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Acta Cryst. (1995). **C51**, 871–873

An Unexpected By-Product in the Friedel–Crafts Acrylation of Ferrocene

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(Received 20 April 1994; accepted 27 October 1994)

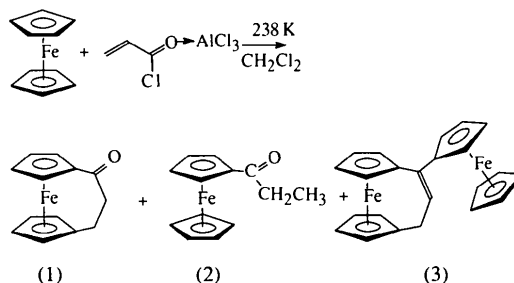
Abstract

The structure of an unsaturated [3]ferrocenophane derivative, 1,1'-(1-ferrocenyl-1,3-propenediyl)ferrocene, $[\text{Fe}_2(\text{C}_5\text{H}_5)(\text{C}_{18}\text{H}_{15})]$, has been determined. Because of the double bond, the three-carbon bridge and the directly attached C atoms are essentially coplanar. Strain in the bridged structure is manifested in a ring-tilt angle of 12.3° and in opening of the angles in the bridge.

Comment

The Friedel–Crafts reaction of ferrocene with acrylyl chloride and aluminium chloride constitutes a very convenient one-pot synthetic route to the bridged [3]ferrocenophane system (Turbit & Watts, 1972). We obtained results somewhat inconsistent with the published procedure in which a dichloromethane solution of acrylyl chloride was added to a solution containing aluminium chloride and ferrocene, but were able to obtain higher and more consistent yields of the desired [3]ferrocenophane-1-one (1) by initial formation of an acid–base complex of acrylyl chloride and aluminium chloride, followed by addition of the complex in dichloromethane solution to a solution of ferrocene at 238 K. Under these conditions, 30–60% yields of the ferrocenophanone were obtained, along with about 10% of propanoylferrocene (2) and a less polar by-product (3). The latter material, (3), melted with decomposition at 423 K. Mass spectral data suggested the composition to be $\text{Fc}_2\text{C}_3\text{H}_2$ ($\text{Fc} = \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$), but good NMR spectra were not obtainable because of insufficient solubility. The product formed clusters of red crystals upon

recrystallization from a hexane–dichloromethane mixture and these crystals were used for the structure analysis.



The crystal structure reveals the by-product to be an unsaturated [3]ferrocenophane derivative, 1-(ferrocenyl)- Δ^1 -[3]ferrocenophene. Formation of this product from the [3]ferrocenophanone by acid coordination to the keto group, attack of the cation on an unsubstituted ferrocene and dehydration of the resulting tertiary alcohol is readily envisaged.

Because of the double bond in the three-carbon bridge, atoms C1, C23, C11, C22 and C21 form a plane approximately orthogonal to the planes of the two cyclopentadienyl rings of the bridged ferrocene. The tilt angle between the two rings of the bridged ferrocene unit is 12.3° ; this value falls within the normal range of about 7 – 14° found in other [3]ferrocenophanes, e.g. 7.4° in 1,1'-trimethyleneferrocene (Hillman & Austin, 1987), 8.8° in [3]ferrocenophan-1-one (Jones, Marsh & Richards, 1965), 10° in 1,1'-(α -keto- γ -phenyltrimethylene)-2'-methylferrocene (Lecomte, Dusausoy, Protas & Moïse, 1973), 10° in 3,3'-trimethylene[1.1]ferrocenophane (Singletary, Hillman, Dauplaise, Kwick & Kerber, 1984), 12° in 2,2'-trimethylene[1.1]ferrocenophane (Singletary *et al.*, 1984), 12.9 and 13.6° in 1,1'-(propane-1,3-diyl)ferrocenium iodide (Dong *et al.*, 1991) and 13.6° in 2-benzylidene[3]ferrocenophane-1,3-dione (Gyepes, Glowiak & Toma, 1986). In addition, both ferrocene units are eclipsed, and the disorder

