Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2013

Vanadium-Iron Complexes Featuring Metal-Metal Multiple Bonds

Subramaniam Kuppuswamy,[†] Tamara M. Powers,[‖] Jeremy P. Krogman,[†] Mark W. Bezpalko,[†] Bruce M. Foxman,[†] Christine M. Thomas*[,†]

[†]*Department of Chemistry, Brandeis University, 415 South Street, MS 015, Waltham, Masschusetts 02454, United States.* [‖]*Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02139.*

Index *Page*

NMR, IR, Mössbauer Spectra and Cyclic voltammograms (CVs)

X-ray Crystallography Experimental Details

Computational Details

Figure S1. ^{1}H NMR spectrum of **1** in benzene-d_6.

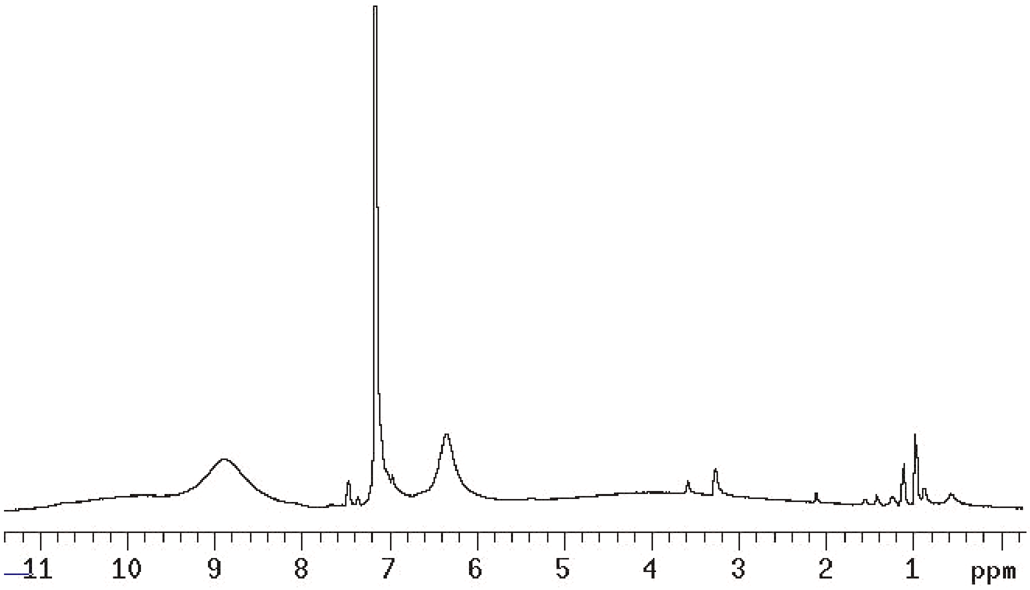


Figure S2. IR spectrum of **1** (KBr solution cell, benzene).

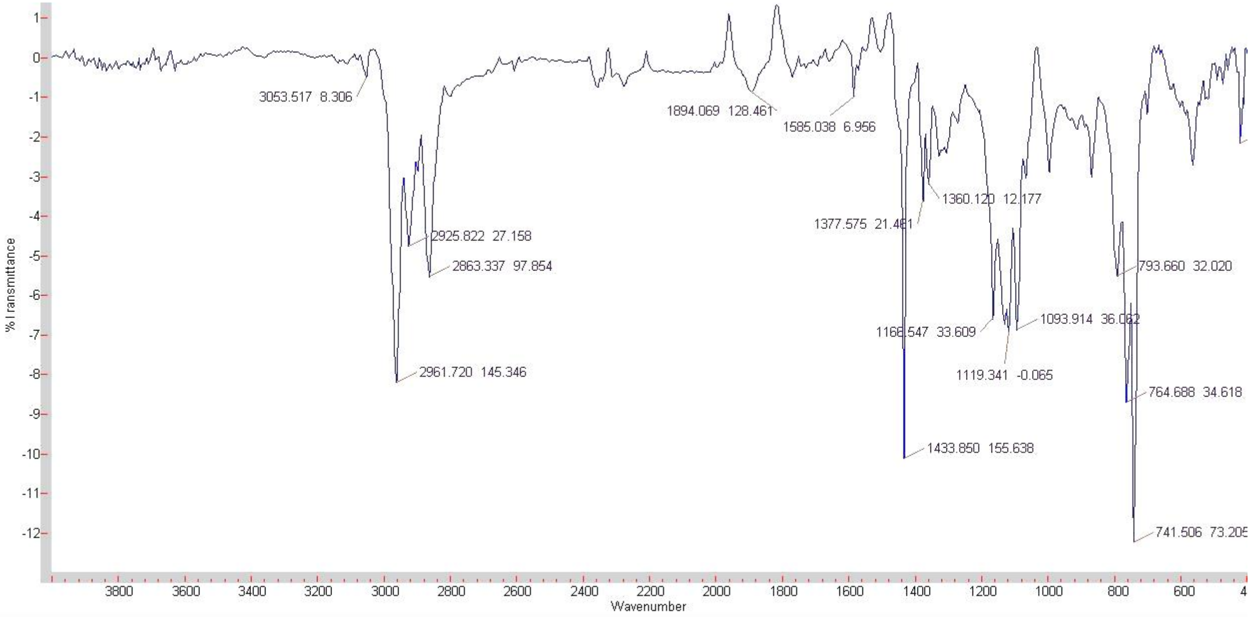


Figure S3. Cyclic Voltammogram of **1** (2 mM in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s).

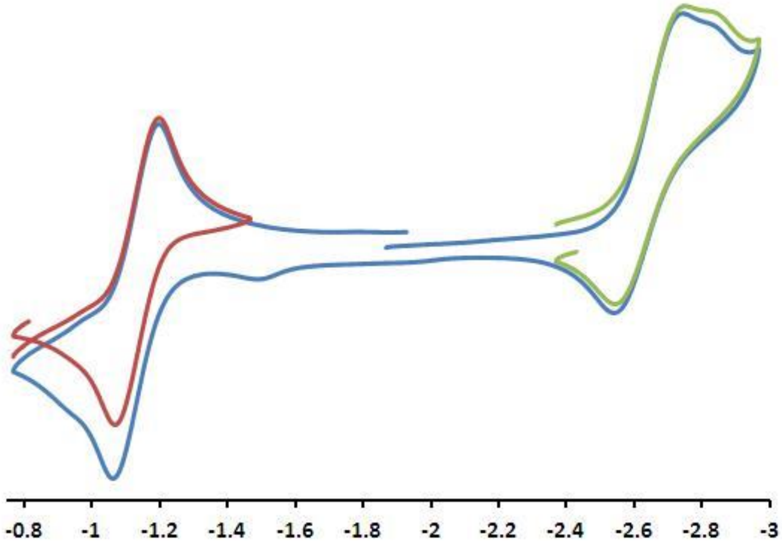


Figure S4. ^{1}H NMR spectrum of **2** in C_6D_6.

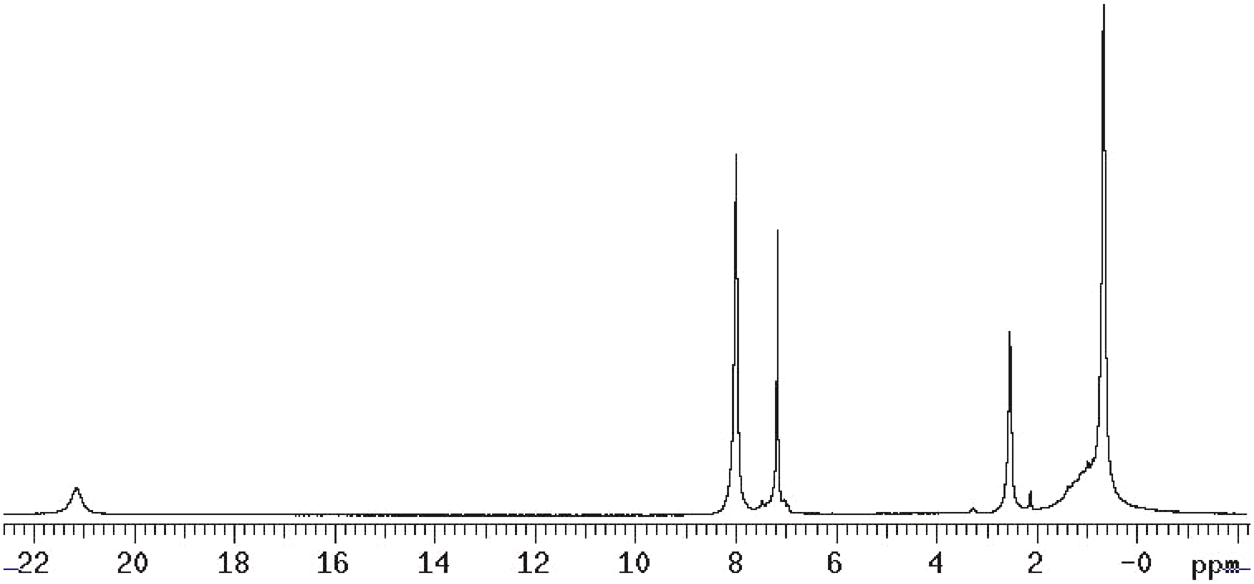


Figure S5. IR spectrum of **2** (KBr solution cell, benzene).

Figure S6. Cyclic Voltammogram of **2** (2 mM in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s).

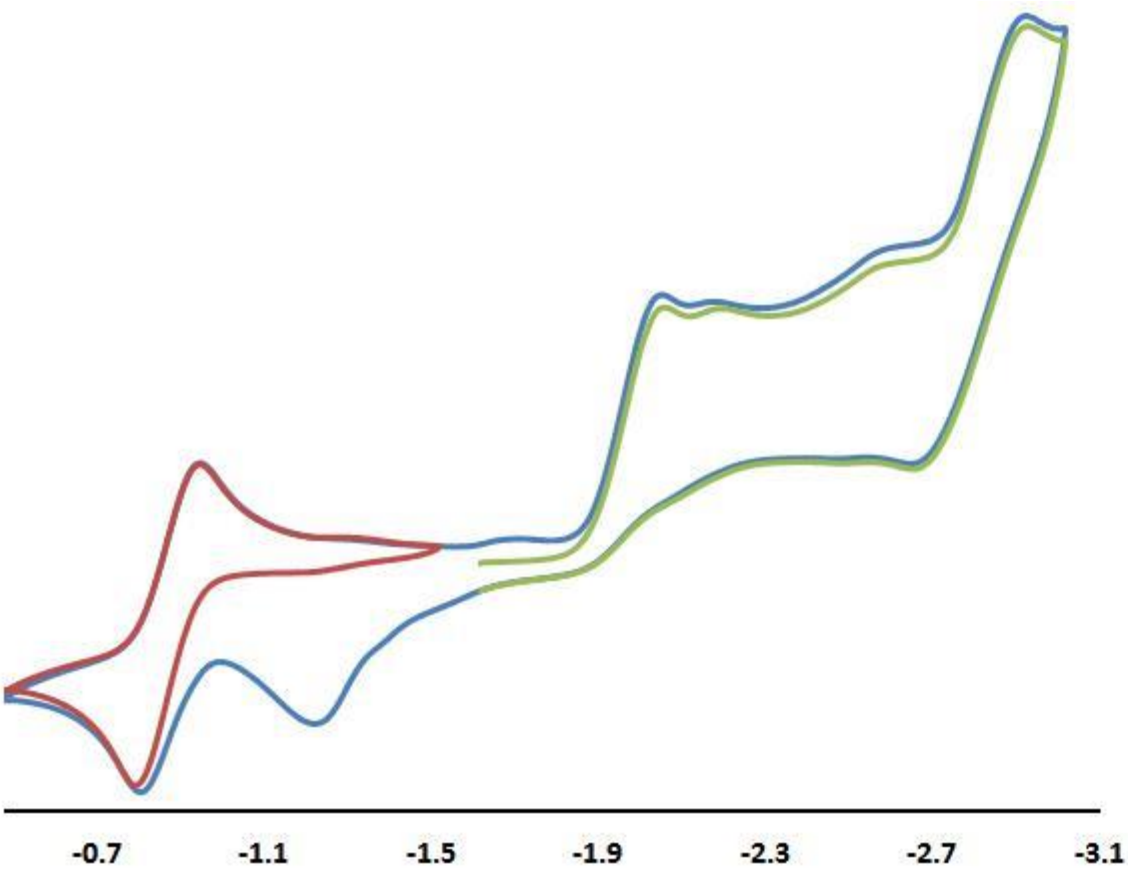


Figure S7. ^{1}H NMR spectrum of **3** in C_6D_6.

