

## Supporting Information for:

# Into the second dimension with ferrocene *bis*-amidinium salts

Francesca A. Stokes,<sup>a</sup> Martyn P. Coles,<sup>\*b</sup> and Peter B. Hitchcock<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Sussex, Falmer, Brighton, UK.

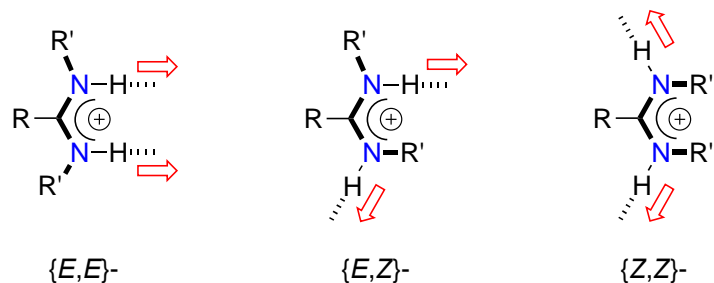
<sup>b</sup> School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand.

Fax: +64 (0)4 4635241; Tel: +64 (0)4 463 6357; E-mail: martyn.coles@vuw.ac.nz

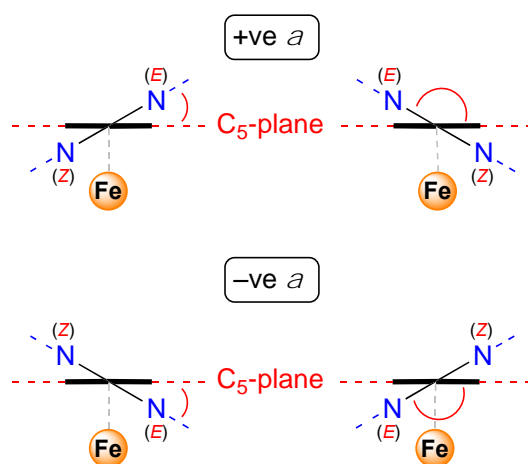
## Contents

p2	Fig S1	Definition of <i>E</i> - and <i>Z</i> -
p2	Fig S2	Definition of $\alpha$
p3	Fig S3	Definition of <i>l</i>
p3	Fig S4	Definition of $\phi_{\text{O}}$ and $\phi_{\text{N}}$
p3	Fig S5	Definition of $d_{\text{O}}$ and $d_{\text{N}}$
p4	Fig S6	Definition <i>ss-S<sub>p</sub></i> and <i>ss-R<sub>p</sub></i>
p5	Table S1	Summary of geometric data for [1] <sub>∞</sub> and [2] <sub>∞</sub>
p6	Fig S7	Disorder in [ <sup>t</sup> BuCO <sub>2</sub> ⋯H⋯O <sub>2</sub> C <sup>t</sup> Bu] <sup>-</sup>
p7	Fig S8	Contour map showing hydrogen H3x

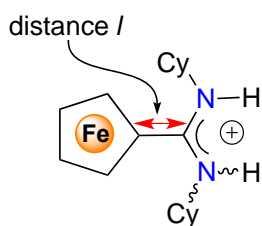
**Figure S1** Definition of *E*- and *Z*- with respect distribution of substituents about a tri-substituted amidinium cation (for **1** and **2**, R = ferrocenyl, R' = Cy)



**Figure S2** Definition of  $\alpha$  (dihedral angle between the amidinium and  $C_5$ -ring, with +ve and -ve values defined relative to the *E*- and *Z*-nitrogen groups)



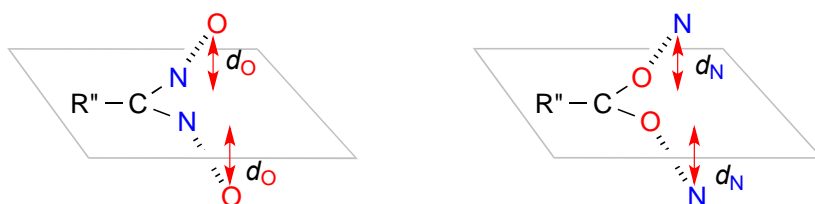
**Figure S3** Definition of  $l$  (the C<sub>5</sub>–CN<sub>2</sub> bond length)



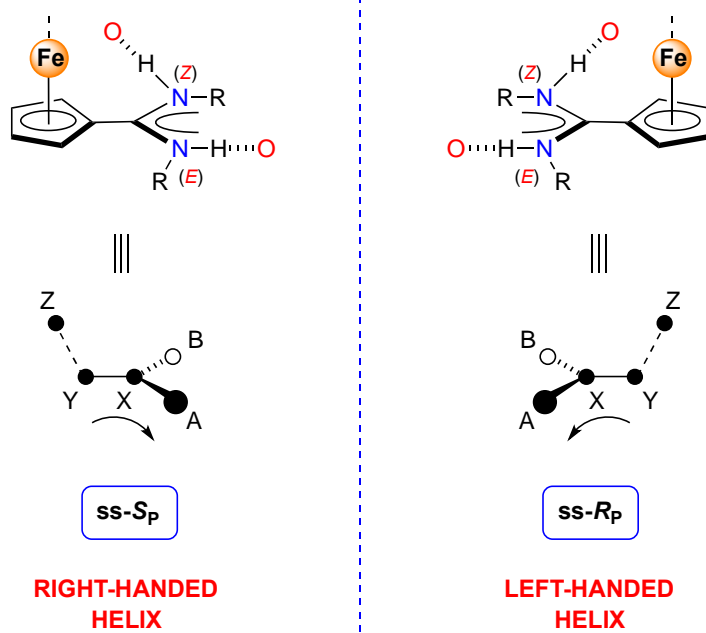
**Figure S4** Definition of  $\phi_{\text{O}}$  and  $\phi_{\text{N}}$  (the bond angle at oxygen and nitrogen subtending the amidinium:carboxylate bridge)