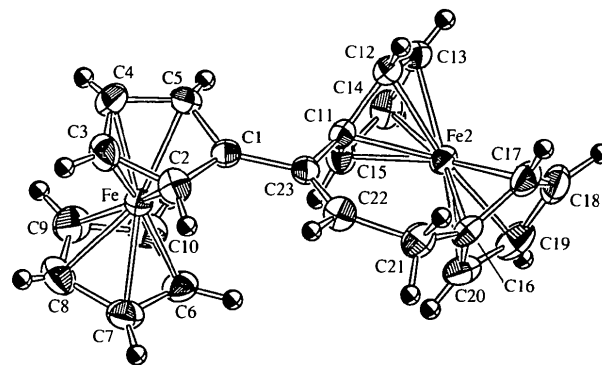


Fig. 1. ORTEP (Johnson, 1976) drawing of 1-(ferrocenyl)- Δ^1 -[3]ferrocenophene with 50% probability displacement ellipsoids.

commonly found in saturated trimethylene-bridged ferrocenophanes (Singletary *et al.*, 1984) is absent. Strain in the bridge is manifested in the C—C—C bond angles of 119.2(2)° for the *sp*³ C atom (C21) and 131.1(3) and 123.9(2)° for the *sp*² C atoms (C22 and C23).

The C—H distances in the final structure range from 0.81 to 1.04 Å (average 0.91 Å) and the isotropic *B* values range from 1.9 to 5.6 Å².

Experimental

Crystal data

[Fe₂(C₅H₅)(C₁₈H₁₅)]

M_r = 408.11

Triclinic

*P*1̄

a = 7.652(2) Å

b = 9.716(2) Å

c = 11.757(3) Å

α = 94.66(3)°

β = 98.25(4)°

γ = 104.17(4)°

V = 832.52(4) Å³

Z = 2

D_x = 1.628 Mg m⁻³

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

empirical, based on 8 ψ scans

T_{min} = 0.793, *T_{max}* = 0.997

3078 measured reflections

2923 independent reflections

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 13–17°

μ = 1.744 mm⁻¹

T = 298 K

Irregular

0.2 × 0.2 × 0.1 mm

Red

2275 observed reflections

[*F_o* > 3σ(*F_o*)]

R_{int} = 0.015

θ_{max} = 25°

h = 0 → 9

k = -11 → 11

l = -13 → 13

3 standard reflections

frequency: 100 min

intensity decay: 2%

Refinement

Refinement on *F*

R = 0.038

wR = 0.048

S = 1.082

2920 reflections

306 parameters

All H atoms refined

isotropically

$w = 1/[\sigma^2(I) + (0.04F^2)^2]^{1/2}$

(Δ/σ)_{max} = 0.04

Δρ_{max} = 0.93(17) e Å⁻³

Δρ_{min} = 0.00(17) e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

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

| | $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}a_i.a_j.$ | | | |
|-----|--|------------|------------|-----------------------|
| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B_{eq}</i> |
| Fe1 | 0.03706(5) | 0.32999(4) | 0.68219(3) | 2.233(8) |
| Fe2 | 0.60510(5) | 0.84004(4) | 0.78998(3) | 2.156(7) |
| C1 | 0.0842(3) | 0.5224(3) | 0.7839(2) | 2.35(5) |
| C2 | -0.0198(4) | 0.4074(3) | 0.8347(2) | 2.82(6) |
| C3 | -0.1831(4) | 0.3420(3) | 0.7567(3) | 3.33(6) |
| C4 | -0.1831(4) | 0.4136(3) | 0.6575(3) | 3.49(7) |
| C5 | -0.0197(4) | 0.5235(3) | 0.6731(3) | 2.78(6) |
| C6 | 0.2830(4) | 0.2882(3) | 0.6708(3) | 3.06(6) |
| C7 | 0.1691(4) | 0.1747(3) | 0.7145(3) | 3.18(6) |
| C8 | 0.0105(4) | 0.1192(3) | 0.6306(3) | 3.62(7) |

