Electronic Supplementary Material (ESI) for Chemical Communications

Synthesis and reactions of β-diketiminate-supported complexes with Mg-Fe or Yb-Fe bonds

Matthew P. Blake, Nikolas Kaltsoyannis and Philip Mountford

SUPPORTING INFORMATION

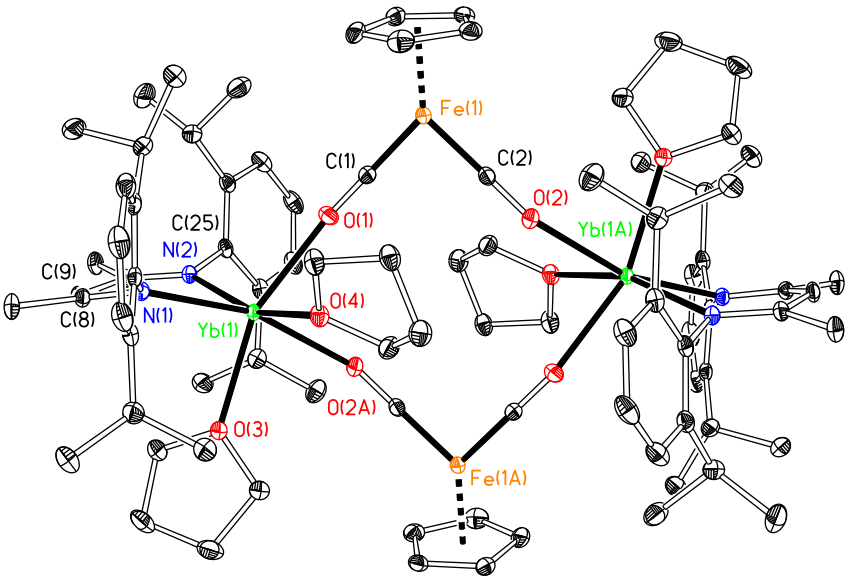


Figure S1. Displacement ellipsoid plot (20% probability) of $[Yb(NacNac)(\mu\text{-}Fp)(THF)_2]_2$ (**10·THF**). H atoms omitted for clarity. Atoms carrying the suffix "A" are related to their counterparts by the operator 1-*x*, 2-*y*, 1-*z*.

Table S1. Selected distances (Å) and angles (°) for [Yb(NacNac)Fp(THF)$_2$]$_2$ (**10·THF**).

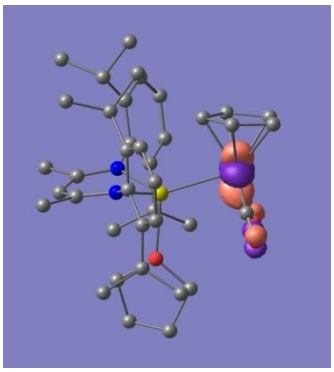
Yb(1)···Fe(1)	5.1718(5)	Yb(1A)···Fe(1)	5.2267(4)
Yb(1)-O(1)	2.437(2)	Yb(1)-O(2A)	2.4617(19)
Yb(1)-O(3)	2.469(2)	Yb(1)-O(4)	2.4671(19)
Yb(1)-N(1)	2.422(2)	Yb(1)-N(2)	2.434(2)
Fe(1)-C(1)	1.709(3)	Fe(1)-C(2)	1.707(3)
Fe(1)-Cp$_{cent(1)}$	1.742	C(1)-O(1)	1.191(3)
C(2)-O(2)	1.190(3)	O(1)-Yb(1)-O(2A)	80.58(7)
O(1)-Yb(1)-O(3)	157.21(7)	O(2A)-Yb(1)-O(4)	82.23(7)
O(4)-Yb(1)-N(1)	94.65(7)	N(1)-Yb(1)-N(2)	77.97(7)
N(2)-Yb(1)-O(2A)	109.56(7)	C(1)-Fe(1)-C(2)	90.31(13)
C(1)-Fe(1)-Cp$_{cent(1)}$	134.31	C(2)-Fe(1)-Cp$_{cent(1)}$	135.35

DFT calculations for Mg(NacNac)Fp(THF) (9). DFT calculations were carried out on Mg(NacNac)Fp(THF) (**9**). The computed geometric parameters are in good agreement with those determined experimentally. For example, the DFT Mg-Fe distance (2.581 Å) is only 0.05 Å shorter than that measured (2.6326(4) Å), and the N-Mg-N angle (92.4 ^{o}) is very similar to that for **9** (90.97(4) ^{o}). The Mg atom lies 0.72 Å out of the plane of the NacNac backbone, again consistent with that observed for **9** (0.76 Å). As with the calculations for [MgFp$_2$(THF)$_3$]$_2$[1] the low values at the Mg–Fe bond critical point for the electron density (0.03 au), its Laplacian (0.062 au) and the energy density (-0.005 au) are consistent with a predominantly ionic Mg-Fe interaction.

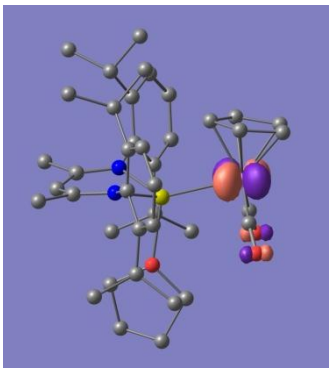
Selected molecular orbitals (MOs) for **9** are shown in Fig. S2 together with their associated energies. By way of comparison, the geometric and electronic structure of FpH was also computed and selected MOs and energies are given in Fig. S3. These are comparable to those reported previously.[2] The HOMO, HOMO-1 and HOMO-2 of FpH are predominantly metal-based, as expected for the formal Fe(+2), d^6 electronic description. MO-5 (-7.59 eV) corresponds to the Fe–H σ-bond. The LUMO of FpH (-1.99 eV) is Fe-ligand antibonding. The HOMO-4 and HOMO-3 (not illustrated) are Fe-Cp bonding MOs. The electronic structure of **9** with respect to the Fe centre is related to that of FpH but with some important differences. The LUMO of **9** resembles that of FpH but lies at higher energy (-1.66 eV *vs.* -1.99 eV in FpH). The MOs corresponding to the d^6 electronic set of FpH (HOMO, HOMO-1, HOMO-2) find their counterparts as HOMO, HOMO-3 and HOMO-5 of **9**. However, as for the LUMOs of the two systems, the average energy of these

MOs for **9** (-4.72 eV) is somewhat less negative than for the corresponding MOs of FpH (av. -5.40 eV). The Mulliken atomic charge for Fe in **9** (-0.164) is also more negative than that for FpH (-0.002). Finally, whereas the Fe–H bonding MO of FpH (HOMO-5, -7.59 eV) is significantly stabilised relative to the three MOs housing the d^6 electrons, the corresponding MO (HOMO-1) of **9** is much less stable (-4.44 eV) and is predominantly Fe-based with negligible contribution from Mg (in contrast to the HOMO-5 for FpH which features a significant H 1s contribution).

