Unusual Structural and Spectroscopic Features of Some PNP-Pincer Complexes of Iron

Elizabeth M. Pelczar, Thomas J. Emge, Karsten Krogh-Jespersen*, and Alan S. Goldman*

Department of Chemistry and Chemical Biology,

Rutgers-The State University of New Jersey, New Brunswick, New Jersey 08903

alan.goldman@rutgers.edu, kroghjes@rutgers.edu

Supporting Information

I. Structural Data for (PNP)$FeCl_2$ (**1**)

Figure S-1 : ORTEP Diagram of (PNP)$FeCl_2$

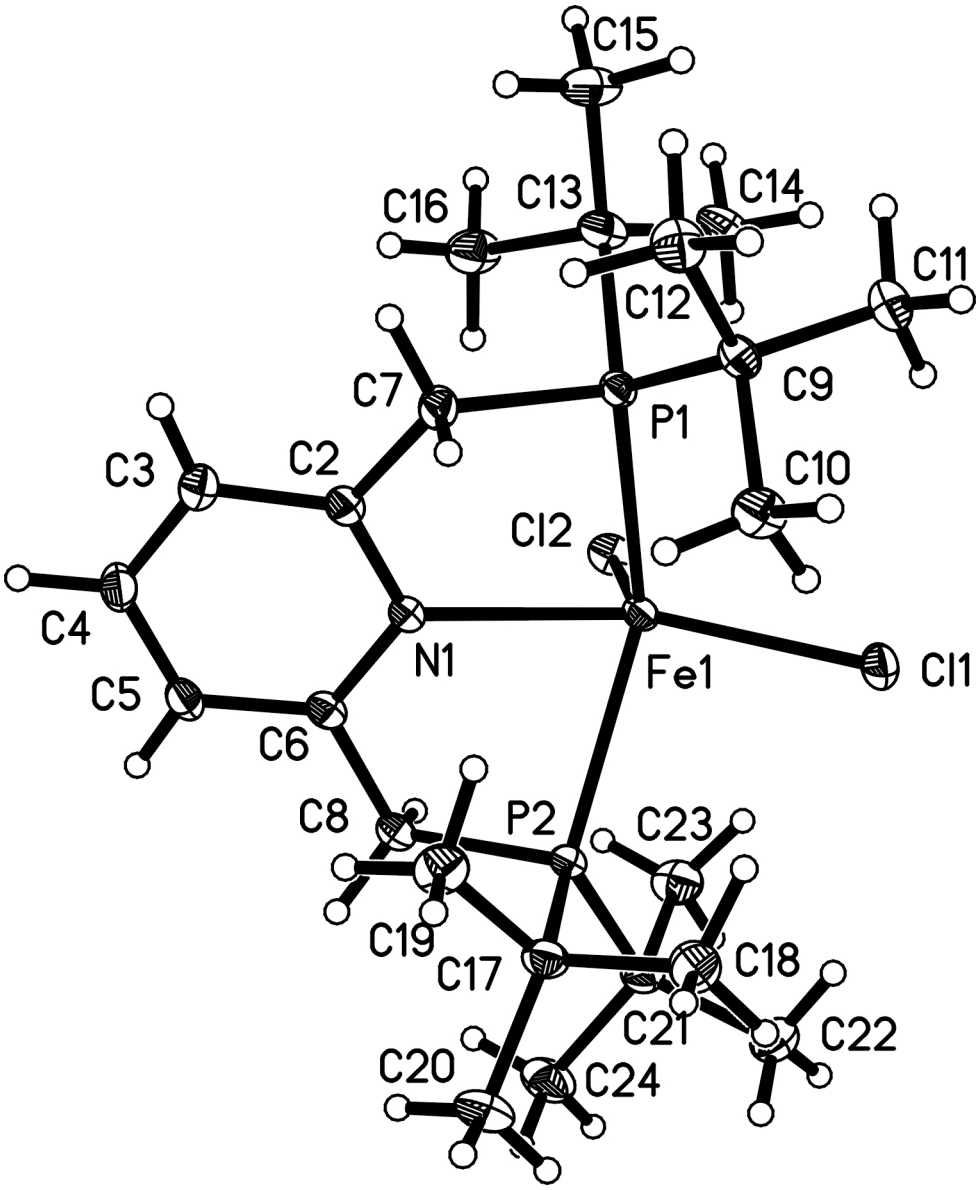


Table S1. Crystal data and structure refinement for (PNP)$FeCl_2$

Identification code	fecl2pnp	
Empirical formula	C23 H43 Cl2 Fe N P2	
Formula weight	522.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.0831(9) Å	α= 90°.
	b = 15.5084(12) Å	β= 91.093(2)°.
	c = 14.5049(11) Å	γ = 90°.
Volume	2717.6(4) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	1112	
Crystal size	0.21 x 0.06 x 0.03 mm^3	
Theta range for data collection	1.92 to 30.57°.	
Index ranges	-17<=h<=17, -22<=k<=22, -20<=l<=20	
Reflections collected	31924	
Independent reflections	8292 [R(int) = 0.0456]	
Completeness to theta = 30.57°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.8338	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8292 / 0 / 434	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0753	
R indices (all data)	R1 = 0.0534, wR2 = 0.0823	
Largest diff. peak and hole	0.618 and -0.300 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (PNP)$FeCl_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	8902(1)	1834(1)	2298(1)	13(1)
Cl(1)	8608(1)	2923(1)	3425(1)	20(1)
Cl(2)	8730(1)	2469(1)	867(1)	19(1)
P(1)	7206(1)	916(1)	2484(1)	13(1)
P(2)	10955(1)	1773(1)	2619(1)	13(1)
N(1)	9490(1)	482(1)	1808(1)	13(1)
C(2)	8794(1)	-194(1)	1749(1)	15(1)
C(3)	9046(1)	-930(1)	1246(1)	19(1)
C(4)	10064(1)	-988(1)	830(1)	20(1)
C(5)	10802(1)	-314(1)	935(1)	17(1)
C(6)	10498(1)	412(1)	1426(1)	14(1)
C(7)	7772(1)	-171(1)	2327(1)	17(1)
C(8)	11313(1)	1140(1)	1592(1)	16(1)
C(9)	6593(1)	837(1)	3661(1)	15(1)
C(10)	7587(2)	882(1)	4339(1)	21(1)
C(11)	5855(2)	1621(1)	3833(1)	21(1)
C(12)	5950(2)	6(1)	3844(1)	22(1)
C(13)	6114(1)	1012(1)	1552(1)	19(1)
C(14)	5786(2)	1964(1)	1461(1)	24(1)
C(15)	5083(2)	452(1)	1692(1)	26(1)
C(16)	6662(2)	723(1)	652(1)	26(1)
C(17)	11459(1)	1121(1)	3641(1)	18(1)
C(18)	11005(2)	1531(1)	4521(1)	24(1)
C(19)	10964(2)	211(1)	3560(1)	22(1)
C(20)	12720(2)	1040(1)	3730(1)	25(1)
C(21)	11799(1)	2785(1)	2480(1)	18(1)
C(22)	11831(2)	3290(1)	3385(1)	26(1)
C(23)	11167(2)	3335(1)	1764(1)	24(1)
C(24)	12976(2)	2632(1)	2138(2)	27(1)

Table S3. Bond lengths [Å] and angles [°] for (PNP)$FeCl_2$.

Fe(1)-Cl(2)	2.3028(5)	C(13)-C(14)	1.533(3)
Fe(1)-N(1)	2.3286(13)	C(13)-C(15)	1.535(2)
Fe(1)-Cl(1)	2.3816(5)	C(13)-C(16)	1.541(2)
Fe(1)-P(1)	2.5149(5)	C(14)-H(14A)	0.97(2)
Fe(1)-P(2)	2.5168(5)	C(14)-H(14B)	0.97(2)
P(1)-C(7)	1.8351(16)	C(14)-H(14C)	0.943(19)
P(1)-C(9)	1.8772(16)	C(15)-H(15A)	0.998(19)
P(1)-C(13)	1.8774(17)	C(15)-H(15B)	1.00(2)
P(2)-C(8)	1.8438(17)	C(15)-H(15C)	0.96(2)
P(2)-C(21)	1.8843(17)	C(16)-H(16A)	0.98(2)
P(2)-C(17)	1.8851(17)	C(16)-H(16B)	0.96(2)
N(1)-C(2)	1.346(2)	C(16)-H(16C)	0.98(2)
N(1)-C(6)	1.3520(19)	C(17)-C(20)	1.531(2)
C(2)-C(3)	1.392(2)	C(17)-C(19)	1.537(2)
C(2)-C(7)	1.507(2)	C(17)-C(18)	1.538(2)
C(3)-C(4)	1.383(2)	C(18)-H(18A)	1.00(2)
C(3)-H(3)	0.917(19)	C(18)-H(18B)	1.02(2)
C(4)-C(5)	1.382(2)	C(18)-H(18C)	0.95(2)
C(4)-H(4)	0.967(19)	C(19)-H(19A)	0.94(2)
C(5)-C(6)	1.385(2)	C(19)-H(19B)	0.96(2)
C(5)-H(5)	0.912(19)	C(19)-H(19C)	0.97(2)
C(6)-C(8)	1.514(2)	C(20)-H(20A)	0.95(2)
C(7)-H(7A)	0.95(2)	C(20)-H(20B)	0.93(2)
C(7)-H(7B)	0.95(2)	C(20)-H(20C)	0.96(2)
C(8)-H(8A)	0.97(2)	C(21)-C(22)	1.530(3)
C(8)-H(8B)	0.982(19)	C(21)-C(24)	1.533(2)
C(9)-C(12)	1.531(2)	C(21)-C(23)	1.537(2)
C(9)-C(11)	1.532(2)	C(22)-H(22A)	0.94(2)
C(9)-C(10)	1.539(2)	C(22)-H(22B)	0.95(2)
C(10)-H(10A)	0.96(2)	C(22)-H(22C)	0.97(2)
C(10)-H(10B)	0.96(2)	C(23)-H(23A)	0.96(2)
C(10)-H(10C)	0.96(2)	C(23)-H(23B)	0.96(2)
C(11)-H(11A)	0.98(2)	C(23)-H(23C)	1.02(2)
C(11)-H(11B)	1.00(2)	C(24)-H(24A)	0.97(2)
C(11)-H(11C)	0.94(2)	C(24)-H(24B)	0.97(2)
C(12)-H(12A)	0.96(2)	C(24)-H(24C)	0.98(2)
C(12)-H(12B)	0.99(2)	Cl(2)-Fe(1)-N(1)	97.61(3)
C(12)-H(12C)	0.96(2)	Cl(2)-Fe(1)-Cl(1)	107.628(17)

N(1)-Fe(1)-Cl(1)	153.95(3)	P(1)-C(7)-H(7A)	107.1(12)
Cl(2)-Fe(1)-P(1)	106.190(16)	C(2)-C(7)-H(7B)	110.1(12)
N(1)-Fe(1)-P(1)	77.13(3)	P(1)-C(7)-H(7B)	114.3(12)
Cl(1)-Fe(1)-P(1)	101.249(16)	H(7A)-C(7)-H(7B)	105.2(16)
Cl(2)-Fe(1)-P(2)	104.774(16)	C(6)-C(8)-P(2)	111.32(11)
N(1)-Fe(1)-P(2)	73.59(3)	C(6)-C(8)-H(8A)	109.3(12)
Cl(1)-Fe(1)-P(2)	93.402(16)	P(2)-C(8)-H(8A)	103.1(12)
P(1)-Fe(1)-P(2)	139.582(16)	C(6)-C(8)-H(8B)	109.7(11)
C(7)-P(1)-C(9)	101.98(7)	P(2)-C(8)-H(8B)	113.2(11)
C(7)-P(1)-C(13)	104.04(8)	H(8A)-C(8)-H(8B)	110.0(16)
C(9)-P(1)-C(13)	112.11(7)	C(12)-C(9)-C(11)	109.97(14)
C(7)-P(1)-Fe(1)	101.54(5)	C(12)-C(9)-C(10)	108.67(14)
C(9)-P(1)-Fe(1)	118.08(5)	C(11)-C(9)-C(10)	108.01(14)
C(13)-P(1)-Fe(1)	116.14(5)	C(12)-C(9)-P(1)	115.00(12)
C(8)-P(2)-C(21)	102.74(7)	C(11)-C(9)-P(1)	109.71(11)
C(8)-P(2)-C(17)	105.80(8)	C(10)-C(9)-P(1)	105.18(11)
C(21)-P(2)-C(17)	111.33(7)	C(9)-C(10)-H(10A)	110.0(12)
C(8)-P(2)-Fe(1)	96.66(5)	C(9)-C(10)-H(10B)	112.0(12)
C(21)-P(2)-Fe(1)	118.84(5)	H(10A)-C(10)-H(10B)	104.1(16)
C(17)-P(2)-Fe(1)	117.92(5)	C(9)-C(10)-H(10C)	111.6(12)
C(2)-N(1)-C(6)	118.54(13)	H(10A)-C(10)-H(10C)	105.5(16)
C(2)-N(1)-Fe(1)	121.78(10)	H(10B)-C(10)-H(10C)	113.2(16)
C(6)-N(1)-Fe(1)	118.70(10)	C(9)-C(11)-H(11A)	111.0(12)
N(1)-C(2)-C(3)	122.02(14)	C(9)-C(11)-H(11B)	109.2(12)
N(1)-C(2)-C(7)	117.67(14)	H(11A)-C(11)-H(11B)	109.7(17)
C(3)-C(2)-C(7)	120.02(14)	C(9)-C(11)-H(11C)	109.5(12)
C(4)-C(3)-C(2)	119.14(16)	H(11A)-C(11)-H(11C)	106.9(17)
C(4)-C(3)-H(3)	123.0(12)	H(11B)-C(11)-H(11C)	110.5(18)
C(2)-C(3)-H(3)	117.8(12)	C(9)-C(12)-H(12A)	108.1(12)
C(5)-C(4)-C(3)	118.72(15)	C(9)-C(12)-H(12B)	113.3(12)
C(5)-C(4)-H(4)	120.6(11)	H(12A)-C(12)-H(12B)	107.9(17)
C(3)-C(4)-H(4)	120.6(11)	C(9)-C(12)-H(12C)	112.8(12)
C(4)-C(5)-C(6)	119.66(15)	H(12A)-C(12)-H(12C)	106.8(16)
C(4)-C(5)-H(5)	121.7(12)	H(12B)-C(12)-H(12C)	107.8(17)
C(6)-C(5)-H(5)	118.7(12)	C(14)-C(13)-C(15)	110.29(15)
N(1)-C(6)-C(5)	121.73(15)	C(14)-C(13)-C(16)	108.82(15)
N(1)-C(6)-C(8)	117.59(14)	C(15)-C(13)-C(16)	108.04(15)
C(5)-C(6)-C(8)	120.62(14)	C(14)-C(13)-P(1)	108.40(12)
C(2)-C(7)-P(1)	113.70(11)	C(15)-C(13)-P(1)	114.86(12)
C(2)-C(7)-H(7A)	105.7(12)	C(16)-C(13)-P(1)	106.22(11)

