

Utilization of Phosphinoamide Ligands in Homobimetallic Fe and Mn Complexes: The Effect of Vastly Different Coordination Environments on Metal-Metal Interactions and Magnetic and Redox Properties

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Figure S1. ^1H NMR spectrum of $[\text{}^i\text{PrNKPPH}_2]_2$ (**1**) in $\text{THF-}d_8$.

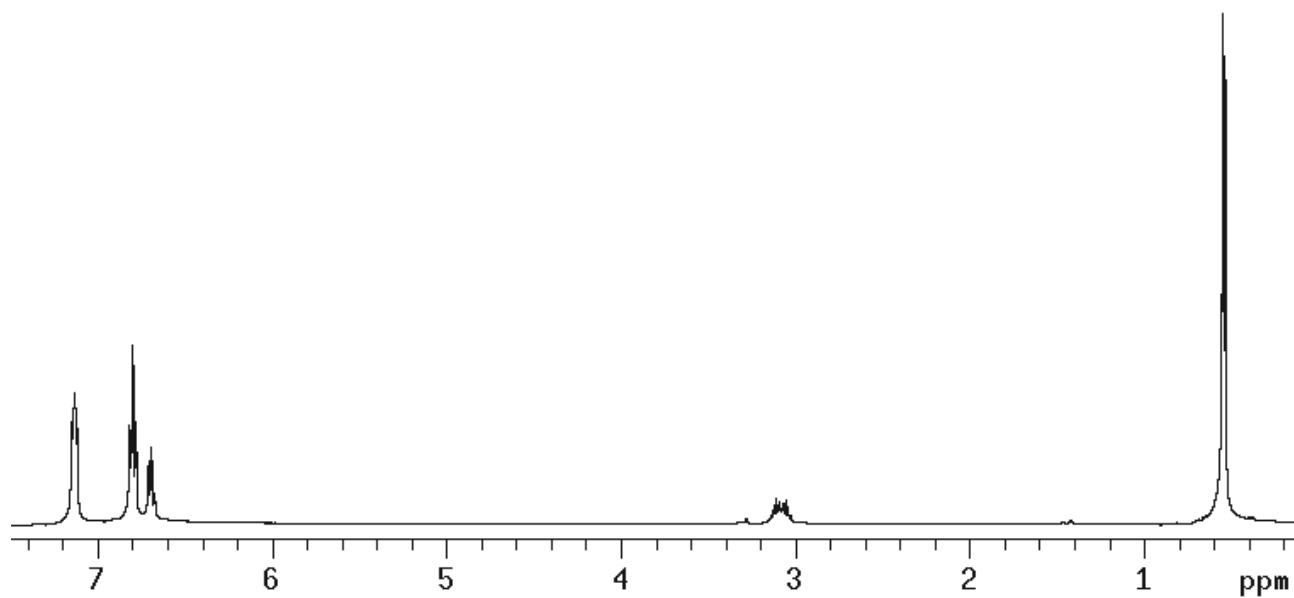


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\textit{i}\text{PrNKPPh}_2]_2$ (**1**) in $\text{THF-}d_8$.

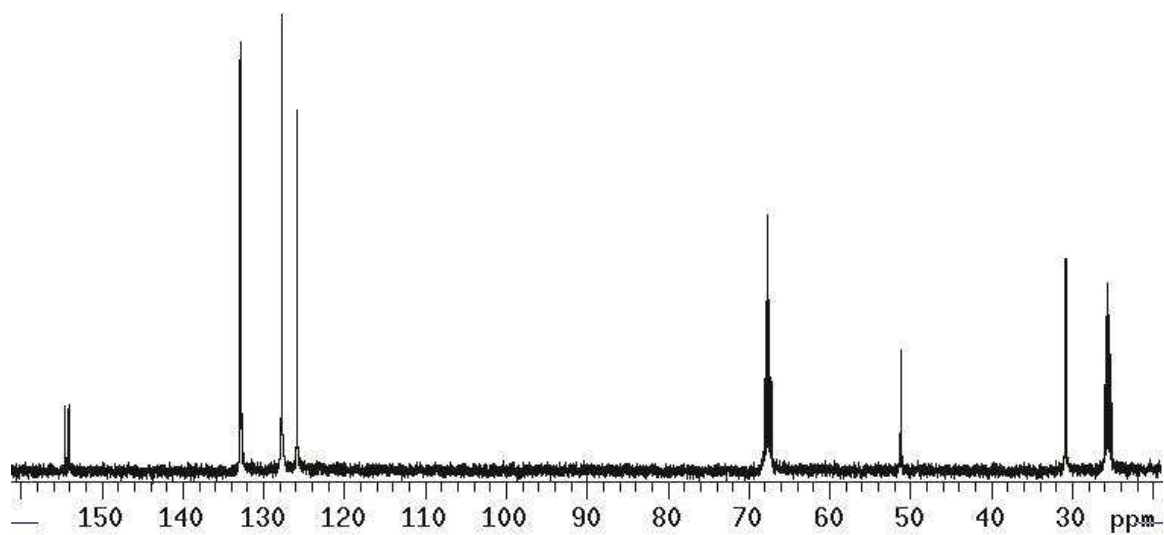


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\textit{i}\text{PrNKPPh}_2]_2$ (**1**) in $\text{THF-}d_8$.

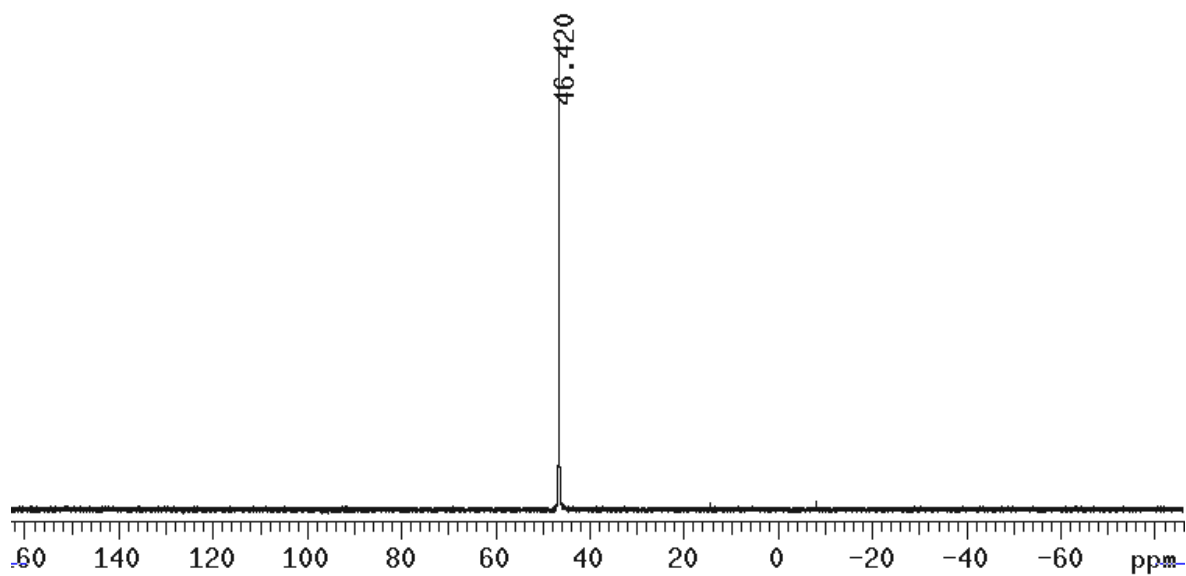


Figure S4. ^1H NMR spectrum of $[\text{MesNKP}^i\text{Pr}_2]_2$ (**2**) in $\text{THF-}d_8$

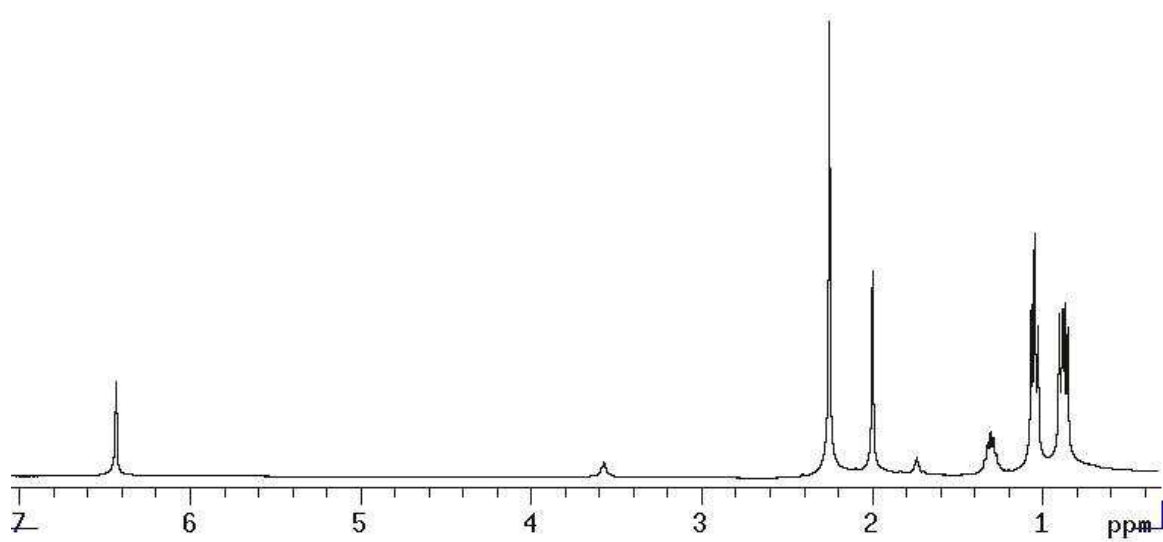


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{MesNKP}^i\text{Pr}_2]_2$ (**2**) in $\text{THF-}d_8$.

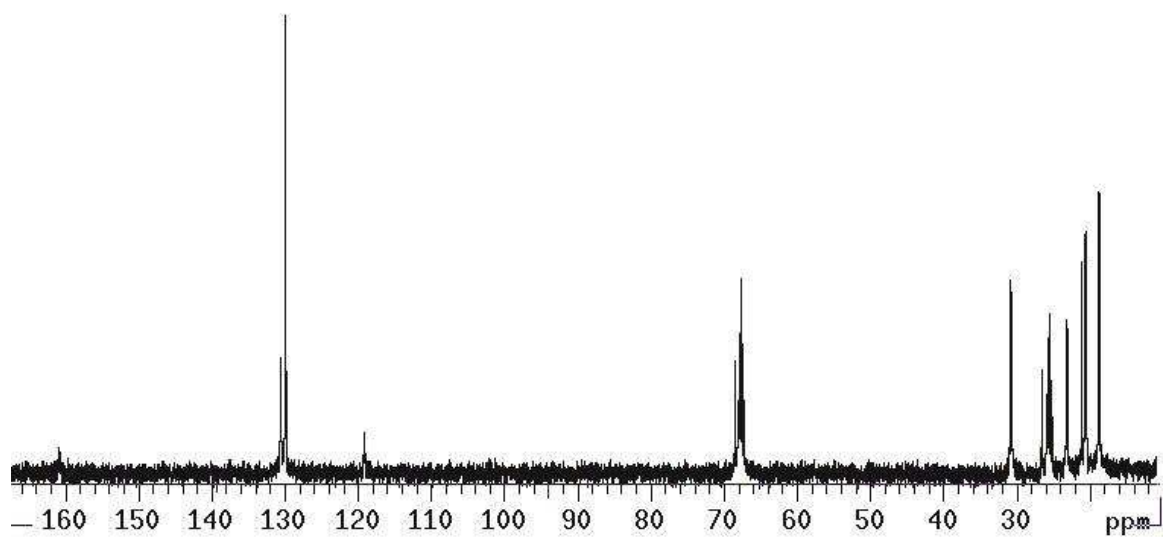


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{MesNKP}^i\text{Pr}_2]_2$ (**2**) in $\text{THF-}d_8$.

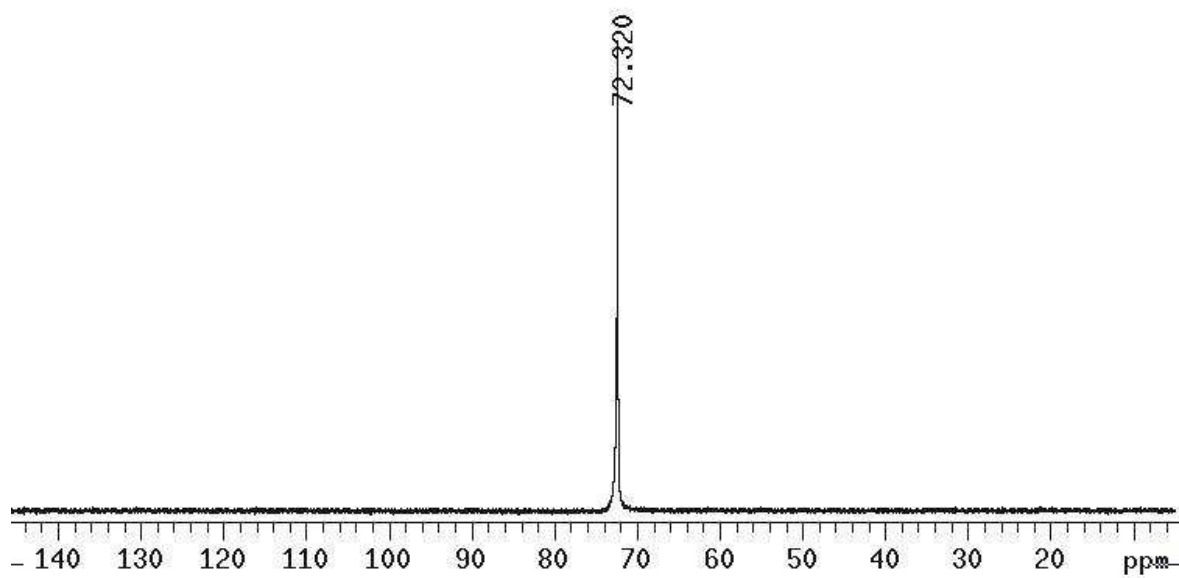


Figure S7. ^1H NMR spectrum of $[\text{Fe}(^i\text{PrNPh}_2)_3\text{Fe}(^i\text{PrNPh}_2)]$ (**4**) in C_6D_6 .

