

The one-electron oxidation product of a metallocenyl-terminated cyanine

Stephen Barlow,^{a*†} Michael W. Day^a and Seth R. Marder^{b‡}

^aBeckman Institute, 139-74 California Institute of Technology, Pasadena, CA 91125, USA, and ^bBeckman Institute and Jet Propulsion Laboratory, 139-74 California Institute of Technology, Pasadena, CA 91125, USA

Correspondence e-mail: stephen.barlow@chem.ox.ac.uk

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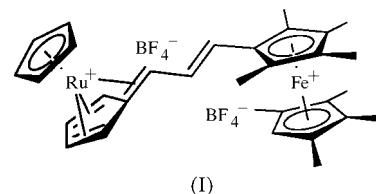
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The 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyloxy)allylium cation readily undergoes one-electron oxidation to a dication in which an octamethylferrocenium moiety is bridged by a vinylene group to a $[(\eta^6\text{-fulvene})(\eta^5\text{-cyclopentadienyl})\text{ruthenium}]^+$ moiety. In the title compound, 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyloxy)prop-1-enium(2+) bis(tetrafluoroborate), $[\text{FeRu}(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_{13})(\text{C}_{17}\text{H}_{19})](\text{BF}_4)_2$, the C—C bond lengths in the bridge (average for two independent molecules) are, starting from the *ipso* octamethylferrocenium carbon and ending at the *exo* carbon of the coordinated fulvene, 1.455 (6), 1.344 (3) and 1.449 (8) Å, indicating a localized electronic structure.

Comment

In the course of our work on symmetrical and unsymmetrical metallocene-terminated polymethines (Barlow *et al.*, 2000), aimed at understanding Peierls distortion effects in cyanines (Tolbert, 1992, and references therein), we attempted to isolate 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyloxy)allylium tetrafluoroborate by treating 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyloxy)prop-2-en-1-ol with anhydrous HBF_4 . We found the product contained comparable amounts of the target compound and its one-electron oxidation product, (I), which is the subject of the present structure determination (Fig. 1). We did not encounter complications from oxidation in the analogous synthesis of a variety of related ferrocene and octamethylferrocene allylium salts. Significantly, electrochemistry shows 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyloxy)allylium is more easily oxidized ($E_{1/2} = -190$ mV *versus* ferrocenium/ferrocene in tetrahydrofuran) than these other species ($E_{1/2} = -140$ to $+145$ mV). Presumably the oxidant is

H^+ . Several cases of similar acids effecting the oxidation of organometallics with similar potentials have been reported (Connelly & Geiger, 1996, and references therein).



The octamethylferrocenyl moiety has clearly been oxidized; the average Fe—C distance of 2.098 (3) Å [range 2.065 (5)–2.120 (5) Å] may be compared with average Fe—C distances of 2.050 (2) Å for decamethylferrocene (Freyberg *et al.*, 1979) and between 2.086 (2) and 2.096 (1) Å for a variety of decamethylferrocenium salts (Miller *et al.*, 1987, and references therein). The ruthenium coordination is best described as $(\eta^6\text{-fulvene})(\eta^5\text{-cyclopentadienyl})$ and is similar to that in other ruthenocenyloxy carbocations. The Ru— α -C distances of 2.367 (6) (molecule A) and 2.337 (6) Å (molecule B) can be compared with literature values ranging from 2.270 (3) to 2.571 (4) Å (Yanovsky *et al.*, 1989; Watanabe *et al.*, 1996a,b; Sato *et al.*, 1998; Barlow *et al.*, 1999), while the Ru—C(ring) distances fall in the range 2.082 (5) to 2.232 (5) Å. The allylium bridging group shows clear bond-length alternation [0.100 (10) Å in molecule A and 0.111 (11) Å in molecule B] between the formally single C29—C30 bond and the formally double C30—C31 bond, similar in magnitude to that in the structures of the Peierls-distorted cation 1,3-bis(ruthenocenyloxy)allylium [0.100 (6) Å] (Barlow *et al.*, 1999) and of 1-(ferrocenyl)-3-ruthenocenyloxyallylium [0.100 (7) Å] (Barlow *et al.*, 2000), both of which can be considered as a $(\eta^6\text{-fulvene})(\eta^5\text{-cyclopentadienyl})\text{ruthenium}$ cation vinylene-bridged to a 'normal' metallocene. Unfortunately, we have no direct evidence for the structure of our original target compound. However, electrochemical data suggest the structure may be similar to that of 1-(ferrocenyl)-3-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)allylium (Barlow *et al.*, 2000), in which the cationic charge is shared, albeit

