

Supporting Information — X-Ray Crystallography

Manuscript: B616191J *In vitro* DNA Scission Activity of Heterometallocenes

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The cation in the structure of **8** has crystallographic C_s symmetry about a plane that includes the iron centre, N(1), C(4) and C(6). The methyl protons on C(4) are disordered across this mirror plane, and this was modelled by placing three 50% occupancy protons on C(4) in an idealised tetrahedral geometry and allowing free rotation about the C(4)–N(1) bond (*i.e.* by using the SHEXL AFIX 137 command). The PF_6 anion was found to be significantly disordered. The anion is located near a centre of symmetry, and was modelled with two unique orientations with the phosphorus centre slightly off of the special position with occupancies of *ca.* 36 and 14%. Two further orientations are present in this region of the structure, related to the first two by the centre of symmetry.

The possibility that this structure could be better modelled using the non-centrosymmetric space group $P2_1$ was considered, and rejected because

- (i) refinements using the space group $P2_1$ did not remove the disorder in the hexafluorophosphate anion, and
- (ii) though the same refinements as for (i) above gave (not unexpectedly) lower final R -factors, they also very strongly suggested that the $P2_1$ structure would be a polar twin, x^+ and x^- being 0.498(13) and 0.502(13) respectively (R_1^+ and R_1^- were 0.0275 and 0.0274 respectively).
- (iii) the thermal ellipsoids of the ferrocenyl unit do not show any pronounced asymmetry that could indicate a breaking of the mirror symmetry.

Fig. S1 The molecular structure of **8** showing the two unique orientations of the disordered PF_6 anion (the other two orientations, which occupy the same region of the structure, are related to these two by the centre of symmetry proximal to the

phosphorus centres). The major orientation, shown with dark bonds, has *ca.* 36% occupancy, the minor orientation (open bonds) has *ca.* 14% occupancy.

Fig. S2 The molecular structure of **8** (50% probability ellipsoids); see caption for Fig. S1.

Fig. S3 The molecular structure of **8** viewed in parallel projection perpendicular to the mirror plane, showing the distortion of the methyl groups out of the pyrrole ring plane.

