Supplementary Material (ESI) for Chemical Communications

Supporting information

Reactions of a β-Diketiminate Zinc Hydride Complex with Heterocumulenes

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Experimental Section

Manipulations were performed in a glove box under an Ar-atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. MesnacnacZnH was prepared according to the literature method,[1] C(N*i*-Pr)$_2$ and *t*-BuNCO were commercially available from Acros and dried before use. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to internal C_6D_5H (^{1}H: δ = 7.154; ^{13}C: δ = 128.0). IR spectra were recorded on a Alpha-T FT-IR spectrometer with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Essen.

[MesnacnacZnO$_2$CH]$_2$ (2)

A solution of 0.40 g (1.0 mmol) MesnacnacZnH in 50 mL of toluene was cooled to -78 °C, evacuated and pressurized with one atmosphere of CO_2. The closed reaction vessel was slowly warmed to ambient temperature and stirred for additional 10 min. Storage of the solution at 25 °C gave colorless crystals of **2** within 12 h, yield 0.39 g (88 %).

M.p. 215 - 217 °C. – Anal. Found (calcd) for $C_{48}H_{60}N_4O_4Zn_2$ (887.77 g/mol): H, 6.77 (6.81); C, 64.87 (64.94); N, 6.24 (6.31). – IR: ν = 2918, 2854, 1697, 1598, 1521, 1453, 1390, 1370, 1259, 1202, 1085, 1012, 856 cm^{-1}. – ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 1.51 (s, 6H, β-*CH$_3$*), 2.00 (s, 12H, *o*-Ar *CH$_3$*), 2.28 (s, 6H, *p*-Ar *CH$_3$*), 4.72 (s, 1H, γ-C*H*), 6.75 (s, 4H, *m*-Ar C*H*), 8.01 (s, 1H, *H*CO$_2$). – ^{13}C NMR (500 MHz, C_6D_6, 298 K): δ = 18.1 (*o*-Ar *C*H$_3$), 21.0 (*β*-C*C*H$_3$), 22.9 (*p*-Ar *C*H$_3$), 94.1 (*γ-C*), 129.4 (*m*-Ar), 131.8 (*o*-Ar), 133.2 (*p*-Ar), 144.4 (*ipso*-Ar), 167.4 (*C*O$_2$), 168.3 (*β*-C).

[MesnacnacZn(t-BuN)C(H)O] (3)

0.10 g (1.0 mmol) *t*-BuNCO was added at ambient temperature via syringe to a solution of 0.40 g (1.0 mmol) MesnacnacZnH in 50 mL of toluene and stirred for 6 h. The solvent was removed in vacuum yielding a slightly yellow solid, which was washed with *n*-pentane. The remaining colorless solid was analytically pure **3**, yield 0.42 g (83 %).

M.p. 160 °C (decomp.) – Anal. Found (calcd) for $C_{28}H_{39}N_3OZn$ (499.01 g/mol): H, 7.82 (7.88); C, 67.32 (67.40); N, 8.34 (8.42). – IR: ν = 2962, 2918, 2862, 1604, 1545, 1515, 1450, 1391, 1338, 1259, 1197, 1083, 1010, 855, 792, 746, 705, 464 cm^{-1}. – ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.67 (s, 9 H, C*Me*$_3$), 1.65 (s, 6 H, β-*CH*$_3$), 2.12 (s, 6 H, *p*-Ar *CH*$_3$), 2.32 (s, 12 H, *o*-Ar *CH*$_3$), 4.92 (s, 1 H, γ-C*H*), 6.81 (s, 4 H, *m*-Ar C*H*), 7.91 (s, 1H, NCO*H*). – ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ = 18.7 (*o*-Ar *C*H$_3$), 20.9 (β-C*C*H$_3$), 22.8 (*p*-Ar *C*H$_3$), 28.7 (C*Me*$_3$), 31.4 (*C*Me$_3$), 94.6 (γ-*C*), 128.7 (*m*-Ar), 132.8 (*o*-Ar), 133.8 (*p*-Ar), 146.0 (*ipso*-Ar), 167.3 (N*C*O), 168.4 (β-C). – $C_{28}H_{39}N_3OZn$ (499.01).

[MesnacnacZn(i-PrN)$_2$CH] (4)

0.26 g (1.0 mmol) (*i*-PrN)$_2$C was added at ambient temperature via syringe to a solution of 0.79 g (1.0 mmol) MesnacnacZnH in 50 mL of toluene and stirred for additional 2 h. Thereafter, the solvent was evacuated in vacuum and the remaining solid dissolved in *n*-hexane and stored at -30 °C. Colorless crystals of **4** were formed within 72 h, yield 0.70 g (62 %).

M.p. 225 °C. – Anal. Found (calcd) for $C_{30}H_{44}N_4Zn$ (526.08 g/mol): H, 8.39 (8.43); C, 68.42 (68.50); N, 10.48 (10.65). – IR: ν = 2962, 2918, 1644, 1555, 1521, 1450, 1396, 1375, 1259, 1198, 1094, 1015, 857 cm^{-1}. – ^1H NMR (500 MHz, C_6D_6, 298 K): δ = 0.90 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(*CH*$_3$)$_2$), 1.67 (s, 6H, β-*CH*$_3$), 2.13 (s, 6H, *p*-Ar *CH*$_3$), 2.33 (s, 12H, *o*-Ar *CH*$_3$), 3.20 (sep, 2H, $^3J_{HH}$ = 6.4 Hz, *CH*(CH$_3$)$_2$), 4.88 (s, 1H, *CH*), 6.82 (s, 4H, *m*-Ar C*H*), 7.30 (*H*CN$_2$). – ^{13}C NMR (500 MHz, C_6D_6, 298 K): δ = 19.4 (*o*-Ar *C*H$_3$), 21.2 (β-C*C*H$_3$), 23.3 (*p*-Ar *C*H$_3$), 26.2 (CH(*CH*$_3$)$_2$), 48.8 (*C*H(CH$_3$)$_2$), 94.5 (γ-*C*), 129.5 (*m*-Ar), 131.9 (*o*-Ar), 133.7 (*p*-Ar), 145.9 (*ipso*-Ar), 165.4 (*C*N$_2$), 168.0 (β-C).

Crystal structure determination

Data were collected on a Bruker AXS SMART APEX CCD diffractometer for **2** and **4** (MoK$_\alpha$ radiation, λ = 0.71073 Å). The structures were solved by Direct Methods SHELXL-97 [2] and refined by full-matrix least-squares on F^2. Semi-empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97, Program for Crystal Structure Refinement).[3]

CCDC 776239 (**2**) and 776240 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

References

[1] S. Schulz, T. Eisenmann, D. Schuchmann, M. Bolte, M. Kirchner, R. Boese, J. Spielmann and S. Harder, *Z. Naturforsch.* 2009, **64b***,* 1397.