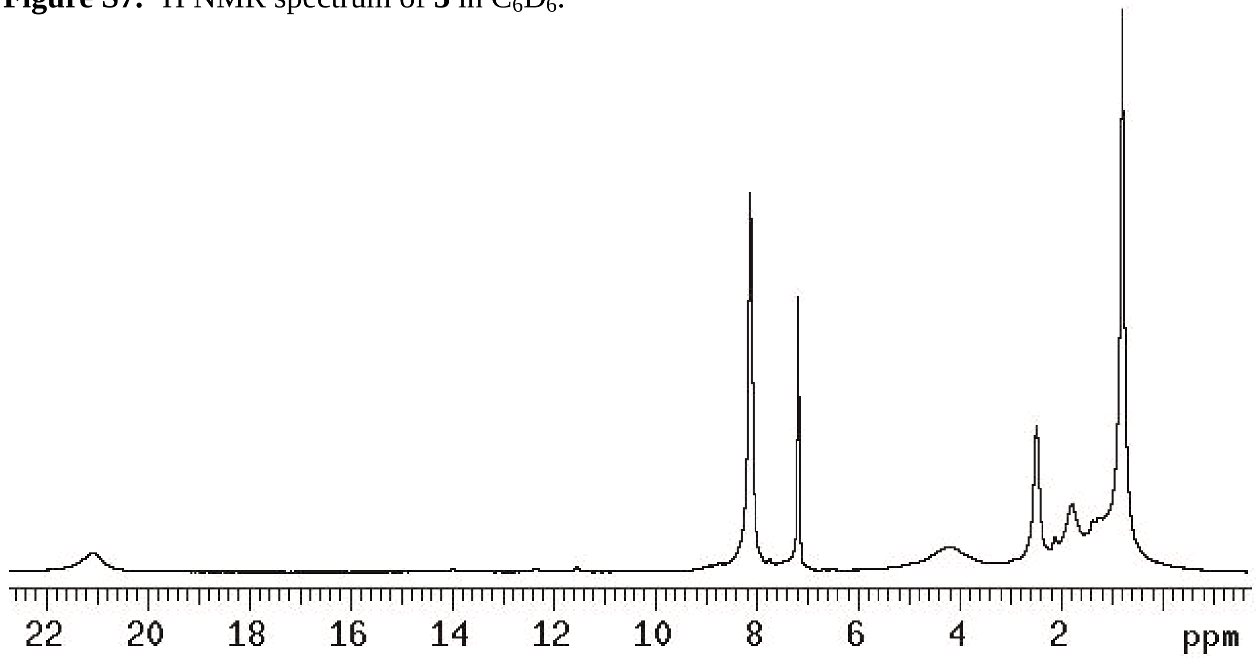


Figure S8. IR spectrum of **3** (KBr solution cell, benzene).

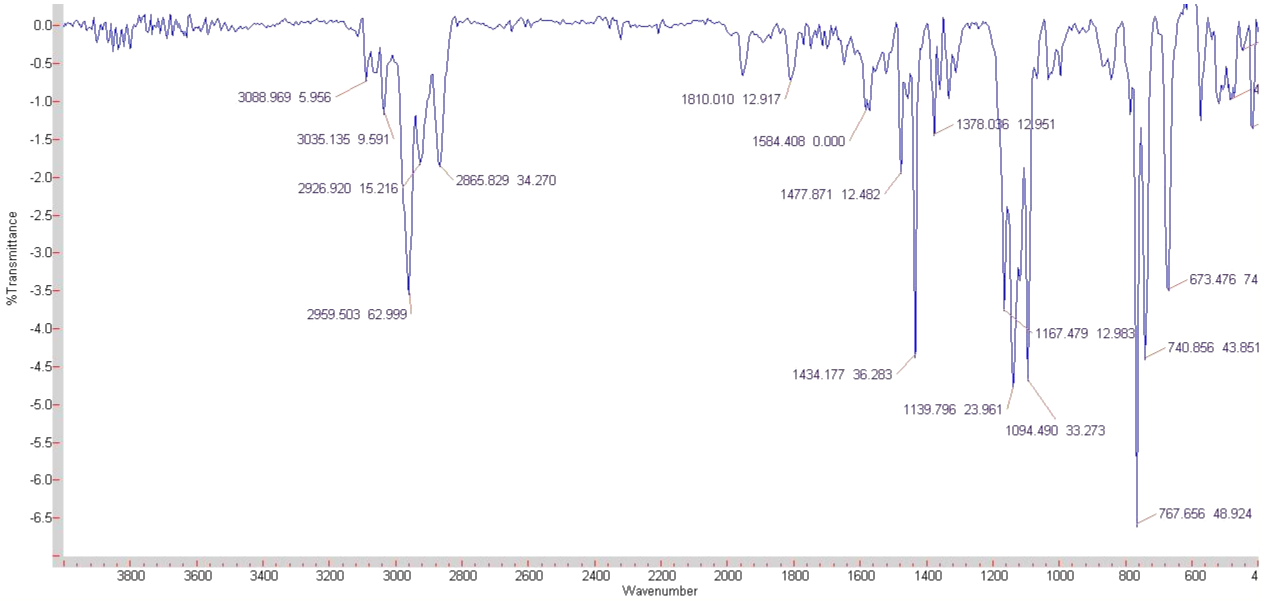


Figure S9. Cyclic Voltammogram of **3** (2 mM in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s).

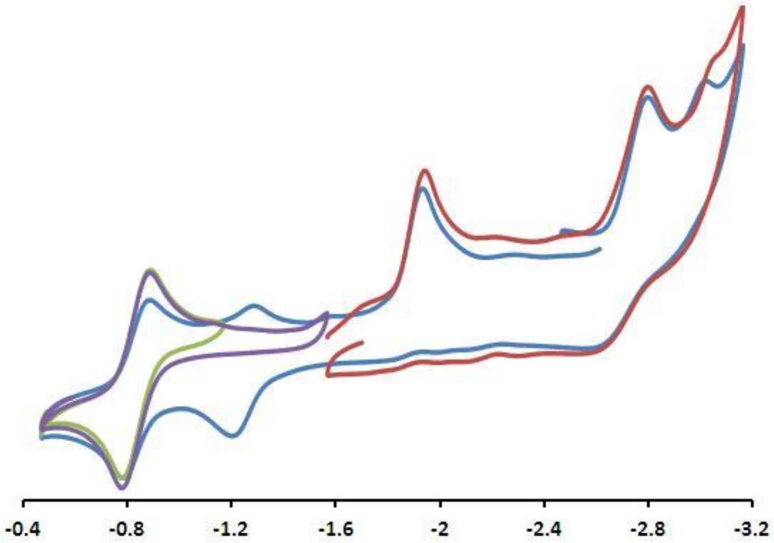


Figure S10. ^{1}H NMR spectrum of **4** in C_6D_6.

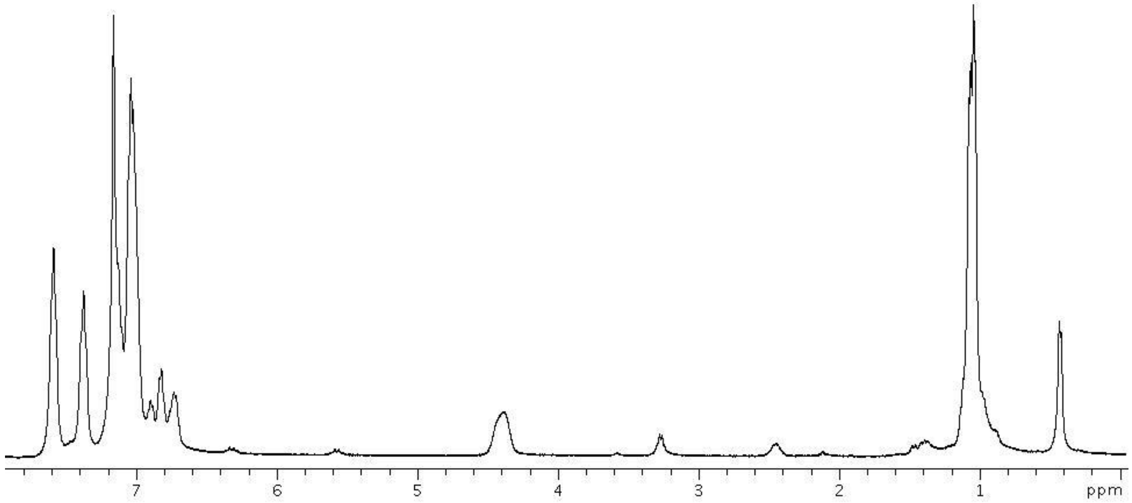


Figure S11. ^{31}P{^{1}H} NMR spectrum of **4** in C_6D_6.

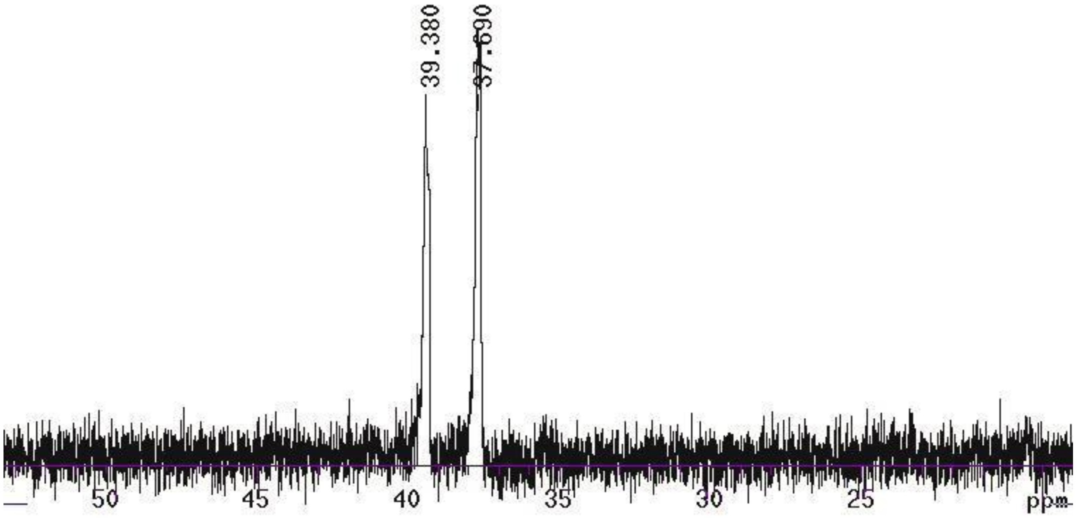


Figure S12. IR spectrum of **4** (KBr solution cell, benzene).

