and 88.9 (1)°] and Br—Fe—P angles in (2) [84.8 (1) and 86.5 (1)°].

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Structure of Bis[ferrocenyl(*p*-tolyl)methyl] Ether

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Abstract. $C_{36}H_{34}Fe_2O$, $M_r = 594.36$, monoclinic, $C2/c$, $a = 17.316$ (5), $b = 11.328$ (2), $c = 14.837$ (4) Å, $\beta = 109.18$ (3)°, $V = 2749$ (1) Å^3, $Z = 4$, $D_x = 1.436$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 10.8$ cm^{-1}, $F(000) = 1240$, room temperature, $R = 0.038$ for 1795 unique reflections with $I > 2\sigma(I)$. The molecule lies on a crystallographic twofold axis which passes through the O atom. The cyclopentadienyl rings are twisted 7.6 (1)° from the eclipsed conformation. In the ferrocene moiety, the Fe—C distances are in the range 2.030 (5)–2.074 (4) Å and C—C distances in the range 1.402 (6)–1.428 (4) Å. The substitution of one cyclopentadienyl ring causes some distortion within the ferrocene moiety.

Introduction. The title compound is the major product from the reaction of ferrocene with tolualdehyde, whereas the corresponding carbinol (α-*p*-tolyl)ferrocenylmethanol was obtained as the by-product. We decided to carry out a single-crystal X-ray study of several related ferrocenyl ethers and carbinols of this type in order to investigate the influence of different substituents on the ferrocene geometry. In this work we describe the structure of bis[ferrocenyl(*p*-tolyl)methyl] ether. As far as we know, the X-ray diffraction studies of ethers of this type have not been described so far.

Experimental. Condensation of *p*-tolualdehyde with ferrocene in conc. H_2SO_4 at 265 K gave a 42% yield of the title compound (Kovač & Rapić, 1990). Orange crystals (0.06 × 0.07 × 0.20 mm) were obtained by recrystallization from ethanol. Data were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Intensities were measured using the θ–2θ scan mode, scan width of 1.4° and scan speed of 0.04° s^{-1}. Unit-cell parameters were determined by the least-squares procedure from 18 reflections, $8.5 < \theta < 14.1$°. Three standard reflections (400, $\bar{4}2\bar{3}$, $\bar{6}\bar{4}\bar{3}$) measured every 2 h showed no significant intensity variations. 1884 reflections were measured within the range $2 \leq \theta \leq 30$° ($-24 \leq h \leq 22$, $0 \leq k \leq 15$, $0 \leq l \leq 18$), 1825 unique ($R_{\rm int} = 0.029$), 1795 with $I > 2\sigma(I)$ were used in the refinement. Intensities were corrected for Lorentz and polarization effects. No absorption or extinction corrections were applied. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). H-atom positions were determined from a difference Fourier map. The structure was refined by the full-matrix least-squares procedure based on F with anisotropic temperature factors for all non-H atoms and isotropic for H atoms. Refinement (245 parameters)

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Table 1. *Positional parameters and isotropic or equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses*