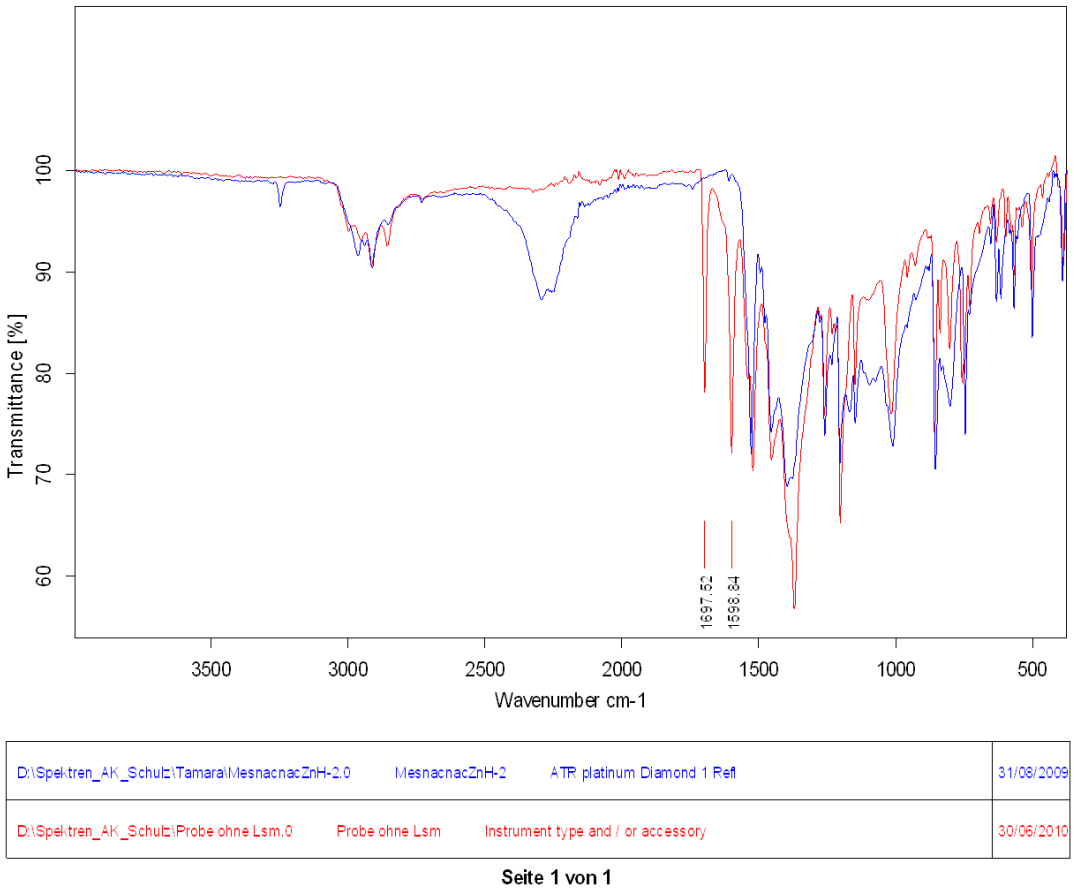
[2] G. M. Sheldrick, *Acta Crystallogr.* 1990, **A46**, 467.

[3] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **1997**.

IR spectroscopic studies

IR spectra of pure **2** as well as solutions of **2** in THF and toluene were recorded. Pure **2** shows two strong absorption bands due to ν_{as}(CO) and ν_{sy}(CO). The difference $\Delta\nu$ between both is typically used in order to verify the binding mode of the formiate group. While a large difference of about 200 cm^{-1} indicates a η^1-coordination, difference of 100 cm^{-1} are typical for bridging and chelating formiate groups. **2** shows a difference of about 99 cm^{-1}, which points to a bridging/chelating mode as observed in the solid state structure. No further symmetrical or asymmetrical CO absorption bands could be identified; however, they might be overlapped by absorption bands of the diketiminato group as a comparison of **2** (in red) with the starting hydride (in blue) shows (spectrum 1).

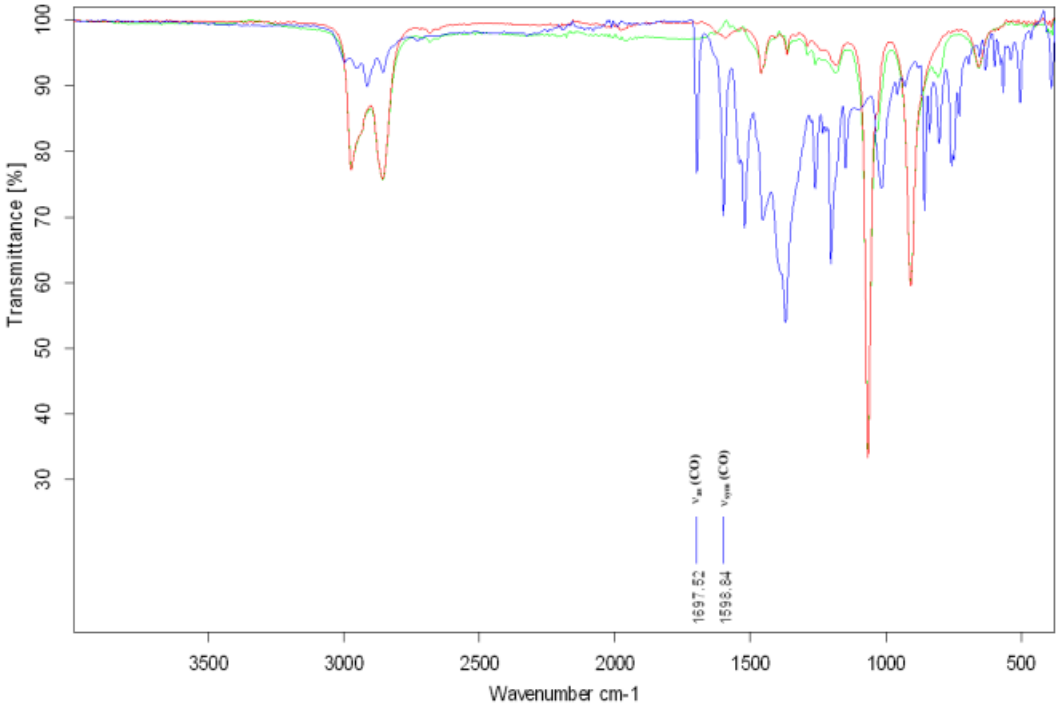
Spectrum 1



IR spectra recorded in solution not really provide any useful information in order to distinguish between both coordination modes (spectrum 2). However, two bands observed at

1591 and 1697 cm^{-1} (enlarged representation see spectrum 3) correspond well to those observed in crystalline **2** (1599, 1698 cm^{-1}).

Spectra 2 and 3



D:\Spektren_AK_Schulz\MEAS\Probe ohne Lsm.0	Probe ohne Lsm	Instrument type and / or accessory	30/06/2010
D:\Spektren_AK_Schulz\MEAS\Probe in THF konz.0	Probe in THF konz	Instrument type and / or accessory	30/06/2010
D:\Spektren_AK_Schulz\THF.0	THF	Instrument type and / or accessory	30/06/2010