| | | | | |
|-----|-----------|-----------|-----------|---------|
| C9 | 0.0268(4) | 0.1983(3) | 0.5356(3) | 3.72(7) |
| C10 | 0.1954(4) | 0.3036(3) | 0.5606(3) | 3.34(6) |
| C11 | 0.3490(3) | 0.7188(3) | 0.7536(2) | 2.17(5) |
| C12 | 0.3494(4) | 0.8655(3) | 0.7517(2) | 2.47(5) |
| C13 | 0.4520(4) | 0.9223(3) | 0.6680(2) | 2.97(6) |
| C14 | 0.5131(4) | 0.8117(3) | 0.6148(2) | 3.02(6) |
| C15 | 0.4486(4) | 0.6864(3) | 0.6657(2) | 2.76(6) |
| C16 | 0.6606(4) | 0.7937(3) | 0.9520(2) | 2.72(6) |
| C17 | 0.7109(4) | 0.9444(3) | 0.9513(2) | 3.11(6) |
| C18 | 0.8436(4) | 0.9784(4) | 0.8775(3) | 3.61(7) |
| C19 | 0.8761(4) | 0.8499(4) | 0.8346(3) | 3.86(7) |
| C20 | 0.7672(4) | 0.7367(3) | 0.8813(3) | 3.39(6) |
| C21 | 0.5153(4) | 0.7117(3) | 1.0137(2) | 3.13(6) |
| C22 | 0.3367(4) | 0.6243(3) | 0.9437(2) | 2.74(6) |
| C23 | 0.2634(3) | 0.6221(3) | 0.8333(2) | 2.20(5) |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|------------|----------|-------------|----------|
| Fe1—C1 | 2.059(3) | C2—C3 | 1.412(4) |
| Fe1—C2 | 2.034(3) | C3—C4 | 1.406(5) |
| Fe1—C3 | 2.031(3) | C4—C5 | 1.410(4) |
| Fe1—C4 | 2.037(3) | C6—C7 | 1.410(4) |
| Fe1—C5 | 2.038(3) | C6—C10 | 1.408(4) |
| Fe1—C6 | 2.040(3) | C7—C8 | 1.410(4) |
| Fe1—C7 | 2.042(3) | C8—C9 | 1.409(5) |
| Fe1—C8 | 2.040(3) | C9—C10 | 1.413(4) |
| Fe1—C9 | 2.042(3) | C11—C12 | 1.426(4) |
| Fe1—C10 | 2.042(3) | C11—C15 | 1.428(4) |
| Fe2—C11 | 1.989(2) | C11—C23 | 1.486(4) |
| Fe2—C12 | 2.023(3) | C12—C13 | 1.410(4) |
| Fe2—C13 | 2.057(3) | C13—C14 | 1.409(5) |
| Fe2—C14 | 2.052(3) | C14—C15 | 1.411(4) |
| Fe2—C15 | 2.017(2) | C16—C17 | 1.421(4) |
| Fe2—C16 | 2.003(3) | C16—C20 | 1.416(5) |
| Fe2—C17 | 2.031(3) | C16—C21 | 1.513(4) |
| Fe2—C18 | 2.057(3) | C17—C18 | 1.423(4) |
| Fe2—C19 | 2.041(3) | C18—C19 | 1.400(5) |
| Fe2—C20 | 2.025(3) | C19—C20 | 1.409(4) |
| C1—C2 | 1.432(4) | C21—C22 | 1.504(3) |
| C1—C5 | 1.427(4) | C22—C23 | 1.335(4) |
| C1—C23 | 1.479(3) | | |
| C1—Fe1—C2 | 41.0(1) | C11—Fe2—C20 | 110.1(1) |
| C1—Fe1—C3 | 68.7(1) | C12—Fe2—C13 | 40.4(1) |
| C1—Fe1—C4 | 68.6(1) | C12—Fe2—C14 | 68.0(1) |
| C1—Fe1—C5 | 40.8(1) | C12—Fe2—C15 | 68.8(1) |
| C1—Fe1—C6 | 108.3(1) | C12—Fe2—C16 | 112.2(1) |
| C1—Fe1—C7 | 125.4(1) | C12—Fe2—C17 | 106.5(1) |
| C1—Fe1—C8 | 162.1(1) | C12—Fe2—C18 | 131.0(1) |
| C1—Fe1—C9 | 156.2(1) | C12—Fe2—C19 | 170.6(1) |
| C1—Fe1—C10 | 121.2(1) | C12—Fe2—C20 | 145.8(1) |
| C2—Fe1—C3 | 40.7(1) | C13—Fe2—C14 | 40.1(1) |
| C2—Fe1—C4 | 68.3(1) | C13—Fe2—C15 | 68.2(1) |
| C2—Fe1—C5 | 68.3(1) | C13—Fe2—C16 | 150.1(1) |
| C2—Fe1—C6 | 121.7(1) | C13—Fe2—C17 | 122.5(1) |
| C2—Fe1—C7 | 107.9(1) | C13—Fe2—C18 | 116.3(1) |
| C2—Fe1—C8 | 124.8(1) | C13—Fe2—C19 | 135.4(1) |
| C2—Fe1—C9 | 161.5(1) | C13—Fe2—C20 | 168.1(1) |
| C2—Fe1—C10 | 156.6(1) | C14—Fe2—C15 | 40.6(1) |
| C3—Fe1—C4 | 40.4(1) | C14—Fe2—C16 | 160.0(1) |
| C3—Fe1—C5 | 68.1(1) | C14—Fe2—C17 | 158.7(1) |
| C3—Fe1—C6 | 156.4(1) | C14—Fe2—C18 | 126.8(1) |
| C3—Fe1—C7 | 120.9(1) | C14—Fe2—C19 | 114.2(1) |
| C3—Fe1—C8 | 107.4(1) | C14—Fe2—C20 | 128.1(1) |
| C3—Fe1—C9 | 124.6(1) | C15—Fe2—C16 | 119.7(1) |
| C3—Fe1—C10 | 161.5(1) | C15—Fe2—C17 | 158.7(1) |
| C4—Fe1—C5 | 40.5(1) | C15—Fe2—C18 | 156.0(1) |
| C4—Fe1—C6 | 162.2(1) | C15—Fe2—C19 | 119.2(1) |
| C4—Fe1—C7 | 155.6(1) | C15—Fe2—C20 | 103.3(1) |
| C4—Fe1—C8 | 120.5(1) | C16—Fe2—C17 | 41.2(1) |
| C4—Fe1—C9 | 107.6(1) | C16—Fe2—C18 | 69.2(1) |
| C4—Fe1—C10 | 125.0(1) | C16—Fe2—C19 | 69.1(1) |
| C5—Fe1—C6 | 125.9(1) | C16—Fe2—C20 | 41.1(1) |
| C5—Fe1—C7 | 162.6(1) | C17—Fe2—C18 | 40.8(1) |
| C5—Fe1—C8 | 155.6(1) | C17—Fe2—C19 | 68.0(1) |
| C5—Fe1—C9 | 121.0(1) | C17—Fe2—C20 | 68.4(1) |
| C5—Fe1—C10 | 108.1(1) | C18—Fe2—C19 | 40.0(1) |
| C6—Fe1—C7 | 40.4(1) | C18—Fe2—C20 | 68.0(1) |

