Electronic Supplementary Information for Dalton Transactions

Zirconium Complexes Bearing a Tetradentate Dipyrrolyl Ligand

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A. X-ray Diffraction Data for $Zr(NMe_2)_2(enp)$ (**2**)

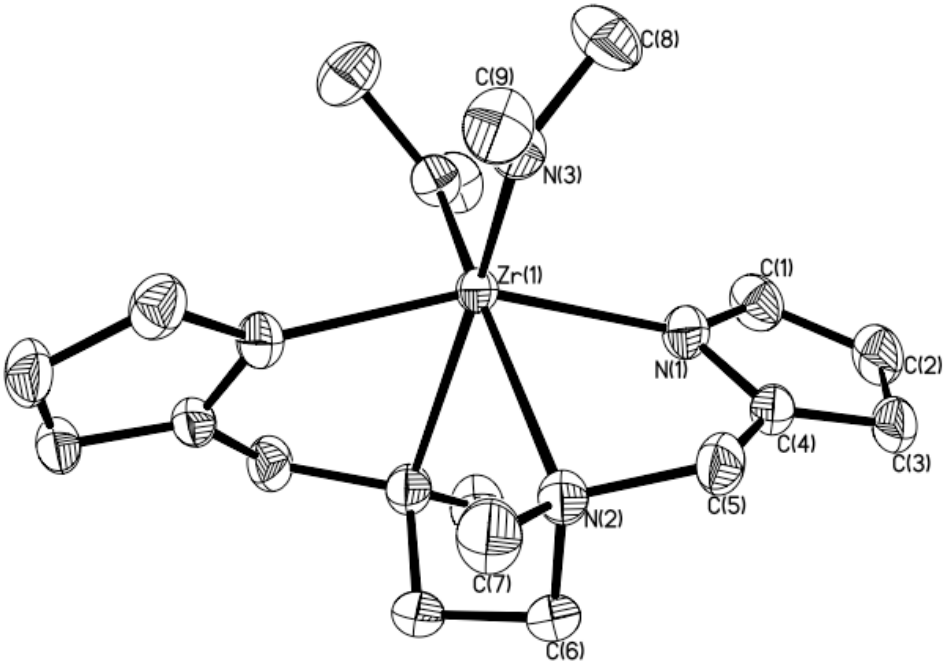


Table 1. Crystal data and structure refinement for ebzrenp.

Identification code	ebzrenp	
Empirical formula	C18 H32 N6 Zr	
Formula weight	423.72	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 29.9669(11) Å	α= 90°.
	b = 10.0542(4) Å	β= 90°.
	c = 13.4751(5) Å	γ = 90°.
Volume	4060.0(3) $Å^3$	
Z	8	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.555 mm^{-1}	
F(000)	1776	
Crystal size	0.28 x 0.27 x 0.20 mm^3	
Theta range for data collection	2.62 to 25.39°.	
Index ranges	-36<=h<=36, -12<=k<=12, -16<=l<=16	
Reflections collected	9124	
Independent reflections	1858 [R(int) = 0.0161]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8976 and 0.8593	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1858 / 1 / 117	
Goodness-of-fit on F^2	1.192	
Final R indices [I>2sigma(I)]	R1 = 0.0129, wR2 = 0.0363	
R indices (all data)	R1 = 0.0132, wR2 = 0.0365	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	0.179 and -0.114 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Zr(1)	10000	10000	8260(1)	19(1)
N(1)	9636(1)	8126(1)	7924(1)	27(1)
N(2)	9532(1)	10363(2)	6779(1)	28(1)
N(3)	9533(1)	10856(1)	9164(1)	27(1)
C(1)	9679(1)	6793(2)	8156(1)	34(1)
C(2)	9342(1)	6075(2)	7726(1)	38(1)
C(3)	9072(1)	6982(2)	7205(1)	36(1)
C(4)	9259(1)	8214(2)	7343(1)	28(1)
C(5)	9121(1)	9555(2)	6995(1)	32(1)
C(6)	9756(1)	9804(2)	5887(1)	35(1)
C(7)	9405(1)	11758(2)	6584(1)	41(1)
C(8)	9430(1)	9937(2)	9968(2)	43(1)
C(9)	9246(1)	12016(2)	9229(2)	39(1)

Table 3. Bond lengths [Å] and angles [°] for ebzrenp.

Zr(1)-N(3)	2.0454(12)
Zr(1)-N(3)#1	2.0454(12)
Zr(1)-N(1)	2.2233(13)
Zr(1)-N(1)#1	2.2234(13)
Zr(1)-N(2)#1	2.4659(15)
Zr(1)-N(2)	2.4659(15)
N(1)-C(4)	1.378(2)
N(1)-C(1)	1.382(2)
N(2)-C(7)	1.477(2)
N(2)-C(6)	1.488(2)
N(2)-C(5)	1.503(2)
N(3)-C(9)	1.451(2)
N(3)-C(8)	1.457(2)
C(1)-C(2)	1.369(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.408(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.373(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.486(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(6)#1	1.515(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800

C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800

N(3)-Zr(1)-N(3)#1	106.86(7)
N(3)-Zr(1)-N(1)	98.20(5)
N(3)#1-Zr(1)-N(1)	95.73(5)
N(3)-Zr(1)-N(1)#1	95.74(5)
N(3)#1-Zr(1)-N(1)#1	98.20(5)
N(1)-Zr(1)-N(1)#1	156.51(6)
N(3)-Zr(1)-N(2)#1	158.99(5)
N(3)#1-Zr(1)-N(2)#1	91.74(5)
N(1)-Zr(1)-N(2)#1	89.36(5)
N(1)#1-Zr(1)-N(2)#1	71.45(5)
N(3)-Zr(1)-N(2)	91.74(5)
N(3)#1-Zr(1)-N(2)	158.99(5)
N(1)-Zr(1)-N(2)	71.45(5)
N(1)#1-Zr(1)-N(2)	89.37(5)
N(2)#1-Zr(1)-N(2)	72.04(7)
C(4)-N(1)-C(1)	105.51(13)
C(4)-N(1)-Zr(1)	117.59(10)
C(1)-N(1)-Zr(1)	136.89(10)
C(7)-N(2)-C(6)	109.32(14)
C(7)-N(2)-C(5)	109.66(13)
C(6)-N(2)-C(5)	108.77(13)
C(7)-N(2)-Zr(1)	115.57(11)
C(6)-N(2)-Zr(1)	109.94(11)
C(5)-N(2)-Zr(1)	103.29(9)
C(9)-N(3)-C(8)	109.85(14)
C(9)-N(3)-Zr(1)	141.18(12)
C(8)-N(3)-Zr(1)	108.71(11)
C(2)-C(1)-N(1)	110.30(14)
C(2)-C(1)-H(1)	124.8
N(1)-C(1)-H(1)	124.8
C(1)-C(2)-C(3)	107.10(14)