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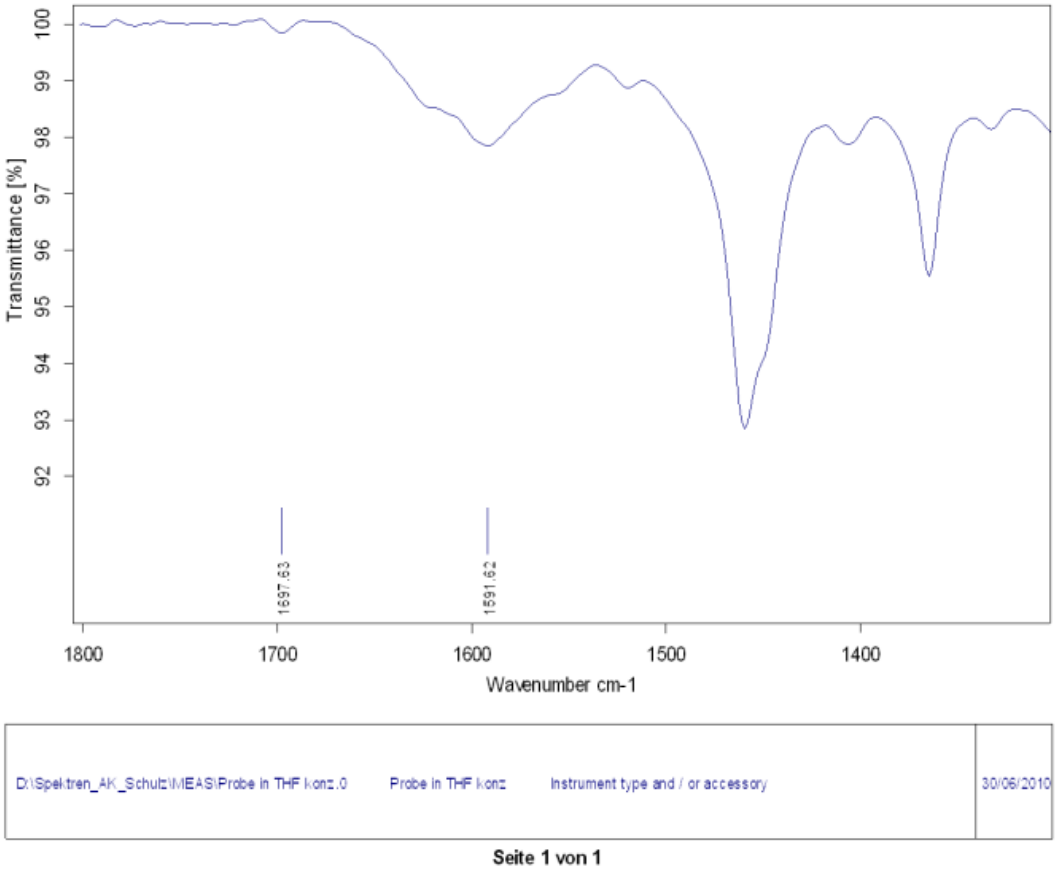


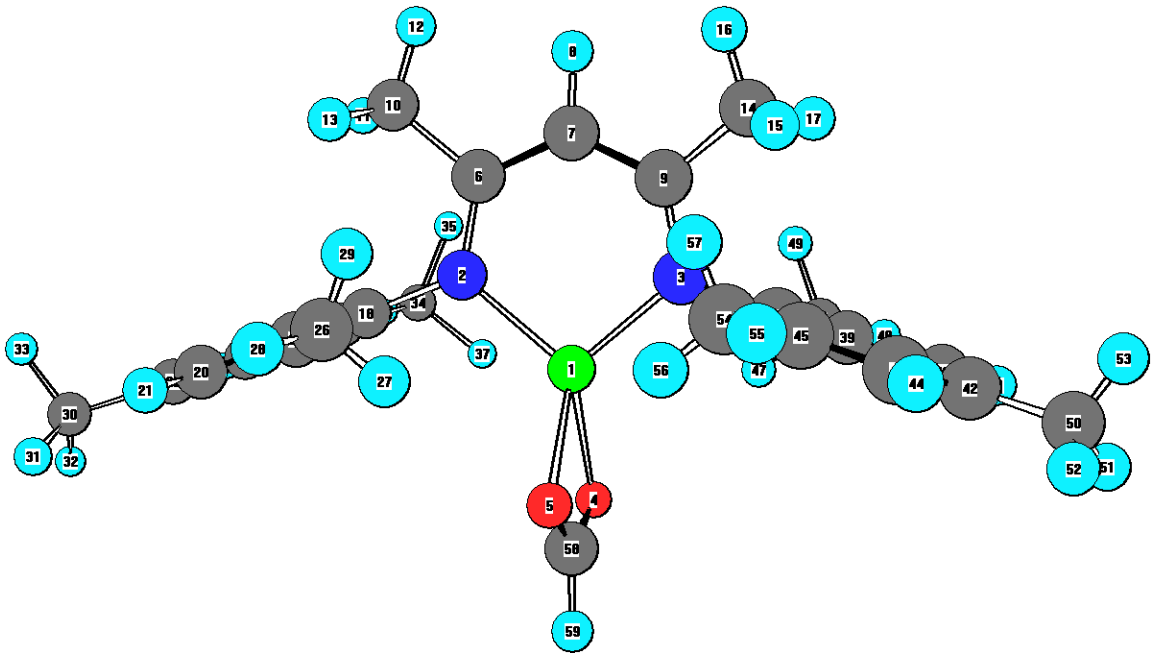
Computational Calculations

DFT calculations were carried out with the Gaussian09 suite of programs (Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009).

The molecular structures and energies of the monomeric **2'** and dimeric form **2"** of compound **2** were obtained by performing a complete energy optimization of all geometric parameters at

the b3lyp/sdd level (input keywords "# b3lyp/sdd opt pop=nbo"), using the atomic coordinates of the crystal structure determinations of **4** (for **2'**) and **2** (for **2"**) as starting points. Population analysis was carried out with the NBO module as implemented in Gaussian03. The final molecular structure and list of the final atomic coordinates and energy, selected bond distances, and NBO atomic populations are given below.

Calculated parameters for 2'



HF=-2971.0363126

! Optimized Parameters !
! (Angstroms and Degrees) !

Name	Definition	Value	Derivative Info.
R1	R(1,2)	1.9609	-DE/DX = 0.0
R2	R(1,3)	1.9609	-DE/DX = 0.0
R3	R(1,4)	2.0969	-DE/DX = 0.0
R4	R(1,5)	2.0969	-DE/DX = 0.0
R5	R(1,58)	2.4	-DE/DX = 0.0
R6	R(2,6)	1.3348	-DE/DX = 0.0
R7	R(2,18)	1.4304	-DE/DX = 0.0
R8	R(3,9)	1.3348	-DE/DX = 0.0
R9	R(3,38)	1.4304	-DE/DX = 0.0
R10	R(4,58)	1.2613	-DE/DX = 0.0
R11	R(5,58)	1.2613	-DE/DX = 0.0
R12	R(6,7)	1.4153	-DE/DX = 0.0
R13	R(6,10)	1.5157	-DE/DX = 0.0
R14	R(7,8)	1.0891	-DE/DX = 0.0
R15	R(7,9)	1.4153	-DE/DX = 0.0
R16	R(9,14)	1.5157	-DE/DX = 0.0
R17	R(10,11)	1.101	-DE/DX = 0.0
R18	R(10,12)	1.0971	-DE/DX = 0.0
R19	R(10,13)	1.101	-DE/DX = 0.0
R20	R(14,15)	1.101	-DE/DX = 0.0
R21	R(14,16)	1.0971	-DE/DX = 0.0
R22	R(14,17)	1.101	-DE/DX = 0.0
R23	R(18,19)	1.4116	-DE/DX = 0.0
R24	R(18,25)	1.4127	-DE/DX = 0.0
R25	R(19,20)	1.4016	-DE/DX = 0.0
R26	R(19,26)	1.5093	-DE/DX = 0.0
R27	R(20,21)	1.0944	-DE/DX = 0.0
R28	R(20,22)	1.4	-DE/DX = 0.0
R29	R(22,23)	1.4011	-DE/DX = 0.0
R30	R(22,30)	1.51	-DE/DX = 0.0
R31	R(23,24)	1.0945	-DE/DX = 0.0
R32	R(23,25)	1.4005	-DE/DX = 0.0
R33	R(25,34)	1.5093	-DE/DX = 0.0
R34	R(26,27)	1.1035	-DE/DX = 0.0
R35	R(26,28)	1.0996	-DE/DX = 0.0
R36	R(26,29)	1.1019	-DE/DX = 0.0
R37	R(30,31)	1.1006	-DE/DX = 0.0
R38	R(30,32)	1.1014	-DE/DX = 0.0
R39	R(30,33)	1.1045	-DE/DX = 0.0
R40	R(34,35)	1.1019	-DE/DX = 0.0
R41	R(34,36)	1.0996	-DE/DX = 0.0
R42	R(34,37)	1.1035	-DE/DX = 0.0
R43	R(38,39)	1.412	-DE/DX = 0.0
R44	R(38,45)	1.4122	-DE/DX = 0.0
R45	R(39,40)	1.4012	-DE/DX = 0.0
R46	R(39,46)	1.5093	-DE/DX = 0.0
R47	R(40,41)	1.0944	-DE/DX = 0.0
R48	R(40,42)	1.4005	-DE/DX = 0.0
R49	R(42,43)	1.4006	-DE/DX = 0.0
R50	R(42,50)	1.51	-DE/DX = 0.0
R51	R(43,44)	1.0945	-DE/DX = 0.0
R52	R(43,45)	1.401	-DE/DX = 0.0
R53	R(45,54)	1.5093	-DE/DX = 0.0
R54	R(46,47)	1.1035	-DE/DX = 0.0
R55	R(46,48)	1.0996	-DE/DX = 0.0
R56	R(46,49)	1.1019	-DE/DX = 0.0
R57	R(50,51)	1.1009	-DE/DX = 0.0
R58	R(50,52)	1.101	-DE/DX = 0.0
R59	R(50,53)	1.1046	-DE/DX = 0.0
R60	R(54,55)	1.0996	-DE/DX = 0.0

