

Electronic Structure Determination of Pyridine *N*-Heterocyclic Carbene Iron Dinitrogen Complexes and Neutral Ligand Derivatives.

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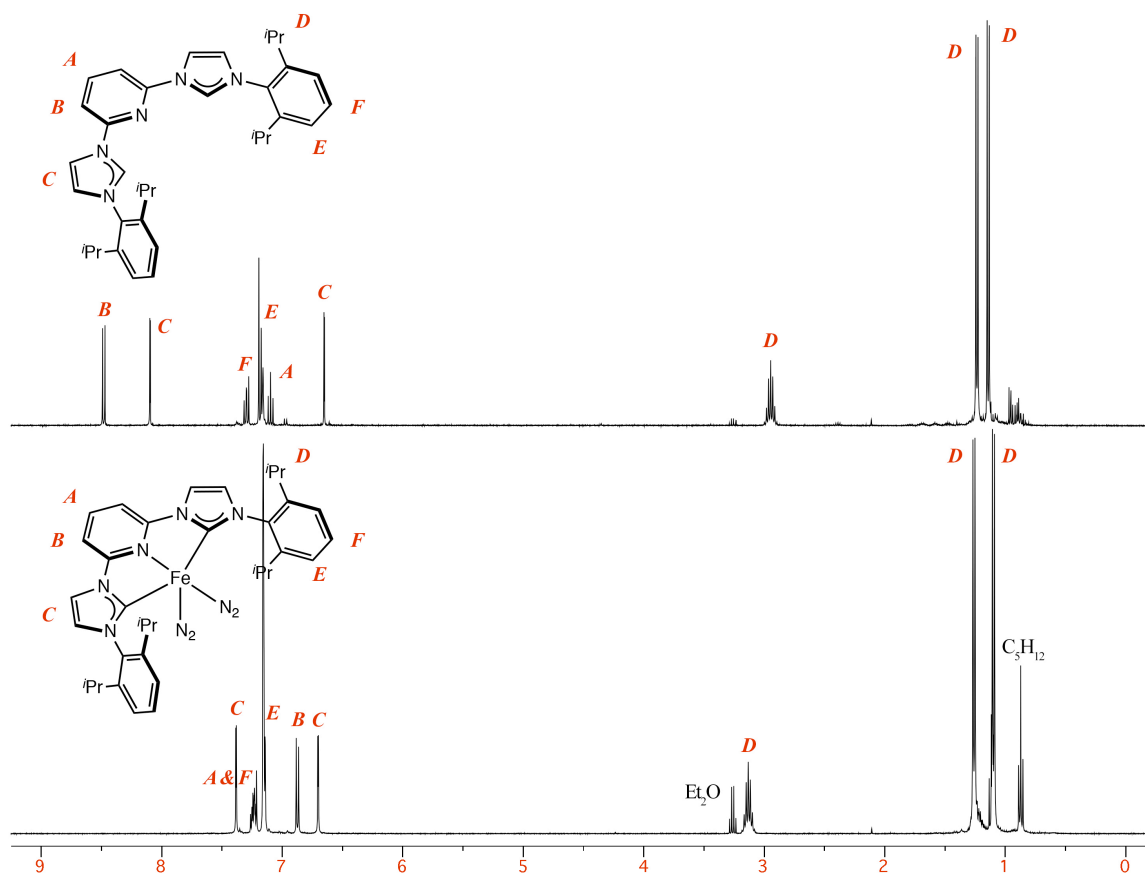


Figure S1. Benzene- d_6 ^1H NMR spectra of $i\text{PrCNC}$ (top) and $(i\text{PrCNC})\text{Fe}(\text{N}_2)_2$ (bottom) recorded at 22 $^\circ\text{C}$.

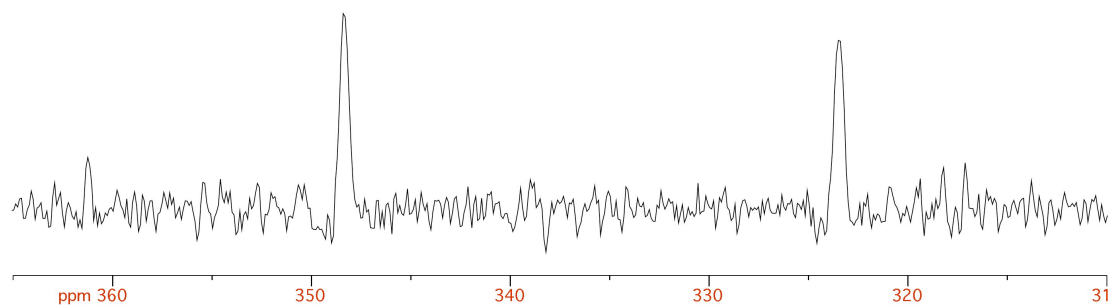


Figure S2. Benzene- d_6 ^{15}N NMR spectra of $(i\text{PrCNC})\text{Fe}(^{15}\text{N}_2)_2$ (bottom) recorded at 22 $^\circ\text{C}$.