C(1)-C(2)-H(2)	126.4
C(3)-C(2)-H(2)	126.4
C(4)-C(3)-C(2)	106.36(15)
C(4)-C(3)-H(3)	126.8
C(2)-C(3)-H(3)	126.8
C(3)-C(4)-N(1)	110.72(16)
C(3)-C(4)-C(5)	131.49(17)
N(1)-C(4)-C(5)	117.78(14)
C(4)-C(5)-N(2)	108.87(13)
C(4)-C(5)-H(5A)	109.9
N(2)-C(5)-H(5A)	109.9
C(4)-C(5)-H(5B)	109.9
N(2)-C(5)-H(5B)	109.9
H(5A)-C(5)-H(5B)	108.3
N(2)-C(6)-C(6)#1	109.75(11)
N(2)-C(6)-H(6A)	109.7
C(6)#1-C(6)-H(6A)	109.7
N(2)-C(6)-H(6B)	109.7
C(6)#1-C(6)-H(6B)	109.7
H(6A)-C(6)-H(6B)	108.2
N(2)-C(7)-H(7A)	109.5
N(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
N(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(3)-C(8)-H(8A)	109.5
N(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(3)-C(9)-H(9A)	109.5
N(3)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5
N(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for ebzrenp. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	19(1)	18(1)	20(1)	0	0	0(1)
N(1)	31(1)	21(1)	31(1)	-1(1)	0(1)	-3(1)
N(2)	27(1)	30(1)	28(1)	4(1)	-3(1)	-6(1)
N(3)	24(1)	28(1)	30(1)	-5(1)	2(1)	2(1)
C(1)	39(1)	25(1)	38(1)	2(1)	6(1)	-1(1)
C(2)	50(1)	23(1)	42(1)	-4(1)	8(1)	-13(1)
C(3)	39(1)	36(1)	32(1)	-8(1)	6(1)	-18(1)
C(4)	27(1)	33(1)	25(1)	-5(1)	3(1)	-10(1)
C(5)	23(1)	36(1)	35(1)	3(1)	-5(1)	-7(1)
C(6)	40(1)	44(1)	21(1)	0(1)	-2(1)	-13(1)
C(7)	39(1)	35(1)	49(1)	13(1)	-14(1)	-2(1)
C(8)	42(1)	44(1)	42(1)	4(1)	19(1)	2(1)
C(9)	32(1)	38(1)	47(1)	-7(1)	2(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ebzrenp.

	x	y	z	U(eq)
H(1)	9909	6428	8557	41
H(2)	9299	5141	7771	46
H(3)	8811	6781	6832	43
H(5A)	8940	10000	7512	38
H(5B)	8937	9474	6387	38
H(6A)	9610	10146	5279	42
H(6B)	9729	8823	5889	42
H(7A)	9674	12288	6465	61
H(7B)	9244	12115	7159	61
H(7C)	9211	11796	5998	61
H(8A)	9477	10381	10607	64
H(8B)	9626	9159	9923	64
H(8C)	9118	9651	9915	64
H(9A)	8937	11755	9094	58
H(9B)	9342	12679	8740	58
H(9C)	9266	12397	9897	58

Table 6. Torsion angles [°] for ebzrenp.

N(3)-Zr(1)-N(1)-C(4)	68.89(12)
N(3)#1-Zr(1)-N(1)-C(4)	176.89(11)
N(1)#1-Zr(1)-N(1)-C(4)	-56.90(11)
N(2)#1-Zr(1)-N(1)-C(4)	-91.43(12)
N(2)-Zr(1)-N(1)-C(4)	-20.19(11)
N(3)-Zr(1)-N(1)-C(1)	-110.11(14)
N(3)#1-Zr(1)-N(1)-C(1)	-2.11(14)
N(1)#1-Zr(1)-N(1)-C(1)	124.09(14)
N(2)#1-Zr(1)-N(1)-C(1)	89.57(14)
N(2)-Zr(1)-N(1)-C(1)	160.81(15)
N(3)-Zr(1)-N(2)-C(7)	57.62(12)
N(3)#1-Zr(1)-N(2)-C(7)	-149.74(13)
N(1)-Zr(1)-N(2)-C(7)	155.68(13)
N(1)#1-Zr(1)-N(2)-C(7)	-38.10(12)
N(2)#1-Zr(1)-N(2)-C(7)	-108.78(13)
N(3)-Zr(1)-N(2)-C(6)	-178.07(10)
N(3)#1-Zr(1)-N(2)-C(6)	-25.4(2)
N(1)-Zr(1)-N(2)-C(6)	-80.01(11)
N(1)#1-Zr(1)-N(2)-C(6)	86.21(11)
N(2)#1-Zr(1)-N(2)-C(6)	15.53(7)
N(3)-Zr(1)-N(2)-C(5)	-62.13(11)
N(3)#1-Zr(1)-N(2)-C(5)	90.51(16)
N(1)-Zr(1)-N(2)-C(5)	35.93(10)
N(1)#1-Zr(1)-N(2)-C(5)	-157.85(11)
N(2)#1-Zr(1)-N(2)-C(5)	131.47(14)
N(3)#1-Zr(1)-N(3)-C(9)	143.34(19)
N(1)-Zr(1)-N(3)-C(9)	-118.08(18)
N(1)#1-Zr(1)-N(3)-C(9)	42.96(18)
N(2)#1-Zr(1)-N(3)-C(9)	-8.0(3)
N(2)-Zr(1)-N(3)-C(9)	-46.57(18)
N(3)#1-Zr(1)-N(3)-C(8)	-43.43(12)
N(1)-Zr(1)-N(3)-C(8)	55.15(13)