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 ! R61   R(54,56)               1.1035         -DE/DX =    0.0                 !
 ! R62   R(54,57)               1.1019         -DE/DX =    0.0                 !
 ! R63   R(58,59)               1.1101         -DE/DX =    0.0                 !
```

Standard orientation:

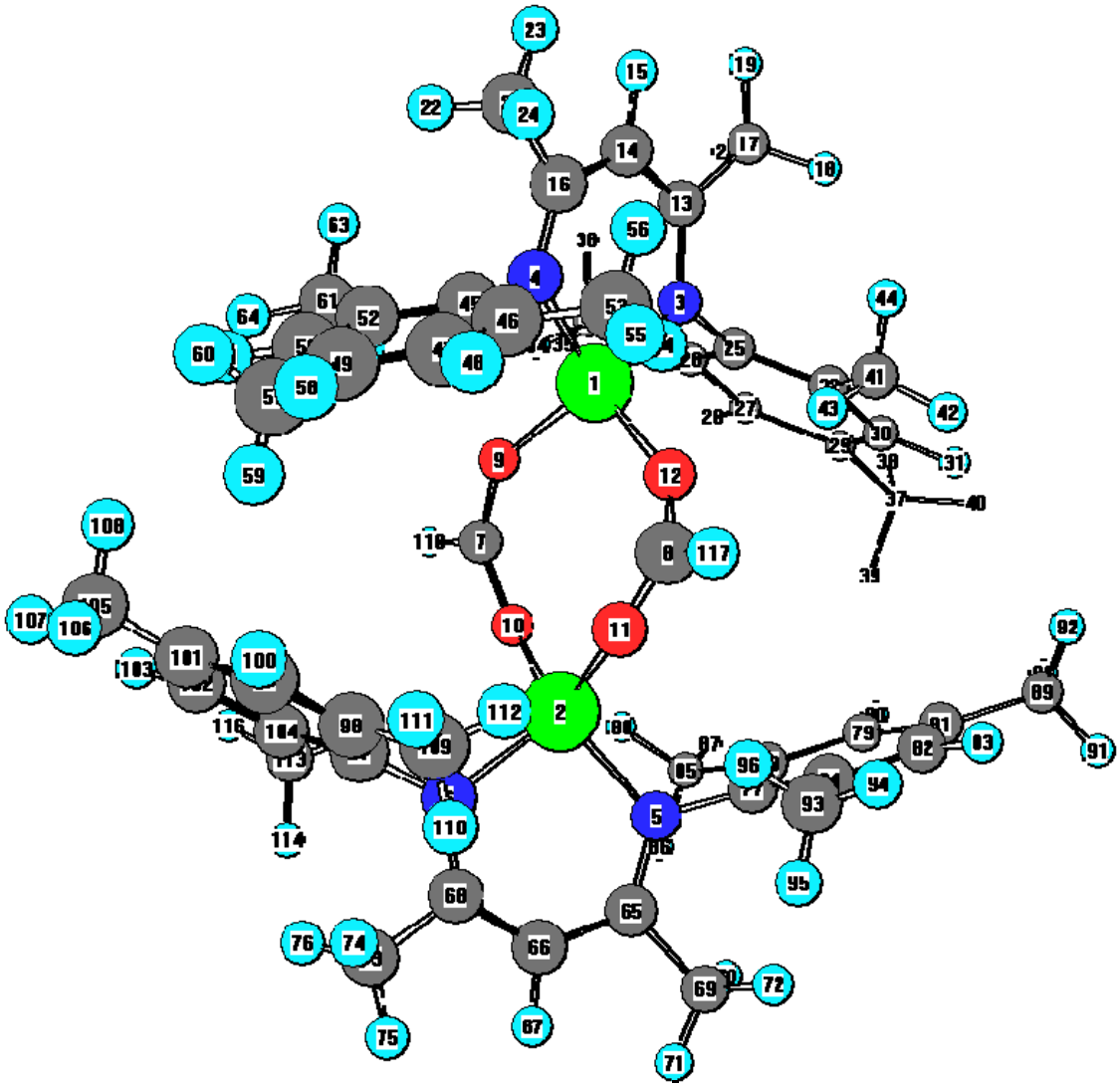
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.000084	-0.436614	0.000817
2	7	0	-1.518377	0.804154	0.001006
3	7	0	1.518344	0.804430	0.000085
4	8	0	-0.000374	-2.221314	-1.100068
5	8	0	0.001216	-2.221155	1.101916
6	6	0	-1.286793	2.118673	0.001180
7	6	0	-0.000174	2.708347	0.000811
8	1	0	-0.000272	3.797456	0.000962
9	6	0	1.286554	2.118902	0.000192
10	6	0	-2.470936	3.064770	0.001876
11	1	0	-3.108926	2.891422	-0.878506
12	1	0	-2.147034	4.112942	0.002115
13	1	0	-3.108319	2.890776	0.882567
14	6	0	2.470540	3.065190	-0.000403
15	1	0	3.108714	2.891617	0.879800
16	1	0	2.146469	4.113311	-0.000231
17	1	0	3.107792	2.891620	-0.881276
18	6	0	-2.848027	0.276848	0.001004
19	6	0	-3.479983	-0.027697	1.225942
20	6	0	-4.766083	-0.584284	1.199453
21	1	0	-5.255217	-0.818378	2.150040
22	6	0	-5.434119	-0.859140	0.000186
23	6	0	-4.765891	-0.581831	-1.199629
24	1	0	-5.255057	-0.814394	-2.150741
25	6	0	-3.480815	-0.025553	-1.225286
26	6	0	-2.766982	0.194720	2.537471
27	1	0	-1.873220	-0.448654	2.608552
28	1	0	-3.421944	-0.045210	3.387511
29	1	0	-2.420788	1.233915	2.657826
30	6	0	-6.833516	-1.426398	-0.003939
31	1	0	-7.062277	-1.947580	0.938091
32	1	0	-6.979169	-2.138721	-0.831220
33	1	0	-7.587701	-0.629051	-0.128005
34	6	0	-2.767349	0.199533	-2.536103
35	1	0	-2.422117	1.239252	-2.654688
36	1	0	-3.421626	-0.039782	-3.386843
37	1	0	-1.872894	-0.442796	-2.607583
38	6	0	2.848049	0.277266	-0.000520
39	6	0	3.479684	-0.026609	-1.226306
40	6	0	4.765164	-0.583546	-1.200766
41	1	0	5.253669	-0.817413	-2.151795
42	6	0	5.433785	-0.859572	-0.001587
43	6	0	4.766321	-0.582955	1.198311
44	1	0	5.255773	-0.816443	2.148973
45	6	0	3.481026	-0.026101	1.224916
46	6	0	2.765821	0.196846	-2.537188
47	1	0	1.871750	-0.446122	-2.607951
48	1	0	3.420069	-0.042846	-3.387845
49	1	0	2.419946	1.236247	-2.656658
50	6	0	6.833497	-1.426062	-0.001579
51	1	0	7.026125	-2.029937	-0.901713
52	1	0	7.013440	-2.061176	0.879622
53	1	0	7.590372	-0.621777	0.018320
54	6	0	2.768374	0.197884	2.536368
55	1	0	3.423476	-0.041292	3.386514
56	1	0	1.874485	-0.445208	2.608282
57	1	0	2.422423	1.237274	2.655671
58	6	0	0.000560	-2.836610	0.000967
59	1	0	0.000802	-3.946681	0.001045

Summary of Natural Population Analysis:

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
Zn	1	1.22083	17.99727	10.77831	0.00359	28.77917
N	2	-0.73679	1.99925	5.72160	0.01593	7.73679
N	3	-0.73677	1.99925	5.72159	0.01593	7.73677
O	4	-0.73561	1.99978	6.72581	0.01002	8.73561
O	5	-0.73563	1.99978	6.72583	0.01002	8.73563
C	6	0.32994	1.99894	3.65019	0.02093	5.67006
C	7	-0.41861	1.99886	4.40327	0.01648	6.41861
H	8	0.22133	0.00000	0.77612	0.00255	0.77867
C	9	0.32995	1.99894	3.65018	0.02093	5.67005
C	10	-0.66106	1.99919	4.65440	0.00746	6.66106
H	11	0.23860	0.00000	0.75903	0.00237	0.76140
H	12	0.22725	0.00000	0.77077	0.00197	0.77275
H	13	0.23866	0.00000	0.75896	0.00237	0.76134
C	14	-0.66106	1.99919	4.65440	0.00746	6.66106
H	15	0.23862	0.00000	0.75900	0.00237	0.76138
H	16	0.22725	0.00000	0.77077	0.00197	0.77275
H	17	0.23864	0.00000	0.75899	0.00237	0.76136
C	18	0.15241	1.99869	3.82677	0.02213	5.84759
C	19	-0.03107	1.99879	4.01669	0.01560	6.03107
C	20	-0.21851	1.99882	4.20509	0.01460	6.21851
H	21	0.21669	0.00000	0.78043	0.00287	0.78331
C	22	-0.02922	1.99885	4.01527	0.01510	6.02922
C	23	-0.21781	1.99882	4.20431	0.01468	6.21781
H	24	0.21647	0.00000	0.78065	0.00289	0.78353
C	25	-0.03095	1.99879	4.01659	0.01557	6.03095
C	26	-0.63809	1.99921	4.62989	0.00899	6.63809
H	27	0.23625	0.00000	0.76052	0.00323	0.76375
H	28	0.22120	0.00000	0.77654	0.00225	0.77880
H	29	0.22170	0.00000	0.77584	0.00246	0.77830
C	30	-0.63178	1.99921	4.62392	0.00866	6.63178
H	31	0.22053	0.00000	0.77709	0.00238	0.77947
H	32	0.22231	0.00000	0.77524	0.00244	0.77769
H	33	0.22529	0.00000	0.77208	0.00262	0.77471
C	34	-0.63805	1.99921	4.62985	0.00899	6.63805
H	35	0.22169	0.00000	0.77585	0.00246	0.77831
H	36	0.22120	0.00000	0.77655	0.00225	0.77880
H	37	0.23623	0.00000	0.76054	0.00323	0.76377
C	38	0.15240	1.99869	3.82678	0.02213	5.84760
C	39	-0.03102	1.99879	4.01664	0.01559	6.03102
C	40	-0.21823	1.99882	4.20478	0.01464	6.21823
H	41	0.21660	0.00000	0.78052	0.00288	0.78340
C	42	-0.02921	1.99885	4.01526	0.01510	6.02921
C	43	-0.21811	1.99882	4.20464	0.01465	6.21811
H	44	0.21657	0.00000	0.78055	0.00288	0.78343
