Insertion reactions of dicyclohexylcarbodiimide with amino-boranes, -boryls and -borylenes

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Supporting Information (25 pages)

Contents

1. Synthetic and characterizing data for 2b

To a solution of $^{i}Pr_2NH$ (1.23 cm^3, 15 mmol) in diethyl ether (10 cm^3) was added dropwise a solution of $^{n}BuLi$ (9.38 cm^3 of a 1.6M in hexanes, 15 mmol) at -30°C. The reaction mixture was allowed to stir for 1 h, cooled to -80°C and CyNCNCy (3.16 g, 15.3 mmol) in diethyl ether (20 cm^3) added. Slow warming to room temperature and stirring for 12 h was followed by the addition of water and the removal of volatiles *in vacuo*. The residue was then dissolved in water (20cm^3), extracted repeatedly with dichloromethane (3 x 30cm^3) and the combined extracts dried over $MgSO_4$. Filtration, removal of solvent *in vacuo* and recrystallization from hot hexanes yielded $^{i}Pr_2NC(NCy)(NHCy)$ as a white crystalline solid which was used in subsequent chemistry without further purification (isolated yield: 1.26 g, 27 %). To a solution of $^{i}Pr_2NC(NCy)(NHCy)$ (1.26 g, 4.08 mmol) in diethyl ether (20 cm^3) was added $^{n}BuLi$ (2.55 cm^3 of a 1.6 M solution in hexanes, 4.08 mmol) at -30°C. The reaction mixture was stirred for 1 h, cooled to -80°C and added dropwise to a solution of BCl_3 (4.08 cm^3, 4.08 mmol) in diethyl ether (40 cm^3). After warming to room temperature for and stirring for 12 h, volatiles were removed *in vacuo* and the residue extracted with hexanes, concentrated to ca. 20 cm^3 and cooled to -30°C to yield **2b** as a white microcrystalline solid. Isolated yield (for second step): 0.477 g, 30 %.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.86 – 1.79 (m, 32H, CH_2 of Cy and CH_3 of ^{i}Pr), 2.29 (q, $^{3}J_{HH}$= 7.9 Hz, 2H, CH of Cy), 3.22 (m, 2H, CH of ^{i}Pr). ^{13}C NMR (76 MHz, C_6D_6) δ 22.4 (CH_3 of ^{i}Pr), 25.3 (4-CH_2 of NCy), 25.5 (3-CH_2 of NCy), 33.2 (2-CH_2 of NCy), 53.1 (CH of Cy), 176.2 (guanidinate quaternary). ^{11}B NMR (96 MHz, $C_6D_5CD_3$) δ 4.6 (s, fwhm ca. 11 Hz). IR (benzene soln, cm^{-1}) 1650 [ν(CN)]. EI-MS, m/z (%): 387 (weak) M^+, 344 (25 %) $(M-^{i}Pr)^+$, 309 (100 %) $(M-^{i}Pr-Cl)^+$. Elemental analysis: (calc. for $C_{19}H_{36}BCl_2N_3$) C 58.78, H 9.35, N 10.82; (obs.) C 58.72, H 9.11, N 10.46.

2. Synthetic and characterizing data for $CpFe(CO)_2B(NBz_2)Cl$

A solution of Bz_2NBCl_2[§] (0.40 g, 1.43 mmol) in diethyl ether (20 cm^3) was added to a suspension of $Na[CpFe(CO)_2]$ (0.29 g, 1.44 mmol) in diethyl ether (20 cm^3) and the mixture stirred for 12 h. Volatiles were removed *in vacuo* and the residue extracted into hexanes, concentrated (to ca. 5 cm^3) and cooled to -30°C yielding crystals suitable for X-ray diffraction. Yield of crystalline product: 0.063 g, 11%.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.25 (s, 5H, Cp), 4.68 (s, 2H, *CH_2*Ph), 4.87 (s, 2H, *CH_2*Ph), 7.13 – 7.47 (m, 10H, CH_2*Ph*). ^{13}C NMR (76 MHz, CD_2Cl_2), δ 51.8 (CH_2), 55.0 (CH_2), 83.4 (Cp), 126.1 (*ortho*-C of Ph), 126.3 (*ortho*-C of Ph), 126.8 (*para*-C of Ph), 127.7 (*meta*-C of Ph), 127.8 (*meta*-C of Ph), 137.9 (*ipso*-C of Ph), 138.3 (ipso-C of Ph), 214.4 (CO). ^{11}B NMR (96 MHz, CD_2Cl_2) δ 58.3 (b, fwhm ca. 377 Hz). IR (CD_2Cl_2 soln, cm^{-1}) ν (CO) 1996, 1933. MS (EI): M^+ = 419 (weak), $(M-2CO)^+$ = 362 (100%); exact mass (calc.) m/z 419.0541, (obs.) 419.0544.

[§] Bz_2NBCl_2: W. Gerard, H.R. Hudson, E.F. Mooney, *J. Chem. Soc.*, 1960, 5168.

3. Crystallographic data for $CpFe(CO)_2B(NBz_2)Cl$

Table 1. Crystal data and structure refinement for $CpFe(CO)_2B(NBz_2)Cl$.

