Supporting Information

XAS Characterization of a Nitridoiron(IV) Complex with a Very Short Fe–N Bond

Jan-Uwe Rohde,[†,‡] Theodore A. Betley,[§,‖] Timothy A. Jackson,[†]
Caroline T. Saouma,[§] Jonas C. Peters,[§] and Lawrence Que, Jr.[†]

[†] *Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, MN 55455, USA*

[‡] *Current address: Department of Chemistry, The University of Iowa, Iowa City, IA 52242, USA*

[§] *Department of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA 91125, USA*

[‖] *Current address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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Table S1. XAS pre-edge peak energies and intensities for the [PhBP$^{i\mathrm{Pr}}_3$]Fe(N_x) complexes in this study from refinements with multiple peaks.[a]

complex	E_0 (eV)	$E_{\text{pre-edge}}$ (eV)	area	$E_{\text{pre-edge}}$ (eV) (centroids)	total area
1	7117.3	7112.2	13.3	7112.6	16.8
		7113.9	3.5		
2	7119.0	7111.1	2.0	7112.4	24.5
		7112.3	17.1		
		7113.4	5.4		
3	7118.0	7111.6	7.9	7112.4	16.2
		7113.1	8.3		
4A (0.01 M Fe)	7120.2	7111.6	4.9	7113.1	64.5
		7113.2	59.6		
4B (0.03 M Fe)	7120.0	7111.7	7.7	7112.8	59.8
		7113.0	52.1		

[a] E_0 is conventionally defined as the first inflection point of the Fe K-edge. Pre-edge peak intensities are reported as peak areas (normalized to the edge jump) and were multiplied by 100.

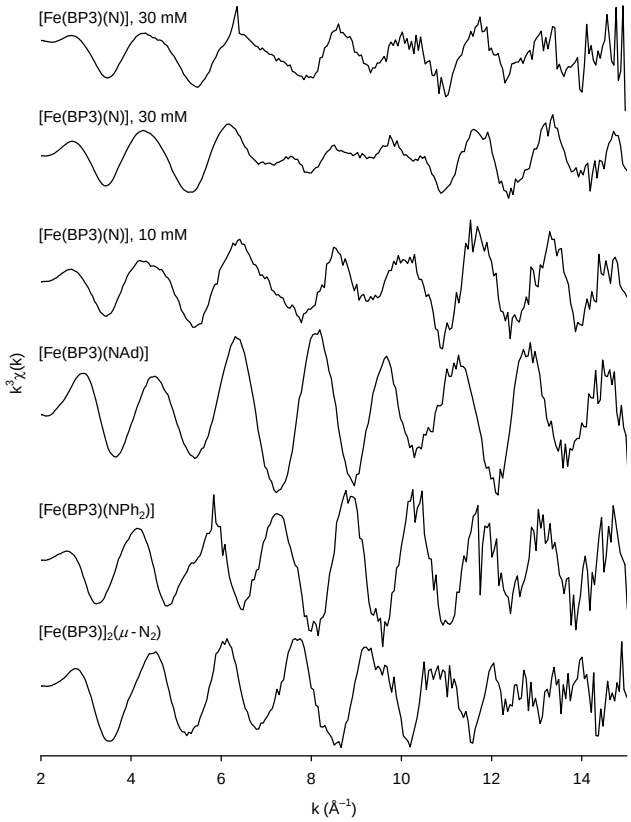

Figure S1. Fe K-edge EXAFS spectra ($k^3\chi(k)$) of $\{[PhBP^{iPr}_3]Fe\}_2(\mu\text{-}N_2)$, **1**, $[PhBP^{iPr}_3]Fe(NPh_2)$, **2**, $[PhBP^{iPr}_3]Fe(NAd)$, **3**, and three samples of $[PhBP^{iPr}_3]Fe(N)$, **4**.

Table S2. EXAFS fitting results for [PhBP$^{i\mathrm{Pr}}_3$]Fe(NPh$_2$), **2**, [PhBP$^{i\mathrm{Pr}}_3$]Fe(NAd), **3**, and {[PhBP$^{i\mathrm{Pr}}_3$]Fe}$_2$(μ-N$_2$), **1**.[a]