C	45	-0.03099	1.99879	4.01662	0.01558	6.03099
C	46	-0.63807	1.99921	4.62987	0.00899	6.63807
H	47	0.23624	0.00000	0.76054	0.00323	0.76376
H	48	0.22120	0.00000	0.77655	0.00225	0.77880
H	49	0.22169	0.00000	0.77584	0.00246	0.77831
C	50	-0.63172	1.99921	4.62386	0.00866	6.63172
H	51	0.22122	0.00000	0.77637	0.00240	0.77878
H	52	0.22152	0.00000	0.77607	0.00241	0.77848
H	53	0.22534	0.00000	0.77204	0.00262	0.77466
C	54	-0.63807	1.99921	4.62987	0.00899	6.63807
H	55	0.22120	0.00000	0.77655	0.00225	0.77880
H	56	0.23625	0.00000	0.76052	0.00323	0.76375
H	57	0.22169	0.00000	0.77585	0.00246	0.77831
C	58	0.68356	1.99953	3.26904	0.04788	5.31644
H	59	0.13792	0.00000	0.85800	0.00407	0.86208

* Total *	0.00000	73.97075	159.52574	0.50350	234.00000

Calculated parameters for 2"



HF=-5942.1111045

Optimized Parameters
(Angstroms and Degrees)

Name	Definition	Value	Derivative Info.
R1	R(1,3)	1.9934	-DE/DX = 0.0
R2	R(1,4)	1.9944	-DE/DX = 0.0
R3	R(1,9)	1.9984	-DE/DX = 0.0
R4	R(1,11)	3.7349	-DE/DX = 0.0
R5	R(1,12)	1.9996	-DE/DX = 0.0
R6	R(2,5)	1.9936	-DE/DX = 0.0
R7	R(2,6)	1.9942	-DE/DX = 0.0
R8	R(2,10)	1.9994	-DE/DX = 0.0
R9	R(2,11)	1.9977	-DE/DX = 0.0
R10	R(3,13)	1.3336	-DE/DX = 0.0
R11	R(3,25)	1.4293	-DE/DX = 0.0
R12	R(4,16)	1.3332	-DE/DX = 0.0
R13	R(4,45)	1.4291	-DE/DX = 0.0
R14	R(5,65)	1.3336	-DE/DX = 0.0
R15	R(5,77)	1.4291	-DE/DX = 0.0
R16	R(6,68)	1.3333	-DE/DX = 0.0
R17	R(6,97)	1.4292	-DE/DX = 0.0
R18	R(7,9)	1.2536	-DE/DX = 0.0
R19	R(7,10)	1.2529	-DE/DX = 0.0
R20	R(7,11)	3.9495	-DE/DX = 0.0
R21	R(7,34)	3.1082	-DE/DX = 0.0
R22	R(7,118)	1.1146	-DE/DX = 0.0
R23	R(8,11)	1.2537	-DE/DX = 0.0
R24	R(8,12)	1.253	-DE/DX = 0.0
R25	R(8,117)	1.1146	-DE/DX = 0.0
R26	R(9,11)	3.9325	-DE/DX = 0.0
R27	R(9,34)	2.5441	-DE/DX = 0.0
R28	R(9,62)	2.5245	-DE/DX = 0.0
R29	R(10,11)	3.2726	-DE/DX = 0.0
R30	R(13,14)	1.414	-DE/DX = 0.0
R31	R(13,17)	1.5175	-DE/DX = 0.0
R32	R(14,15)	1.089	-DE/DX = 0.0
R33	R(14,16)	1.4142	-DE/DX = 0.0
R34	R(16,21)	1.5175	-DE/DX = 0.0
R35	R(17,18)	1.101	-DE/DX = 0.0
R36	R(17,19)	1.0972	-DE/DX = 0.0
R37	R(17,20)	1.1008	-DE/DX = 0.0
R38	R(21,22)	1.101	-DE/DX = 0.0
R39	R(21,23)	1.0972	-DE/DX = 0.0
R40	R(21,24)	1.1006	-DE/DX = 0.0
R41	R(25,26)	1.4146	-DE/DX = 0.0
R42	R(25,32)	1.4112	-DE/DX = 0.0
R43	R(26,27)	1.4003	-DE/DX = 0.0
R44	R(26,33)	1.5098	-DE/DX = 0.0
R45	R(27,28)	1.0949	-DE/DX = 0.0
R46	R(27,29)	1.4013	-DE/DX = 0.0
R47	R(29,30)	1.3994	-DE/DX = 0.0
R48	R(29,37)	1.5102	-DE/DX = 0.0
R49	R(30,31)	1.094	-DE/DX = 0.0
R50	R(30,32)	1.4022	-DE/DX = 0.0
R51	R(32,41)	1.5093	-DE/DX = 0.0
R52	R(33,34)	1.1007	-DE/DX = 0.0
R53	R(33,35)	1.1	-DE/DX = 0.0
R54	R(33,36)	1.1035	-DE/DX = 0.0
R55	R(37,38)	1.102	-DE/DX = 0.0
R56	R(37,39)	1.1043	-DE/DX = 0.0
R57	R(37,40)	1.1004	-DE/DX = 0.0
R58	R(41,42)	1.0997	-DE/DX = 0.0
R59	R(41,43)	1.1013	-DE/DX = 0.0

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 ! R60   R(41,44)              1.1033         -DE/DX =    0.0                 !
 ! R61   R(45,46)              1.4123         -DE/DX =    0.0                 !
 ! R62   R(45,52)              1.4139         -DE/DX =    0.0                 !
 ! R63   R(46,47)              1.4026         -DE/DX =    0.0                 !
 ! R64   R(46,53)              1.5099         -DE/DX =    0.0                 !
 ! R65   R(47,48)              1.0945         -DE/DX =    0.0                 !
 ! R66   R(47,49)              1.3989         -DE/DX =    0.0                 !
 ! R67   R(49,50)              1.4017         -DE/DX =    0.0                 !
 ! R68   R(49,57)              1.5099         -DE/DX =    0.0                 !
 ! R69   R(50,51)              1.0947         -DE/DX =    0.0                 !
 ! R70   R(50,52)              1.3997         -DE/DX =    0.0                 !
 ! R71   R(52,61)              1.5093         -DE/DX =    0.0                 !
 ! R72   R(53,54)              1.1002         -DE/DX =    0.0                 !
 ! R73   R(53,55)              1.1            -DE/DX =    0.0                 !
 ! R74   R(53,56)              1.1037         -DE/DX =    0.0                 !
 ! R75   R(57,58)              1.1004         -DE/DX =    0.0                 !
 ! R76   R(57,59)              1.1038         -DE/DX =    0.0                 !
 ! R77   R(57,60)              1.1022         -DE/DX =    0.0                 !
 ! R78   R(61,62)              1.1014         -DE/DX =    0.0                 !
 ! R79   R(61,63)              1.1031         -DE/DX =    0.0                 !
 ! R80   R(61,64)              1.0998         -DE/DX =    0.0                 !
 ! R81   R(65,66)              1.414          -DE/DX =    0.0                 !