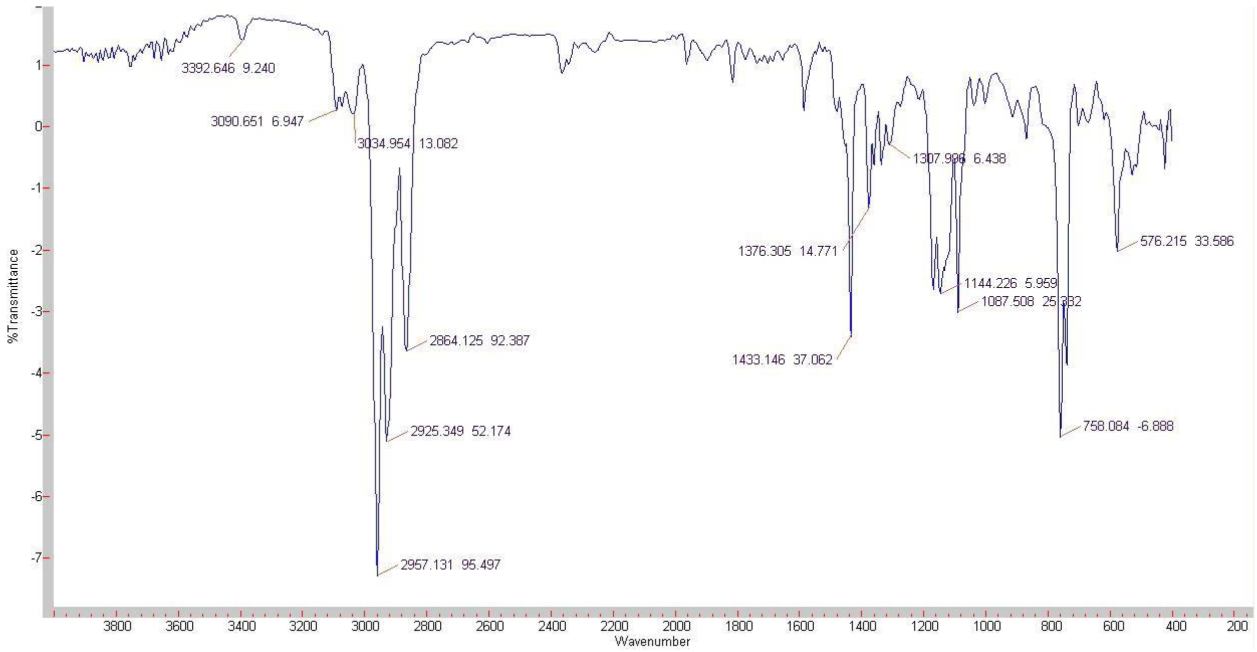


Figure S13. ^{1}H NMR spectrum of **5** in C_6D_6.

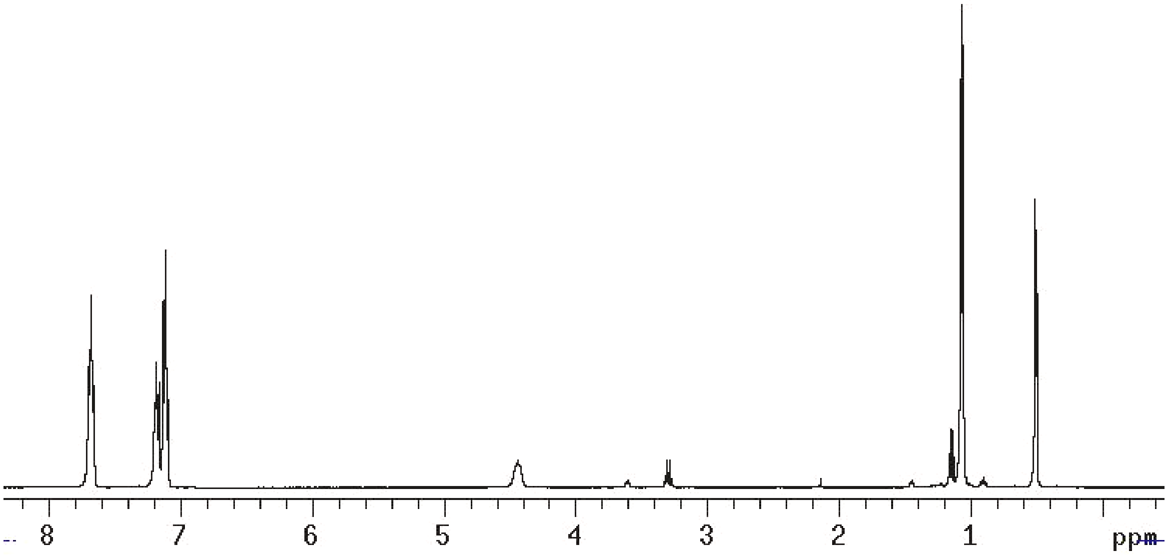


Figure S14. ^{31}P{^{1}H} NMR spectrum of **5** in C_6D_6.

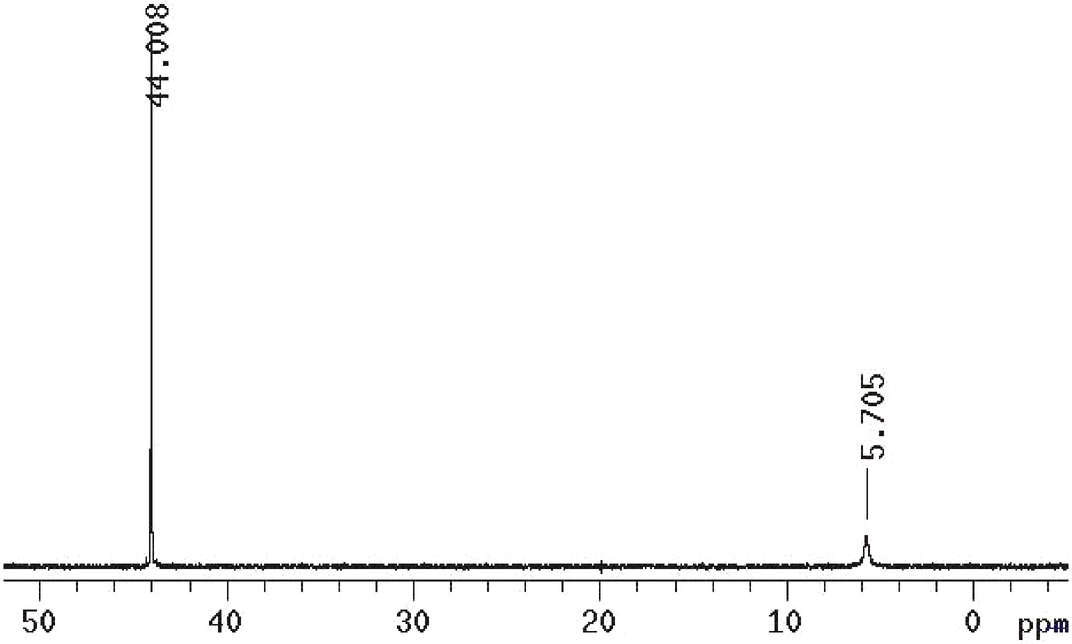


Figure S15. IR spectrum of **5** (KBr solution cell, benzene).

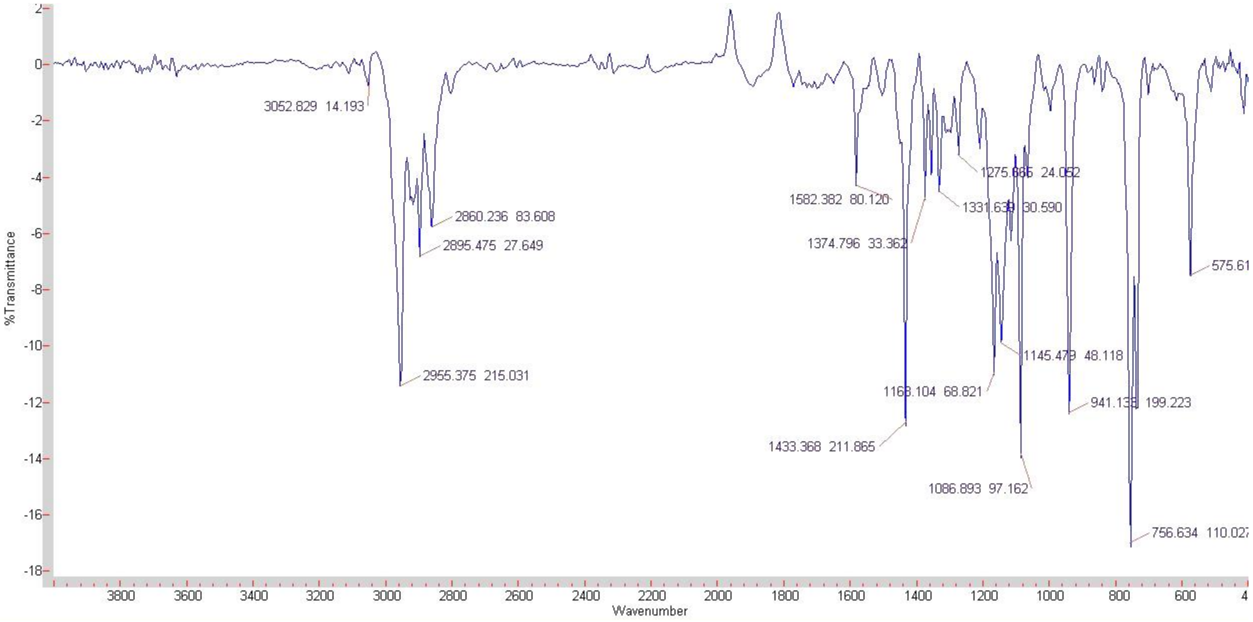


Figure S16. Cyclic Voltammogram of **5** (2 mM in 0.4 M [^{n}Bu$_4$N][PF$_6$] in THF, scan rate = 100 mV/s).

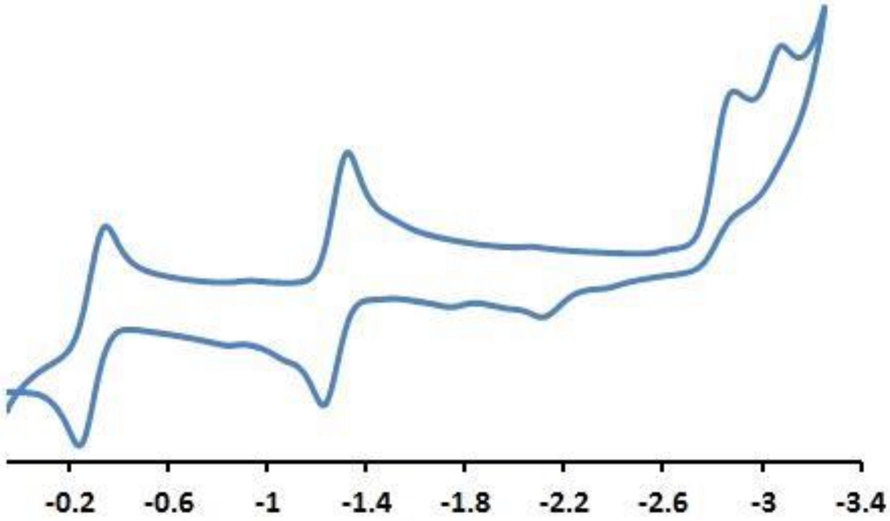


Figure S17. ^{1}H NMR spectrum of **6** in C_6D_6.

