Jun-Hong Wang, Hong-Bo Tong*, Meng-Liang Wang and Hai-Yan Yuan

Crystal structure of bis(3,3-dimethyl-1-phenylbut-1-en-2-yl)(trimethylsilyl)amido- k^1N zinc(II), $Zn(C_{15}H_{24}NSi)_2$

<https://doi.org/10.1515/ncrs-2021-0057>

Received February 7, 2021; accepted February 26, 2021;
published online March 15, 2021

Abstract

$Zn(C_{15}H_{24}NSi)_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.828(3)$ Å, $b = 9.458(3)$ Å, $c = 10.786(3)$ Å, $\alpha = 74.609(4)^\circ$, $\beta = 73.915(4)^\circ$, $\gamma = 64.888(4)^\circ$, $V = 772.1(4)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0476$, $wR_{ref}(F^2) = 0.1225$, $T = 293$ K.

CCDC no.: 2065271

The molecular structure is shown in the figure ($' = -x, 2-y, 1-z$). Table 1 contains crystallographic data and Table 2

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.60 × 0.40 × 0.30 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.89 mm ⁻¹
Diffractometer, scan mode:	SMART, ϕ and ω
θ_{max} , completeness:	25.0°, 97 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	3179, 2659, 0.022
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I > 2\sigma(I)$, 2158
$N(param)_{refined}$:	166
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Zn	0.000000	1.000000	0.500000	0.0339 (2)
N	0.1660 (3)	0.9424 (3)	0.3550 (2)	0.0296 (5)
Si	0.27684 (10)	1.06528 (9)	0.28675 (8)	0.0334 (2)
C1	0.1988 (4)	0.7902 (3)	0.3315 (3)	0.0298 (6)
C2	0.2465 (4)	0.6594 (3)	0.4208 (3)	0.0356 (7)
H2	0.264847	0.566341	0.394734	0.043*
C3	0.2748 (4)	0.6390 (3)	0.5540 (3)	0.0347 (7)
C4	0.2409 (4)	0.5162 (4)	0.6472 (3)	0.0444 (8)
H4	0.203962	0.450956	0.622463	0.053*
C5	0.2608 (5)	0.4893 (4)	0.7747 (3)	0.0502 (9)
H5	0.235882	0.407553	0.834725	0.060*
C6	0.3174 (5)	0.5828 (4)	0.8139 (3)	0.0497 (9)
H6	0.329959	0.565499	0.900147	0.060*
C7	0.3547 (5)	0.7010 (4)	0.7240 (3)	0.0476 (8)
H7	0.394316	0.763611	0.749597	0.057*
C8	0.3348 (4)	0.7302 (4)	0.5952 (3)	0.0395 (7)
H8	0.361727	0.811312	0.535910	0.047*
C9	0.1602 (4)	0.7837 (3)	0.2024 (3)	0.0347 (7)
C10	0.1624 (5)	0.6221 (4)	0.1988 (3)	0.0495 (9)
H10A	0.081193	0.596215	0.271236	0.074*
H10B	0.274186	0.542724	0.204634	0.074*
H10C	0.133282	0.626000	0.118211	0.074*
C11	-0.0166 (4)	0.9079 (4)	0.1859 (3)	0.0511 (9)
H11A	-0.041458	0.904804	0.105717	0.077*
H11B	-0.019318	1.011123	0.183458	0.077*
H11C	-0.100091	0.885702	0.258270	0.077*
C12	0.2941 (4)	0.8167 (4)	0.0858 (3)	0.0419 (8)
H12A	0.265705	0.817405	0.005856	0.063*
H12B	0.404214	0.735475	0.094402	0.063*
H12C	0.296201	0.917840	0.084185	0.063*

*Corresponding author: Hong-Bo Tong, Institute of Applied Chemistry, Shanxi University, Wucheng Rd. 92#, Taiyuan, Shanxi Province, P. R. China, E-mail: tong@sxu.edu.cn. <https://orcid.org/0000-0001-9222-9563>