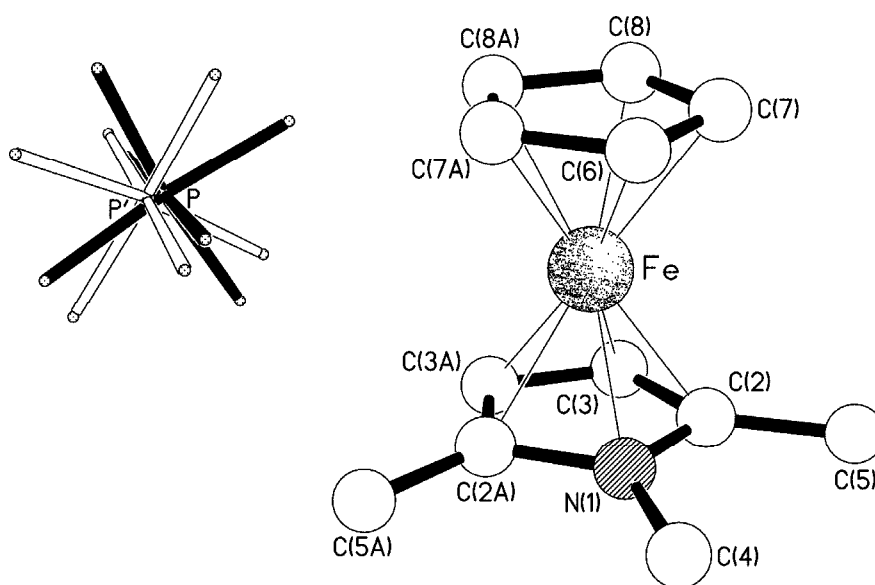


Fig. S1

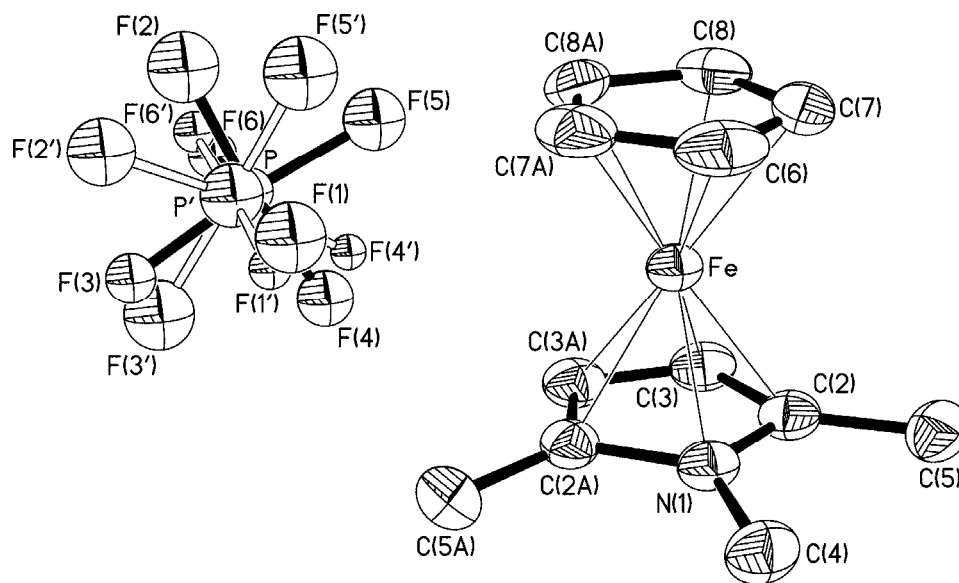


Fig. S2

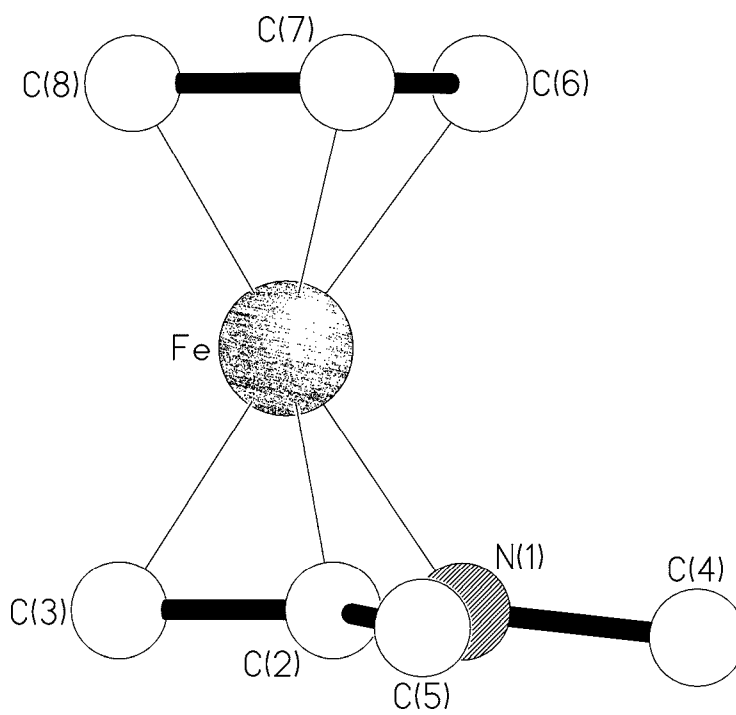


Fig. S3

DNA Cleavage Experiments

Figure S4 Ferrocene **1** fails to cleave DNA *in vitro*. Supercoiled plasmid DNA was treated with the indicated amount of ferrocene and the reaction products were resolved by agarose gel electrophoresis as described in the Experimental section. Gels were viewed under UV illumination (a typical example is shown in the left hand panel) and the proportion of supercoiled DNA from three independent experiments was quantified (right hand panel). The histogram shows means + standard errors.

Figure S5 *N*-methyl-2,5-dimethylazaferrocene iodide **6** is a potent DNA cleaving reagent. Samples were treated as described in the legend to Figure 3.

Figure S6 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene-dependent **7** DNA cleavage is markedly potentiated by DTT. Samples were treated as described in the legend to Figure 3 except DTT treated samples could not be quantified due to complete degradation of the DNA at the lowest dose used.