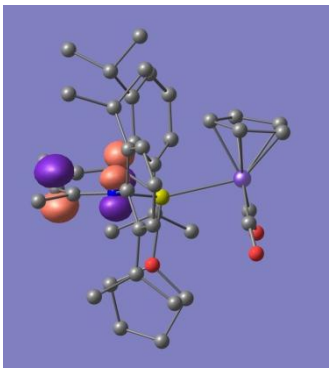
For comparison the electronic structure of the $[Fp]^-$ anion in the geometry found for FpH (which is also very close to that for **9**) was also computed. As expected, the frontier MOs of $[Fp]^-$ feature four Fe-based MOs for the d^8 electron configuration. The HOMO (Fig. S4) of $[Fp]^-$ resembles the HOMO-1 of **9** and lies 1.06 eV *above* the HOMO-1. This in turn closely resembles the HOMO of **9**. Coordination of $[Mg(NacNac)(THF)]^+$ to $[Fp]^-$ in **9** stabilises the HOMO of $[Fp]^-$ by *ca.* 1.3 eV relative to the anion's HOMO-1. The Fe–Mg interaction is nonetheless substantially ionic, as evidenced by the AIM data discussed above and the composition of the HOMO-1. Mulliken population analysis of the HOMO-1 of **9** calculated in ADF gives its composition as 42.2% Fe d, 9.0% Fe p, 4.3% Fe s, 7.5% Mg p and 6.2% Mg s, *i.e.* strongly polarised toward the Fe centre. Since the DFT results show that the MO of **9** (HOMO-1) most responsible for any covalency lies within the manifold for the Fe-based electrons (HOMO, HOMO-3, HOMO-5), the electronic structure of Fe in **9** is best viewed as being between that of the Fe(0) in $[Fp]^-$ (d^8 configuration) and the formal Fe(+2) in FpH (d^6).



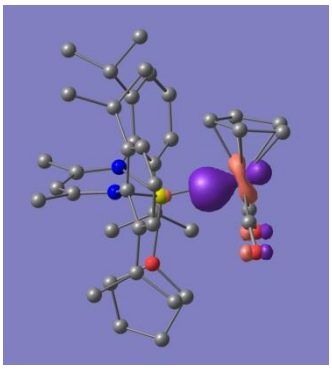
HOMO-5: -5.36 eV



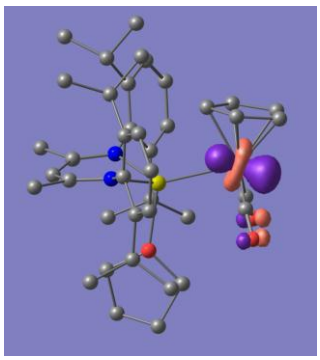
HOMO-3: -4.60 eV



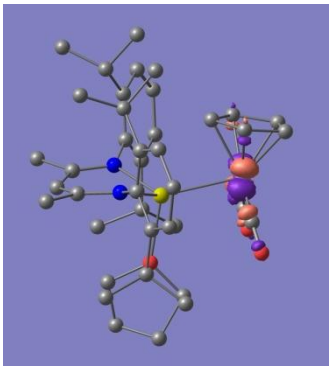
HOMO-2: -4.57 eV



HOMO-1: -4.44 eV

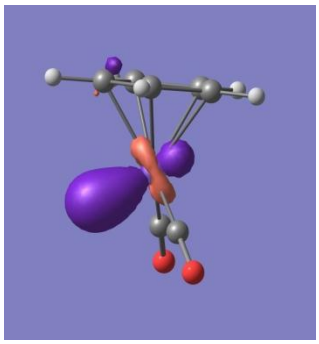


HOMO: -4.20eV

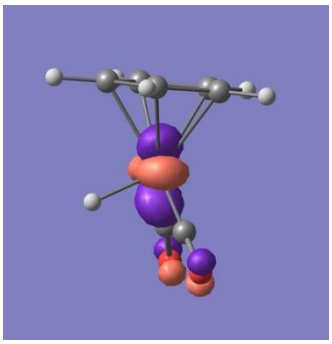


LUMO: -1.66 eV

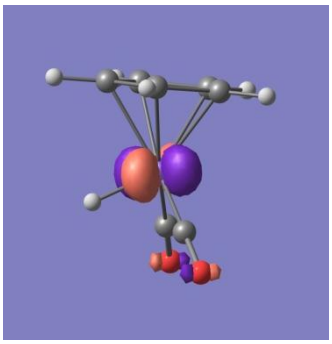
Figure S2. Isosurfaces and associated energies of selected MOs of Mg(NacNac)Fp(THF) (**9**). HOMO-2 and HOMO-4 (not shown) are ligand-based MOs associated with NacNac. The value for the isosurfaces is 0.06 au.



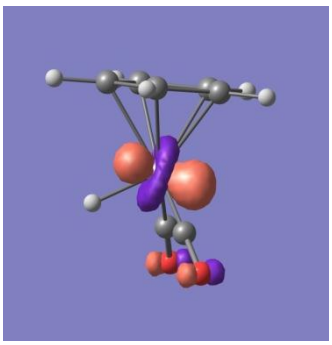
HOMO-5: -7.59 eV



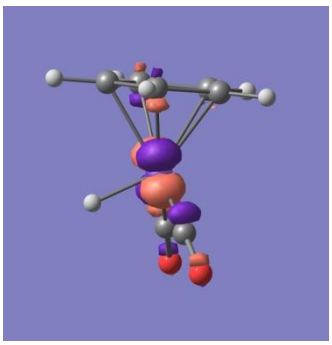
HOMO-2: -6.15 eV



HOMO-1: -5.52 eV

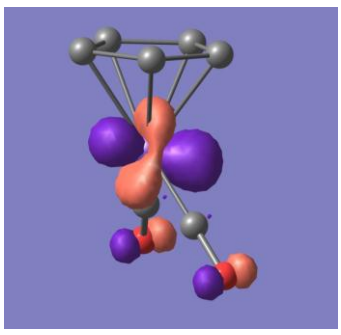


HOMO: -4.54 eV

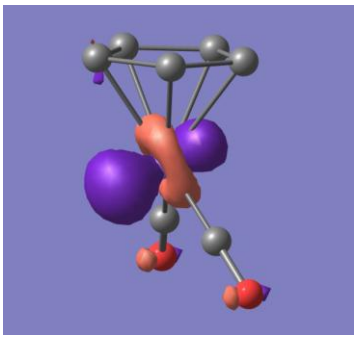


LUMO: -1.99 eV

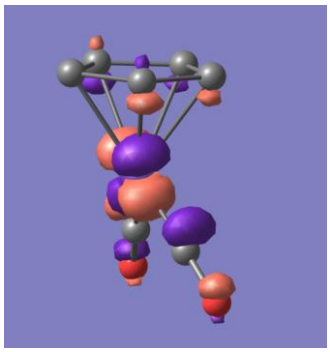
Figure S3. Isosurfaces and associated energies of selected molecular orbitals of FpH. The value for the isosurfaces is 0.06 au.