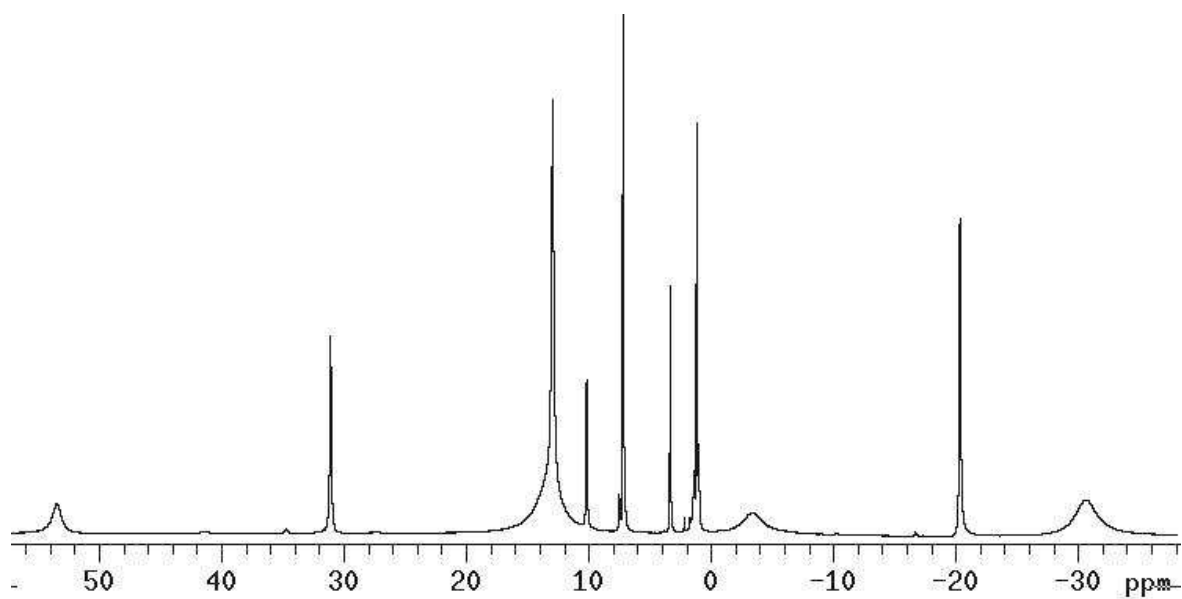


Figure S8. ^1H NMR spectrum of $[\text{Fe}(\text{MesNP}^i\text{Pr}_2)_3\text{FeCl}]$ (**6**) in C_6D_6 .

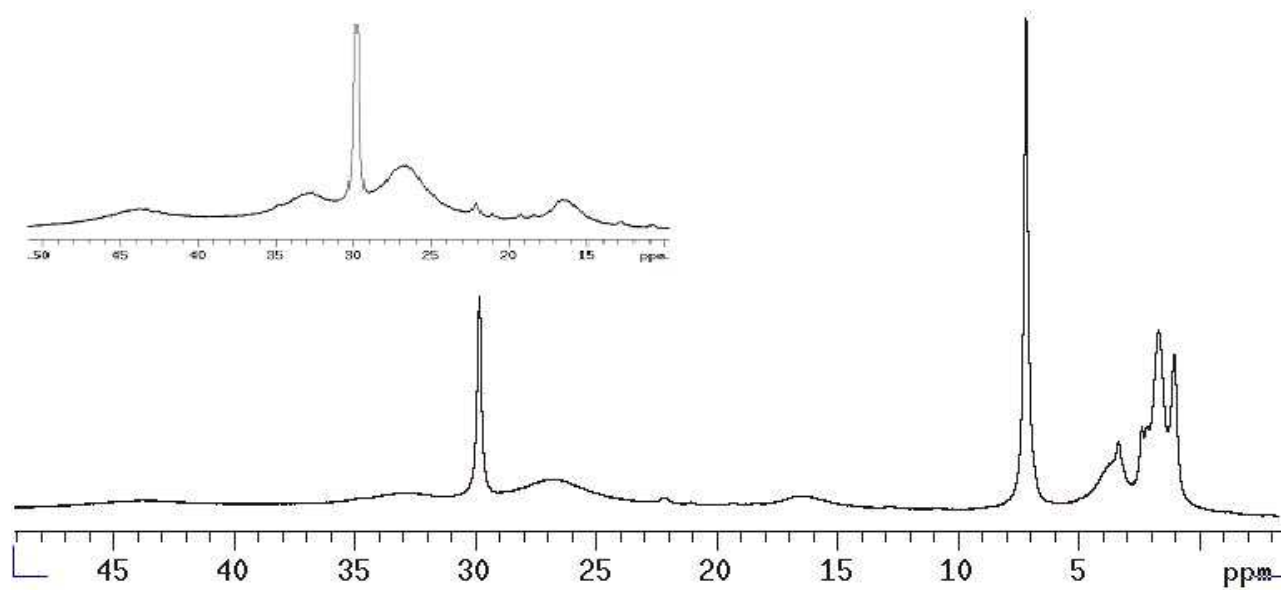


Figure S9. ^1H NMR spectrum of $[(\text{THF})\text{Fe}(\mu\text{-I})(\text{MesNP}^i\text{Pr}_2)_3\text{FeI}]$ (**7**) in C_6D_6 .

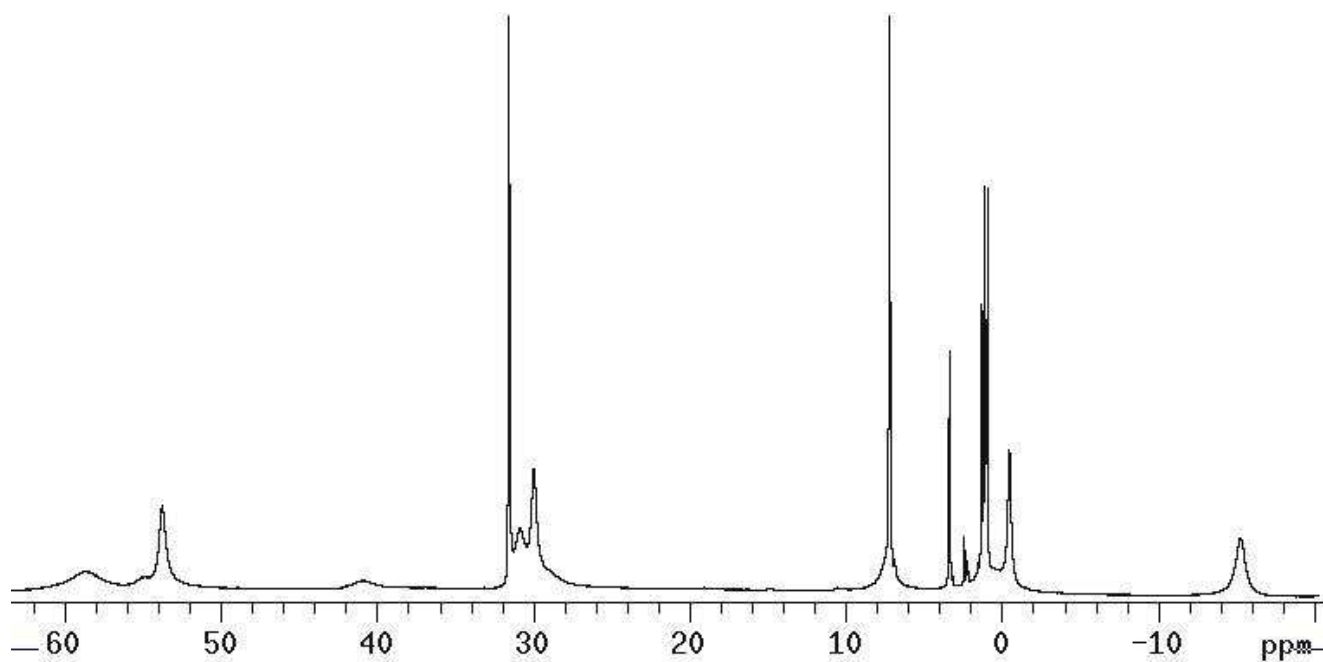


Figure S10. ^1H NMR spectrum of $[\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}]$ (**9**) in C_6D_6 .

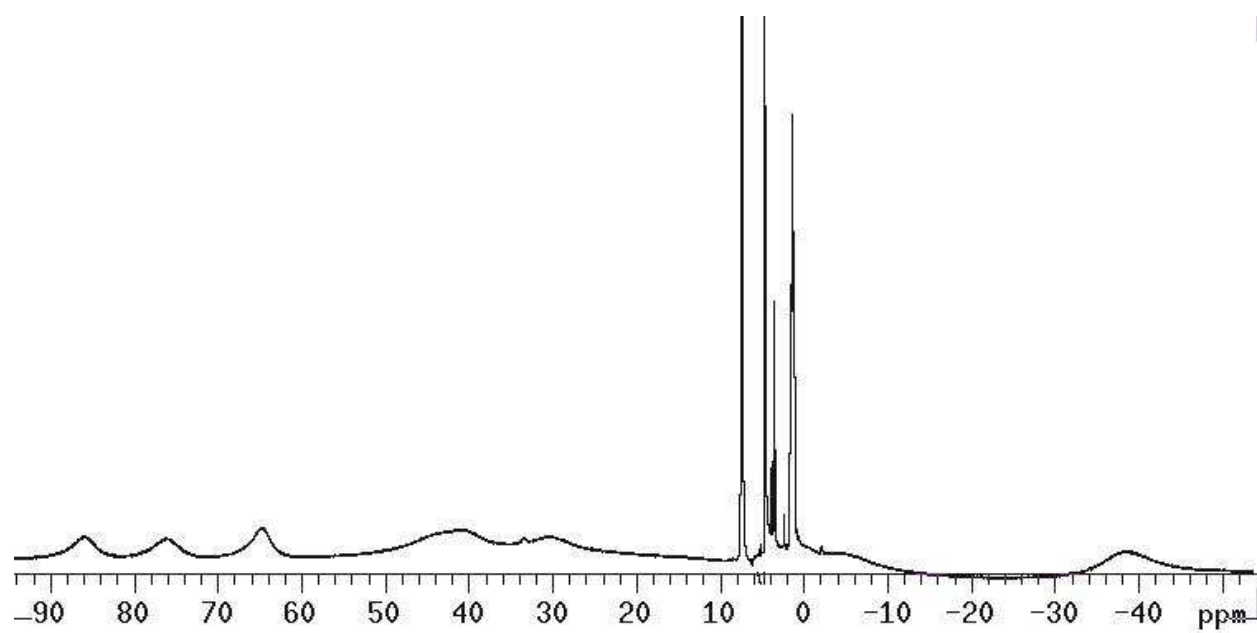


Figure S11. Full cyclic voltammogram of $[\text{Mn}(^i\text{PrNPPh}_2)_3\text{Mn}(^i\text{PrNPPh}_2)]$ (**3**) (2 mM in 0.4 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ in THF, scan rate = 100 mV/s).

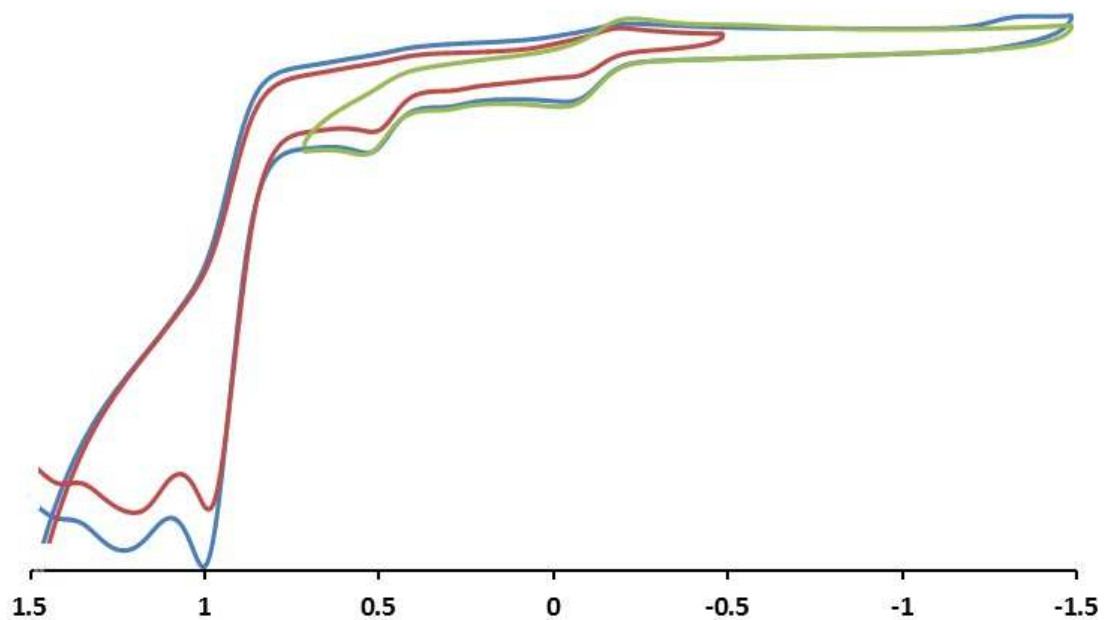


Figure S12. Cyclic voltammogram of $[\text{Fe}(\text{}^i\text{PrNPPH}_2)_3\text{Fe}(\text{}^i\text{PrNPPH}_2)]$ (**4**) (2 mM in 0.4 M $[\text{}^n\text{Bu}_4\text{N}][\text{PF}_6]$ in THF, scan rate = 100 mV/s), including scans of several different potential windows to identify artifacts of irreversible processes.