N(1)#1-Zr(1)-N(3)-C(8)	-143.81(13)
N(2)#1-Zr(1)-N(3)-C(8)	165.25(16)
N(2)-Zr(1)-N(3)-C(8)	126.65(13)
C(4)-N(1)-C(1)-C(2)	0.57(17)
Zr(1)-N(1)-C(1)-C(2)	179.65(12)
N(1)-C(1)-C(2)-C(3)	-0.42(19)
C(1)-C(2)-C(3)-C(4)	0.09(19)
C(2)-C(3)-C(4)-N(1)	0.26(18)
C(2)-C(3)-C(4)-C(5)	-178.69(17)
C(1)-N(1)-C(4)-C(3)	-0.51(17)
Zr(1)-N(1)-C(4)-C(3)	-179.80(10)
C(1)-N(1)-C(4)-C(5)	178.60(14)
Zr(1)-N(1)-C(4)-C(5)	-0.69(19)
C(3)-C(4)-C(5)-N(2)	-145.19(16)
N(1)-C(4)-C(5)-N(2)	35.9(2)
C(7)-N(2)-C(5)-C(4)	-171.23(14)
C(6)-N(2)-C(5)-C(4)	69.27(17)
Zr(1)-N(2)-C(5)-C(4)	-47.50(15)
C(7)-N(2)-C(6)-C(6)#1	82.92(19)
C(5)-N(2)-C(6)-C(6)#1	-157.37(15)
Zr(1)-N(2)-C(6)-C(6)#1	-44.94(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,z

B. X-ray Diffraction Data for $Zr(NHPh)_2(enp)$ (**3a**)

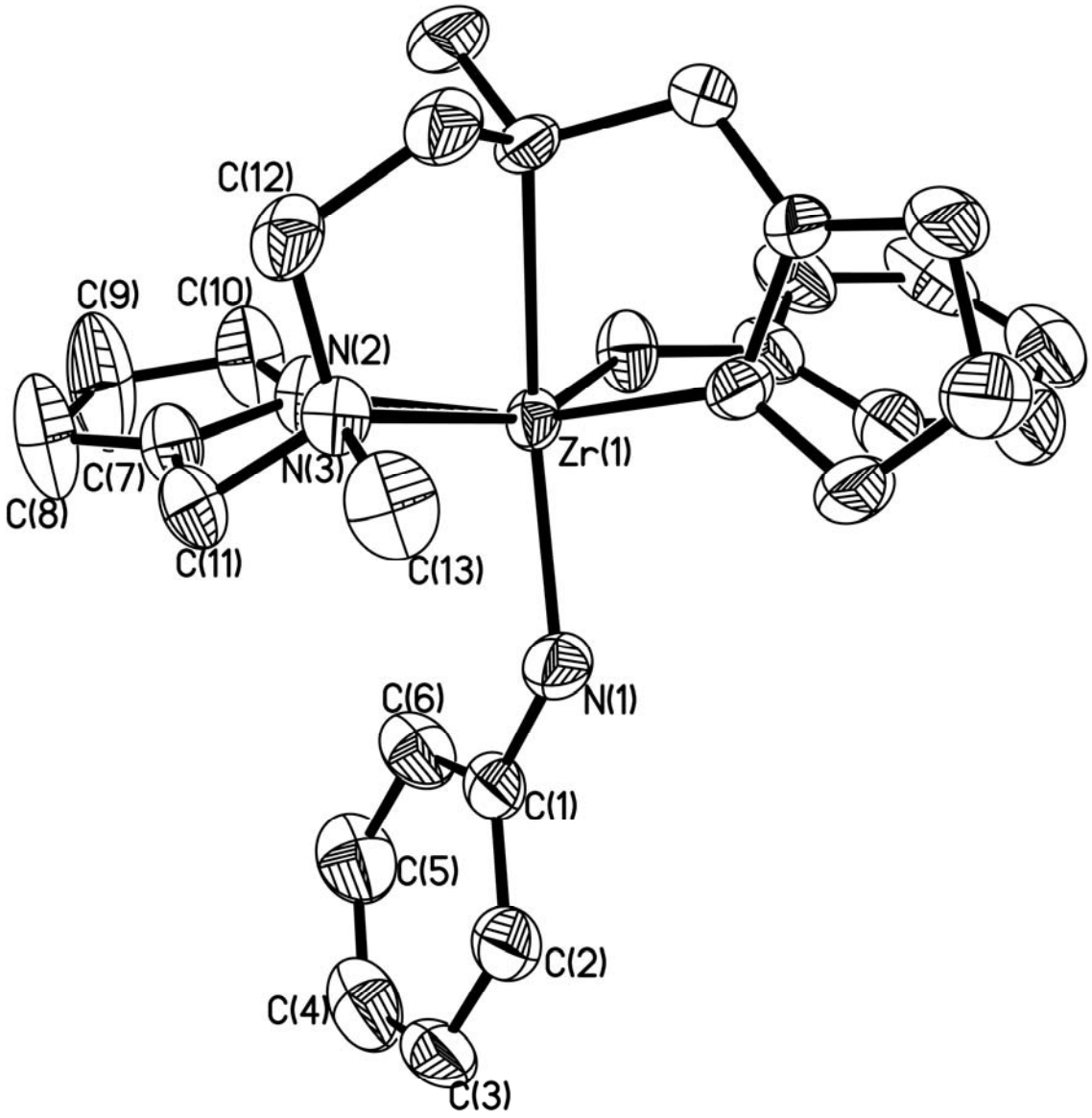


Table 1. Crystal data and structure refinement for ebzrenpphnh2_0m.