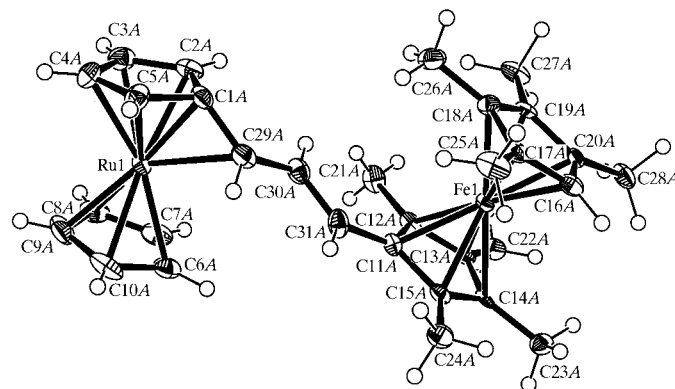


Figure 1

View of one of the two independent cations (A) in the asymmetric unit of (I), showing 50% displacement probability ellipsoids. The other cation is labeled in an analogous fashion and has a similar structure.

[†] Current address: Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, England.

[‡] Current address: Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA.

unevenly, between the two metallocenes. Thus, it appears that, in this case, it is the oxidation which leads to the shift of the ruthenium to full fulvene coordination.

Experimental

Attempts were made to isolate 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyl)allylium tetrafluoroborate by the method we used for a range of other bis(metallocenyl)allylium salts (Barlow *et al.*, 2000). Specifically, a diethyl ether solution of 1-(2,3,4,5,1',2',3',4'-octamethylferrocen-1-yl)-3-(ruthenocenyl)prop-2-en-1-ol (Barlow *et al.*, 2000) was treated with ethereal HBF₄. The resulting precipitate was washed with diethyl ether and extracted into dichloromethane solution. Layering of this solution with diethyl ether afforded a crystalline product, which was found to be a mixture of the desired compound and its one-electron oxidation product by elemental analysis (which indicated approximately half the material to be oxidized) and ¹H NMR (which indicated paramagnetic species present). Both compounds are reasonably stable in the solid state and in solution in deoxygenated dichloromethane, but solutions exposed to air, or in more polar solvents such as Me₂SO, slowly decompose. We were unable to separate the two compounds in bulk. However, a number of crystals were found to be the oxidation product and are the subject of the present structure determination.

Crystal data

[FeRu(C ₅ H ₅)(C ₉ H ₁₃)(C ₁₇ H ₁₉)]-(BF ₄) ₂	$D_x = 1.657 \text{ Mg m}^{-3}$
$M_r = 740.16$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 19.178 (4) \text{ \AA}$	$\theta = 13.5\text{--}14.2^\circ$
$b = 10.988 (3) \text{ \AA}$	$\mu = 1.071 \text{ mm}^{-1}$
$c = 28.728 (7) \text{ \AA}$	$T = 85 \text{ K}$
$\beta = 101.75 (2)^\circ$	Blade, dark green-brown
$V = 5927 (2) \text{ \AA}^3$	$0.39 \times 0.33 \times 0.14 \text{ mm}$
$Z = 8$	

Data collection

CAD-4 diffractometer	$R_{\text{int}} = 0.037$
ω scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -22 \rightarrow 22$
$T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.861$	$k = -13 \rightarrow 13$
22 328 measured reflections	$l = 0 \rightarrow 34$
10 404 independent reflections	3 standard reflections
7469 reflections with $I > 2\sigma(I)$	frequency: 75 min
	intensity decay: 0.36%

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R(F) = 0.052$	$w = 1/\sigma^2(F_o^2)$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.751$	$\Delta\rho_{\text{max}} = 1.927 \text{ e \AA}^{-3}$
10 403 reflections	$\Delta\rho_{\text{min}} = -0.851 \text{ e \AA}^{-3}$
832 parameters	

Refined C—H distances are in the range 0.78 (4)–1.14 (4) Å.

Data reduction: CRYM (Duchamp, 1964); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to

Table 1

Selected geometric parameters (Å, °).

C1A—C29A	1.428 (7)	C1B—C29B	1.405 (7)
C11A—C31A	1.461 (7)	C11B—C31B	1.450 (7)
C29A—C30A	1.441 (7)	C29B—C30B	1.457 (8)
C30A—C31A	1.341 (7)	C30B—C31B	1.346 (8)
C1A—C29A—C30A	125.6 (6)	C1B—C29B—C30B	123.9 (6)
C31A—C30A—C29A	120.6 (5)	C31B—C30B—C29B	122.0 (6)
C30A—C31A—C11A	128.5 (5)	C30B—C31B—C11B	128.0 (5)

refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1066). Services for accessing these data are described at the back of the journal.

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