C(13)-C(14)-H(14A)	108.9(13)
C(13)-C(14)-H(14B)	113.2(13)
H(14A)-C(14)-H(14B)	107.1(18)
C(13)-C(14)-H(14C)	112.4(12)
H(14A)-C(14)-H(14C)	107.1(17)
H(14B)-C(14)-H(14C)	107.9(17)
C(13)-C(15)-H(15A)	111.2(11)
C(13)-C(15)-H(15B)	110.9(11)
H(15A)-C(15)-H(15B)	110.3(15)
C(13)-C(15)-H(15C)	106.9(12)
H(15A)-C(15)-H(15C)	108.7(16)
H(15B)-C(15)-H(15C)	108.7(16)
C(13)-C(16)-H(16A)	105.1(12)
C(13)-C(16)-H(16B)	112.7(13)
H(16A)-C(16)-H(16B)	109.1(17)
C(13)-C(16)-H(16C)	113.2(12)
H(16A)-C(16)-H(16C)	109.0(17)
H(16B)-C(16)-H(16C)	107.7(17)
C(20)-C(17)-C(19)	108.45(15)
C(20)-C(17)-C(18)	109.54(14)
C(19)-C(17)-C(18)	107.36(15)
C(20)-C(17)-P(2)	114.61(12)
C(19)-C(17)-P(2)	108.27(11)
C(18)-C(17)-P(2)	108.37(12)
C(17)-C(18)-H(18A)	113.2(12)
C(17)-C(18)-H(18B)	112.4(12)
H(18A)-C(18)-H(18B)	106.0(17)
C(17)-C(18)-H(18C)	108.8(13)
H(18A)-C(18)-H(18C)	106.5(17)
H(18B)-C(18)-H(18C)	109.7(17)
C(17)-C(19)-H(19A)	109.5(14)
C(17)-C(19)-H(19B)	111.2(12)
H(19A)-C(19)-H(19B)	108.3(18)
C(17)-C(19)-H(19C)	113.6(12)
H(19A)-C(19)-H(19C)	104.9(18)
H(19B)-C(19)-H(19C)	108.9(16)
C(17)-C(20)-H(20A)	108.8(13)
C(17)-C(20)-H(20B)	112.3(13)
H(20A)-C(20)-H(20B)	108.8(18)
C(17)-C(20)-H(20C)	111.1(12)
H(20A)-C(20)-H(20C)	107.6(18)
H(20B)-C(20)-H(20C)	108.1(18)
C(22)-C(21)-C(24)	110.43(15)
C(22)-C(21)-C(23)	107.41(15)
C(24)-C(21)-C(23)	108.62(15)
C(22)-C(21)-P(2)	109.81(12)
C(24)-C(21)-P(2)	114.43(12)
C(23)-C(21)-P(2)	105.80(11)
C(21)-C(22)-H(22A)	112.1(13)
C(21)-C(22)-H(22B)	110.0(14)
H(22A)-C(22)-H(22B)	110.8(19)
C(21)-C(22)-H(22C)	109.0(12)
H(22A)-C(22)-H(22C)	108.3(17)
H(22B)-C(22)-H(22C)	106.4(18)
C(21)-C(23)-H(23A)	110.6(12)
C(21)-C(23)-H(23B)	111.7(13)
H(23A)-C(23)-H(23B)	111.5(17)
C(21)-C(23)-H(23C)	107.5(11)
H(23A)-C(23)-H(23C)	108.4(16)
H(23B)-C(23)-H(23C)	106.9(16)
C(21)-C(24)-H(24A)	108.5(12)
C(21)-C(24)-H(24B)	110.4(13)
H(24A)-C(24)-H(24B)	106.6(17)
C(21)-C(24)-H(24C)	110.7(14)
H(24A)-C(24)-H(24C)	108.8(18)
H(24B)-C(24)-H(24C)	111.7(19)

Table S4. Torsion angles [°] for (PNP)$FeCl_2$.

Cl(2)-Fe(1)-P(1)-C(7)	105.57(6)	Fe(1)-N(1)-C(2)-C(3)	163.34(12)
N(1)-Fe(1)-P(1)-C(7)	11.26(7)	C(6)-N(1)-C(2)-C(7)	168.58(14)
Cl(1)-Fe(1)-P(1)-C(7)	-142.14(6)	Fe(1)-N(1)-C(2)-C(7)	-22.87(19)
P(2)-Fe(1)-P(1)-C(7)	-33.06(7)	N(1)-C(2)-C(3)-C(4)	3.1(3)
Cl(2)-Fe(1)-P(1)-C(9)	-144.00(6)	C(7)-C(2)-C(3)-C(4)	-170.52(15)
N(1)-Fe(1)-P(1)-C(9)	121.70(7)	C(2)-C(3)-C(4)-C(5)	0.5(3)
Cl(1)-Fe(1)-P(1)-C(9)	-31.71(6)	C(3)-C(4)-C(5)-C(6)	-1.9(2)
P(2)-Fe(1)-P(1)-C(9)	77.37(6)	C(2)-N(1)-C(6)-C(5)	3.7(2)
Cl(2)-Fe(1)-P(1)-C(13)	-6.51(6)	Fe(1)-N(1)-C(6)-C(5)	-165.18(12)
N(1)-Fe(1)-P(1)-C(13)	-100.82(7)	C(2)-N(1)-C(6)-C(8)	-173.33(14)
Cl(1)-Fe(1)-P(1)-C(13)	105.78(6)	Fe(1)-N(1)-C(6)-C(8)	17.76(18)
P(2)-Fe(1)-P(1)-C(13)	-145.14(6)	C(4)-C(5)-C(6)-N(1)	-0.2(2)
Cl(2)-Fe(1)-P(2)-C(8)	-57.79(6)	C(4)-C(5)-C(6)-C(8)	176.79(15)
N(1)-Fe(1)-P(2)-C(8)	35.94(6)	N(1)-C(2)-C(7)-P(1)	33.51(19)
Cl(1)-Fe(1)-P(2)-C(8)	-167.03(6)	C(3)-C(2)-C(7)-P(1)	-152.57(13)
P(1)-Fe(1)-P(2)-C(8)	81.18(6)	C(9)-P(1)-C(7)-C(2)	-148.41(12)
Cl(2)-Fe(1)-P(2)-C(21)	50.74(6)	C(13)-P(1)-C(7)-C(2)	94.87(13)
N(1)-Fe(1)-P(2)-C(21)	144.47(7)	Fe(1)-P(1)-C(7)-C(2)	-26.10(13)
Cl(1)-Fe(1)-P(2)-C(21)	-58.50(6)	N(1)-C(6)-C(8)-P(2)	21.16(18)
P(1)-Fe(1)-P(2)-C(21)	-170.29(6)	C(5)-C(6)-C(8)-P(2)	-155.93(13)
Cl(2)-Fe(1)-P(2)-C(17)	-169.64(6)	C(21)-P(2)-C(8)-C(6)	-164.36(11)
N(1)-Fe(1)-P(2)-C(17)	-75.91(7)	C(17)-P(2)-C(8)-C(6)	78.79(12)
Cl(1)-Fe(1)-P(2)-C(17)	81.13(6)	Fe(1)-P(2)-C(8)-C(6)	-42.74(11)
P(1)-Fe(1)-P(2)-C(17)	-30.66(7)	C(7)-P(1)-C(9)-C(12)	-43.06(14)
Cl(2)-Fe(1)-N(1)-C(2)	-100.96(11)	C(13)-P(1)-C(9)-C(12)	67.66(14)
Cl(1)-Fe(1)-N(1)-C(2)	93.31(13)	Fe(1)-P(1)-C(9)-C(12)	-153.25(10)
P(1)-Fe(1)-N(1)-C(2)	3.99(11)	C(7)-P(1)-C(9)-C(11)	-167.62(12)
P(2)-Fe(1)-N(1)-C(2)	155.81(12)	C(13)-P(1)-C(9)-C(11)	-56.90(13)
Cl(2)-Fe(1)-N(1)-C(6)	67.57(11)	Fe(1)-P(1)-C(9)-C(11)	82.19(12)
Cl(1)-Fe(1)-N(1)-C(6)	-98.16(12)	C(7)-P(1)-C(9)-C(10)	76.43(12)
P(1)-Fe(1)-N(1)-C(6)	172.52(11)	C(13)-P(1)-C(9)-C(10)	-172.85(11)
P(2)-Fe(1)-N(1)-C(6)	-35.66(10)	Fe(1)-P(1)-C(9)-C(10)	-33.76(12)
C(6)-N(1)-C(2)-C(3)	-5.2(2)	C(7)-P(1)-C(13)-C(14)	-166.07(11)

C(9)-P(1)-C(13)-C(14)	84.51(13)
Fe(1)-P(1)-C(13)-C(14)	-55.43(12)
C(7)-P(1)-C(13)-C(15)	70.08(14)
C(9)-P(1)-C(13)-C(15)	-39.34(15)
Fe(1)-P(1)-C(13)-C(15)	-179.28(11)
C(7)-P(1)-C(13)-C(16)	-49.27(14)
C(9)-P(1)-C(13)-C(16)	-158.69(12)
Fe(1)-P(1)-C(13)-C(16)	61.37(13)
C(8)-P(2)-C(17)-C(20)	67.31(14)
C(21)-P(2)-C(17)-C(20)	-43.58(15)
Fe(1)-P(2)-C(17)-C(20)	173.95(11)
C(8)-P(2)-C(17)-C(19)	-53.87(13)
C(21)-P(2)-C(17)-C(19)	-164.77(11)
Fe(1)-P(2)-C(17)-C(19)	52.77(13)
C(8)-P(2)-C(17)-C(18)	-170.03(12)
C(21)-P(2)-C(17)-C(18)	79.08(13)
Fe(1)-P(2)-C(17)-C(18)	-63.39(13)
C(8)-P(2)-C(21)-C(22)	-165.99(12)
C(17)-P(2)-C(21)-C(22)	-53.16(14)
Fe(1)-P(2)-C(21)-C(22)	88.92(12)
C(8)-P(2)-C(21)-C(24)	-41.17(15)
C(17)-P(2)-C(21)-C(24)	71.67(15)
Fe(1)-P(2)-C(21)-C(24)	-146.25(12)
C(8)-P(2)-C(21)-C(23)	78.37(13)
C(17)-P(2)-C(21)-C(23)	-168.79(12)
Fe(1)-P(2)-C(21)-C(23)	-26.71(14)

