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Rare example of structurally characterized mononuclear N-heterocyclic carbene containing zinc carboxylate

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General considerations

All operations were carried out in evacuated Schenk flasks or tubes using standard vacuum-line techniques. The compounds were handled in an argon-filled glovebox. All glassware was oven-dried at 150°C overnight. Solvents were distilled in inert atmosphere over common drying agents (THF – K/benzophenone, hexane – Na metal) and transferred under vacuum. IMes (1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was synthesized according to known procedure[S1]. [Zn(piv)$_2$] was synthesized as reported[S2] and dried at 105°C overnight. IR spectra of the compounds were recorded on a Perkin Elmer Spectrum 65 spectrophotometer equipped with a Quest ATR Accessory (Specac) by the attenuated total reflectance (ATR) in the range of 400—4000 cm^{-1}. NMR spectra were recorded with a Bruker Avance 600 (600.22 MHz) spectrometer. The samples for NMR spectroscopy were prepared in dry argon atmosphere using Schleck technique with J. Young valve NMR tube and dried toluene-d$_8$ (Sigma-Aldrich) was used as a solvent. ^{1}H NMR chemical shifts are reported versus SiMe$_4$ and were calculated by reference to the residual ^{1}H solvent peaks[S3].

Synthesis of [Zn(O$_2$CCMe$_3$)$_2$(IMes)]

In a Schlenk tube with J.Young PTFE stopcock IMes (0.200 g, 0.657 mmol), and [Zn(O$_2$CCMe$_3$)$_2$] (0.175 g, 0.657 mmol) were placed in the glove box. The tube was evacuated, and *ca.* 10 mL of THF was vacuum-transferred at –196°C. Spontaneous warming to room temperature afforded a clear colourless solution, which was stirred for 24 h without heating and then evaporated. 25 ml of hexane was vacuum-transferred to the residue, the resulting colourless suspension was transferred to a glass ampoule. The latter was fire-sealed, heated at 110 °C for 2 hours (until the precipitate was completely dissolved) and then slowly (by *ca*. 10 °C/hour) cooled to RT. White needle-like crystals were collected in 24 h (0.283 g, 78%). Anal. Calcd for $C_{31}H_{42}N_2O_4Zn$ (572.06) C, 65.09; H, 7.40; N, 4.90. Found: C, 64.97; H, 7.22; N, 4.83. IR, ν/cm^{-1}: 3160 w, 3124 w, 3089 w, 2956 m, 2921 m, 1549 vs, 1484 vs, 1419 vs, 1377 s, 1360 s, 1224 s, 1116 m, 1033 w, 931 w, 903 s, 854 m, 812 m, 793 m, 772 m, 704 w, 609 s, 576 w, 536 w, 473 w, 455 w, 444 w, 426 w, 412 s. ^{1}H NMR (600.22 MHz, 293 K, toluene-d$_8$), δ, ppm: 1.18 (18H, s, Me(*tert*-Bu)), 2.02–2.26 (18H, m, o-/p-CH$_3$(Mes)), 6.06 (2H, s, HCN), 6.66–6.84 (4H, m, m-CH(Mes)).

[S1] A.J. Arduengo, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 1992, **114**, 5530–5534.

[S2] I.G.Fomina, V.V. Chernyshev, Yu.A. Velikodnyi, M.A. Bykov, I.P. Malkerova, A.S. Alikhanyan, Yu.S. Zavorotnyi, Zh.V. Dobrokhotova, I.L. Eremenko, *Russ. Chem. Bull.* 2013, **62**, 427-434.