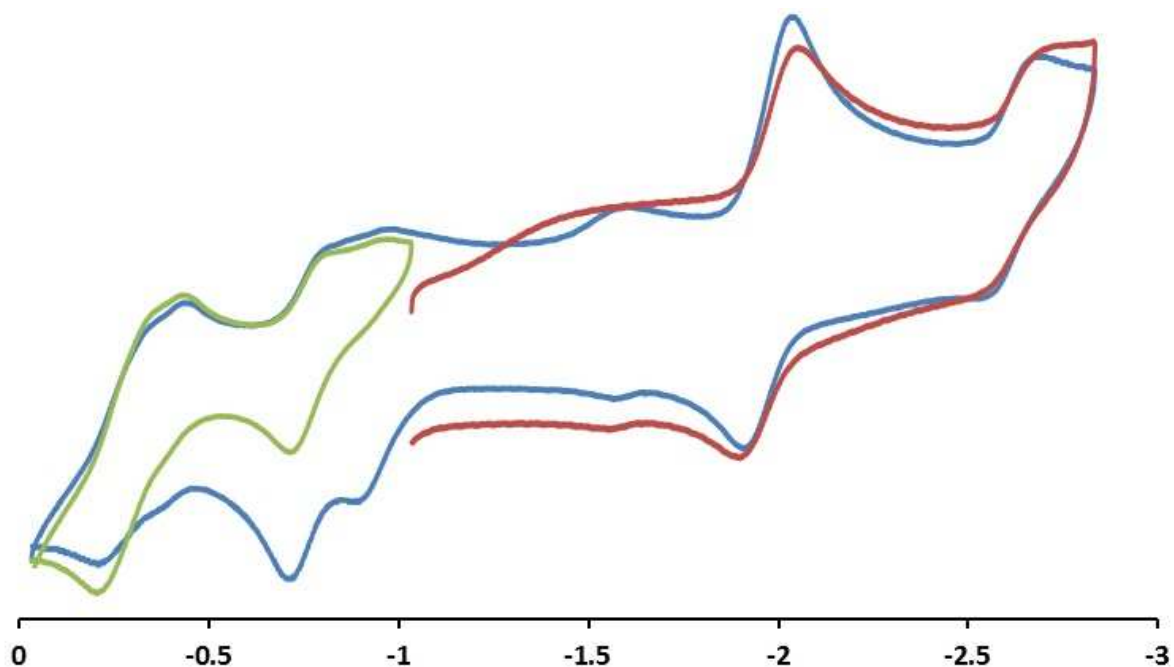


Figure S13. Cyclic voltammogram of $[\text{Fe}(\text{MesNP}^i\text{Pr}_2)_3\text{FeCl}]$ (**6**) (2 mM in 0.4 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ in THF, scan rate = 100 mV/s).

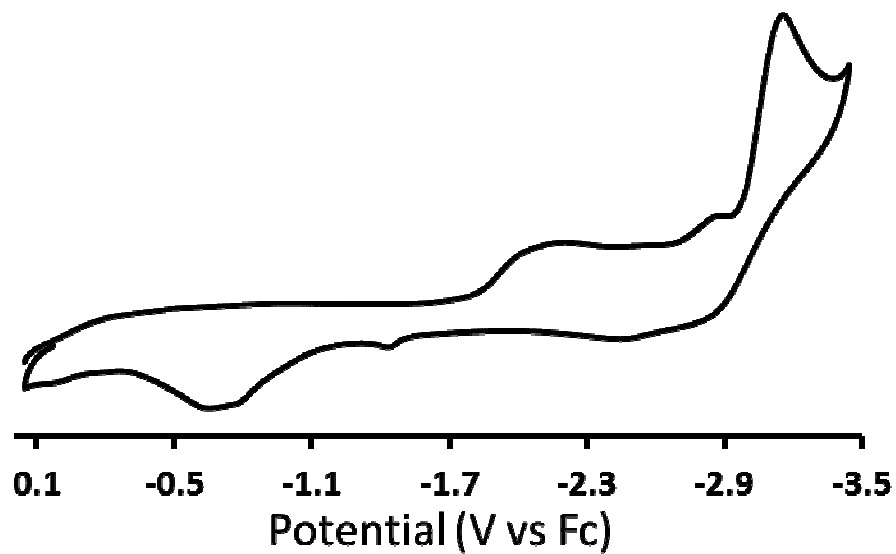


Figure S14. Cyclic voltammogram of $(\text{THF})_3\text{LiCl}[\text{Mn}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{MnCl}]$ (**8**) (2 mM in 0.4 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ in THF, scan rate = 100 mV/s).

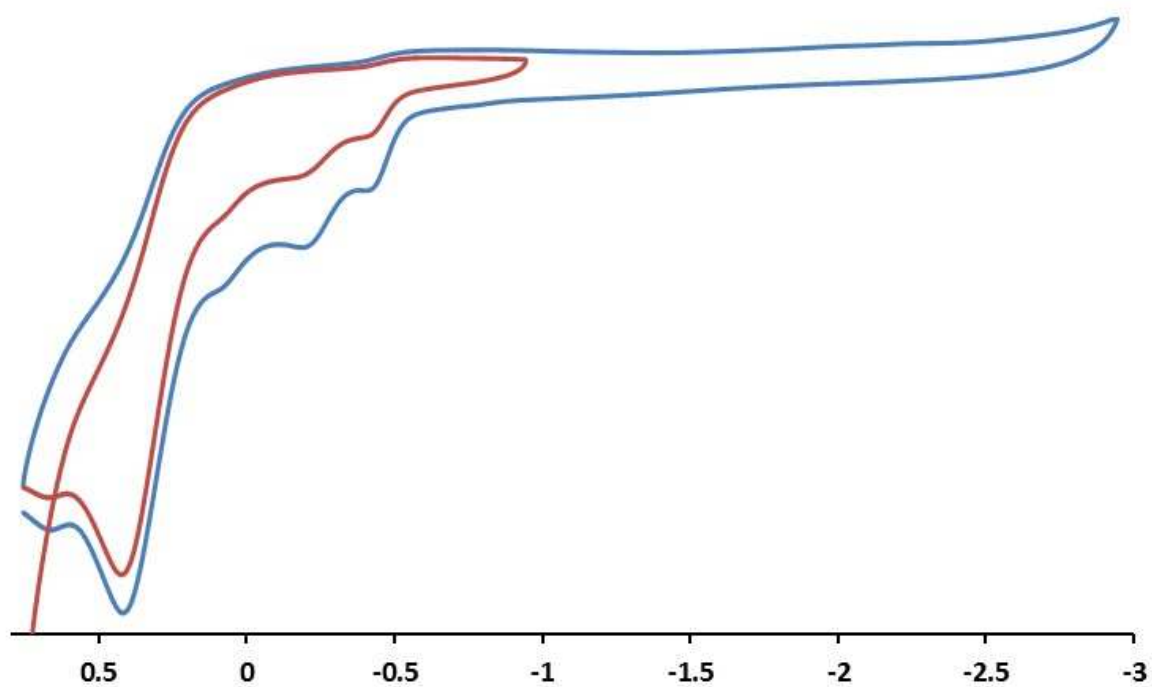


Figure S15. Plot of magnetization as a function of field collected for **3**.

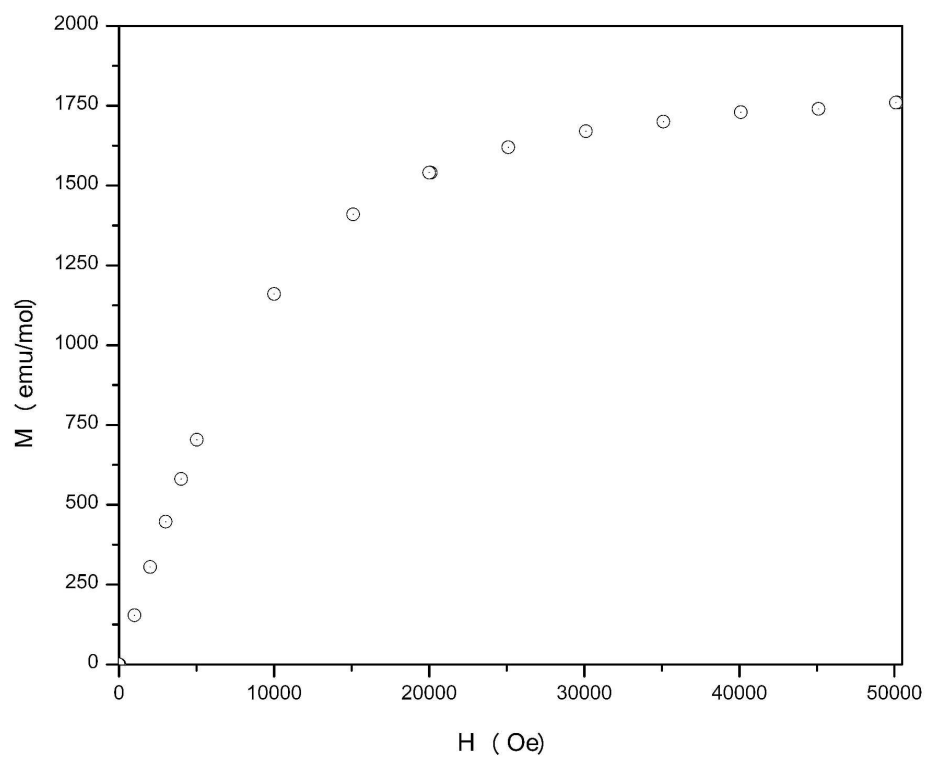


Figure S16. Plot of magnetization as a function of field collected for **5**.

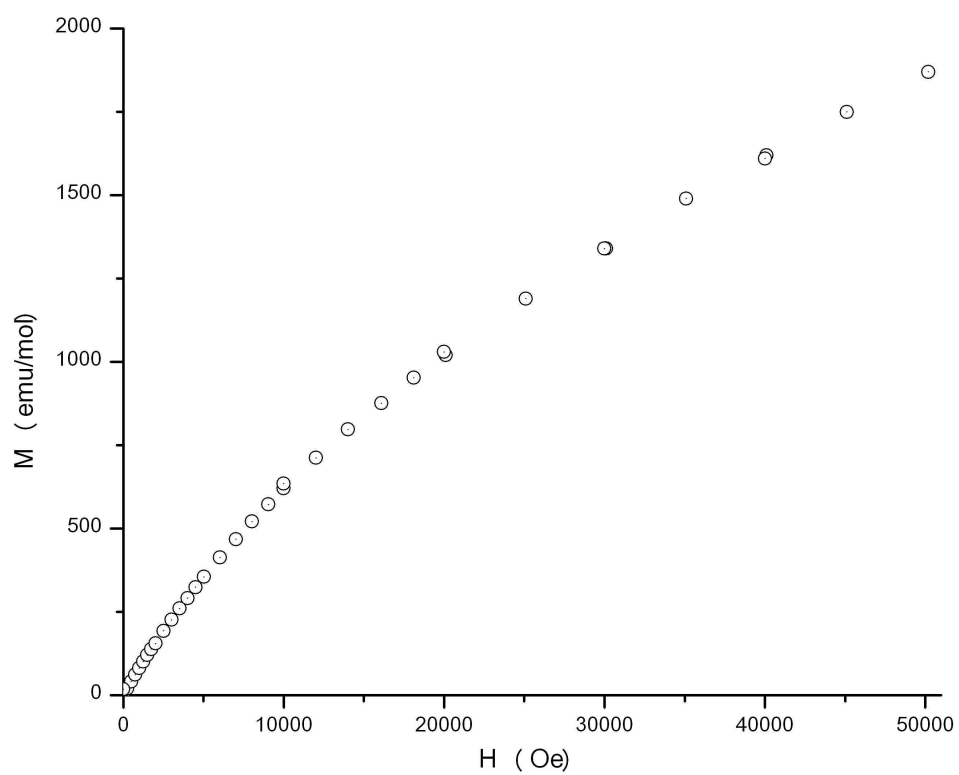


Figure S17. Uncorrected plot of magnetic susceptibility as a function of temperature for **5**.

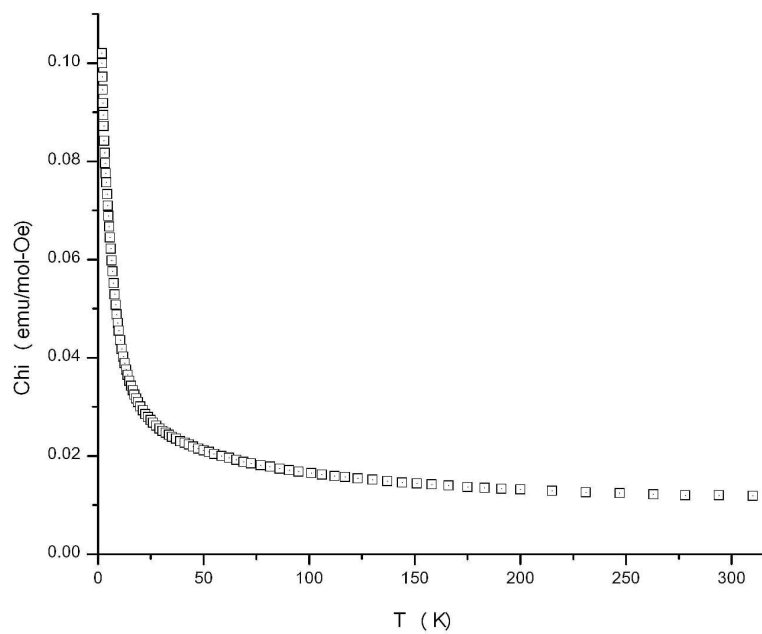


Figure S18. Plot of magnetization as a function of field collected for **8**.