II. Structural Data for (PNP)Fe(CO)$_2$ (**3**)

Figure S-2 : ORTEP Diagram of (PNP)Fe(CO)$_2$

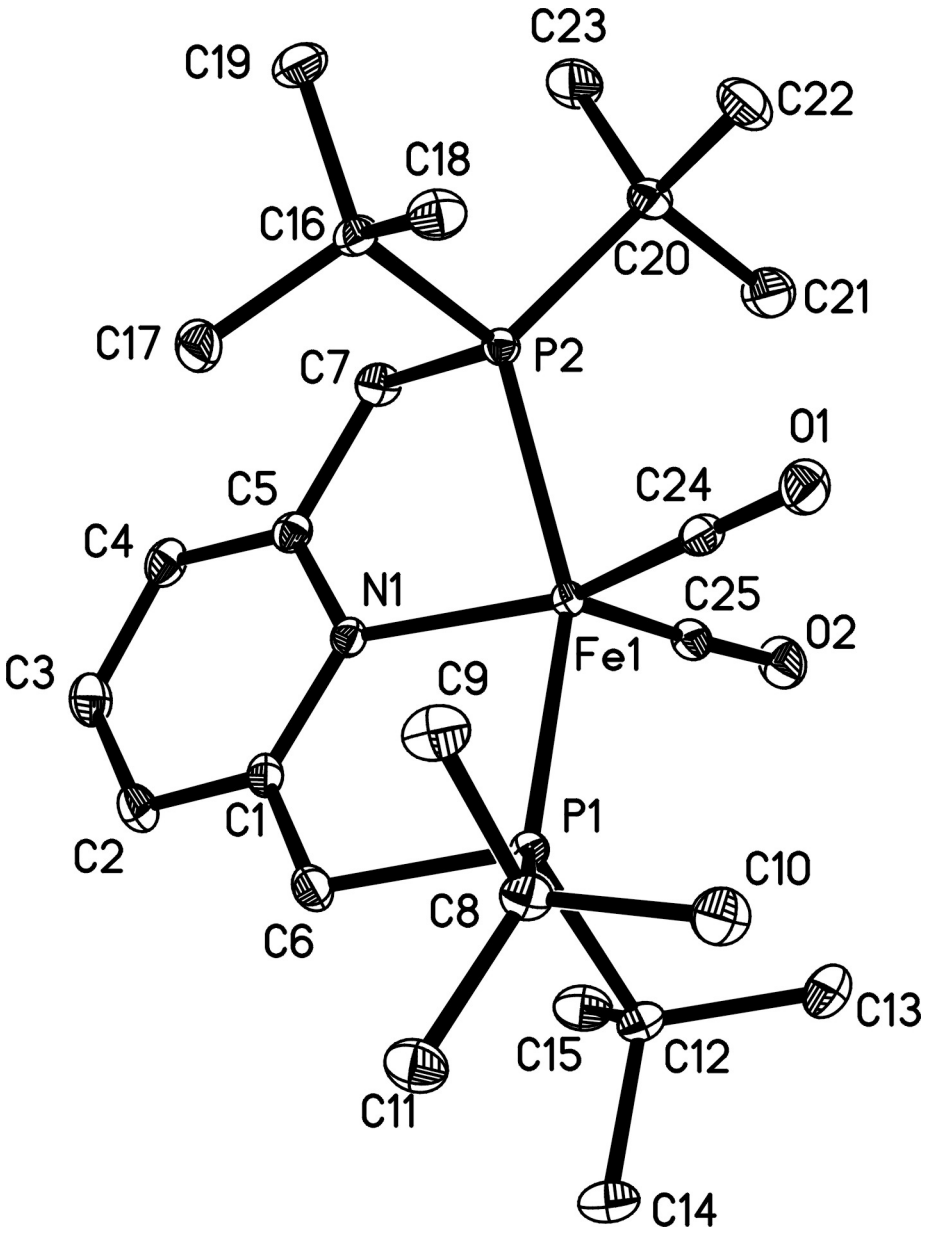


Table S5. Crystal data and structure refinement for $(PNP)Fe(CO)_2$

Identification code	fehco	
Empirical formula	C25 H43 Fe N O2 P2	
Formula weight	507.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.7404(12) Å	α= 90°.
	b = 14.5944(14) Å	β= 90°.
	c = 15.3327(15) Å	γ = 90°.
Volume	2627.2(4) $Å^3$	
Z	4	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	0.717 mm^{-1}	
F(000)	1088	
Crystal size	0.29 x 0.25 x 0.18 mm^3	
Theta range for data collection	1.93 to 30.56°.	
Index ranges	-16<=h<=16, -20<=k<=20, -21<=l<=21	
Reflections collected	31387	
Independent reflections	8025 [R(int) = 0.0228]	
Completeness to theta = 30.56°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.9146	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8025 / 0 / 335	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0561	
R indices (all data)	R1 = 0.0230, wR2 = 0.0565	
Absolute structure parameter	0.002(6)	
Largest diff. peak and hole	0.362 and -0.180 $e.Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (PNP)Fe$(CO)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	3493(1)	4841(1)	9565(1)	9(1)
P(1)	2067(1)	5699(1)	9055(1)	10(1)
P(2)	5170(1)	4168(1)	9449(1)	10(1)
N(1)	3159(1)	4041(1)	8496(1)	10(1)
C(1)	2293(1)	4234(1)	7931(1)	12(1)
C(2)	1947(1)	3624(1)	7289(1)	16(1)
C(3)	2524(1)	2802(1)	7180(1)	17(1)
C(4)	3448(1)	2624(1)	7717(1)	16(1)
C(5)	3742(1)	3242(1)	8367(1)	12(1)
C(6)	1801(1)	5174(1)	7981(1)	14(1)
C(7)	4723(1)	3068(1)	8967(1)	14(1)
C(8)	2292(1)	6946(1)	8743(1)	13(1)
C(9)	3489(1)	7025(1)	8344(1)	19(1)
C(10)	2236(1)	7554(1)	9555(1)	19(1)
C(11)	1447(1)	7309(1)	8056(1)	19(1)
C(12)	639(1)	5577(1)	9622(1)	14(1)
C(13)	767(1)	5821(1)	10594(1)	20(1)
C(14)	-346(1)	6139(1)	9240(1)	19(1)
C(15)	310(1)	4556(1)	9548(1)	19(1)
C(16)	6179(1)	4661(1)	8607(1)	13(1)
C(17)	5556(1)	4679(1)	7724(1)	18(1)
C(18)	6463(1)	5661(1)	8835(1)	17(1)
C(19)	7292(1)	4124(1)	8485(1)	19(1)
C(20)	6023(1)	3804(1)	10437(1)	14(1)
C(21)	5177(1)	3552(1)	11164(1)	24(1)
C(22)	6769(1)	4589(1)	10781(1)	22(1)
C(23)	6768(1)	2949(1)	10267(1)	22(1)
C(24)	4126(1)	5771(1)	10071(1)	13(1)
O(1)	4551(1)	6377(1)	10452(1)	18(1)
C(25)	2844(1)	4198(1)	10409(1)	13(1)
O(2)	2449(1)	3862(1)	11030(1)	19(1)

Table S7. Bond lengths [Å] and angles [°] for (PNP)Fe(CO)$_2$.

Fe(1)-C(24)	1.7310(12)	C(10)-H(10B)	0.9800
Fe(1)-C(25)	1.7708(12)	C(10)-H(10C)	0.9800
Fe(1)-N(1)	2.0503(9)	C(11)-H(11A)	0.9800
Fe(1)-P(2)	2.2066(4)	C(11)-H(11B)	0.9800
Fe(1)-P(1)	2.2322(3)	C(11)-H(11C)	0.9800
P(1)-C(6)	1.8427(11)	C(12)-C(14)	1.5340(16)
P(1)-C(12)	1.8974(11)	C(12)-C(13)	1.5404(17)
P(1)-C(8)	1.8985(12)	C(12)-C(15)	1.5428(16)
P(2)-C(7)	1.8439(12)	C(13)-H(13A)	0.9800
P(2)-C(20)	1.8930(12)	C(13)-H(13B)	0.9800
P(2)-C(16)	1.8939(12)	C(13)-H(13C)	0.9800
N(1)-C(1)	1.3648(14)	C(14)-H(14A)	0.9800
N(1)-C(5)	1.3664(14)	C(14)-H(14B)	0.9800
C(1)-C(2)	1.3885(16)	C(14)-H(14C)	0.9800
C(1)-C(6)	1.4905(16)	C(15)-H(15A)	0.9800
C(2)-C(3)	1.3878(17)	C(15)-H(15B)	0.9800
C(2)-H(2)	0.9500	C(15)-H(15C)	0.9800
C(3)-C(4)	1.3859(18)	C(16)-C(19)	1.5342(16)
C(3)-H(3)	0.9500	C(16)-C(18)	1.5370(16)
C(4)-C(5)	1.3871(15)	C(16)-C(17)	1.5399(16)
C(4)-H(4)	0.9500	C(17)-H(17A)	0.9800
C(5)-C(7)	1.4965(16)	C(17)-H(17B)	0.9800
C(6)-H(6A)	0.9900	C(17)-H(17C)	0.9800
C(6)-H(6B)	0.9900	C(18)-H(18A)	0.9800
C(7)-H(7A)	0.9900	C(18)-H(18B)	0.9800
C(7)-H(7B)	0.9900	C(18)-H(18C)	0.9800
C(8)-C(10)	1.5296(17)	C(19)-H(19A)	0.9800
C(8)-C(9)	1.5375(17)	C(19)-H(19B)	0.9800
C(8)-C(11)	1.5413(16)	C(19)-H(19C)	0.9800
C(9)-H(9A)	0.9800	C(20)-C(22)	1.5365(17)
C(9)-H(9B)	0.9800	C(20)-C(21)	1.5377(17)
C(9)-H(9C)	0.9800	C(20)-C(23)	1.5452(16)
C(10)-H(10A)	0.9800	C(21)-H(21A)	0.9800

C(21)-H(21B)	0.9800	C(23)-H(23A)	0.9800
C(21)-H(21C)	0.9800	C(23)-H(23B)	0.9800
C(22)-H(22A)	0.9800	C(23)-H(23C)	0.9800
C(22)-H(22B)	0.9800	C(24)-O(1)	1.1717(14)
C(22)-H(22C)	0.9800	C(25)-O(2)	1.1679(14)

C(24)-Fe(1)-C(25)	105.78(5)	C(1)-C(2)-H(2)	120.1
C(24)-Fe(1)-N(1)	152.52(5)	C(4)-C(3)-C(2)	118.15(11)
C(25)-Fe(1)-N(1)	101.57(4)	C(4)-C(3)-H(3)	120.9
C(24)-Fe(1)-P(2)	90.13(4)	C(2)-C(3)-H(3)	120.9
C(25)-Fe(1)-P(2)	101.94(4)	C(3)-C(4)-C(5)	120.01(11)
N(1)-Fe(1)-P(2)	81.55(3)	C(3)-C(4)-H(4)	120.0
C(24)-Fe(1)-P(1)	92.21(4)	C(5)-C(4)-H(4)	120.0
C(25)-Fe(1)-P(1)	103.35(4)	N(1)-C(5)-C(4)	122.26(11)
N(1)-Fe(1)-P(1)	84.04(3)	N(1)-C(5)-C(7)	116.23(10)
P(2)-Fe(1)-P(1)	152.917(13)	C(4)-C(5)-C(7)	121.51(10)
C(6)-P(1)-C(12)	102.72(5)	C(1)-C(6)-P(1)	111.32(7)
C(6)-P(1)-C(8)	101.37(5)	C(1)-C(6)-H(6A)	109.4
C(12)-P(1)-C(8)	109.18(5)	P(1)-C(6)-H(6A)	109.4
C(6)-P(1)-Fe(1)	101.92(4)	C(1)-C(6)-H(6B)	109.4
C(12)-P(1)-Fe(1)	116.69(4)	P(1)-C(6)-H(6B)	109.4
C(8)-P(1)-Fe(1)	121.45(4)	H(6A)-C(6)-H(6B)	108.0
C(7)-P(2)-C(20)	103.07(5)	C(5)-C(7)-P(2)	108.48(8)
C(7)-P(2)-C(16)	103.63(5)	C(5)-C(7)-H(7A)	110.0
C(20)-P(2)-C(16)	108.70(5)	P(2)-C(7)-H(7A)	110.0
C(7)-P(2)-Fe(1)	99.58(4)	C(5)-C(7)-H(7B)	110.0
C(20)-P(2)-Fe(1)	122.20(4)	P(2)-C(7)-H(7B)	110.0
C(16)-P(2)-Fe(1)	116.38(4)	H(7A)-C(7)-H(7B)	108.4
C(1)-N(1)-C(5)	117.24(9)	C(10)-C(8)-C(9)	108.60(10)
C(1)-N(1)-Fe(1)	122.15(7)	C(10)-C(8)-C(11)	109.19(10)
C(5)-N(1)-Fe(1)	120.37(7)	C(9)-C(8)-C(11)	106.84(10)
N(1)-C(1)-C(2)	122.33(11)	C(10)-C(8)-P(1)	110.21(8)
N(1)-C(1)-C(6)	116.48(10)	C(9)-C(8)-P(1)	107.42(8)
C(2)-C(1)-C(6)	120.96(10)	C(11)-C(8)-P(1)	114.37(8)
C(3)-C(2)-C(1)	119.83(11)	C(8)-C(9)-H(9A)	109.5
C(3)-C(2)-H(2)	120.1	C(8)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5	H(15A)-C(15)-H(15B)	109.5
C(8)-C(9)-H(9C)	109.5	C(12)-C(15)-H(15C)	109.5
H(9A)-C(9)-H(9C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(9B)-C(9)-H(9C)	109.5	H(15B)-C(15)-H(15C)	109.5
C(8)-C(10)-H(10A)	109.5	C(19)-C(16)-C(18)	109.15(10)
C(8)-C(10)-H(10B)	109.5	C(19)-C(16)-C(17)	107.80(10)
H(10A)-C(10)-H(10B)	109.5	C(18)-C(16)-C(17)	106.62(9)
C(8)-C(10)-H(10C)	109.5	C(19)-C(16)-P(2)	114.97(8)
H(10A)-C(10)-H(10C)	109.5	C(18)-C(16)-P(2)	109.96(8)
H(10B)-C(10)-H(10C)	109.5	C(17)-C(16)-P(2)	107.99(8)
C(8)-C(11)-H(11A)	109.5	C(16)-C(17)-H(17A)	109.5
C(8)-C(11)-H(11B)	109.5	C(16)-C(17)-H(17B)	109.5
H(11A)-C(11)-H(11B)	109.5	H(17A)-C(17)-H(17B)	109.5
C(8)-C(11)-H(11C)	109.5	C(16)-C(17)-H(17C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(11B)-C(11)-H(11C)	109.5	H(17B)-C(17)-H(17C)	109.5
C(14)-C(12)-C(13)	108.59(9)	C(16)-C(18)-H(18A)	109.5
C(14)-C(12)-C(15)	107.44(9)	C(16)-C(18)-H(18B)	109.5
C(13)-C(12)-C(15)	108.62(11)	H(18A)-C(18)-H(18B)	109.5
C(14)-C(12)-P(1)	116.19(8)	C(16)-C(18)-H(18C)	109.5
C(13)-C(12)-P(1)	109.57(8)	H(18A)-C(18)-H(18C)	109.5
C(15)-C(12)-P(1)	106.19(8)	H(18B)-C(18)-H(18C)	109.5
C(12)-C(13)-H(13A)	109.5	C(16)-C(19)-H(19A)	109.5
C(12)-C(13)-H(13B)	109.5	C(16)-C(19)-H(19B)	109.5
H(13A)-C(13)-H(13B)	109.5	H(19A)-C(19)-H(19B)	109.5
C(12)-C(13)-H(13C)	109.5	C(16)-C(19)-H(19C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(13B)-C(13)-H(13C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(12)-C(14)-H(14A)	109.5	C(22)-C(20)-C(21)	107.32(11)
C(12)-C(14)-H(14B)	109.5	C(22)-C(20)-C(23)	109.74(10)
H(14A)-C(14)-H(14B)	109.5	C(21)-C(20)-C(23)	107.18(10)
C(12)-C(14)-H(14C)	109.5	C(22)-C(20)-P(2)	111.53(8)
H(14A)-C(14)-H(14C)	109.5	C(21)-C(20)-P(2)	107.75(8)
H(14B)-C(14)-H(14C)	109.5	C(23)-C(20)-P(2)	113.04(8)
C(12)-C(15)-H(15A)	109.5	C(20)-C(21)-H(21A)	109.5
C(12)-C(15)-H(15B)	109.5	C(20)-C(21)-H(21B)	109.5

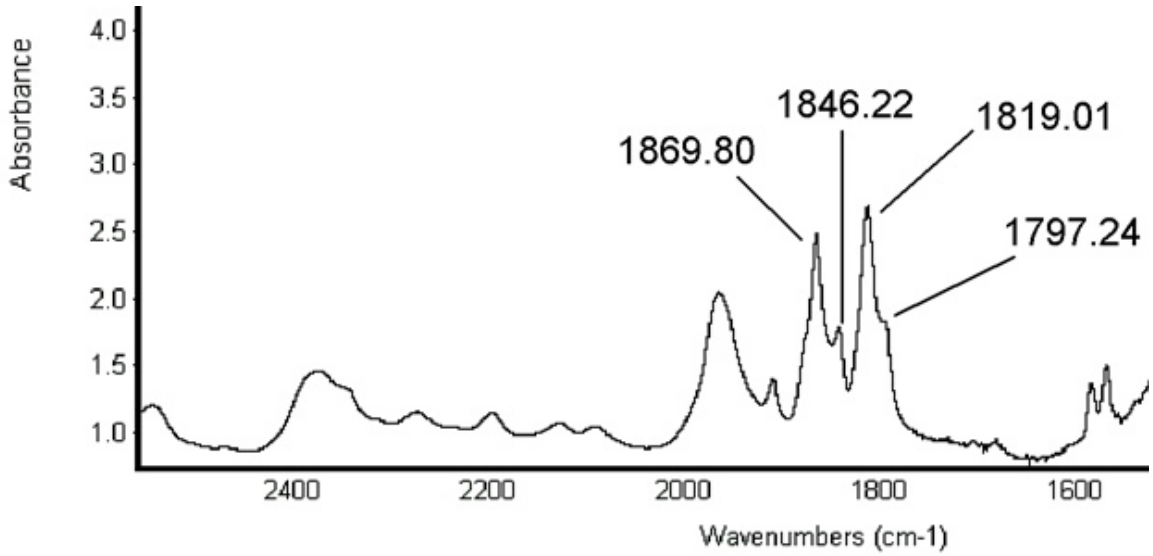
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(1)-C(24)-Fe(1)	176.68(10)
O(2)-C(25)-Fe(1)	171.87(10)

Table S8. Torsion angles [°] for (PNP)Fe(CO)$_2$.

