Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
4095 measured reflections
3188 independent reflections
1906 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 15$
$k = -1 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.111$
$S = 0.919$
3188 reflections
232 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.180$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.139$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0226 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O(3)—C(13)	1.246 (2)	C(7)—C(8)	1.474 (2)
O(4)—C(13)	1.250 (2)	C(14)—C(15)	1.379 (3)
N(1)—C(8)	1.314 (2)	C(14)—C(19)	1.385 (3)
N(1)—C(1)	1.468 (2)	C(15)—C(16)	1.373 (3)
N(1)—C(12)	1.482 (2)	C(16)—C(17)	1.367 (4)
N(2)—C(8)	1.325 (2)	C(17)—C(18)	1.370 (3)
N(2)—C(2)	1.466 (2)	C(18)—C(19)	1.383 (3)
N(2)—C(4)	1.480 (2)		
C(8)—N(1)—C(1)	110.0 (2)	N(2)—C(8)—C(7)	123.7 (2)
C(8)—N(1)—C(12)	126.0 (2)	C(15)—C(14)—C(19)	118.1 (2)
C(1)—N(1)—C(12)	123.1 (2)	C(16)—C(15)—C(14)	121.3 (2)
C(8)—N(2)—C(2)	109.4 (2)	C(17)—C(16)—C(15)	119.9 (3)
C(8)—N(2)—C(4)	123.8 (2)	C(16)—C(17)—C(18)	120.2 (2)
C(2)—N(2)—C(4)	122.4 (2)	C(17)—C(18)—C(19)	119.8 (2)
N(1)—C(8)—N(2)	112.5 (2)	C(18)—C(19)—C(14)	120.7 (2)
N(1)—C(8)—C(7)	123.7 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)—H(O1)···O(4)	0.82	1.906 (2)	2.642 (2)	149.0 (1)
O(2)—H(O2)···O(3)	0.82	1.980 (2)	2.681 (2)	143.1 (2)
C(1)—H(1*A*)···O(3$^{\rm i}$)	0.97	2.781 (3)	3.319 (3)	115.7 (3)
C(1)—H(1*B*)···O(2$^{\rm i}$)	0.97	2.579 (3)	3.325 (3)	133.8 (3)
C(7)—H(7)···O(3$^{\rm ii}$)	0.98	2.571 (2)	3.361 (2)	137.7 (3)
C(7)—H(7)···O(4$^{\rm ii}$)	0.98	2.642 (3)	3.574 (3)	159.0 (2)

Symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

All non-H atoms were refined anisotropically. H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *XP* (Siemens, 1991). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1059). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bruno, G. & Randaccio, L. (1980). *Acta Cryst.* B**36**, 1711–1712.
Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Huang, Z.-T. & Wang, M.-X. (1994*a*). *Heterocycles*, **37**, 1233–1262.
Huang, Z.-T. & Wang, M.-X. (1994*b*). *The Chemistry of Enamines*, edited by Z. Rappoport, pp. 1303–1363. New York: Wiley.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1991). *XP. Molecular Graphics Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Ammonium and Isopropylammonium Salts of the Fumaric Acid Dianion

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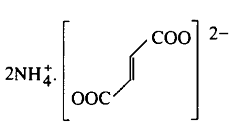
Abstract

The crystal structures of diammonium fumarate, $2NH_4^+.C_4H_2O_4^{2-}$, (I), and bis(isopropylammonium) fumarate, $2C_3H_7NH_3^+.C_4H_2O_4^{2-}$, (II), have been determined. The intermolecular N—H···O hydrogen bonds form a three-dimensional network in (I), whereas two-dimensional sheets are formed in (II) separated by layers of isopropyl groups. The N···O distances are 2.790 (1)–2.903 (1) Å in (I) and 2.747 (1)–2.807 (1) Å in (II). Differences between the solid-state photoreactivities of the fumaric acid ions in (I) and (II) are rationalized based on the crystal structures.

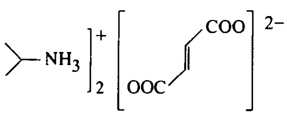
Comment

Organic solid-state reactions have the potential to control the stereoselectivity of chemical reactions. Many practical applications have been developed (Ramamurthy & Venkatesan, 1987; Toda, 1995; Gamlin *et al.*, 1996), since the topochemical photodimerization of *trans*-cinnamic acid was studied by Schmidt (1964).

Salt formation is one way of designing the molecular arrangement in crystals (Ito *et al.*, 1995; Ito & Olovsson, 1997). In the crystal of the ammonium salt, (I), the fumaric acid ions underwent facile *syn*-[2+2]-photodimerization, while in the isopropylammonium salt, (II), only *trans-cis* photoisomerization occurred (Ito, 1998).