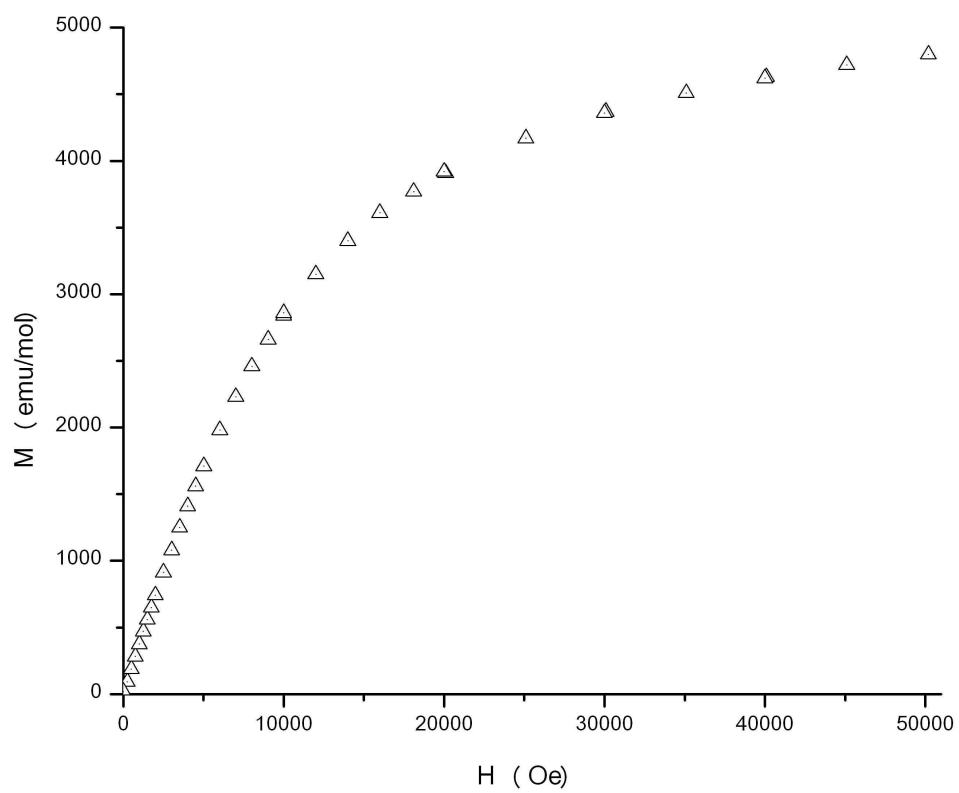


Figure S19. Uncorrected plot of magnetic susceptibility as a function of temperature for **8**.

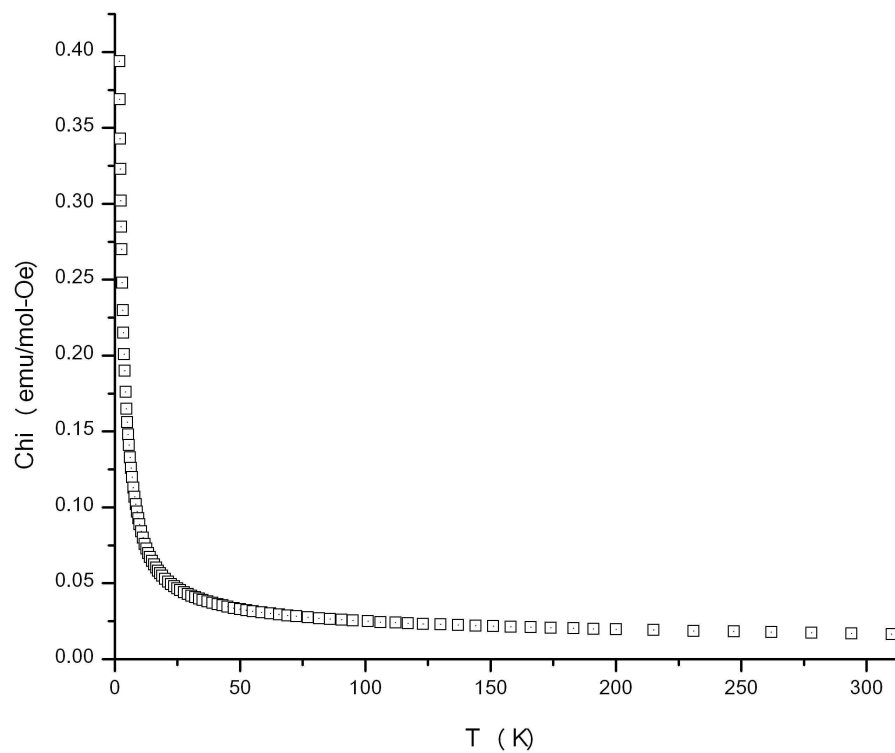
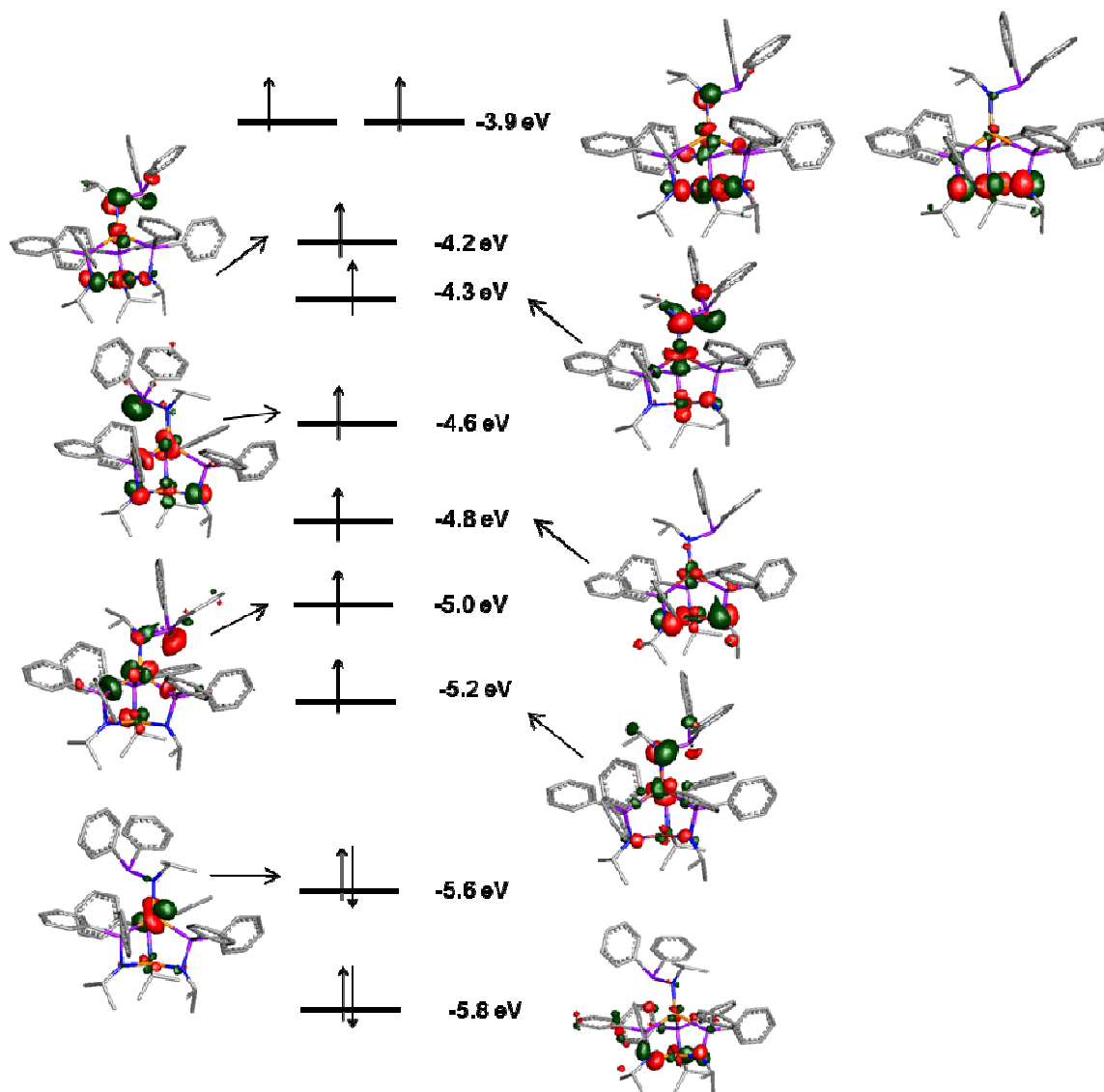


Figure S20. Calculated frontier molecular orbital energies and representations of **4** derived from DFT calculations using Gaussian 09 (BP86/LANL2TZ(f)/6-311+G(d)/D95V).



Discussion of alternative fits for Mössbauer spectra of **6** and **7**

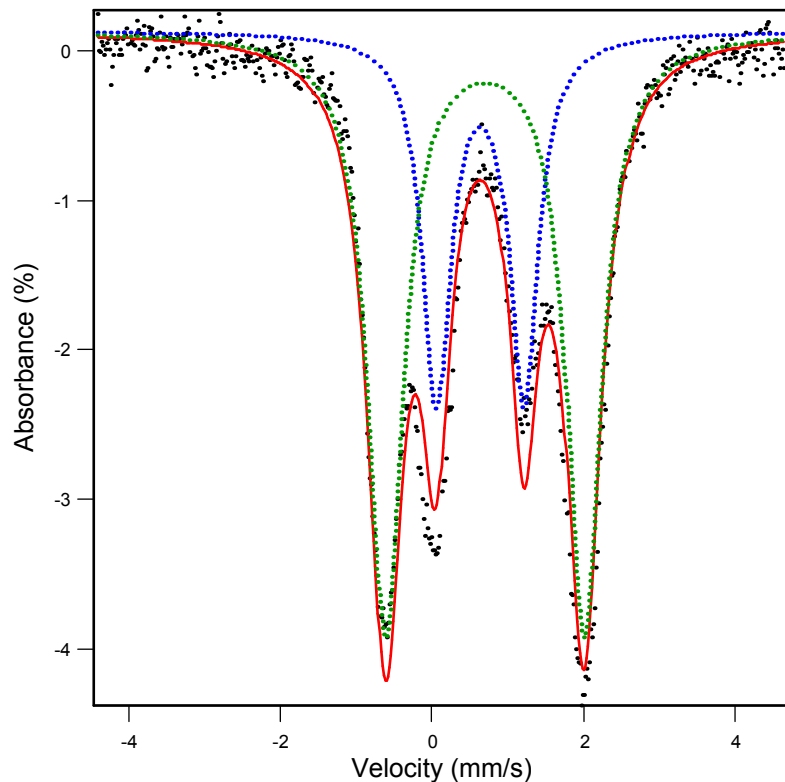
For both compounds **6** and **7**, two alternative fits of the zero-field ^{57}Fe Mössbauer can be considered. For example, compound **6** contains two iron centers in disparate coordination environments. The first simulation fits the Mössbauer spectrum with two quadrupole doublets with essentially the same quadrupole splitting, suggesting that the two iron centers are electronically equivalent. This fitting is most consistent with a zwitterionic description of the diiron core. In this case, both iron centers would be in the 2+ oxidation state. Fe1 is bound to three amides and would therefore bear an overall negative charge. Fe2, bound to two neutral phosphines, two amides and one chloride, would bear an overall positive charge to complete the zwitterionic pair.

The alternate simulation of **6** fits the Mössbauer spectrum with two quadrupole doublets with very different quadrupole splittings ($\delta = 0.27$ and 0.99 mm/s) more consistent with a mixed valent diiron compound (Fe(III) and Fe(I) respectively).

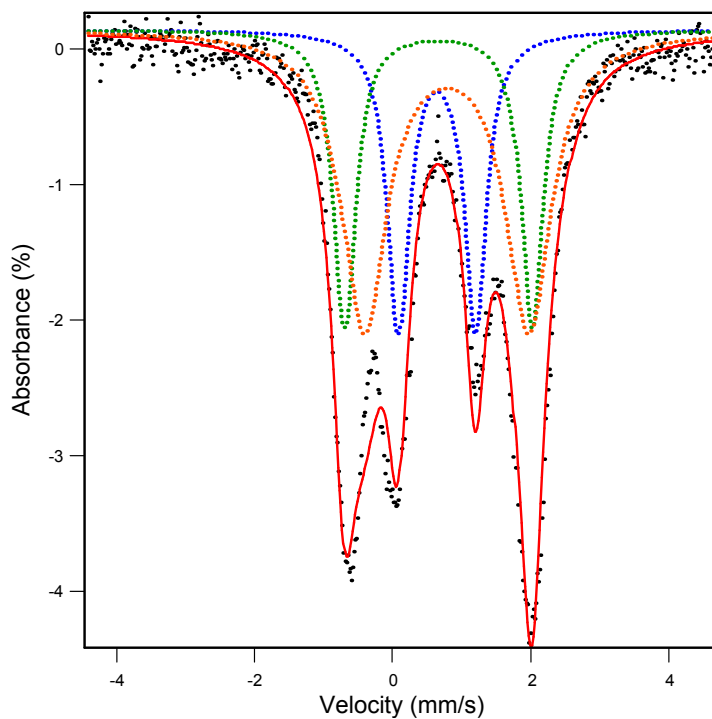
In both **6** and **7**, we favor the Mössbauer simulation that is consistent with the zwitterionic pair. Single crystal x-ray crystallography shows that the Fe-amide bond distances are consistent with previously reported compounds that feature Fe(II)-amide distances. Both the Mössbauer spectrum and the x-ray diffraction data were collected at similar temperatures (~ 100 K) and it is therefore appropriate to correlate these data.

Compound **6**

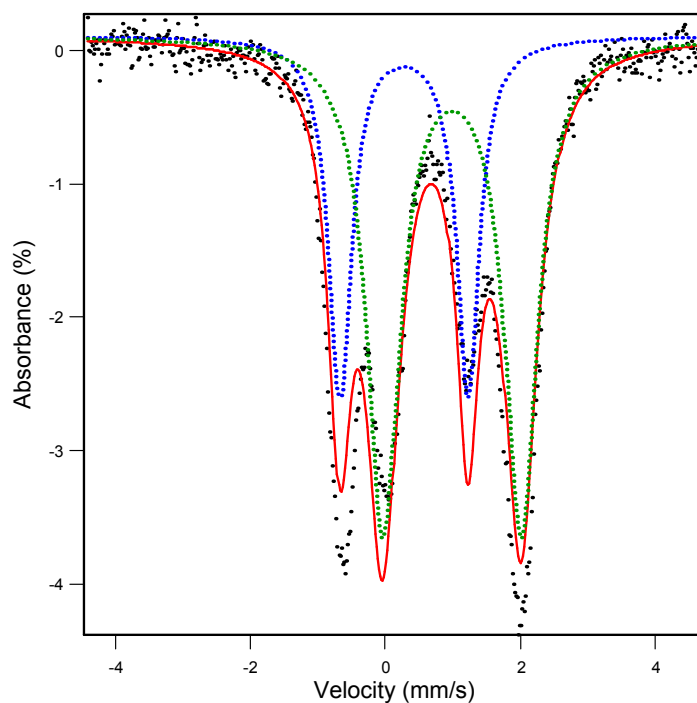
Zero-field Mössbauer spectrum of compound **6** obtained at 110 K. Simulation (without impurity) yields the following parameters: δ , $|AE_Q|$ (mm/s) component 1 (blue, 38%) 0.63 , 1.16 ($\gamma = 0.23$ mm/s); component 2 (green, 62%) 0.69 , 2.04 ($\gamma = 0.28$ mm/s).



