430 (6)	6.5 (18)	H(63)	0.072 (3)	0.517 (6)	−0.286 (6)	4.4 (15)
H(35)	−0.083 (3)	−0.033 (7)	0.365 (7)	7.6 (21)	H(64)	0.054 (2)	0.413 (5)	−0.475 (5)	3.5 (13)
H(36)	−0.059 (2)	0.001 (5)	0.195 (5)	3.1 (12)	H(65)	−0.006 (4)	0.240 (8)	−0.506 (8)	9.2 (23)
H(42)	−0.197 (3)	0.425 (6)	−0.109 (6)	6.1 (17)	H(66)	−0.049 (2)	0.159 (5)	−0.356 (5)	4.1 (14)

[a] The temperature factors for heavier atoms are of the form, $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and those for the hydrogen atoms are, $T = \exp[-\beta(\sin\theta/\lambda)^2]$.

in an aqueous solution of potassium iodide.]

The crystal with six faces of the forms {100}, {010}, and {10$\bar{1}$} was mounted such that the c axis was nearly parallel to the ϕ axis of a Rigaku four-circle diffractometer. The perpendicular distances to each of these faces were 0.0072, 0.0438, and 0.0151 cm, respectively. Intensity data were collected by he 2θ–ω scan method using Cu Kα radiation filtered through a nickel foil.[4] A scan rate of 4° min^{-1} was used. Ten-second stationary background counts were taken at the lower and upper limits of each scan. Three standard reflections were monitored before every 52 measurements. A total of 3355 independent intensities in the range $2\theta \leq 130°$ was measured. The 2939 reflections for which $F_o > 3\sigma(F_o)$ were used in the solution and refinement of the structure.

Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient of this compound for Cu Kα radiation is 50.66 cm^{-1}, and an absorption correction was made.[5] The calculated transmission factors varied from 0.405 to 0.700.

Solution and Refinement of Structure. The iron atom was located from a three-dimensional Patterson map. A subsequent Fourier map phased by the iron atom gave the positions of all of the carbon atoms. Six cycles of a block-diagonal least-squares refinement of all the positional and isotropic thermal parameters resulted in the residual factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ of 10.49 and 11.27%, respectively. Further six cycles of a refinement with anisotropic thermal parameters converged to R_1 = 7.35% and R_2 = 8.83%. At this stage a difference-Fourier synthesis revealed all of the 28 hydrogen atoms in the molecule. Six more cycles of block-diagonal least-squares calculations completed the refinement, in which the 28 hydrogen atoms were included. The hydrogen atoms were given isotropic thermal parameters. This refinement converged