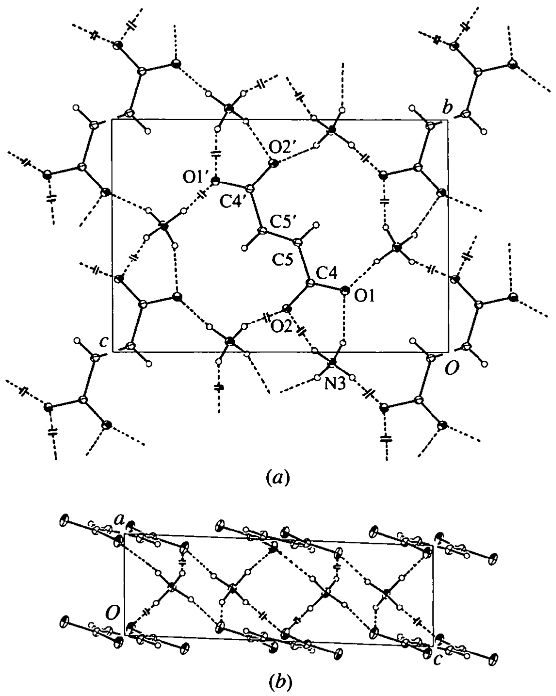


(I)



(II)

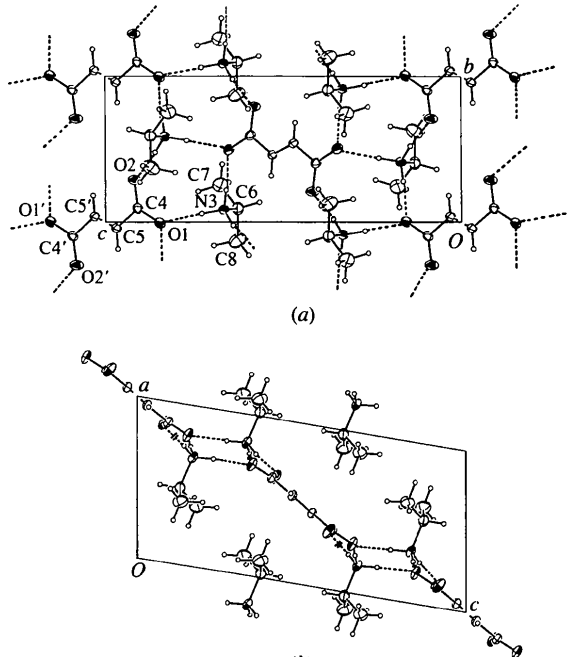
In both crystals, fumaric acid ions lie on centres of symmetry and all ammonium H atoms participate in the N—H···O hydrogen bonds. In (I), cation and anion layers are arranged alternately parallel to (100) to form a three-dimensional hydrogen-bonding network (Fig. 1). The shortest intermolecular distance between the C═C double bonds of fumarate ions is 3.733 (3) Å, which is one lattice translation along **a**. This arrangement is suitable for *syn*-photodimerization. In (II), anions and NH$_3^+$ moieties of the cations lie near (101) to form two-dimensional hydrogen-bonded sheets, which are separated by the layers of isopropyl groups of the cations (Fig. 2). The distance between the C═C bonds is longer than 6.2 Å, which corresponds with the lack of photodimerization in (II).



(*a*)

(*b*)

Fig. 1. The projections of the crystal structure of compound (I) (*a*) along **a** and (*b*) along **b**. Displacement ellipsoids are plotted at the 20% probability level. Dashed lines represent hydrogen bonds. The symbol - - -||- - - indicates that the two lines - - -| and |- - - are parallel but heights are different.



(*a*)

(*b*)

Fig. 2. The projections of the crystal structure of compound (II) (*a*) along **a** and (*b*) along **b**. Displacement ellipsoids are plotted at the 20% probability level.

Experimental

The title salts were prepared by mixing 1 mol equivalent of fumaric acid with 2 mol equivalents of aqueous ammonia or isopropylamine as described previously (Ito & Olovsson, 1997). Crystals of (I) were grown from methanol–2-propanol–water (13:1:2) and those of (II) from ethanol.