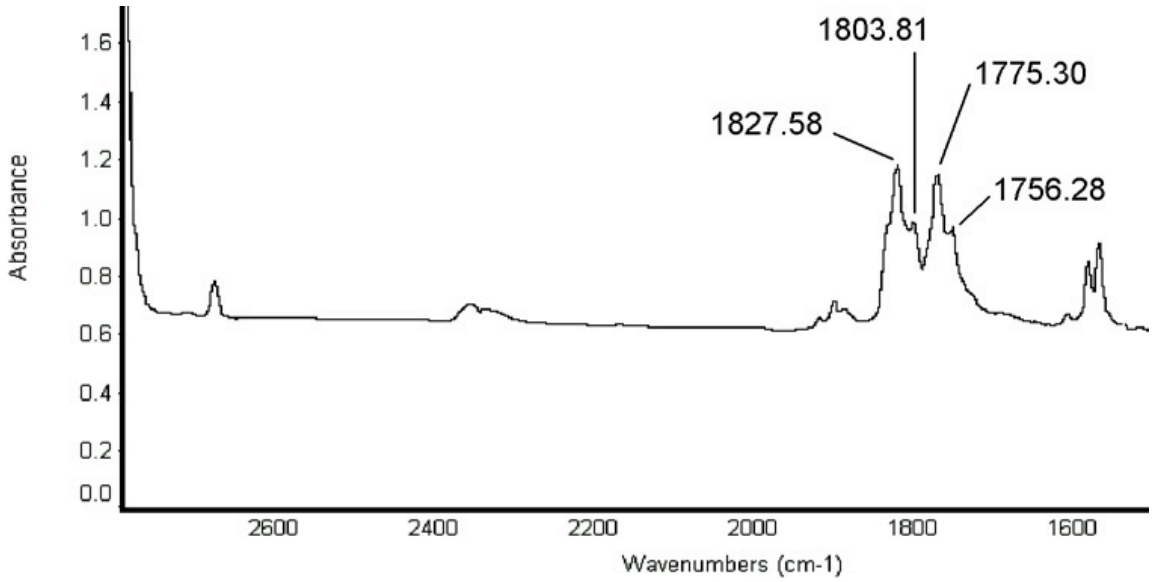
C(24)-Fe(1)-P(1)-C(6)	144.06(5)	Fe(1)-N(1)-C(1)-C(2)	-169.54(9)
C(25)-Fe(1)-P(1)-C(6)	-109.16(6)	C(5)-N(1)-C(1)-C(6)	-169.65(9)
N(1)-Fe(1)-P(1)-C(6)	-8.64(5)	Fe(1)-N(1)-C(1)-C(6)	15.93(13)
P(2)-Fe(1)-P(1)-C(6)	49.44(5)	N(1)-C(1)-C(2)-C(3)	-3.12(18)
C(24)-Fe(1)-P(1)-C(12)	-104.96(6)	C(6)-C(1)-C(2)-C(3)	171.17(11)
C(25)-Fe(1)-P(1)-C(12)	1.83(6)	C(1)-C(2)-C(3)-C(4)	-0.79(18)
N(1)-Fe(1)-P(1)-C(12)	102.34(5)	C(2)-C(3)-C(4)-C(5)	2.71(18)
P(2)-Fe(1)-P(1)-C(12)	160.42(4)	C(1)-N(1)-C(5)-C(4)	-2.87(16)
C(24)-Fe(1)-P(1)-C(8)	32.64(6)	Fe(1)-N(1)-C(5)-C(4)	171.65(9)
C(25)-Fe(1)-P(1)-C(8)	139.43(6)	C(1)-N(1)-C(5)-C(7)	177.09(10)
N(1)-Fe(1)-P(1)-C(8)	-120.06(5)	Fe(1)-N(1)-C(5)-C(7)	-8.38(13)
P(2)-Fe(1)-P(1)-C(8)	-61.98(5)	C(3)-C(4)-C(5)-N(1)	-0.89(18)
C(24)-Fe(1)-P(2)-C(7)	176.47(5)	C(3)-C(4)-C(5)-C(7)	179.15(11)
C(25)-Fe(1)-P(2)-C(7)	70.30(5)	N(1)-C(1)-C(6)-P(1)	-22.69(12)
N(1)-Fe(1)-P(2)-C(7)	-29.82(5)	C(2)-C(1)-C(6)-P(1)	162.70(9)
P(1)-Fe(1)-P(2)-C(7)	-88.41(5)	C(12)-P(1)-C(6)-C(1)	-102.66(8)
C(24)-Fe(1)-P(2)-C(20)	64.30(6)	C(8)-P(1)-C(6)-C(1)	144.46(8)
C(25)-Fe(1)-P(2)-C(20)	-41.86(6)	Fe(1)-P(1)-C(6)-C(1)	18.56(8)
N(1)-Fe(1)-P(2)-C(20)	-141.99(5)	N(1)-C(5)-C(7)-P(2)	-20.12(12)
P(1)-Fe(1)-P(2)-C(20)	159.42(5)	C(4)-C(5)-C(7)-P(2)	159.84(9)
C(24)-Fe(1)-P(2)-C(16)	-73.02(6)	C(20)-P(2)-C(7)-C(5)	161.49(8)
C(25)-Fe(1)-P(2)-C(16)	-179.18(5)	C(16)-P(2)-C(7)-C(5)	-85.24(8)
N(1)-Fe(1)-P(2)-C(16)	80.69(5)	Fe(1)-P(2)-C(7)-C(5)	35.06(8)
P(1)-Fe(1)-P(2)-C(16)	22.10(5)	C(6)-P(1)-C(8)-C(10)	165.99(8)
C(24)-Fe(1)-N(1)-C(1)	-85.57(13)	C(12)-P(1)-C(8)-C(10)	58.07(10)
C(25)-Fe(1)-N(1)-C(1)	100.18(9)	Fe(1)-P(1)-C(8)-C(10)	-82.31(9)
P(2)-Fe(1)-N(1)-C(1)	-159.27(9)	C(6)-P(1)-C(8)-C(9)	-75.86(9)
P(1)-Fe(1)-N(1)-C(1)	-2.27(8)	C(12)-P(1)-C(8)-C(9)	176.22(8)
C(24)-Fe(1)-N(1)-C(5)	100.18(12)	Fe(1)-P(1)-C(8)-C(9)	35.85(9)
C(25)-Fe(1)-N(1)-C(5)	-74.07(9)	C(6)-P(1)-C(8)-C(11)	42.54(10)
P(2)-Fe(1)-N(1)-C(5)	26.48(8)	C(12)-P(1)-C(8)-C(11)	-65.39(10)
P(1)-Fe(1)-N(1)-C(5)	-176.52(8)	Fe(1)-P(1)-C(8)-C(11)	154.24(7)
C(5)-N(1)-C(1)-C(2)	4.88(16)	C(6)-P(1)-C(12)-C(14)	-66.90(10)

C(8)-P(1)-C(12)-C(14)	40.10(10)
Fe(1)-P(1)-C(12)-C(14)	-177.42(7)
C(6)-P(1)-C(12)-C(13)	169.60(8)
C(8)-P(1)-C(12)-C(13)	-83.40(9)
Fe(1)-P(1)-C(12)-C(13)	59.09(9)
C(6)-P(1)-C(12)-C(15)	52.47(9)
C(8)-P(1)-C(12)-C(15)	159.48(8)
Fe(1)-P(1)-C(12)-C(15)	-58.04(9)
C(7)-P(2)-C(16)-C(19)	-66.51(9)
C(20)-P(2)-C(16)-C(19)	42.62(10)
Fe(1)-P(2)-C(16)-C(19)	-174.65(7)
C(7)-P(2)-C(16)-C(18)	169.84(8)
C(20)-P(2)-C(16)-C(18)	-81.03(9)
Fe(1)-P(2)-C(16)-C(18)	61.70(8)
C(7)-P(2)-C(16)-C(17)	53.87(9)
C(20)-P(2)-C(16)-C(17)	163.00(8)
Fe(1)-P(2)-C(16)-C(17)	-54.27(9)
C(7)-P(2)-C(20)-C(22)	163.05(8)
C(16)-P(2)-C(20)-C(22)	53.54(9)
Fe(1)-P(2)-C(20)-C(22)	-86.59(9)
C(7)-P(2)-C(20)-C(21)	-79.41(9)
C(16)-P(2)-C(20)-C(21)	171.08(9)
Fe(1)-P(2)-C(20)-C(21)	30.95(10)
C(7)-P(2)-C(20)-C(23)	38.83(10)
C(16)-P(2)-C(20)-C(23)	-70.68(10)
Fe(1)-P(2)-C(20)-C(23)	149.19(7)
C(25)-Fe(1)-C(24)-O(1)	18.6(17)
N(1)-Fe(1)-C(24)-O(1)	-155.6(17)
P(2)-Fe(1)-C(24)-O(1)	-83.9(17)
P(1)-Fe(1)-C(24)-O(1)	123.1(17)
C(24)-Fe(1)-C(25)-O(2)	8.3(7)
N(1)-Fe(1)-C(25)-O(2)	-174.4(7)
P(2)-Fe(1)-C(25)-O(2)	101.9(7)
P(1)-Fe(1)-C(25)-O(2)	-87.9(7)

III. Infrared spectra of (PNP)Fe$(CO)_2$ and (PNP)Fe$(^{13}CO)_2$



Infrared spectrum of (PNP)Fe$(CO)_2$ (THF solvent)



Infrared spectrum of (PNP)Fe$(^{13}CO)_2$ (THF solvent)

IV. Optimized geometries and absolute energies (a.u.) for (^{tBu}PNP)$FeCl_2$, **1**; quintet, triplet and singlet states.

PBEPBE Structures and Energetics for (^{tBu}PNP)$FeCl_2$, **1**.

(^{tBu}PNP)$FeCl_2$, square planar, 1-SQP, quintet

Charge = 0 Multiplicity = 5

Fe,0,0.0057356183,-0.4801111418,-0.6954081588
N,0,-0.0200472272,1.6975773747,0.220279995
P,0,2.3336477344,-0.2033186129,0.2231186498
P,0,-2.3529930192,-0.1430813564,0.0845952036
C,0,2.2582642706,1.4551814839,1.1035002346
C,0,2.9731450577,-1.373840662,1.6120614309
C,0,3.6477612435,0.058522425,-1.1565150728
C,0,-2.419296898,1.6830515497,-0.3683272181
C,0,-3.7479027517,-0.8984755902,-1.0074236569
C,0,-2.8049565259,-0.2471983922,1.9556161458
C,0,1.1050485917,2.3263957199,0.6441744184
C,0,1.1739549021,3.7275713763,0.763160348
C,0,0.0264567002,4.4924150877,0.4906949466
C,0,-1.1482297594,2.423930296,0.0104758673
C,0,-1.158963188,3.8267849392,0.1386177765
H,0,2.1108390828,4.2029143129,1.0862372906
H,0,0.0504612629,5.5886134905,0.5731105321
H,0,-2.0878403696,4.3832028715,-0.0505439058
H,0,2.0835686751,1.2230168872,2.1753940958
H,0,3.2167154588,2.0068827641,1.053547081
H,0,-2.504728514,1.6893842747,-1.4753043601
H,0,-3.3049131617,2.2100159888,0.040097868
Cl,0,0.045776094,-2.7986925744,-0.7211545219
Cl,0,-0.1101521631,0.5545203454,-2.7651485854
C,0,5.1047215936,0.1138724204,-0.6570955454
H,0,5.4546272093,-0.8569141525,-0.2591963963
H,0,5.7634570391,0.3745627521,-1.5121455112
H,0,5.2549366293,0.8879924874,0.1218162359
C,0,3.4734879965,-1.0866453584,-2.1816084018
H,0,2.4529319219,-1.0887793301,-2.6092652618
H,0,4.1938955289,-0.9370008411,-3.0130560298
H,0,3.663465017,-2.083492481,-1.7426256937
C,0,3.3133780209,1.3967711558,-1.8571183261
H,0,3.527147567,2.2737539665,-1.2144065009
H,0,3.9542241452,1.4869354593,-2.758984339
H,0,2.2586345153,1.4413448315,-2.190760798
C,0,-3.1688530697,-1.0291465565,-2.4352305422
H,0,-2.8784926368,-0.0587362484,-2.8787692111
H,0,-2.2748338033,-1.6795137755,-2.4567494571
H,0,-3.9473713827,-1.4833433526,-3.0841292191
C,0,-5.0340391556,-0.0467823748,-1.069142715
H,0,-5.7590778918,-0.5477450623,-1.7448306347
H,0,-5.5261612959,0.0739316588,-0.0875710579
H,0,-4.8440655881,0.9597136872,-1.4895540867
C,0,-4.0697881466,-2.3245895784,-0.5084546253
H,0,-4.7249750395,-2.8205735728,-1.2544188628
H,0,-3.1506513711,-2.9355257751,-0.4105977578

H,0,-4.6101940383,-2.3290952896,0.4571017374
C,0,-4.2725643696,0.0873634108,2.2853629801
H,0,-4.9763846568,-0.6621317863,1.8791849205
H,0,-4.4030227393,0.0971845406,3.3883129095
H,0,-4.5680475481,1.0864275104,1.9086283681
C,0,-2.4573350979,-1.6745940096,2.4401300646
H,0,-1.4164583522,-1.9460235402,2.1796917447
H,0,-2.5623140643,-1.7188030197,3.54450161
H,0,-3.1202101916,-2.444964314,2.0085195895
C,0,-1.8941101195,0.7425582442,2.716872901
H,0,-0.8244499981,0.5575963276,2.5048121882
H,0,-2.1185455319,1.7991856167,2.4745550916
H,0,-2.0582196238,0.6066499068,3.8064294115
C,0,3.4096234593,-2.7133366141,0.9790361219
H,0,4.344540309,-2.6180727865,0.3944617315
H,0,3.6003469447,-3.4486783845,1.7886585365
H,0,2.6160047603,-3.1247282072,0.3253259135
C,0,4.1110058765,-0.7974645187,2.4811478356
H,0,4.35244213,-1.527210644,3.2826414346
H,0,5.0372535726,-0.6176769652,1.9081390156
H,0,3.8252651817,0.1487647997,2.9812490215
C,0,1.7409671744,-1.6479162836,2.5059488739
H,0,0.9340875762,-2.1319874338,1.9232008852
H,0,2.0348665925,-2.3311142009,3.3302137328
H,0,1.3363688125,-0.7257564982,2.9718722755

SCF Done: E(UPBE-PBE) = -2682.18345057 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2681.579631
Sum of electronic and thermal Energies= -2681.540116
Sum of electronic and thermal Enthalpies= -2681.539172
Sum of electronic and thermal Free Energies= -2681.649424