Table II. Interatomic Distances (Å) with Esd's

Atoms	Distance	Atoms	Distance
(A) Distances from Iron Atom			
Fe–C(21)	1.975 (6)	Fe–C(11)	1.976 (5)
Fe–C(22)	2.041 (7)	Fe–C(12)	2.036 (6)
Fe–C(23)	2.079 (7)	Fe–C(13)	2.083 (7)
Fe–C(24)	2.078 (7)	Fe–C(14)	2.081 (7)
Fe–C(25)	2.024 (7)	Fe–C(15)	2.036 (7)
Fe-Cp2	1.638 (1)	Fe–Cp1	1.638 (1)
(B) Carbon–Carbon Distances in π-Cyclopentadienyl Rings			
C(11)–C(12)	1.441 (7)	C(21)–C(22)	1.443 (8)
C(11)–C(15)	1.439 (8)	C(21)–C(25)	1.431 (8)
C(12)–C(13)	1.433 (8)	C(22)–C(23)	1.431 (7)
C(13)–C(14)	1.411 (10)	C(23)-C(24)	1.401 (10)
C(14)–C(15)	1.437 (7)	C(24)–C(25)	1.431 (7)
(C) Carbon–Carbon Distances around Central Benzene Ring			
C(1)–C(2)	1.388 (9)	C(1)–C(11)	1.514 (7)
C(1)–C(6)	1.404 (6)	C(2)–C(21)	1.508 (6)
C(2)–C(3)	1.402 (7)	C(3)–C(31)	1.489 (9)
C(3)–C(4)	1.425 (7)	C(4)–C(41)	1.504 (7)
C(4)–C(5)	1.400 (9)	C(5)–C(51)	1.501 (7)
C(5)–C(6)	1.421 (7)	C(6)-C(61)	1.486 (9)
(D) Carbon–Carbon Distances in Outer Phenyls			
C(31)-C(32)	1.396 (10)	C(51)–C(52)	1.382 (9)
C(31)–C(36)	1.388 (8)	C(51)–C(56)	1.415 (8)
C(32)–C(33)	1.402 (12)	C(52)–C(53)	1.381 (8)
C(33)–C(34)	1.370 (12)	C(53)–C(54)	1.382 (9)
C(34)–C(35)	1.352 (12)	C(54)–C(55)	1.386 (11)
C(35)–C(36)	1.393 (11)	C(55)–C(56)	1.402 (7)
C(41)–C(42)	1.392 (9)	C(61)–C(62)	1.397 (8)
C(41)–C(46)	1.385 (9)	C(61)–C(66)	1.386 (8)
C(42)–C(43)	1.405 (10)	C(62)–C(63)	1.383 (11)
C(43)–C(44)	1.377 (13)	C(63)–C(64)	1.358 (10)
C(44)–C(45)	1.410 (13)	C(64)–C(65)	1.383 (10)
C(45)–C(46)	1.383 (10)	C(65)–C(66)	1.389 (11)
(E) Selected Interannular Distances			
C(11)–C(21)	2.729 (9)	Fe- - -C(1)	2.871 (4)
C(12)–C(22)	3.142 (10)	Fe- - -C(2)	2.863 (5)
C(13)–C(23)	3.653 (10)	Cp1- - -C(1)	2.636 (5)
C(14)–C(24)	3.627 (10)	Cp1- - -C(2)	3.370 (5)
C(15)–C(25)	3.066 (10)	Cp2- - -C(1)	3.377 (5)
Cp1- - -Cp2	3.211 (0)	Cp2- - -C(2)	2.627 (4)
(F) Carbon-Hydrogen Distances in π-Cyclopentadienyl Rings			
C(12)-H(12)	1.06 (5)	C(22)-H(22)	1.23 (8)
C(13)-H(13)	1.12 (6)	C(23)-H(23)	1.02 (6)
C(14)-H(14)	1.13 (6)	C(24)-H(24)	1.07 (6)
C(15)-H(15)	1.12 (6)	C(25)-H(25)	0.96 (5)

Table III. Interatomic Angles (deg)