Empirical formula	C21 H19 B Cl Fe N O2	
Formula weight	419.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.1425(3) Å	α= 91.3820(10)°.
	b = 12.7613(3) Å	β= 105.8800(10)°.
	c = 13.5593(4) Å	γ = 102.8330(10)°.
Volume	1962.32(9) $Å^3$	
Z	4	
Density (calculated)	1.420 Mg/m^3	
Absorption coefficient	0.920 mm^{-1}	
F(000)	864	
Crystal size	0.25 x 0.13 x 0.05 mm^3	
Theta range for data collection	3.51 to 26.37°.	
Index ranges	-15<=h<=15, -15<=k<=15, -16<=l<=16	
Reflections collected	14830	
Independent reflections	7986 [R(int) = 0.0575]	
Completeness to theta = 26.37°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9554 and 0.8026	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7986 / 0 / 472	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0563, wR2 = 0.1108	
R indices (all data)	R1 = 0.0901, wR2 = 0.1231	
Largest diff. peak and hole	1.424 and -0.589 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $CpFe(CO)_2B(NBz_2)Cl$.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7392(4)	-1037(3)	6692(3)	37(1)
C(2)	7973(4)	-869(3)	7766(3)	36(1)
C(3)	9072(4)	-1121(3)	7925(3)	33(1)
C(4)	9181(4)	-1426(3)	6957(3)	33(1)
C(5)	8138(4)	-1373(3)	6203(3)	38(1)
C(6)	8438(4)	1282(3)	7191(3)	35(1)
C(7)	9540(4)	755(3)	6029(3)	32(1)
C(8)	12719(3)	1336(3)	8994(3)	31(1)
C(9)	13121(3)	559(3)	9767(3)	28(1)
C(10)	12433(4)	-452(3)	9794(3)	35(1)
C(11)	12832(4)	-1128(3)	10536(3)	40(1)
C(12)	13909(4)	-792(4)	11254(3)	43(1)
C(13)	14609(4)	218(4)	11228(3)	41(1)
C(14)	14218(3)	889(3)	10491(3)	32(1)
C(15)	12016(3)	343(3)	7294(3)	25(1)
C(16)	12830(3)	1108(3)	6823(3)	25(1)
C(17)	13610(4)	719(3)	6420(3)	35(1)
C(18)	14395(4)	1408(4)	6007(3)	48(1)
C(19)	14403(4)	2492(4)	6004(3)	51(1)
C(20)	13626(4)	2881(4)	6387(3)	46(1)
C(21)	12839(4)	2193(3)	6796(3)	33(1)
C(22)	10862(4)	4146(3)	7084(3)	42(1)
C(23)	10819(4)	3902(3)	8078(4)	40(1)
C(24)	11879(4)	4415(4)	8775(4)	49(1)
C(25)	12578(5)	4988(4)	8239(4)	58(1)
C(26)	11954(4)	4839(4)	7184(4)	48(1)
C(27)	11701(4)	6909(3)	7860(3)	34(1)
C(28)	10517(3)	5950(3)	8987(3)	31(1)
C(29)	7425(3)	5358(3)	5908(3)	27(1)
C(30)	6935(3)	4361(3)	5147(3)	24(1)
C(31)	7485(3)	3522(3)	5174(3)	32(1)

C(32)	7007(4)	2634(4)	4445(3)	43(1)
C(33)	5964(4)	2574(4)	3698(3)	43(1)
C(34)	5403(4)	3404(4)	3668(3)	40(1)
C(35)	5883(3)	4287(3)	4379(3)	28(1)
C(36)	7979(3)	4626(3)	7562(3)	24(1)
C(37)	7245(3)	5136(3)	8072(2)	22(1)
C(38)	6301(3)	4486(3)	8335(3)	29(1)
C(39)	5636(3)	4937(3)	8824(3)	34(1)
C(40)	5878(3)	6039(3)	9045(3)	30(1)
C(41)	6805(3)	6695(3)	8785(3)	27(1)
C(42)	7479(3)	6244(3)	8302(3)	24(1)
N(1)	11685(3)	870(2)	8110(2)	25(1)
N(2)	8400(3)	5275(2)	6796(2)	22(1)
O(1)	8051(3)	2010(2)	7309(2)	51(1)
O(2)	9869(3)	1156(2)	5375(2)	50(1)
O(3)	12149(3)	7779(2)	7786(2)	52(1)
O(4)	10201(3)	6225(2)	9656(2)	47(1)
Cl(1)	10369(1)	1434(1)	9278(1)	34(1)
Cl(2)	9863(1)	6321(1)	5744(1)	33(1)
Fe(1)	8983(1)	164(1)	6996(1)	24(1)
Fe(2)	11062(1)	5568(1)	7997(1)	23(1)
B(1)	10524(4)	843(3)	8088(3)	26(1)
B(2)	9598(4)	5671(3)	6877(3)	24(1)

Table 3. Bond lengths [Å] and angles [°] for $CpFe(CO)_2B(NBz_2)Cl$.

C(1)-C(5)	1.391(6)
C(1)-C(2)	1.422(6)
C(1)-Fe(1)	2.115(4)
C(2)-C(3)	1.403(6)
C(2)-Fe(1)	2.093(4)
C(3)-C(4)	1.409(5)
C(3)-Fe(1)	2.095(3)
C(4)-C(5)	1.409(6)
C(4)-Fe(1)	2.096(4)
C(5)-Fe(1)	2.111(4)
C(6)-O(1)	1.156(5)
C(6)-Fe(1)	1.744(4)
C(7)-O(2)	1.154(4)
C(7)-Fe(1)	1.747(4)
C(8)-N(1)	1.476(4)
C(8)-C(9)	1.519(5)
C(9)-C(10)	1.380(5)
C(9)-C(14)	1.390(5)
C(10)-C(11)	1.397(5)
C(11)-C(12)	1.370(6)
C(12)-C(13)	1.384(6)
C(13)-C(14)	1.385(6)
C(15)-N(1)	1.472(4)
C(15)-C(16)	1.511(5)
C(16)-C(21)	1.383(5)
C(16)-C(17)	1.387(5)
C(17)-C(18)	1.391(6)
C(18)-C(19)	1.382(7)
C(19)-C(20)	1.367(7)
C(20)-C(21)	1.390(5)
C(22)-C(26)	1.390(6)
C(22)-C(23)	1.403(6)
C(22)-Fe(2)	2.102(4)
C(23)-C(24)	1.381(6)
C(23)-Fe(2)	2.090(4)
C(24)-C(25)	1.367(6)