(^{tBu}PNP)$FeCl_2$, square planar, 1-SQP, triplet

Charge = 0 Multiplicity = 3
Fe,0,0.0096417299,-0.2688205695,-0.4456991384
N,0,-0.0145970855,1.6331934323,0.1610063552
P,0,2.260042963,-0.2112925792,0.2167366477
P,0,-2.26516919,-0.1321344438,0.0438396524
C,0,2.2435399697,1.4184448277,1.1351137483
C,0,2.8967385071,-1.4477900764,1.5491635317
C,0,3.5318919364,0.0298944085,-1.2059822373
C,0,-2.398447475,1.6657721289,-0.4712495826
C,0,-3.5707747429,-1.0135325909,-1.0675749537
C,0,-2.7723124821,-0.230604318,1.9047893257
C,0,1.0917098389,2.2761380154,0.66965921
C,0,1.1343641756,3.6683059293,0.8453591466
C,0,0.0049248762,4.4501091872,0.5515888513
C,0,-1.1449305954,2.3922746491,-0.0526469334
C,0,-1.1561245827,3.7836675674,0.1246500659
H,0,2.0560303653,4.1256176134,1.2308774034
H,0,0.0214981311,5.5418327772,0.6743004009
H,0,-2.0818543335,4.3365365568,-0.0862449977
H,0,2.0701068703,1.1725419281,2.2048484883
H,0,3.2031593625,1.9675894696,1.0855059696

H,0,-2.4267760358,1.6214935694,-1.5804312751
H,0,-3.3040328145,2.1958191715,-0.115396195
Cl,0,-0.022915937,-2.53280858,-0.685117226
Cl,0,-0.0694803353,0.5370840632,-2.6786886585
C,0,5.0000115959,0.0082257309,-0.735896321
H,0,5.3206399238,-0.9879026386,-0.3786794391
H,0,5.6454177091,0.269273335,-1.6006522131
H,0,5.2015769961,0.7523132073,0.0604117252
C,0,3.2859272672,-1.0770030046,-2.2565080108
H,0,2.2539698571,-1.0264708134,-2.6505487938
H,0,3.9888719706,-0.9240305651,-3.1022666442
H,0,3.4567740979,-2.0919022969,-1.8519078482
C,0,3.2462914433,1.4048703584,-1.8531101113
H,0,3.5167206684,2.2479806028,-1.1869308357
H,0,3.8732120778,1.4920245558,-2.7649364023
H,0,2.1883119052,1.5037070509,-2.1627363036
C,0,-2.9667760129,-1.1587723333,-2.4818734943
H,0,-2.7338426014,-0.187142382,-2.9544170241
H,0,-2.0318329459,-1.7468734257,-2.4687946231
H,0,-3.7123829203,-1.6826068869,-3.1169902856
C,0,-4.8871264048,-0.2111680298,-1.1781250934
H,0,-5.5793778623,-0.7685330578,-1.8435065329
H,0,-5.3996929382,-0.0698306733,-0.2102578315
H,0,-4.7298159044,0.7831123062,-1.6386138202
C,0,-3.8535021956,-2.432743955,-0.5279396857
H,0,-4.4627715142,-2.9769369415,-1.2789834241
H,0,-2.9149139408,-3.0007105247,-0.3795252522
H,0,-4.4289816986,-2.4262843529,0.4171345089
C,0,-4.2599460105,0.064989911,2.1777525359
H,0,-4.9264629309,-0.7138116133,1.7646113764
H,0,-4.4261142674,0.0907343223,3.2755259996
H,0,-4.5742418702,1.0474240846,1.7734166964
C,0,-2.4003525104,-1.6361800225,2.4307817723
H,0,-1.3582123091,-1.9007975333,2.1710397137
H,0,-2.4966531617,-1.6454192387,3.5366598755
H,0,-3.0554708703,-2.428614318,2.0295338737
C,0,-1.9202685757,0.8021960787,2.6771636287
H,0,-0.8383086889,0.6408595964,2.5119265046
H,0,-2.1627780899,1.8464683173,2.4019150097
H,0,-2.1233566594,0.6852505139,3.7620950913
C,0,3.2761988066,-2.7854528058,0.8764242495
H,0,4.1867974537,-2.7023204479,0.253523004
H,0,3.4854920877,-3.5364640343,1.6668968905
H,0,2.4459066304,-3.1662540894,0.251272911
C,0,4.0811469521,-0.9167767384,2.3867554736
H,0,4.3137928648,-1.6615449055,3.1766729499
H,0,4.9984578014,-0.7712579086,1.7906770652
H,0,3.8464240395,0.0359505464,2.9012096159
C,0,1.7005631108,-1.7103479117,2.4928780688
H,0,0.8519870665,-2.1478915506,1.9351085443
H,0,2.0137644847,-2.4313630738,3.2768264868
H,0,1.3516052981,-0.7929653771,3.0099791752

SCF Done: E(UPBE-PBE) = -2682.17696240 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -2681.571737

Sum of electronic and thermal Energies= -2681.534089
Sum of electronic and thermal Enthalpies= -2681.533144
Sum of electronic and thermal Free Energies= -2681.636211

(^{tBu}PNP)$FeCl_2$, square planar, 1-SQP, singlet

Charge = 0 Multiplicity = 1

26	0	-0.0113	-0.28017	-0.21015
7	0	-0.00053	1.6319	0.1978
15	0	2.27613	-0.20071	0.13314
15	0	-2.26755	-0.11997	-0.03637
6	0	2.31111	1.45163	1.03088
6	0	2.95573	-1.37572	1.51172
6	0	3.54236	-0.02587	-1.30756
6	0	-2.37335	1.68492	-0.51983
6	0	-3.56518	-0.98777	-1.17486
6	0	-2.85879	-0.1883	1.80839
6	0	1.13004	2.29324	0.62332
6	0	1.18451	3.69149	0.73894
6	0	0.05175	4.4673	0.44486
6	0	-1.11794	2.39537	-0.07272
6	0	-1.11453	3.79409	0.04837
1	0	2.12182	4.15848	1.07129
1	0	0.07575	5.56284	0.52659
1	0	-2.03398	4.34648	-0.18993
1	0	2.20538	1.21321	2.1099
1	0	3.25958	2.01111	0.92016
1	0	-2.38694	1.66738	-1.62947
1	0	-3.27963	2.21836	-0.17105
17	0	-0.12365	-2.56217	-0.29733
17	0	-0.02663	0.32763	-2.41746
6	0	5.0234	-0.05925	-0.8834
1	0	5.33292	-1.04507	-0.48984
1	0	5.64656	0.14586	-1.7795
1	0	5.26729	0.71688	-0.13091
6	0	3.24987	-1.17108	-2.30442
1	0	2.19598	-1.14531	-2.63801
1	0	3.90325	-1.04862	-3.19392
1	0	3.45424	-2.16733	-1.86907
6	0	3.27109	1.3315	-1.998
1	0	3.55803	2.19036	-1.3592
1	0	3.8923	1.38329	-2.91677
1	0	2.21205	1.43714	-2.296
6	0	-2.91457	-1.21702	-2.55712
1	0	-2.62946	-0.27436	-3.05829
1	0	-2.00405	-1.83753	-2.4805
1	0	-3.65491	-1.74154	-3.19829
6	0	-4.83815	-0.13413	-1.37239
1	0	-5.53011	-0.68831	-2.04105
1	0	-5.37961	0.07267	-0.4324
1	0	-4.6166	0.83132	-1.8671
6	0	-3.9358	-2.37369	-0.60249
1	0	-4.53385	-2.91725	-1.36324
1	0	-3.03014	-2.97377	-0.39048
1	0	-4.55331	-2.309	0.31281
6	0	-4.34348	0.17586	2.01238
1	0	-5.0269	-0.5778	1.58027

1	0	-4.55572	0.22376	3.10155
1	0	-4.5981	1.16602	1.58405
6	0	-2.5753	-1.59474	2.38586
1	0	-1.53476	-1.91566	2.19053
1	0	-2.73346	-1.56908	3.48462
1	0	-3.24066	-2.37002	1.96915
6	0	-2.0044	0.8203	2.61186
1	0	-0.92341	0.59278	2.54134
1	0	-2.15711	1.86744	2.28848
1	0	-2.29438	0.75347	3.68129
6	0	3.27036	-2.75866	0.90077
1	0	4.15075	-2.72971	0.23098
1	0	3.50224	-3.47189	1.71971
1	0	2.40172	-3.15178	0.33815
6	0	4.19337	-0.83531	2.26259
1	0	4.44092	-1.54306	3.08193
1	0	5.08735	-0.75036	1.62204
1	0	4.01106	0.15051	2.73411
6	0	1.80998	-1.55027	2.53809
1	0	0.92429	-2.01641	2.06864
1	0	2.15837	-2.21732	3.35449
1	0	1.50637	-0.59285	3.01066

SCF Done: E(RPBE-PBE) = -2682.15844641 A.U. after 6 cycles

Sum of electronic and zero-point Energies= -2681.552782
Sum of electronic and thermal Energies= -2681.514574
Sum of electronic and thermal Enthalpies= -2681.513630
Sum of electronic and thermal Free Energies= -2681.617679

(^{tBu}PNP)$FeCl_2$, trigonal bipyramid, 1-TBP, quintet, C2 sym

Charge = 0 Multiplicity = 5
Fe,0,0.,0.,0.7428801824
N,0,0.,0.,-1.6710823404
P,0,0.8385918073,-2.2822782441,0.0794065226
P,0,-0.8385918073,2.2822782441,0.0794065226
C,0,1.6415296115,-1.8293988576,-1.5616497524
C,0,2.2739776887,-3.0490096475,1.1066513389
C,0,-0.4792720356,-3.60740881,-0.3963807323
C,0,-1.6415296115,1.8293988576,-1.5616497524
C,0,-2.2739776887,3.0490096475,1.1066513389
C,0,0.4792720356,3.60740881,-0.3963807323
C,0,0.7649659101,-0.8896782322,-2.3584756239
C,0,0.781516079,-0.9210480286,-3.7681519202
C,0,0.,0.,-4.4827236163
C,0,-0.7649659101,0.8896782322,-2.3584756239
C,0,-0.781516079,0.9210480286,-3.7681519202
H,0,1.413992154,-1.654221352,-4.2872429204
H,0,0.,0.,-5.5824574295
H,0,-1.413992154,1.654221352,-4.2872429204
H,0,2.563887977,-1.2819951663,-1.2806021941
H,0,1.9480617615,-2.6969803614,-2.1772340158
H,0,-2.563887977,1.2819951663,-1.2806021941
H,0,-1.9480617615,2.6969803614,-2.1772340158
C,0,-2.6762032955,4.4841931823,0.7105458005
H,0,-3.5572725573,4.7832126978,1.3165865572

H,0,-1.8776679754,5.2224394307,0.9106416609
H,0,-2.9692638727,4.5603659059,-0.3555299414
C,0,-3.512925495,2.1352999882,0.9530815268
H,0,-4.0048825657,2.255983024,-0.0328790937
H,0,-3.2652828563,1.0688413604,1.1220363228
H,0,-4.255508254,2.4269830137,1.7244656853
C,0,-1.8267014098,3.0040549345,2.5881828003
H,0,-0.9195736227,3.6060196851,2.7784574183
H,0,-2.6433299453,3.4117793528,3.220390339
H,0,-1.6265661178,1.9643715218,2.9090937262
C,0,0.,4.6597559756,-1.4170284227
H,0,-0.851644542,5.2602816286,-1.052887132
H,0,0.8359226673,5.3598620682,-1.6277673157
H,0,-0.2843096492,4.2000621702,-2.3844728098
C,0,0.9751592884,4.2905781002,0.8980296701
H,0,1.8496021173,4.9289650479,0.6525798949
H,0,0.2092611707,4.943915995,1.35693623
H,0,1.3022041544,3.5384146755,1.6426473359
C,0,1.680281932,2.8448043712,-1.0092907436
H,0,2.0565867806,2.064319959,-0.3200661434
H,0,1.4326401523,2.381524865,-1.9836218891
H,0,2.5026147898,3.5695455023,-1.1879922669
C,0,3.512925495,-2.1352999882,0.9530815268
H,0,3.2652828563,-1.0688413604,1.1220363228
H,0,4.255508254,-2.4269830137,1.7244656853
H,0,4.0048825657,-2.255983024,-0.0328790937
C,0,2.6762032955,-4.4841931823,0.7105458005
H,0,3.5572725573,-4.7832126978,1.3165865572
H,0,1.8776679754,-5.2224394307,0.9106416609
H,0,2.9692638727,-4.5603659059,-0.3555299414
C,0,1.8267014098,-3.0040549345,2.5881828003
H,0,0.9195736227,-3.6060196851,2.7784574183
H,0,2.6433299453,-3.4117793528,3.220390339
H,0,1.6265661178,-1.9643715218,2.9090937262
C,0,0.,-4.6597559756,-1.4170284227
H,0,0.851644542,-5.2602816286,-1.052887132
H,0,-0.8359226673,-5.3598620682,-1.6277673157
H,0,0.2843096492,-4.2000621702,-2.3844728098
C,0,-0.9751592884,-4.2905781002,0.8980296701
H,0,-1.8496021173,-4.9289650479,0.6525798949
H,0,-0.2092611707,-4.943915995,1.35693623
H,0,-1.3022041544,-3.5384146755,1.6426473359
C,0,-1.680281932,-2.8448043712,-1.0092907436
H,0,-2.0565867806,-2.064319959,-0.3200661434
H,0,-1.4326401523,-2.381524865,-1.9836218891
H,0,-2.5026147898,-3.5695455023,-1.1879922669
Cl,0,-1.7192342388,-0.7781543889,2.1072367322
Cl,0,1.7192342388,0.7781543889,2.1072367322

SCF Done: E(UPBE-PBE) = -2682.18342516 A.U. after 4 cycles

Sum of electronic and zero-point Energies= -2681.578626
Sum of electronic and thermal Energies= -2681.539474
Sum of electronic and thermal Enthalpies= -2681.538530
Sum of electronic and thermal Free Energies= -2681.647303

V. Optimized geometries and absolute energies (a.u.) for (^{tBu}PNP)FeHCl, **2**; quintet, triplet and singlet states.

PBEPBE Structure and Energy for (^{tBu}PNP)FeHCl, **2**.