HOMO-1: 0.51 eV



HOMO: 1.57 eV



LUMO: 3.37 eV

Figure S4. Isosurfaces and associated energies of the LUMO, HOMO and HOMO-1 of $[Fp]^-$ in the geometry of the $CpFe(CO)_2$ moiety in **9** and FpH. The value for the isosurfaces is 0.06 au.

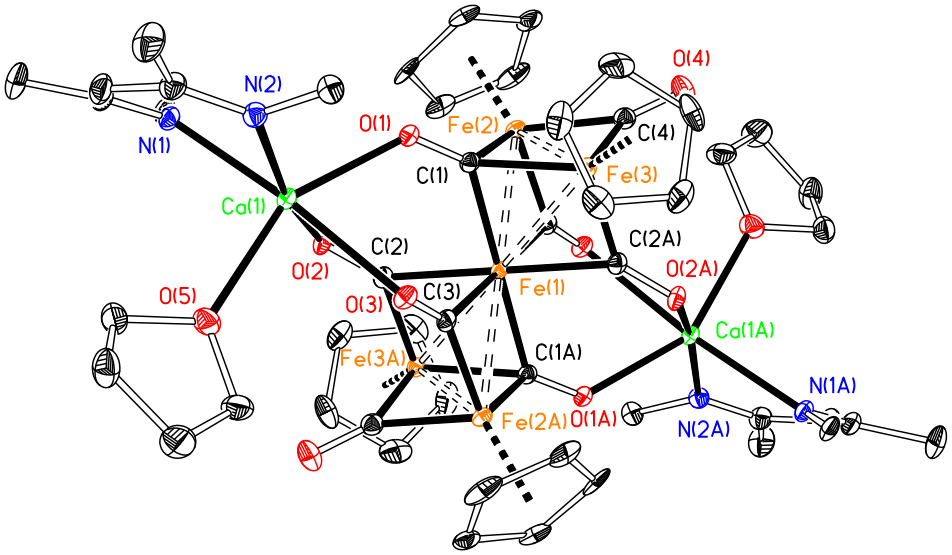


Figure S5. Displacement ellipsoid plot (20% probability) of [{Ca(NacNac)(THF)}$_2${$Cp_4Fe_5(CO)_8$}] (**11**). H atoms and minor disorder component omitted and only the *ispo* carbons of the $C_6H_3{}^{i}Pr_2$ rings are shown. Atoms carrying the suffix 'A' are related to their counterparts by the operator 1–*x*, 1–*y*, 1–*z*.

Table S2. Selected distances (Å) and angles (°) for [{Ca(NacNac)(THF)}$_2${$Cp_4Fe_5(CO)_8$}] (**11**).

Ca(1)···Fe(1)	4.1872(3)	Ca(1)···Fe(2)	4.8967(3)
Ca(1)···Fe(3)	4.9247(3)	Ca(1)-O(1)	2.2895(9)
Ca(1)-O(2)	2.4384(9)	Ca(1)-O(3)	2.4669(9)
Ca(1)-O(5)	2.4148(10)	Ca(1)-N(1)	2.3911(11)
Ca(1)-N(2)	2.3855(11)	Fe(1)-C(1)	2.0221(12)
Fe(1)-C(2)	1.9875(12)	Fe(1)-C(3)	1.9976(12)
Fe(1)···Fe(2)	2.5524(2)	Fe(1)···Fe(3)	2.5412(2)
Fe(2)···Fe(3)	2.5307(3)	Fe(2)-$Cp_{cent(1)}$	1.744
Fe(2)-C(4)	1.9202(14)	Fe(2)-C(1)	1.9674(13)
Fe(2)-C(3A)	1.8591(13)	Fe(3)-$Cp_{cent(2)}$	1.745
Fe(3)-C(1)	1.9535(13)	Fe(3)-C(4)	1.9133(14)
Fe(3)-C(2A)	1.8724(13)	C(1)-O(1)	1.2295(16)
C(2)-O(2)	1.1971(16)	C(3)-O(3)	1.2032(16)
C(4)-O(4)	1.1794(17)	O(1)-Ca(1)-O(2)	71.49(3)
O(1)-Ca(1)-O(3)	72.14(3)	O(1)-Ca(1)-O(5)	151.50(4)
O(2)-Ca(1)-O(3)	80.30(3)	O(2)-Ca(1)-N(1)	93.44(4)
O(3)-Ca(1)-N(2)	107.33(4)	N(1)-Ca(1)-N(2)	79.79(4)
C(1)-Fe(1)-C(1A)	179.994	C(1)-Fe(1)-C(2)	84.21(5)
C(1)-Fe(2)-C(4)	97.42(5)	C(1)-Fe(2)-C(3A)	101.99(5)
C(1)-Fe(2)-$Cp_{cent(1)}$	120.89	C(1)-Fe(3)-C(2A)	102.05(5)
C(1)-Fe(3)-C(4)	98.12(5)	C(1)-Fe(3)-$Cp_{cent(2)}$	121.86
C(2)-Fe(1)-C(3)	73.47(5)	C(2)-Fe(1)-C(3A)	106.53(5)
C(2A)-Fe(3)-C(4)	83.49(5)	C(2A)-Fe(3)-$Cp_{cent(2)}$	121.95
C(3A)-Fe(2)-C(4)	84.73(6)	C(3A)-Fe(2)-$Cp_{cent(1)}$	123.39
C(4)-Fe(2)-$Cp_{cent(1)}$	120.47	C(4)-Fe(3)-$Cp_{cent(2)}$	121.07

For $Cp_{cent(2)}$ average distances and angles are given to accommodate both orientations of the Cp rings.

DFT calculations for 13 (*cf.* Fig. S6). These find an electronic structure consistent with a formal Fe(2+) centre and d^6 configuration. The Mulliken charge for Fe in **13** (-0.040) is significantly increased relative to that in **9** (-0.164) and is comparable to the value for FpH (0.0). The MO corresponding to the Fe-CN_2 σ-bonding interaction is found at -6.32 eV (*cf.* -7.59 eV for the Fe–H bond in FpH).

