

A Homologous Series of Homoleptic Zinc Bis(1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene) Complexes: $K_x[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]$, $Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2$, and $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2](OTf)_x$ ($x = 1, 2$)

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A homologous series of mono- and dicationic, neutral, and mono- and dianionic zinc diazabutadiene complexes, $K_x[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]$, $Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2$, and $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2](OTf)_x$ ($x = 1, 2$), have been prepared and isolated in pure form. The crystal structures of the mono- and dicationic as well as of the monoanionic complexes are reported. In this series, the formal charge on the *t*-BuNCHCHN-*t*-Bu ligands ranges from -2 to $+2$, and the way in which the molecular geometry of the ligands varies with the charge is discussed. $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2](OTf)_2$ reacts with methanol to give 1,3-di-*tert*-butylimidazolium triflate. Crystal data: dicationic **2** ($[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2](OTf)_2$, $C_{22}H_{40}F_6S_2N_4O_6Zn$), monoclinic, space group $C2/c$, with $a = 18.015(6)$ Å, $b = 9.257(6)$ Å, $c = 20.012(5)$ Å, $\beta = 109.63(3)^\circ$, and $Z = 4$; monocationic **3**·thf ($[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]OTf\cdot thf$, $C_{25}H_{48}F_3N_4O_3SZn$), orthorhombic, space group $P2_12_12_1$, with $a = 10.3077(6)$ Å, $b = 17.1974(6)$ Å, $c = 17.8241(13)$ Å, and $Z = 4$; monoanionic **5**·thf ($K(thf)_3[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]$, $C_{36}H_{72}KN_4O_3Zn$), triclinic, space group $P\bar{1}$, with $a = 10.8702(10)$ Å, $b = 11.5175(9)$ Å, $c = 18.2815(13)$ Å, $\alpha = 73.795(6)^\circ$, $\beta = 74.227(6)^\circ$, $\gamma = 75.736(7)^\circ$, and $Z = 2$; **7** (1,3-di-*tert*-butylimidazolium triflate, $C_{12}H_{21}F_3N_2O_3S$), orthorhombic, space group $Pbca$, with $a = 14.4086(8)$ Å, $b = 12.0293(8)$ Å, $c = 18.6985(12)$ Å, and $Z = 8$.

Introduction

The preparation and characterization of a number of neutral homoleptic main group metal bis(1,4-disubstituted 1,4-diaza-1,3-butadiene) complexes, $M(RNCHCHNR)_2$, have been reported. Such $M(RNCHCHNR)_2$ complexes have been studied by EPR or X-ray diffraction methods for the metals Li, Be, Mg, Ca, Sr, Zn, Al, and Ga.¹

On the basis of EPR measurements, it has been suggested that the zinc complex $Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2$ (**4**) exists at room temperature as a radical-cation/radical-anion pair, $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]^{+\bullet}[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]^{-\bullet}$.^{1a} Although a representative model for the radical-cationic $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]^{+\bullet}$ part of the latter complex was generated electrochemically in 1976 by von Zelewsky and co-workers,^{1d} attempts to synthesize it separately failed. Also, the homoleptic radical-

anionic zinc complex has not yet been synthesized. Comparable radical-anionic complexes containing aluminum with three chelating monoanionic 1,3-disubstituted triazenide ligands have been reported by Braddock-Wilking *et al.*² Our recent isolation of the 1:1 coordination complex $ZnMe(OTf)(t\text{-BuNCHCHN-}t\text{-Bu})_3$ ($OTf = SO_3CF_3$) and the heteroleptic (organodiamido)-zincate complexes $K[ZnR(t\text{-BuNCHCHN-}t\text{-Bu})]$ ($R = Me, CH_2Ph$)^{4,5} showed that the *t*-BuNCHCHN-*t*-Bu ligand is able to stabilize both electron-deficient and electron-rich zinc complexes. Therefore, we decided to investigate the independent synthesis of radical-monocationic $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]^{+\bullet}$ and radical-monoanionic $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]^{-\bullet}$, as parts of a homologous series of zinc bis(1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene) complexes. A comparison of the structural features of the $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]$ unit in the solid-state structures of these complexes offers a unique opportunity to study the effect of changes in the electronic charge of the $[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]$ unit on the nature of the *t*-BuNCHCHN-*t*-Bu ligands without complications due to changes in the coordination number of the central zinc atom. Moreover, the structural aspects of these relatively simple model systems may

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provide information on the biological redox behavior of zinc ions in the active site of macromolecular enzymatic systems.