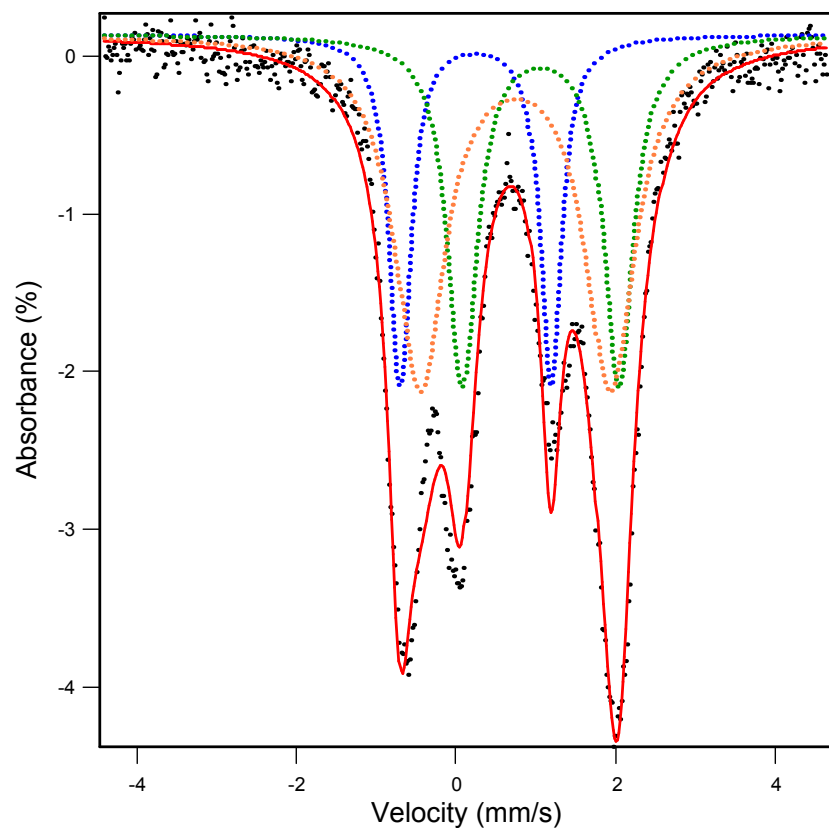
Simulation (with impurity) yields the following parameters: δ , $|AE_Q|$ (mm/s) component 1 (blue, 33%) 0.64, 1.12 ($\gamma = 0.19 \text{ mm/s}$); component 2 (green, 33%) 0.66, 2.72 ($\gamma = 0.19 \text{ mm/s}$); component 3 (orange – impurity) 0.78, 2.38 ($\gamma = 0.30 \text{ mm/s}$).



An alternate simulation (without impurity) yields the following parameters: δ , $|AE_Q|$ (mm/s) component 1 (blue, 42%) 0.27, 1.90 ($\gamma = 0.20 \text{ mm/s}$); component 2 (green, 58%) 0.99, 2.04 ($\gamma = 0.30 \text{ mm/s}$).

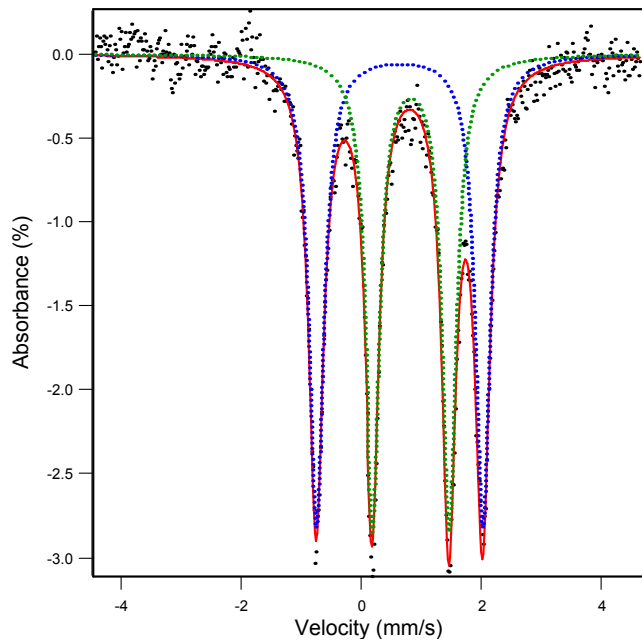


Simulation (with impurity) yields the following parameters: δ , $|AE_Q|$ (mm/s) component 1 (blue, 33%) 0.24, 1.89 ($\gamma = 0.16 \text{ mm/s}$); component 2 (green, 33%) 1.05, 1.96 ($\gamma = 0.22 \text{ mm/s}$); component 3 (orange – impurity) 0.74, 2.39 ($\gamma = 0.38 \text{ mm/s}$).



Compound 7

Zero-field Mössbauer spectrum of compound **7** obtained at 110 K. Simulation yields the following parameters: δ , $|AE_Q|$ (mm/s) component 1 (blue, 50%) 0.64, 2.77 ($\gamma = 0.15$ mm/s); component 2 (green, 50%) 0.83, 1.27 ($\gamma = 0.14$ mm/s).



An alternative simulation yields the following parameters: δ , $|AE_Q|$ (mm/s) component 1 (blue, 50%) 0.36, 2.22 ($\gamma = 0.14$ mm/s); component 2 (green, 50%) 1.11, 1.83 ($\gamma = 0.15$ mm/s).

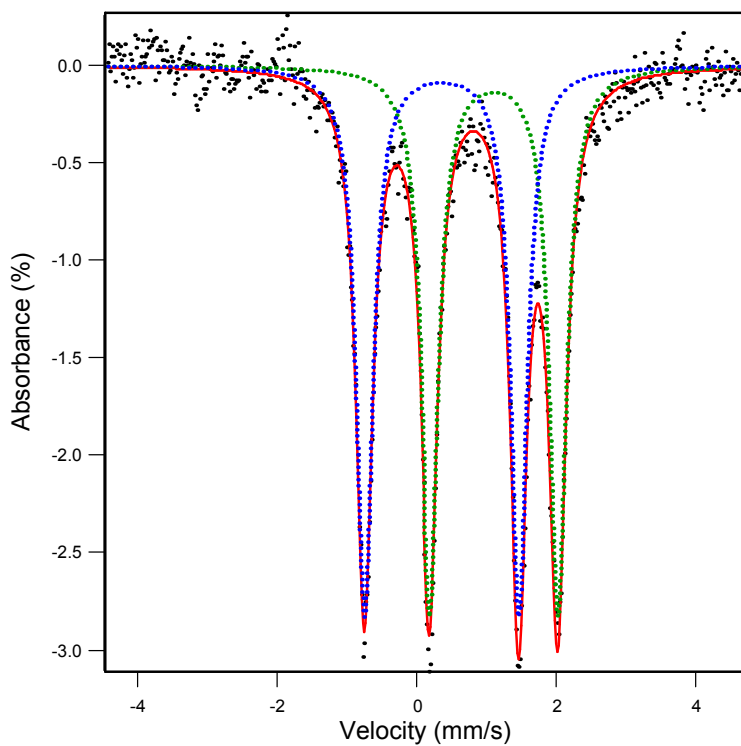
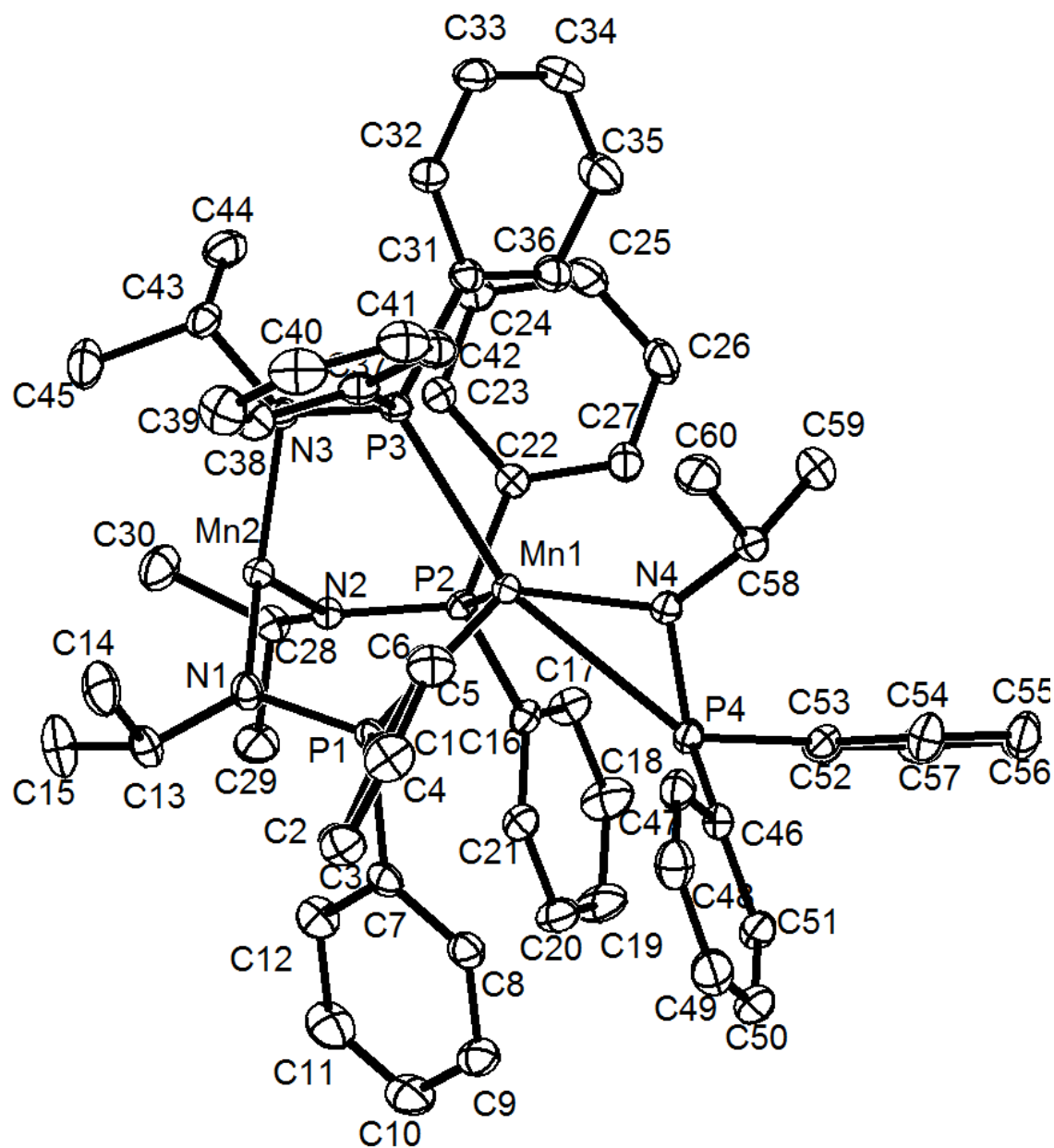


Figure S21. Molecular structure of $\text{Mn}(\text{iPrNPPh}_2)_3\text{Mn}(\text{iPrNPPh}_2)$ (**3**). A lattice ether molecule and all hydrogen atoms have been omitted for clarity.



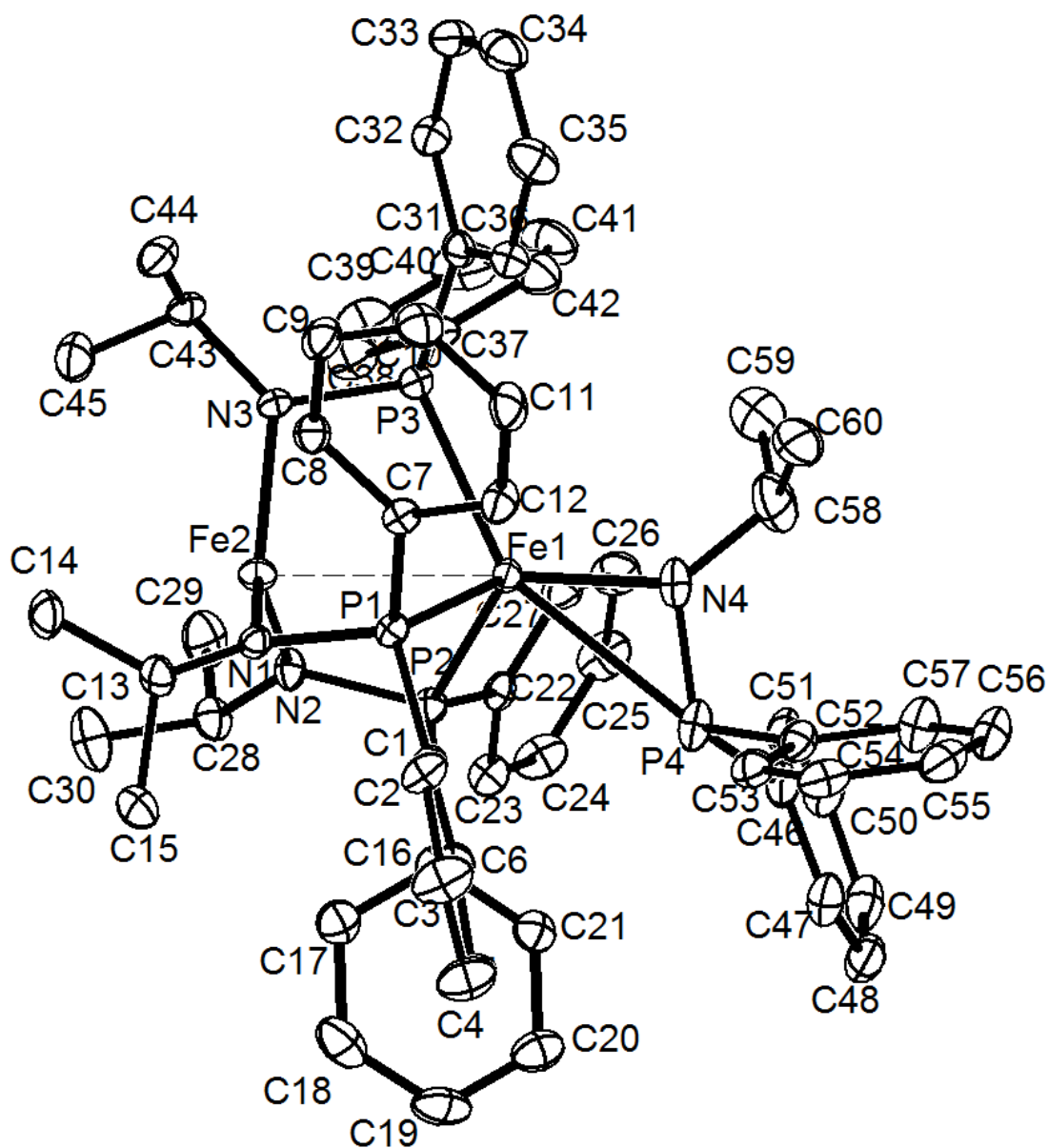
X-ray data collection, solution, and refinement for $\text{Mn}(\text{}^i\text{PrNPPPh}_2)_3\text{Mn}(\text{}^i\text{PrNPPPh}_2)$