 ! R82   R(65,69)              1.5175         -DE/DX =    0.0                 !
 ! R83   R(66,67)              1.089          -DE/DX =    0.0                 !
 ! R84   R(66,68)              1.4142         -DE/DX =    0.0                 !
 ! R85   R(68,73)              1.5174         -DE/DX =    0.0                 !
 ! R86   R(69,70)              1.1008         -DE/DX =    0.0                 !
 ! R87   R(69,71)              1.0972         -DE/DX =    0.0                 !
 ! R88   R(69,72)              1.1008         -DE/DX =    0.0                 !
 ! R89   R(73,74)              1.1012         -DE/DX =    0.0                 !
 ! R90   R(73,75)              1.0972         -DE/DX =    0.0                 !
 ! R91   R(73,76)              1.1006         -DE/DX =    0.0                 !
 ! R92   R(77,78)              1.4109         -DE/DX =    0.0                 !
 ! R93   R(77,84)              1.4151         -DE/DX =    0.0                 !
 ! R94   R(78,79)              1.4026         -DE/DX =    0.0                 !
 ! R95   R(78,85)              1.5092         -DE/DX =    0.0                 !
 ! R96   R(79,80)              1.0939         -DE/DX =    0.0                 !
 ! R97   R(79,81)              1.3989         -DE/DX =    0.0                 !
 ! R98   R(81,82)              1.4016         -DE/DX =    0.0                 !
 ! R99   R(81,89)              1.5102         -DE/DX =    0.0                 !
 ! R100  R(82,83)              1.0949         -DE/DX =    0.0                 !
 ! R101  R(82,84)              1.3998         -DE/DX =    0.0                 !
 ! R102  R(84,93)              1.5098         -DE/DX =    0.0                 !
 ! R103  R(85,86)              1.1034         -DE/DX =    0.0                 !
 ! R104  R(85,87)              1.0997         -DE/DX =    0.0                 !
 ! R105  R(85,88)              1.1012         -DE/DX =    0.0                 !
 ! R106  R(89,90)              1.1002         -DE/DX =    0.0                 !
 ! R107  R(89,91)              1.1028         -DE/DX =    0.0                 !
 ! R108  R(89,92)              1.1037         -DE/DX =    0.0                 !
 ! R109  R(93,94)              1.1            -DE/DX =    0.0                 !
 ! R110  R(93,95)              1.1035         -DE/DX =    0.0                 !
 ! R111  R(93,96)              1.1005         -DE/DX =    0.0                 !
 ! R112  R(97,98)              1.413          -DE/DX =    0.0                 !
 ! R113  R(97,104)             1.4131         -DE/DX =    0.0                 !
 ! R114  R(98,99)              1.4007         -DE/DX =    0.0                 !
 ! R115  R(98,109)             1.5093         -DE/DX =    0.0                 !
 ! R116  R(99,100)             1.0946         -DE/DX =    0.0                 !
 ! R117  R(99,101)             1.4009         -DE/DX =    0.0                 !
 ! R118  R(101,102)            1.3999         -DE/DX =    0.0                 !
 ! R119  R(101,105)            1.51           -DE/DX =    0.0                 !
 ! R120  R(102,103)            1.0947         -DE/DX =    0.0                 !
 ! R121  R(102,104)            1.4018         -DE/DX =    0.0                 !
 ! R122  R(104,113)            1.51           -DE/DX =    0.0                 !
 ! R123  R(105,106)            1.1014         -DE/DX =    0.0                 !
 ! R124  R(105,107)            1.1008         -DE/DX =    0.0                 !
 ! R125  R(105,108)            1.1045         -DE/DX =    0.0                 !
 ! R126  R(109,110)            1.103          -DE/DX =    0.0                 !
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 ! R127  R(109,111)              1.0998         -DE/DX =    0.0                 !
 ! R128  R(109,112)              1.1015         -DE/DX =    0.0                 !
 ! R129  R(113,114)              1.1038         -DE/DX =    0.0                 !
 ! R130  R(113,115)              1.1004         -DE/DX =    0.0                 !
 ! R131  R(113,116)              1.1            -DE/DX =    0.0                 !
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.303365	2.221392	-0.014122
2	30	0	-0.314117	-2.220641	-0.016174
3	7	0	1.953769	3.284479	-0.359898
4	7	0	-0.974757	3.702900	0.372039
5	7	0	1.031358	-3.645555	0.349773
6	7	0	-1.912535	-3.355190	-0.382967
7	6	0	-0.057442	0.019097	-2.178627
8	6	0	-0.056350	-0.004736	2.137452
9	8	0	-0.140041	1.148324	-1.640645
10	8	0	0.062436	-1.100329	-1.628907
11	8	0	-0.476726	-1.055776	1.598626
12	8	0	0.393973	1.026825	1.586916
13	6	0	1.920800	4.613754	-0.257747
14	6	0	0.771547	5.372449	0.063402
15	1	0	0.932794	6.449079	0.093192