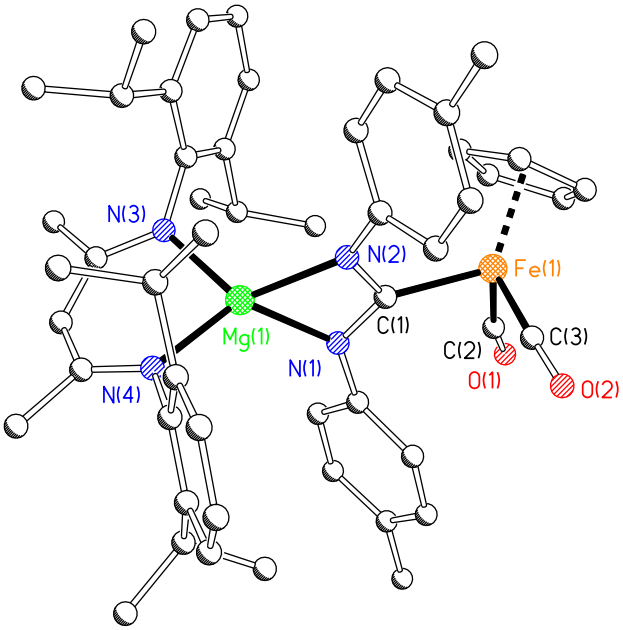


Figure S6. DFT calculated structure of Mg(NacNac){$(NTol)_2$CFp} (**13**). H atoms omitted for clarity. Selected distances (Å) and angles (°): Fe(1)–C(1) 2.059, Fe(1)–C(2) 1.769, Fe(1)–C(3) 1.746, Fe(1)–Cp_{cent} 1.758, Mg(1)–N(1) 2.114, Mg(1)–N(2) 2.106, Mg(1)–N(3) 2.083, Mg(1)–N(4) 2.086; Cp_{cent}–Fe(1)–C(1) 123.3, N(1)–Mg(1)–N(2) 64.1, N(3)–Mg(1)–N(4) 94.2.

Experimental Details

General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. THF was refluxed over sodium and distilled. NMR spectra were recorded in C_6D_6 or THF-d_8 which were dried over potassium, distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on Varian Mercury-VX 300 spectrometer at ambient temperature and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two-dimensional ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Perkin Elmer Paragon 1000 FTIR or Thermo Scientific Nicolet iS5 FTIR spectrometer. Samples were prepared in a dry-box as Nujol mulls between NaCl plates or as a toluene or THF solution in a NaCl cell. The data are quoted in wavenumbers (cm^{-1}). Elemental analyses were carried out by the Elemental Analysis Service at London Metropolitan University.

Starting materials. KFp,[3] Mg(NacNac)I(THF),[4] [Ca(NacNac)I(THF)]$_2$,[5] [Yb(NacNac)I(THF)]$_2$[6] and [YbFp$_2$(THF)$_3$]$_2$[1] were prepared according to published procedures. Other reagents were purchased from Sigma Aldrich and used without further purification. A slightly modified synthesis of [Ca(NacNac)(μ-Fp)(THF)]$_2$ (**8**) was reported previously.[1]

Mg(NacNac)Fp(THF) (9). To KFp (0.674 g, 3.12 mmol) and Mg(NacNac)I(THF) (2.00 g, 3.12 mmol) was added THF (30 mL). The red-brown solution was stirred for 16 h at RT. Volatiles were removed under reduced pressure to give a brown solid. The solid was extracted into benzene (30 mL), filtered and volatiles were removed under reduced pressure. The resulting red solid was washed with pentane (2 x 10 mL) to afford **9** as a pale yellow-green solid. Yield: 1.69 g (78%). Diffraction-quality crystals were grown from a concentrated benzene solution at RT.

^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.19 (6 H, 3,4,5-C_6H_3), 4.80 (1 H, s, NC(Me)C<u>H</u>), 4.35 (5 H, s, Cp), 3.65 (4 H, m, OCH_2), 3.29 (4 H, sept, ^{3}J = 6.8 Hz, C<u>H</u>Me$_2$), 1.67 (6 H, s, Me), 1.39 (12 H, d, ^{3}J = 6.8 Hz, CH<u>Me</u>$_2$), 1.26 (12 H, d, ^{3}J = 6.8 Hz, CH<u>Me</u>$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 221.3 (CO), 168.8 (CN), 146.9 (1-C_6H_3), 142.6 (2,6-C_6H_3), 125.7 (4-C_6H_3), 124.3 (3,5-C_6H_3), 96.1 (NC(Me)<u>C</u>H), 78.1 Cp, 71.1 (OCH_2), 28.7 (<u>C</u>HMe$_2$), 25.5 (OCH_2<u>C</u>H$_2$), 25.3 (CH<u>Me</u>$_2$), 25.2(Me), 24.8 (CH<u>Me</u>$_2$). EI-MS: *m/z* = 441 (100%) [(NacNac)Mg]$^{+}$. IR (NaCl plates, Nujol mull, cm^{-1}): 2020 (m), 1963 (m), 1926 (s), 1857 (s), 1519 (s), 1307 (m), 1261 (m), 1226 (w), 1172 (w), 1107 (m), 1055 (w), 1017 (s), 926 (m), 867 (m), 846 (m), 814 (m), 793 (s), 722 (m), 758 (m), 667 (s). IR

(NaCl cell, THF, ν(CO), cm^{-1}): 1926 (m), 1871 (s). Anal. found (calcd. for $C_{40}H_{54}FeMgN_2O_3$): C, 69.31 (69.52) ; H, 7.66 (7.88) ; N, 4.17 (4.05)%.

NMR tube scale reaction of Mg(NacNac)Fp(THF) (9) with MeI. To a solution of Mg(NacNac)Fp(THF) (9, 20.0 mg, 28.9 μmol) in C_6D_6 (0.6 mL) was added MeI (2.7 μL, 43 μmol). The ^{1}H NMR spectrum recorded after 10 min showed quantitative formation of FpMe and Mg(NacNac)I(THF) as judged by comparison with the spectra for authentic samples.[4,7] ^{1}H NMR data for FpMe in C_6D_6 (299.9 MHz): 3.99 (5 H, s, Cp), 1.41 (3 H, s, Me).

Mg(NacNac){(NTol)$_2$CFp} (13). To Mg(NacNac)Fp(THF) (**9**, 0.500 g, 0.724 mmol) and TolNCNTol (0.161 g, 0.724 mmol) was added C_6H_6 (10 mL). The resulting red solution was stirred for 16 h at RT, filtered and volatiles removed under reduced pressure to give a red solid. The solid was washed with pentane (2 x 5 mL) and dried *in vacuo* to afford **13** as a yellow solid. Yield: 0.404 g (66%).