	Fe–N			Fe–P			Fe···C			Fe···C			GOF
Fit	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	$\varepsilon^2 \cdot 10^3$ [b]
1	**1**	**1.959**	**2.5**	**3**	**2.463**	**0.6**	**2**	**2.938**	**0.9**				**0.512**
(*1*	*1*	*1.959*	*2.8*	*3*	*2.463*	*0.6*	*2*	*2.936*	*0.6*				*0.686*) [c]
2	1	1.961	2.8	3	2.463	0.7							0.656
3				3	2.463	0.7	2	2.935	1.4				0.709
4				3	2.463	0.8							0.779
1	**1**	**1.637**	**0.7**	**3**	**2.269**	**0.9**	**1**	**3.163**	**–2.9**	**3**	**3.443**	**4**	**0.528**
(*1*	*1*	*1.636*	*0.8*	*3*	*2.269*	*0.8*	*1*	*3.168*	*–2.9*	*3*	*3.454*	*3.9*	*0.696*) [c]
2	1	1.638	0.7	3	2.269	0.9	1	3.163	–3.2				0.612
3	1	1.636	0.6	3	2.269	0.9				3	3.436	1.1	0.609
4	1	1.637	0.6	3	2.269	1.0							0.668
5				3	2.268	0.8	1	3.167	–3.3	3	3.44	5	1.112
6				3	2.269	0.9							1.122
1	**1**	**1.794**	**4.1**	**3**	**2.352**	**3.8**							**0.557**
(*1*	*1*	*1.789*	*5.1*	*3*	*2.353*	*3.8*							*0.818*) [c]
2				3	2.351	3.8							0.725

[a] Fourier-transformed range **1**, **2**, and **3**: k = 2–15 Å^{-1} (resolution 0.12 Å). r is in units Å, $\Delta\sigma^2$ in 10^3 Å^2. The typical error of analysis for interatomic distances (r) is approximately ±0.02 Å. [b] Back-transformation ranges for **2**: r' = 0.80–3.80 Å; for **3**: r' = 0.60–3.80 Å; and for **1**: r' = 0.60–3.60 Å. [c] Fits to unfiltered data corresponding to the best fits to filtered data.

Table S3. Distances (Å) in **2**, **3**, and **1** revealed by crystal structure determination.

	2		**3**		**1**	
	d (Å)	average	*d* (Å)	average	*d* (Å)	average
Fe–N	1.953		1.638		1.761–1.818 (4 x)	1.793
Fe–P	2.443 2.462 2.467	2.457	2.260 2.263 2.297	2.273	2.333–2.394 (12 x)	2.357
Fe···C[a]	2.936 2.982	2.959	3.074			
Fe···C[b]	3.434–3.733 (9 x)	3.592	3.366–3.545 (9 x)	3.45		

[a] *Ipso* carbon atoms of the *N*-phenyl (**2**) and *N*-adamantyl substituents (**3**). [b] Carbon atoms adjacent to the ligating phosphorus atoms.

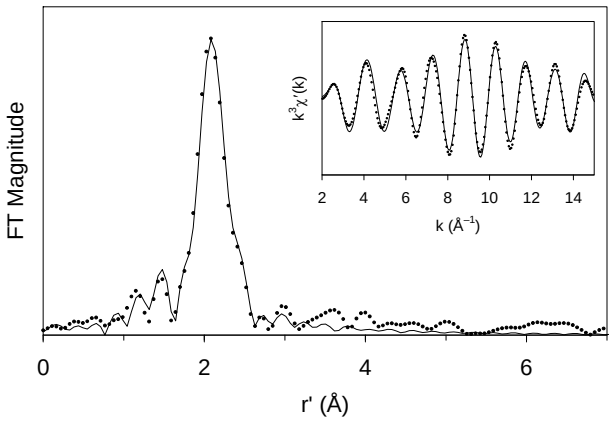

Figure S2. Fourier transform of the Fe K-edge EXAFS data ($k^3\chi(k)$) and Fourier-filtered EXAFS spectrum ($k^3\chi'(k)$, inset) of [PhBP$^{i\mathrm{Pr}}_3$]Fe(NPh$_2$), **2**, Fourier-transformed range k = 2–15 Å^{-1}; experimental data (•••) and fit 1, Table S2 (—); Back-transformation range: r' = 0.80–3.80 Å.