Atoms	Angle	Atoms	Angle
(A) Angles around 1,1′-Ferrocenylene Part			
C(12)-C(11)–C(15)	108.4 (5)	C(22)-C(21)–C(25)	108.3 (5)
C(13)-C(12)-C(11)	107.3 (5)	C(23)-C(22)–C(21)	106.8 (5)
C(14)-C(13)–C(12)	108.4 (5)	C(24)–C(23)–C(22)	108.7 (6)
C(15)–C(14)–C(13)	109.2 (5)	C(25)–C(24)-C(23)	109.2 (6)
C(11)-C(15)–C(14)	106.7 (5)	C(21)-C(25)–C(24)	107.0 (5)
C(12)–C(11)-C(1)	123.5 (5)	C(22)–C(21)–C(2)	123.9 (5)
C(1)–C(11)–C(15)	125.9 (5)	C(2)–C(21)-C(25)	125.5 (5)
Cp1· · ·Fe· · ·Cp2	157.2 (1)		
(B) Angles around Central Benzene Ring			
C(2)-C(1)–C(6)	121.2 (5)	C(2)–C(1)–C(11)	116.0 (5)
C(3)–C(2)–C(1)	121.5 (5)	C(6)–C(1)–C(11)	122.7 (5)
C(4)–C(3)–C(2)	117.7 (5)	C(3)–C(2)–C(21)	121.8 (5)
C(5)–C(4)–C(3)	120.9 (5)	C(1)–C(2)–C(21)	116.7 (5)
C(6)–C(5)–C(4)	120.3 (5)	C(4)-C(3)–C(31)	122.8 (5)
C(1)–C(6)–C(5)	118.2 (5)	C(2)–C(3)–C(31)	119.2 (5)
		C(5)–C(4)–C(41)	120.4 (5)
		C(3)–C(4)–C(41)	118.8 (5)
		C(6)–C(5)–C(51)	119.2 (5)
		C(4)–C(5)–C(51)	120.4 (5)
		C(61)–C(6)–C(1)	118.8 (5)
		C(61)–C(6)–C(5)	122.9 (5)
(C) Angles Involving Outer Phenyls			
C(32)-C(31)–C(36)	118.7 (6)	C(52)-C(51)–C(56)	119.2 (5)
C(33)–C(32)-C(31)	119.1 (6)	C(53)-C(52)–C(51)	121.5 (6)
C(34)–C(33)–C(32)	120.8 (7)	C(54)–C(53)–C(52)	120.1 (6)
C(35)–C(34)–C(33)	120.5 (7)	C(55)–C(54)–C(53)	119.5 (7)
C(36)–C(35)–C(34)	120.0 (7)	C(56)–C(55)–C(54)	121.2 (6)
C(31)-C(36)–C(35)	120.9 (6)	C(51)–C(56)-C(55)	118.5 (6)
C(32)–C(31)–C(3)	119.8 (5)	C(52)–C(51)–C(5)	121.9 (5)
C(3)–C(31)–C(36)	121.4 (5)	C(5)–C(51)–C(56)	119.0 (5)
C(42)–C(41)–C(46)	119.7 (6)	C(62)–C(61)–C(66)	118.7 (5)
C(43)–C(42)–C(41)	120.1 (6)	C(63)–C(62)–C(61)	120.0 (6)
C(44)–C(43)–C(42)	119.0 (7)	C(64)–C(63)–C(62)	121.1 (6)
C(45)–C(44)–C(43)	121.5 (8)	C(65)–C(64)–C(63)	119.9 (7)
C(46)–C(45)–C(44)	118.2 (8)	C(66)–C(65)–C(64)	119.9 (7)
C(41)–C(46)–C(45)	121.5 (7)	C(61)–C(66)–C(65)	120.5 (6)
C(42)–C(41)–C(4)	118.8 (5)	C(62)–C(61)–C(6)	120.4 (5)
C(4)–C(41)–C(46)	121.5 (6)	C(6)-C(61)–C(66)	121.0 (5)
(D) Angles Involving Hydrogen Atoms of 1,1′-Ferrocenylene Part			
C(13)–C(12)-H(12)	127 (3)	C(23)–C(22)-H(22)	127 (4)
C(11)–C(12)-H(12)	126 (3)	C(21)–C(22)-H(22)	126 (4)
C(14)-C(13)-H(13)	134 (4)	C(24)–C(23)-H(23)	126 (4)
C(12)–C(13)-H(13)	117 (3)	C(22)–C(23)-H(23)	125 (4)
C(15)–C(14)-H(14)	116 (3)	C(25)–C(24)-H(24)	119 (3)
C(13)–C(14)-H(14)	134 (3)	C(23)–C(24)-H(24)	131 (3)
C(11)–C(15)-H(15)	126 (3)	C(21)–C(25)-H(25)	123 (3)
C(14)–C(15)-H(15)	127 (3)	C(24)–C(25)-H(25)	129 (3)