Identification code	ebzrenpphnh2_0m	
Empirical formula	C26 H32 N6 Zr	
Formula weight	519.80	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 12.0136(2) Å	α= 90°.
	b = 12.4957(2) Å	β= 90°.
	c = 16.9666(3) Å	γ = 90°.
Volume	2547.00(7) $Å^3$	
Z	4	
Density (calculated)	1.356 Mg/m^3	
Absorption coefficient	0.456 mm^{-1}	
F(000)	1080	
Crystal size	0.24 x 0.18 x 0.06 mm^3	
Theta range for data collection	2.35 to 28.00°.	
Index ranges	-15<=h<=15, -16<=k<=15, -22<=l<=19	
Reflections collected	24698	
Independent reflections	3014 [R(int) = 0.0619]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3014 / 0 / 151	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0756	
R indices (all data)	R1 = 0.0802, wR2 = 0.0899	
Extinction coefficient	0.00017(17)	
Largest diff. peak and hole	0.326 and -0.386 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ebzrenpphnh2_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	2500	2500	4654(1)	26(1)
N(1)	2500(2)	3852(2)	3928(1)	39(1)
N(2)	4266(2)	2273(2)	4884(1)	33(1)
N(3)	2982(2)	3559(2)	5786(1)	31(1)
C(9)	6095(3)	1919(3)	4914(3)	81(1)
C(8)	5911(3)	2871(3)	5340(2)	66(1)
C(4)	4866(4)	5167(4)	2387(2)	65(1)
C(5)	4989(3)	4160(4)	2669(2)	60(1)
C(3)	3944(3)	5761(3)	2595(2)	61(1)
C(13)	2233(2)	4487(2)	5917(2)	51(1)
C(10)	5091(2)	1574(3)	4657(2)	51(1)
C(2)	3135(3)	5328(3)	3107(2)	49(1)
C(6)	4203(3)	3723(3)	3169(2)	48(1)
C(12)	2996(2)	2867(2)	6499(2)	41(1)
C(1)	3263(2)	4301(2)	3402(2)	38(1)
C(11)	4122(2)	3966(2)	5614(2)	37(1)
C(7)	4807(2)	3066(2)	5311(2)	36(1)

Table 3. Bond lengths [Å] and angles [°] for ebzrenpphnh2_0m.

Zr(1)-N(1)	2.091(2)
Zr(1)-N(1)#1	2.091(2)
Zr(1)-N(2)	2.176(2)
Zr(1)-N(2)#1	2.176(2)
Zr(1)-N(3)	2.403(2)
Zr(1)-N(3)#1	2.403(2)
N(1)-C(1)	1.398(3)
N(1)-H(1A)	0.8800
N(2)-C(10)	1.376(3)
N(2)-C(7)	1.390(3)
N(3)-C(12)	1.486(3)
N(3)-C(11)	1.491(3)
N(3)-C(13)	1.485(3)
C(9)-C(10)	1.353(4)
C(9)-C(8)	1.409(5)
C(9)-H(9A)	0.9500
C(8)-C(7)	1.349(4)
C(8)-H(8A)	0.9500
C(4)-C(5)	1.354(5)
C(4)-C(3)	1.378(5)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.382(4)
C(5)-H(5A)	0.9500
C(3)-C(2)	1.410(5)
C(3)-H(3A)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(10)-H(10A)	0.9500
C(2)-C(1)	1.385(4)
C(2)-H(2A)	0.9500
C(6)-C(1)	1.398(4)

C(6)-H(6A)	0.9500
C(12)-C(12)#1	1.504(6)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(11)-C(7)	1.485(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900

N(1)-Zr(1)-N(1)#1	107.83(13)
N(1)-Zr(1)-N(2)	102.18(9)
N(1)#1-Zr(1)-N(2)	89.99(9)
N(1)-Zr(1)-N(2)#1	89.99(9)
N(1)#1-Zr(1)-N(2)#1	102.19(9)
N(2)-Zr(1)-N(2)#1	159.38(12)
N(1)-Zr(1)-N(3)	91.49(8)
N(1)#1-Zr(1)-N(3)	156.29(9)
N(2)-Zr(1)-N(3)	72.18(7)
N(2)#1-Zr(1)-N(3)	91.14(8)
N(1)-Zr(1)-N(3)#1	156.29(9)
N(1)#1-Zr(1)-N(3)#1	91.49(8)
N(2)-Zr(1)-N(3)#1	91.14(8)
N(2)#1-Zr(1)-N(3)#1	72.18(7)
N(3)-Zr(1)-N(3)#1	73.86(11)
C(1)-N(1)-Zr(1)	134.5(2)
C(1)-N(1)-H(1A)	112.8
Zr(1)-N(1)-H(1A)	112.8
C(10)-N(2)-C(7)	105.2(2)
C(10)-N(2)-Zr(1)	137.35(18)
C(7)-N(2)-Zr(1)	117.13(17)
C(12)-N(3)-C(11)	110.3(2)
C(12)-N(3)-C(13)	109.9(2)
C(11)-N(3)-C(13)	108.6(2)
C(12)-N(3)-Zr(1)	109.45(16)
C(11)-N(3)-Zr(1)	104.64(15)

C(13)-N(3)-Zr(1)	113.81(17)
C(10)-C(9)-C(8)	107.1(3)
C(10)-C(9)-H(9A)	126.5
C(8)-C(9)-H(9A)	126.5
C(7)-C(8)-C(9)	106.8(3)
C(7)-C(8)-H(8A)	126.6
C(9)-C(8)-H(8A)	126.6
C(5)-C(4)-C(3)	119.8(4)
C(5)-C(4)-H(4A)	120.1
C(3)-C(4)-H(4A)	120.1
C(4)-C(5)-C(6)	120.6(4)
C(4)-C(5)-H(5A)	119.7
C(6)-C(5)-H(5A)	119.7
C(4)-C(3)-C(2)	120.3(4)
C(4)-C(3)-H(3A)	119.8
C(2)-C(3)-H(3A)	119.8
N(3)-C(13)-H(13A)	109.5
N(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
N(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(9)-C(10)-N(2)	110.5(3)
C(9)-C(10)-H(10A)	124.8
N(2)-C(10)-H(10A)	124.8
C(1)-C(2)-C(3)	120.1(4)
C(1)-C(2)-H(2A)	120.0
C(3)-C(2)-H(2A)	120.0
C(5)-C(6)-C(1)	121.4(3)
C(5)-C(6)-H(6A)	119.3
C(1)-C(6)-H(6A)	119.3
N(3)-C(12)-C(12)#1	110.2(2)
N(3)-C(12)-H(12A)	109.6
C(12)#1-C(12)-H(12A)	109.6