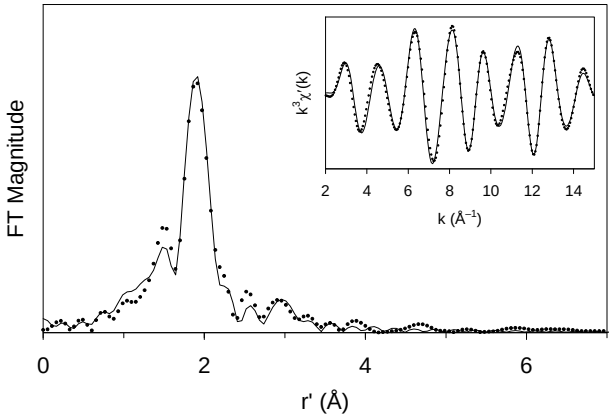

Figure S3. Fourier transform of the Fe K-edge EXAFS data ($k^3\chi(k)$) and Fourier-filtered EXAFS spectrum ($k^3\chi'(k)$, inset) of [PhBP$^{i\mathrm{Pr}}_3$]Fe(NAd), **3**, Fourier-transformed range k = 2–15 Å^{-1}; experimental data (•••) and fit 1, Table S2 (—); Back-transformation range: r' = 0.60–3.80 Å.

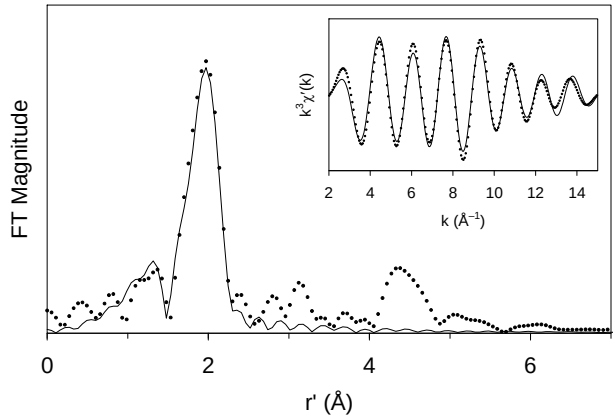

Figure S4. Fourier transform of the Fe K-edge EXAFS data ($k^3\chi(k)$) and Fourier-filtered EXAFS spectrum ($k^3\chi'(k)$, inset) of $\{[PhBP^{iPr}_3]Fe\}_2(\mu\text{-}N_2)$, **1**, Fourier-transformed range k = 2–15 Å^{-1}; experimental data (•••) and fit 1, Table S2 (—); Back-transformation range: r' = 0.60–3.60 Å.

Table S4. EXAFS fitting results for a sample of [PhBP$^{i\mathrm{Pr}}_3$]Fe(N), **4** (**4A**, [Fe] = 0.01 M).[a]

	Fe–N			Fe–N			Fe–P			Fe–P			Fe···C			GOF
Fit	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	$\varepsilon^2 \cdot 10^3$ [b]
1							3	2.210	6.0							1.744
2							2	2.216	2.5	1	2.442	–0.5				0.934
3							1.5	2.210	0.3	1.5	2.434	2.7				0.885
4							1	2.203	–1.6	2	2.418	8.1				0.951
5	1	1.510	4.3				1.5	2.209	0.2	1.5	2.432	2.9				0.816
6	0.5	1.515	0.2				1.5	2.209	0.1	1.5	2.431	2.8				0.671
7				1	2.05	9	1.5	2.208	0.7	1.5	2.441	2.4				0.842
8				0.5	2.03	1	1.5	2.214	0.7	1.5	2.441	2.1				0.854
9	0.55	1.517	0.8	0.45	2.02	4	1.65	2.213	1.0	1.35	2.439	1.3				0.600
10	**0.5**	**1.518**	**0.2**	**0.5**	**2.00**	**4**	**1.5**	**2.212**	**0.3**	**1.5**	**2.435**	**2.3**				**0.573**
11	0.45	1.518	–0.3	0.55	1.98	3	1.35	2.211	–0.4	1.65	2.432	3.4				0.558
12	**0.5**	**1.518**	**0.3**	**0.5**	**2.00**	**4**	**1.5**	**2.212**	**0.3**	**1.5**	**2.435**	**2.4**	**1**	**3.03**	**9**	**0.555**
													3	**3.470**	**2.2**	
													3	**3.71**	**5**	
(*12*	*0.5*	*1.523*	*0.7*	*0.5*	*2.025*	*0.1*	*1.5*	*2.216*	*0.9*	*1.5*	*2.443*	*2.1*	*1*	*3.02*	*8*	*0.602*) [c]
													3	*3.470*	*1.0*	
													3	*3.702*	*3.4*	
13	0.5	1.515	0.3				1.5	2.209	0.1	1.5	2.431	2.9	0.7	3.08	3	0.693
													3	3.473	2.0	
													3	3.71	4	
14				0.5	2.03	1	1.5	2.214	0.8	1.5	2.441	2.2	1	3.06	5	0.922
													3	3.47	2	
													3	3.71	4	
15							1.5	2.209	0.3	1.5	2.433	2.9	1	3.06	6	0.952
													3	3.47	2	
													3	3.71	4	

[a] Fourier-transformed range: k = 2–15 Å^{-1} (resolution 0.12 Å). r is in units Å, $\Delta\sigma^2$ in 10^3 Å^2. The typical error of analysis for interatomic distances (r) is approximately ±0.02 Å. [b] Back-transformation range: r' = 0.60–3.80 Å. [c] Fits to unfiltered data corresponding to the best fits to filtered data.