to the lower residual factors $R_1 = 5.40\%$ and $R_2 = 6.25\%$. In these refinements, the $\sum w(|F_o| - |F_c|)^2$ function was minimized, where the weight, w, was $1/\sigma(F_o)$. No unusual trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of either $\sin\theta/\lambda$ or $|F_o|$. In the final cycles of a refinement, no positional parameter exhibited shifts of more than 0.33 and 0.56 times its estimated standard deviation for nonhydrogen atoms and for hydrogen atoms, respectively. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 2.29, where the number of reflections (m) and refined parameters (n) were 2939 and 482, respectively. Anomalous dispersion effects for Fe were included in the calculation of *Fe* using $\Delta f'$ and $\Delta f''$ calculated by Cromer.[6] The atomic scattering factors for Fe, C, and H were from the usual tabulation.[7]

A list of observed and calculated structure factor amplitudes is available.[8] The final atomic coordinates and thermal parameters are listed in Table I.

Discussion of the Molecular Structure

Figure 1 shows a perspective view of the molecule 1,1′-(tetraphenyl-*o*-phenylene)ferrocene from a direction almost perpendicular to the central benzene ring (ring C), which shows also the numbering scheme and the 30% probability envelopes of the atomic thermal ellipsoids (hydrogen atoms are omitted). Interatomic distances and their estimated standard deviations (esd) are collected in Table II; bond angles, with esd, are shown in Table III, from which bond distances and angles involving hydrogen atoms of the outer four phenyls are excluded [the average C–H = 1.01 (9) Å, ∠C–C–H = 120 (7)°]. The least-squares planes through each of the seven rings are given in Table IV. Each ring does not deviate significantly from planarity. An examination of the unit cell packing (Figure 2) shows no carbon–carbon intermolecular contact less than 3.50 Å.

Figure 1 clearly shows the tilt of the cyclopentadienyl rings. This tilt is defined in two ways: the dihedral angle of 23.7° between the two cyclopentadienyl rings, ring 1 and ring 2 (the numbering represents the carbon atom's number of the central benzene to which the ring attaches); and the angle Cp(1)···Fe···Cp(2) of 157.2 (1)° [Cp(1) and Cp(2) are the centroids of ring 1 and ring 2].

The dihedral angle between the planes of ring 1 (ring 2) and ring C is 90.6° (94.9°). Figure 3 shows that rings 1 and 2 are almost eclipsed. The bond distances of the bridging atoms are: C(1)–C(11), 1.514 (7); C(2)–C(21), 1.508 (6); and C(1)–C(2), 1.388 (9) Å. The ferrocenylene attaches to the benzene ring in a way with slight distortion which can be shown as the internal rotation angle C(11)–C(1)–C(2)–C(21) of 3° and the deviations of the atoms from the plane of ring

Table IV. Least-Squares Planes within the 1,1′-(Tetraphenyl-*o*-phenylene)ferrocene Molecule

(A) Planes Defines by $Lx + My + Nz = D^a$

Plane	L	M	N	D
Ring C	0.0010	0.9471	0.3209	2.478
Ring 1	−0.1449	−0.3435	0.9279	−1.538
Ring 2	−0.5254	−0.3518	0.7747	0.5711
Ring 3	0.8242	0.4573	0.3341	−0.0901
Ring 4	0.1944	0.1100	0.9747	−0.0056
Ring 5	−0.5851	0.3708	0.7212	1.554
Ring 6	0.8318	−0.5054	0.2294	−2.524

