Data collection

Stoe IPDS diffractometer
Image plate, Stoe IPDS scans
Absorption correction: integration (*XPREP*; Siemens, 1996*a*)
$T_{\min} = 0.425$, $T_{\max} = 0.875$
16 171 measured reflections
3788 independent reflections
2729 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 25.97°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.080$
$S = 1.018$
3788 reflections
241 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.279$ e Å^{-3}
$\Delta\rho_{\min} = -0.276$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.000 (13); 1799 Friedel pairs

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.882 (2)	Cu—O2	1.940 (3)
Cu—N1	1.924 (3)	Cu—S	2.2791 (11)
O1—Cu—N1	93.34 (12)	O1—Cu—S	101.49 (8)
O1—Cu—O2	162.05 (15)	N1—Cu—S	160.74 (11)
N1—Cu—O2	83.92 (12)	O2—Cu—S	85.57 (8)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···O1	0.90	1.85	2.722 (4)	160
N3—H31···O3$^{\rm i}$	0.90	1.99	2.865 (4)	165

Symmetry code: (i) $1 - y, x, z - \frac{1}{4}$.

An analytical absorption correction was based on face-indexing and was carried out with the following faces and distances (mm): $\bar{1}00$ 0.0578; 100 0.0578; 001 0.4312; $00\bar{1}$ 0.4351; $\bar{1}10$ 0.0770; $1\bar{1}0$ 0.0770. The contributions of the H atoms of the two butyl groups were included at calculated positions using *SHELXL*97 (Sheldrick, 1997) and refined using a riding model. All other H atoms were found from difference Fourier syntheses. $U_{\rm iso}$ values for H atoms of CH, NH and CH_2 or the methyl groups were taken as $1.2U_{\rm eq}$ or $1.5U_{\rm eq}$ of the parent atoms, respectively. The positions of the H21 and H31 atoms were refined using N—H distance restraints. Atoms C14 and C18 display slight disorder. Nonetheless, no disorder model was employed because of the insignificance of the positions of these atoms with respect to the overall structure.

Data collection: *EXPOSE* (Stoe, 1997*b*). Cell refinement: *CELL* (Stoe, 1997*a*). Data reduction: *INTEGRATE* (Stoe, 1997*c*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1262). Services for accessing these data are described at the back of the journal.

Acta Cryst. (1998). C**54**, 462–464

2-[(2,5-Dimethoxyphenyl)(ferrocenyl)methyl]-3,6-dimethoxybenzonitrile†

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Abstract

The cyano group of ferrocenylacetonitrile migrates to the phenyl ring of an aryne during a tandem addition–rearrangement reaction that yields the title compound, [$Fe(C_5H_5)(C_{23}H_{22}NO_4)$]. The two cyclopentadienyl rings of the ferrocenyl moiety are in a staggered conformation.

Comment

We have found that the reaction of ferrocenylacetonitrile with 2-bromo-1,4-dimethoxybenzene, (1), in the presence of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) gives a significant amount (63%) of a solid material, which was identified as the title compound,

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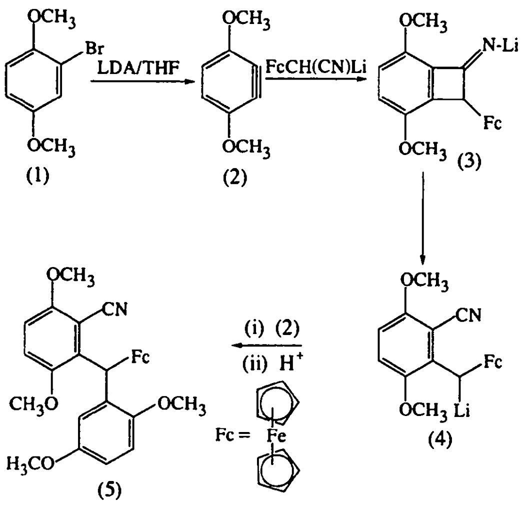
† Alternative name: [1-(2-cyano-3,6,2′,5′-tetramethoxybenzhydryl)-η^5-cyclopentadienyl](η^5-cyclopentadienyl)iron(II).

