

X-Ray Structure Determination of [1,4-di (4- methylphenyl) 1,4-Diazabutadiene] zinc (II) chloride

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Abstract

Compound [1,4-di (4-methylphenyl) 1,4-Diazabutadiene] Zinc (II) Chloride (**1**) was obtained by reaction of zinc chloride with N, N'-bis (p-tolyl) ethylendiimine. X-ray crystallography shows the molecule to possess distorted tetrahedral geometry and together with NMR data it suggests to be a unique example of **1** complex. The crystal are monoclinic, spacegroup P2_{1/n}, with a =11.4859(1), b=7.5185(5), c=20.2110 (25)Å, β=106.23(°), V=1675 (3), D_c=1.474 g cm⁻³ and Z=4.1525 unique observed reflections [F_o>3σ (F_o)] have been used to solve and refine the structure down to R = 0.0439

Keywords: [1,4-di (4- methylphenyl) 1,4-Diazabutadiene] zinc (II) chloride, N,N'-bis (p-tolyl) ethylendiimine, zinc chloride complexes.

Introduction

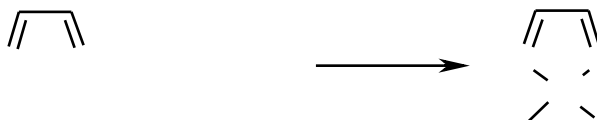
Diazabutadienes (RN=CH-CH=NR=RDAB) have been shown to stabilize both low valent and divalent homoleptic and heteroleptic compounds of transition metals (Wissing *et al.*, 1994; Kaupp *et al.*, 1991; Rijnberg *et al.*, 1995; Geoffrey *et al.*, 1990 & 1986; Tom Dieck *et al.*, 1987&1980; Sinnema *et al.*, 1990). Investigations are generally performed with bulky alkyl-R groups, but very few examples are shown with aryl-R groups, which generally tend to reduce the nitrogen σ and π-donating ability to metal atoms and destabilize low valent dab complexes. We therefore set out to prepare

a new aryl diazadiene complex of zinc and to explore further the possibility that this ligand system might stabilize low valent complexes of zinc. In this study we used a new approach for synthesis [1,4-di (4-methylphenyl) 1,4-Diazabutadiene] zinc (II) chloride (Hsieh, 1976). In addition the X-ray structure is also presented.

Result and Discussion

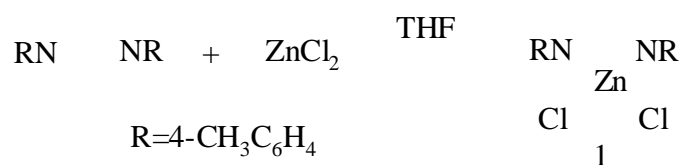
Reaction of N,N'-bis (p-tolyl) ethylenediimine (Kliegman, 1970) and zinc chloride in THF gives a yellow reaction mixture. On work-up, air sensitive yellow crystals of [1,4-di (4-methylphenyl) 1,4-Diazabutadiene] zinc (II) chloride (**1**) are obtained in ca. 60% yield. The zinc (II) complex is soluble in a variety of solvents such as CH₂Cl₂ and benzene. The solvents have to be completely dry in order to avoid hydrolysis or decomposition and therefore reactions are carried out under atmosphere of nitrogen. Scheme 1 shows reaction pathway.

A complete uv-vis spectrum of **1** recorded in CH₂Cl₂ shows two strong absorptions due to π→π*, and n→σ* transitions 232 and 426nm, respectively. No absorption at 289nm were observed



Scheme 1

indicating the absence of n→π* transitions. In the IR spectrum of (**1**) a moderate C=N absorption is observed at 1591 cm⁻¹. Characteristics of the proton spectra are a singlet for imine protons at δ 8.4 ppm and two singlets at δ 2.48, 7.2 ppm for methyl groups and aromatic hydrogens, respectively. The data suggests a symmetric environment for aromatic and iminic groups. X-ray crystallographic analysis was used to establish the solid state structure of **1**. The crystal structure confirms the expected C_{2v} symmetry and shows that molecules lie on mirror planes with nitrogen and adjacent carbon atoms restricted to the planes (Fig. 1).