| | | | |
|-------------|-----------|-------------|-----------|
| C6—Fe1—C8 | 67.8 (1) | C19—Fe2—C20 | 40.5 (1) |
| C6—Fe1—C9 | 67.8 (1) | Fe1—C1—C2 | 68.6 (1) |
| C6—Fe1—C10 | 40.4 (1) | C3—C4—C5 | 108.1 (2) |
| C7—Fe1—C8 | 40.4 (1) | Fe1—C1—C5 | 68.8 (1) |
| C7—Fe1—C9 | 67.9 (1) | Fe1—C1—C23 | 127.2 (2) |
| C7—Fe1—C10 | 68.1 (1) | C2—C1—C5 | 106.3 (2) |
| C8—Fe1—C9 | 40.4 (1) | C2—C1—C23 | 128.1 (2) |
| C8—Fe1—C10 | 68.1 (1) | C5—C1—C23 | 125.6 (2) |
| C9—Fe1—C10 | 40.5 (1) | Fe1—C2—C1 | 70.4 (2) |
| C11—Fe2—C12 | 41.6 (1) | Fe1—C2—C3 | 69.5 (2) |
| C11—Fe2—C13 | 69.6 (1) | C1—C2—C3 | 108.4 (2) |
| C11—Fe2—C14 | 69.6 (1) | Fe1—C3—C2 | 69.8 (2) |
| C11—Fe2—C15 | 41.8 (1) | Fe1—C3—C4 | 70.0 (2) |
| C11—Fe2—C16 | 97.0 (1) | C2—C3—C4 | 108.3 (2) |
| C11—Fe2—C17 | 120.9 (1) | Fe1—C4—C3 | 69.5 (2) |
| C11—Fe2—C18 | 161.5 (1) | Fe1—C4—C5 | 69.8 (2) |
| C11—Fe2—C19 | 147.6 (1) | Fe1—C5—C1 | 70.4 (2) |
| Fe1—C5—C4 | 69.7 (2) | Fe2—C14—C13 | 70.1 (2) |
| C1—C5—C4 | 108.9 (3) | Fe2—C14—C15 | 68.4 (1) |
| Fe1—C6—C7 | 69.9 (2) | C13—C14—C15 | 108.1 (3) |
| Fe1—C6—C10 | 69.9 (2) | Fe2—C15—C11 | 68.1 (1) |
| C7—C6—C10 | 108.5 (2) | Fe2—C15—C14 | 71.1 (1) |
| Fe1—C7—C6 | 69.7 (2) | C11—C15—C14 | 108.7 (3) |
| Fe1—C7—C8 | 69.7 (2) | Fe2—C16—C17 | 70.4 (2) |
| C6—C7—C8 | 107.7 (3) | Fe2—C16—C20 | 70.2 (2) |
| Fe1—C8—C7 | 69.9 (2) | Fe2—C16—C21 | 122.7 (2) |
| Fe1—C8—C9 | 69.9 (2) | C17—C16—C20 | 106.9 (3) |
| C7—C8—C9 | 108.1 (3) | C17—C16—C21 | 125.8 (3) |
| Fe1—C9—C8 | 69.8 (2) | C20—C16—C21 | 127.3 (3) |
| C12—C11—C23 | 126.0 (2) | Fe2—C17—C16 | 68.4 (1) |
| C15—C11—C23 | 127.8 (2) | Fe2—C19—C18 | 70.6 (2) |
| Fe2—C12—C11 | 67.9 (2) | Fe2—C19—C20 | 69.1 (2) |
| Fe2—C12—C13 | 71.1 (2) | C18—C19—C20 | 108.7 (3) |
| C11—C12—C13 | 109.0 (3) | Fe2—C20—C16 | 68.6 (2) |
| Fe1—C9—C10 | 69.8 (2) | Fe2—C20—C19 | 70.3 (2) |
| C8—C9—C10 | 108.2 (3) | C16—C20—C19 | 108.5 (3) |
| Fe1—C10—C6 | 69.8 (2) | Fe2—C17—C18 | 70.6 (2) |
| Fe1—C10—C9 | 69.8 (2) | C16—C17—C18 | 108.4 (3) |
| C6—C10—C9 | 107.5 (3) | Fe2—C18—C17 | 68.6 (1) |
| Fe2—C11—C12 | 70.5 (1) | Fe2—C18—C19 | 69.4 (2) |
| Fe2—C11—C15 | 70.1 (1) | C17—C18—C19 | 107.5 (3) |
| Fe2—C11—C23 | 123.5 (2) | C16—C21—C22 | 119.2 (2) |
| C12—C11—C15 | 106.2 (2) | C21—C22—C23 | 131.1 (3) |
| Fe2—C13—C12 | 68.5 (2) | C1—C23—C11 | 115.7 (2) |
| Fe2—C13—C14 | 69.8 (2) | C1—C23—C22 | 120.4 (2) |
| C12—C13—C14 | 107.9 (3) | C11—C23—C22 | 123.9 (2) |

