Supporting Information

for

Synthesis and structure of a zinc–zinc-bonded compound with a monoanionic α-diimine ligand, [LZn–ZnL] (L = [(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)]$_2^-$)

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S1. DFT computations

The structure optimization and NBO bonding analysis for the model compounds [(CMeNAr')$_2$Zn–Zn(NAr'CMe)$_2$] (**3'**, Ar' = 2,6-$C_6H_3Me_2$) and Na_2[(CMeNAr')$_2$Zn–Zn(NAr'CMe)$_2$] (**1a'**) were carried out at the B3LYP/GEN level using the Gaussian 03 program. The optimized structures and selected frontier molecular orbitals are given in Figures S1–S4.

The model compound [(CMeNAr')$_2$Zn–Zn(NAr'CMe)$_2$] (**3'**), where the isopropyl groups on the *N*-2,6-diisopropylphenyl were replaced by methyl groups, was used for the compound **3**. Geometrical optimizations were carried out using DFT methods, specifically the B3LYP functional with DZP basis sets. This combination has been demonstrated to be efficient to predict reasonable theoretical results for metal-ligand complex systems.[1-4] The B3LYP method is a hybrid of the HF and DFT methods, incorporating Becke's three-parameter exchange functional (B3)[5] with the Lee, Yang, and Parr (LYP) correlation functional.[4]

The double-ζ plus polarization (DZP) basis sets were used for carbon and nitrogen add one set of pure spherical harmonic *d* functions with orbital exponents α_d(C) = 0.75 and α_d(N) = 0.80 to the Huzinaga-Dunning standard contracted DZ sets and were designated (9s5p1d/4s2p1d).[6,7] For Zn, in our loosely contracted DZP basis set, the Wachters' primitive set is used but is augmented by two sets of p functions and one set of d functions, contracted following Hood et al., and designated (14s11p6d/10s8p3d).[8,9] DZP basis set for Na is McLean and Chandler's DZ set plus a set of d functions with exponent αd(Na) = 0.175, and designated (12s9p1d/6s5p1d). For K, the Wachters' primitive set was used but was augmented by two sets of *p* functions and one set of *d* functions, contracted following Hood et al.[10]

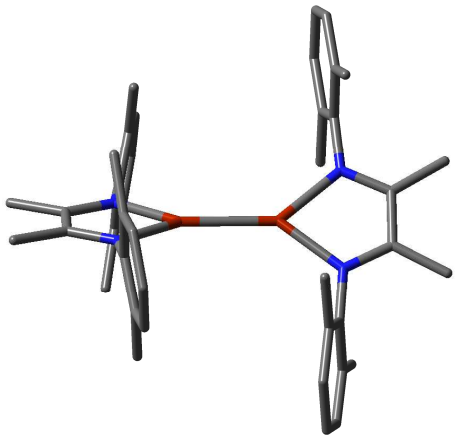
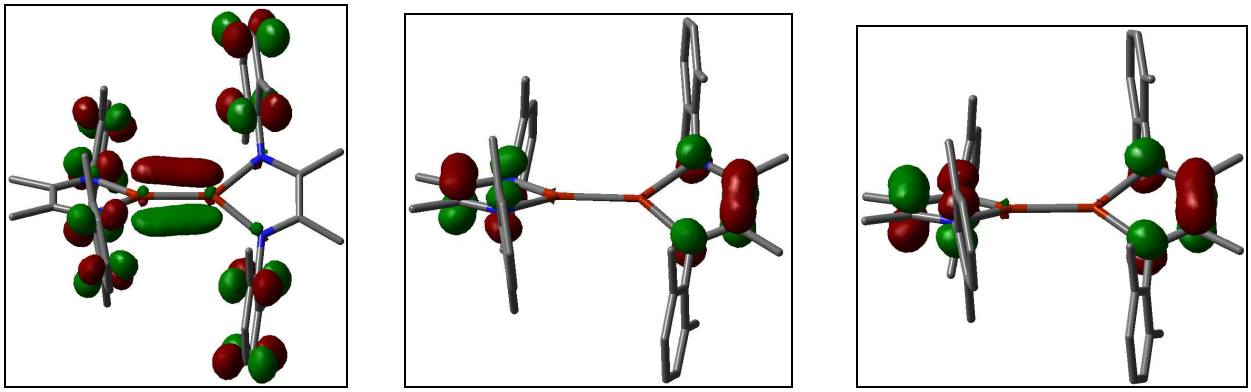


Figure S1. The optimized structure of **3'**.



