

Natalie Bratych, Kathryn Hassall
and Jonathan White*School of Chemistry, University of Melbourne,
Parkville, Victoria 3010, AustraliaCorrespondence e-mail:
whitejm@unimelb.edu.au

Key indicators

Single-crystal X-ray study
 $T = 130\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.034
 wR factor = 0.094
Data-to-parameter ratio = 12.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Redetermination of the structure of
diferrocenyl ketone at low temperature

The structure of diferrocenyl ketone, $[\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{C}_{11}\text{H}_8\text{O})]$, was redetermined as part of our investigations of carbon–iron hyperconjugation. The title ketone lies on a twofold axis of symmetry. Lengthening of the carbonyl $\text{C}=\text{O}$ bond [$1.237(3)\text{ \AA}$ compared with that expected for simple ketones, 1.210 \AA] and slight slippage of the Fe atom towards the carbonyl carbon are consistent with the presence of strong hyperconjugation of the carbonyl group with the adjacent Fe–C bond. The structure was determined at 130 K .

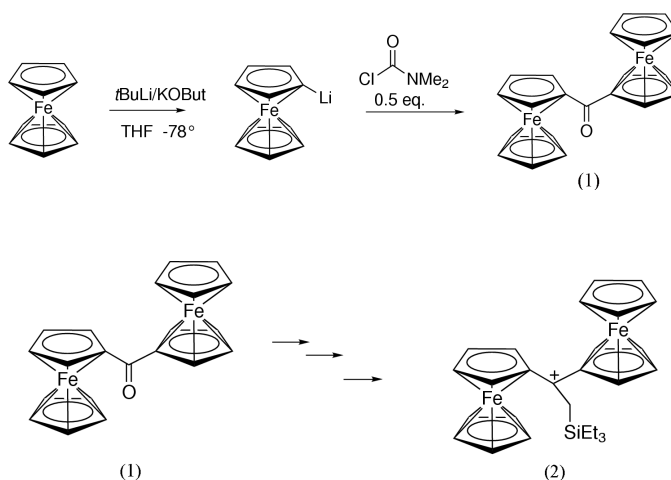
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Comment

The title compound, (1), is an intermediate in the synthesis of the β -silyl-substituted diferrocenyl cation (2).



Upon full characterization of (1), we observed that the IR carbonyl-stretching frequency of (1), 1609 cm^{-1} , was very low for a ketone; normally values lie in the range $1650\text{--}1750\text{ cm}^{-1}$. Furthermore, the ^{13}C NMR chemical shift occurred at 199 p.p.m. , which is at a high field for a typical ketone carbon. The low stretching frequency in the IR spectrum, and the high-field resonance in the ^{13}C NMR implied that the resonance form (1a) (Fig. 1) was making a significant contribution to the ground state structure of (1). The resonance form (1a) is

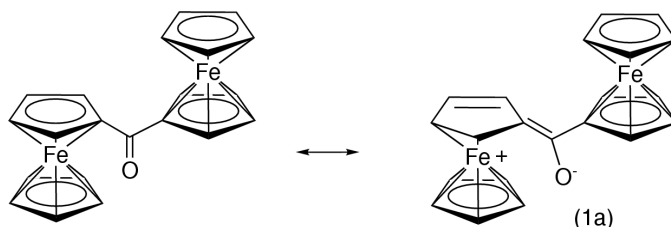


Figure 1
Hyperconjugation in diferrocenyl ketone, (1).

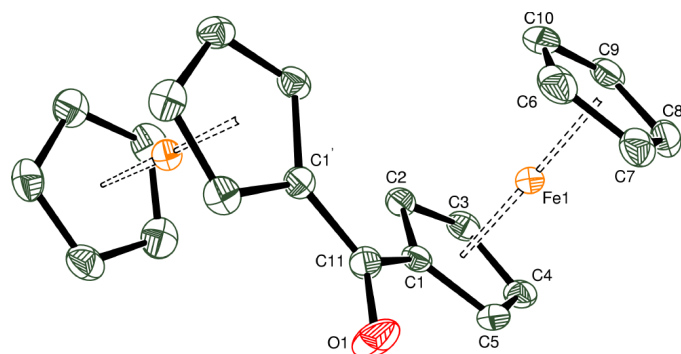


Figure 2
Displacement ellipsoid plot of (1); ellipsoids are at the 20% probability level.

presumably stabilized by hyperconjugation with the carbon–iron bonds of the two attached ferrocenyl substituents. Our interest in the structural effects of carbon–metal hyperconjugation (Pool *et al.*, 1998; Chan *et al.*, 1996; White & Robertson, 1992; White *et al.*, 2000), we determined the structure of (1) at low temperature to establish whether there were any significant structural effects consistent with hyperconjugation between the ferrocenyl substituents and the carbonyl group. A previous room-temperature determination of the structure of (1) (Trotter & Macdonald, 1966) was not deemed sufficiently precise for our requirements.