C(24)-Fe(2)	2.101(5)
C(25)-C(26)	1.410(6)
C(25)-Fe(2)	2.082(5)
C(26)-Fe(2)	2.076(5)
C(27)-O(3)	1.142(4)
C(27)-Fe(2)	1.752(4)
C(28)-O(4)	1.153(4)
C(28)-Fe(2)	1.753(4)
C(29)-N(2)	1.465(4)
C(29)-C(30)	1.517(5)
C(30)-C(31)	1.379(5)
C(30)-C(35)	1.392(5)
C(31)-C(32)	1.391(5)
C(32)-C(33)	1.374(6)
C(33)-C(34)	1.378(6)
C(34)-C(35)	1.374(5)
C(36)-N(2)	1.473(4)
C(36)-C(37)	1.506(5)
C(37)-C(42)	1.389(5)
C(37)-C(38)	1.394(5)
C(38)-C(39)	1.380(5)
C(39)-C(40)	1.379(5)
C(40)-C(41)	1.381(5)
C(41)-C(42)	1.383(5)
N(1)-B(1)	1.394(5)
N(2)-B(2)	1.402(5)
Cl(1)-B(1)	1.837(4)
Cl(2)-B(2)	1.835(4)
Fe(1)-B(1)	2.036(4)
Fe(2)-B(2)	2.030(4)

C(5)-C(1)-C(2)	107.9(4)
C(5)-C(1)-Fe(1)	70.6(2)
C(2)-C(1)-Fe(1)	69.4(2)
C(3)-C(2)-C(1)	107.8(4)
C(3)-C(2)-Fe(1)	70.5(2)
C(1)-C(2)-Fe(1)	71.1(2)
C(2)-C(3)-C(4)	107.9(3)

C(2)-C(3)-Fe(1)	70.4(2)
C(4)-C(3)-Fe(1)	70.4(2)
C(5)-C(4)-C(3)	107.9(4)
C(5)-C(4)-Fe(1)	71.0(2)
C(3)-C(4)-Fe(1)	70.3(2)
C(1)-C(5)-C(4)	108.4(4)
C(1)-C(5)-Fe(1)	70.9(2)
C(4)-C(5)-Fe(1)	69.9(2)
O(1)-C(6)-Fe(1)	178.4(4)
O(2)-C(7)-Fe(1)	177.5(4)
N(1)-C(8)-C(9)	116.1(3)
C(10)-C(9)-C(14)	118.7(4)
C(10)-C(9)-C(8)	122.8(3)
C(14)-C(9)-C(8)	118.5(3)
C(9)-C(10)-C(11)	120.6(4)
C(12)-C(11)-C(10)	120.4(4)
C(11)-C(12)-C(13)	119.4(4)
C(12)-C(13)-C(14)	120.4(4)
C(13)-C(14)-C(9)	120.6(4)
N(1)-C(15)-C(16)	113.7(3)
C(21)-C(16)-C(17)	118.6(3)
C(21)-C(16)-C(15)	122.2(3)
C(17)-C(16)-C(15)	119.2(3)
C(16)-C(17)-C(18)	120.7(4)
C(19)-C(18)-C(17)	119.8(4)
C(20)-C(19)-C(18)	120.0(4)
C(19)-C(20)-C(21)	120.3(4)
C(16)-C(21)-C(20)	120.7(4)
C(26)-C(22)-C(23)	107.1(4)
C(26)-C(22)-Fe(2)	69.6(3)
C(23)-C(22)-Fe(2)	70.0(2)
C(24)-C(23)-C(22)	108.8(4)
C(24)-C(23)-Fe(2)	71.2(2)
C(22)-C(23)-Fe(2)	70.9(2)
C(25)-C(24)-C(23)	108.0(4)
C(25)-C(24)-Fe(2)	70.2(3)
C(23)-C(24)-Fe(2)	70.3(2)
C(24)-C(25)-C(26)	108.8(5)

C(24)-C(25)-Fe(2)	71.7(3)
C(26)-C(25)-Fe(2)	70.0(3)
C(22)-C(26)-C(25)	107.3(4)
C(22)-C(26)-Fe(2)	71.6(3)
C(25)-C(26)-Fe(2)	70.4(3)
O(3)-C(27)-Fe(2)	178.0(4)
O(4)-C(28)-Fe(2)	177.4(4)
N(2)-C(29)-C(30)	114.6(3)
C(31)-C(30)-C(35)	118.0(4)
C(31)-C(30)-C(29)	123.2(3)
C(35)-C(30)-C(29)	118.8(3)
C(30)-C(31)-C(32)	120.8(4)
C(33)-C(32)-C(31)	120.2(4)
C(32)-C(33)-C(34)	119.6(4)
C(35)-C(34)-C(33)	120.2(4)
C(34)-C(35)-C(30)	121.2(4)
N(2)-C(36)-C(37)	113.8(3)
C(42)-C(37)-C(38)	118.1(3)
C(42)-C(37)-C(36)	122.2(3)
C(38)-C(37)-C(36)	119.7(3)
C(39)-C(38)-C(37)	120.5(3)
C(40)-C(39)-C(38)	120.6(3)
C(39)-C(40)-C(41)	119.6(4)
C(40)-C(41)-C(42)	119.9(3)
C(41)-C(42)-C(37)	121.3(3)
B(1)-N(1)-C(15)	123.9(3)
B(1)-N(1)-C(8)	124.2(3)
C(15)-N(1)-C(8)	111.7(3)
B(2)-N(2)-C(29)	124.8(3)
B(2)-N(2)-C(36)	123.3(3)
C(29)-N(2)-C(36)	111.7(3)
C(6)-Fe(1)-C(7)	91.26(18)
C(6)-Fe(1)-B(1)	90.01(18)
C(7)-Fe(1)-B(1)	91.13(17)
C(6)-Fe(1)-C(2)	95.43(17)
C(7)-Fe(1)-C(2)	162.28(17)
B(1)-Fe(1)-C(2)	105.23(16)
C(6)-Fe(1)-C(3)	126.35(17)