N(3)-C(12)-H(12B)	109.6
C(12)#1-C(12)-H(12B)	109.6
H(12A)-C(12)-H(12B)	108.1
C(2)-C(1)-C(6)	117.8(3)
C(2)-C(1)-N(1)	122.0(3)
C(6)-C(1)-N(1)	120.2(3)
C(7)-C(11)-N(3)	108.6(2)
C(7)-C(11)-H(11A)	110.0
N(3)-C(11)-H(11A)	110.0
C(7)-C(11)-H(11B)	110.0
N(3)-C(11)-H(11B)	110.0
H(11A)-C(11)-H(11B)	108.4
C(8)-C(7)-N(2)	110.5(3)
C(8)-C(7)-C(11)	132.0(3)
N(2)-C(7)-C(11)	117.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for ebzrenpphnh2_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	23(1)	34(1)	21(1)	0	0	-1(1)
N(1)	33(1)	50(2)	35(1)	13(1)	1(1)	-1(1)
N(2)	26(1)	41(2)	31(1)	-11(1)	-2(1)	4(1)
N(3)	30(1)	35(1)	28(1)	-9(1)	3(1)	4(1)
C(9)	26(2)	86(3)	131(4)	-59(3)	-10(2)	15(2)
C(8)	31(2)	74(3)	94(3)	-47(2)	-6(2)	-2(2)
C(4)	71(3)	93(4)	31(2)	0(2)	-2(2)	-39(3)
C(5)	59(2)	85(3)	36(2)	-1(2)	10(2)	-20(2)
C(3)	87(3)	60(2)	37(2)	18(2)	-24(2)	-41(2)
C(13)	46(2)	45(2)	61(2)	-23(2)	9(2)	10(1)
C(10)	33(2)	52(2)	67(2)	-30(2)	1(2)	8(1)
C(2)	59(2)	53(2)	36(2)	7(2)	-17(2)	-19(2)
C(6)	55(2)	57(2)	32(2)	-3(2)	7(2)	-18(2)
C(12)	40(2)	58(2)	23(1)	-4(1)	-2(1)	0(1)
C(1)	45(2)	47(2)	22(1)	4(1)	-8(1)	-16(2)
C(11)	33(2)	38(2)	40(2)	-12(1)	3(1)	-7(1)
C(7)	29(1)	42(2)	37(2)	-13(2)	2(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ebzrenpphnh2_0m.

	x	y	z	U(eq)
H(1A)	1879	4223	3962	47
H(9A)	6793	1583	4824	97
H(8A)	6458	3293	5598	79
H(4A)	5413	5464	2047	78
H(5A)	5622	3751	2522	72
H(3A)	3853	6464	2393	73
H(13A)	2476	4881	6386	76
H(13B)	1469	4233	5994	76
H(13C)	2260	4961	5457	76
H(10A)	4973	938	4362	61
H(2A)	2503	5741	3249	59
H(6A)	4303	3014	3358	57
H(12A)	2982	3320	6978	49
H(12B)	3689	2438	6507	49
H(11A)	4085	4545	5217	44
H(11B)	4461	4260	6100	44

Table 6. Torsion angles [°] for ebzrenpphnh2_0m.

N(1)#1-Zr(1)-N(1)-C(1)	-66.9(2)
N(2)-Zr(1)-N(1)-C(1)	27.1(3)
N(2)#1-Zr(1)-N(1)-C(1)	-169.7(3)
N(3)-Zr(1)-N(1)-C(1)	99.2(3)
N(3)#1-Zr(1)-N(1)-C(1)	150.0(2)
N(1)-Zr(1)-N(2)-C(10)	-106.9(3)
N(1)#1-Zr(1)-N(2)-C(10)	1.3(3)
N(2)#1-Zr(1)-N(2)-C(10)	128.1(3)
N(3)-Zr(1)-N(2)-C(10)	165.4(3)
N(3)#1-Zr(1)-N(2)-C(10)	92.8(3)
N(1)-Zr(1)-N(2)-C(7)	65.1(2)
N(1)#1-Zr(1)-N(2)-C(7)	173.4(2)
N(2)#1-Zr(1)-N(2)-C(7)	-59.84(19)
N(3)-Zr(1)-N(2)-C(7)	-22.50(19)
N(3)#1-Zr(1)-N(2)-C(7)	-95.1(2)
N(1)-Zr(1)-N(3)-C(12)	176.05(18)
N(1)#1-Zr(1)-N(3)-C(12)	-38.7(3)
N(2)-Zr(1)-N(3)-C(12)	-81.63(17)
N(2)#1-Zr(1)-N(3)-C(12)	86.03(17)
N(3)#1-Zr(1)-N(3)-C(12)	14.96(13)
N(1)-Zr(1)-N(3)-C(11)	-65.70(17)
N(1)#1-Zr(1)-N(3)-C(11)	79.5(3)
N(2)-Zr(1)-N(3)-C(11)	36.62(16)
N(2)#1-Zr(1)-N(3)-C(11)	-155.72(16)
N(3)#1-Zr(1)-N(3)-C(11)	133.2(2)
N(1)-Zr(1)-N(3)-C(13)	52.7(2)
N(1)#1-Zr(1)-N(3)-C(13)	-162.1(2)
N(2)-Zr(1)-N(3)-C(13)	155.0(2)
N(2)#1-Zr(1)-N(3)-C(13)	-37.3(2)
N(3)#1-Zr(1)-N(3)-C(13)	-108.4(2)
C(10)-C(9)-C(8)-C(7)	-1.0(5)
C(3)-C(4)-C(5)-C(6)	-0.5(5)