Compound (I)

Crystal data

2NH$_4^+$.C$_4$H$_2$O$_4^{2-}$
M_r = 150.13
Monoclinic
$P2_1/c$
a = 3.733 (3) Å
b = 8.009 (2) Å
c = 11.508 (2) Å
β = 92.46 (3)°
V = 343.7 (3) Å^3
Z = 2
D_x = 1.451 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14.1–14.9°
μ = 0.129 mm^{-1}
T = 298 K
Prism
0.5 × 0.5 × 0.4 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: none
1146 measured reflections
1008 independent reflections
908 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{\rm int} = 0.009$
$\theta_{\rm max} = 30.0°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: 6.1%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.048$
$S = 1.06$
908 reflections
66 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

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

	x	y	z	$U_{\rm eq}$
O1	0.11270 (7)	0.26340 (3)	0.30750 (2)	0.0312 (1)
O2	−0.07190 (7)	0.18730 (3)	0.48060 (2)	0.0295 (1)
N3	0.50400 (8)	−0.04600 (4)	0.34760 (3)	0.0262 (1)
C4	0.02290 (8)	0.29600 (4)	0.40990 (3)	0.0210 (1)
C5	0.03340 (9)	0.47490 (4)	0.44720 (3)	0.0241 (1)

Table 2. *Selected geometric parameters (Å, °) for (I)*

O1—C4	1.266 (1)	C4—C5	1.496 (1)
O2—C4	1.253 (1)	C5—C5$^{\rm i}$	1.314 (1)
O1—C4—O2	123.7 (1)	O2—C4—C5	118.9 (1)
O1—C4—C5	117.4 (1)	C4—C5—C5$^{\rm i}$	123.7 (1)

Symmetry code: (i) $-x, 1-y, 1-z$.

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O2$^{\rm i}$	0.931 (5)	1.963 (5)	2.852 (1)	159.1 (5)
N3—H3B···O1$^{\rm ii}$	0.970 (6)	1.828 (5)	2.790 (1)	170.8 (5)
N3—H3C···O2$^{\rm iii}$	0.881 (6)	1.991 (6)	2.840 (1)	161.5 (5)
N3—H3D···O1	0.936 (5)	2.022 (5)	2.903 (1)	156.2 (5)

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $-x, -y, 1-z$.

Compound (II)

Crystal data

$2C_3H_{10}N^+.C_4H_2O_4^{2-}$
$M_r = 234.30$
Monoclinic
$P2_1/n$
$a = 7.236$ (2) Å
$b = 6.275$ (2) Å
$c = 15.460$ (2) Å
$\beta = 99.55$ (1)°
$V = 692.3$ (3) Å^3
$Z = 2$
$D_x = 1.124$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.2$–$15.0°$
$\mu = 0.086$ mm^{-1}
$T = 298$ K
Plate
0.6 × 0.6 × 0.2 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
ω scans
Absorption correction: none
2164 measured reflections
2020 independent reflections
1258 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 30.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = -21 \rightarrow 21$
3 standard reflections every 100 reflections intensity decay: 10.7%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.045$
$S = 0.97$
1258 reflections
117 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\rm max} = 0.05$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

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

	x	y	z	$U_{\rm eq}$
O1	0.19240 (8)	−0.00410 (8)	0.84680 (3)	0.0640 (2)
O2	0.13830 (8)	0.29040 (8)	0.91750 (4)	0.0743 (2)
N3	0.1774 (1)	0.0859 (1)	0.66790 (5)	0.0499 (2)
C4	0.1320 (1)	0.0941 (1)	0.90750 (5)	0.0461 (2)
C5	0.0451 (1)	−0.0391 (1)	0.97000 (4)	0.0429 (2)
C6	−0.0251 (1)	0.0940 (2)	0.62810 (6)	0.0637 (3)
C7	−0.1217 (2)	0.2556 (2)	0.67760 (9)	0.0919 (5)
C8	−0.1075 (2)	−0.1253 (2)	0.6293 (1)	0.1063 (6)

Table 5. *Selected geometric parameters (Å, °) for (II)*

O1—C4	1.260 (1)	C5—C5$^{\rm i}$	1.315 (1)
O2—C4	1.241 (1)	C6—C7	1.510 (2)
N3—C6	1.493 (2)	C6—C8	1.501 (2)
C4—C5	1.493 (1)		
O1—C4—O2	124.6 (1)	N3—C6—C7	108.6 (1)
O1—C4—C5	116.3 (1)	N3—C6—C8	109.2 (1)
O2—C4—C5	119.1 (1)	C7—C6—C8	113.0 (1)
C4—C5—C5$^{\rm i}$	124.0 (1)		

Symmetry code: (i) $-x, -y, 2-z$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O2$^{\rm i}$	0.941 (8)	1.809 (8)	2.747 (1)	174.7 (8)
N3—H3B···O1	0.957 (8)	1.852 (8)	2.807 (1)	175.6 (8)
N3—H3C···O1$^{\rm ii}$	0.963 (10)	1.815 (9)	2.762 (1)	167.2 (8)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Both crystals gradually lose their transparency in air, which may be due to the vaporization of ammonia or amine. Therefore, the crystal specimen was coated with adhesive. The intensity decays of (I) (6.1%) and (II) (10.7%) were corrected based on the standard reflections.