Jun-Hong Wang, Meng-Liang Wang and Hai-Yan Yuan, Institute of Applied Chemistry, Shanxi University, Wucheng Rd. 92#, Taiyuan, Shanxi Province, P. R. China. <https://orcid.org/0000-0002-9293-0525> (H.-Y. Yuan)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C13	0.2354 (5)	1.1830 (4)	0.4164 (3)	0.0457 (8)
H13A	0.115473	1.243516	0.437481	0.069*
H13B	0.295589	1.253399	0.384511	0.069*
H13C	0.273949	1.112222	0.493349	0.069*
C14	0.2062 (5)	1.2154 (4)	0.1408 (3)	0.0528 (9)
H14A	0.235205	1.162900	0.067720	0.079*
H14B	0.262029	1.288802	0.119801	0.079*
H14C	0.085110	1.271523	0.159965	0.079*
C15	0.5104 (4)	0.9464 (4)	0.2456 (4)	0.0494 (9)
H15A	0.551479	0.884554	0.324307	0.074*
H15B	0.569795	1.016588	0.204339	0.074*
H15C	0.529884	0.877254	0.186961	0.074*

contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All manipulations were carried out under argon using standard Schlenk techniques. The title complex was synthesized according to literature methods [6, 8, 9]. To a solution of trimethylsilylmethyltolulithium ($(\text{Me}_3\text{Si})\text{PhCH}_2\text{Li}$) (6 mmol) in diethyl ether (20 ml), *tert*-butyl nitrile (6 mmol) was added at *ca.* 273 K and the solution was stirred for 15 min and then kept stirring for 5 h at room temperature. To this solution, ZnCl_2 (3 mmol) was added at *ca.* 200 K and the suspension was stirred for 15 min and then for 5 h at room temperature. The solvent was removed under reduced pressure and then we used CH_2Cl_2 to extract the solid. The filtrate was concentrated under vacuum until colorless crystals of the title compound appeared.

Experimental details

All hydrogen atoms were added, using the standard procedures for riding atoms in the SHELX system.

Comment

Metal- η^3 -allyl complexes are well known and play an important role in many metal-mediated reactions [5]. Lappert and co-workers prepared various 1-azaallyl complexes including some main group element and transition metal [6–9]. Many years ago we have got a example of

η^3 -azaallyl cobalt complex [10]. As part of a subsequent investigation, we have prepared the title complex, and present its structure here (the Figure). The title compound shows not enlarged η^3 -coordination mode but a coordination of the N atoms to Zn. Thus it is a comparing object to study the transformation between η^3 -carbon coordination to a coordination of the amido nitrogen. The centrosymmetric title complex contains two amido ligands bound to the Zn, with $\text{Zn}\cdots\text{N}$ bond length of 1.842(2) Å. The two ligands form a perfect straight line (N/Zn/N') due to symmetry (the Figure).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Key Research and Development Projects in Shanxi Province No. 201803D121040.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. SAINT (version 6.02), SADABS (version 2.03); Bruker AXS Inc.: Madison, 2002.
2. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
5. Blystone S. L. Synthetic applications of enantioselective organotransition-metal-mediated reactions. *Chem. Rev.* 1989, *89*, 1663–1679.
6. Avent A. G., Hitchcock P. B., Lappert M. F., Sablong R., Severn J. R. Synthesis, structures, characterization, dynamic behavior, and reactions of novel late transition metal(II) 1-azaallyls. *Organometallics* 2004, *23*, 2591–2600.
7. Caro C. F., Lappert M. F., Merle P. G. Review of metal 1-azaallyl complexes. *Coord. Chem. Rev.* 2001, *219*, 605–663.
8. Hitchcock P. B., Lappert M. F., Layh M., Liu D.-S., Sablong R., Shun J. Reactions of LiCHR_2 and related lithium alkyls with α -H free nitriles and the crystal structures of eleven representative lithium 1,3-diazaallyls, 1-azaallyls and β -diketiminates. *J. Chem. Soc. Dalton Trans.* 2000, 2301–2312; <https://doi.org/10.1039/b002376k>.
9. Hitchcock P. B., Lappert M. F., Wei X.-H. Synthesis and structures of crystalline lithium 1-azaallyls and a 1,3-diazaallyl derived from $\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_{3-n}(\text{OMe})_n)\}$ ($n=1$ or 2) and $\text{Li}\{\text{CH}(\text{SiMe}_2\text{OMe})_2\}$ and RCN ($\text{R}=\text{Bu}$, Ph , 2,5- $\text{Me}_2\text{C}_6\text{H}_3$, or Ad). *J. Organomet. Chem.* 2003, *683*, 83–91.
10. Yuan H.-Y., Tong H.-B., Wei X.-H. Bis(η^3 -2-*tert*-butyl-3-phenyl-1-trimethylsilyl-1-azaallyl)cobalt(II). *Acta Crystallogr.* 2007, *E63*, m1325–m1327.