^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.20 (6 H, s , 3,4,5-C_6H_3), 6.97 (4 H, d, ^3J = 8.2 Hz, 2,6-C_6H_4), 6.36 (4 H, d, ^3J = 8.2 Hz, 3,5-C_6H_4), 4.93 (1 H, s, NC(Me)C<u>H</u>), 3.79 (5 H, s, Cp), 3.33 (4 H, sept, ^3J = 6.8 Hz, C<u>H</u>Me$_2$), 2.24 (6 H, s, <u>Me</u>C_6H_4) 1.71 (6 H, s, NCMe), 1.20 (12 H, d, ^3J = 6.8 Hz, CH<u>Me</u>$_2$), 1.12 (12 H, d, ^3J = 6.8 Hz, CH<u>Me</u>$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 214.4 (CO), 200.7 (N_2<u>C</u>-Fp) 168.8 (N<u>C</u>Me), 170 (1-C_6H_4), 146.3 (1-C_6H_3), 142.6 (2,6-C_6H_3), 130.5 (4-C_6H_4), 129.0 (2,6-C_6H_4), 128.0 (3,5-C_6H_4), 125.2 (4-C_6H_3), 124.1 (3,5-C_6H_3), 95.4 (NC(Me)<u>C</u>H), 85.7 Cp, 28.7 (<u>C</u>HMe$_2$), 24.5 (CH<u>Me</u>$_2$), 24.4 (Me), 21.1 (C_6H_4Me). EI-MS: *m/z* = 441 (20%) $[(NacNac)Mg]^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 2010 (s), 1956 (s), 1791 (w), 1600 (m), 1543 (m), 1522 (s), 1504 (s), 1406 (s), 1317 (m), 1262 (m), 1212 (w), 1179 (m), 1158 (m), 1018 (m), 951 (m), 933 (m), 848 (m), 821 (m), 759 (m). (NaCl cell, toluene, ν(CO), cm^{-1}): 2015 (s), 1970 (s). Anal. found (calcd. for $C_{51}H_{60}FeMgN_4O_2$): C, 72.64 (72.82); H, 7.32 (7.19); N, 6.79 (6.66)%.

[Ca(NacNac)(μ-Fp)(THF)]$_2$ (8). To KFp (0.329 g, 1.52 mmol) and [Ca(NacNac)I(THF)]$_2$ (1.00 g, 0.760 mmol) was added THF (20 mL). The red solution was stirred for 5 h at RT. Volatiles were removed under reduced pressure. The orange solid was extracted into THF (15 mL) and the resulting solution filtered, layered with pentane (15 mL) and allowed to stand for 16 h at RT. The resulting orange microcrystalline solid was isolated by filtration, washed with pentane (2 x 5 mL) then dried *in vacuo* to afford **8** as an orange solid. Yield: 0.728 g (68%). Diffraction-quality crystals of [Ca(NacNac)(μ-Fp)(THF)$_2$]$_2$ (**8·THF**) were grown from a concentrated THF solution at RT. Attempted crystallisation from a concentrated C_6H_6 solution at RT gave a few diffraction-quality crystals of [{Ca(NacNac)(THF)}$_2${$Cp_4Fe_5(CO)_8$}] (**11**).

^{1}H NMR (THF-d_8, 299.9 MHz): δ 7.09 (8 H, d, ^3J = 6.4 Hz, 3,5-C_6H_3), 7.02 (4 H, d, ^3J = 6.4 Hz, 4-C_6H_3), 4.73 (2 H, s, NC(Me)C<u>H</u>), 4.20 (s, 10 H, Cp), 3.20 (8 H, sept, ^3J = 6.8 Hz, C<u>H</u>Me$_2$), 1.58 (12

H, s, Me), 1.28 (24 H, d, ^3J = 6.8 Hz, CHMe$_2$), 1.12 (24 H, d, ^3J = 6.8 Hz, CHMe$_2$). ^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.18 (24 H, s, 3,4,5-C_6H_3), 4.85 (2 H, s, NC(Me)CH), 4.04 (s, 10 H, Cp), 3.92 (8 H, m, OCH_2), 3.32 (8 H, sept, ^3J = 6.8 Hz, CHMe$_2$), 1.66 (12 H, s, Me), 1.42 (24 H, d, ^3J = 6.8 Hz, CHMe$_2$), 1.39 (8 H, m, OCH_2CH_2), 1.19 (24 H, d, ^3J = 6.8 Hz, CHMe$_2$). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ 231.0 (CO), 166.3 (CN), 149.9 (1-C_6H_3), 143.1 (2,6-C_6H_3), 124.9 (4-C_6H_3), 124.5 (3,5-C_6H_3), 95.0 (NC(Me)CH), 78.0 Cp, 29.0 (CHMe$_2$), 26.5 (Me), 25.7 (CHMe$_2$), 25.5 (CHMe$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 166.2 (CN), 146.6 (1-C_6H_3), 142.0 (2,6-C_6H_3), 125.0 (4-C_6H_3), 124.1 (3,5-C_6H_3), 94.4 (NC(Me)CH), 79.5 Cp, 69.6 (OCH_2), 28.5 (CHMe$_2$), 25.4 (OCH_2CH_2), 25.3 (CHMe$_2$), 24.8 (Me), 25.5 (CHMe$_2$) (δ(CO) not observed). EI-MS: *m/z* = 457 (100%) [(NacNac)Ca]$^+$. IR (NaCl plates, Nujol mull, cm^{-1}): 1905 (w), 1823 (s), 1780 (s), 1721 (m), 1540 (m), 1513 (m), 1408 (s), 1313 (m), 1253 (w), 1225 (w), 1167 (m), 1105 (w), 1032 (m), 922 (m), 892 (w), 787 (m), 759 (w). IR (NaCl cell, THF, ν(CO) cm^{-1}): 1958 (s), 1810 (s). Anal. found (calcd. for $C_{80}H_{108}Ca_2Fe_2N_4O_6$): C, 67.91 (67.97) ; H, 7.70 (7.70) ; N, 3.97 (3.96)%.

[Yb(NacNac)(μ-Fp)(THF)]$_2$ (10). To KFp (0.137 g, 0.633 mmol) and [Yb(NacNac)I(THF)]$_2$ (0.500 g, 0.317 mmol) was added THF (20 mL). The red solution was stirred for 16 h at RT. Volatiles were removed under reduced pressure. The red solid was dissolved in THF (20 mL) and the solution filtered and volatiles removed under reduced pressure. The resulting solid was dried *in vacuo* to afford **12** as a spectroscopically pure red solid. Yield: 0.471 g (88%). An analytically pure sample was obtained by further recrystallisation from a THF:pentane mixture and thoroughly drying *in vacuo*. Diffraction-quality crystals of [Yb(NacNac)(μ-Fp)(THF)$_2$]$_2$ (**10·THF**) were grown from a concentrated THF solution at RT. Attempted crystallisation from a dilute pentane solution at -30 ºC gave a number of diffraction-quality crystals of [{Yb(NacNac)(THF)}$_2$(μ-$YbFp_4$)] (**12**) which was independently prepared as described below.