For both compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs. Program(s) used to solve structures: *CRYSTAN-GM* (Edwards *et al.*, 1996) for (I); *CRYSTAN* (Edwards *et al.*, 1995) for (II). Program(s) used to refine structures: *CRYSTAN-GM* for (I); *CRYSTAN* for (II). Molecular graphics: *CRYSTAN-GM* for (I); *CRYSTAN* for (II). Software used to prepare material for publication: *CRYSTAN-GM* for (I); *CRYSTAN* for (II).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1034). Services for accessing these data are described at the back of the journal.

References

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1995). *CRYSTAN6.3. A Computer Program for the Solution and Refinement of Crystal Structures*. MacScience, Japan.
Gamlin, J. N., Jones, R., Leibovitch, M., Patrick, B., Scheffer, J. R. & Trotter, J. (1996). *Acc. Chem. Res.* **29**, 203–209.
Ito, Y. (1998). In preparation.
Ito, Y., Borecka, B., Scheffer, J. R. & Trotter, J. (1995). *Tetrahedron Lett.* **36**, 6083–6086.
Ito, Y. & Olovsson, G. (1997). *J. Chem. Soc. Perkin Trans.* pp. 127–133.
Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.
Rigaku Corporation (1993). *AFC/MSC Diffractometer Control System*. Rigaku Corporation, Tokyo, Japan.
Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 2014–2021.
Toda, F. (1995). *Acc. Chem. Res.* **28**, 480–486.

Acta Cryst. (1998). C**54**, 145–146

(±)-7,7,9,9-Tetramethyl-2,3:4,5-dinaphtho-1,6,8-trioxa-7,9-disilacyclonona-2,4-diene

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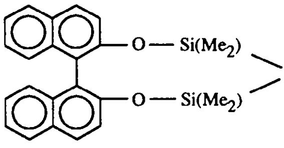
Abstract

The title compound, $C_{24}H_{24}O_3Si_2$, is a twofold symmetric silicocrown ether with the two dimethylsilyl groups attached to the O atoms of 1,1′-bi-2-naphthol, and bridged by another O atom.

Comment

Optically active 1,1′-bi-2-naphthol and its derivatives are excellent ligands of chiral catalysts and have a C_2 symmetry axis (Narasaka, 1991; Stock & Kellogg, 1996). Their high stereoselectivity stems from their flexible chiral axis which can adapt to the coordination requirements of various substrates and multidentate ligands. Complexes of these molecules with Lewis acids are used as asymmetric catalysts for organic reactions such as Diels–Alder addition (Markó *et al.*, 1996), Michael addition and aldol reactions (Shibasaki & Sasai, 1996). The title compound, (I), is one such molecule (Stock, 1994).



(I)

In this molecule, each Si atom is bonded to two O atoms and two methyl groups with a distorted tetrahedral configuration. The angles around Si1 and Si2 are in the ranges 105.8 (2)–111.7 (2) and 107.2 (2)–112.5 (2)°, respectively. The bond distances Si1—O1 [1.657 (2) Å] and Si2—O3 [1.647 (2) Å] are longer than Si1—O2 [1.626 (2) Å] and Si2—O2 [1.625 (2) Å]. The dihedral angle between the two naphthalene rings is 72.96 (6)°, and that between the least-squares planes through O1, Si1, O2, Si2 and O3 (with a maximum deviation of 0.206 Å), and the two naphthalene rings (C1–C10 and C11–C20) are 74.73 (8) and 78.75 (7)°, respectively.

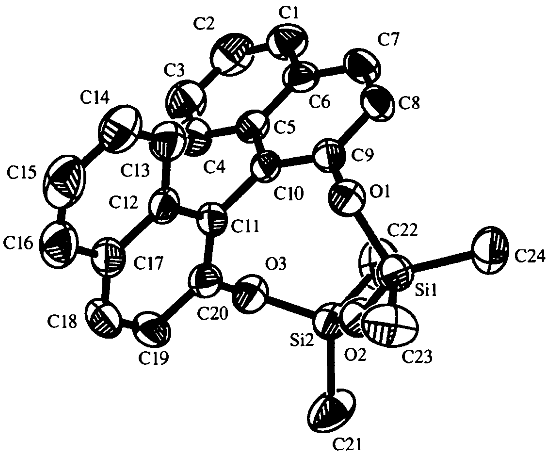


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was synthesized by treatment of racemic 1,1′-bi-2-naphthol with excess dichlorodimethylsilane in the presence of triethylamine, and then subsequent reaction with sodium cyclopentadienide in tetrahydrofuran at room temperature. Compound (I) was obtained as yellow prismatic crystals by slow evaporation from a petroleum ether and tetrahydrofuran mixed solution.

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