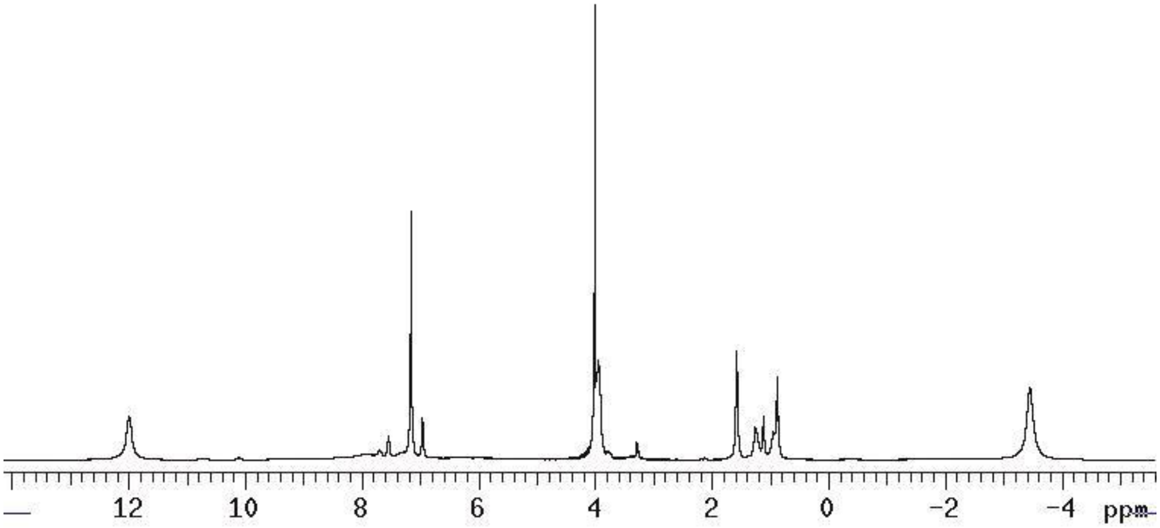


Figure S18. IR spectrum of **6** (KBr solution cell, benzene).

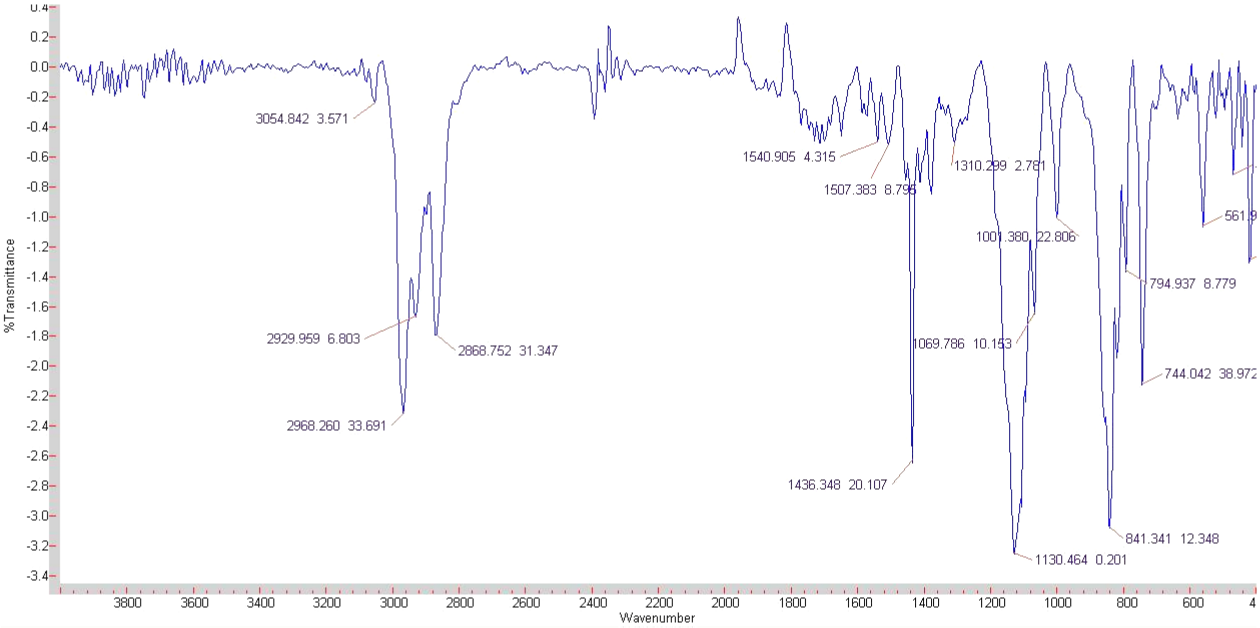
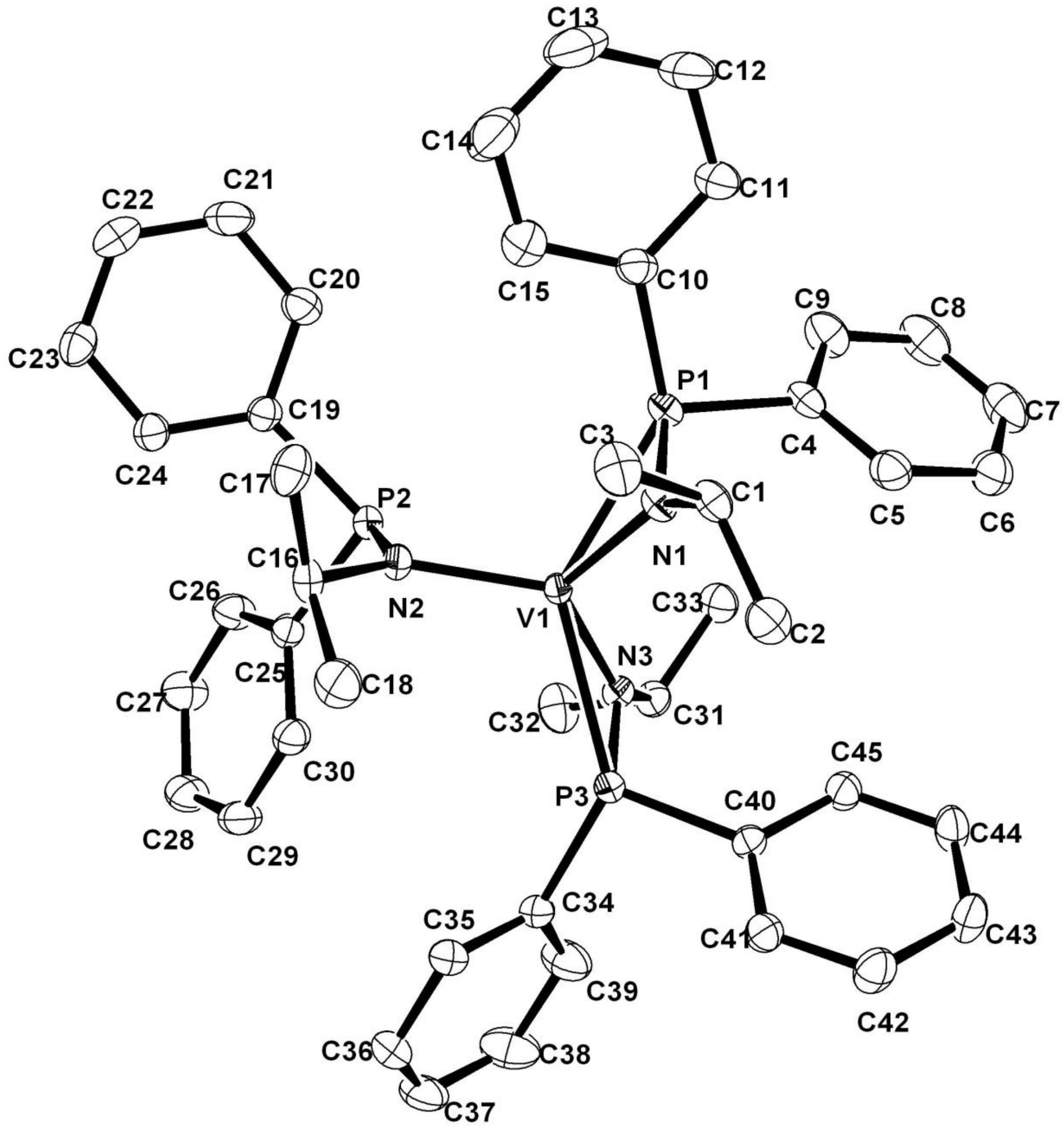


Table S1. X-ray Diffraction Experimental Details for **1**, **3-6**.

	1	**3**●1.5THF	**4**	**5**	**6**●1.5THF
chemical formula	$C_{45}H_{51}N_3P_3V$	$C_{48}H_{57}FeIN_3O_{0.75}P_3V$	$C_{60}H_{69}FeN_4P_4V$	$C_{48}H_{60}FeN_3P_4V$	$C_{48}H_{57}FFeIN_3O_{0.75}P_3V$
fw	777.78	1014.61	1076.92	909.71	1033.61
T (K)	120 K	120 K	120 K	120 K	120 K
λ (Å)	0.71073 Å	0.71073 Å	0.71073	0.71073	0.71073
a (Å)	10.0198(3)	10.7003(3)	13.0944(3)	16.3841(5)	10.7611(3)
b (Å)	11.1462(3)	22.3479(5)	14.5742(4)	16.3841(5)	22.0867(6)
c (Å)	19.6789(5)	22.5190(5)	28.4690(8)	22.8729(9)	22.4678(7)
α (deg)	85.018(1)	62.001(1)	90	90	63.2680(10)
β (deg)	79.607(2)	81.313(1)	95.9356(14)	90	80.585(2)
γ (deg)	74.258(1)	88.637(1)	90	120	85.642(2)
V (Å^3)	2078.99(10)	4693.3(2)	5403.9(2)	5317.4(3)	4705.1(2)
space group	P-1	P-1	$P2_1/c$	P-3c1	P-1
Z	2	4 (Z' = 2)	4	4 (Z' = 1/3)	4 (Z' = 2)
D_{calcd} (g/cm^3)	1.242	1.436	1.324	1.136	1.459
μ (cm^{-1})	0.388	1.306	0.603	0.600	1.307
$R1$, $wR2^a$ (I > 2σ)	0.0322, 0.0834	0.0364, 0.0802	0.0487, 0.1004	0.0324, 0.0993	0.0356, 0.0745

$^a R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

Figure S19. Displacement ellipsoid (50%) representations of **1**. Hydrogen atoms have been omitted for clarity.



X-ray data collection, solution, and refinement for 1. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 135K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of seven phi and three omega scan sets, with 0.5° steps in phi or omega; completeness was 99.9 %. A total of 4162 frames were collected. Final cell constants were obtained from the xyz centroids of 9871 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group P-1 was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuperFlip*,[2] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] The asymmetric unit contains one vanadium complex (Z = 2; Z' = 1). All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] The final least-

---

[1] Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

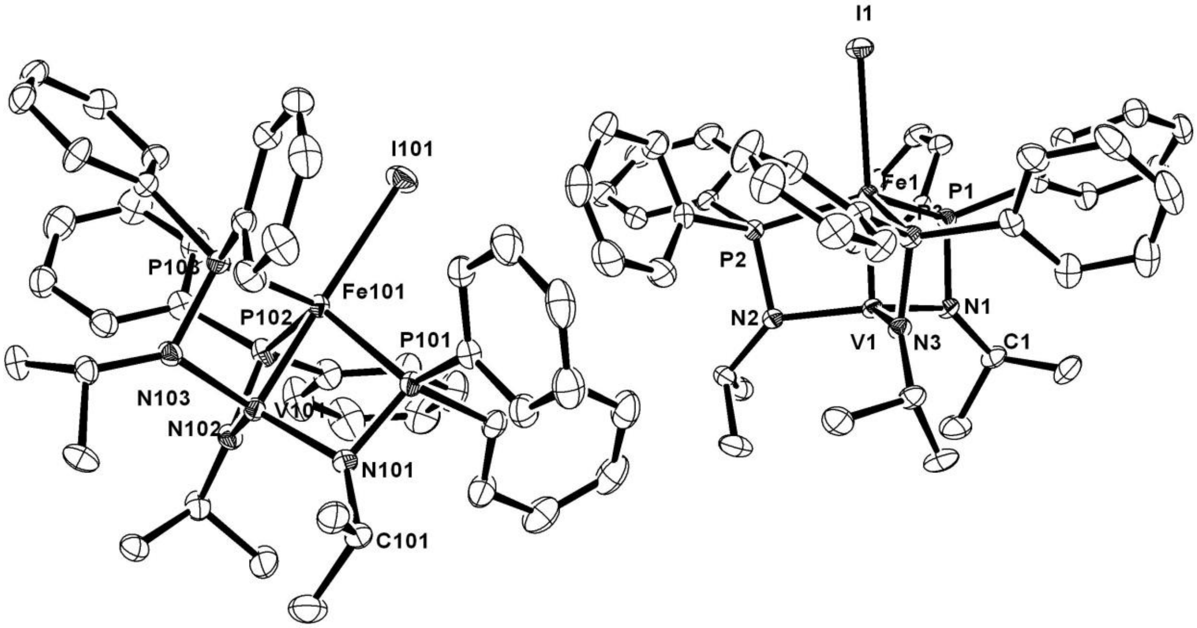
[2] Palatinus, L.; Chapuis, G.; *J. Appl. Cryst*. **2007**, 40, 786.