Table S1. Comparison of the experimental and computational bond distances (Å) and angles (deg) for (ⁱPrCNC)Fe(N₂)₂.

	ⁱ PrCNC)Fe(N ₂) ₂ ^a	ⁱ PrCNC)Fe(N ₂)		
		RKS	BS(2,2)	Triplet
Fe–N _{pyr}	1.890(2)	1.902	1.927	1.921
Fe–C _{carbene}	1.915(3)	1.942	1.971	1.968
	1.912(3)	1.942	1.971	1.968
Fe–N _{N2,basal}	1.820(2)	1.794	1.804	1.803
Fe–N _{N2,apical}	1.847(2)			
N _{pyr} –C _{ipso}	1.367(3)	1.358	1.366	1.366
	1.364(3)	1.358	1.366	1.366
C _{ipso} –N _{carbene}	1.377(3)	1.390	1.392	1.392
	1.383(3)	1.390	1.392	1.392
N _{carbene} –C _{carbene}	1.402(3)	1.398	1.398	1.398
	1.394(3)	1.398	1.399	1.398
N≡N _{basal}	1.115(3)	1.116	1.119	1.116
N–C _{carbene} –N	102.3(2)	102.08	102.45	102.40
	102.0(2)	102.08	102.46	102.40

^a Data from Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B. *Chem. Commun.* **2005**, 784.

Table S2. Comparison of the experimental and computational bond distances (Å) and angles (deg) for (ⁱPrCNC)Fe(DMAP)(N₂).

	ⁱ PrCNC)Fe(DMAP)(N ₂)		
	Exp.	RKS	BS(1,1)
Fe–N _{pyr}	1.8903(14)	1.897	1.926
Fe–C _{carbene}	1.9156(17)	1.960	1.976
	1.9179(17)	1.959	1.982
Fe–N _{N₂}	1.7797(14)	1.806	1.801
Fe–N _{DMAP}	2.0467(16)	2.043	2.209
N _{pyr} –C _{ipso}	1.369(2)	1.370	1.366
	1.369(2)	1.370	1.367
C _{ipso} –N _{carbene}	1.388(2)	1.383	1.390
	1.382(2)	1.383	1.390
N _{carbene} –C _{carbene}	1.406(2)	1.403	1.401
	1.405(2)	1.403	1.401
N≡N	1.1323(19)	1.117	1.119
N–C _{carbene} –N	101.73(13)	102.00	102.11
	101.55(13)	101.95	102.04

Table S3. Computational bond distances (Å) and angles (deg) for various electronic structure possibilities for the hypothetical (ⁱPrCNC)Fe(N₂).

	(ⁱ PrCNC)Fe(N ₂) ₂ ^a	RKS	(ⁱ PrCNC)Fe(N ₂) BS(2,2)	Triplet
Fe–N _{pyr}	1.890(2)	1.902	1.927	1.921
Fe–C _{carbene}	1.915(3)	1.942	1.971	1.968
	1.912(3)	1.942	1.971	1.968
Fe–N _{N2,basal}	1.820(2)	1.794	1.804	1.803
Fe–N _{N2,apical}	1.847(2)			
N _{pyr} –C _{ipso}	1.367(3)	1.358	1.366	1.366
	1.364(3)	1.358	1.366	1.366
C _{ipso} –N _{carbene}	1.377(3)	1.390	1.392	1.392
	1.383(3)	1.390	1.392	1.392
N _{carbene} –C _{carbene}	1.402(3)	1.398	1.398	1.398
	1.394(3)	1.398	1.399	1.398
N≡N _{basal}	1.115(3)	1.116	1.119	1.116
N–C _{carbene} –N	102.3(2)	102.08	102.45	102.40
	102.0(2)	102.08	102.46	102.40

^a Data from Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B. *Chem. Commun.* **2005**, 784.