The ketone group of (1) lies on a crystallographic twofold axis of symmetry. The attached ferrocenyl substituents are slightly twisted from coplanarity with the ketone carbonyl [C5–C1–C11–O1 = $-17.7(2)^\circ$], a conformation which is a compromise between maximizing hyperconjugation of the carbonyl group with the ferrocenyl substituents [the Fe1–C1–C11–O1 dihedral angle is $105.4(1)^\circ$, whereas maximum overlap occurs when this angle is 90°], and minimizing non-bonded repulsions involving the C2 and C5 H atoms on each ferrocenyl substituent with the second ferrocenyl substituent and the carbonyl O atom. The carbonyl bond distance (C11–O1) is $1.237(3) \text{ \AA}$, which is significantly longer than a typical ketone carbonyl, 1.210 \AA (Allen *et al.*, 1987). There are also some interesting differences in the Fe–Cp bond distances in the substituted cyclopentadienyl ring (Table 1). These distances show that the Fe atom has slipped slightly toward the carbonyl-bearing carbon (C1); by contrast there are no significant differences in the Fe–Cp distances in the unsubstituted cyclopentadienyl ring, which is, in addition, essentially parallel to the substituted cyclopentadienyl [angle between the planes defined by C1–C5 and C6–C10 is $1.8(1)^\circ$]. The slipping of Fe1 towards C1 presumably occurs to maximize the overlap between the Fe1–C1 bond and the carbonyl π orbital.

Experimental

The title compound was prepared according to the reaction *Scheme*. Thus, ferrocene was converted into lithioferrocene by treatment with *tert*-butyllithium and potassium *tert*-butoxide in tetrahydrofuran. Reaction with *N*-(dimethylamino)chlorocarbamate afforded (1) in 55% yield. Crystals of (1) were grown from pentane.

Crystal data

[Fe₂(C₅H₅)₂(C₁₁H₈O)]
 $M_r = 398.05$
 Monoclinic, $P2_1/c$
 $a = 10.4058(11) \text{ \AA}$
 $b = 6.1448(7) \text{ \AA}$
 $c = 12.9773(14) \text{ \AA}$
 $\beta = 110.835(2)^\circ$
 $V = 775.53(15) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.705 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 2038 reflections
 $\theta = 3.3\text{--}28.8^\circ$
 $\mu = 1.87 \text{ mm}^{-1}$
 $T = 130.0(2) \text{ K}$
 Rod, red
 $0.35 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Blessing, 1995; Sheldrick, 2001)
 $T_{\min} = 0.86, T_{\max} = 1.0$
 3879 measured reflections

1368 independent reflections
 1228 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.078$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -12 \rightarrow 12$
 $k = -7 \rightarrow 4$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.094$
 $S = 1.02$
 1368 reflections
 111 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.80 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.007(2)

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1–C5	1.424 (3)	C6–C7	1.413 (3)
C1–C2	1.444 (3)	C6–C10	1.420 (3)
C1–C11	1.477 (2)	C6–Fe1	2.046 (3)
C1–Fe1	2.0344 (19)	C7–C8	1.422 (3)
C2–C3	1.411 (3)	C7–Fe1	2.045 (2)
C2–Fe1	2.039 (2)	C8–C9	1.418 (3)
C3–C4	1.427 (3)	C8–Fe1	2.045 (3)
C3–Fe1	2.052 (2)	C9–C10	1.412 (3)
C4–C5	1.418 (3)	C9–Fe1	2.043 (2)
C4–Fe1	2.056 (2)	C10–Fe1	2.038 (2)
C5–Fe1	2.0495 (19)	C11–O1	1.237 (3)
C5–C1–C11	122.32 (17)	O1–C11–C1	118.37 (12)
C2–C1–C11	130.15 (18)	C1–Fe1–C10	124.53 (9)
C11–C1–Fe1	125.69 (12)		
C5–C1–C11–O1	$-17.7(2)$	Fe1–C1–C11–O1	$-105.38(13)$
C2–C1–C11–O1	$162.34(17)$	Fe1–C1–C11–C1 ¹	$74.62(13)$

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

H atoms were fixed in idealized positions.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 1999); program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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