Experimental Section

General Data. All experiments were carried out under a dry and oxygen-free nitrogen atmosphere, using standard techniques. Et₂O, thf, and pentane were dried and distilled from Na/benzophenone, and MeCN was dried and distilled from CaH₂. All standard chemicals were purchased from Aldrich and Acros. The starting materials ZnCl₂⁶ and 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene (*t*-BuNCHCHN-*t*-Bu)⁷ were prepared according to literature procedures. ¹H (200 MHz), ¹⁹F (188.2 MHz), and ¹³C (50.3 MHz) NMR spectra were recorded in CD₃CN or thf-*d*₈ at room temperature, using SiMe₄ (¹H, ¹³C) or CClF₃ (¹⁹F) as the external standard (0.00 ppm). EPR spectra were recorded in thf at room temperature. Melting points are uncorrected. Elemental analyses were obtained from Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. There have been some problems with the elemental analyses of complexes **2**, **3**, **5**, and **6**, because of the extreme air, and moisture sensitivity of these complexes. For **2** and **3**, the atomic ratios C:H:N are within acceptable limits, but the individual values are 3.5% low. For **5**, we have been unable to obtain reproducible elemental analyses, and for **6**, the value for hydrogen is too low. For **2**, **3**, and **5**, the X-ray data are presented, and for **3** and **5**, the ESR spectra are also presented. As extra evidence for **2** and **6**, we have included the ¹H, ¹³C, and ¹⁹F NMR spectra of **2** and the variable-temperature ¹H NMR spectra of **6** as Supporting Information.

Preparation of Zn(OTf)₂(*t*-BuNCHCHN-*t*-Bu) (1**).** To a stirred solution of HOTf (2.40 g, 15.89 mmol) in Et₂O (30 mL) at 195 K was added dropwise ZnEt₂ (8.0 mL of a 1.0 M solution in hexane; 8.0 mmol). The resulting suspension was allowed to warm to room temperature, after which a solution of *t*-BuNCHCHN-*t*-Bu (1.35 g, 8.02 mmol) in Et₂O (20 mL) was added. The suspension was stirred for 15 min before the solvents were evaporated. The resulting colorless solid was washed with pentane (2 × 50 mL) and dried *in vacuo*; yield 4.18 g (99%) of **1**. ¹H NMR (MeCN-*d*₃): δ 8.20 (s, 2 H, N=CH), 1.43 (s, 18 H, C(CH₃)₃). ¹³C NMR (MeCN-*d*₃): δ 157.5 (N=CH), 62.9 (C(CH₃)₃), 29.2 (C(CH₃)₃). ¹⁹F NMR (MeCN-*d*₃): δ -78.3 (OTf).

Preparation of [Zn(*t*-BuNCHCHN-*t*-Bu)₂](OTf)₂ (2**).** To a stirred solution of HOTf (4.32 g, 28.79 mmol) in Et₂O (30 mL) at 195 K was added dropwise ZnEt₂ (14.40 mL of a 1.0 M solution in hexane; 14.40 mmol). The resulting suspension was allowed to warm to room temperature, after which a solution of *t*-BuNCHCHN-*t*-Bu (4.84 g, 28.78 mmol) in Et₂O (20 mL) was added. The suspension was stirred for 15 min before the solvents were evaporated. The resulting colorless solid was washed with pentane (2 × 50 mL) and dried *in vacuo*; yield 9.22 g (92%). Crystallization from MeCN at 243 K gave colorless crystals of **2** suitable for an X-ray structure determination. ¹H NMR (MeCN-*d*₃): δ 8.65 (s, 2 H, N=CH), 1.43 (s, 18 H, C(CH₃)₃). ¹³C NMR (MeCN-*d*₃): δ 165.6 (N=CH), 62.7 (C(CH₃)₃), 30.7 (C(CH₃)₃). ¹⁹F NMR (CD₃CN): δ -78.3 (OSO₂CF₃). Anal. Calcd for C₂₂H₄₀F₆N₄O₆S₂Zn: C, 37.74; H, 5.76; N, 8.00. Found: C, 36.40; H, 5.54; N, 7.56. Mp: >180 °C.

Preparation of [Zn(*t*-BuNCHCHN-*t*-Bu)₂](OTf) (3**).** To a stirred suspension of **2** (1.12 g, 1.60 mmol) in Et₂O (20 mL) was added a solution of **4** (0.62 g, 1.55 mmol) in Et₂O (20 mL) at room temperature. After the mixture was stirred for 68 h, the mother liquor was decanted. The resulting yellow-green solid was washed with Et₂O (2 × 30 mL) and dried *in vacuo*; yield 1.60 g (94%). Crystallization from thf at room temperature gave brown crystals of **3**·thf suitable for an X-ray structure determination. Anal. Calcd for C₂₁H₄₀F₃N₄O₃SZn: C, 45.78; H, 7.32; N, 10.17. Found: C, 44.31; H, 7.16; N, 9.70. Mp: >180 °C.