[3] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487; Prout, C.K;. Pearce, L. J. CAMERON, Chemical Crystallography Laboratory, Oxford, UK, 1996.

[4] Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100–1107.

squares refinement converged to $R_1 = 0.0322$ ($I > 2\sigma(I)$, 9598 data) and $wR_2 = 0.0834$ (F^2, 12100 data, 469 parameters). The final CIF is available as supporting material.

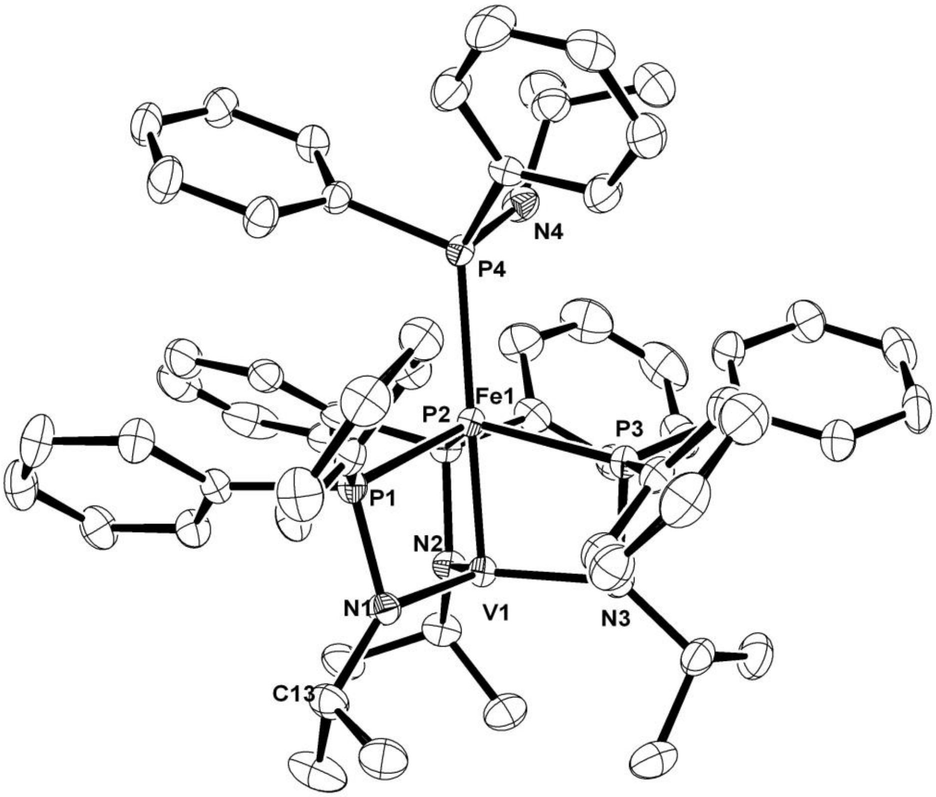
Figure S20. Displacement ellipsoid (50%) representations of **3**. 1.5 THF solvates and hydrogen atoms have been omitted for clarity.



X-ray data collection, solution, and refinement for 3. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 30 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 99.6%. A total of 3034 frames were collected. Final cell constants were obtained from the xyz centroids of 9976 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group *P*-1 was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using the coordinates of the isomorphous F-V-Fe-I analogue (**6**), and simply deleting the F atom. The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] The asymmetric unit contains two complexes and 1.5 THF solvate molecules (Z = 4; *Z'* = 2). All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] One of the two THF solvate molecules was disordered about a center of symmetry; occupancies of atoms O(1), C(500), and C(501) (required to be 0.5) were fixed in the refinement. All the modeled disordered components were refined using isotropic displacement parameters. The final least-squares refinement converged to $R_1 = 0.0364$ ($I > 2\sigma(I)$, 19306 data) and $wR_2 = 0.0802$ (F^2, 24941 data, 1039 parameters). The final CIF is available as supporting material. The CheckCIF report contained one Alert B item, related to the disorder of the THF solvate molecule about a center of symmetry; accordingly, a validation reply form item appears in the CIF to explain this issue in detail.

Figure S21. Displacement ellipsoid (50%) representations of **4**. Hydrogen atoms have been omitted for clarity.

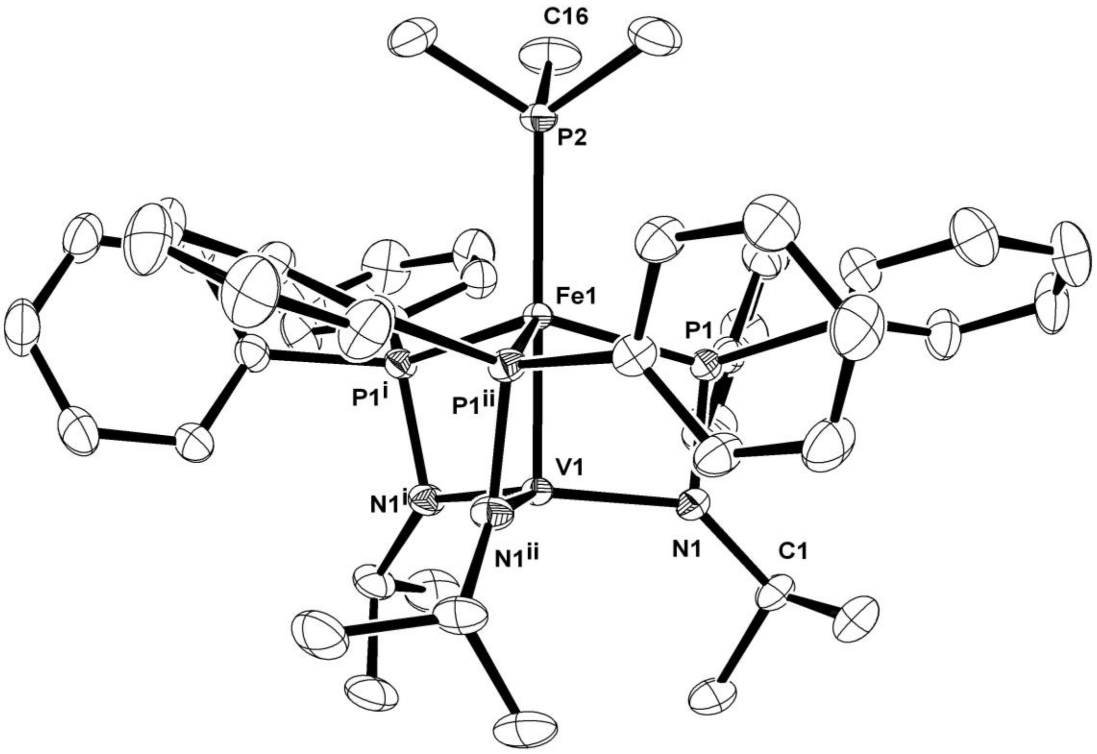


X-ray data collection, solution, and refinement for 4. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 135K, using a frame time of 30 sec and a detector distance of 65 mm. The optimized strategy used for data collection consisted of four phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 99.3 %. A total of 1930 frames were collected. Final cell constants were obtained from the xyz centroids of 7457 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1/c$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*,[2] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] The original solution failed to refine below R *ca.* 20%. The data were analyzed using the CELL_NOW program in the Apex2 package,[1] and an unusual result, *viz.,* that the crystal was composed of two domains rotated about the -0.235 1 0 reciprocal axis by the small amount of 2.0 degrees (twin law (1.011, 0.003, 0.016 / 0.000, 1.000, 0.005 / -0.083, -0.020, 0.988). The result implies that the crystal was either a composite of two grown together or a cracked sample; visual inspection suggested the former. Integration using the orientation matrices for the two components, followed by scaling and absorption correction using TWINABS,1 yielded an HKLF4 file that contained only contributions from component 1. Since this produced a highly satisfactory result, with low R factors and a clean electron density difference map, no further processing of the data or analysis of the composite crystal was attempted. The asymmetric unit contains one molecule of complex

(Z = 4; *Z'* = 1). All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] The final least-squares refinement converged to $R_1 = 0.0487$ ($I > 2\sigma(I)$, 9252 data) and $wR_2 = 0.1004$ (F^2, 13563 data, 631 parameters). The final CIF is available as supporting material.

Figure S22. Displacement ellipsoid (50%) representations of **5**. Hydrogen atoms have been omitted for clarity.



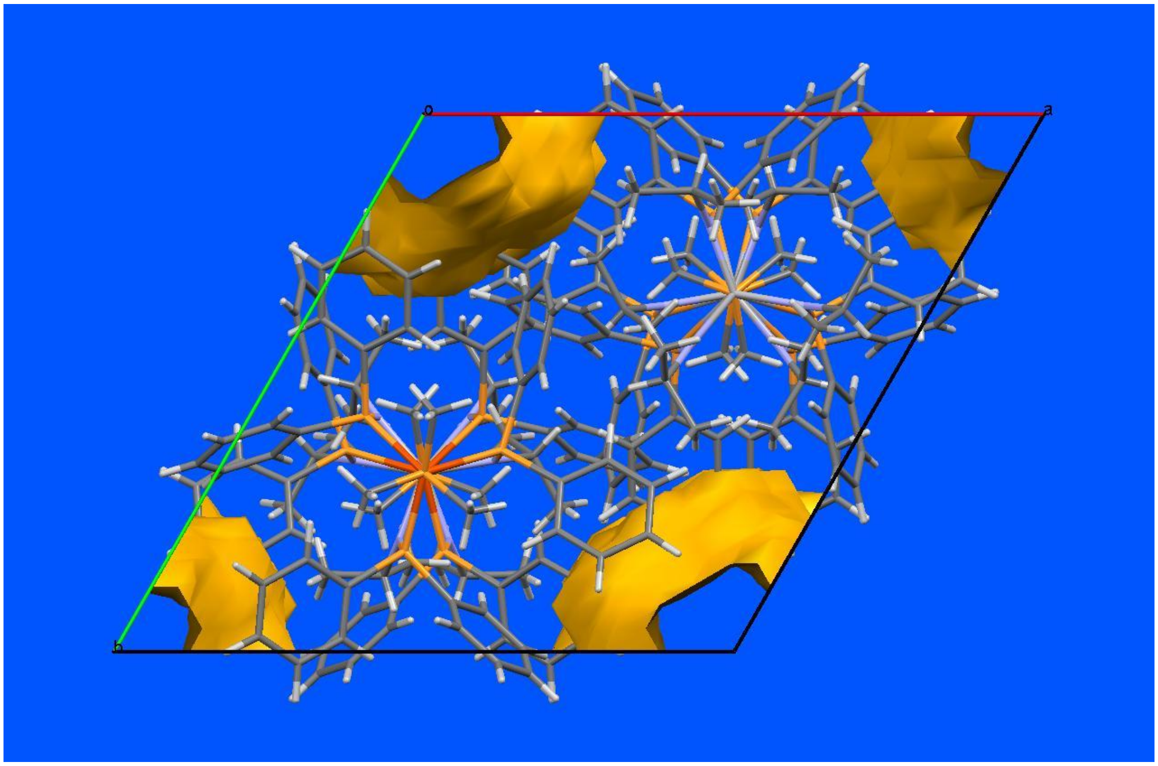
X-ray data collection, solution, and refinement for 5. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.1 Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of two phi and four omega scan sets, with 0.5° steps in phi or omega; completeness was 99.8%. A total of 1561 frames were collected. Final cell constants were obtained from the xyz centroids of 9966 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group *P*-3*c*1 was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *Superflip*,[2] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] The asymmetric unit contains one molecule of complex (Z = 4; Z' = 1/3). All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] During the structure solution, electron density difference maps revealed that there were disordered solvent molecule(s) which could not be successfully modeled. The diethyl-ether solvate was highly disordered in a volume of PLATON SQUEEZE[5,6] reported the solvent void volume to be 948.6

---

[5] (a) Spek, A. L. Acta Crystallogr., Sect A 1990, A46, C34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.