Table S5. EXAFS fitting results for a second sample of [PhBP$^{i\mathrm{Pr}}_3$]Fe(N), **4** (**4B**, [Fe] = 0.03 M).[a]

	Fe–N			Fe–N			Fe–P			Fe–P			Fe···C			GOF
Fit	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	*n*	*r* (Å)	$\Delta\sigma^2$	$\varepsilon^2 \cdot 10^3$ [b]
1										3	2.34	19				1.087
3							1.5	2.235	2.2	1.5	2.429	1.6				0.656
5	0.8	1.513	9				1.5	2.233	2.2	1.5	2.428	1.7				0.684
6	0.5	1.529	2.9				1.5	2.234	2.1	1.5	2.428	1.6				0.601
8				0.5	1.824	–0.6	1.5	2.239	2.7	1.5	2.434	1.8				0.685
9	**0.5**	**1.535**	**3.7**	**0.5**	**1.819**	**–0.2**	**1.5**	**2.238**	**2.5**	**1.5**	**2.433**	**1.7**				**0.524**
10	0.45	1.538	2.6	0.55	1.824	1.2	1.35	2.231	1.6	1.65	2.426	2.5				0.512
11	0.4	1.541	1.3	0.6	1.836	4	1.2	2.225	0.7	1.8	2.419	3.3				0.498
12	**0.5**	**1.535**	**3.8**	**0.5**	**1.820**	**–0.2**	**1.5**	**2.237**	**2.4**	**1.5**	**2.432**	**1.7**	**1**	**3.12**	**0**	**0.559**
													3	**3.47**	**6**	
													3	**3.73**	**6**	
(*12*	*0.5*	*1.535*	*3.7*	*0.5*	*1.817*	*–0.3*	*1.5*	*2.240*	*2.6*	*1.5*	*2.435*	*1.6*	*1*	*3.113*	*1.1*	*0.551*) [c]
													3	*3.490*	*6.9*	
													3	*3.743*	*6.4*	
13	0.5	1.528	3.0				1.5	2.234	2.0	1.5	2.428	1.5	1	3.12	0	0.657
													3	3.48	6	
													3	3.73	6	
14				0.5	1.826	–0.6	1.5	2.238	2.6	1.5	2.433	1.7	1	3.12	0	0.751
													3	3.47	6	
													3	3.73	6	
15							1.5	2.234	2.1	1.5	2.429	1.6	1	3.12	0	0.709
													3	3.48	6	
													3	3.73	6	

[a] Fourier-transformed range: k = 2–15 Å^{-1} (resolution 0.12 Å). r is in units Å, $\Delta\sigma^2$ in 10^3 Å^2. The typical error of analysis for interatomic distances (r) is approximately ±0.02 Å. [b] Back-transformation range: r' = 0.60–3.80 Å. [c] Fits to unfiltered data corresponding to the best fits to filtered data.