(B) Deviations (Å) of the Atoms from the Plane

	Atom	Dev	Atom	Dev
Ring C	C(1)	0.014	C(31)	0.112
	C(2)	−0.012	C(41)	0.077
	C(3)	−0.005	C(51)	−0.002
	C(4)	−0.021	C(61)	−0.039
	C(5)	−0.019		
	C(6)	0.002	Fe	0.186
			Cp(1)	0.333
	C(11)	0.126	Cp(2)	0.155
	C(21)	0.001		
Ring 1	C(11)	0.009	Fe	1.637
	C(12)	−0.009	C(1)	0.389
	C(13)	0.005	H(12)	0.052
	C(14)	0.001	H(13)	0.080
	C(15)	−0.006	H(14)	0.056
			H(15)	0.068
Ring 2	C(21)	−0.008	Fe	−1.636
	C(22)	0.009	C(2)	−0.388
	C(23)	−0.008	H(22)	−0.055
	C(24)	0.003	H(23)	0.104
	C(25)	0.003	H(24)	−0.083
			H(25)	−0.144

(C) Dihedral Angles between these Rings (deg)

Ring C/ring 1	90.6	Ring C/ring 5	62.1
Ring C/ring 2	94.9	Ring C/ring 6	66.2
Ring C/ring 3	57.2		
Ring C/ring 4	65.3	Ring 1/ring 2	23.7

[a] x, y, and z are the orthogonal coordinates measured in Å units along the crystallographic a^*, b, and c axes, respectively.

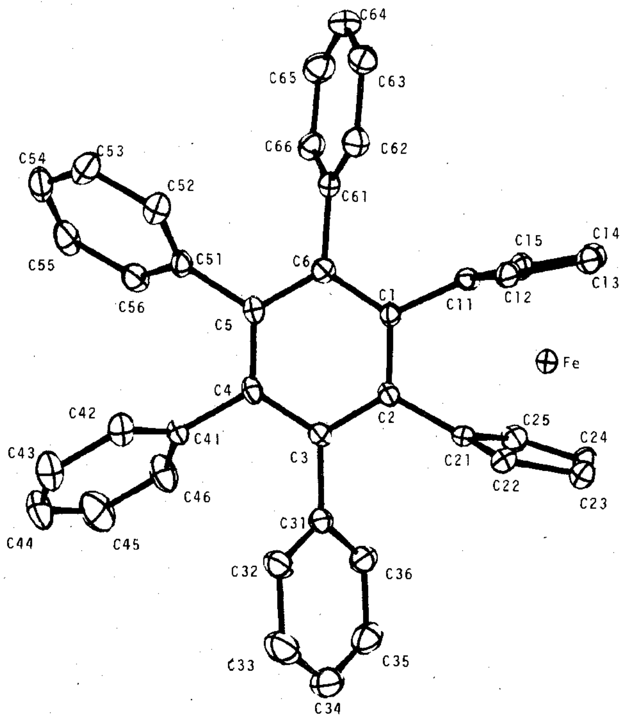


Figure 1. The molecular structure and numbering of the carbon atoms in the 1,1′-(tetraphenyl-*o*-phenylene)ferrocene. Ellipsoids are scaled to include 30% probability.

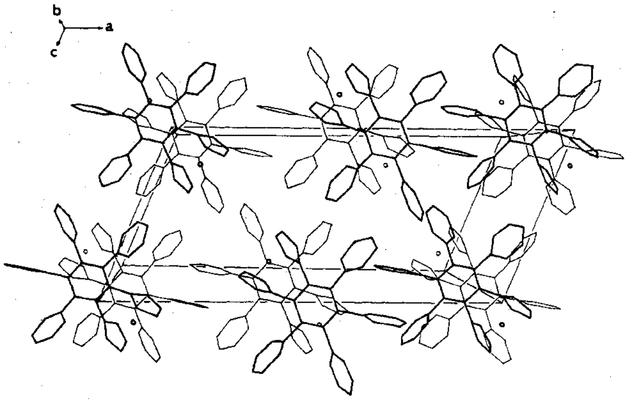
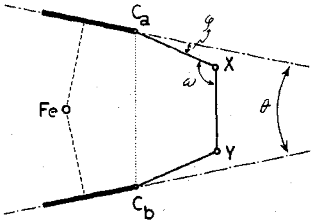


Figure 2. A stereoscopic view of the unit cell.