H atoms isotropic; for non-H atoms $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} or U_{iso}
Fe	0.22517 (3)	−0.03311 (4)	0.29833 (4)	0.0349 (2)
O	0	0.0542 (3)	0.25	0.032 (1)
C1	0.1354 (2)	0.0321 (3)	0.3492 (2)	0.034 (1)
C2	0.2152 (2)	0.0549 (4)	0.4148 (3)	0.042 (1)
C3	0.2552 (2)	−0.0549 (4)	0.4423 (3)	0.050 (2)
C4	0.2021 (3)	−0.1446 (4)	0.3935 (3)	0.049 (2)
C5	0.1278 (2)	−0.0919 (4)	0.3348 (3)	0.039 (1)
C6	0.2216 (3)	0.0528 (4)	0.1755 (3)	0.048 (2)
C7	0.3011 (3)	0.0592 (4)	0.2437 (3)	0.049 (2)
C8	0.3299 (3)	−0.0572 (4)	0.2657 (4)	0.053 (2)
C9	0.2689 (3)	−0.1359 (4)	0.2124 (3)	0.057 (2)
C10	0.2017 (3)	−0.0678 (4)	0.1566 (3)	0.055 (2)
C11	0.0674 (2)	0.1213 (3)	0.3089 (2)	0.033 (1)
C12	0.0461 (2)	0.1837 (3)	0.3884 (2)	0.031 (1)
C13	−0.0069 (2)	0.1312 (4)	0.4282 (3)	0.042 (2)
C14	−0.0267 (2)	0.1866 (4)	0.5012 (3)	0.046 (2)
C15	0.0065 (2)	0.2942 (3)	0.5375 (2)	0.038 (1)
C16	0.0604 (3)	0.3452 (4)	0.4985 (3)	0.049 (2)
C17	0.0794 (2)	0.2921 (3)	0.4240 (3)	0.044 (2)
C18	−0.0144 (3)	0.3521 (5)	0.6179 (3)	0.052 (2)
H2	0.235 (2)	0.132 (3)	0.434 (3)	0.04 (1)
H3	0.313 (3)	−0.063 (3)	0.487 (3)	0.06 (1)
H4	0.212 (2)	−0.225 (3)	0.395 (3)	0.04 (1)
H5	0.084 (2)	−0.132 (3)	0.294 (2)	0.03 (1)
H6	0.187 (2)	0.120 (3)	0.149 (3)	0.05 (1)
H7	0.328 (2)	0.136 (3)	0.271 (3)	0.04 (1)
H8	0.378 (3)	−0.078 (4)	0.312 (3)	0.08 (2)
H9	0.273 (3)	−0.217 (4)	0.216 (3)	0.06 (1)
H10	0.154 (3)	−0.094 (4)	0.114 (3)	0.06 (1)
H11	0.082 (2)	0.180 (3)	0.271 (2)	0.04 (1)
H13	−0.028 (2)	0.061 (3)	0.409 (3)	0.05 (1)
H14	−0.060 (2)	0.149 (3)	0.527 (3)	0.05 (1)
H16	0.085 (3)	0.423 (4)	0.524 (3)	0.07 (1)
H17	0.112 (2)	0.331 (3)	0.395 (3)	0.04 (1)
H181	−0.003 (4)	0.441 (5)	0.626 (5)	0.14 (2)
H182	0.019 (3)	0.321 (4)	0.680 (4)	0.09 (2)
H183	−0.070 (4)	0.338 (5)	0.617 (4)	0.11 (2)

converged at $R = 0.038$, $wR = 0.045$, $w = 1/[\sigma^2(F) + 0.000197F^2]$, $S = 0.94$, $(\Delta/\sigma)_{max} = 0.001$; max. and min. electron density in the final difference Fourier map 0.29 and -0.32 e $Å^{-3}$. Atomic scattering factors and anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). *SHELX76* (Sheldrick, 1976) and the *CRYSRULER* crystallographic package (Rizzoli, Sangermano, Calestani & Andreetti, 1987) were used for the refinement and general calculations.

Discussion. The atomic coordinates are given in Table 1[*] and interatomic distances and angles in Table 2. An *ORTEP* (Johnson, 1976) drawing of the molecule with the atom-labelling scheme is shown in Fig. 1. The molecular packing in the unit cell drawn with *PLUTON* (Spek, 1982) is shown in Fig. 2.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Fe—C1	2.074 (4)	C4—C5	1.426 (6)
Fe—C2	2.051 (5)	C6—C7	1.417 (6)
Fe—C3	2.041 (4)	C6—C10	1.414 (6)
Fe—C4	2.030 (5)	C7—C8	1.410 (6)
Fe—C5	2.044 (4)	C8—C9	1.410 (6)
Fe—C6	2.049 (5)	C9—C10	1.415 (6)
Fe—C7	2.044 (5)	C1—C11	1.517 (5)
Fe—C8	2.043 (6)	C11—C12	1.521 (5)
Fe—C9	2.047 (5)	C12—C13	1.379 (6)
Fe—C10	2.045 (5)	C12—C17	1.385 (5)
O—C11	1.426 (4)	C13—C14	1.389 (7)
C1—C2	1.428 (4)	C14—C15	1.379 (5)
C1—C5	1.420 (6)	C15—C16	1.376 (7)
C2—C3	1.417 (6)	C16—C17	1.390 (7)
C3—C4	1.402 (6)	C15—C18	1.506 (6)