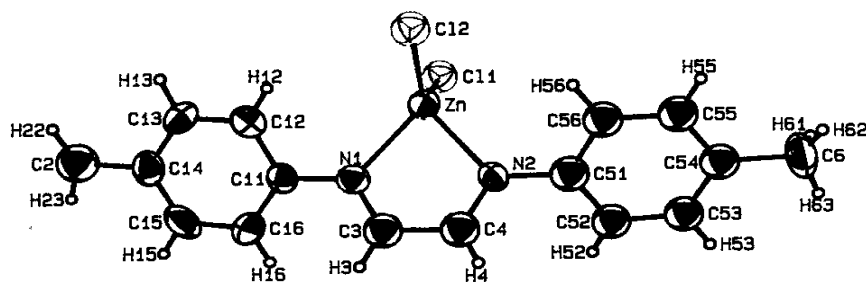


Figure 1 - Molecular projection of 1.

The molecule exhibits a distorted tetrahedral geometry. Average C=N and C-C bond lengths in dad ligand (1.27 and 1.47 Å respectively) are typical of those found with other transition metal analogues, such as [Ni (dab) (C₃H₄)] (Sinnema *et al.*, 1990), in which the corresponding bond lengths are 1.306 and 1.423 Å (Table 1, 2, 3). The observations showed that is condition reaction leads to the formation of a divalent zinc complex and no low valent zinc complex formed.

Table1: Fractional coordinates values with e.s.d's in parentheses.

Atom	X	Y	Z
Zn	0.81168(8)	0.2257(1)	0.62763(5)
Cl-1	0.8637(2)	0.2113(4)	0.5327(1)
Cl-2	0.7840(2)	-0.0260(3)	0.6778(1)
N1	0.6737(6)	0.4011(9)	0.6303(3)
N2	0.9087(5)	0.4053(9)	0.6996(3)
C2	0.1713(9)	0.2950(2)	0.4907(5)
C4	0.7146(7)	0.5330(1)	0.6691(4)
C3	0.8434(7)	0.5350(1)	0.7068(4)
C6	1.4028(8)	0.3250(2)	0.8588(5)
C11	0.5473(7)	0.3810(1)	0.5968(4)
C12	0.5152(7)	0.2710(1)	0.5401(4)
C13	0.3932(7)	0.2430(1)	0.5061(4)
C14	0.3048(7)	0.3240(1)	0.5274(5)
C15	0.3380(8)	0.4290(1)	0.5841(6)
C16	0.4591(7)	0.4630(1)	0.6188(5)
H3	0.867(5)	0.619(8)	0.732(3)
H4	0.671(5)	0.624(8)	0.672(3)
H12	0.567(5)	0.217(8)	0.524(3)
H13	0.379(6)	0.180(1)	0.465(4)
H15	0.288(5)	0.492(8)	0.597(3)
H16	0.478(5)	0.524(9)	0.655(3)
H21	0.137(6)	0.310(1)	0.522(4)
H22	0.168(6)	0.300(1)	0.446(3)
H23	0.160(1)	0.170(2)	0.478(5)

Table 2- Selected Bond Distances (Å) with e.s.d;s in parentheses.

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
Zn	Cl-1	2.168(3)	C4	H4	0.860(6)
Zn	Cl-2	2.213(3)	C3	H3	0.810(6)
Zn	N1	2.075(7)	C11	C12	1.380(1)
Zn	N2	2.069(6)	C11	C16	1.360(1)
N1	C3	1.270(1)	C12	C13	1.390(1)
N1	C11	1.428(9)	C12	H12	0.850(6)
N2	C4	1.260(1)	C13	C14	1.360(1)
N2	C51	1.430(9)	C13	H13	0.950(7)
C2	C14	1.520(1)	C14	C15	1.350(1)
C2	H21	0.840(8)	C15	C16	1.400(1)
C2	H22	0.900(7)	C15	H15	0.850(6)
C2	H23	1.00(1)	C16	H16	0.840(6)
C4	C3	1.460(1)			

Table 3: Selected Bond Angles (°) with e.s.d.'s in parentheses.