C(7)-Fe(1)-C(3)	141.31(18)
B(1)-Fe(1)-C(3)	81.24(15)
C(2)-Fe(1)-C(3)	39.14(15)
C(6)-Fe(1)-C(4)	160.87(17)
C(7)-Fe(1)-C(4)	105.88(17)
B(1)-Fe(1)-C(4)	97.93(16)
C(2)-Fe(1)-C(4)	65.73(16)
C(3)-Fe(1)-C(4)	39.29(15)
C(6)-Fe(1)-C(5)	131.45(18)
C(7)-Fe(1)-C(5)	97.91(17)
B(1)-Fe(1)-C(5)	136.94(17)
C(2)-Fe(1)-C(5)	65.50(15)
C(3)-Fe(1)-C(5)	65.61(15)
C(4)-Fe(1)-C(5)	39.12(16)
C(6)-Fe(1)-C(1)	98.40(18)
C(7)-Fe(1)-C(1)	123.24(17)
B(1)-Fe(1)-C(1)	144.12(16)
C(2)-Fe(1)-C(1)	39.50(15)
C(3)-Fe(1)-C(1)	65.65(16)
C(4)-Fe(1)-C(1)	65.25(16)
C(5)-Fe(1)-C(1)	38.42(16)
C(27)-Fe(2)-C(28)	92.48(18)
C(27)-Fe(2)-B(2)	88.81(18)
C(28)-Fe(2)-B(2)	93.16(17)
C(27)-Fe(2)-C(26)	97.39(18)
C(28)-Fe(2)-C(26)	161.88(18)
B(2)-Fe(2)-C(26)	102.17(17)
C(27)-Fe(2)-C(25)	97.3(2)
C(28)-Fe(2)-C(25)	124.05(19)
B(2)-Fe(2)-C(25)	141.73(18)
C(26)-Fe(2)-C(25)	39.64(18)
C(27)-Fe(2)-C(23)	160.89(18)
C(28)-Fe(2)-C(23)	102.30(17)
B(2)-Fe(2)-C(23)	102.23(17)
C(26)-Fe(2)-C(23)	65.27(17)
C(25)-Fe(2)-C(23)	64.40(18)
C(27)-Fe(2)-C(24)	128.47(19)
C(28)-Fe(2)-C(24)	96.58(18)

B(2)-Fe(2)-C(24)	140.71(18)
C(26)-Fe(2)-C(24)	65.41(18)
C(25)-Fe(2)-C(24)	38.14(17)
C(23)-Fe(2)-C(24)	38.49(16)
C(27)-Fe(2)-C(22)	129.94(18)
C(28)-Fe(2)-C(22)	136.86(18)
B(2)-Fe(2)-C(22)	81.91(16)
C(26)-Fe(2)-C(22)	38.87(17)
C(25)-Fe(2)-C(22)	65.25(19)
C(23)-Fe(2)-C(22)	39.10(16)
C(24)-Fe(2)-C(22)	65.18(17)
N(1)-B(1)-Cl(1)	114.2(3)
N(1)-B(1)-Fe(1)	130.3(3)
Cl(1)-B(1)-Fe(1)	115.4(2)
N(2)-B(2)-Cl(2)	113.7(3)
N(2)-B(2)-Fe(2)	130.6(3)
Cl(2)-B(2)-Fe(2)	115.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $CpFe(CO)_2B(NBz_2)Cl$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