C2—C1—C5	107.6 (3)	O—C11—C12	111.4 (3)
C2—C1—C11	126.9 (3)	C1—C11—C12	111.0 (3)
C5—C1—C11	125.3 (3)	C11—C12—C13	119.8 (3)
C1—C2—C3	108.0 (4)	C11—C12—C17	122.1 (3)
C2—C3—C4	108.2 (4)	C13—C12—C17	118.1 (3)
C3—C4—C5	108.6 (4)	C12—C13—C14	120.6 (4)
C1—C5—C4	107.6 (4)	C13—C14—C15	121.7 (4)
C7—C6—C10	107.9 (4)	C14—C15—C18	121.1 (4)
C6—C7—C8	107.7 (4)	C14—C15—C16	117.4 (3)
C7—C8—C9	108.6 (4)	C16—C15—C18	121.5 (4)
C8—C9—C10	107.7 (4)	C15—C16—C17	121.6 (4)
C6—C10—C9	108.1 (4)	C12—C17—C16	120.6 (4)
O—C11—C1	105.0 (3)	C11—O—C11'	115.6 (3)

Symmetry code: (i) $-x, y, 0.5-z$.

The crystal structure consists of discrete molecules of bis[ferrocenyl(*p*-tolyl)methyl] ether held together by van der Waals interactions. The molecule has twofold symmetry with the twofold axis passing through the O atom. C atoms in the cyclopentadienyl (Cp) rings do not deviate significantly from coplanarity. The cyclopentadienyl rings are slightly twisted from the eclipsed conformation: the torsion angles C—Cp1—Cp2—C range from 7.5 (4) to 8.0 (5)° [mean value 7.6 (1)°; Cp1 and Cp2 are centroids of the Cp rings]. In the structure of ferrocene the two Cp rings are rotated about 12° from the eclipsed position (Seiler & Dunitz, 1979*a*; Takusagawa & Koetzle, 1979*a*). The Cp1—Fe—Cp2 angle is 178.1 (2)°. The least-squares best planes through the Cp rings make an angle of 3.0 (2)°. The Fe atom is equidistant from the Cp ring planes with the Fe—Cp1 and Fe—Cp2 distances being 1.654 (5) and 1.655 (5) Å, respectively. This distance is somewhat longer than that of 1.645 (2) Å found in ferrocene itself (Takusagawa & Koetzle, 1979*a*) but is close to those found in 1,6-diferrocenyl-1,3,5-hexa-2,5-dicarbonitrile [1.650 (3) and 1.657 (3) Å] (Amer, Sadler, Henry, Ferguson & Ruhl, 1985). The mean Fe—C distance of 2.047 (4) Å[*] is the same as in the room-temperature structure of 1,1'-ferrocenedicarboxylic acid (Takusagawa & Koetzle, 1979*b*). The Fe—C distances in the unsubstituted Cp ring are all similar, ranging from 2.044 (5) to 2.049 (5) Å [mean 2.046 (1) Å], while those in the substituted Cp ring are considerably different and range from 2.030 (5) to 2.074 (4) Å. [mean 2.048 (7) Å], thus indicating distortion of the ferrocene moiety caused by substi-

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[*] Lists of structure factors, anisotropic thermal parameters, least-squares planes, selected torsion angles and bond lengths involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55530 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] Standard deviations of the mean values have been estimated as $\sigma(\bar{d}) = [\sum(d-\bar{d})^2/n(n-1)]^{1/2}$.