(^{tBu}PNP)FeHCl, square planar, singlet

Charge = 0 Multiplicity = 1
Fe,0,-0.0089213837,-0.28084041,-0.0374453627
N,0,0.0616747984,1.6388291123,0.1252609599
P,0,2.2038251372,-0.2506616338,0.1029090293
P,0,-2.236538172,-0.0456536475,-0.0709302088
C,0,2.3962173573,1.426909586,0.9121143216
C,0,3.174636179,-1.413180458,1.300131501
C,0,3.1385762372,-0.0744195365,-1.5830442496
C,0,-2.3156109626,1.771173707,-0.5426875686
C,0,-3.2963330302,-0.8428578487,-1.4770602097
C,0,-3.1389284692,-0.1597438806,1.6285005768
C,0,1.2194820871,2.2901720768,0.5337563542
C,0,1.307654924,3.6839697189,0.6488578777
C,0,0.1899710987,4.4960465404,0.3860469642
C,0,-1.0411011404,2.4496400978,-0.1092442755
C,0,-0.9995423042,3.8459419291,0.0154560013
H,0,2.2626369851,4.1238556107,0.9695079259
H,0,0.2415782703,5.5894563485,0.477596686
H,0,-1.9150714821,4.4174183964,-0.1932720367
H,0,2.3506787912,1.2280727772,2.0038888483
H,0,3.3577679137,1.9392542504,0.7119076435
H,0,-2.3791691567,1.7909945604,-1.6509971745
H,0,-3.2062165159,2.3099102971,-0.1623799919
Cl,0,-0.047163439,-2.5198428098,-0.5123625862
H,0,0.0043472245,-0.3419289502,1.4306109908
C,0,4.6611019589,0.1334515139,-1.4690505202
H,0,5.1772160537,-0.7681584317,-1.0896567678
H,0,5.076050649,0.3490491116,-2.4768787218
H,0,4.9257616326,0.9881868478,-0.8151630927
C,0,2.8428991062,-1.3120139312,-2.4598589032
H,0,1.7564837562,-1.5046884646,-2.5402698698
H,0,3.246223135,-1.1356453052,-3.4796463701
H,0,3.3101731455,-2.2324590618,-2.0674090987
C,0,2.5211290151,1.1576581549,-2.2865735673
H,0,2.7439025066,2.108218145,-1.7642400834
H,0,2.9412262753,1.2330325591,-3.3114959464
H,0,1.4205520981,1.068459654,-2.3780897139
C,0,-2.3786863358,-0.8603868139,-2.7236186777
H,0,-2.0659209104,0.157381304,-3.0371701756
H,0,-1.4730958031,-1.4685866439,-2.5412837728
H,0,-2.9346863241,-1.3063874524,-3.575282943
C,0,-4.5859069511,-0.067243827,-1.8245676054
H,0,-5.0773142089,-0.5661104161,-2.6868803021
H,0,-5.314905685,-0.05057608,-0.9955971598
H,0,-4.3844664578,0.9784430409,-2.128896189
C,0,-3.643745595,-2.3021039907,-1.1117480309
H,0,-4.0914337493,-2.800626909,-1.9975666814
H,0,-2.737109799,-2.866653762,-0.8211812756

H,0,-4.3856136303,-2.3617063779,-0.2921062871
C,0,-4.6616337166,0.0667690565,1.5733079993
H,0,-5.1866537695,-0.7453969751,1.0369821461
H,0,-5.0613742983,0.0893566241,2.6093199526
H,0,-4.9284000673,1.0318743302,1.0974286348
C,0,-2.8264122844,-1.5461886623,2.2347877285
H,0,-1.7347720273,-1.7230553204,2.2702457098
H,0,-3.227113124,-1.5908989101,3.269571288
H,0,-3.2823678195,-2.3720428485,1.6585873408
C,0,-2.511178924,0.9215175996,2.5374356972
H,0,-1.409728253,0.8228905144,2.5764613586
H,0,-2.7592020002,1.9492611925,2.2071182526
H,0,-2.9078307927,0.7971652078,3.5668579446
C,0,3.5055515658,-2.7474018811,0.5976556757
H,0,4.2944741036,-2.6337029939,-0.1705917791
H,0,3.8850823259,-3.4664967993,1.3538857754
H,0,2.6041768377,-3.1849914696,0.127429607
C,0,4.4682256552,-0.7746397696,1.8531235451
H,0,4.9597915036,-1.5017814463,2.5336688915
H,0,5.1966915409,-0.5160872392,1.0643233589
H,0,4.2661540511,0.1377759104,2.4474659463
C,0,2.2294779138,-1.7180263267,2.4850901637
H,0,1.31904488,-2.2429498715,2.1435648783
H,0,2.7665140027,-2.3654705316,3.2107724275
H,0,1.9135642552,-0.8018088904,3.0232294057

SCF Done: E(RPBE-PBE) = -2222.72113716 A.U. after 4 cycles

Sum of electronic and zero-point Energies= -2222.109818
Sum of electronic and thermal Energies= -2222.073116
Sum of electronic and thermal Enthalpies= -2222.072172
Sum of electronic and thermal Free Energies= -2222.172637

(^{tBu}PNP)FeHCl, square planar, triplet

Charge = 0 Multiplicity = 3
Fe,0,0.0129581456,-0.3935698206,0.0744218772
N,0,-0.0183433088,1.6401632195,-0.3438145083
P,0,2.2414829141,-0.1297334812,0.1694477052
P,0,-2.2448594205,-0.2107712633,-0.0142099983
C,0,2.2579767724,1.6979777216,0.6126202649
C,0,3.2991242506,-0.9324803136,1.5676819012
C,0,3.1897925544,-0.1801975418,-1.522429628
C,0,-2.3595029242,1.4028494986,-1.0106232006
C,0,-3.3129976444,-1.3733974703,-1.1331768331
C,0,-3.1520698059,0.1663078753,1.6530443082
C,0,1.0529825323,2.4097414267,0.0418060052
C,0,1.0147705062,3.8131464634,-0.0033501393
C,0,-0.1541179069,4.46965639,-0.4283212933
C,0,-1.1788421615,2.2824671179,-0.7041449567
C,0,-1.2715952217,3.6822528696,-0.7607496887
H,0,1.9023693046,4.3819275318,0.3075773165
H,0,-0.2000897877,5.5665695382,-0.4775079037
H,0,-2.2192169469,4.1450369349,-1.0696013656
H,0,2.1645507934,1.715948567,1.719559569
H,0,3.1960487522,2.2290237332,0.3552154274
H,0,-2.3187462041,1.079966668,-2.0714098726

H,0,-3.3101579396,1.9546657711,-0.8747323532
Cl,0,0.1771462623,-2.6541633073,-0.4862047021
H,0,-0.0351525423,-0.1260287644,1.6175436119
C,0,4.6650680968,0.2614587198,-1.4341960146
H,0,5.2877336255,-0.4717156398,-0.8881794875
H,0,5.0784223971,0.3382227847,-2.4623224722
H,0,4.7906392295,1.2531681105,-0.9553754137
C,0,3.1098135822,-1.5909799596,-2.1476135341
H,0,2.0677930516,-1.9582009678,-2.1949252426
H,0,3.5200478924,-1.5439046732,-3.1788440629
H,0,3.6992195742,-2.3387027381,-1.58803203
C,0,2.4395363956,0.7884408836,-2.467070739
H,0,2.5116612949,1.8454289817,-2.1455831477
H,0,2.8900183814,0.7166929152,-3.479069354
H,0,1.3677204078,0.5251109537,-2.5532329384
C,0,-2.4998940877,-1.6262514372,-2.4268272424
H,0,-2.4144303797,-0.7182942048,-3.0584193497
H,0,-1.4874926932,-2.0107491676,-2.2072065635
H,0,-3.035807316,-2.388050176,-3.0312844575
C,0,-4.6841116706,-0.7969894111,-1.5529458337
H,0,-5.1350913503,-1.4797526205,-2.3038532309
H,0,-5.3979618049,-0.7137022663,-0.7165022519
H,0,-4.5936716346,0.1968932182,-2.0338260189
C,0,-3.5002399152,-2.7186597858,-0.3992215497
H,0,-3.9709681734,-3.4495621057,-1.0900811449
H,0,-2.5256274318,-3.1317155762,-0.0752728104
H,0,-4.1647080706,-2.6224945924,0.4812136742
C,0,-4.682026575,0.3246046534,1.5649488073
H,0,-5.1918002286,-0.6345670155,1.3566986348
H,0,-5.0601214308,0.6874767404,2.5441364027
H,0,-4.9918624926,1.0627490235,0.7991971397
C,0,-2.7991953675,-0.9701618842,2.6385141196
H,0,-1.7012448151,-1.08356956,2.723414914
H,0,-3.2076256405,-0.7229074621,3.6412290587
H,0,-3.2236750595,-1.944316303,2.3312385246
C,0,-2.5527071166,1.4822741101,2.1992439257
H,0,-1.4468773852,1.4325861908,2.2307688608
H,0,-2.8559187509,2.3647266473,1.6024210599
H,0,-2.9200759116,1.6381467059,3.2352216576
C,0,3.7625378101,-2.3354546635,1.1181518825
H,0,4.5736727361,-2.2899310131,0.3662655832
H,0,4.1610068038,-2.8803941926,1.9994064762
H,0,2.9220320963,-2.9241696258,0.7017394055
C,0,4.5157500621,-0.0827108149,1.9962070021
H,0,5.059367311,-0.6195529821,2.8020384486
H,0,5.2315757454,0.0935393024,1.1742338778
H,0,4.2147017019,0.8999957464,2.4089228568
C,0,2.3692577484,-1.1095394475,2.7893199065
H,0,1.5185269826,-1.7749368059,2.5543278854
H,0,2.957735696,-1.5568973342,3.618678919
H,0,1.9482732407,-0.1498700904,3.1476544332

SCF Done: E(UPBE-PBE) = -2222.70537765 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -2222.095841
Sum of electronic and thermal Energies= -2222.058742

Sum of electronic and thermal Enthalpies= -2222.057797
Sum of electronic and thermal Free Energies= -2222.160599

(^{tBu}PNP)FeHCl, square planar, quintet

Charge = 0 Multiplicity = 5
Fe,0,-0.0050034537,-0.5665441901,-0.4085370795
N,0,0.0094176345,1.6595205388,0.1485085243
P,0,-2.4152952808,-0.1423373057,-0.1135835876
P,0,2.4319950839,-0.1978270899,0.0275886351
C,0,-2.3409185386,1.663583593,-0.6354100386
C,0,-3.6506818565,-0.8866516507,-1.3913545401
C,0,-3.1973567852,-0.0958263203,1.6532300008
C,0,2.3604020746,1.4754005803,0.8930287847
C,0,3.3467702055,-1.2593091847,1.3463444017
C,0,3.5081574571,0.1253622503,-1.5332321803
C,0,-1.0978241412,2.3893426189,-0.1598414945
C,0,-1.0944011895,3.7966153793,-0.1093491808
C,0,0.0864553733,4.4721902774,0.2414167377
C,0,1.1555951603,2.3072237078,0.4974676762
C,0,1.2290650786,3.7138636264,0.540792967
H,0,-2.0103949005,4.3485254795,-0.3628322198
H,0,0.1151114365,5.5707640585,0.2788941839
H,0,2.1741314662,4.1986619327,0.8232394415
H,0,-2.2898156323,1.6206094246,-1.7445304421
H,0,-3.2469418719,2.2439897169,-0.3699057306
H,0,2.2778992836,1.2458459468,1.9762438316
H,0,3.2883189716,2.0671134554,0.7671393508
Cl,0,-0.1083837125,-2.8528709757,-0.0067030099
H,0,-0.0278829755,-0.077169908,-1.9870129401
C,0,-4.6747188602,0.3354763702,1.7264330964
H,0,-5.3510037222,-0.401472604,1.2543758415
H,0,-4.9790065017,0.4227147928,2.7915890868
H,0,-4.8499237166,1.3224541444,1.2536638037
C,0,-3.0166123416,-1.4961016737,2.2845745638
H,0,-1.9672456238,-1.8405583534,2.2061339288
H,0,-3.293407157,-1.4501936307,3.3590482767
H,0,-3.6526207449,-2.2623922713,1.8068928973
C,0,-2.3511270471,0.8993105755,2.4808626562
H,0,-2.471569442,1.9464706154,2.1411487497
H,0,-2.6779071463,0.8527541825,3.5408461793
H,0,-1.272987378,0.6464155875,2.4477849827
C,0,2.3006468133,-1.5349921917,2.4530348332
H,0,1.9605558072,-0.6080241633,2.9591125017
H,0,1.4146864938,-2.0596230494,2.0474302593
H,0,2.7619212723,-2.1794863871,3.2308102948
C,0,4.5860632708,-0.5947162723,1.982819999
H,0,4.9923952109,-1.2681183307,2.7670336598
H,0,5.39342298,-0.4103506483,1.2527836056
H,0,4.3417459586,0.3666936708,2.4767486547
C,0,3.7346969924,-2.6081487871,0.7029756945
H,0,4.0974196906,-3.2974690963,1.4939199034
H,0,2.8629397444,-3.0840394582,0.2126621556
H,0,4.549014951,-2.4983031934,-0.0391679791
C,0,5.0077904818,0.3642214221,-1.2792157785

H,0,5.5204349016,-0.5447462762,-0.9108318217
H,0,5.495822833,0.651888629,-2.2345648111
H,0,5.1901418796,1.1857661694,-0.5573280078
C,0,3.3001291384,-1.0850415416,-2.4720840957
H,0,2.2213117169,-1.2413255261,-2.6685380962
H,0,3.808522952,-0.8898128793,-3.4397552984
H,0,3.7147359446,-2.0217577895,-2.055332
C,0,2.8966303751,1.369080607,-2.2180561766
H,0,1.804435324,1.2444045644,-2.3636340335
H,0,3.0819354523,2.3007576358,-1.6477722999
H,0,3.3643683416,1.4930829106,-3.2172833072
C,0,-4.1322661763,-2.2615894321,-0.8790235337
H,0,-4.8287825657,-2.1753840121,-0.0233969162
H,0,-4.6767194151,-2.7779082405,-1.6969774057
H,0,-3.2792461727,-2.9033361405,-0.5830855064
C,0,-4.8603398703,0.0146348727,-1.7191336739
H,0,-5.4996394949,-0.4993110105,-2.4679872361
H,0,-5.490670758,0.2307024937,-0.8378345399
H,0,-4.5492420797,0.9785128231,-2.167415852
C,0,-2.8374535958,-1.1278651673,-2.6844556474
H,0,-1.9899994581,-1.8146694711,-2.5039680574
H,0,-3.5091448768,-1.5777003201,-3.4467758442
H,0,-2.413140673,-0.1965797379,-3.1062418166

SCF Done: E(UPBE-PBE) = -2222.69626798 A.U. after 12 cycles

Sum of electronic and zero-point Energies= -2222.088125
Sum of electronic and thermal Energies= -2222.050219
Sum of electronic and thermal Enthalpies= -2222.049275
Sum of electronic and thermal Free Energies= -2222.155496