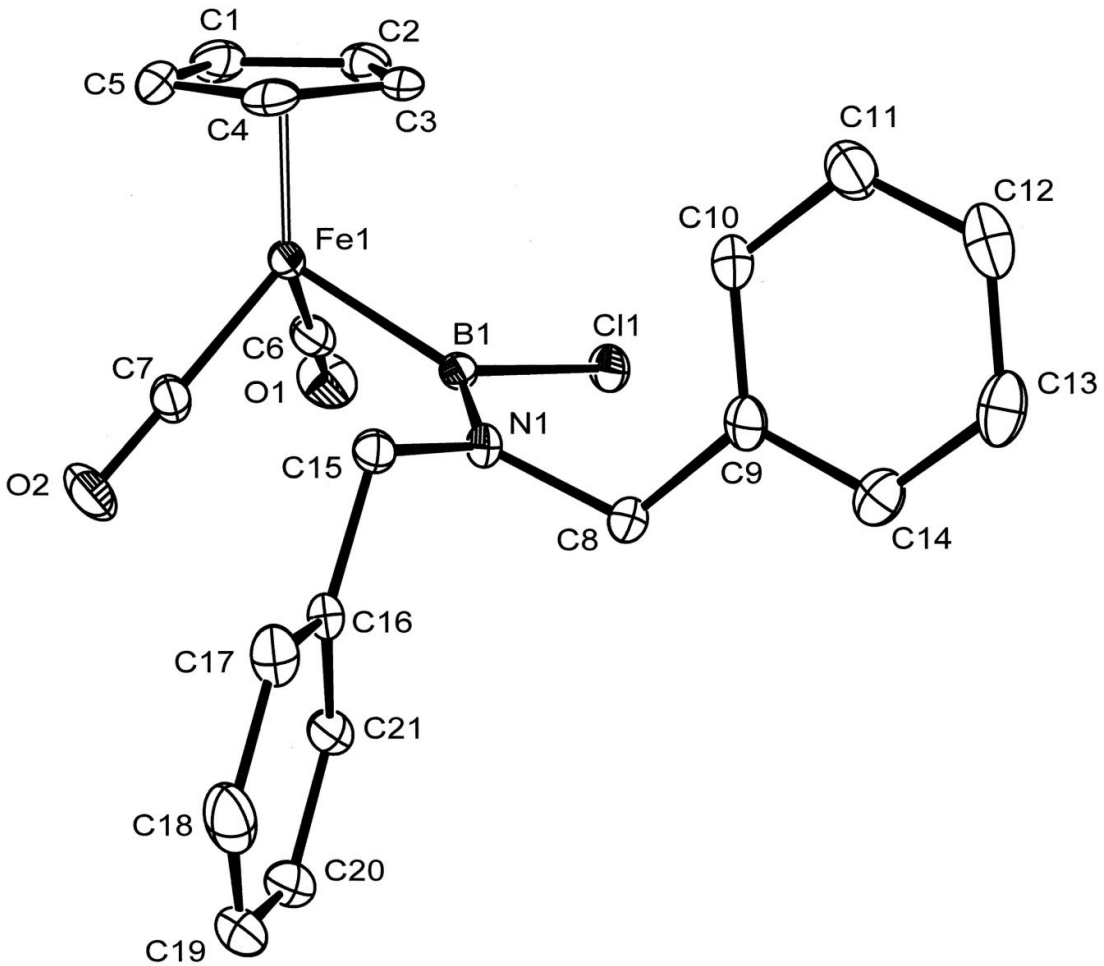
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(2)	35(2)	49(3)	7(2)	9(2)	0(2)
C(2)	51(3)	25(2)	37(2)	0(2)	26(2)	3(2)
C(3)	45(3)	17(2)	28(2)	6(2)	3(2)	-4(2)
C(4)	38(2)	16(2)	47(2)	1(2)	18(2)	2(2)
C(5)	48(3)	30(2)	27(2)	-5(2)	11(2)	-8(2)
C(6)	44(3)	30(2)	32(2)	9(2)	14(2)	8(2)
C(7)	43(2)	30(2)	22(2)	3(2)	9(2)	9(2)
C(8)	33(2)	32(2)	21(2)	-1(2)	5(2)	-2(2)
C(9)	32(2)	36(2)	20(2)	-3(2)	11(2)	11(2)
C(10)	38(2)	41(2)	22(2)	3(2)	4(2)	5(2)
C(11)	49(3)	42(2)	32(2)	9(2)	12(2)	12(2)
C(12)	54(3)	56(3)	27(2)	8(2)	10(2)	31(2)
C(13)	34(2)	57(3)	32(2)	-6(2)	0(2)	22(2)
C(14)	33(2)	33(2)	31(2)	-7(2)	10(2)	9(2)
C(15)	31(2)	20(2)	23(2)	3(2)	6(2)	6(2)
C(16)	27(2)	28(2)	16(2)	2(2)	4(2)	4(2)
C(17)	36(2)	44(2)	26(2)	3(2)	7(2)	12(2)
C(18)	35(3)	82(4)	29(2)	6(2)	13(2)	11(2)
C(19)	47(3)	65(3)	30(2)	12(2)	12(2)	-14(3)
C(20)	61(3)	35(2)	32(2)	5(2)	14(2)	-9(2)
C(21)	43(3)	27(2)	27(2)	4(2)	12(2)	2(2)
C(22)	51(3)	39(2)	32(2)	-15(2)	-8(2)	32(2)
C(23)	41(3)	22(2)	69(3)	11(2)	28(2)	13(2)
C(27)	37(2)	33(2)	34(2)	-2(2)	13(2)	8(2)
C(28)	34(2)	30(2)	29(2)	0(2)	8(2)	9(2)
C(29)	27(2)	29(2)	28(2)	1(2)	6(2)	12(2)
C(30)	22(2)	32(2)	21(2)	3(2)	10(2)	5(2)
C(31)	28(2)	39(2)	28(2)	-2(2)	5(2)	11(2)
C(32)	40(3)	46(3)	42(3)	-9(2)	12(2)	13(2)
C(33)	44(3)	47(3)	31(2)	-15(2)	11(2)	-4(2)
C(34)	36(2)	55(3)	25(2)	6(2)	5(2)	4(2)
C(35)	26(2)	38(2)	21(2)	7(2)	9(2)	4(2)
C(36)	24(2)	20(2)	28(2)	2(2)	8(2)	5(2)

C(37)	20(2)	27(2)	17(2)	4(2)	3(1)	6(2)
C(38)	27(2)	26(2)	31(2)	-2(2)	9(2)	4(2)
C(39)	24(2)	40(2)	38(2)	7(2)	14(2)	2(2)
C(40)	28(2)	43(2)	23(2)	2(2)	8(2)	16(2)
C(41)	34(2)	25(2)	20(2)	0(2)	4(2)	8(2)
C(42)	22(2)	26(2)	26(2)	1(2)	10(2)	4(2)
N(1)	30(2)	26(2)	17(2)	0(1)	5(1)	3(1)
N(2)	26(2)	24(2)	19(2)	1(1)	5(1)	11(1)
O(1)	71(2)	36(2)	60(2)	10(2)	27(2)	30(2)
O(2)	69(2)	53(2)	35(2)	20(2)	25(2)	15(2)
O(3)	69(2)	26(2)	58(2)	0(1)	23(2)	-2(2)
O(4)	54(2)	56(2)	33(2)	-9(1)	16(2)	17(2)
Cl(1)	49(1)	32(1)	22(1)	-4(1)	15(1)	4(1)
Cl(2)	43(1)	41(1)	24(1)	10(1)	16(1)	16(1)
Fe(1)	31(1)	21(1)	20(1)	3(1)	8(1)	5(1)
Fe(2)	24(1)	23(1)	23(1)	1(1)	7(1)	7(1)
B(1)	39(3)	15(2)	20(2)	0(2)	8(2)	2(2)
B(2)	34(3)	24(2)	18(2)	-1(2)	9(2)	12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $CpFe(CO)_2B(NBz_2)Cl$.

	x	y	z	U(eq)
H(1)	6644	-939	6372	45
H(2)	7677	-633	8274	43
H(3)	9630	-1092	8557	40
H(4)	9826	-1627	6836	40
H(5)	7977	-1535	5498	45
H(8A)	12540	1914	9354	37
H(8B)	13372	1657	8731	37
H(10)	11697	-686	9313	42
H(11)	12363	-1810	10543	48
H(12)	14168	-1238	11754	52
H(13)	15345	447	11708	50
H(14)	14695	1566	10480	39
H(15A)	11305	1	6755	30
H(15B)	12398	-218	7578	30
H(17)	13609	-10	6425	42
H(18)	14911	1139	5734	58
H(19)	14937	2958	5741	62
H(20)	13624	3609	6373	55
H(21)	12314	2464	7054	40
H(22)	10271	3893	6472	50
H(23)	10182	3467	8241	49
H(24)	12082	4377	9484	58
H(25)	13340	5406	8524	69
H(26)	12223	5147	6653	58
H(29A)	7693	5968	5550	33
H(29B)	6792	5506	6156	33
H(31)	8183	3549	5685	39
H(32)	7396	2080	4464	51
H(33)	5640	1977	3216	52
H(34)	4696	3368	3164	48
H(35)	5499	4845	4348	34
H(36A)	8654	4512	8088	29
H(36B)	7514	3926	7227	29
H(38)	6118	3742	8179	34