tution at C1. The longest Fe—C1 bond length of 2.074 (4) Å and the deviations of C1 and C11 from the plane of the Cp ring by 0.007 (3) and 0.149 (3) Å, respectively, show displacement of these atoms away from the Fe atom. The C—C bond lengths in the unsubstituted Cp ring are in the range 1.410 (6)–1.417 (6) Å [mean 1.413 (3) Å]. Substitution of the other Cp ring affects the electron density within its π system showing evidence of some double-bond localization. The C—C distances vary from 1.402 (6) to 1.428 (4) Å [mean 1.419 (10) Å], similar to some other ferrocene derivatives, for example benzoylferrocene (Butler, Cullen, Rettig & Trotter, 1988). Comparison of the mean values of the C—C bond lengths in the unsubstituted and the substituted ring shows that the latter are longer. However, this difference is not significant and similar values were also found in the structure of ferrocenecarboxaldoxime (Ferguson, Bell & Glidewell, 1991) or ferrocenecarboxylic acid (Cotton & Reid, 1985).

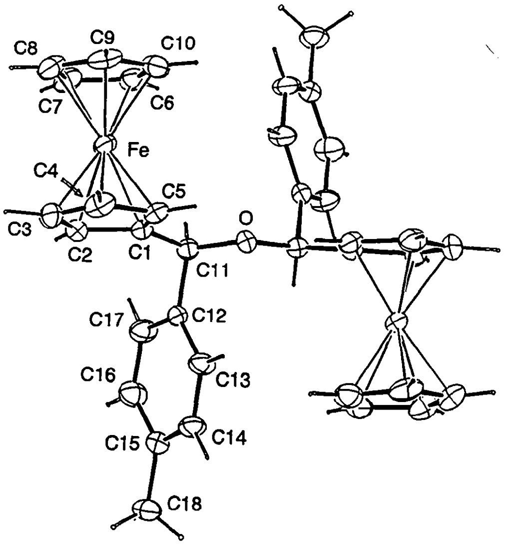

Fig. 1. *ORTEP* drawing of the molecule showing the atom-labelling scheme. The thermal ellipsoids are drawn at the 40% probability level.

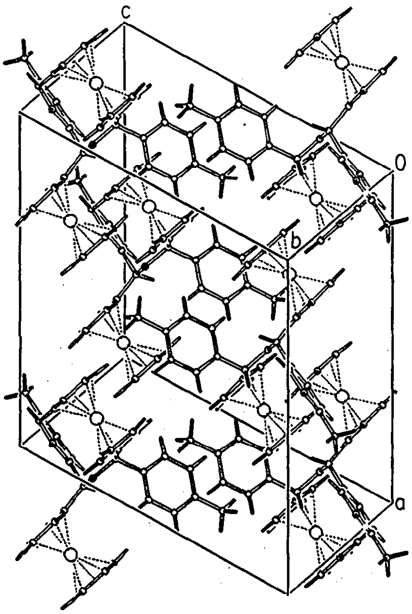

Fig. 2. Packing diagram of the molecules in the unit cell.

The atoms of the Cp ring, except H4, are displaced out of the Cp planes toward the Fe atom [the mean displacement is 0.027 (8) Å]. These values are similar, within experimental error, to those already noticed in the X-ray structure of low-temperature ferrocene (mean displacement is 0.018 Å) (Seiler & Dunitz, 1979*b*). The most accurate values were found in the neutron diffraction study of ferrocene [mean displacement 0.030 (7) Å] (Takusagawa & Koetzle, 1979*a*) and ferrocenedicarboxylic acid [mean displacement 0.027 (5) Å] (Takusagawa & Koetzle, 1979*b*). The bond lengths and angles within the tolyl ring and those involving the O atom are as expected. The mean value of the C—H bond lengths is 0.95 (1) Å.

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