(5), by X-ray crystallography. The formation of (5) is consistent with the following multi-step pathway (see scheme below). A tandem addition–rearrangement aryne (TARA) reaction (Pansegrau *et al.*, 1988) of aryne (2) with α-lithioferrocenylacetonitrile gives adduct (3); subsequent ring opening gives intermediate (4), which then reacts with another molecule of aryne (2) (Roberts *et al.*, 1956) to give title compound (5) after proton quench. This is the first reported case of a TARA product from the reaction of 2-bromo-1,4-dimethoxybenzene.



The structure determination of (5) showed that the ferrocenyl and two anisyl groups are linked *via* the methylene C1 atom (Fig. 1). For steric reasons, the methoxy groups of the two *p*-methoxybenzene groups adopt a *cis* conformation, with C17—O12···O15—C18 −3.9 (3) and C27—O22···O25—C28 −23.3 (3)°, which is different from the *trans* conformation found in the structures of 1,4-diethoxybenzene (Haisa & Kashino, 1977), 2,3,5,6-tetrabromo-1,4-dimethoxybenzene (Wieczorek, 1982) and lactisole (Mathlouthi *et al.*, 1994). The dihedral angle between the two phenyl planes is 78.2 (1)°. The two cyclopentadienyl (Cp) planes are parallel, forming a dihedral angle of 0.2 (2)°. The short contact N30···C28^{i} [symmetry code: (i) $-\frac{1}{2}+x, y, \frac{1}{2}-z$] results in the cyano group being slightly tilted out of the phenyl plane, with deviations of 0.017 (5) and 0.063 (6) Å for atoms C29 and N30, respectively. An intermolecular short contact also exists between the cyano group and a cyclopentadienyl H atom, *i.e* C34—H34···N30^{ii} with C34···N30 3.331 (5) Å [symmetry code: (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, z$]. The length of the triple bond C29≡N30 [1.151 (4) Å] is very close to those we have found previously (Zhang *et al.*, 1995, 1997).

The two Cp rings in the ferrocenyl moiety are in a staggered conformation with the torsion angle C31—*Cnt*1—*Cnt*2—C36 being −39.5 (3)° (*Cnt*1 is the centroid of the Cp ring C31–C35 and *Cnt*2 is the centroid of the Cp ring C36–C40) (Zhang *et al.*, 1997). The Fe···*Cnt*1 and Fe···*Cnt*2 distances of 1.653 (1) and 1.657 (2) Å, respectively, are close to the distances of 1.643 (1) and 1.653 (2) Å found in 2-(ferrocenylmethyl)-3-methyl-6-methoxybenzonitrile, and those of 1.645 (2) and 1.649 (2) Å found in 10-(ferrocenylmethyl)-9-phenanthrenecarbonitrile (Zhang *et al.*, 1997).

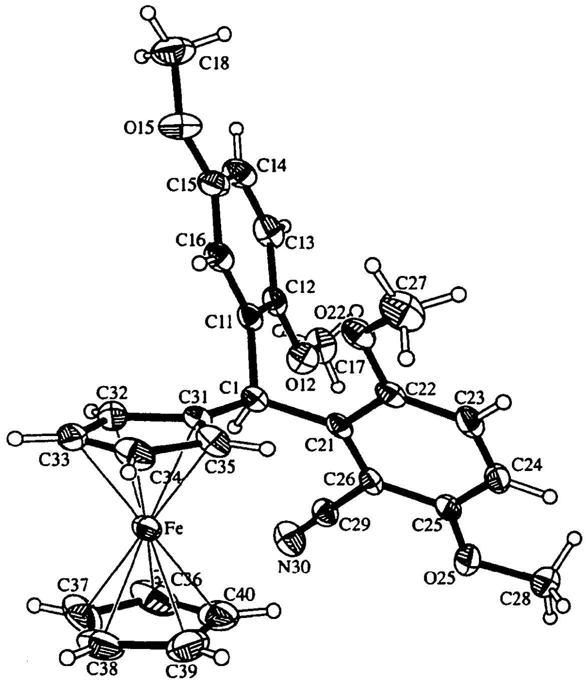


Fig. 1. The structure of (5) showing 40% probability displacement ellipsoids. The H atoms are drawn as small circles of arbitrary radii for clarity.

Experimental

The title compound was prepared as described in the *Comment* and recrystallized from hexane–methylene chloride.