C(5)-C(4)-C(3)-C(2)	0.7(5)
C(8)-C(9)-C(10)-N(2)	1.3(5)
C(7)-N(2)-C(10)-C(9)	-1.1(4)
Zr(1)-N(2)-C(10)-C(9)	171.6(3)
C(4)-C(3)-C(2)-C(1)	-0.1(5)
C(4)-C(5)-C(6)-C(1)	-0.3(5)
C(11)-N(3)-C(12)-C(12)#1	-158.1(3)
C(13)-N(3)-C(12)-C(12)#1	82.2(3)
Zr(1)-N(3)-C(12)-C(12)#1	-43.5(3)
C(3)-C(2)-C(1)-C(6)	-0.6(4)
C(3)-C(2)-C(1)-N(1)	178.0(3)
C(5)-C(6)-C(1)-C(2)	0.8(4)
C(5)-C(6)-C(1)-N(1)	-177.9(3)
Zr(1)-N(1)-C(1)-C(2)	-167.1(2)
Zr(1)-N(1)-C(1)-C(6)	11.5(4)
C(12)-N(3)-C(11)-C(7)	72.0(3)
C(13)-N(3)-C(11)-C(7)	-167.6(2)
Zr(1)-N(3)-C(11)-C(7)	-45.7(2)
C(9)-C(8)-C(7)-N(2)	0.3(5)
C(9)-C(8)-C(7)-C(11)	-176.8(4)
C(10)-N(2)-C(7)-C(8)	0.5(4)
Zr(1)-N(2)-C(7)-C(8)	-174.0(2)
C(10)-N(2)-C(7)-C(11)	178.0(3)
Zr(1)-N(2)-C(7)-C(11)	3.6(3)
N(3)-C(11)-C(7)-C(8)	-151.8(4)
N(3)-C(11)-C(7)-N(2)	31.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z

C. Structure from X-ray diffraction of H_2enp (**1**)

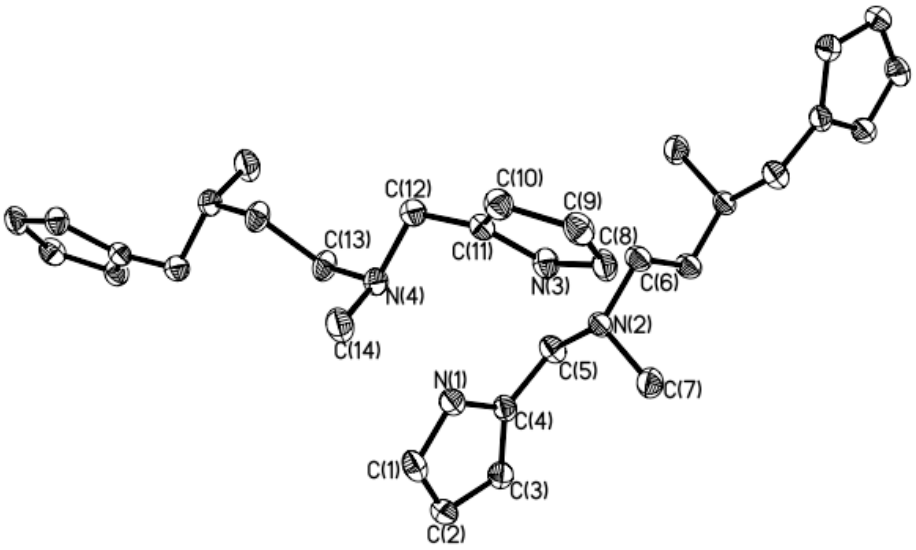


Table 1. Crystal data and structure refinement for eb050608_0m.

Identification code	eb050608_0m	
Empirical formula	C14 H22 N4	
Formula weight	246.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.5186(5) Å	α= 109.351(4)°.
	b = 9.2912(5) Å	β= 104.362(4)°.
	c = 9.5647(6) Å	γ = 92.986(4)°.
Volume	684.43(7) $Å^3$	
Z	2	
Density (calculated)	1.195 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	268	
Crystal size	0.62 x 0.13 x 0.11 mm^3	
Theta range for data collection	2.35 to 27.92°.	
Index ranges	-10<=h<=11, -12<=k<=11, -12<=l<=12	
Reflections collected	9942	
Independent reflections	3150 [R(int) = 0.0326]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9921 and 0.9559	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3150 / 0 / 165	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.0967	
R indices (all data)	R1 = 0.0753, wR2 = 0.1088	
Largest diff. peak and hole	0.216 and -0.181 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for eb050608_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	25(2)	2528(1)	5462(1)	28(1)
N(3)	4297(2)	2663(1)	7864(1)	24(1)
N(4)	1141(2)	3478(1)	8869(1)	22(1)
N(2)	3389(2)	3503(1)	5089(1)	22(1)
C(14)	506(2)	2065(2)	9037(2)	33(1)
C(1)	-1413(2)	1537(2)	4866(2)	32(1)
C(7)	3532(2)	2091(2)	3885(2)	31(1)
C(2)	-2005(2)	1334(2)	3345(2)	30(1)
C(8)	5484(2)	1733(2)	7742(2)	27(1)
C(3)	-871(2)	2229(2)	3000(2)	28(1)
C(9)	5961(2)	1426(2)	9070(2)	28(1)
C(12)	2847(2)	4029(2)	9798(2)	26(1)
C(5)	1844(2)	4070(2)	4605(2)	26(1)
C(6)	4823(2)	4700(2)	5613(2)	25(1)
C(10)	5026(2)	2204(2)	10041(2)	26(1)
C(13)	92(2)	4694(2)	9177(2)	25(1)
C(11)	4010(2)	2962(2)	9274(2)	23(1)
C(4)	373(2)	2963(2)	4324(2)	23(1)

Table 3. Bond lengths [Å] and angles [°] for eb050608_0m.