(LUMO+5) (HOMO) (LUMO)

Figure S2. Selected frontier molecular orbitals of **3'**.

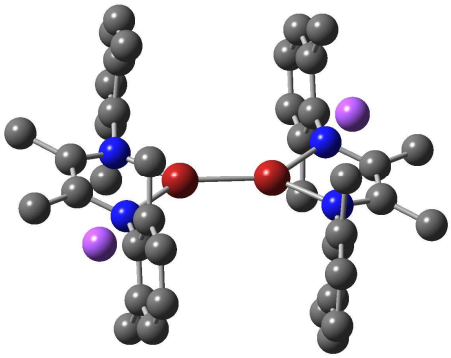


Figure S3. The optimized structure of **1a'**.

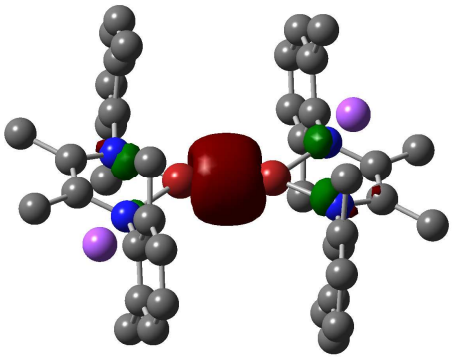


Figure S4. The Zn–Zn bond orbital HOMO–2 of **1a'**.

Table S1. Selected bond distances and angles of **3** and **3'** (at B3LYP/GEN level)

	3	**3'**
Zn1–Zn2	2.3403	2.3565
Zn–N (*av.*)	1.995	2.034
C–C (*av.*)	1.420	1.438
N–C (*av.*)	1.332	1.345
N–Zn–N (*av.*)	81.500	81.421
N–Zn–Zn (*av.*)	139.250	139.285

Table S2. Cartesian coordinates of the optimized geometry for **3'**

Zn	0.21352500	-1.15872600	0.02213900
Zn	-0.21351300	1.15872600	0.02213700
N	-0.73019200	-2.89006200	-0.48109400
N	1.70420900	-2.46148200	0.48260500
C	1.35553000	-3.74144900	0.25962400
C	0.04944400	-3.97071500	-0.29768900
N	-1.70420600	2.46146500	0.48262700
N	0.73018400	2.89007500	-0.48108200
C	-0.04945800	3.97072000	-0.29765900
C	-1.35554000	3.74143700	0.25965700
H	-3.58504800	2.53863500	-1.65241500
C	-2.01199000	-2.98331600	-1.09015000
C	2.94147800	-2.11609000	1.09305700
C	2.27707200	-4.90319900	0.55297500
C	-0.40344200	-5.37320300	-0.63453900
C	-2.94147200	2.11605900	1.09307800
C	2.01198300	2.98334700	-1.09013400
C	0.40341800	5.37321500	-0.63449300
C	-2.27708800	4.90317600	0.55303100
C	-3.84974400	1.56520800	-1.21969300
C	-3.16831200	-2.94665200	-0.27360500
C	-2.12902600	-3.03426000	-2.50101000
C	4.00300500	-1.64601300	0.28224600
C	3.08197100	-2.17062200	2.50169900
H	3.30130100	-4.55555000	0.71402100
H	2.28150800	-5.62434300	-0.27313800
H	1.96715300	-5.45286500	1.45475000
H	-1.47941400	-5.39745100	-0.82686000
H	-0.18225400	-6.06947700	0.18376400
H	0.10434600	-5.76200300	-1.53008100
C	-4.00300800	1.64600800	0.28226400
C	-3.08195200	2.17055200	2.50172300
C	2.12902200	3.03429800	-2.50099400
C	3.16830300	2.94669300	-0.27358700
H	1.47938900	5.39747200	-0.82681700
H	0.18222900	6.06947800	0.18381800
H	-0.10437500	5.76202200	-1.53002900
H	-3.30132000	4.55552000	0.71404800
H	-2.28151200	5.62434700	-0.27305900
H	-1.96718600	5.45281200	1.45482900
C	-3.04575400	-2.86929900	1.23104100
C	-4.43173000	-2.98685600	-0.88392200
C	-0.89949500	-3.02480900	-3.38159700
C	-3.40950200	-3.06999400	-3.07500700