(3). All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.⁴ Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 5 sec and a detector distance of 75 mm. The optimized strategy used for data collection consisted of four phi and three omega scan sets, with 0.5° steps in phi or omega; completeness was 99.9%. A total of 2857 frames were collected. Final cell constants were obtained from the xyz centroids of 9734 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 *SuperFlip*,⁵ and the remaining atoms were located on electron density difference maps. The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁶ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. Except as described below, after location of H atoms on electron-density difference maps, the H atoms attached to ordered atoms were initially refined with soft restraints on the bond lengths and angles to regularise 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.⁷ A disordered ether solvate molecule resides near a center of symmetry; C atoms were refined by using anisotropic displacement parameters with fixed occupancies of 0.5. The O atom, very near a center of symmetry at (0, $\frac{1}{2}$, 0) was

refined by using an isotropic displacement parameter. Most H atoms were treated as described above, but those attached to C(61) were placed at geometric positions and refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0349$ ($I > 2\sigma(I)$, 14249 data) and $wR_2 = 0.0829$ (F^2 , 17214 data, 662 parameters). The final CIF is available as supporting material.

Figure S22. Molecular structure of $\text{Fe}(^i\text{PrNPPH}_2)_3\text{Fe}(^i\text{PrNPPH}_2)$ (**4**). All hydrogen atoms have been omitted for clarity.

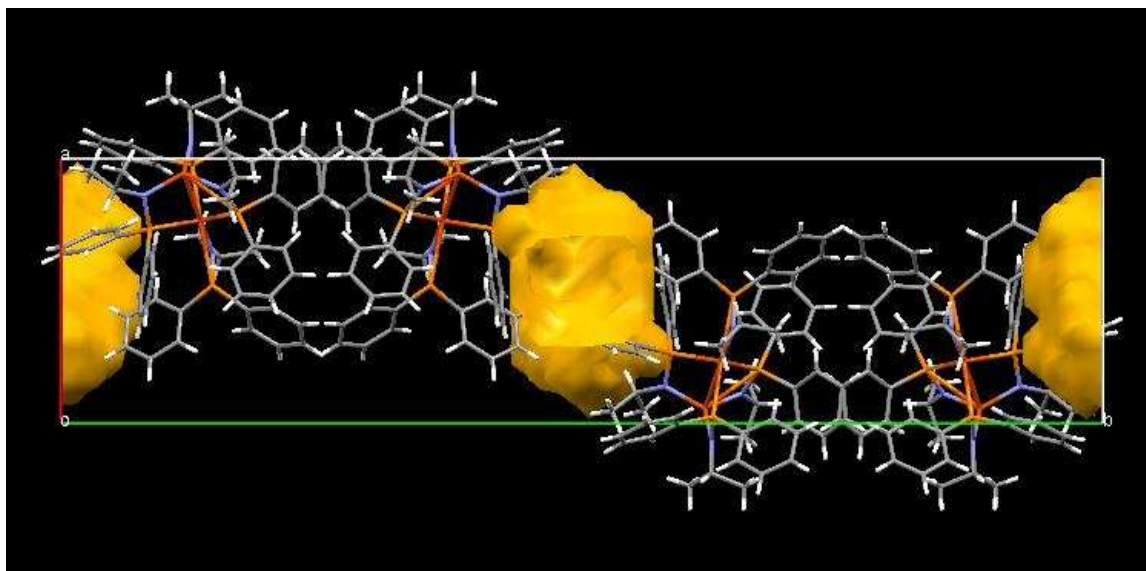


X-Ray data collection, solution, and refinement for $\text{Fe}(\text{}^i\text{PrNPPPh}_2)_3\text{Fe}(\text{}^i\text{PrNPPPh}_2)$ (4).

All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.⁴ Preliminary cell constants were obtained from three sets of 12 frames. Data collection carried out at 120K, using a frame time of 40 sec and a detector distance of 65 mm. The optimized strategy used for data collection consisted of two phi and three omega scan sets, with 0.5° steps in phi or omega; completeness was 99.5%. A total of 1648 frames were collected. Final cell constants were obtained from the xyz centroids of 6331 reflections after integration.

From the systematic absences and 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 *SuperFlip* and subsequent electron-density difference syntheses.⁵ Refinement (full-matrix-least squares) was carried out using the Oxford University *Crystals for Windows* program.⁶ 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 regularise 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.⁷ During the structure solution, electron density difference maps revealed that there were considerable disordered solvent molecules. From history, the solvate was likely Et_2O in a volume of 470.6 Å^3 per unit cell (8.1%); the peaks could not be modeled successfully. It appeared that the cavity areas

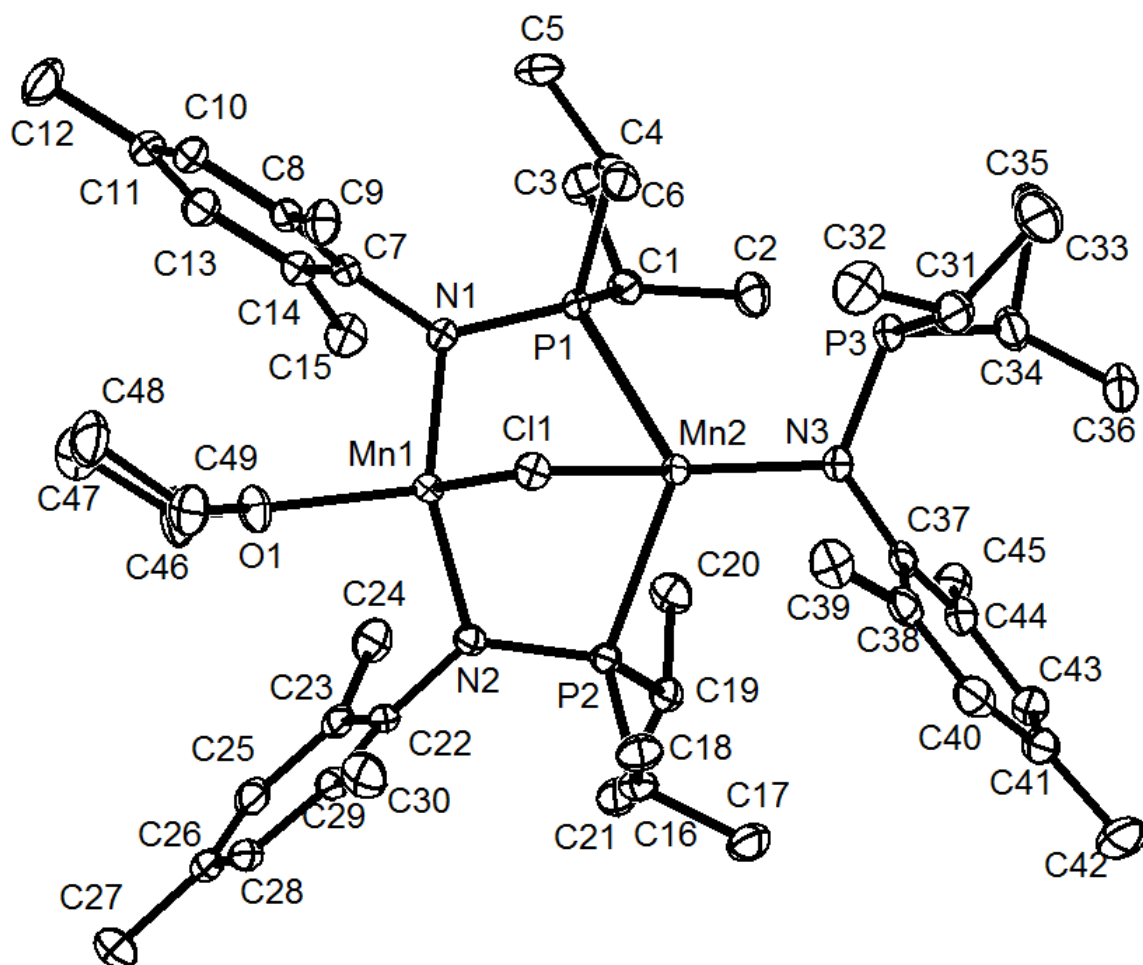
contained about two diethyl ether molecules, located near the centers of symmetry



at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$ as shown in the *ab* projection above.⁸ 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^{9,10} technique, in order to produce a “solvate-free” structure factor set. PLATON reported a total electron density of 97 e⁻ per unit cell, likely representing 2-3 diethyl ether molecules, consistent with our earlier observations. Use of the SQUEEZE technique resulted in a decrease of ca 2.1 % in *R*. The final least-squares refinement converged to $R_1 = 0.0476$ ($I > 2\sigma(I)$, 8253 data) and $wR_2 = 0.0959$ (F^2 , 12677 data, 631 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced an alert G item, related to the void volume described above. Accordingly, the CIF file contains a section (`_platon_squeeze_details`) which explains the issue in detail.

Figure S23. Molecular structure of $[(\text{THF})\text{Mn}(\mu\text{-Cl})(\text{MesNP}^i\text{Pr}_2)_3\text{Mn}(\text{MesNP}^i\text{Pr}_2)]$ (**5**).

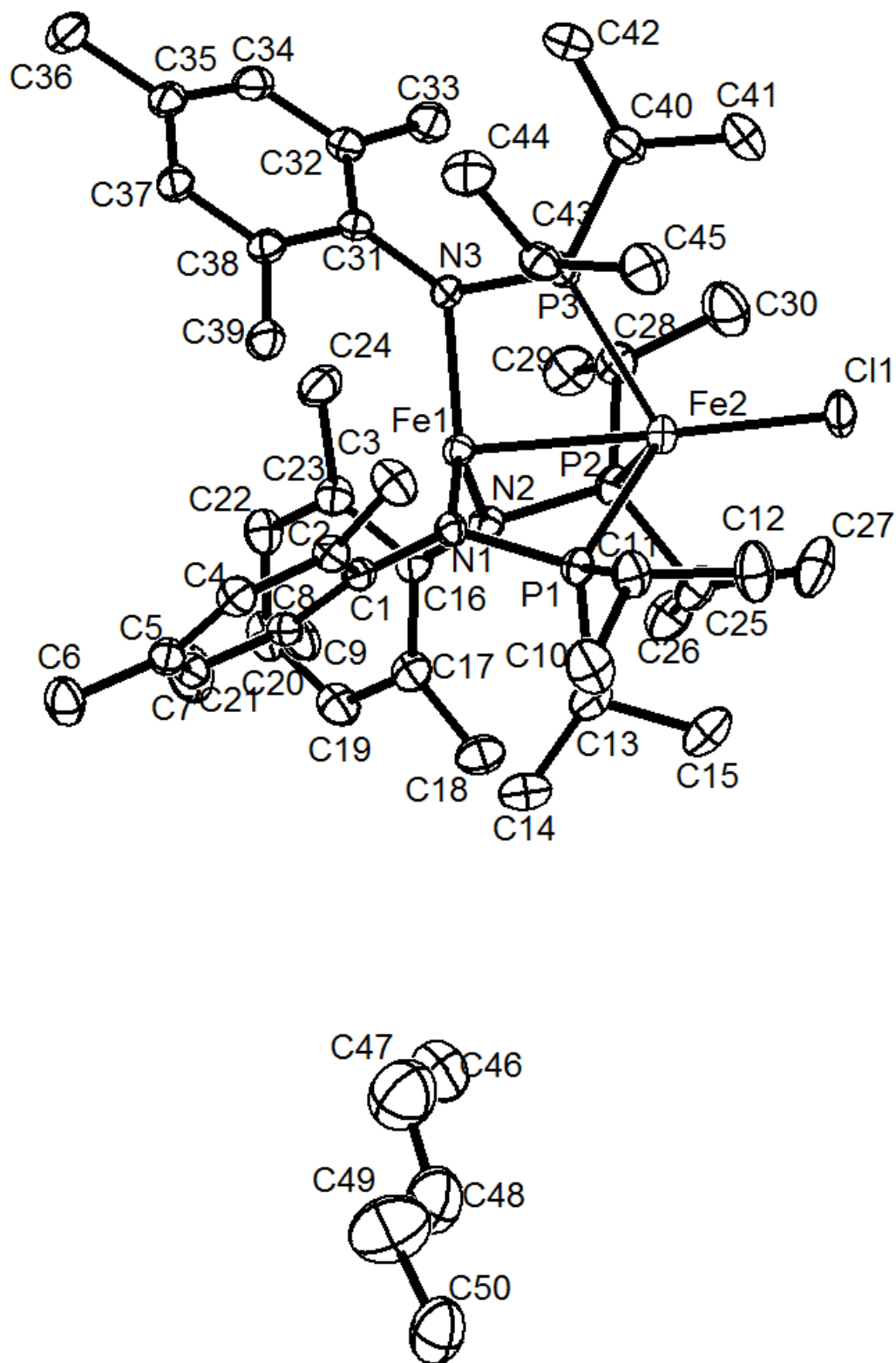
All hydrogen atoms have been omitted for clarity.