N(1)-C(1)	1.3642(19)
N(1)-C(4)	1.3696(18)
N(1)-H(1)	0.8800
N(3)-C(8)	1.3663(18)
N(3)-C(11)	1.3706(17)
N(3)-H(3)	0.8800
N(4)-C(12)	1.4641(19)
N(4)-C(14)	1.4669(18)
N(4)-C(13)	1.4754(17)
N(2)-C(7)	1.4653(17)
N(2)-C(5)	1.4675(19)
N(2)-C(6)	1.4721(18)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(1)-C(2)	1.360(2)
C(1)-H(1A)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(2)-C(3)	1.411(2)
C(2)-H(2)	0.9500
C(8)-C(9)	1.362(2)
C(8)-H(8)	0.9500
C(3)-C(4)	1.371(2)
C(3)-H(3A)	0.9500
C(9)-C(10)	1.415(2)
C(9)-H(9)	0.9500
C(12)-C(11)	1.4956(19)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(5)-C(4)	1.489(2)

C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(6)#1	1.538(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(10)-C(11)	1.369(2)
C(10)-H(10)	0.9500
C(13)-C(13)#2	1.538(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900

C(1)-N(1)-C(4)	109.33(13)
C(1)-N(1)-H(1)	125.3
C(4)-N(1)-H(1)	125.3
C(8)-N(3)-C(11)	109.28(12)
C(8)-N(3)-H(3)	125.4
C(11)-N(3)-H(3)	125.4
C(12)-N(4)-C(14)	111.32(12)
C(12)-N(4)-C(13)	112.06(11)
C(14)-N(4)-C(13)	112.80(12)
C(7)-N(2)-C(5)	111.11(12)
C(7)-N(2)-C(6)	112.76(12)
C(5)-N(2)-C(6)	112.44(11)
N(4)-C(14)-H(14A)	109.5
N(4)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
N(4)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(2)-C(1)-N(1)	108.62(14)
C(2)-C(1)-H(1A)	125.7
N(1)-C(1)-H(1A)	125.7
N(2)-C(7)-H(7A)	109.5
N(2)-C(7)-H(7B)	109.5

H(7A)-C(7)-H(7B)	109.5
N(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(1)-C(2)-C(3)	106.82(14)
C(1)-C(2)-H(2)	126.6
C(3)-C(2)-H(2)	126.6
C(9)-C(8)-N(3)	108.41(13)
C(9)-C(8)-H(8)	125.8
N(3)-C(8)-H(8)	125.8
C(4)-C(3)-C(2)	108.10(14)
C(4)-C(3)-H(3A)	125.9
C(2)-C(3)-H(3A)	125.9
C(8)-C(9)-C(10)	107.04(13)
C(8)-C(9)-H(9)	126.5
C(10)-C(9)-H(9)	126.5
N(4)-C(12)-C(11)	113.54(11)
N(4)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12A)	108.9
N(4)-C(12)-H(12B)	108.9
C(11)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.7
N(2)-C(5)-C(4)	113.01(12)
N(2)-C(5)-H(5A)	109.0
C(4)-C(5)-H(5A)	109.0
N(2)-C(5)-H(5B)	109.0
C(4)-C(5)-H(5B)	109.0
H(5A)-C(5)-H(5B)	107.8
N(2)-C(6)-C(6)#1	116.35(15)
N(2)-C(6)-H(6A)	108.2
C(6)#1-C(6)-H(6A)	108.2
N(2)-C(6)-H(6B)	108.2
C(6)#1-C(6)-H(6B)	108.2
H(6A)-C(6)-H(6B)	107.4

C(11)-C(10)-C(9)	107.78(13)
C(11)-C(10)-H(10)	126.1
C(9)-C(10)-H(10)	126.1
N(4)-C(13)-C(13)#2	116.07(15)
N(4)-C(13)-H(13A)	108.3
C(13)#2-C(13)-H(13A)	108.3
N(4)-C(13)-H(13B)	108.3
C(13)#2-C(13)-H(13B)	108.3
H(13A)-C(13)-H(13B)	107.4
C(10)-C(11)-N(3)	107.49(12)
C(10)-C(11)-C(12)	130.16(13)
N(3)-C(11)-C(12)	122.24(13)
N(1)-C(4)-C(3)	107.13(13)
N(1)-C(4)-C(5)	122.86(13)
C(3)-C(4)-C(5)	130.00(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for eb050608_0m. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	23(1)	33(1)	24(1)	9(1)	7(1)	0(1)
N(3)	22(1)	28(1)	26(1)	13(1)	8(1)	6(1)
N(4)	19(1)	24(1)	24(1)	7(1)	8(1)	6(1)
N(2)	19(1)	22(1)	24(1)	8(1)	6(1)	2(1)
C(14)	29(1)	28(1)	45(1)	11(1)	19(1)	5(1)
C(1)	25(1)	37(1)	37(1)	14(1)	14(1)	-1(1)
C(7)	31(1)	25(1)	38(1)	8(1)	16(1)	4(1)
C(2)	22(1)	30(1)	32(1)	4(1)	7(1)	-1(1)
C(8)	21(1)	29(1)	34(1)	10(1)	13(1)	5(1)
C(3)	25(1)	32(1)	25(1)	9(1)	8(1)	3(1)
C(9)	22(1)	27(1)	36(1)	13(1)	7(1)	7(1)
C(12)	21(1)	26(1)	26(1)	5(1)	7(1)	3(1)
C(5)	22(1)	26(1)	33(1)	13(1)	7(1)	4(1)
C(6)	23(1)	30(1)	23(1)	10(1)	5(1)	-2(1)
C(10)	24(1)	29(1)	26(1)	13(1)	7(1)	3(1)
C(13)	25(1)	31(1)	24(1)	11(1)	11(1)	13(1)
C(11)	18(1)	23(1)	25(1)	6(1)	7(1)	0(1)
C(4)	20(1)	23(1)	28(1)	9(1)	9(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for eb050608_0m.

	x	y	z	U(eq)
H(1)	633	2838	6427	33
H(3)	3796	3016	7149	29
H(14A)	1095	1228	8600	49
H(14B)	-665	1783	8488	49
H(14C)	664	2240	10134	49
H(1A)	-1917	1067	5420	39
H(7A)	2686	1260	3748	47
H(7B)	4617	1795	4191	47
H(7C)	3389	2273	2912	47
H(2)	-2992	709	2649	36
H(8)	5905	1362	6877	32
H(3A)	-955	2310	2020	33
H(9)	6769	808	9301	33
H(12A)	2921	4172	10886	31
H(12B)	3185	5048	9760	31
H(5A)	1802	4278	3647	32
H(5B)	1818	5056	5415	32
H(6A)	5801	4284	6040	30
H(6B)	4674	5587	6467	30
H(10)	5091	2201	11046	31
H(13A)	-1013	4287	8444	30
H(13B)	542	5573	8956	30

Table 6. Torsion angles [°] for eb050608_0m.