H(39)	5018	4493	9007	41
H(40)	5420	6338	9367	36
H(41)	6977	7439	8934	33
H(42)	8101	6691	8129	29


C1
C2
C5
C4
C3
Fe1
C11
C12
C10
C6
B1
Cl1
C7
O1
C13
N1
C15
C9
O2
C8
C14
C16
C17
C21
C18
C20
C19

4. X, y, z file and total energy for the fully optimized (DFT) geometry of 4a

H	−3.105924	2.973043	−3.448855
H	−3.023318	0.447191	1.048427
H	−2.481262	−2.015546	2.044033
H	−1.277386	−3.784807	−3.082734
H	−2.330823	0.635329	−2.955800
H	−0.965424	−4.726409	−1.625784
H	−1.773748	−2.405519	−1.073603
C	−2.439939	0.231863	1.935384
C	−2.157366	−1.068918	2.463281
H	−2.447313	1.603620	−1.479131
C	−2.040325	2.781611	−3.265586
C	−0.608517	−3.868674	−2.211716
C	−1.891462	1.490488	−2.423888
H	−1.576423	2.629385	−4.252797
C	−0.725486	−2.584482	−1.353678
C	−1.407389	−0.896126	3.684237
C	−1.842731	1.198314	2.804793
H	−0.807701	−1.173601	−2.981864
H	−1.933661	4.226837	−1.643615
H	−1.047093	−1.694403	4.323253
H	−1.883387	2.275009	2.685989
H	−1.453940	4.881920	−3.208588
C	−1.381718	3.992613	−2.568816
H	0.877790	−4.989927	−3.344051
C	−1.214112	0.493616	3.895253
H	−0.153769	−2.731471	−0.423453
C	−0.170785	−1.355824	−2.104799
C	0.839414	−4.105714	−2.694012
H	0.826604	−2.729159	−4.378471
N	−0.273785	−0.076969	−1.277678
C	−0.408886	1.209869	−2.087192
H	−0.684234	0.947922	4.724301
B	−0.265052	−0.074781	0.074386
Fe	−0.265052	−0.074781	1.969431
H	0.137910	1.013438	−3.019275
H	1.483690	−4.324627	−1.827277
C	1.388174	−2.870868	−3.441312
H	−0.229228	2.570852	−0.405189
C	0.096241	3.705577	−2.226068
C	1.283063	−1.588815	−2.577724
C	0.251046	2.414588	−1.385913
C	0.909748	−1.453837	1.928924
H	0.675936	3.602478	−3.156854
H	2.436714	−3.026795	−3.727202
H	1.643905	−0.720189	−3.145401
H	0.537575	4.547783	−1.676789
O	1.665665	−2.328722	1.894829
H	1.929351	−1.686479	−1.691602
C	1.042731	1.181881	1.964805
H	1.312778	2.202350	−1.199844
O	1.879047	1.980182	1.962946

E = -27528.71 kJ mol^{-1}

5. X, y, z file and total energy for the fully optimized (DFT) geometry of CyNCNCy

N	2.175202	−1.478995	0.734799
C	3.070384	−1.801067	−0.046673
N	3.961563	−2.020395	−0.868581
C	1.283496	−2.447181	1.434459
C	5.322578	−2.462284	−0.442993
C	0.745106	−1.780577	2.718141
C	−0.122142	−2.750293	3.553454
C	0.635635	−4.057259	3.881142
C	1.144187	−4.741458	2.593167
C	2.008215	−3.779304	1.747437
C	5.763770	−3.665712	−1.301044
C	7.158961	−4.170214	−0.866054
C	8.212581	−3.038355	−0.896766
C	7.748047	−1.800503	−0.093332
C	6.347130	−1.312473	−0.538951
H	0.176467	−0.880719	2.446295
H	1.606520	−1.442943	3.315784
H	−0.443966	−2.252473	4.479288
H	−1.040391	−2.996429	2.995115
H	1.495609	−3.824867	4.531378
H	−0.011408	−4.743514	4.446590
H	1.731047	−5.638780	2.839113
H	0.282561	−5.084609	1.997443
H	2.932620	−3.540239	2.298544
H	2.309237	−4.262061	0.806368
H	0.432460	−2.653556	0.764631
H	7.473033	−5.002177	−1.512628
H	7.092396	−4.577734	0.156644
H	5.277766	−2.788144	0.609230
H	5.782522	−3.351701	−2.356665
H	5.017296	−4.468325	−1.219824
H	8.393121	−2.743442	−1.943118
H	9.171413	−3.405392	−0.502002
H	6.016057	−0.470093	0.084495
H	6.380251	−0.952908	−1.579389
H	7.713549	−2.056462	0.978818
H	8.477343	−0.984201	−0.195091