16	6	0	-0.554416	4.967788	0.342719
17	6	0	3.197145	5.398186	-0.499429
18	1	0	3.996569	5.060840	0.178221
19	1	0	3.039068	6.473424	-0.349038
20	1	0	3.571717	5.238672	-1.522162
21	6	0	-1.551619	6.077383	0.620379
22	1	0	-2.393660	6.028733	-0.087255
23	1	0	-1.081797	7.065594	0.539922
24	1	0	-1.987871	5.976841	1.625832
25	6	0	3.151174	2.613050	-0.757771
26	6	0	3.418680	2.412502	-2.132297
27	6	0	4.579021	1.719284	-2.498184
28	1	0	4.785959	1.569030	-3.562784
29	6	0	5.476979	1.214823	-1.548017
30	6	0	5.180097	1.417818	-0.195602
31	1	0	5.862971	1.029550	0.565873
32	6	0	4.030260	2.103440	0.221561
33	6	0	2.474098	2.937480	-3.186664
34	1	0	1.439245	2.620780	-2.986081
35	1	0	2.763592	2.580724	-4.186104
36	1	0	2.463571	4.040476	-3.219053
37	6	0	6.708122	0.452534	-1.976747
38	1	0	7.223226	0.951592	-2.813470
39	1	0	6.450259	-0.564609	-2.320952
40	1	0	7.427430	0.347710	-1.150618
41	6	0	3.741440	2.295777	1.690430
42	1	0	4.499106	1.792632	2.308604
43	1	0	2.752447	1.893576	1.960519
44	1	0	3.732511	3.362720	1.971042
45	6	0	-2.324688	3.388051	0.719860
46	6	0	-2.676473	3.205515	2.075460
47	6	0	-3.996427	2.848004	2.387391
48	1	0	-4.266769	2.708464	3.438809
49	6	0	-4.971440	2.665069	1.401074
50	6	0	-4.591443	2.846041	0.064103
51	1	0	-5.335073	2.706803	-0.727101
52	6	0	-3.286505	3.198811	-0.299089
53	6	0	-1.656856	3.397321	3.172423
54	1	0	-0.730732	2.843573	2.957526
55	1	0	-2.053558	3.059402	4.141184
56	1	0	-1.368975	4.456797	3.285969
57	6	0	-6.382400	2.259758	1.754384
58	1	0	-6.573797	2.355659	2.833720
59	1	0	-6.576719	1.209784	1.474702

60	1	0	-7.125579	2.875836	1.222329
61	6	0	-2.913557	3.376339	-1.750778
62	1	0	-2.083680	2.710343	-2.035064
63	1	0	-2.577119	4.404715	-1.965632
64	1	0	-3.770245	3.159938	-2.405602
65	6	0	0.681185	-4.929018	0.257719
66	6	0	-0.616003	-5.392272	-0.061954
67	1	0	-0.717306	-6.476309	-0.085794
68	6	0	-1.807427	-4.683718	-0.341954
69	6	0	1.731754	-5.994165	0.511708
70	1	0	2.592513	-5.861044	-0.161524
71	1	0	1.322381	-7.001460	0.365004
72	1	0	2.127994	-5.922808	1.536227
73	6	0	-3.043235	-5.523995	-0.605246
74	1	0	-3.841777	-5.275161	0.110957
75	1	0	-2.821850	-6.595685	-0.525917
76	1	0	-3.453445	-5.322845	-1.606533
77	6	0	2.349732	-3.275811	0.758953
78	6	0	3.333440	-2.989442	-0.211073
79	6	0	4.606136	-2.585518	0.218200
80	1	0	5.367843	-2.366893	-0.535862
81	6	0	4.927476	-2.450697	1.573009
82	6	0	3.926839	-2.729059	2.514167
83	1	0	4.151103	-2.624297	3.580740
84	6	0	2.642275	-3.137247	2.136565
85	6	0	3.024002	-3.117209	-1.682693
86	1	0	2.781717	-4.156705	-1.962246
87	1	0	3.880587	-2.796739	-2.293423
88	1	0	2.151157	-2.507327	-1.963561
89	6	0	6.300320	-2.005340	2.017553
90	1	0	6.991300	-1.914395	1.166311
91	1	0	6.742599	-2.715318	2.736205
92	1	0	6.261001	-1.024264	2.521576
93	6	0	1.590838	-3.425469	3.181011
94	1	0	1.944566	-3.142731	4.183460
95	1	0	1.324461	-4.495831	3.213969
96	1	0	0.659662	-2.878701	2.968797
97	6	0	-3.152884	-2.729176	-0.718222
98	6	0	-4.031441	-2.317925	0.309221
99	6	0	-5.223403	-1.671850	-0.042647
100	1	0	-5.906849	-1.364413	0.755207
101	6	0	-5.565059	-1.409693	-1.375672
102	6	0	-4.670056	-1.817505	-2.371813
103	1	0	-4.912551	-1.622600	-3.421342
104	6	0	-3.467028	-2.471533	-2.071668
105	6	0	-6.840185	-0.678918	-1.722219
106	1	0	-7.653822	-0.930120	-1.023692
107	1	0	-7.180909	-0.917839	-2.741349
108	1	0	-6.698545	0.415374	-1.673350
109	6	0	-3.692960	-2.570930	1.758142
110	1	0	-3.592147	-3.647665	1.975224
111	1	0	-4.472482	-2.166018	2.419883
112	1	0	-2.732328	-2.105545	2.030091
113	6	0	-2.531024	-2.897442	-3.177377
114	1	0	-2.497582	-3.995066	-3.288775
115	1	0	-1.499641	-2.572264	-2.973872
116	1	0	-2.848547	-2.478953	-4.143883
117	1	0	-0.086892	0.012705	3.251457
118	1	0	-0.094735	0.011311	-3.292579

Summary of Natural Population Analysis:

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
Zn	1	1.27313	17.99729	10.72585	0.00373	28.72687
Zn	2	1.27291	17.99729	10.72606	0.00374	28.72709
N	3	-0.73296	1.99926	5.71727	0.01642	7.73296
N	4	-0.73214	1.99926	5.71644	0.01643	7.73214
N	5	-0.73280	1.99926	5.71712	0.01642	7.73280
N	6	-0.73219	1.99926	5.71649	0.01644	7.73219
C	7	0.76425	1.99950	3.19067	0.04558	5.23575
C	8	0.76385	1.99950	3.19097	0.04568	5.23615
O	9	-0.76360	1.99971	6.75403	0.00985	8.76360
O	10	-0.76450	1.99971	6.75493	0.00986	8.76450
O	11	-0.76357	1.99971	6.75401	0.00985	8.76357
O	12	-0.76446	1.99971	6.75489	0.00985	8.76446
C	13	0.32767	1.99894	3.65209	0.02131	5.67233
C	14	-0.42270	1.99886	4.40705	0.01679	6.42270
H	15	0.21800	0.00000	0.77941	0.00259	0.78200
C	16	0.32789	1.99894	3.65184	0.02133	5.67211
C	17	-0.66008	1.99919	4.65339	0.00750	6.66008
H	18	0.23627	0.00000	0.76131	0.00242	0.76373