Å^3 per unit cell (17.8%). It appeared that the cavity area contained *ca.* one or two diethyl-ether molecules, located near the center of symmetry at (0, 0, 0) as shown in the *ab* projection below.[7]



Modeling with or without restraints was unsuccessful, as was step by step acquisition of peaks using successive electron density difference maps. Thus, the structure factors were modified using the PLATON SQUEEZE[5,6] technique, in order to produce a "solvate-free" structure factor set. PLATON reported a total electron density of 70 e$^-$ per unit cell, likely representing one or two diethyl-ether molecules, consistent with our earlier observations. Use of the SQUEEZE technique resulted in a decrease of *ca.* 1.6 % in *R*. The final least-squares refinement converged to R_1 =

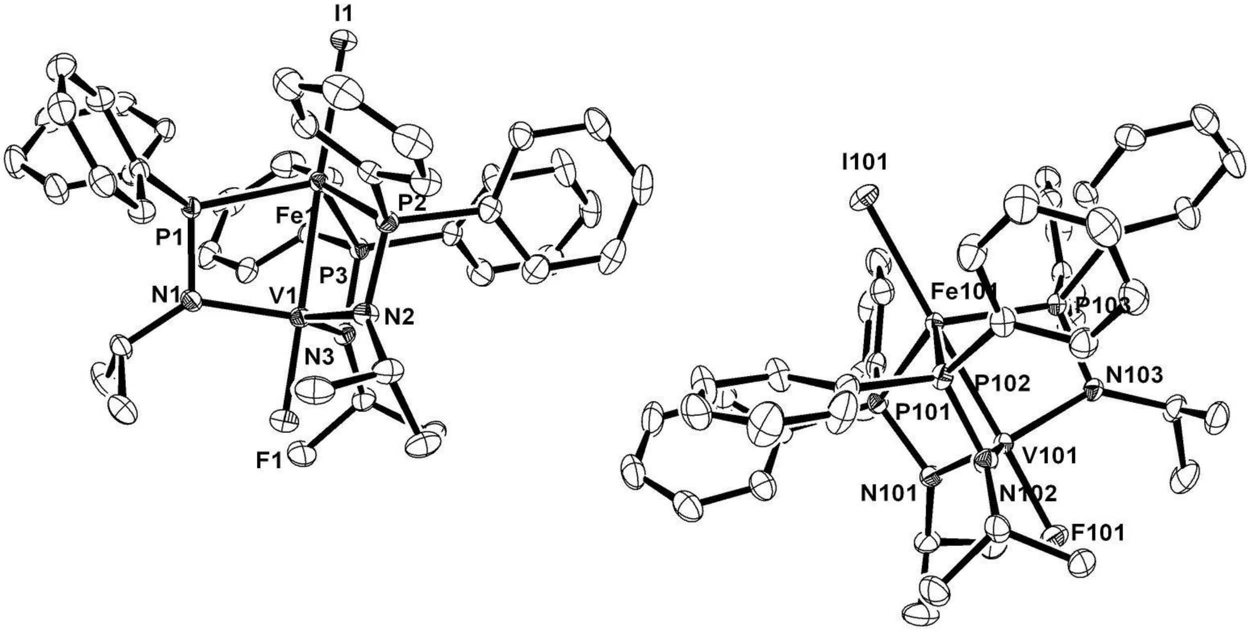
---

[6] v. d. Sluis, P.; Spek, A. Acta Crystallogr., Sect. A **1990**, A46, 194-201.

[7] Macrae, C. F; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.*, **41**, 466-470, 2008

0.0324 ($I > 2\sigma(I)$, 4019 data) and $wR_2 = 0.0993$ (F^2, 5179 data, 172 parameters). The final CIF is available as supporting material.

Figure S23. Displacement ellipsoid (50%) representations of **6**. 1.5 THF solvates and hydrogen atoms have been omitted for clarity.



X-ray data collection, solution, and refinement for 6. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of five phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 99.3%. A total of 3624 frames were collected. Final cell constants were obtained from the xyz centroids of 9566 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group *P*-1was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuperFlip*,[2] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] The asymmetric unit contains two complexes and 1.5 THF solvate molecules (Z = 4; *Z'* = 2). All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.4 One of the two THF solvate molecules was disordered about a center of symmetry; occupancies of atoms O(1), C(500), and C(501) (required to be 0.5) were fixed in the refinement. All the modeled disordered components were refined using isotropic displacement parameters. The final least-squares refinement converged to $R_1 = 0.0356$ ($I > 2\sigma(I)$, 19036 data) and $wR_2 = 0.0745$ (F^2, 25039 data, 1057 parameters). The final CIF is available as supporting material.

Complete Gaussian09 Reference:

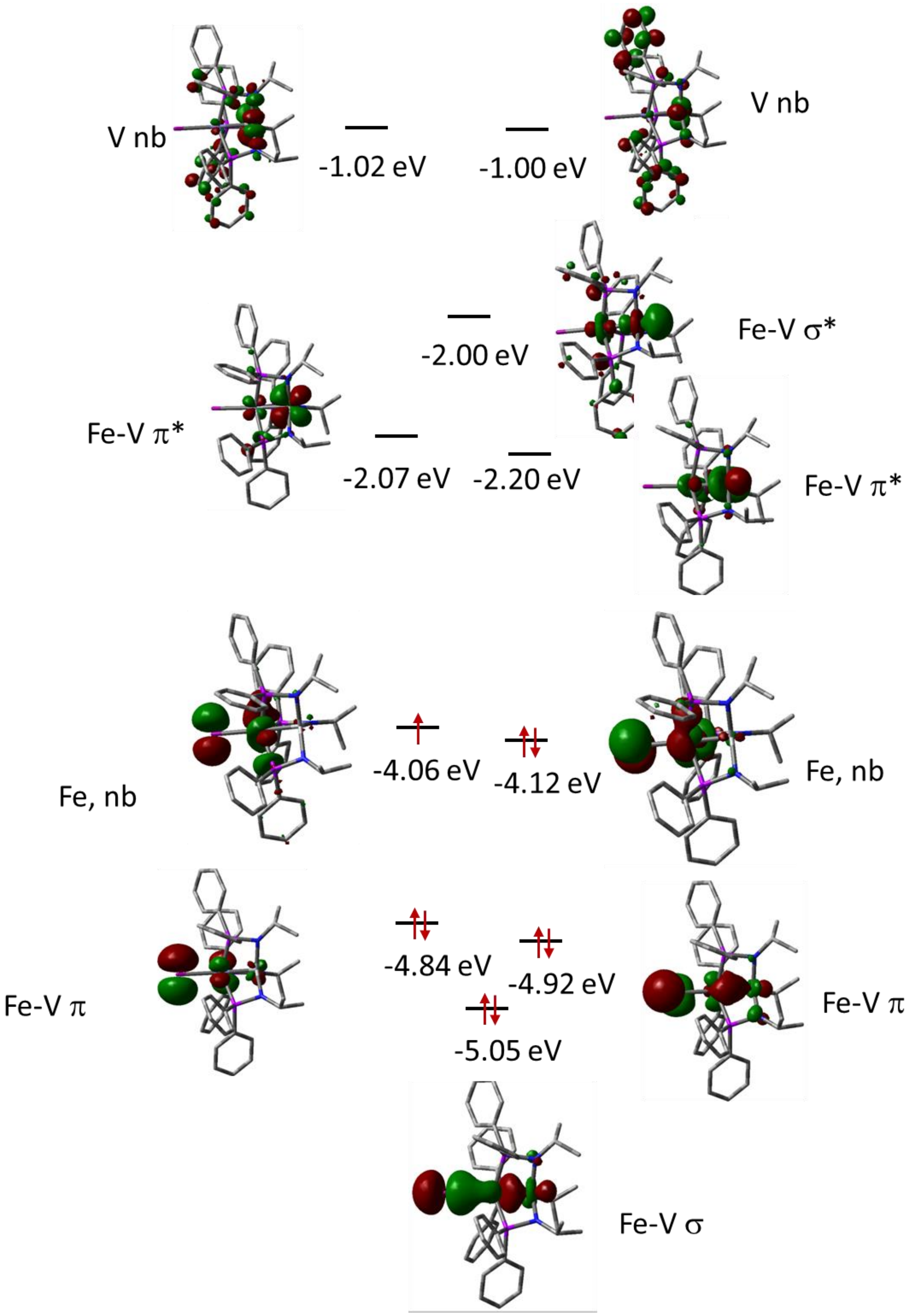
Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji,

H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

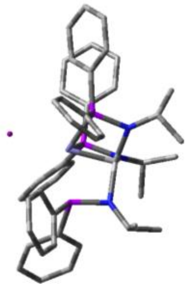
Table S2. Comparison of calculated (DFT) vs experimental (X-ray) bond metrics for complexes **3**, **5**, and **6**.

	3		**5**		**6**	
	Calc.	**exp.**	**Calc.**	**exp.**	**Calc.**	**exp.**
Fe-V	2.12 Å	2.07 Å	2.06 Å	2.05 Å	2.45 Å	2.46 Å
Fe-P(avg)	2.31 Å	2.29 Å	2.23 Å	2.22 Å	2.32 Å	2.31 Å
V-N (avg)	1.92 Å	1.92 Å	1.91 Å	1.91 Å	1.94 Å	1.93 Å
Fe-I	2.64 Å	2.66 Å	------	------	2.60 Å	2.57
Fe-PMe_3	------	------	2.30 Å	2.32 Å	------	------
V-F	------	------	------	------	1.87 Å	1.87 Å
N-V-N (avg)	119.1°	119.1°	119.0°	119.2°	120.0°	120.0°
P-Fe-P (avg)	112.9°	112.9°	114.1°	113.7°	109.0°	108.5°

Figure S24. Calculated frontier molecular orbital diagram of **3** and pictorial representations of molecular orbitals.