C, C(11), C(21), and Fe, and the centroids Cp(1) and Cp(2) of 0.126, 0.001, 0.186, 0.333, and 0.155 Å, respectively.

The magnitude of the cyclopentadienyl ring tilt accords well with those observed in three known [2]ferrocenophanes (in Table V) irrespective of the divergent geometries of their two-atom bridging groups. In those three with longer bridges, **4**,[9] **5**,[10] and **6**,[11] the configurations of the cyclopentadienyl rings are intermediate between the eclipsed and staggered extremes (~9 and ~10° rotated from the eclipsed extremes in **4** and **6**). Also, in **4** and **6**, appreciable lengthening of the bond

Table V. Geometries of Known [2]Ferrocenophanes:



	Compd	Angles, deg				Distances, Å			
		θ	φ	ω	∠Ca-X-Y-Cb	Ca-Fe	Ca-Cb	Ca-X	X-Y
3a	Present molecule	23.7	14.9	116.4 (5)	3	1.976 (5)	2.729 (9)	1.511 (7)	1.388 (9)
4	1,1′-Tetramethylethylene-ferrocene [X, Y = $C(CH_3)_2$]	23.2	12.7	110	25	1.97	2.70	1.548	1.584 (14)
5	[2]Ferrocenophanethiazine 1,1-dioxide[10] [X = SO_2; Y = NH]	23	NSC SNC	104.5 (4) 112.5 (6)	29	1.976 (8)	2.78 (1)	C-S 1.740 (9) C-N 1.419 (11)	1.671 (5)
6	1,1′-Dihydro-1,1′-bipentalenyliron[11] [X, Y = CHCH=CHR]	23.6	12.6	109.0 (4)	(20)	1.985 (5)	2.723 (6)	1.524 (7)	1.568 (7)

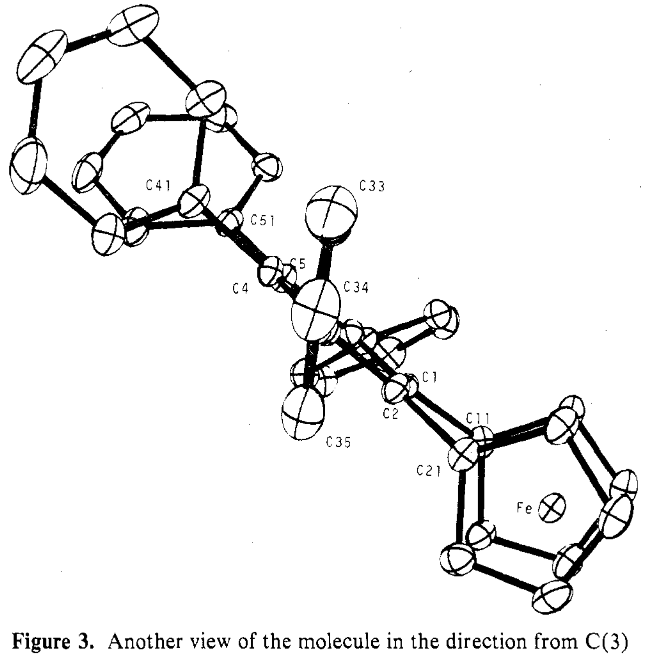


Figure 3. Another view of the molecule in the direction from C(3) to C(6).

between the two bridged carbons (sp^3) has been observed. In the present molecule, there is no lengthening of the bridging $C(sp^2)$=$C(sp^2)$ aromatic bond whereas appreciable angle deformation of ∠C(11)–C(1)–C(2) and ∠C(21)–C(2)–C(1) of average 116.4 (5)° from 120° for the normal sp^2 carbon emerges. The angle φ defined (in Table V) by the plane of ring 1 (or 2) and the bond C(11)–C(1) (or C(21)–C(2)) is 14.9°. The C–C bond distances in rings 1 and 2 range from 1.411 (10) to 1.441 (7) Å (average 1.432 (12) Å) and from 1.401 (10) to 1.443 (8) Å (average 1.429 (16) Å), respectively. These average values may be compared with the accepted C–C (π-cyclopentadienyl) bond length of ~1.43 Å. The C–H bond distances in rings 1 and 2 range from 0.96 (5) to 1.23 (8) Å (average 1.09 (6) Å).