Figure S4

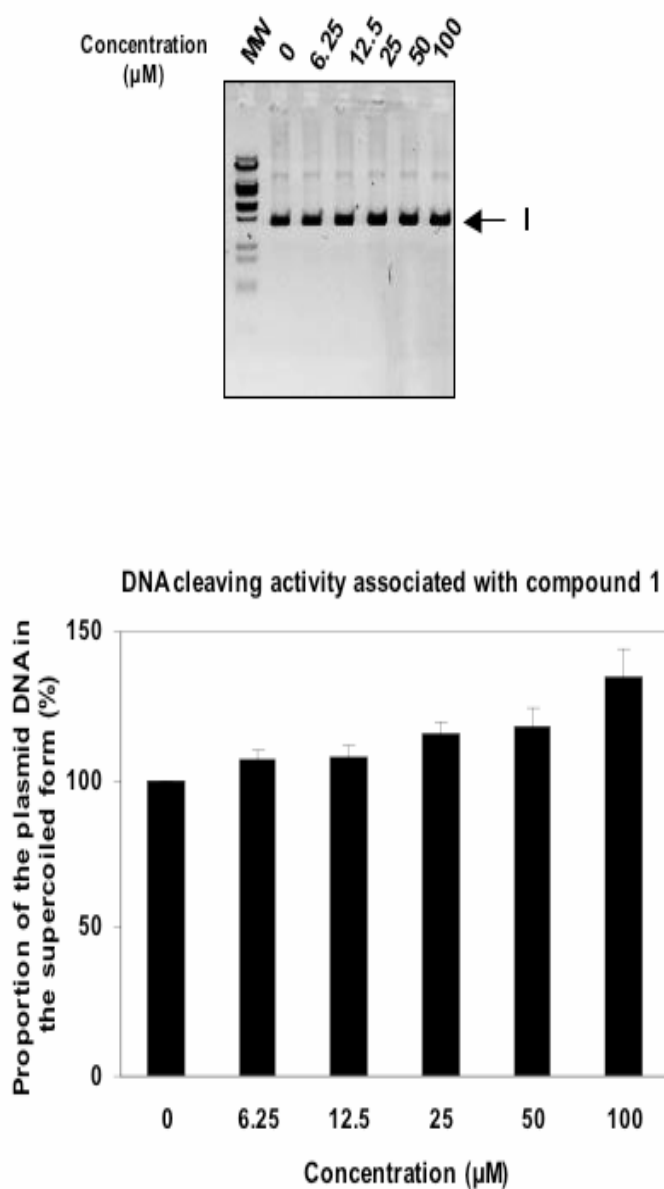


Figure S5

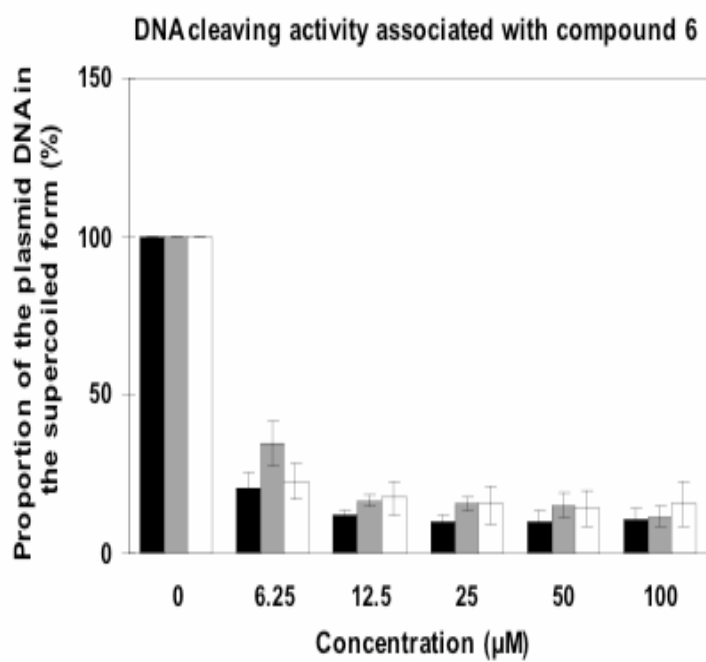
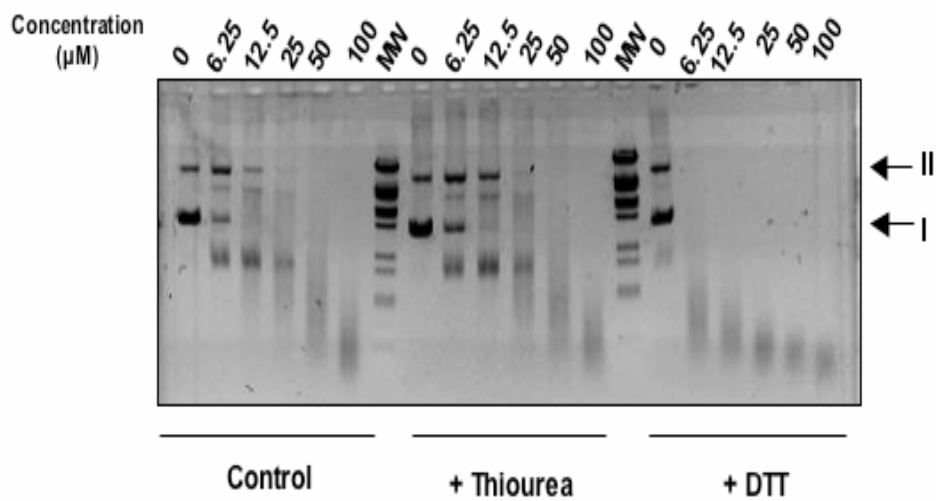


Figure S6