[S3] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

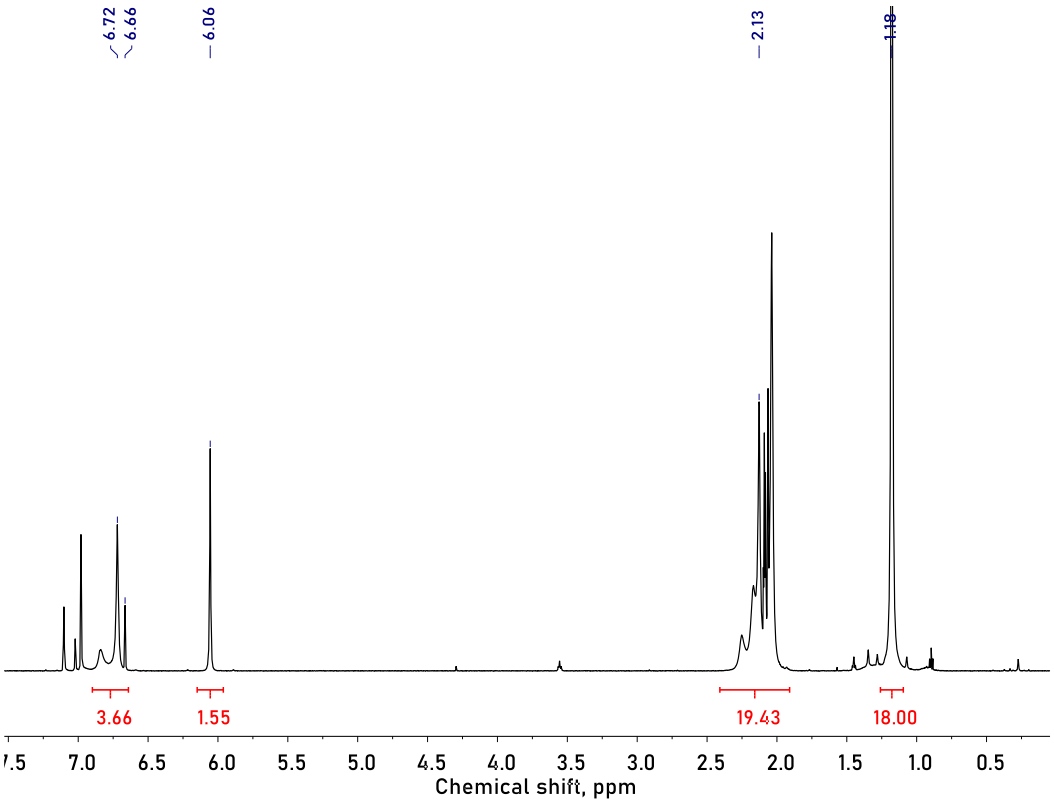

Figure S1. ^{1}H NMR spectrum of **1** in d$_8$-toluene solution (600.22 MHz).

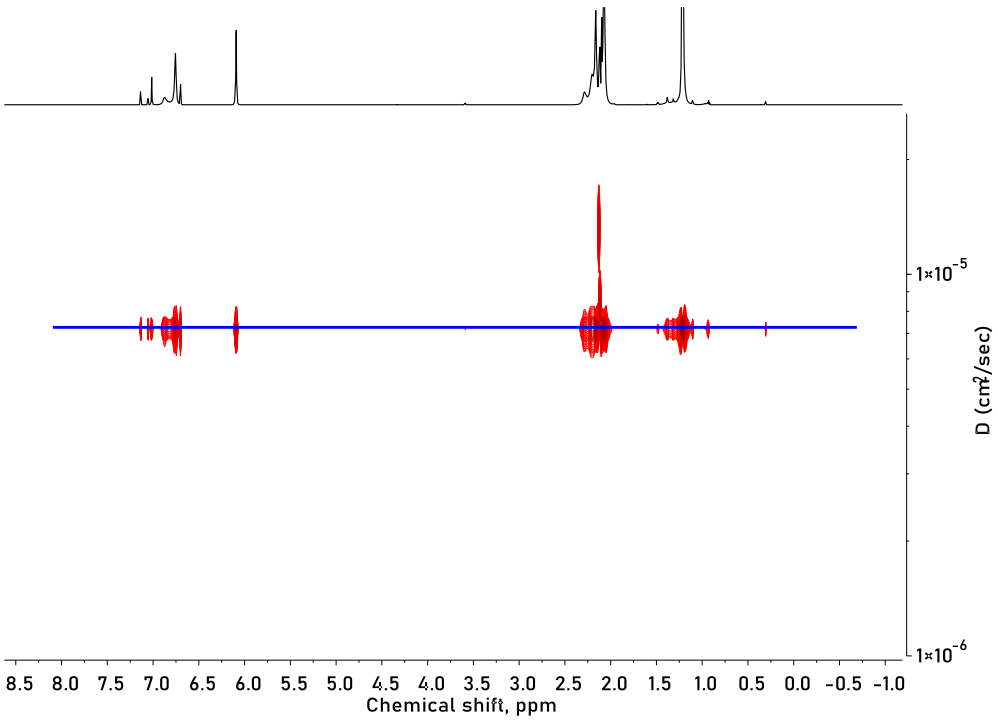

Figure S2. DOSY NMR spectrum of **1** in d$_8$-toluene solution (600.22 MHz). The blue horizontal line shows the signals with equal diffusion coefficient $7.2 \cdot 10^{-6}$ cm^{2}s^{-1}.