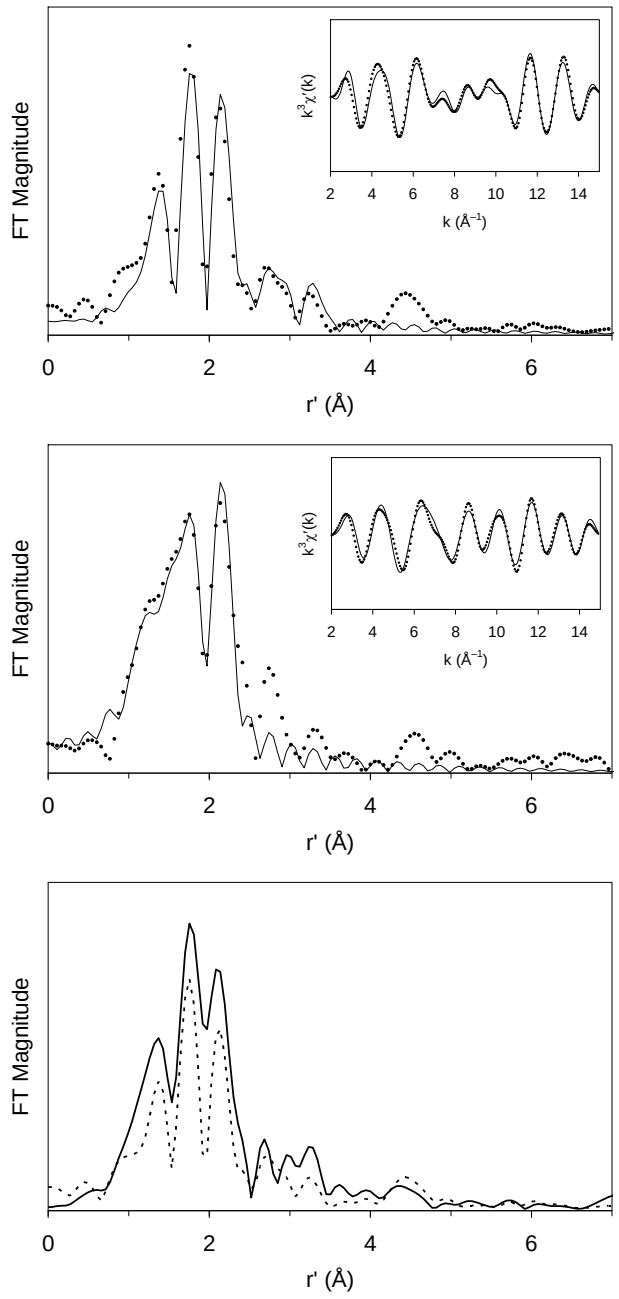

Figure S5. Fourier transforms of the Fe K-edge EXAFS data ($k^3\chi(k)$) and Fourier-filtered EXAFS spectra ($k^3\chi'(k)$, inset) of additional samples of [PhBP$^{i\mathrm{Pr}}_3$]Fe(N), **4** ([Fe] = 0.03 M); top, **4B**, Fourier-transformed range k = 2–15 Å^{-1}; experimental data (•••) and fit 12, Table S5 (—); Back-transformation range: r' = 0.60–3.80 Å; middle, **4C**, Fourier-transformed range k = 2–14.9 Å^{-1}; experimental data (•••) and fit 4c, Table 2 (—); Back-transformation range: r' = 0.60–3.60 Å; bottom, comparison of the Fourier transforms of the Fe K-edge EXAFS data ($k^3\chi(k)$) of samples **4A** (—, [Fe] = 0.01 M) and **4B** (---, [Fe] = 0.03 M).

Table S6. EXAFS fitting results for a sample of [PhBP$^{CH2Cy}{}_3$]Fe(N), **5** ([Fe] = 0.035 M).[a]

	Fe–N			Fe–P			GOF [b]
Fit	*n*	*r* (Å)	σ^2	*n*	*r* (Å)	σ^2	
1				5	2.18	6.0	0.547
2				4	2.18	4.1	0.512
3				3	2.19	2.3	0.486
4				2	2.19	0.6	0.472
5	1	1.56	7.9	4	2.19	4.2	0.649
6	1	1.55	8.1	3	2.19	2.4	0.548
7	**1**	**1.55**	**7.4**	**2**	**2.19**	**0.6**	**0.455**
8	0.8	1.56	4.2	2	2.19	0.6	0.452
9	0.7	1.55	3.8	2.1	2.19	0.8	0.458
10	0.8	1.56	4.7	2.4	2.19	1.3	0.486
							GOF [b]
11				4	2.19	4.2	0.962
12				3	2.19	3.9	0.653
13				2	2.18	3.2	0.483
14	1	1.55	8.1	3	2.19	2.4	0.470
15	**1**	**1.56**	**7.7**	**2**	**2.19**	**0.6**	**0.340**
16	0.8	1.55	6.8	2	2.19	1.3	0.325

[a] Fourier-transformed range: k = 2–15 Å^{-1} (resolution 0.12 Å). r is in units Å, σ^2 in 10^3 Å^2. The typical error of analysis for interatomic distances (r) is approximately ±0.02 Å. [b] GOF = $[\Sigma k^6(\chi_{exptl}-\chi_{sim})^2 / \Sigma k^6\chi_{exptl}{}^2]^{1/2}$. Fits 1–10 are to unfiltered $k^3\chi(k)$ EXAFS data, fits 11–16 to unfiltered $k\chi(k)$ EXAFS data.