C	3.84972800	-1.56517300	-1.21970700
C	5.20448100	-1.25737700	0.89531100
C	4.29738000	-1.77012500	3.07854900
C	1.93723100	-2.62659000	3.37852800
C	-5.20448000	1.25735900	0.89532900
C	-4.29735600	1.77004200	3.07857300
C	-1.93720300	2.62649400	3.37855300
C	3.40949900	3.07004900	-3.07498700
C	0.89949300	3.02483700	-3.38158300
C	3.04574300	2.86933300	1.23105900
C	4.43172300	2.98691400	-0.88390100
H	-2.51448500	-1.95854700	1.53629700
H	-5.32284800	-2.96497300	-0.25644400
C	-4.55933700	-3.05215200	-2.27647100
H	-3.50224400	-3.10633600	-4.16066000
H	3.05170100	-0.86432600	-1.49771000
C	5.35925700	-1.31954200	2.28522500
H	6.02479500	-0.90147700	0.27183600
H	4.40703700	-1.80810500	4.16255900
H	1.69332500	-3.68469200	3.21720700
C	-5.35924200	1.31948500	2.28524600
H	-6.02480000	0.90147800	0.27185200
H	-4.40700400	1.80799300	4.16258500
H	-1.69328300	3.68459400	3.21724300
H	3.50224300	3.10639700	-4.16064000
C	4.55933200	3.05221700	-2.27644900
H	0.29390700	3.93066100	-3.24893400
H	2.51448100	1.95857500	1.53630900
H	5.32283900	2.96503900	-0.25642100
H	-5.54665100	-3.08197600	-2.73623400
H	6.29726300	-1.01336300	2.74727300
H	-6.29724500	1.01329600	2.74729400
H	5.54664700	3.08205400	-2.73620900
H	-0.24970900	-2.17278400	-3.14178200
H	-0.29393100	-3.93064900	-3.24896500
H	-1.18042700	-2.95987900	-4.43836100
H	-4.03507500	-2.85915400	1.70101500
H	-2.47948000	-3.71887400	1.63447600
H	-4.77927900	1.22078000	-1.68557900
H	-3.05172900	0.86435800	-1.49772100
H	-2.18533900	2.49681600	4.43757700
H	-1.02415400	2.05579500	3.16360500
H	4.03506300	2.85919400	1.70103500
H	2.47946200	3.71890100	1.63449600
H	1.18042800	2.95993400	-4.43834800
H	0.24972500	2.17279300	-3.14178600
H	4.77925400	-1.22072100	-1.68559100

H	3.58504000	-2.53859200	-1.65245300
H	2.18537000	-2.49692100	4.43755300
H	1.02417400	-2.05590100	3.16359000

Table S3. Cartesian coordinates of the optimized geometry for **1a'**

Zn	-0.10914300	1.19354600	-0.02821100
Zn	0.10914200	-1.19354100	0.02818700
N	1.07421700	2.83695200	-0.16641500
N	-1.54423600	2.61950100	-0.14427100
C	0.35318700	4.02545300	0.13909800
C	-1.02384800	3.91108800	0.14850800
N	-1.07421600	-2.83694500	0.16640800
N	1.54423500	-2.61949400	0.14424500
C	-0.35318900	-4.02544900	-0.13909900
C	1.02384600	-3.91108300	-0.14851800
Na	-0.27303800	3.09535600	-2.14583300
C	2.47691200	2.81842100	0.03384400
C	-2.92992600	2.38502100	0.04059600
C	1.11981700	5.32055100	0.30121200
C	-1.99002800	5.06188400	0.33143900
Na	0.27305200	-3.09533900	2.14582300
C	-2.47691500	-2.81842100	-0.03382900
C	2.92992700	-2.38501900	-0.04061200
C	-1.11981800	-5.32054800	-0.30120100
C	1.99002600	-5.06187900	-0.33145300
C	3.35382200	2.77807900	-1.08076400
C	3.02717100	2.78761600	1.34394900
C	-3.47678600	2.23655700	1.34352600
C	-3.78578500	2.24938300	-1.08274000
H	1.77898300	5.29990500	1.17925800
H	0.45367500	6.18015200	0.40935600
H	1.77856600	5.50889300	-0.56114500
H	-2.61747200	4.93101200	1.22325500
H	-2.68851800	5.14195200	-0.51607900
H	-1.47184200	6.01883500	0.43151600
C	-3.35380800	-2.77808400	1.08079100
C	-3.02719300	-2.78761800	-1.34392600
C	3.47679500	-2.23654800	-1.34353800
C	3.78578200	-2.24939600	1.08272900
H	-1.77898700	-5.29990900	-1.17924500
H	-0.45367700	-6.18015000	-0.40934000
H	-1.77856600	-5.50888400	0.56115900
H	2.61745600	-4.93101400	-1.22328000
H	2.68852900	-5.14193900	0.51605500
H	1.47184000	-6.01883200	-0.43151400