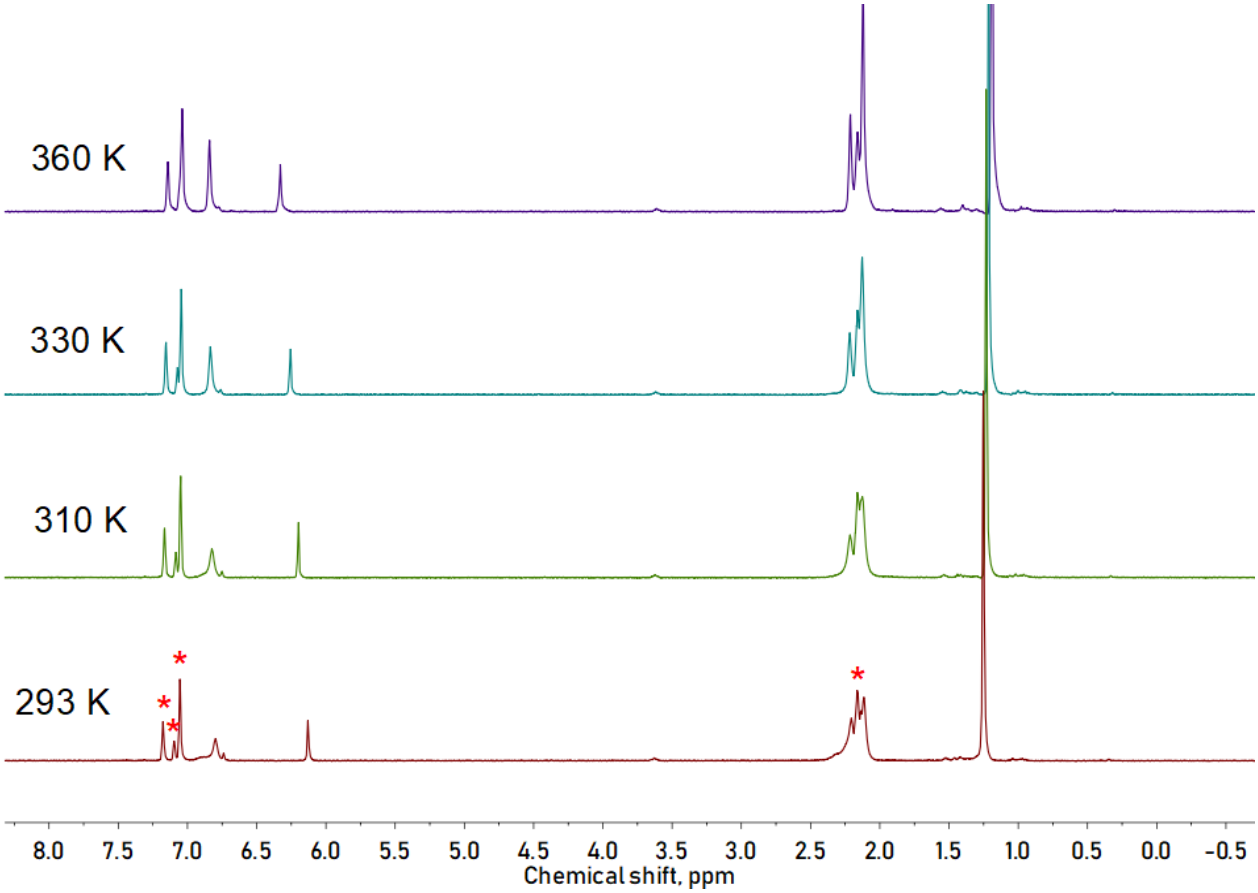

Figure S3. Variable temperature ^{1}H NMR spectra of **1** in d_8-toluene solution (300.15 MHz). The residual signals of tolene-d_8 are marked by red stars.

DFT calculations

The density functional theory (DFT) calculations were performed applying the Gaussian 09 program package[S4] with the use of UB3LYP functional[S5] and Def2TZVP

[S4] 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, T. Keith, 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, D. J. Fox, *Gaussian 09 (Revision E.01)*, Gaussian, Inc., Wallingford CT, 2013

[S5] Density-functional thermochemistry. III. The role of exact exchange /A.D. Becke // J. Chem. Phys. 1993. V. 98. P. 5648-5652

basis set[S6]. The stationary points on the potential energy surfaces were located by full geometry optimization with the calculation of the force constants matrix and checked for the stabilities of the DFT wave function. The solvent effects were considered using the SMD continuum solvation model[S7] with hexane as solvent. Structural visualizations of molecular structures were produced with the program suite ChemCraft[S8].