^{1}H NMR (THF-d_8, 299.9 MHz): δ 7.13 (8 H, d, ^3J = 6.4 Hz, 3,5-C_6H_3), 7.06 (4 H, d, ^3J = 6.4 Hz, 4-C_6H_3), 4.75 (2 H, s, NC(Me)CH), 4.20 (s, 10 H, Cp), 3.22 (8 H, sept, ^3J = 6.8 Hz, CHMe$_2$), 1.59 (12 H, s, Me), 1.30 (24 H, d, ^3J = 6.8 Hz, CHMe$_2$), 1.16 (24 H, d, ^3J = 6.8 Hz, CHMe$_2$). ^{1}H NMR (C_6D_6, 299.9 MHz): δ 7.20 (24 H, m, 3,4,5-C_6H_3), 4.74 (2 H, s, NC(Me)CH), 4.24 (s, 10 H, Cp), 3.76 (8 H, m, OCH_2), 3.29 (8 H, sept, CHMe$_2$), 1.61 (12 H, s, Me), 1.41 (32 H, overlapping 2 x m, CHMe$_2$ & OCH_2CH_2), 1.23 (24 H, d, CHMe$_2$). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ 230.6 (CO), 165.7 (CN), 149.2 (1-C_6H_3), 142.9 (2,6-C_6H_3), 124.8 (4-C_6H_3), 124.4 (3,5-C_6H_3), 95.4 (NC(Me)CH), 77.7 Cp, 28.9 (CHMe$_2$), 26.5 (Me), 25.3 (CHMe$_2$).^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 165.7 (CN), 146.0 (1-C_6H_3), 141.7 (2,6-C_6H_3), 125.1 (4-C_6H_3), 124.2 (3,5-C_6H_3), 93.9 (NC(Me)CH), 78.9 Cp, 69.7 (OCH_2), 28.7 (CHMe$_2$), 25.4 (OCH_2CH_2), 25.1 (CHMe$_2$), 24.8 (Me & CHMe$_2$) (δ(CO) not observed). IR (NaCl plates, Nujol mull, cm^{-1}): 1908 (m), 1837 (s), 1821 (s), 1779 (s), 1737 (s), 1717 (m), 1541 (m), 1514 (m), 1406 (s), 1314 (m), 1260 (w), 1228 (w), 1170 (w), 1107 (w), 1027

(m), 923 (w), 875 (w). IR (NaCl cell, THF, ν(CO) cm^{-1}): 1873 (s), 1721 (s). Anal. found (calcd. for $C_{80}H_{108}Fe_2N_4O_6Yb_2$): C, 57.59 (57.21) ; H, 6.93 (6.48) ; N, 2.93 (3.34)%.

[{Yb(NacNac)(THF)}$_2$(μ-YbFp$_4$)] (19). To [Yb(NacNac)(μ-Fp)(THF)]$_2$ (0.200 g, 0.238 mmol) and (0.177 mg, 0.199 mmol) was added THF (15 mL). The resulting red-brown solution was stirred for 16 h at RT then volatiles were removed under reduced pressure. To the resulting solid was added pentane (10 mL) and the suspension stirred for 15 min. Volatiles were removed under reduced pressure and the resulting solid was dried in vacuo to afford **19** as a beige solid. Yield 0.194 g (74%). ^{1}H NMR (THF-d_8, 299.9 MHz): δ 7.13 (8 H, m, 3,5-C_6H_3), 7.07 (4 H, d, ^3J = 6.7 Hz, 4-C_6H_3), 4.86 (2 H, s, NC(Me)C<u>H</u>), 4.31 (20 H, s, Cp), 3.21 (8 H, m, C<u>H</u>Me$_2$), 1.58 (12 H, s, Me), 1.32 (m, 24, CH<u>Me$_2$</u>), 1.16 (24 H, d, ^3J = 6.4 Hz, CH<u>Me$_2$</u>).^{13}C{^{1}H} NMR not recorded due to poor solubility. IR (NaCl plates, Nujol mull, cm^{-1}): 2019 (s), 1962 (s), 1905 (m), 1761 (m), 1623 (w), 1576 (m), 1552 (m), 1314 (m), 1260 (m), 1099 (m), 1017 (m), 754 (w). IR (NaCl cell, THF, ν(CO), cm^{-1}): 1874 (m), 1782 (s). Anal. found (calcd. for $C_{94}H_{118}Fe_4N_4O_{10}Yb_3$): C, 50.88 (51.17); H, 5.23 (5.39); N, 2.67 (2.54)%.

Computational Details

Gradient corrected, gas-phase density functional theory calculations were carried out using the PBE functional,[8] as implemented in the Amsterdam Density Functional 2012.01[9] (ADF) and the Gaussian 09 Rev. C.01 (G09)[10] quantum chemistry codes. Atoms in molecules analyses were performed using the AIMALL programme,[11] using formatted G09 checkpoint files as input.

Geometry optimisations were carried out in G09, without symmetry constraints. The cc-pVDZ basis set of Dunning *et al.* was used for all atoms. The ultrafine grid was employed, together with default geometry convergence criteria. The scf convergence criterion was set to 10^{-6} in all cases. Frequencies calculations were performed at all optimised geometries, yielding no imaginary frequencies in all cases, and were used in the calculation of $\Delta_r G$ for **9** + TolNCNTol → **13** + THF (SCF total energies modified with zero point energies, thermal corrections to 298.15 K, and entropic corrections). The SCF total energies for the species involved in this reaction were obtained from B3LYP single point calculations at the PBE optimised geometries.

Single point calculations were performed in the ADF code using the Zeroth Order Regular Approximation (ZORA) Hamiltonian. Slater Type Orbital ZORA basis sets of TZP quality were used for all atoms bar H, for which a DZP ZORA basis set was employed. The frozen core approximation was employed for all atoms; Fe(2p) and 1s for all other atoms bar H. The default SCF convergence criteria were used, together with an integration grid of 4.5. Quoted Mulliken charges are from ADF.

References

1. M. P. Blake, N. Kaltsoyannis and P. Mountford, *J. Am. Chem. Soc.*, 2011, **113**, 15358–15361.
2. B. E. Bursten and M. G. Gatter, *J. Am. Chem. Soc.*, 1984, **106**, 2554.
3. J. S. Plotkin and S. G. Shore, *Inorg. Chem.*, 1981, **20**, 284-285.
4. S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938-955.
5. S. Pillai Sarish, A. Jana, H. W. Roesky, T. Schulz, M. John and D. Stalke, *Inorg. Chem.*, 2010, **49**, 3816-3820.
6. P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, *Dalton Trans.*, 2009, 2383-2391.
7. H. J. Li and M. M. Turnbull, *J. Organomet. Chem.*, 1991, **419**, 245-249
8. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
9. C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, Theo. Chem. Acc. 1998, 99, 391; G. te Velde, F. M. Bickelhaupt, S. Van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* 2001, **22**, 931.
10. Gaussian 09, Revision C.01, M. J. Frisch, G.W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
11. AIMALL, 11.03.14, T. A. Keith, 2011 (aim.tkgristmill.com).