Other bond distances and angles involving ring C are noticeably symmetrical about the line bisecting the cental benzene through the Fe atom: The bond distances C(2)–C(3) and C(6)–C(1) are 1.402 (7) and 1.404 (6) Å, C(3)–C(4) and C(5)–C(6) are 1.425 (7) and 1.421 (7) Å, and C(4)–C(5) is 1.400 (9) Å (average 1.407 (14) Å, which agrees with the accepted value of 1.395 (3) Å for the benzene ring 7). It would be noteworthy that the bond C(1)–C(2) is the shortest and the difference between the distances C(3)–C(4) and C(1)–C(2) is $>3\sigma$, although the difference may not be significant because similar but not so systematic deviations as in the present molecule in bond lengths and angles have been shown in hexaphenylbenzene.[12]

Registry No. **3a**, 61332-68-1.

Supplementary Material Available: Listings of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(5) The absorption correction program ABSIO (by T. Ito) used the Gaussian integration method of Busing and Levy. The following programs were used during the course of the structural analyses: FANDFR, structure factor calculation and Fourier synthesis, Y. Iitaka; HBLS, structure factor calculation and block-diagonal least-squares refinement, T. Ashida; BOND, distances, angles, and least-squares planes, Y. Iitaka; ORTEP, thermal ellipsoid drawings, C. K. Johnson.
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Studies in Heavy-Metal Molybdates. 2. Crystal Structure of Disodium Di-μ-hydroxo-dizinc(II) Molybdate

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Sodium μ-hydroxo-μ-aquo-dizinc(II) molybdate, $NaZn_2(OH)(H_2O)(MoO_4)_2$, was found to form a compound of composition $NaZn(OH)MoO_4$ when allowed to react in a pressure bomb with 4 M sodium molybdate. The crystals are orthorhombic with $a = 7.850$ (1), $b = 9.2922$ (8), $c = 6.148$ (1) Å, and $V = 444.4$ Å^3. Systematic absences fixed the space group as $Pna2_1$. The density, determined by flotation in a thallous formate–thallous malonate solution, was ~4 g cm^{-3} compared to a calculated density with $Z = 4$ of 3.965 g cm^{-3}. A total of 843 intensities above background were collected by counter diffractometry using the θ–2θ scan technique. The structure was solved by a combination of Patterson and Fourier methods. Refinement by block-diagonal least-squares procedures led to a final R_F of 0.038 and a weighted residual R_{wF} of 0.036. The zinc atoms are octahedrally coordinated by oxygen atoms which share edges forming infinite chains of octahedra. These chains are linked by molybdate tetrahedra to form zinc molybdate sheets. The sheets are not separated by sodium ions as in $NaZn_2(OH)(H_2O)MoO_4$ but are interconnected through both molybdate groups and sodium ions. The hydrogen atom was placed on the oxygen which bridges zinc atoms based upon electrostatic bond strength considerations. This made the structure a disodium di-μ-hydroxo-dizinc(II) molybdate.

Introduction

Pezerat has reported that at least three well-defined phases can be obtained from the reaction of a soluble zinc salt with sodium molybdate.[2] Two of the phases are sodium zinc molybdates designated by him as Φ_x and Φ_y. The crystal structure of the Φ_x phase was reported upon in paper 1 of this series.[3] It has the composition $NaZn_2OH(H_2O)(MoO_4)_2$. We have now isolated single crystals of phase Φ_y and its structure is reported upon here.

Phase Φ_y was described by Pezerat as having the ideal