C	4.74203200	2.73738200	-0.88225600
C	2.80822600	2.78989600	-2.49382000
C	4.41973100	2.75525600	1.51082700
C	2.12108000	2.73929500	2.55277600
C	-4.85030000	1.99474900	1.49598400
C	-2.58056500	2.29315100	2.55924100
C	-5.15394800	1.99802800	-0.89963200
C	-3.24201100	2.38571100	-2.49012200
C	-4.74202100	-2.73739300	0.88230400
C	-2.80819100	-2.78990300	2.49383900
C	-4.41975600	-2.75526300	-1.51078300
C	-2.12111900	-2.73929700	-2.55276600
C	4.85031000	-1.99474300	-1.49598800
C	2.58058000	-2.29313500	-2.55925900
C	5.15394700	-1.99804400	0.89963000
C	3.24200100	-2.38573700	2.49010700
H	5.40554700	2.70998500	-1.74725000
C	5.28249500	2.73456000	0.40836700
H	2.16233700	1.91886800	-2.68038900
H	4.83194600	2.73318200	2.52038900
H	1.45490600	1.86628900	2.49663700
H	-5.26111100	1.88516500	2.50040600
C	-5.69449200	1.87798700	0.38517800
H	-1.80822600	1.51278500	2.50060400
H	-5.80114700	1.89831400	-1.77155800
H	-2.47556300	1.62379800	-2.69810900
H	-5.40552300	-2.70999900	1.74730800
C	-5.28250300	-2.73457100	-0.40831100
H	-2.16230000	-1.91887500	2.68040000
H	-4.83198500	-2.73319000	-2.52033900
H	-1.46606400	-3.61665100	-2.62121400
H	5.26112700	-1.88515400	-2.50040700
C	5.69449700	-1.87799400	-0.38517700
H	2.04450500	-3.24679600	-2.63968800
H	5.80114200	-1.89834200	1.77156000
H	2.47554300	-1.62383400	2.69809400
H	6.36177500	2.70383800	0.55294300
H	-6.75821000	1.68463500	0.51885900
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H	6.75821700	-1.68464500	-0.51885000
H	-2.22789100	-3.70785200	2.69279800
H	-3.61957400	-2.76092200	3.22997100
H	-3.15835000	2.14192900	3.47840400
H	-2.04448500	3.24681000	2.63966100
H	-2.70615200	-2.67194800	-3.47723700
H	-1.45495000	-1.86628600	-2.49664000
H	4.03694700	-2.26114000	3.23411200

H	2.80346200	-3.38514600	2.65675700
H	3.15836900	-2.14190400	-3.47841800
H	1.80823700	-1.51277300	-2.50062000
H	2.70610000	2.67193700	3.47725600
H	1.46603000	3.61665300	2.62122000
H	2.22793000	3.70784600	-2.69278800
H	3.61962000	2.76091400	-3.22993900
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S2. EPR study of 3.

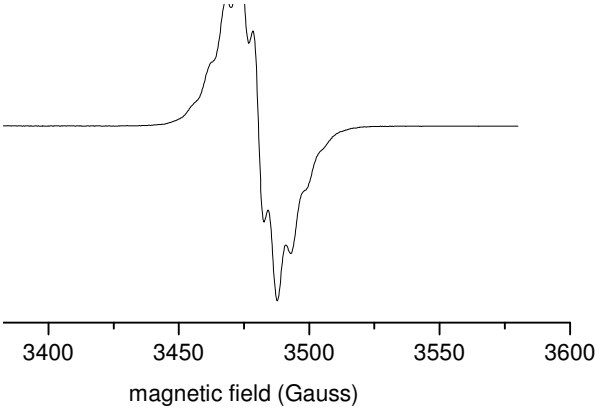

Figure S5. EPR signal of compound **3** in THF at room temperature.

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