**Figure S5** Definition of  $d_{\text{O}}$  and  $d_{\text{N}}$  (the distance of the oxygen and nitrogen atoms from the C–CN<sub>2</sub> and C–CO<sub>2</sub> planes, respectively)



**Figure S6** Definition  $ss-S_p$  and  $ss-R_p$  chirality, prioritizing the (*E*)-nitrogen group

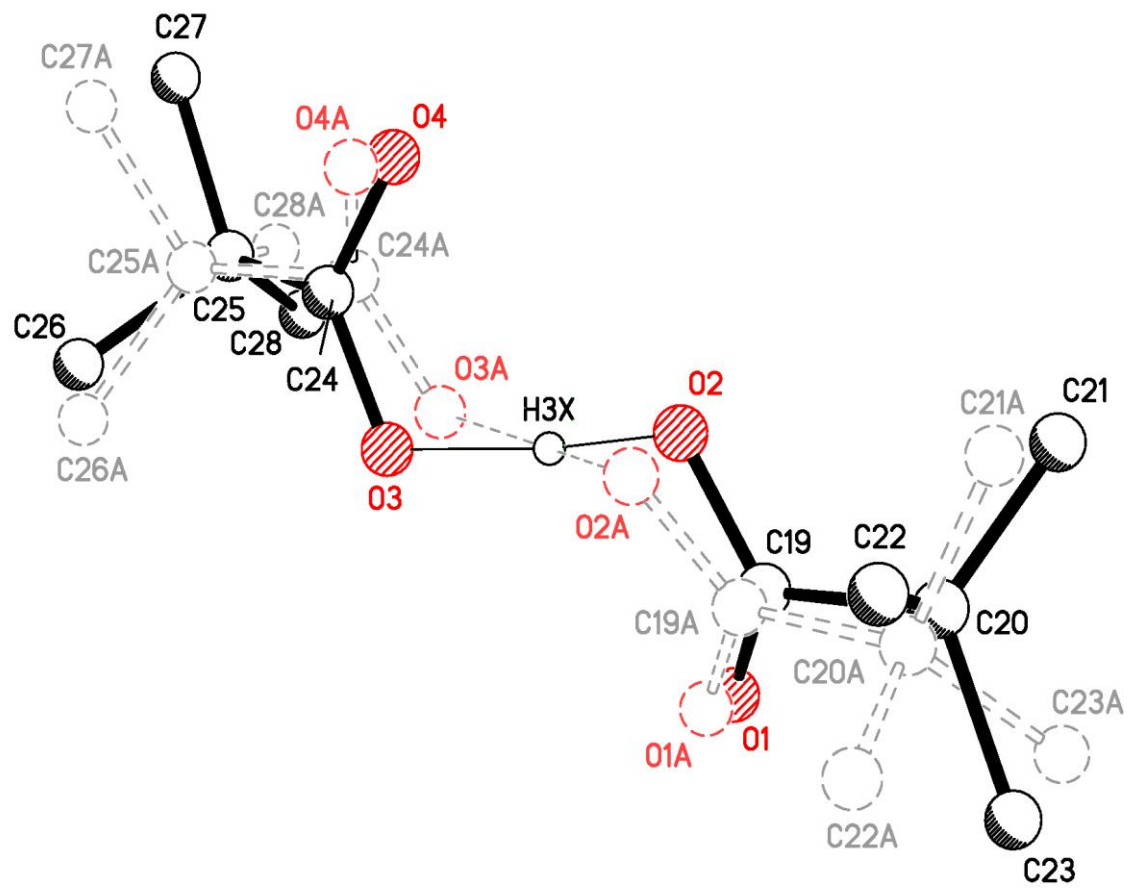


**Table S1** Summary of geometric data for [1]<sub>∞</sub> and [2]<sub>∞</sub>

	$\alpha$ , deg	$l$ , Å		$\phi_{\text{O}}$ , deg	$d_{\text{O}}$ , Å		$\phi_{\text{N}}$ , deg	$d_{\text{N}}$ , Å
<b>1</b>	+26.3(2)	1.480(3)	O1	116.41(15)	-0.343(5)	N1	130.34(16)	-0.293(5)
	+153.7(2)		O2	140.26(18)	-0.367(5)	N2	129.69(15)	2.590(4)
<b>2</b>	+39.8(1)	1.477(2)	O1	~135 <sup>a</sup>	~0.1 <sup>a</sup>	N1	~101 <sup>a</sup>	~1.9 <sup>a</sup>
	+39.8(1)		O2	~110 <sup>a</sup>	-	N2	~133 <sup>a</sup>	~1.0 <sup>a</sup>
			O3	~109 <sup>a</sup>	-			
			O4	~147 <sup>a</sup>	~0.1 <sup>a</sup>			

<sup>a</sup> disorder in the [<sup>t</sup>BuCO<sub>2</sub>⋯H⋯O<sub>2</sub>C<sup>t</sup>Bu]<sup>-</sup> anion precludes accurate determination of these distances and angle. The values provided are meant simply as an indication and should not be used for meaningful comparisons.

**Figure S7** Representation of the disorder in the  $[\text{}^i\text{BuCO}_2\cdots\text{H}\cdots\text{O}_2\text{C}^i\text{Bu}]^-$  anion



**Figure S8** Contour map showing residual electron density corresponding to hydrogen H3x between the two pivalate anions.