VI. Optimized geometry and absolute energies (a.u.) for the (^{tBu}PNP)FeHCl:MeCN adduct.

(^{tBu}PNP)FeHCl:MeCN Adduct, octahedral, singlet

Charge = 0 Multiplicity = 1

Fe,0,-0.007571188,-0.2252176868,0.1863017619
N,0,0.0238375277,1.5459247702,-0.5824921278
P,0,-2.1873302646,-0.2825340967,-0.2895239054
P,0,2.2187846118,-0.1758482047,-0.1092615261
C,0,-2.1772400258,1.0975605561,-1.5731034112
C,0,-2.9305095708,-1.7790893957,-1.2667392856
C,0,-3.4910638769,0.3306969047,1.0129412592
C,0,2.3927405413,1.6961025505,0.0822141532
C,0,3.5154630685,-0.8444050862,1.1660565615
C,0,2.8370361321,-0.5611794099,-1.9044040451
C,0,-1.0634681694,2.0620087444,-1.2556117862
C,0,-1.1049567238,3.3951956991,-1.691681152
C,0,0.0056084306,4.2365175204,-1.4973560342
C,0,1.1455931948,2.3421843201,-0.475253903
C,0,1.1525717388,3.6788192516,-0.9059238844
H,0,-2.0079856351,3.7577874026,-2.2022811273
H,0,-0.0117045502,5.2847709074,-1.8264898287
H,0,2.0687716184,4.2721023199,-0.7767558792
H,0,-1.9224106444,0.5925831016,-2.5297158475
H,0,-3.1434960248,1.6176860096,-1.7205709616
H,0,2.4530964234,1.8579265565,1.1790712517
H,0,3.3013479993,2.1446173248,-0.3677677275
Cl,0,-0.0076516607,-2.410381702,1.1263067614
H,0,-0.0171933192,-0.8066277219,-1.1972038983
C,0,-4.9665241788,0.3305881967,0.5648441543
H,0,-5.366201226,-0.6885379629,0.4105794843
H,0,-5.5816488213,0.8040334124,1.3602534906
H,0,-5.1257454756,0.9157551508,-0.3628184918
C,0,-3.3356487203,-0.5366139625,2.2832638566
H,0,-2.2763149424,-0.6357157395,2.5803762105
H,0,-3.9013594086,-0.0692312322,3.1179517041
H,0,-3.7327603892,-1.5579378243,2.1403813166
C,0,-3.1131851188,1.7916910515,1.3563662026
H,0,-3.2899790124,2.4808153515,0.5079999117
H,0,-3.752355626,2.1362960192,2.1972838633
H,0,-2.0593004251,1.8896028677,1.6689171087
C,0,2.8726169396,-0.7260481382,2.5655570669
H,0,2.6989376164,0.330665053,2.853902958
H,0,1.911890408,-1.2731118986,2.6083874848
H,0,3.5712105655,-1.1646398232,3.3096316248
C,0,4.8444539061,-0.0578933481,1.1808788633
H,0,5.4908805716,-0.4715911658,1.9842627128
H,0,5.4075878189,-0.1300849021,0.2350326696
H,0,4.6897641563,1.0147326055,1.4101558505
C,0,3.7787979568,-2.3432668271,0.9039537895
H,0,4.3780661088,-2.7525693938,1.7446925309
H,0,2.8285839336,-2.9098230382,0.8544786274
H,0,4.3558130031,-2.5165361327,-0.0237730607
C,0,4.3496828441,-0.3623392292,-2.1300774741
H,0,4.9621183184,-1.1012326852,-1.5810285599

H,0,4.5706035762,-0.4959501876,-3.2103555351
H,0,4.6900794557,0.6547646589,-1.8505033289
C,0,2.4388267646,-2.0137338656,-2.2509986628
H,0,1.3587860844,-2.173948077,-2.0741077432
H,0,2.6526697956,-2.2023709246,-3.3242929074
H,0,2.9943742624,-2.761823982,-1.658329231
C,0,2.0863236902,0.3768242022,-2.8771035497
H,0,0.9908089293,0.2714800625,-2.7693859897
H,0,2.3559720525,1.4418854846,-2.7378500625
H,0,2.3591135511,0.0963564863,-3.9162412855
C,0,-3.3960856624,-2.8635811572,-0.26858973
H,0,-4.2979223824,-2.5634863141,0.2979799422
H,0,-3.6563130191,-3.7823926084,-0.8353991269
H,0,-2.5856451914,-3.1153584285,0.4427476413
C,0,-4.0931295368,-1.3804704058,-2.2038333129
H,0,-4.444113742,-2.2895619449,-2.7363834985
H,0,-4.9604063051,-0.9569455842,-1.6696445915
H,0,-3.7766968879,-0.6550484065,-2.9784767238
C,0,-1.8120715473,-2.4011321896,-2.1317603673
H,0,-0.9877511126,-2.7780018359,-1.4992907999
H,0,-2.2458234974,-3.2515728171,-2.700480474
H,0,-1.3919120303,-1.6860784346,-2.8675170505
N,0,0.0079671272,0.508546016,1.9469522019
C,0,0.0138286169,0.9754627895,3.0322616726
C,0,0.0396478499,1.4972263596,4.3953996932
H,0,0.0552361209,2.6054793919,4.3926134442
H,0,-0.8547901932,1.1639290082,4.9592517857
H,0,0.9407475597,1.1367469095,4.9324082692

SCF Done: E(RPBE-PBE) = -2355.33657024 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -2354.677387
Sum of electronic and thermal Energies= -2354.636683
Sum of electronic and thermal Enthalpies= -2354.635739
Sum of electronic and thermal Free Energies= -2354.744630

---

acetonitrile

Charge = 0 Multiplicity = 1
C,0,0.,0.,0.276666693
N,0,0.,0.,1.4556633582
C,0,0.,0.,-1.1900641343
H,0,1.0389861803,0.,-1.5697529533
H,0,-0.5194930902,-0.8997884264,-1.5697529533
H,0,-0.5194930902,0.8997884264,-1.5697529533

SCF Done: E(RPBE-PBE) = -132.588967303 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -132.544964
Sum of electronic and thermal Energies= -132.541300
Sum of electronic and thermal Enthalpies= -132.540356
Sum of electronic and thermal Free Energies= -132.568015

VII. Optimized geometries and absolute energies (a.u.) for (^{tBu}PNP)Fe(CO)$_2$, **3-SQP** and **3-TBP**, and the TS for their interconversion. Electronic transition energies for **3-SQP** and **3-TBP**.

(^{tBu}PNP)Fe(CO)$_2$, square planar, 3-SQP

Charge = 0 Multiplicity = 1

Fe,0,-0.0053603688,-0.2809316565,-0.4410325224
N,0,-0.0362882246,1.6811942212,0.0676130001
P,0,2.1612409284,-0.1978649518,0.1650913464
P,0,-2.1964410719,-0.1231666589,-0.0215066964
C,0,2.2282752982,1.496200026,0.9751358161
C,0,2.8783856185,-1.3200958675,1.5805207565
C,0,3.4617092066,-0.0682713514,-1.2702204511
C,0,-2.4150233741,1.6714457546,-0.5318826793
C,0,-3.5091914868,-1.0430200475,-1.1058641101
C,0,-2.7528776228,-0.1851478614,1.8429552983
C,0,1.0847349208,2.3538155661,0.5046369574
C,0,1.1361645158,3.7519393572,0.5997676416
C,0,0.000010615,4.522885016,0.2918284618
C,0,-1.1687845241,2.4354720402,-0.1581193507
C,0,-1.1743310253,3.8330961448,-0.0669598061
H,0,2.0667618465,4.2267446868,0.9411090591
H,0,0.0201958756,5.6191949217,0.3558448939
H,0,-2.1052036479,4.3751817513,-0.2853264934
H,0,2.0817544061,1.3150935106,2.0619446065
H,0,3.2051475978,2.0040100937,0.859781256
H,0,-2.5088987251,1.6386025062,-1.6388583345
H,0,-3.3223036692,2.1661028415,-0.1319314209
C,0,-0.0523765721,-1.9943515997,-0.231643495
O,0,-0.0971942919,-3.1878135443,-0.164208171
C,0,0.0207561888,-0.1053169061,-2.1863589125
O,0,0.0501732429,-0.1131261674,-3.3773753903
C,0,4.9340226904,0.014199922,-0.8208835143
H,0,5.2999999444,-0.9357587667,-0.3889625201
H,0,5.5643352426,0.2312127462,-1.7091355939
H,0,5.1114117875,0.8268163051,-0.0885839773
C,0,3.2797603464,-1.2768969878,-2.2145166678
H,0,2.2451345563,-1.3427536084,-2.5948674014
H,0,3.9558158972,-1.1593263872,-3.0873856077
H,0,3.5288994295,-2.2361913164,-1.7240891921
C,0,3.1291748089,1.2278917321,-2.0454887981
H,0,3.3954521246,2.1373780173,-1.4717968781
H,0,3.7192830003,1.2432914569,-2.9853466434
H,0,2.0607833832,1.2859616965,-2.3199582703
C,0,-2.9115916001,-1.2249558847,-2.5169784878
H,0,-2.6497802519,-0.2656038062,-3.0013780729
H,0,-2.0005995486,-1.8488491277,-2.4989301359
H,0,-3.6683101746,-1.7283237863,-3.1551008763
C,0,-4.8320309851,-0.2545968705,-1.2445142843
H,0,-5.5270416343,-0.839445529,-1.8830343845
H,0,-5.339442419,-0.077077756,-0.2807934641
H,0,-4.6824470122,0.7228635264,-1.7420950188
C,0,-3.7963861799,-2.4496686088,-0.535968116
H,0,-4.408105514,-3.0112380466,-1.2725409559

H,0,-2.8663805893,-3.025686231,-0.3680805571
H,0,-4.3703326178,-2.419033147,0.4087790119
C,0,-4.2471969063,0.1034868453,2.0838659942
H,0,-4.9021972232,-0.701246559,1.701850529
H,0,-4.4271414746,0.1779815755,3.1773874679
H,0,-4.5715297927,1.0634079678,1.6344536451
C,0,-2.3739278603,-1.5604146068,2.4325099836
H,0,-1.3004432648,-1.7717470405,2.2706614088
H,0,-2.5614114903,-1.5487824381,3.5268281522
H,0,-2.9548243307,-2.3945414698,2.0018872172
C,0,-1.9200713725,0.8787686237,2.5927998476
H,0,-0.8385309534,0.7302759532,2.4094457708
H,0,-2.1868737251,1.9136439047,2.3039857133
H,0,-2.1066299672,0.7745822707,3.6822365637
C,0,3.2520118707,-2.7052034278,1.0093486254
H,0,4.1420653738,-2.6607542898,0.3536993478
H,0,3.4954390355,-3.3904055808,1.8483277163
H,0,2.4178287741,-3.1579489109,0.4415747365
C,0,4.0973674854,-0.7157349985,2.3152008031
H,0,4.3719159348,-1.3892839737,3.1544737201
H,0,4.9887706695,-0.6140916415,1.6741861252
H,0,3.8769652781,0.2745325108,2.7597375452
C,0,1.7545029207,-1.5105452314,2.6230485905
H,0,0.8674108947,-1.9940817422,2.1795659472
H,0,2.1348043255,-2.1536515151,3.4445982003
H,0,1.4272884932,-0.5520848689,3.0749698689

SCF Done: E(RPBE-PBE) = -1988.62264938 A.U. after 9 cycles

Sum of electronic and zero-point Energies= -1988.002607
Sum of electronic and thermal Energies= -1987.963934
Sum of electronic and thermal Enthalpies= -1987.962990
Sum of electronic and thermal Free Energies= -1988.067295

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 1.8920 eV 655.29 nm f=0.0557
131 ->132 0.56012
131 ->135 0.34176

Excited State 2: Singlet-A 2.2730 eV 545.47 nm f=0.0423
131 ->132 -0.35428
131 ->135 0.52556
131 ->141 -0.12218

Excited State 3: Singlet-A 2.4695 eV 502.07 nm f=0.0010
131 ->133 -0.67927
131 ->137 0.11622

(^{tBu}PNP)Fe(CO)$_2$, trigonal-bipyramidal symmetry, 3-TBP

Charge = 0 Multiplicity = 1
Fe,0,0.,0.,0.4475034659
N,0,0.,0.,-1.5962165017
P,0,0.7766758096,-2.0910958556,0.1316805923
P,0,-0.7766758096,2.0910958556,0.1316805923

C,0,1.6573112583,-1.7816407548,-1.4968252042
C,0,2.1372905397,-2.8325813718,1.2879929881
C,0,-0.5429204651,-3.4584302515,-0.2978614945
C,0,-1.6573112583,1.7816407548,-1.4968252042
C,0,-2.1372905397,2.8325813718,1.2879929881
C,0,0.5429204651,3.4584302515,-0.2978614945
C,0,0.7866773075,-0.8718969629,-2.3192782349
C,0,0.8081421579,-0.8928157145,-3.7208803301
C,0,0.,0.,-4.4504554338
C,0,-0.7866773075,0.8718969629,-2.3192782349
C,0,-0.8081421579,0.8928157145,-3.7208803301
H,0,1.4693795786,-1.6056257187,-4.233021071
H,0,0.,0.,-5.548927099
H,0,-1.4693795786,1.6056257187,-4.233021071
H,0,2.5725177682,-1.2214216664,-1.2112716569
H,0,1.9666859435,-2.683941866,-2.0576230253
H,0,-2.5725177682,1.2214216664,-1.2112716569
H,0,-1.9666859435,2.683941866,-2.0576230253
C,0,1.2927185216,0.5156458488,1.4839991104
C,0,-1.2927185216,-0.5156458488,1.4839991104
O,0,2.0559559987,0.8670053844,2.3373932714
O,0,-2.0559559987,-0.8670053844,2.3373932714
C,0,-2.4828488091,4.3122484224,1.0173877392
H,0,-3.3275132255,4.599095486,1.6784007476
H,0,-1.6466800257,4.9978160873,1.2439567344
H,0,-2.8109768103,4.4841951913,-0.0264059663
C,0,-3.444486629,2.0239766081,1.110978094
H,0,-3.948505139,2.2574963423,0.1523174061
H,0,-3.2909081388,0.9336867462,1.179542334
H,0,-4.1414075876,2.3115366288,1.925339208
C,0,-1.645679287,2.6773493952,2.7467035503
H,0,-0.7021703156,3.2220911609,2.9346711281
H,0,-2.416263262,3.0904748367,3.4309239275
H,0,-1.4862533492,1.6173678536,3.0110274958
C,0,0.,4.5978722023,-1.1899742123
H,0,-0.818730873,5.1742980545,-0.7284339173
H,0,0.8290599216,5.3083276013,-1.3935390296
H,0,-0.3465730398,4.2222078658,-2.1722305071
C,0,1.1299475472,4.0389966861,1.0085172788
H,0,1.9850099282,4.6995963628,0.7531015284
H,0,0.4017615007,4.6528842775,1.571029859
H,0,1.5125462977,3.2452833653,1.6767430276
C,0,1.692718891,2.778806782,-1.0779213087
H,0,2.095579317,1.9070284341,-0.5323735449
H,0,1.3706780592,2.4423329046,-2.0815731179
H,0,2.5082158073,3.5193325124,-1.2169219207
C,0,3.444486629,-2.0239766081,1.110978094
H,0,3.2909081388,-0.9336867462,1.179542334
H,0,4.1414075876,-2.3115366288,1.925339208
H,0,3.948505139,-2.2574963423,0.1523174061
C,0,2.4828488091,-4.3122484224,1.0173877392
H,0,3.3275132255,-4.599095486,1.6784007476
H,0,1.6466800257,-4.9978160873,1.2439567344
H,0,2.8109768103,-4.4841951913,-0.0264059663
C,0,1.645679287,-2.6773493952,2.7467035503
H,0,0.7021703156,-3.2220911609,2.9346711281