X-Ray data collection, solution, and refinement for [(THF)Mn(μ -Cl)(MesNPⁱPr₂)₃Mn(MesNPⁱPr₂)] (5). All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.⁴ 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 three phi scan sets, with 0.5° steps in phi; completeness was 99.1%. A total of 1915 frames were collected. Final cell constants were obtained from the xyz centroids of 9909 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*,⁵ and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁶ 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.⁷ The final least-squares refinement converged to $R_1 = 0.0336$ ($I > 2\sigma(I)$, 9411 data) and $wR_2 = 0.0836$ (F^2 , 12814 data, 532 parameters). The final CIF is available as supporting material.

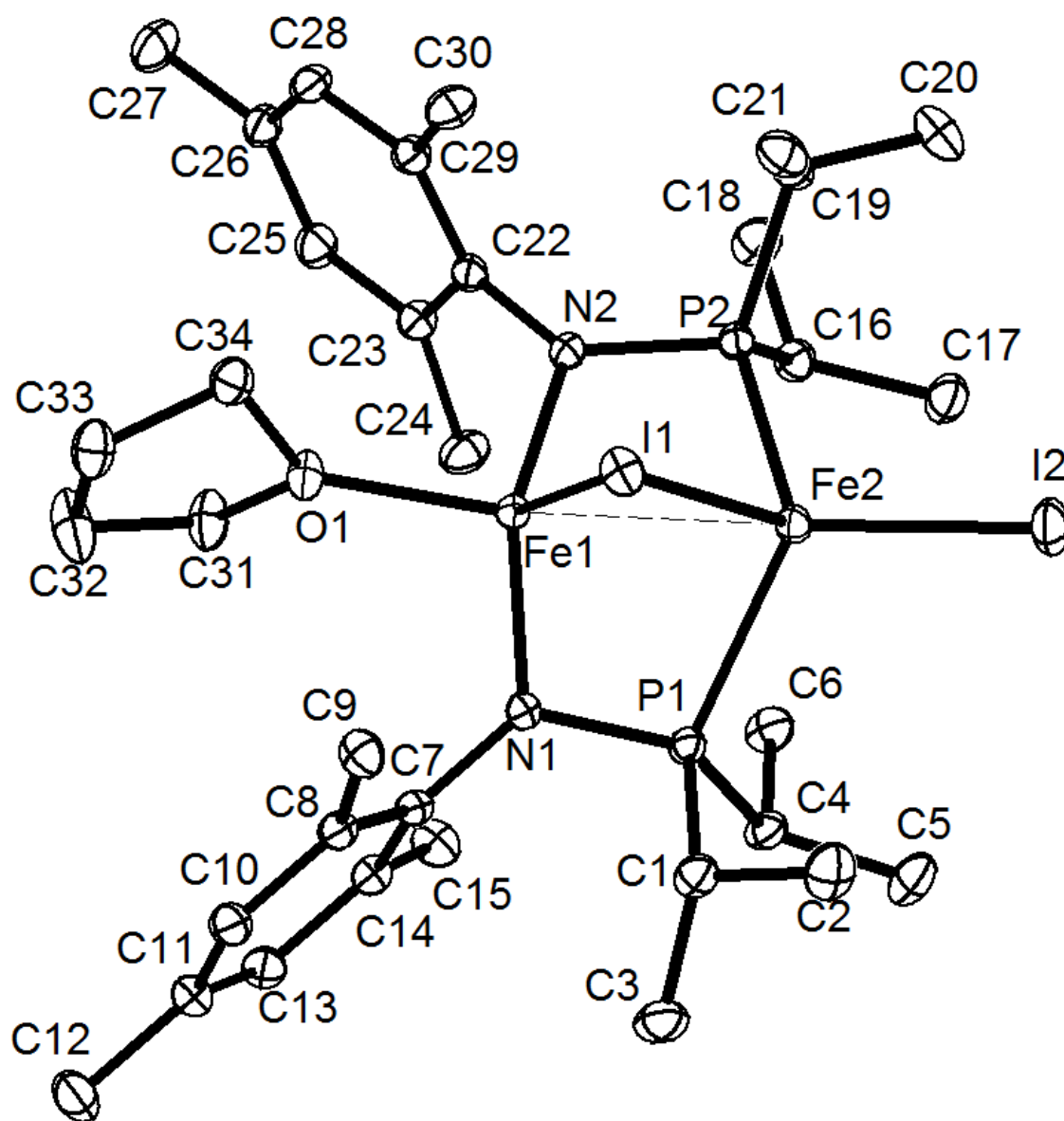
Figure S24. Molecular structure of $[\text{Fe}(\text{MesNP}^i\text{Pr}_2)_3\text{FeCl}]$ (**6**). A lattice pentane molecule and all hydrogen atoms have been omitted for clarity.



X-Ray data collection, solution, and refinement for [Fe(MesNPⁱPr₂)₃FeCl] (6). All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.⁴ 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 six phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 99.4 %. A total of 3623 frames were collected. Final cell constants were obtained from the xyz centroids of 9944 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuperFlip*,⁵ and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁶ 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.⁷ The final least-squares refinement converged to $R_1 = 0.0410$ ($I > 2\sigma(I)$, 11542 data) and $wR_2 = 0.1198$ (F^2 , 15469 data, 532 parameters). The final CIF is available as supporting material.

Figure S25. Molecular structure of $[(\text{THF})\text{Fe}(\mu\text{-I})(\text{MesNP}^i\text{Pr}_2)_2\text{FeI}]$ (**7**). All hydrogen atoms have been omitted for clarity.

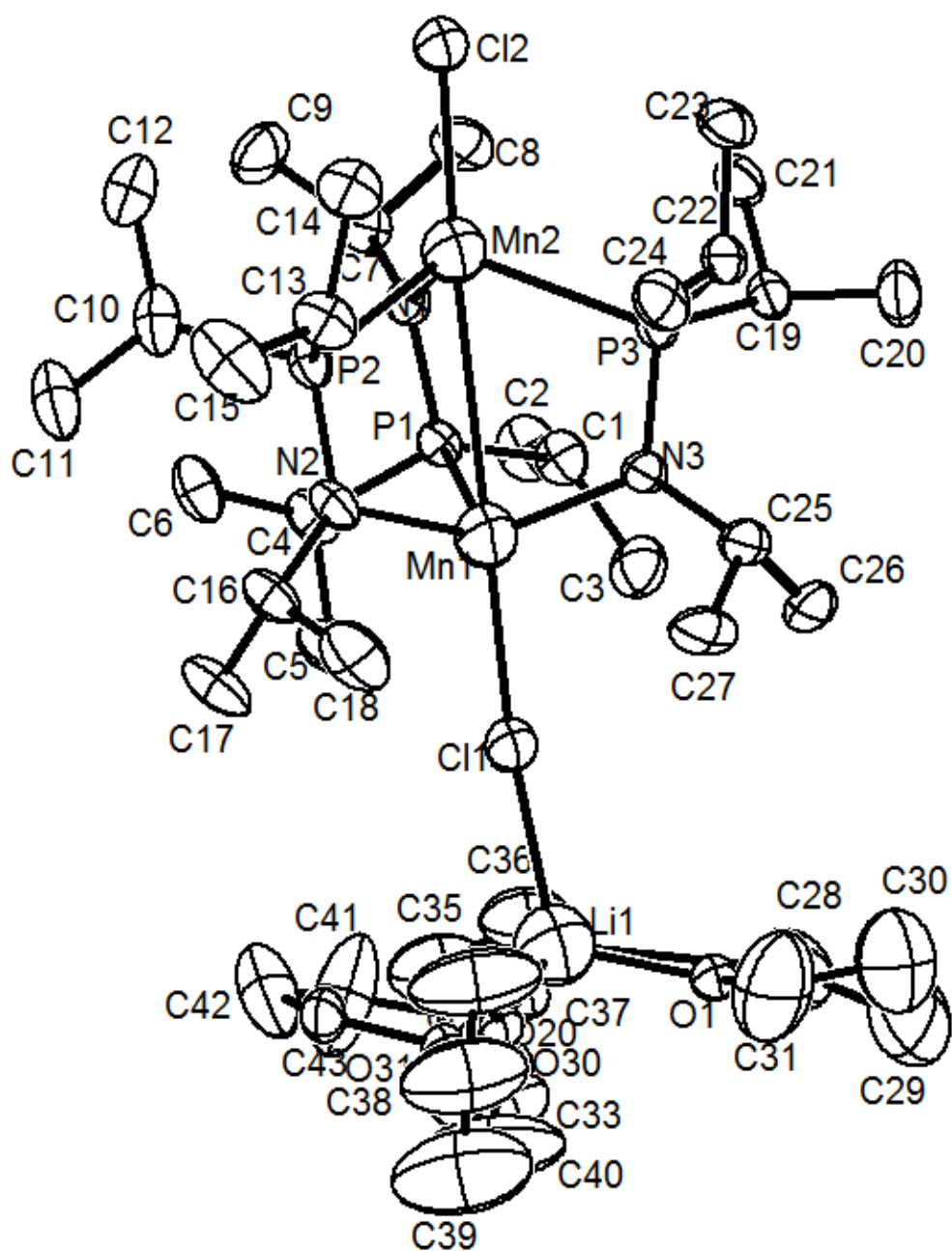


X-Ray data collection, solution, and refinement for [(THF)Fe(μ -I)(MesNP^{*i*}Pr₂)₂FeI]

(7). All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.⁴ 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 six phi and three omega scan sets, with 0.5° steps in phi or omega; completeness was 98.8%. A total of 4166 frames were collected. Final cell constants were obtained from the xyz centroids of 9768 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuperFlip*,⁵ and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁶ 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.⁷ The final least-squares refinement converged to $R_1 = 0.0195$ ($I > 2\sigma(I)$, 9938 data) and $wR_2 = 0.0465$ (F^2 , 11290 data, 388 parameters). The final CIF is available as supporting material.

Figure S26. Molecular structure of $(\text{THF})_3\text{LiCl}[\text{Mn}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{MnCl}]$ (**8**). Cationic part of $(\text{THF})_3\text{Li}$, and all hydrogen atoms have been omitted for clarity.

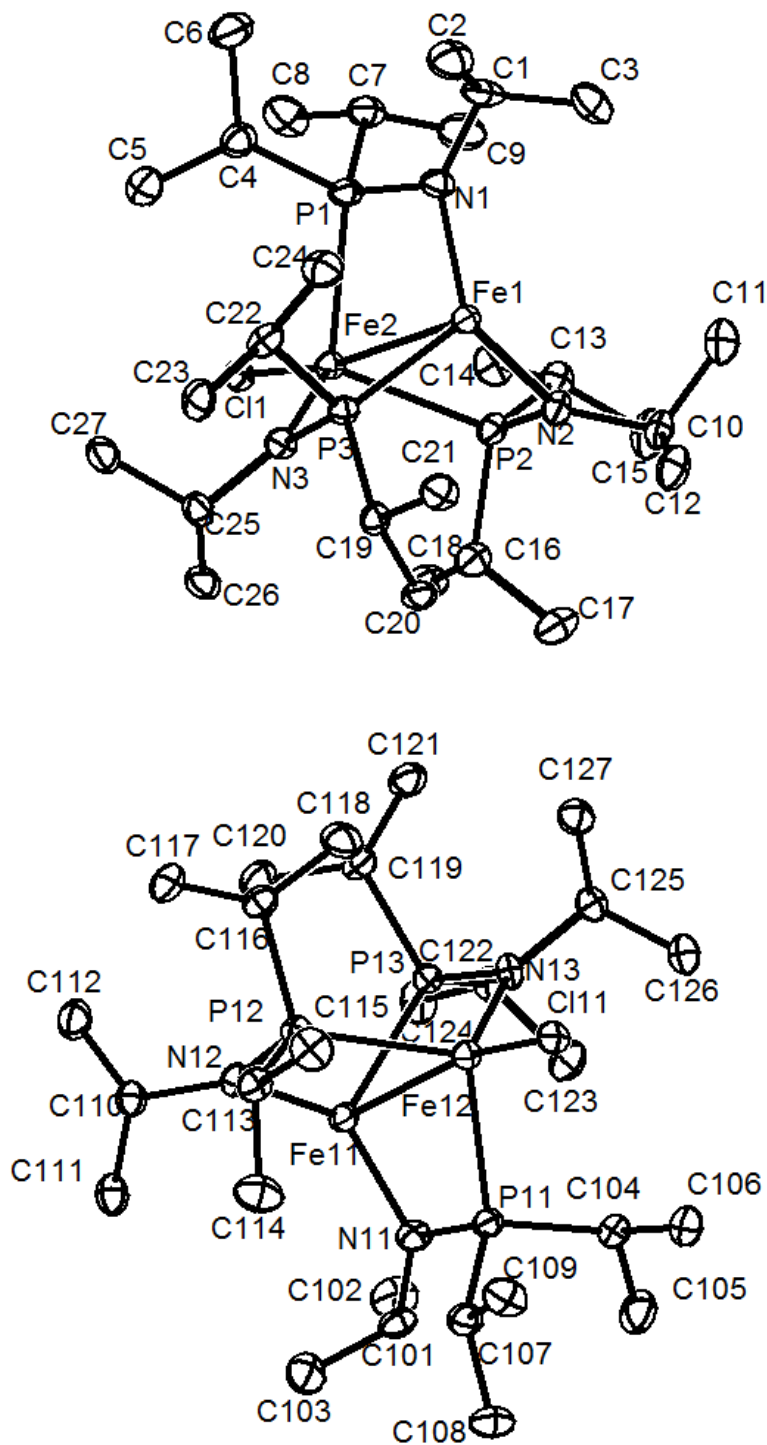


X-Ray data collection, solution, and refinement for (THF)₃LiCl[Mn(NⁱPrPⁱPr₂)₂(PⁱPr₂NⁱPr)MnCl] (8). All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.^{1.a.i.4} Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, 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 three omega scan sets, with 0.5° steps in phi or omega; completeness was 98.2%. A total of 2757 frames were collected. Final cell constants were obtained from the xyz centroids of 8213 reflections after integration.