DFT (PBE) converged Cartesian coordinates and total energies (H)

Compound 9

(-3353.3040016)

Mg	0.037055	0.483577	0.068790
Fe	-0.119971	0.569156	2.643662
N	-1.527084	-0.297654	-1.183256
N	1.566071	-0.472801	-1.092846
C	-1.157714	1.939248	2.436977
C	1.272027	1.595765	2.652784
C	0.796877	-1.249732	3.108259
C	-0.264597	-1.455226	2.155240
C	-1.486656	-1.017295	2.780526
C	-1.172317	-0.539532	4.104061
C	0.231012	-0.683731	4.307904
C	-1.243938	-0.547007	-2.477869
C	0.064057	-0.588254	-3.023642
C	1.336352	-0.686394	-2.402488
C	-2.345513	-0.813160	-3.496594
C	2.459465	-1.069372	-3.357992
C	-2.856348	-0.556766	-0.693709
C	-3.277961	-1.898480	-0.429948
C	-4.556630	-2.111047	0.124000
C	-5.412445	-1.047971	0.422014
C	-4.996943	0.261432	0.154057
C	-3.734979	0.535333	-0.406101
C	-2.419480	-3.128195	-0.741720
C	-2.242692	-4.055426	0.477719
C	-3.013055	-3.948237	-1.907361
C	-3.360410	1.979530	-0.745952
C	-4.085277	3.030569	0.109902
C	-3.614867	2.285780	-2.237507
C	2.843051	-0.839785	-0.532035
C	3.065589	-2.188033	-0.109608
C	4.295949	-2.514848	0.493668
C	5.295145	-1.555608	0.685732
C	5.072318	-0.241076	0.264089
C	3.862814	0.143254	-0.346210
C	2.039558	-3.301996	-0.333019
C	1.831071	-4.193763	0.905781
C	2.431842	-4.191169	-1.532168
C	3.709997	1.581071	-0.845281
C	4.252007	2.631762	0.140041
C	4.391482	1.770963	-2.217476
C	0.408777	3.738292	-0.008573
C	0.776432	4.786953	-1.053611
C	0.020205	4.289910	-2.294433
C	0.218723	2.781074	-2.200033
O	-1.840705	2.906002	2.378591
O	2.202837	2.323382	2.745075

O	0.239663	2.482605	-0.764157
H	1.858100	-1.464572	2.940296
H	-0.179807	-1.985234	1.199824
H	-2.480866	-1.032188	2.320289
H	-1.889910	-0.123194	4.819143
H	0.787859	-0.403515	5.208226
H	0.087775	-0.733823	-4.113627
H	-2.218512	-1.814004	-3.954088
H	-2.268036	-0.078873	-4.324585
H	-3.357494	-0.749916	-3.061188
H	2.198145	-1.988401	-3.918311
H	2.588395	-0.267461	-4.114057
H	3.423903	-1.226616	-2.845703
H	-4.885774	-3.141336	0.327023
H	-6.403714	-1.236952	0.859615
H	-5.675038	1.094830	0.382394
H	-1.415625	-2.770727	-1.050148
H	-1.550541	-4.886557	0.229131
H	-3.206346	-4.516224	0.778762
H	-1.837910	-3.524297	1.359598
H	-2.340980	-4.790519	-2.173038
H	-3.994426	-4.382261	-1.622044
H	-3.173872	-3.337473	-2.815156
H	-2.269646	2.087766	-0.564308
H	-3.651298	4.033306	-0.080229
H	-5.163547	3.095107	-0.146651
H	-3.988278	2.826704	1.191679
H	-3.347582	3.338520	-2.469931
H	-4.689124	2.152026	-2.484457
H	-3.032516	1.630467	-2.910689
H	4.474950	-3.551162	0.816798
H	6.247695	-1.832686	1.160805
H	5.861126	0.511393	0.408094
H	1.072458	-2.815251	-0.578183
H	0.998210	-4.904728	0.728365
H	1.589331	-3.608300	1.813002
H	2.732002	-4.802502	1.127597
H	1.658371	-4.966517	-1.712998
H	2.556853	-3.609309	-2.463987
H	3.391689	-4.712936	-1.332878
H	2.623900	1.762684	-0.976738
H	4.004920	3.652440	-0.221285
H	3.823955	2.511488	1.152021
H	5.358234	2.587778	0.220513
H	4.252917	2.811149	-2.581590
H	5.484018	1.588196	-2.138304
H	3.994144	1.083971	-2.987475
H	-0.553961	3.962254	0.493789
H	1.187011	3.570903	0.758330
H	0.481416	5.805608	-0.737095
H	1.870478	4.787063	-1.241080
H	-1.057541	4.545150	-2.221678

H 0.410125 4.703166 -3.244446
H -0.587046 2.177797 -2.656736
H 1.191175 2.461036 -2.633202

Compound 13

(-3809.8488655)

Mg	-0.743394	0.480420	0.487380
Fe	3.220316	-1.263853	-0.971728
N	-1.599927	-0.225404	2.250605
N	-2.226983	1.908557	0.156326
C	4.308500	-0.189830	-0.081533
C	3.316253	-0.378145	-2.473829
C	4.023294	-3.050270	-1.802326
C	2.608374	-3.223645	-1.597246
C	2.349184	-3.078788	-0.197024
C	3.584650	-2.809049	0.461586
C	4.629653	-2.797589	-0.539417
C	-2.367929	0.608007	2.986875
C	-2.937462	1.805303	2.494176
C	-2.983806	2.344832	1.179257
C	-2.655551	0.291094	4.444806
C	-3.978838	3.477031	0.988339
C	-1.333458	-1.561262	2.708883
C	-2.219299	-2.609625	2.299891
C	-1.903956	-3.935090	2.652959
C	-0.752995	-4.240930	3.391042
C	0.096643	-3.208509	3.798808
C	-0.172307	-1.862407	3.476741
C	-3.506307	-2.305219	1.529642
C	-3.936610	-3.419203	0.560811
C	-4.674793	-1.990630	2.488010
C	0.770844	-0.777478	3.994879
C	2.196390	-0.934923	3.435828
C	0.800551	-0.746482	5.536393
C	-2.406093	2.443751	-1.167710
C	-3.076890	1.636893	-2.137175
C	-3.197423	2.120190	-3.452705
C	-2.673745	3.365346	-3.821134
C	-2.011361	4.142876	-2.867306
C	-1.859431	3.707468	-1.535503
C	-3.699569	0.296444	-1.750062
C	-3.728770	-0.730963	-2.891583
C	-5.114848	0.496778	-1.169718
C	-1.094852	4.597276	-0.555992
C	0.385175	4.717166	-0.962550
C	-1.726022	5.997280	-0.423965
O	5.201758	0.289536	0.501463
O	3.425245	0.196817	-3.488873
H	4.541514	-3.093868	-2.766766
H	1.869894	-3.445398	-2.372533
H	1.369111	-3.134580	0.285920
H	3.719930	-2.646059	1.535292
H	5.694355	-2.615615	-0.356334
H	-3.545876	2.353080	3.226755