E = --**19632.65** kJ mol^{-1}

6. X, y, z file and total energy for the fully optimized (DFT) geometry of 4a·CyNCNCy

H	−0.073034	4.405516	−3.281292
H	−1.689325	0.300239	0.765096
H	−0.625667	−0.547148	3.109951
H	−1.042533	−3.697750	−2.569998
H	−0.940781	2.333205	−2.144492
H	−0.508952	−3.585479	−4.245880
H	1.099319	−2.428001	−2.684991
C	−1.179956	0.915397	1.495934
C	−0.611142	0.465998	2.728457
H	0.482520	2.984950	−1.333417
C	0.414371	3.436516	−3.455242
C	−0.890292	−2.992532	−3.404238
C	0.139652	2.497003	−2.250815
H	−0.049329	3.012875	−4.361386
C	0.170062	−1.932163	−2.999381
C	−0.096429	1.617468	3.424034
C	−0.996039	2.326576	1.414217
H	−0.496710	−1.665443	−0.978960
H	2.372326	4.164007	−2.847749
H	0.387827	1.607579	4.393897
H	−1.326053	2.966717	0.604767
H	2.083688	4.269109	−4.586212
C	1.926776	3.633276	−3.703708
H	−2.980283	−3.128486	−4.022436
C	−0.333486	2.760919	2.619631
H	0.417701	−1.322215	−3.880318
C	−0.343348	−1.026449	−1.855114
C	−2.247464	−2.350802	−3.767185
H	−3.006463	−2.125677	−1.741389
N	0.622003	0.062471	−1.406857
C	0.861019	1.139031	−2.446107
H	−0.064964	3.781545	2.865953
B	1.133689	0.008486	−0.082137
Fe	1.011322	1.364020	1.490857
H	0.448063	0.716137	−3.370256
H	−2.129297	−1.723067	−4.665350
C	−2.771313	−1.482624	−2.605402
H	2.866214	1.714291	−1.803775
C	2.641005	2.278008	−3.893662
C	−1.732768	−0.410730	−2.199526
C	2.379090	1.320313	−2.707210
C	2.532702	0.821995	2.239655
H	2.285421	1.806156	−4.824493
H	−3.709807	−0.984141	−2.886594
H	−2.101894	0.174340	−1.346791
H	3.723534	2.425579	−4.013363
H	−1.624449	0.293187	−3.035941
C	1.911190	2.640562	0.627828
H	2.823216	0.335980	−2.912148
O	3.547913	0.552989	2.747542
O	2.527376	3.522999	0.183301
N	1.824419	−1.488245	0.215206
C	2.994907	−1.657442	−0.287704
N	4.051925	−1.964388	−0.747871
C	1.531907	−2.701717	1.187650
C	5.434405	−2.356009	−0.308031

C	0.051137	−3.098988	1.220673
C	−0.139626	−4.326009	2.155782
C	0.430527	−4.081956	3.569873
C	1.917431	−3.677970	3.504248
C	2.123229	−2.448137	2.587651
C	5.728874	−3.746592	−0.914952
C	7.096159	−4.276970	−0.423974
C	8.234115	−3.273859	−0.716999
C	7.903955	−1.866122	−0.167689
C	6.531681	−1.336240	−0.674681
H	−0.293737	−3.352964	0.211370
H	−0.557171	−2.257856	1.580170
H	−1.207812	−4.574322	2.203060
H	0.364814	−5.197207	1.708240
H	−0.144176	−3.283842	4.066884
H	0.308926	−4.983501	4.184309
H	2.305346	−3.445794	4.505136
H	2.512945	−4.524442	3.126279
H	1.635824	−1.573540	3.035064
H	3.191965	−2.209372	2.506005
H	2.084858	−3.531279	0.724081
H	7.297745	−5.243203	−0.905349
H	7.044227	−4.471997	0.659193
H	5.383085	−2.430883	0.787434
H	5.729429	−3.650711	−2.011206
H	4.925047	−4.446063	−0.648569
H	8.397482	−3.214776	−1.804415
H	9.173260	−3.636120	−0.276738
H	6.312280	−0.360663	−0.221529
H	6.558725	−1.201544	−1.765912
H	7.893400	−1.898358	0.933936
H	8.689730	−1.152862	−0.449191

E = -47113.37 kJ mol^{-1}

7. X, y, z file and total energy for the fully optimized (DFT) geometry of 5a

H	-4.019941	2.466927	-3.582507
H	0.492077	4.548321	-3.437982
H	0.807203	2.092360	-2.924688
O	3.691257	1.014651	-2.800836
H	2.020344	4.239146	-2.619024
H	-2.821222	3.332281	-2.624294
C	-3.650581	2.608647	-2.557433
C	0.928183	4.233255	-2.479962
H	-2.288616	0.895523	-2.632446
H	-5.075056	4.179334	-2.039026
C	0.458980	2.792841	-2.153309
H	-0.636939	2.760576	-2.164776
H	-3.920179	0.509560	-2.082247
C	-3.121219	1.258456	-2.013157
H	-5.647265	2.545445	-1.698054
C	-4.759445	3.198167	-1.658763
H	0.942409	6.229079	-1.598878
C	3.561717	0.552455	-1.744511
C	0.549026	5.230226	-1.362219
H	-0.546601	5.328740	-1.311542
O	3.473150	-2.901774	-1.444944
H	-3.401475	-1.743247	-1.459902
H	0.527019	-3.342983	-1.201640
C	3.417294	-1.879099	-0.906232
H	2.073585	2.311852	-0.829167
H	-5.159816	-3.324340	-0.607149
C	0.980649	2.333499	-0.770637
H	-4.667196	-0.895752	-0.556882
C	-3.832827	-1.604089	-0.459878
C	-2.644432	1.393473	-0.538797
H	-1.847526	2.146530	-0.538746
H	-0.244629	-5.601218	-0.367452
C	-4.282080	3.320978	-0.194951
N	0.587809	0.939723	-0.442302
H	-1.015932	-3.261660	-0.355670
H	-3.477903	4.073637	-0.134322
C	0.057003	-3.455072	-0.215175
H	6.028437	1.105824	0.034104
H	2.186121	4.790618	-0.004635
Fe	3.415776	-0.248521	-0.124988
C	1.084465	4.765317	0.010464
C	-4.381613	-2.954000	0.074150
H	-3.573850	-3.703574	0.059426
C	1.420886	-0.108268	-0.111440
B	-0.582452	0.051855	-0.041414
N	-1.969815	0.145325	-0.010343
H	-5.097473	3.686967	0.444403
H	1.318968	-5.151635	0.308011
C	0.246869	-4.895303	0.315355
H	-4.614510	1.267378	0.399039
C	-3.769027	1.968935	0.358979
C	0.607395	3.331397	0.354552
N	0.466291	-1.015607	0.281679
C	5.254650	0.674903	0.660833
H	-0.481475	3.337035	0.501756
C	-2.759635	-1.048808	0.508305