H,0,2.416263262,-3.0904748367,3.4309239275
H,0,1.4862533492,-1.6173678536,3.0110274958
C,0,0.,-4.5978722023,-1.1899742123
H,0,0.818730873,-5.1742980545,-0.7284339173
H,0,-0.8290599216,-5.3083276013,-1.3935390296
H,0,0.3465730398,-4.2222078658,-2.1722305071
C,0,-1.1299475472,-4.0389966861,1.0085172788
H,0,-1.9850099282,-4.6995963628,0.7531015284
H,0,-0.4017615007,-4.6528842775,1.571029859
H,0,-1.5125462977,-3.2452833653,1.6767430276
C,0,-1.692718891,-2.778806782,-1.0779213087
H,0,-2.095579317,-1.9070284341,-0.5323735449
H,0,-1.3706780592,-2.4423329046,-2.0815731179
H,0,-2.5082158073,-3.5193325124,-1.2169219207

SCF Done: E(RPBE-PBE) = -1988.62423932 A.U. after 9 cycles

Sum of electronic and zero-point Energies= -1988.002949
Sum of electronic and thermal Energies= -1987.964596
Sum of electronic and thermal Enthalpies= -1987.963652
Sum of electronic and thermal Free Energies= -1988.066308

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.2008 eV 563.37 nm f=0.1158
131 ->132 0.66034

Excited State 2: Singlet-B 2.3277 eV 532.64 nm f=0.0007
131 ->134 -0.21700
131 ->135 -0.60630
131 ->137 -0.11160

Excited State 3: Singlet-B 2.7178 eV 456.19 nm f=0.0014
131 ->133 -0.69357

(^{tBu}PNP)Fe(CO)$_2$, TS SQP<->TBP

Charge = 0 Multiplicity = 1
Fe,0,-0.014513805,-0.4117402199,-0.2236502336
N,0,-0.0029335051,1.6387673127,-0.1014640323
P,0,-2.2280972939,-0.0829015608,-0.0988725479
P,0,2.2141497785,-0.1881739174,0.1462622691
C,0,-2.2938470225,1.5816410346,-0.9532704502
C,0,-3.4691623445,-1.1913522193,-1.0879906324
C,0,-2.9231931418,0.2504578396,1.6932851248
C,0,2.2436762841,1.5466585787,0.8651415527
C,0,3.1075018691,-1.200640027,1.5420026348
C,0,3.3608153519,-0.0079294743,-1.4196414217
C,0,-1.1014437796,2.3774605713,-0.495549084
C,0,-1.1153515165,3.7784849209,-0.5077677049
C,0,0.0236224635,4.4981905055,-0.1001215507
C,0,1.0948018982,2.3527086867,0.3247608218
C,0,1.1394439457,3.755497726,0.3254114052
H,0,-2.0224684914,4.2976032467,-0.8474233606
H,0,0.036709819,5.5966338798,-0.1045254867
H,0,2.049854373,4.2572511696,0.6822914416

H,0,-2.1636841289,1.3420147995,-2.0293417361
H,0,-3.2392532511,2.1446166643,-0.8345367626
H,0,2.0884945456,1.417732251,1.9562932855
H,0,3.2066120628,2.0757465083,0.7286879329
C,0,0.017594679,-1.0095341051,-1.8632468959
O,0,0.035770739,-1.6145834315,-2.8944402417
C,0,-0.1507970851,-1.8184926156,0.7664510567
O,0,-0.2734827872,-2.8679489575,1.3317584722
C,0,4.5361259391,-0.7100846761,1.8715679962
H,0,4.8617305444,-1.1902331557,2.8181380217
H,0,5.2728937664,-0.9883174957,1.0986311434
H,0,4.5881081122,0.3855353006,2.0271271005
C,0,2.2749442209,-1.0675268903,2.8413004244
H,0,2.406656744,-0.0764301951,3.3196561301
H,0,1.1972647025,-1.2362621774,2.6789027389
H,0,2.6358019856,-1.8264605369,3.5658994809
C,0,3.1642306292,-2.6886714615,1.1303428935
H,0,3.8118894189,-2.8489091155,0.2487553993
H,0,3.5937367037,-3.2782478715,1.9672374931
H,0,2.1637195257,-3.1003882215,0.909310322
C,0,4.7979051708,0.4862011569,-1.1438316148
H,0,5.4500642865,-0.308128927,-0.7405100705
H,0,5.2467798678,0.8156636837,-2.1044175865
H,0,4.838029489,1.351633292,-0.454150108
C,0,3.430114258,-1.3512848333,-2.1776166981
H,0,3.9239816095,-1.1874503615,-3.1584125936
H,0,4.0276279522,-2.1054652565,-1.6316591116
H,0,2.4293286766,-1.773275917,-2.3748935268
C,0,2.672012839,1.0465705534,-2.3194623063
H,0,1.6057910963,0.8132428178,-2.4914966749
H,0,2.7419025636,2.065659706,-1.8909540437
H,0,3.1852571523,1.0625641657,-3.3033890905
C,0,-3.3035200759,-0.9195984323,-2.6024096322
H,0,-2.256736194,-0.9870959186,-2.9416845021
H,0,-3.879577515,-1.6914490113,-3.1542804177
H,0,-3.7182687585,0.0648205071,-2.8957693363
C,0,-4.9572472895,-0.9525250285,-0.7523742488
H,0,-5.5701654744,-1.5846525342,-1.4286425286
H,0,-5.2224932463,-1.2336224561,0.282446686
H,0,-5.2621431205,0.0986412872,-0.9234930078
C,0,-3.0992263631,-2.6670921597,-0.8130423059
H,0,-3.170874771,-2.9345122356,0.2570639437
H,0,-3.7985703131,-3.3215202622,-1.3743057623
H,0,-2.0711317243,-2.892146917,-1.1499797916
C,0,-4.1711370601,1.1588503079,1.7263970003
H,0,-5.0452725619,0.7307418199,1.2072786385
H,0,-4.4630302025,1.3189841732,2.7857947465
H,0,-3.9634995783,2.1585029741,1.2974265484
C,0,-3.2207889924,-1.0977942354,2.3872196076
H,0,-3.4814672937,-0.9025586279,3.4485954622
H,0,-4.0738010107,-1.6378920675,1.9361937874
H,0,-2.3405379752,-1.7673061227,2.3779886873
C,0,-1.8080097782,0.9559362659,2.4985550456
H,0,-0.8528985971,0.4023031484,2.4241998145
H,0,-1.6358828635,1.9922192599,2.1508042467
H,0,-2.1160659405,1.0036886066,3.5642389777

SCF Done: E(RPBE-PBE) = -1988.62118299   A.U. after   4 cycles

Sum of electronic and zero-point Energies=   -1988.001238
Sum of electronic and thermal Energies=   -1987.963246
Sum of electronic and thermal Enthalpies=   -1987.962302
Sum of electronic and thermal Free Energies=   -1988.064707

VIII. Optimized geometry and absolute energies (a.u.) for (^{iPr}PNP)Fe(CO)$_2$, **4**. Electronic transition energies for **4**.

Charge = 0 Multiplicity = 1

26	0	0.	0.	0.4355
7	0	0.	0.	-1.60096
15	0	0.	2.19439	0.18329
15	0	0.	-2.19439	0.18329
6	0	-0.83021	2.29544	-1.50124
6	0	-1.12606	3.28974	1.23609
6	0	1.59788	3.18167	-0.08791
6	0	0.83021	-2.29544	-1.50124
6	0	1.12606	-3.28974	1.23609
6	0	-1.59788	-3.18167	-0.08791
6	0	-0.38798	1.10973	-2.31961
6	0	-0.39752	1.13693	-3.72204
6	0	0.	0.	-4.4498
6	0	0.38798	-1.10973	-2.31961
6	0	0.39752	-1.13693	-3.72204
1	0	-0.72788	2.05056	-4.23569
1	0	0.	0.	-5.54848
1	0	0.72788	-2.05056	-4.23569
1	0	-1.91722	2.20073	-1.28367
1	0	-0.66906	3.24904	-2.04178
1	0	1.91722	-2.20073	-1.28367
1	0	0.66906	-3.24904	-2.04178
6	0	-1.46786	0.05975	1.37094
6	0	1.46786	-0.05975	1.37094
8	0	-2.41274	0.07716	2.10365
8	0	2.41274	-0.07716	2.10365
6	0	1.17853	-4.75962	0.78227
1	0	1.94938	-5.30384	1.36498
1	0	0.21373	-5.2767	0.95282
1	0	1.4382	-4.8623	-0.28982
6	0	0.84329	-3.15955	2.74535
1	0	-0.08247	-3.68802	3.04178
1	0	1.68061	-3.60723	3.31779
1	0	0.75102	-2.10095	3.04876
6	0	-2.37756	-3.42986	1.21745
1	0	-3.32868	-3.95083	0.98419
1	0	-1.81721	-4.06422	1.92876
1	0	-2.63073	-2.48014	1.72496
6	0	-2.48897	-2.47094	-1.12432
1	0	-2.74305	-1.44848	-0.78409
1	0	-2.00503	-2.39104	-2.11645
1	0	-3.43397	-3.03731	-1.25232
6	0	-1.17853	4.75962	0.78227
1	0	-1.94938	5.30384	1.36498
1	0	-0.21373	5.2767	0.95282
1	0	-1.4382	4.8623	-0.28982
6	0	-0.84329	3.15955	2.74535
1	0	0.08247	3.68802	3.04178
1	0	-1.68061	3.60723	3.31779
1	0	-0.75102	2.10095	3.04876
6	0	2.37756	3.42986	1.21745

1	0	3.32868	3.95083	0.98419
1	0	1.81721	4.06422	1.92876
1	0	2.63073	2.48014	1.72496
6	0	2.48897	2.47094	-1.12432
1	0	2.74305	1.44848	-0.78409
1	0	2.00503	2.39104	-2.11645
1	0	3.43397	3.03731	-1.25232
1	0	2.11767	-2.8237	1.05066
1	0	-1.27483	-4.15982	-0.50583
1	0	-2.11767	2.8237	1.05066
1	0	1.27483	4.15982	-0.50583

SCF Done: E(RPBE-PBE) = -1831.63169332 A.U. after 6 cycles

Sum of electronic and zero-point Energies= -1831.120758
Sum of electronic and thermal Energies= -1831.087111
Sum of electronic and thermal Enthalpies= -1831.086166
Sum of electronic and thermal Free Energies= -1831.182072

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.4501 eV 506.03 nm f=0.1249
115 ->116 0.66590

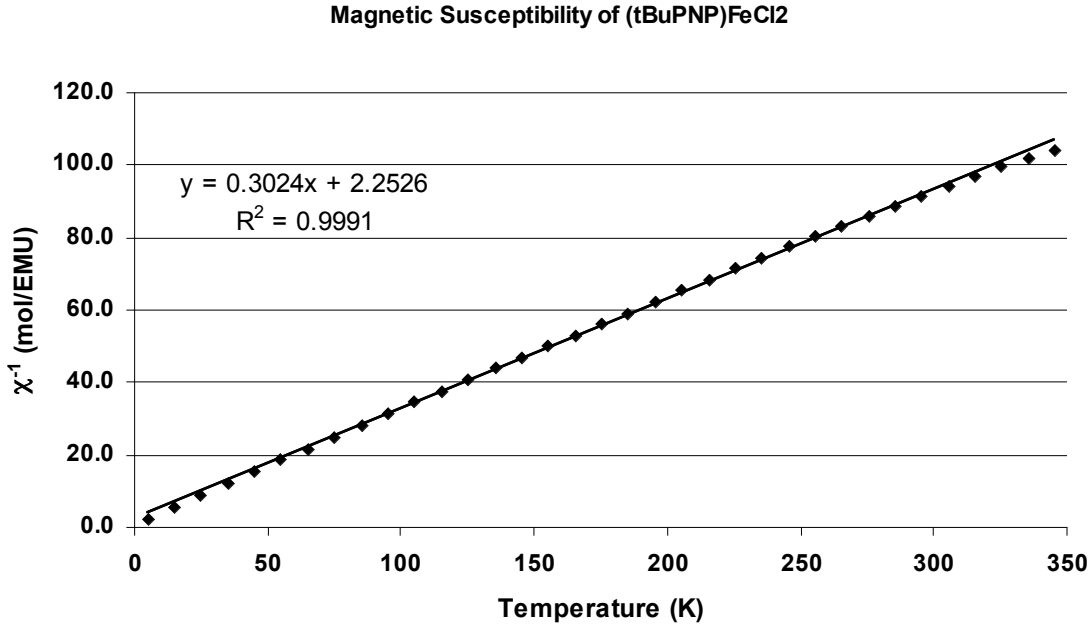
Excited State 2: Singlet-B 2.6679 eV 464.73 nm f=0.0031
115 ->117 -0.10085
115 ->119 0.62338
115 ->121 -0.17656

Excited State 3: Singlet-B 2.9080 eV 426.35 nm f=0.0007
115 ->117 0.68141
115 ->121 -0.11922

IX. Calculation of magnetic moment of (^{tBu}PNP)$FeCl_2$ (**1**).

The plot of magnetic susceptibility of (^{tBu}PNP)$FeCl_2$ versus temperature remained linear at high temperature in accord with the Curie Law (Figure S-3). The value of μ_{eff} was calculated according to $\mu_{eff} = (8C)^{1/2}$, where C is equal to the reciprocal of the slope (1/0.3024 = 3.31), and was found to be 5.143 BM. This value is similar to the value of 5.22 BM measured for (^{Ph}PNP)$FeCl_2$ and 5.38 BM for (^{tBu}PNP)$FeCl_2$ (references 11 and 14). The value is also in good agreement with the calculated magnetic moment of 4.899 BM for a complex with four unpaired electrons.

Figure S-3. Magnetic Susceptibility of (^{tBu}PNP)$FeCl_2$ (**1**)



X. Complete Reference 64.

Gaussian 03, Revision B.03: Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.; Jr,; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M..C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; and Pople, J.A. Gaussian, Inc., Pittsburgh, PA, 2003.