H	-3.608593	0.742708	4.777431
H	-1.847587	0.715764	5.077837
H	-2.680720	-0.796977	4.638898
H	-4.900635	3.285523	1.569810
H	-3.547698	4.428672	1.363037
H	-4.242350	3.625873	-0.074138
H	-2.575560	-4.748793	2.343926
H	-0.524652	-5.284516	3.653364
H	0.991721	-3.448687	4.393072
H	-3.314995	-1.386437	0.934832
H	-4.790587	-3.071457	-0.055692
H	-4.280419	-4.327536	1.098517
H	-3.123221	-3.716598	-0.128789
H	-5.599025	-1.775281	1.912318
H	-4.880274	-2.857437	3.151186
H	-4.468699	-1.113008	3.127747
H	0.376422	0.197508	3.640168
H	2.863791	-0.143179	3.833586
H	2.633396	-1.913976	3.726779
H	2.204453	-0.854432	2.331295
H	1.418108	0.102037	5.896874
H	1.243233	-1.677034	5.949335
H	-0.214271	-0.642795	5.968617
H	-3.713802	1.508389	-4.205528
H	-2.778682	3.726009	-4.855009
H	-1.592910	5.117477	-3.161027
H	-3.074064	-0.130768	-0.934902
H	-4.055952	-1.716647	-2.503702
H	-2.730094	-0.864273	-3.352107
H	-4.445641	-0.443174	-3.689094
H	-5.555327	-0.475662	-0.864189
H	-5.109614	1.159154	-0.282255
H	-5.785697	0.950636	-1.929238
H	-1.126623	4.111057	0.439904
H	0.955060	5.300685	-0.210517
H	0.865340	3.724133	-1.046230
H	0.491604	5.230301	-1.941489
H	-1.196422	6.588116	0.351619
H	-1.652595	6.564514	-1.375281
H	-2.798222	5.950057	-0.148812
C	1.459733	-0.279963	-0.557654
N	1.337490	0.786296	0.275461
N	0.241232	-0.794044	-0.870406
C	-0.058374	-1.704153	-1.890234
C	0.262568	-1.447127	-3.246744
C	-0.788604	-2.880971	-1.602902
C	-0.092222	-2.354813	-4.253268
H	0.786709	-0.516965	-3.504005
C	-1.143369	-3.779206	-2.618835
H	-1.052355	-3.093592	-0.555789
C	-0.798994	-3.542693	-3.965712
H	0.178193	-2.127461	-5.296929

H	-1.698207	-4.694581	-2.356897
C	2.290160	1.775087	0.523118
C	3.070392	2.367384	-0.503690
C	2.407823	2.325837	1.824498
C	3.963295	3.410169	-0.222082
H	2.943976	2.025326	-1.539389
C	3.294843	3.373155	2.089976
H	1.783714	1.912820	2.630430
C	4.107216	3.930250	1.077820
H	4.553529	3.843755	-1.044935
H	3.362740	3.770714	3.115283
C	-1.209969	-4.495501	-5.062290
H	-1.340609	-5.527008	-4.679242
H	-2.177136	-4.193054	-5.519920
H	-0.462192	-4.525959	-5.879897
C	5.091065	5.032654	1.384936
H	6.013326	4.631610	1.859081
H	5.401919	5.568657	0.466696
H	4.666519	5.777873	2.088245

TolNCNTol

(-689.5600471)

C	0.000670	-1.149713	0.008751
N	1.110765	-1.273858	-0.521642
N	-1.110269	-1.264751	0.539781
C	-2.328267	-0.612549	0.276640
C	-2.500679	0.298985	-0.786306
C	-3.424350	-0.899373	1.116052
C	-3.745230	0.905715	-0.994795
H	-1.651718	0.525664	-1.448863
C	-4.661025	-0.284297	0.894988
H	-3.283133	-1.612537	1.940275
C	-4.849373	0.630154	-0.162864
H	-3.863058	1.614482	-1.829206
H	-5.504812	-0.521477	1.561594
C	2.330232	-0.619800	-0.271367
C	2.503377	0.309745	0.779070
C	3.423902	-0.918563	-1.105724
C	3.745192	0.919278	0.977766
H	1.653553	0.546011	1.437266
C	4.662492	-0.298144	-0.893840
H	3.283593	-1.643370	-1.919785
C	4.851118	0.630201	0.147974
H	3.861499	1.641338	1.801250
H	5.506544	-0.543416	-1.556732
C	-6.189708	1.286044	-0.389262
H	-6.984687	0.532115	-0.568441
H	-6.504998	1.879599	0.494470
H	-6.168289	1.966894	-1.261862
C	6.185690	1.295127	0.381737
H	6.098205	2.401467	0.355030
H	6.600612	1.030633	1.377362
H	6.928966	0.996011	-0.382253

THF

(-232.1576236)

O	0.000054	-1.258941	-0.000192
C	-1.164521	-0.427103	0.135790
C	-0.731149	0.995559	-0.236065
C	0.730970	0.995722	0.235952
C	1.164633	-0.426970	-0.135544
H	-1.967258	-0.826367	-0.520632
H	-1.535523	-0.468259	1.188983
H	-0.779722	1.141489	-1.335891
H	-1.354015	1.776811	0.241967
H	1.353724	1.776952	-0.242259
H	0.779502	1.141959	1.335737
H	1.536189	-0.468253	-1.188528
H	1.967070	-0.826049	0.521355

FpH

(-1683.9474625)

Fe	-0.140967	0.000211	-0.203736
C	-1.322588	-1.274353	-0.014998
C	-1.323775	1.273633	-0.014689
C	1.618475	-1.158844	-0.213387
C	1.332053	-0.712825	1.131046
C	1.331872	0.712869	1.131447
C	1.618263	1.159673	-0.212705
C	1.794652	0.000661	-1.034441
O	-2.108921	2.133956	0.094588
O	-2.106687	-2.135612	0.094552
H	1.683247	-2.199790	-0.547469
H	1.141695	-1.358613	1.995043
H	1.141596	1.358101	1.995875
H	1.682730	2.200786	-0.546299
H	2.014129	0.001019	-2.106894
H	-0.567094	0.001378	-1.639871