XYZ Coordinates of Optimized Structure of **3**

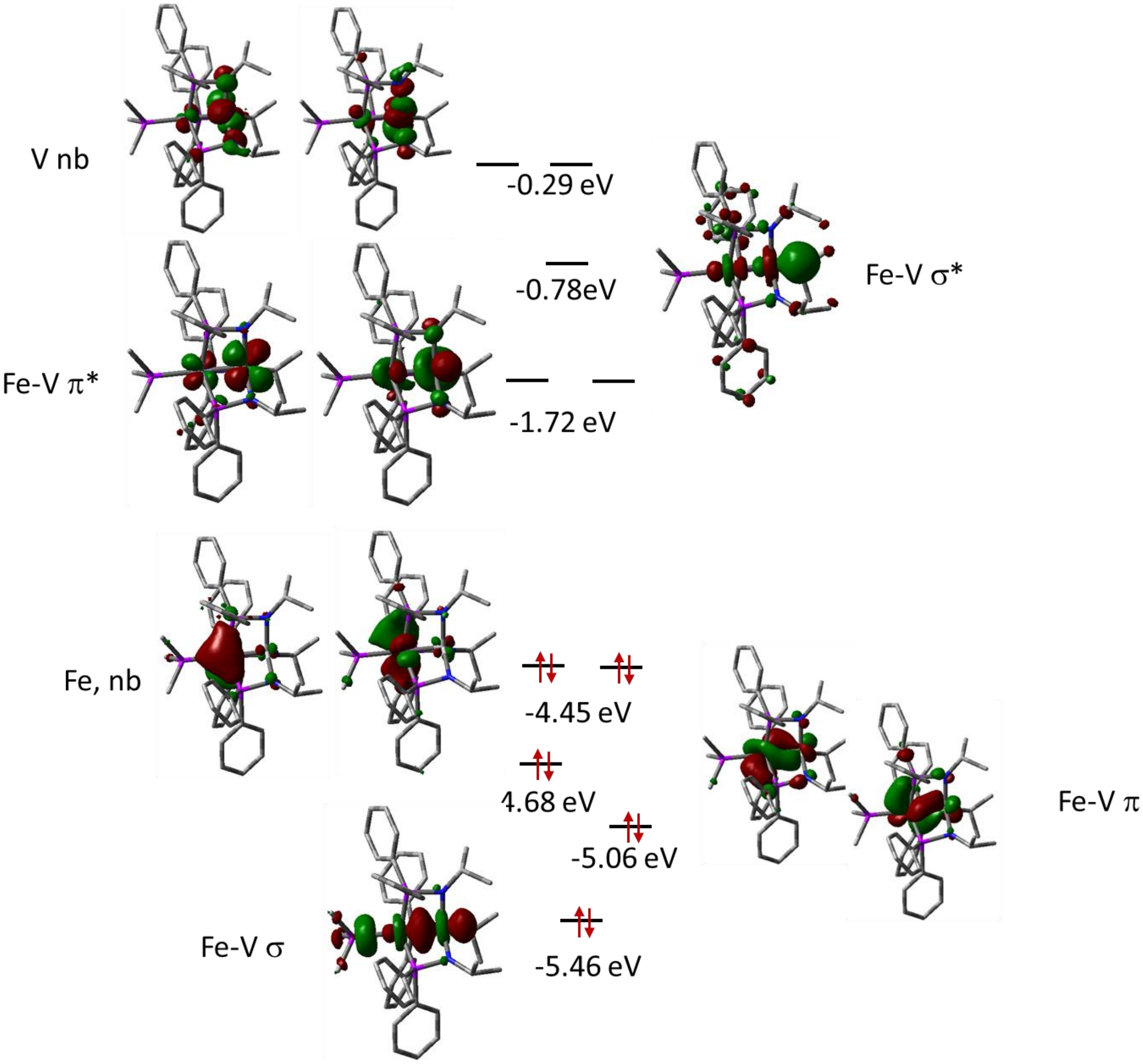


Symbol	X	Y	Z
Fe	0.012505	0.07567	-0.51229
V	-0.03342	0.039906	1.604431
P	-2.05638	0.991712	0.100374
P	0.039492	-2.13111	0.068801
P	1.994588	1.051583	0.165673
N	-1.67427	1.023543	1.772318
N	1.692178	0.859152	1.841703
C	2.713098	3.363815	-1.33145
N	-0.13502	-1.88092	1.749998
C	6.144324	0.685321	-0.29584
C	5.072067	-1.02209	-1.69019
C	1.556951	-3.16941	-0.13913
C	2.757092	4.752567	-1.59125
C	-2.44923	2.70482	-0.49118
C	3.799798	-0.5815	-1.2535
C	-3.69615	0.156966	-0.05766
C	-1.26254	-3.27416	-0.59047
C	1.586574	3.802175	0.79927
C	2.564837	-3.18604	0.86206
C	3.748532	-3.93611	0.679679
C	-3.6699	3.359978	-0.16088
C	-4.14246	-0.76127	0.93118
C	1.773245	-3.89454	-1.34479
C	3.950978	-4.66708	-0.51578
C	-1.73332	4.718355	-1.71074
C	-3.28344	-4.97801	-1.64091
C	-3.91324	4.683199	-0.59205
C	-6.12829	-1.28843	-0.40848
C	-1.31968	-4.64554	-0.21142
C	-2.21615	-2.77293	-1.51369
C	-5.35197	-1.47174	0.761245
C	4.874534	1.132651	0.131433
C	2.607336	1.217603	2.959569
C	-3.22155	-3.62124	-2.03581

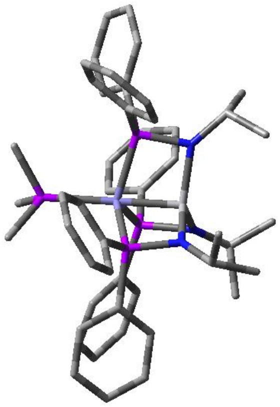
C	-1.48693	3.39482	-1.27469
C	-2.94309	5.366748	-1.3682
C	1.641558	5.191345	0.54409
C	3.690671	0.491784	-0.3318
C	-0.31511	-2.91064	2.806806
C	-2.32727	-5.4903	-0.72738
C	1.78887	1.606631	4.212515
C	-5.68064	-0.39152	-1.41051
C	2.961857	-4.63711	-1.53027
C	-4.47421	0.324469	-1.23944
C	2.228681	5.672205	-0.65105
C	2.13744	2.874714	-0.12496
C	-1.81401	-3.23317	3.042185
C	-2.47927	1.66454	2.847986
C	3.591823	0.065168	3.288279
C	-2.03811	3.13422	3.075803
C	-2.37102	0.851699	4.159363
C	6.245293	-0.3962	-1.20803
C	0.351483	-2.45065	4.124631
H	3.124853	2.662135	-2.06626
H	7.049827	1.184641	0.069738
H	5.139164	-1.84879	-2.40642
H	3.203892	5.11438	-2.52508
H	2.888769	-1.04951	-1.64315
H	1.107252	3.429583	1.711551
H	2.41987	-2.60105	1.777029
H	4.51386	-3.94402	1.465254
H	-4.43655	2.832038	0.419865
H	-3.53311	-0.9229	1.826872
H	1.013141	-3.88322	-2.13499
H	4.869058	-5.24965	-0.65745
H	-0.98192	5.23261	-2.32058
H	-4.0619	-5.63532	-2.04692
H	-4.8576	5.175971	-0.33071
H	-7.06698	-1.83949	-0.54014
H	-0.56683	-5.05924	0.471325
H	-2.15087	-1.7284	-1.83887
H	-5.68475	-2.17153	1.537483
H	4.805817	1.992768	0.809353
H	3.19822	2.105493	2.645761
H	-3.94833	-3.21873	-2.75054
H	-0.55988	2.887239	-1.5663

H	-3.13491	6.391364	-1.70911
H	1.219127	5.895121	1.271484
H	0.194269	-3.83974	2.470243
H	-2.36086	-6.54462	-0.42698
H	2.460251	1.888029	5.045886
H	1.118275	2.458862	4.001043
H	1.172528	0.749935	4.548396
H	-6.27117	-0.24557	-2.32314
H	3.111834	-5.19405	-2.46308
H	-4.14115	1.017417	-2.02155
H	2.270076	6.74967	-0.85057
H	-1.92254	-4.066	3.764405
H	-2.32914	-2.34648	3.457414
H	-2.31282	-3.51711	2.100699
H	-3.54323	1.663365	2.527547
H	4.312534	0.382093	4.067288
H	3.032681	-0.8096	3.668932
H	4.157403	-0.24435	2.393744
H	-2.68876	3.6224	3.827412
H	-2.08872	3.713225	2.138794
H	-0.99657	3.1618	3.447681
H	-2.96492	1.327519	4.962801
H	-2.73724	-0.18106	4.019549
H	-1.31753	0.806607	4.497737
H	7.230957	-0.73766	-1.54682
H	0.202826	-3.20422	4.921298
H	-0.09853	-1.49895	4.46878
H	1.436709	-2.29519	3.99004
I	0.118576	0.174245	-3.15127

Figure S25. Calculated frontier molecular orbital diagram of **5** and pictorial representations of molecular orbitals.



XYZ Coordinates of Optimized Structure of **5**



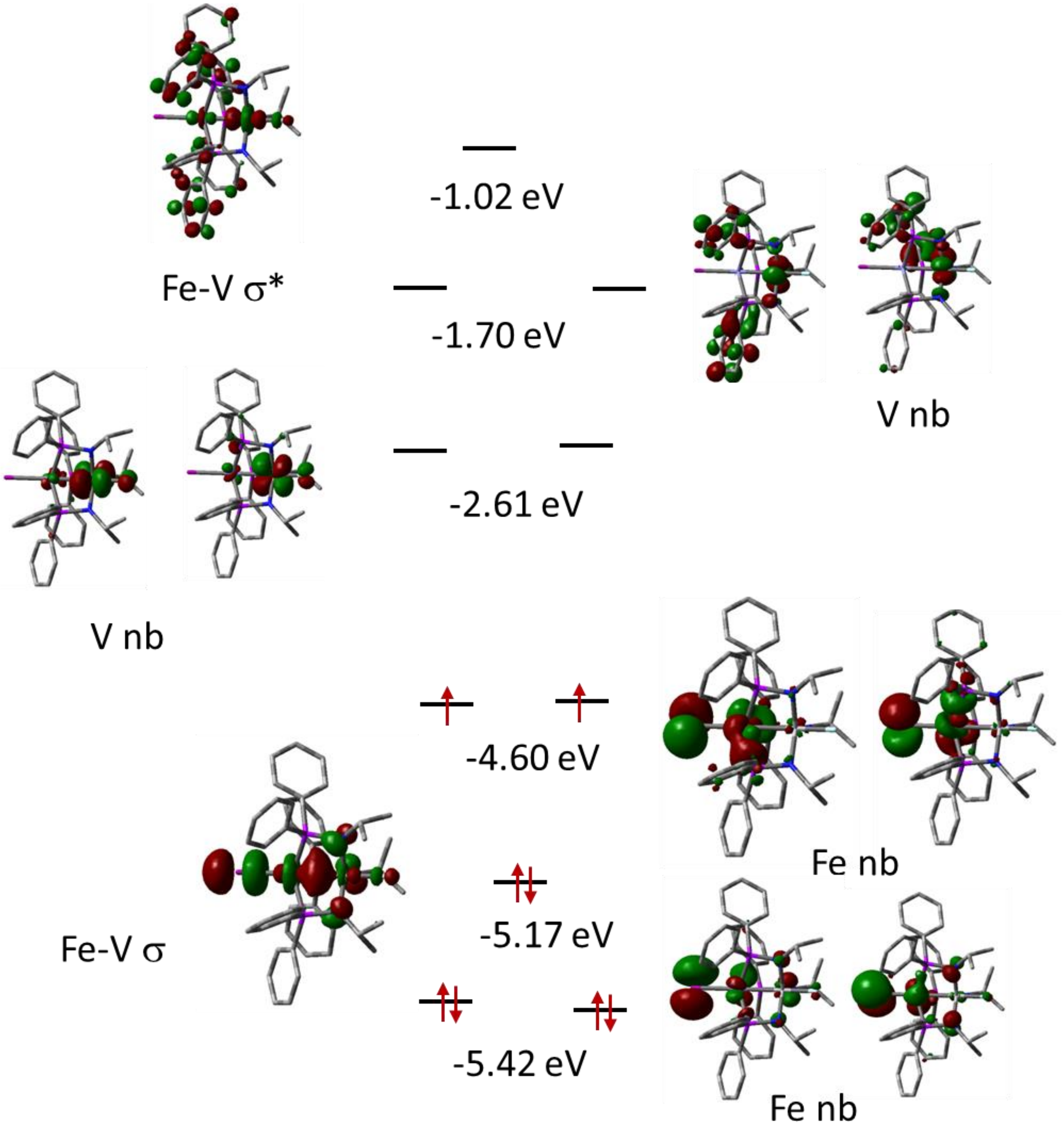
Symbol	X	Y	Z
Fe	0.001111	-0.0006	-0.56377
V	0.000343	-7E-06	1.493401
P	2.042634	0.69701	-0.01331
P	-1.62523	1.419679	-0.01403
P	-0.41732	-2.11651	-0.01249
N	1.838792	0.482084	1.689559
N	-0.50136	-1.83246	1.690647
C	0.865071	-4.36805	-1.27708
N	-1.33611	1.350251	1.688859
C	-3.38068	-5.05052	-0.6104
C	-4.09936	-3.00648	-1.75184
C	-3.43765	1.005455	-0.16241
C	1.886238	-5.33682	-1.41612
C	3.612266	-0.16512	-0.5497
C	-2.91393	-2.35927	-1.33015
C	2.592163	2.472794	-0.1627
C	-1.66438	3.209598	-0.5506
C	1.89128	-3.58306	0.795894
C	-4.04894	0.150292	0.796637
C	-5.40003	-0.24109	0.665935
C	4.911607	0.300282	-0.19866
C	2.15866	3.430466	0.795905
C	-4.21868	1.436854	-1.27301
C	-6.16914	0.200701	-0.43825
C	4.654939	-2.0489	-1.74996
C	-1.60831	5.931923	-1.39921
C	6.066034	-0.40011	-0.61542
C	3.26277	5.239787	-0.44069
C	-2.72096	4.100018	-0.20523
C	-0.58485	3.705937	-1.3258