<u>Atom1</u>	<u>Atom2</u>	<u>Atom3</u>	<u>Angle</u>	<u>Atom1</u>	<u>Atom2</u>	<u>Atom3</u>	<u>Angle</u>
Cl-1	Zn	Cl 2	118.3(1)	N1	C3	C4	118.5(8)
Cl-1	Zn	N1	117.1(2)	N1	C3	C3	123.0(3)
Cl-1	Zn	N2	115.4(2)	C4	C3	C3	118.0(3)
Cl-2	Zn	N1	108.9(2)	N2	C4	C3	118.4(7)
Cl-2	Zn	N2	110.7(2)	N2	C4	H4	124.0(4)
N1	Zn	N2	80.30(2)	C3	C4	H4	117.0(4)
Zn	N1	C3	111.0(5)	N1	C11	C12	117.3(7)
Zn	N1	C11	127.0(5)	N1	C11	C16	123.1(7)
C3	N1	C11	121.9(7)	C12	C11	C16	119.6(7)

Experimental

General. Melting point was determined on an Electrothermal Model 9100. IR(Nujolumull) spectrum was taken on a Shimadzu model 4300 spectrometer. NMR spectrum was recorded on a Bruker 80 MHz spectrometer. MASS analysis of the product was conducted on a Shimadzu QP 1000 EX instruments. Elemental analysis were done with a C, H, N, O Rapid-Hereaus analyzer.

Synthesis of [1,4-di(4-methylphenyl) 1,4-Diazabutadiene] zinc(?)chloride (1)

To a stirred solution of N, N'-di (p-tolyl) ethylenediimine (Kliegman, 1970) (23.6 g, 0.1 mol) in dry THF (10 ml) was added over 20 min a solution of zinc chloride (13.6 g, 0.1 mol) in dry THF (50 ml) at 35°C. The solution was stirred at 35°C for further 2 hrs until yellow precipitates were formed. The precipitates were filtered and washed with cold acetonitrile. Recrystallization from acetonitrile gave yellow

pure crystal of **1** (21.4g, 60% yield), mp 241°C (dec.); ¹H-NMR (80 MHz, CDCl₃), δ : 2.48 (s, 6H), 7.2 (s, 8H), 8.43 (s, 2H). IR : C=N 1590 cm⁻¹. Satisfactory elemental analysis were obtained for **1** (found: C, 51.4 % ; H, 4.3% ; N, 7.4% ; Cl, 19.4% and Zn, 17.7% . Calculated: C, 51.6 % ; H, 4.3% ; N, 7.5% ; Cl, 19.1% and Zn, 17.4%).

X-Ray Structure Analysis of **1**

A yellow crystal with dimension 0.12 × 0.15 × 0.33 mm was used for data collection on a Enraf-Nonius CAD4 diffractometer with monochromated MoK α radiation. C₁₆H₁₆Cl₂N₂Zn, Fw =372.6 gmol⁻¹, monoclinic crystal in a P2_{1/n} space group, a=11.4859(1), b=7.5185 (5), c=20.2110 (25) Å, β =106.235 (8)°, V=1675.7 (3) Å³, Z= 4, D_c=1.474 gcm⁻³, F(000)=4741, T=298.6K. A total number of 4741 unique reflections were measured and 1525 independent reflections [Fo > 3 σ (Fo)] were used in the final refinement. There was no crystal decay and no absorption correction were applied. The structure was solved by a multiple solution procedure with the aid of the program Multan 11/82 and was refined using full matrix least squares. Seven reflections, which were strongly affected by extinction, were excluded from the final refinement. The non- hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations and their parameters were refined (International Tables For X-ray). The final discrepancy indices are R=0.0439 and W_R=0.0501. The final difference map had no peaks greater than ± 0.466 e Å⁻³.

Acknowledgements

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