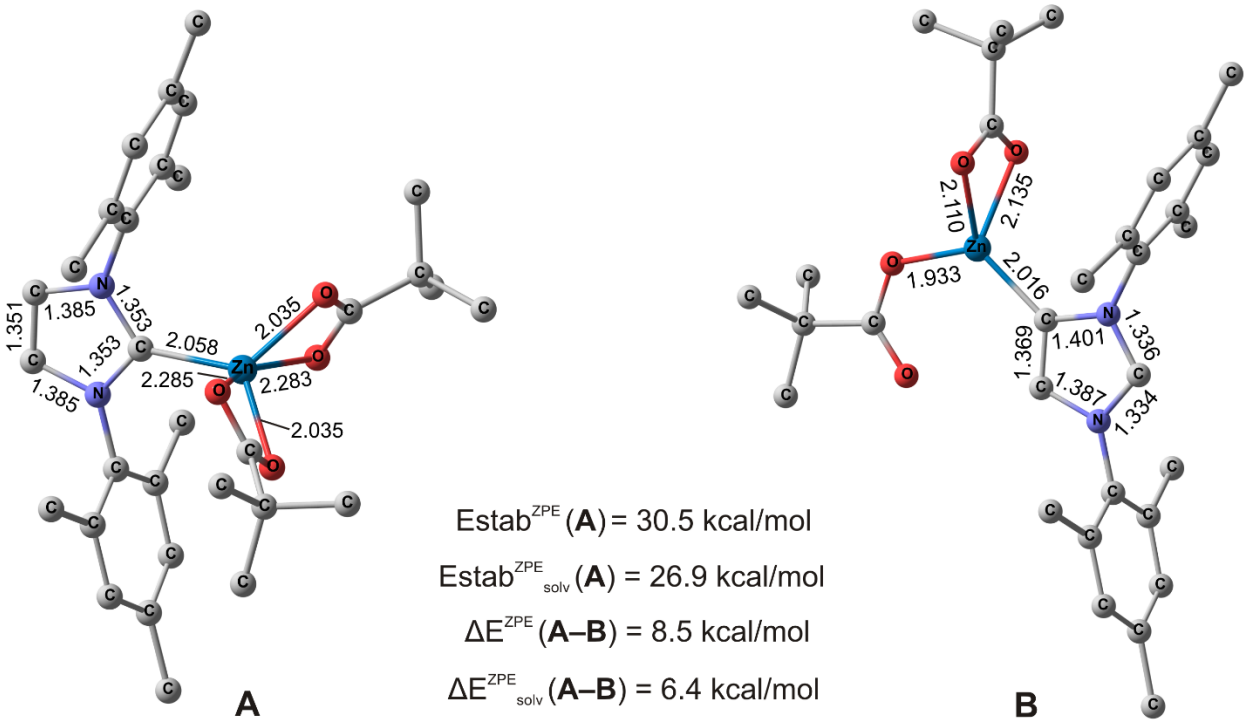

Figure S4. Optimized geometries and energy parameters of the isomers **A** and **B** of [Zn(O_2CCMe_3)$_2$(IMes)] complex calculated by DFT B3LYP/Def2TZVP method. Hydrogen atoms are omitted for clarity, bond lengths are given in Å.

[S6] Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy / F. Weigend, R. Ahlrichs // Phys. Chem. Chem. Phys. 2005. V. 7. P. 3297-3305; F. Accurate Coulomb-fitting basis sets for H to Rn / F. Weigend // Phys. Chem. Chem. Phys. 2006. V. 8. P. 1057-1065

[S7] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.* 2009, 113, 6378−6396.

[S8] Chemcraft: http://www.chemcraftprog.com

Table S1. Total energies without (E), with (E^{ZPE}) taking into account for zero-point harmonic vibrations, total energies without (E_{solv}) and with (E^{ZPE}_{solv}) taking into account for the nonspecific solvation (SMD, solvent – hexane) calculated by the DFT B3LYP/Def2TZVP method.

Molecule	E	E^{ZPE}	E_{solv}	E^{ZPE}_{solv}
$Zn(O_2CCMe_3)_2$	-2472.657891	-2472.386942	-2472.669185	-2472.398621
IMes	-924.505686	-924.110335	-924.530992	-924.135975
$[Zn(O_2CCMe_3)_2(n\text{IMes})]$ (**A**)	-3397.214827	-3396.545902	-3397.246061	-3396.577394
$[Zn(O_2CCMe_3)_2(a\text{IMes})]$ (**B**)	-3397.200289	-3396.532315	-3397.235320	-3396.567133

Cartesian coordinates of the isomers A and B of $[Zn(Piv)_2(IMes)]$ complex calculated by DFT B3LYP/Def2TZVP method

A

30	0.002031000	0.617848000	0.001643000
8	-0.216453000	1.128956000	-2.214763000
8	-1.576518000	1.750136000	-0.605051000
8	0.220581000	1.112004000	2.220213000
8	1.580937000	1.745887000	0.615777000
7	-1.028092000	-2.265290000	0.298543000
7	1.026113000	-2.264852000	-0.316004000
6	-0.000324000	-1.440044000	-0.005830000
6	0.644870000	-3.592285000	-0.207679000
1	1.323064000	-4.400227000	-0.414739000
6	-0.649620000	-3.592564000	0.179039000
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6	2.351409000	-1.836377000	-0.694312000

6	2.624044000	-1.578146000	-2.040404000
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6	-3.535237000	2.378470000	-2.593951000
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6	-1.718536000	4.111043000	-2.464464000
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B

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