From the lack of systematic absences, and the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*.^{1.a.i.5} The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.^{1.a.i.6} All non-hydrogen atoms were refined using anisotropic displacement parameters. The asymmetric unit contains one molecule of complex, and a mixture of THF and ether molecules weakly bound to a lithium ion. There was considerable disorder in the THF and ether molecules, and thermal similarity restraints were used to help model the three (partial) THF molecules. One of the THF moieties (O(1)/C(28)/C(29)/C(30)/C(31)) was refined as a fully-occupied species. The other two THF molecules occupied positions that were shared (in different ratios) with ether molecules. The first shared pair involved THF atoms O(20)/C(35)/C(36), common atoms

C(33)/C(34) (occupancy 1.0), and ether atoms O(21)/C(41), with methyl ether atom C(42) common to the two partial ether molecules(!). The second shared pair involved THF atoms O(30)/C(37)/C(38), common atoms C(39)/C(40) (occupancy 1.0), and ether atoms O(31)/C(43) with methyl ether atom C(42), as stated above, common to the two partial ether molecules. In each case the sum of the ether and THF occupancies were constrained to sum to 1.0. The refined occupancies of the first and second THF:ether pairs were: 0.516(7):0.484(7) and 0.691(7):0.309(7), respectively. The occupancy of common methyl ether atom C(42) was effectively constrained (using a tight restraint, 0.0003) to the sum of the occupancies of the two ether molecule occupancies, $0.48424 + 0.30923 = 0.79346$. Thus, the final composition of the solvate molecules bound to lithium is $\text{Li}(\text{C}_4\text{H}_8\text{O})_{2.207}(\text{C}_4\text{H}_{10}\text{O})_{0.793}$. The fourth coordination position around Li is filled by atom Cl(1). After location of most ordered H atoms on electron-density difference maps, the H atoms attached to ordered C atoms were initially refined with soft restraints on the bond lengths and angles to regularise 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.^{1.a.i.7} The remaining H atoms on disordered THF or ether carbon atoms were placed at geometric positions and refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0550$ ($I > 2\sigma(I)$, 9279 data) and $wR_2 = 0.1444$ (F^2 , 13083 data, 526 parameters). The final CIF is available as supporting material. The CheckCIF routine returned four Alert B messages, related to the disorder described above; accordingly, the CIF and CheckCIF results now contain validation response form (_vrf) items which explain the Alert B items.

Figure S27. Molecular structure of $[\text{Fe}(\text{N}^i\text{PrP}^i\text{Pr}_2)_2(\text{P}^i\text{Pr}_2\text{N}^i\text{Pr})\text{FeCl}]$ (**9**). All hydrogen atoms have been omitted for clarity.

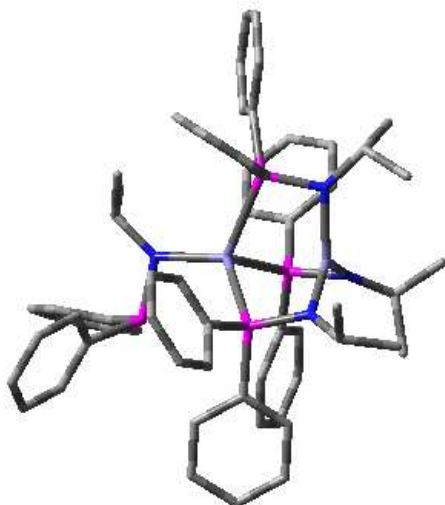


X-Ray data collection, solution, and refinement for [Fe(NⁱPrPⁱPr₂)₂(PⁱPr₂NⁱPr)FeCl] (9). All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.⁴ 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 three phi and five omega scan sets, with 0.5° steps in phi or omega; completeness was 98.6%. A total of 2554 frames were collected. Final cell constants were obtained from the xyz centroids of 7470 reflections after integration. From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*,⁵ and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁶ 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.⁷ The final least-squares refinement converged to $R_1 = 0.0472$ ($I > 2\sigma(I)$, 9411 data) and $wR_2 = 0.1191$ (F^2 , 13823 data, 649 parameters). The final CIF is available as supporting material.

Gaussian 09 Full 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.

XYZ coordinates of DFT optimized structure of **4**



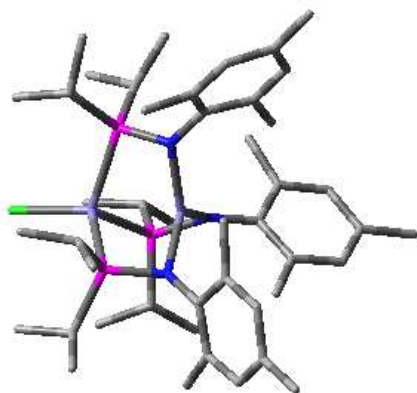
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12	C	-2.12554	-3.8623	2.13041
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15	C	-3.89563	-1.77644	2.836405
16	C	-2.68922	-1.48225	2.160023
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22	C	-0.55428	-4.16736	-0.81581
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24	C	2.429319	-2.84946	4.064665

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27	C	-1.77324	1.648425	3.589336
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XYZ coordinates of DFT optimized structure of **6**



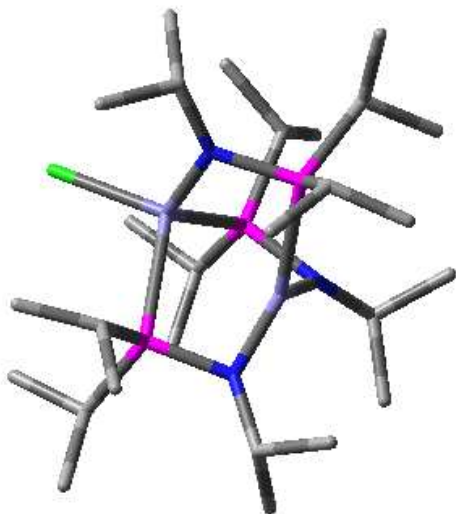
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78	H	2.65654	3.69072	0.255063
79	H	2.966442	4.510156	-1.301
80	H	5.629748	-1.44224	2.868521
81	H	2.024278	-3.20787	4.487133
82	H	-0.00064	-3.13314	3.366562
83	H	-0.05777	-2.816	1.601435
84	H	-0.23857	-1.48361	2.743948
85	H	4.182343	-2.85026	5.938065
86	H	4.945625	-4.0613	4.878055
87	H	5.709452	-2.46338	5.091306
88	H	5.262761	0.384621	1.254687
89	H	5.282722	-0.88557	0.009493
90	H	3.930788	0.280118	0.066658
91	H	-0.11129	-3.225	-0.77984
92	H	-0.03363	-4.85977	-2.61353
93	H	1.611497	-4.36601	-3.08623
94	H	0.241684	-3.23901	-3.32836
95	H	0.879137	-5.35897	-0.15273
96	H	1.82096	-4.09781	0.696488
97	H	2.492237	-4.89729	-0.75228
98	H	3.767788	-0.81405	-1.75437
99	H	4.263189	-1.662	-4.01399
100	H	2.871507	-2.7773	-3.97293
101	H	2.587282	-1.02127	-3.99143
102	H	5.309184	-2.71416	-1.87668
103	H	3.979792	-3.89359	-1.96776
104	H	4.284192	-3.01505	-0.4382
105	H	-4.1716	0.229096	4.180005
106	H	-4.26063	-3.91202	2.922214
107	H	-2.36113	-4.61637	1.510547
108	H	-3.37984	-4.13329	0.134237
109	H	-1.71205	-3.50861	0.265513

110	H	-5.36598	-3.28742	5.016105
111	H	-6.3699	-1.87817	4.582202
112	H	-5.03485	-1.68848	5.746031
113	H	-3.0351	1.860106	2.987404
114	H	-1.4284	1.215478	2.576033
115	H	-2.56232	1.588327	1.277531
116	H	-2.41607	-2.9966	-1.68005
117	H	-4.81739	-3.41571	-1.89923
118	H	-4.66239	-2.2318	-0.56332
119	H	-5.17726	-1.69791	-2.19222
120	H	-3.28985	-3.22134	-3.97815
121	H	-3.53714	-1.46058	-4.12292
122	H	-1.88466	-2.10564	-3.9895
123	H	-2.67391	1.629318	-1.11102
124	H	-3.97412	2.211341	-3.11463
125	H	-4.32379	0.502387	-3.47653
126	H	-2.65124	1.118562	-3.63513
127	H	-5.05439	1.87036	-0.69054
128	H	-5.41831	0.204838	-1.20695
129	H	-4.51676	0.487622	0.30809

XYZ coordinates of DFT optimized structure of **9**



Tag	Symbol	X	Y	Z
1	Fe	0.050013	-0.19241	1.190896
2	Fe	-0.03893	-0.00488	-1.29396
3	Cl	-0.15237	-0.71321	-3.47581
4	P	1.812929	-1.43686	-0.33539
5	P	-2.22659	-0.54396	-0.2066
6	P	0.640722	2.144792	0.545328
7	N	1.621073	-1.30685	1.350131
8	N	-1.86049	-0.37449	1.440416
9	N	0.18991	1.925198	-1.07174
10	C	2.306379	-2.13386	2.379146
11	C	3.446013	-1.35396	3.088672
12	C	1.286932	-2.63214	3.431794
13	C	3.580038	-0.87653	-0.78747
14	C	3.682367	-0.35382	-2.24552
15	C	4.700771	-1.90513	-0.47668
16	C	1.782433	-3.28133	-0.77562
17	C	2.019258	-3.54887	-2.28576
18	C	0.451391	-3.92146	-0.31175
19	C	-2.74998	-0.6176	2.61078
20	C	-2.56483	-2.04173	3.201698
21	C	-2.4748	0.447545	3.700912

22	C	-2.98136	-2.26796	-0.50313
23	C	-2.87049	-2.75052	-1.97634
24	C	-4.42819	-2.47944	0.021607
25	C	-3.49022	0.763841	-0.75237
26	C	-4.67334	1.056493	0.206487
27	C	-3.97407	0.516437	-2.20695
28	C	-0.24614	3.671417	1.248263
29	C	-1.76651	3.621664	0.96951
30	C	0.030126	3.79461	2.771386
31	C	2.478475	2.688335	0.569867
32	C	2.763186	4.187241	0.288116
33	C	3.20796	2.216865	1.855061
34	C	0.196535	2.997721	-2.11411
35	C	-1.09889	2.951635	-2.96285
36	C	1.433218	2.879395	-3.04502
37	H	2.756089	-3.02832	1.893464
38	H	3.024207	-0.50105	3.653524
39	H	3.981692	-2.01053	3.802482
40	H	4.178541	-0.95761	2.363462
41	H	1.786242	-3.24369	4.208386
42	H	0.49466	-3.23925	2.959327
43	H	0.808698	-1.76523	3.928168
44	H	3.713447	-0.01235	-0.10366
45	H	4.673291	0.116086	-2.40874
46	H	2.902104	0.394881	-2.46417
47	H	3.570233	-1.16737	-2.98393
48	H	4.654201	-2.28239	0.560819
49	H	5.691469	-1.42731	-0.61482
50	H	4.658748	-2.77294	-1.16037
51	H	2.612766	-3.74102	-0.1969
52	H	1.302422	-2.98247	-2.90739
53	H	1.879536	-4.62836	-2.49417
54	H	3.040433	-3.27993	-2.60909
55	H	0.201927	-3.64619	0.728441
56	H	-0.37672	-3.596	-0.96513
57	H	0.520083	-5.02533	-0.37591
58	H	-3.80862	-0.51494	2.293777
59	H	-2.70714	-2.81955	2.430507
60	H	-1.54622	-2.15163	3.614624
61	H	-3.29182	-2.22296	4.018311
62	H	-3.0952	0.266711	4.600228
63	H	-2.6875	1.464109	3.323879

64	H	-1.40909	0.408892	4.00184
65	H	-2.29848	-2.89233	0.110612
66	H	-3.0509	-3.84366	-2.02024
67	H	-3.62595	-2.26439	-2.61862
68	H	-1.88155	-2.53853	-2.41874
69	H	-4.69451	-3.55265	-0.06134
70	H	-5.16025	-1.91366	-0.5832
71	H	-4.54949	-2.18432	1.078245
72	H	-2.84533	1.664832	-0.76422
73	H	-5.26159	1.909499	-0.18955
74	H	-5.36048	0.196987	0.302773
75	H	-4.31967	1.33729	1.214177
76	H	-4.72504	-0.29414	-2.25015
77	H	-4.45537	1.433984	-2.5996
78	H	-3.13942	0.255153	-2.8833
79	H	0.170064	4.565401	0.739523
80	H	-2.21428	2.696157	1.374598
81	H	-1.97993	3.660312	-0.11313
82	H	-2.26634	4.487203	1.44855
83	H	-0.51041	4.66961	3.183456
84	H	1.102783	3.928695	2.999017
85	H	-0.32466	2.895548	3.310228
86	H	2.878303	2.101136	-0.28296
87	H	3.85457	4.341645	0.167656
88	H	2.272312	4.548722	-0.63352
89	H	2.434997	4.828796	1.127884
90	H	2.894575	2.798565	2.74256
91	H	3.004781	1.152028	2.055283
92	H	4.303327	2.349907	1.745169
93	H	0.234366	3.984802	-1.60167
94	H	-1.17508	1.978576	-3.48159
95	H	-1.08874	3.754729	-3.72564
96	H	-1.99608	3.084457	-2.33141
97	H	2.377081	2.913791	-2.47133
98	H	1.444703	3.704975	-3.78401
99	H	1.388475	1.920969	-3.59443

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