C(4)-N(1)-C(1)-C(2)	-0.32(17)
N(1)-C(1)-C(2)-C(3)	0.50(17)
C(11)-N(3)-C(8)-C(9)	0.16(17)
C(1)-C(2)-C(3)-C(4)	-0.51(17)
N(3)-C(8)-C(9)-C(10)	-0.04(17)
C(14)-N(4)-C(12)-C(11)	65.67(15)
C(13)-N(4)-C(12)-C(11)	-166.95(12)
C(7)-N(2)-C(5)-C(4)	62.17(16)
C(6)-N(2)-C(5)-C(4)	-170.37(11)
C(7)-N(2)-C(6)-C(6)#1	61.7(2)
C(5)-N(2)-C(6)-C(6)#1	-64.9(2)
C(8)-C(9)-C(10)-C(11)	-0.09(17)
C(12)-N(4)-C(13)-C(13)#2	-63.8(2)
C(14)-N(4)-C(13)-C(13)#2	62.8(2)
C(9)-C(10)-C(11)-N(3)	0.19(16)
C(9)-C(10)-C(11)-C(12)	-175.81(14)
C(8)-N(3)-C(11)-C(10)	-0.22(16)
C(8)-N(3)-C(11)-C(12)	176.17(13)
N(4)-C(12)-C(11)-C(10)	-119.46(17)
N(4)-C(12)-C(11)-N(3)	65.05(18)
C(1)-N(1)-C(4)-C(3)	-0.01(16)
C(1)-N(1)-C(4)-C(5)	178.60(13)
C(2)-C(3)-C(4)-N(1)	0.32(16)
C(2)-C(3)-C(4)-C(5)	-178.15(13)
N(2)-C(5)-C(4)-N(1)	63.12(17)
N(2)-C(5)-C(4)-C(3)	-118.62(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+2

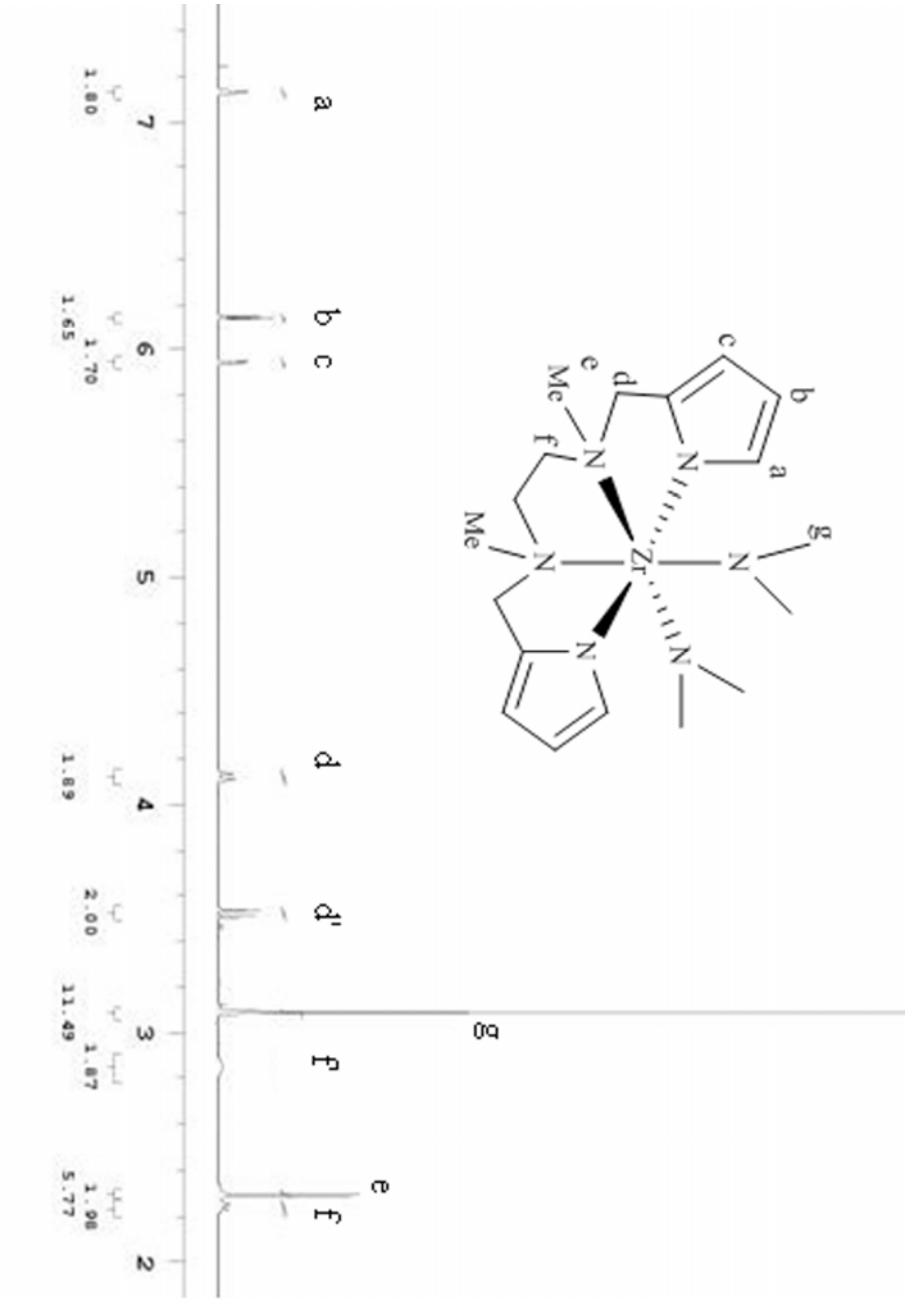
Table 7. Hydrogen bonds for eb050608_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(4)	0.88	2.13	2.9610(17)	156.8
N(3)-H(3)...N(2)	0.88	2.12	2.9443(17)	156.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+2

D. ^{1}H-NMR spectrum of complex **2**, with proton assignment (500 MHz, $CDCl_3$)



E. ^{1}H-NMR spectrum of complex **3c** (500 MHz, $CDCl_3$)