C	2.496278	4.795917	0.66443
C	-2.19691	-4.40102	-0.19373
C	-0.82919	-2.80991	2.756505
C	-0.55388	5.055824	-1.74862
C	3.501816	-1.34533	-1.32901
C	5.940967	-1.57801	-1.39522
C	2.906703	-4.55632	0.664225
C	-1.94936	-3.04375	-0.54689
C	-2.01916	2.122887	2.754062
C	-2.69307	5.449467	-0.62355
C	-0.05096	-2.47776	4.051936
C	3.686578	4.300098	-1.41306
C	-5.56887	1.038549	-1.41065
C	3.355576	2.932025	-1.27437
C	2.910691	-5.44002	-0.44247
C	0.846407	-3.47914	-0.16391
C	-1.30068	3.469767	3.033393
C	2.847998	0.68966	2.755811
C	-2.3544	-2.85372	3.040156
C	3.650708	-0.60736	3.042379
C	2.170641	1.200858	4.0498
C	-4.3364	-4.35442	-1.39351
C	-2.11537	1.284507	4.05115
H	0.068791	-4.31926	-2.02962
H	-3.55467	-6.09688	-0.33059
H	-4.83437	-2.45523	-2.35018
H	1.874209	-6.01606	-2.27787
H	-2.7268	-1.31132	-1.59245
H	1.906227	-2.88574	1.640363
H	-3.45161	-0.21635	1.63838
H	-5.84993	-0.89692	1.421465
H	5.02278	1.219638	0.389266
H	1.543162	3.096744	1.638239
H	-3.77901	2.103628	-2.0247
H	-7.21827	-0.10185	-0.53934
H	4.544757	-2.9631	-2.34514
H	-1.58838	6.978436	-1.72693
H	7.059269	-0.02641	-0.33743
H	3.525465	6.299481	-0.54297
H	-3.57504	3.735693	0.378639
H	0.233525	3.02291	-1.58156
H	2.15433	5.514119	1.419814

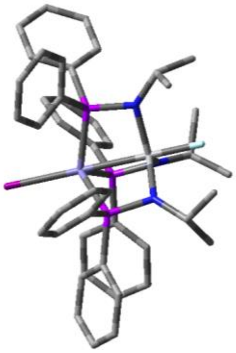
H	-1.45684	-4.95675	0.394984
H	-0.50844	-3.81724	2.411894
H	0.294464	5.418776	-2.3408
H	2.500943	-1.70918	-1.589
H	6.837011	-2.11981	-1.72164
H	3.698383	-4.61983	1.420904
H	-3.05338	2.343153	2.410252
H	-3.51628	6.120984	-0.35003
H	-0.29563	-3.20295	4.851779
H	1.039503	-2.50391	3.877603
H	-0.32278	-1.46651	4.411889
H	4.283402	4.628064	-2.27351
H	-6.15245	1.391233	-2.2704
H	3.712488	2.216987	-2.0255
H	3.698362	-6.19599	-0.54494
H	-1.87019	4.067443	3.772229
H	-0.29187	3.279292	3.445812
H	-1.19475	4.062558	2.109716
H	3.558862	1.471256	2.408965
H	-2.58911	-3.6444	3.77983
H	-2.68759	-1.88307	3.453508
H	-2.92451	-3.05549	2.118096
H	4.45258	-0.41214	3.781528
H	4.111106	-1.0021	2.12148
H	2.977907	-1.38126	3.457395
H	2.920231	1.351559	4.850347
H	1.649786	2.159039	3.873683
H	1.42928	0.461461	4.409698
H	-5.2533	-4.85976	-1.72049
H	-2.62233	1.857748	4.851076
H	-1.10198	1.019243	4.409488
H	-2.67916	0.350245	3.878931
P	0.000338	-0.00283	-2.86837
C	-0.0212	-1.64237	-3.76459
H	-0.92636	-2.20769	-3.47727
H	-0.01566	-1.50427	-4.8642
H	0.864051	-2.23562	-3.47282
C	1.427635	0.798969	-3.76844
H	2.370404	0.29976	-3.48042
H	1.304087	0.73172	-4.8678
H	1.497009	1.863103	-3.47946
C	-1.41176	0.832588	-3.76238

H	-1.4477	1.89926	-3.47596
H	-1.2991	0.757095	-4.86232
H	-2.36701	0.362502	-3.4662

Figure S26. Calculated frontier molecular orbital diagram of **6** and pictorial representations of molecular orbitals.



XYZ Coordinates of Optimized Structure of **6**



Symbol	X	Y	Z
Fe	-0.00085	0.001621	-0.65555
V	0.003236	0.007943	1.797514
I	-0.00435	-0.00947	-3.25614
P	-2.0678	0.697998	0.137373
P	1.639994	1.441119	0.130121
P	0.428953	-2.13441	0.138988
F	0.008654	0.011221	3.665025
N	-1.8471	0.599733	1.806044
N	1.438875	1.312276	1.799241
N	0.41759	-1.8909	1.80722
C	-2.92221	0.736088	2.840856
C	-2.49688	1.622355	4.036048
C	-3.37993	-0.66354	3.319944
C	-2.60006	2.428595	-0.24506
C	-2.35603	3.482732	0.67375
C	-2.73373	4.808202	0.360647
C	-3.34448	5.099242	-0.88255
C	-3.57202	4.055258	-1.81389
C	-3.20197	2.728143	-1.49894
C	-3.55018	-0.25497	-0.44634
C	-4.86737	0.081215	-0.02052
C	-5.98172	-0.6496	-0.48789
C	-5.79885	-1.71522	-1.40494
C	-4.49737	-2.03783	-1.85359
C	-3.37986	-1.31258	-1.37658
C	2.101571	2.178264	2.826189
C	2.658694	1.371615	4.023493
C	1.128481	3.284375	3.301761
C	3.404571	1.024248	-0.23758
C	4.172639	0.274091	0.690795
C	5.50924	-0.07798	0.396551

C	6.088791	0.300184	-0.83821
C	5.320508	1.029699	-1.77988
C	3.986338	1.389904	-1.48335
C	1.562722	3.198182	-0.46341
C	2.530586	4.163851	-0.063
C	2.458238	5.492305	-0.53684
C	1.427522	5.872	-1.4332
C	0.475648	4.914292	-1.85261
C	0.542343	3.585637	-1.37033
C	0.840715	-2.89127	2.839407
C	-0.13645	-2.96897	4.0364
C	2.284056	-2.59289	3.314724
C	-0.81024	-3.45794	-0.23074
C	-1.84707	-3.75409	0.692091
C	-2.8139	-4.74022	0.391568
C	-2.76634	-5.42982	-0.84353
C	-1.74785	-5.1223	-1.7802
C	-0.77601	-4.14173	-1.47794
C	1.990375	-2.94183	-0.45972
C	2.353909	-4.25811	-0.0535
C	3.53837	-4.8573	-0.53565
C	4.3683	-4.15793	-1.44781
C	4.002076	-2.86093	-1.87536
C	2.82156	-2.25559	-1.38309
H	-3.78209	1.2367	2.348171
H	-2.23061	2.642132	3.704531
H	-1.62863	1.179956	4.549845
H	-3.33814	1.705076	4.751478
H	-3.71062	-1.28047	2.465185
H	-2.54111	-1.17257	3.825415
H	-4.22133	-0.57446	4.034469
H	-1.86943	3.261267	1.629283
H	-2.54749	5.611104	1.083858
H	-3.6385	6.127414	-1.1249
H	-4.04063	4.271624	-2.78144
H	-3.38728	1.926971	-2.2243
H	-5.03055	0.928826	0.655683
H	-6.98917	-0.37997	-0.14886
H	-6.6652	-2.27691	-1.77452
H	-4.34371	-2.84778	-2.57545
H	-2.37842	-1.5488	-1.752
H	2.96525	2.663711	2.325009

H	3.406684	0.628687	3.692591
H	3.154298	2.061437	4.734123
H	1.842062	0.844611	4.542177
H	0.27437	2.823728	3.827393
H	1.639251	3.977295	3.998447
H	0.750072	3.86742	2.442883
H	3.71822	-0.03054	1.639683
H	6.093896	-0.64963	1.127125
H	7.126296	0.028355	-1.0663
H	5.759338	1.322259	-2.74134
H	3.402716	1.95872	-2.21687
H	3.357475	3.877067	0.597754
H	3.209973	6.224382	-0.21816
H	1.376676	6.90141	-1.80784
H	-0.31741	5.191066	-2.55633
H	-0.18404	2.844176	-1.72053
H	0.833539	-3.88484	2.344191
H	-0.19054	-1.99524	4.548493
H	0.21713	-3.73676	4.751906
H	-1.15224	-3.25303	3.706899
H	2.981554	-2.57432	2.458116
H	2.311659	-1.61237	3.820753
H	2.626346	-3.36774	4.028099
H	-1.89548	-3.20532	1.638702
H	-3.60516	-4.96409	1.116908
H	-3.51586	-6.19551	-1.07643
H	-1.70676	-5.64675	-2.7424
H	0.009771	-3.91414	-2.20792
H	1.701989	-4.83021	0.617431
H	3.805084	-5.87057	-0.21205
H	5.2836	-4.62675	-1.82868
H	4.626721	-2.31562	-2.5918
H	2.533327	-1.2603	-1.73954