Crystal data

$[\mathrm{Fe}(C_5H_5)(C_{23}H_{22}NO_4)]$
$M_r = 497.36$
Orthorhombic
Pbca
$a = 12.004$ (2) Å
$b = 19.108$ (2) Å
$c = 20.328$ (2) Å
$V = 4662.7$ (10) Å^3
$Z = 8$
$D_x = 1.417$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 0.68$ mm^{-1}
$T = 220$ (2) K
Plate
0.35 × 0.25 × 0.15 mm
Orange

Data collection

R3m/V diffractometer
$\omega/2\theta$ scans

2794 reflections with $F > 4\sigma(F)$

Absorption correction:
ψ scan (*SHELXTL-Plus*; Sheldrick, 1990*b*)
$T_{\min} = 0.77$, $T_{\max} = 0.88$
4108 measured reflections
4108 independent reflections

$\theta_{\max} = 25.01°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 24$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.102$
$S = 1.02$
3674 reflections
307 parameters
H atoms riding (C—H 0.96 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 1.35P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe—C31	2.062 (3)	C14—C15	1.377 (4)
Fe—C32	2.038 (3)	C15—O15	1.380 (4)
Fe—C33	2.042 (3)	C15—C16	1.398 (4)
Fe—C34	2.034 (3)	O12—C17	1.424 (4)
Fe—C35	2.045 (3)	O15—C18	1.429 (4)
Fe—C36	2.041 (4)	C21—C22	1.403 (4)
Fe—C37	2.034 (4)	C21—C26	1.408 (4)
Fe—C38	2.052 (3)	C22—O22	1.379 (4)
Fe—C39	2.051 (3)	C22—C23	1.388 (4)
Fe—C40	2.043 (4)	C23—C24	1.385 (4)
C1—C31	1.516 (4)	C24—C25	1.379 (4)
C1—C21	1.523 (4)	C25—O25	1.365 (4)
C1—C11	1.535 (4)	C25—C26	1.406 (4)
C11—C16	1.391 (4)	C26—C29	1.437 (4)
C11—C12	1.409 (4)	O22—C27	1.428 (4)
C12—O12	1.376 (4)	O25—C28	1.436 (4)
C12—C13	1.388 (4)	C29—N30	1.151 (4)
C13—C14	1.389 (5)		
C31—C1—C21	113.4 (2)	C22—C21—C26	116.7 (3)
C31—C1—C11	113.2 (2)	C22—C21—C1	123.0 (3)
C21—C1—C11	112.3 (2)	C26—C21—C1	120.2 (3)
C16—C11—C12	118.1 (3)	O22—C22—C23	123.3 (3)
C16—C11—C1	123.0 (3)	O22—C22—C21	116.1 (3)
C12—C11—C1	118.9 (3)	C23—C22—C21	120.6 (3)
O12—C12—C13	124.0 (3)	C24—C23—C22	121.3 (3)
O12—C12—C11	115.7 (3)	C25—C24—C23	120.3 (3)
C13—C12—C11	120.2 (3)	O25—C25—C24	126.0 (3)
C12—C13—C14	120.7 (3)	O25—C25—C26	115.8 (3)
C15—C14—C13	119.8 (3)	C24—C25—C26	118.2 (3)
C14—C15—O15	124.9 (3)	C25—C26—C21	122.8 (3)
C14—C15—C16	119.9 (3)	C25—C26—C29	117.1 (3)
O15—C15—C16	115.2 (3)	C21—C26—C29	120.0 (3)
C11—C16—C15	121.3 (3)	C22—O22—C27	117.6 (3)
C12—O12—C17	117.8 (3)	C25—O25—C28	116.9 (3)
C15—O15—C18	116.8 (3)	N30—C29—C26	178.1 (3)

Data were corrected for Lorentz, polarization and absorption effects. All non-H atoms were refined anisotropically; all H atoms were included using a riding model.

Data collection: *R3m/V* diffractometer software. Cell refinement: *R3m/V* diffractometer software. Data reduction: *R3m/V* diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1350). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 464–468

Bis(1,10-phenanthroline-*N*,*N'*)copper(II) Tetrathionate and Tris(1,10-phenanthroline-*N*,*N'*)copper(II) Tetrathionate Pentahydrate

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Abstract

The structures of $[Cu(C_{12}H_8N_2)_2(S_4O_6)]$, (I), and $[Cu(C_{12}H_8N_2)_3](S_4O_6).5H_2O$, (II), are reported. Compound (I) consists of infinite polymeric chains where copper displays a typical (4+2) coordination and S_4O_6 connects Cu(phen)$_2$ (phen is phenanthroline) units through rather long Cu···O contacts. Compound

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