H	0.767763	5.457080	0.803090
H	5.913755	−1.453413	0.866995
H	−2.005631	−1.832714	0.590134
H	1.743028	−2.555808	0.761496
C	0.656172	−2.401871	0.753888
C	5.194459	−0.674929	1.097827
H	3.884340	2.422171	1.059169
C	4.112256	1.371502	1.195445
H	−5.840298	−2.193516	1.494212
H	1.050921	2.996162	1.304109
H	−3.400880	2.096441	1.386742
C	−4.938243	−2.825637	1.508463
H	−5.253533	−3.812456	1.879193
H	−1.395729	−4.907089	1.741531
C	−0.303717	−5.056448	1.749201
C	4.012036	−0.829352	1.911090
H	−0.131064	−6.078973	2.109703
H	−4.144330	−0.122784	1.936769
C	3.359953	0.440373	1.976018
C	−3.337374	−0.864141	1.936863
H	3.695854	−1.737674	2.409959
C	0.168825	−2.584179	2.215245
H	−0.890757	−2.308026	2.286433
C	−3.896167	−2.210737	2.469995
H	2.446150	0.655505	2.516777
H	−3.068191	−2.923699	2.608111
H	−2.553019	−0.484314	2.607805
C	0.346680	−4.038087	2.711586
H	1.420806	−4.269283	2.806377
H	0.715494	−1.885037	2.865337
H	−4.338324	−2.053436	3.463016
H	−0.081039	−4.131739	3.719127

E = -47295.85 kJ mol^{-1}

8. X, y, z file and total energy for the fully optimized (DFT) geometry of 5a'

H	-4.004090	3.453308	-2.541607
O	3.367416	-2.246258	-2.343307
O	3.640898	1.977086	-2.234145
H	-0.303125	-5.195948	-2.243577
H	0.329434	-2.742604	-2.259052
H	-2.187940	1.739720	-2.198139
H	0.640593	3.018424	-2.027484
H	-3.273147	-1.138811	-1.970255
H	-5.120709	-2.811030	-1.716630
H	-3.792834	1.130293	-1.792271
H	0.459046	5.516471	-1.649201
C	-3.607083	3.270953	-1.533962
H	1.251342	-4.900988	-1.468610
C	3.403565	-1.444420	-1.500477
C	0.167322	-4.734053	-1.365126
C	3.574747	1.137245	-1.431602
C	-3.015897	1.835971	-1.482705
H	-1.202810	-3.055082	-1.444431
H	-2.808389	4.011433	-1.377317
C	-0.118338	-3.211115	-1.372049
H	-3.580088	-3.487754	-1.196491
H	1.942770	4.845698	-0.977962
C	-4.346700	-2.739770	-0.940474
H	-0.797958	3.471540	-1.111708
C	0.295746	3.425916	-1.067828
C	-3.721588	-1.321502	-0.984856
C	0.847616	4.858353	-0.860177
H	-5.575159	2.852644	-0.701511
H	-4.523389	-0.585055	-0.844004
H	-5.059437	4.527556	-0.501775
C	-4.705070	3.488288	-0.470594
H	-0.092022	-6.479844	-0.082059
C	-0.329511	-5.407449	-0.066586
H	-1.427828	-5.332015	-0.010080
Fe	3.509100	-0.188403	-0.224933
H	1.548116	-2.693906	-0.164442
B	1.507222	-0.063249	-0.175299
C	0.463405	-2.540083	-0.101307
H	-1.913397	-1.949809	-0.062878
N	0.504655	1.037904	-0.144340
C	-2.514086	1.490909	-0.052662
N	0.397542	-1.049337	-0.066944
H	1.858745	2.509339	0.033665
C	-0.499171	0.044231	-0.038028
H	6.002787	-1.678745	0.370082
H	-5.319853	-4.093685	0.463143
C	0.761899	2.493331	0.075112
N	-1.833351	0.119900	0.031987
C	-2.648942	-1.172766	0.123316
H	6.126160	1.010957	0.480714
C	-4.941270	-3.062109	0.447094
H	-1.719865	2.193812	0.191043
H	-5.807168	-2.406873	0.634161
C	0.488322	5.417983	0.534621
H	0.939641	6.410211	0.669943
H	-0.602535	5.558637	0.605292

C	5.273468	−1.024630	0.833996
C	5.338743	0.390397	0.893063
H	−4.458812	1.011503	0.822092
C	−4.182609	3.146224	0.940515
C	−3.625863	1.701413	1.005336
H	1.384143	−4.927660	1.176385
C	0.297035	−4.746093	1.180950
H	−3.397592	3.862900	1.228852
C	0.027500	−3.221839	1.220159
H	−3.114434	−3.638634	1.464913
H	−1.038069	−3.056085	1.411368
H	−4.985222	3.248185	1.683931
C	4.059384	−1.444186	1.491055
C	−3.893984	−2.868606	1.566388
C	4.166478	0.864818	1.588048
C	0.395558	3.035099	1.479904
C	−3.247646	−1.456041	1.529223
H	2.056753	4.430032	1.666124
H	3.736407	−2.468754	1.633713
C	0.954958	4.469459	1.662345
H	−0.694127	3.056157	1.625033
H	3.940471	1.899773	1.816758
H	−4.016684	−0.719287	1.778860
H	−0.091556	−5.207321	2.099428
H	−3.236190	1.490613	2.010200
C	3.387682	−0.274142	1.968530
H	0.571469	−2.757160	2.055401
H	0.804283	2.363631	2.249027
H	−2.462939	−1.374768	2.294305
H	−4.354563	−3.021904	2.551659
H	0.654088	4.859858	2.643972
H	2.473940	−0.256745	2.551481

E = -47184.05 kJ mol^{-1}