H	19	0.22598	0.00000	0.77202	0.00199	0.77402
H	20	0.23545	0.00000	0.76212	0.00244	0.76455
C	21	-0.65997	1.99919	4.65330	0.00748	6.65997
H	22	0.23632	0.00000	0.76127	0.00241	0.76368
H	23	0.22600	0.00000	0.77201	0.00199	0.77400
H	24	0.23515	0.00000	0.76240	0.00244	0.76485
C	25	0.15436	1.99868	3.82465	0.02230	5.84564
C	26	-0.03405	1.99879	4.01960	0.01566	6.03405
C	27	-0.21991	1.99882	4.20637	0.01472	6.21991
H	28	0.21427	0.00000	0.78281	0.00293	0.78573
C	29	-0.03260	1.99884	4.01857	0.01519	6.03260
C	30	-0.21679	1.99882	4.20331	0.01466	6.21679
H	31	0.21461	0.00000	0.78227	0.00313	0.78539
C	32	-0.02959	1.99878	4.01505	0.01575	6.02959
C	33	-0.63918	1.99920	4.63109	0.00890	6.63918
H	34	0.23671	0.00000	0.75874	0.00455	0.76329
H	35	0.21754	0.00000	0.78019	0.00227	0.78246
H	36	0.22054	0.00000	0.77681	0.00264	0.77946
C	37	-0.63208	1.99920	4.62419	0.00868	6.63208
H	38	0.22285	0.00000	0.77465	0.00250	0.77715
H	39	0.22238	0.00000	0.77489	0.00273	0.77762
H	40	0.21882	0.00000	0.77883	0.00235	0.78118
C	41	-0.63870	1.99920	4.63057	0.00894	6.63870
H	42	0.21727	0.00000	0.78046	0.00227	0.78273
H	43	0.24018	0.00000	0.75608	0.00374	0.75982
H	44	0.22042	0.00000	0.77702	0.00256	0.77958
C	45	0.15381	1.99868	3.82519	0.02232	5.84619
C	46	-0.03488	1.99879	4.02041	0.01568	6.03488
C	47	-0.22075	1.99882	4.20739	0.01454	6.22075
H	48	0.21474	0.00000	0.78236	0.00290	0.78526
C	49	-0.03121	1.99884	4.01717	0.01520	6.03121
C	50	-0.21631	1.99882	4.20279	0.01470	6.21631
H	51	0.21325	0.00000	0.78381	0.00294	0.78675
C	52	-0.02952	1.99879	4.01503	0.01569	6.02952
C	53	-0.63929	1.99920	4.63120	0.00889	6.63929
H	54	0.23603	0.00000	0.75932	0.00465	0.76397
H	55	0.21776	0.00000	0.77997	0.00228	0.78224
H	56	0.22045	0.00000	0.77689	0.00266	0.77955
C	57	-0.63077	1.99920	4.62294	0.00864	6.63077
H	58	0.21852	0.00000	0.77913	0.00235	0.78148
H	59	0.22288	0.00000	0.77424	0.00288	0.77712

H	60	0.22215	0.00000	0.77534	0.00251	0.77785
C	61	-0.63930	1.99920	4.63118	0.00893	6.63930
H	62	0.24011	0.00000	0.75607	0.00382	0.75989
H	63	0.22069	0.00000	0.77676	0.00255	0.77931
H	64	0.21747	0.00000	0.78025	0.00228	0.78253
C	65	0.32764	1.99894	3.65210	0.02132	5.67236
C	66	-0.42271	1.99886	4.40705	0.01679	6.42271
H	67	0.21800	0.00000	0.77941	0.00259	0.78200
C	68	0.32791	1.99894	3.65183	0.02132	5.67209
C	69	-0.65999	1.99919	4.65331	0.00749	6.65999
H	70	0.23612	0.00000	0.76146	0.00242	0.76388
H	71	0.22603	0.00000	0.77198	0.00199	0.77397
H	72	0.23539	0.00000	0.76218	0.00243	0.76461
C	73	-0.66008	1.99919	4.65339	0.00749	6.66008
H	74	0.23654	0.00000	0.76105	0.00240	0.76346
H	75	0.22599	0.00000	0.77201	0.00199	0.77401
H	76	0.23518	0.00000	0.76237	0.00245	0.76482
C	77	0.15420	1.99868	3.82480	0.02231	5.84580
C	78	-0.03006	1.99878	4.01553	0.01575	6.03006
C	79	-0.21626	1.99882	4.20285	0.01458	6.21626
H	80	0.21440	0.00000	0.78251	0.00309	0.78560
C	81	-0.03230	1.99884	4.01826	0.01520	6.03230
C	82	-0.21942	1.99882	4.20585	0.01475	6.21942
H	83	0.21419	0.00000	0.78287	0.00293	0.78581
C	84	-0.03449	1.99879	4.02008	0.01562	6.03449
C	85	-0.63849	1.99920	4.63036	0.00893	6.63849
H	86	0.22052	0.00000	0.77692	0.00256	0.77948
H	87	0.21762	0.00000	0.78010	0.00227	0.78238
H	88	0.23930	0.00000	0.75693	0.00377	0.76070
C	89	-0.63277	1.99920	4.62489	0.00868	6.63277
H	90	0.21844	0.00000	0.77924	0.00232	0.78156
H	91	0.22388	0.00000	0.77356	0.00255	0.77612
H	92	0.22265	0.00000	0.77468	0.00268	0.77735
C	93	-0.63911	1.99920	4.63101	0.00890	6.63911
H	94	0.21767	0.00000	0.78006	0.00227	0.78233
H	95	0.22065	0.00000	0.77670	0.00265	0.77935
H	96	0.23623	0.00000	0.75918	0.00459	0.76377
C	97	0.15403	1.99868	3.82499	0.02230	5.84597
C	98	-0.02913	1.99879	4.01462	0.01572	6.02913
C	99	-0.21793	1.99882	4.20448	0.01464	6.21793
H	100	0.21346	0.00000	0.78362	0.00292	0.78654
C	101	-0.03162	1.99884	4.01759	0.01518	6.03162
C	102	-0.22047	1.99882	4.20703	0.01461	6.22047
H	103	0.21463	0.00000	0.78246	0.00291	0.78537
C	104	-0.03403	1.99879	4.01956	0.01569	6.03403
C	105	-0.63108	1.99920	4.62325	0.00863	6.63108
H	106	0.22054	0.00000	0.77701	0.00244	0.77946
H	107	0.21997	0.00000	0.77764	0.00240	0.78003
H	108	0.22318	0.00000	0.77398	0.00284	0.77682
C	109	-0.63959	1.99920	4.63145	0.00894	6.63959
H	110	0.22056	0.00000	0.77689	0.00255	0.77944
H	111	0.21751	0.00000	0.78022	0.00228	0.78249
H	112	0.24091	0.00000	0.75531	0.00378	0.75909
C	113	-0.63943	1.99920	4.63134	0.00888	6.63943
H	114	0.22043	0.00000	0.77691	0.00265	0.77957
H	115	0.23666	0.00000	0.75873	0.00461	0.76334
H	116	0.21762	0.00000	0.78011	0.00227	0.78238
H	117	0.11713	0.00000	0.87830	0.00457	0.88287
H	118	0.11700	0.00000	0.87845	0.00454	0.88300

Supplementary Material (ESI) for Chemical Communications