The MULTAN11/82 program system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) was used to solve the structure.

We thank Messrs Anthony DiCristifaro and Jens John for carrying out the reactions and isolating the product. The structure was solved under the auspices of the second American Crystallographic Association Summer School at the University of Pittsburgh in August, 1993. We gratefully acknowledge the assistance of Dr John Ruble (Pittsburgh) and Dr Grahame Williams (Enraf-Nonius Co.) in this connection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and r.m.s. amplitudes have been deposited with the IUCr (Reference: BK1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The 7,7,8,8-Tetracyanoquinodimethane Salt of (*C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), [Ni(*C-meso*-Me₆[14]aneN₄)](TCNQ)₂

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(Received 25 February 1994; accepted 12 September 1994)

Abstract

The title compound, [Ni(C₁₆H₃₆N₄)](C₁₂H₄N₄)₂, consists of cationic (*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) entities and 7,7,8,8-tetracyanoquinodimethane anions. The Ni atom is surrounded by four N atoms from the tetraaza macrocycle in a square-planar arrangement. The average Ni—N distance is 1.953 (3) Å. The TCNQ[−] radical anions are arranged so as to form discrete dimers with the usual twist-type π overlap which leads to a diamagnetic ground state. The intra- and interdimer separations between the mean molecular planes within a TCNQ column are 3.081 (5) and 5.113 (5) Å, respectively.