Preparation of Zn(*t*-BuNCHCHN-*t*-Bu)₂ (4**).** A modification of a procedure published by Raston was used.^{1a} It appeared that, for practical purposes, the use of isolated Li(*t*-BuNCHCHN-*t*-Bu)₂ is not necessary. Also, the ZnCl₂(*t*-BuNCHCHN-*t*-Bu) used as the other reagent does not have to be isolated.

An excess of lithium metal (2.2–2.5 equiv) was added to a stirred solution of *t*-BuNCHCHN-*t*-Bu (2.0 g, 11.9 mmol) in Et₂O (50 mL) at room temperature. After the mixture was stirred for 17 h, the remaining lithium metal was removed by filtration and the resulting deep red solution was added to a solution of ZnCl₂(*t*-BuNCHCHN-*t*-Bu), *in situ* prepared from *t*-BuNCHCHN-*t*-Bu (2.0 g, 11.9 mmol) and ZnCl₂ (19.2 mL of a 0.62 M solution in Et₂O; 11.9 mmol), in Et₂O (30 mL) at 195 K. The resulting green suspension was stirred for 2–17 h at room temperature. After the mother liquor had been decanted, the residue was extracted with Et₂O (2 × 30 mL). Evaporation of the combined organic fractions *in vacuo* gave **4** as a green-brown solid; yield 3.73 g (78%). Anal. Calcd for C₂₀H₄₀N₄Zn: C, 59.77; H, 10.03; N, 13.94. Found: C, 59.88; H, 9.92; N, 13.84. Mp: 154 °C.

Preparation of K(thf)₃[Zn(*t*-BuNCHCHN-*t*-Bu)₂] (5**).** To a stirred solution of **4** (0.14 g, 0.34 mmol) in thf (30 mL) at room temperature was added exactly 1 equiv of **6** (0.20 g, 0.34 mmol) in thf (30 mL). After the mixture was stirred for 12 h, the solvent was evaporated. The resulting yellow-green solid was washed with pentane (2 × 30 mL) and dried *in vacuo*; yield 0.39 g (79%). Crystallization from Et₂O/thf at 243 K gave green crystals of **5**·thf suitable for an X-ray structure determination. Mp: 118 °C dec.

Preparation of K₂(thf)₂[Zn(*t*-BuNCHCHN-*t*-Bu)₂] (6**).** To a stirred solution of **4** (0.45 g, 1.12 mmol) in thf (30 mL) was added a more than 2-fold excess of potassium metal. After the mixture was stirred for 17 h at room temperature, the remaining potassium metal was removed. Evaporation of the solvent *in vacuo* gave a yellow solid; yield 0.57 g (87%). ¹H NMR (thf-*d*₈, 204 K): δ 5.21 (br s, 4 H, NCH=), 3.59 (br s, 8 H, thf), 1.76 (br s, 8 H, thf), 1.09 (br s, 18 H, C(CH₃)₃). ¹³C NMR (thf-*d*₈, 204 K): δ 114.2 (br, NCH=), 68.3 (thf), 52.3 (C(CH₃)₃), 33.6 (C(CH₃)₃), 26.3 (thf). Anal. Calcd for C₂₈H₅₆K₂N₄O₂Zn: C, 53.86; H, 9.04; N, 8.97. Found: C, 53.75; H, 8.22; N, 9.10. Mp: 111 °C (dec.).

Preparation of 1,3-Di-*tert*-butylimidazolium Trifluoromethanesulfonate (7**).** **Method A.** To a stirred suspension of paraformaldehyde (0.30 g, 9.99 mmol) in MeCN (25 mL) was added a solution of **1**, *in situ* prepared from Zn(OTf)₂ (3.69 g, 10.15 mmol) and *t*-BuNCHCHN-*t*-Bu (1.70 g, 10.10 mmol) in MeCN (25 mL), at room temperature. After 3 h of stirring, the almost clear reaction mixture was filtered. The volume of the reaction mixture was reduced *in vacuo* to 20 mL, and the concentrate was cooled to 243 K to afford colorless crystals of **7**; yield 1.50 g (45% with respect to *t*-BuNCHCHN-*t*-Bu).

Method B. The reaction of paraformaldehyde (0.30 g, 9.99 mmol) and **2**, *in situ* prepared from Zn(OTf)₂ (1.78 g, 4.90 mmol) and *t*-BuNCHCHN-*t*-Bu (1.65 g, 9.81 mmol), in MeCN (25 mL) at room temperature gave 1.75 g (54% with respect to *t*-BuNCHCHN-*t*-Bu) of **7** after crystallization. Recrystallization from MeOH at 243 K gave colorless crystals of **7** suitable for an X-ray structure determination. ¹H NMR (MeOH-*d*₄): δ 9.00 (t, 1 H, NCHN), 7.93 (d, 2 H, NCHC), 1.77 (s, 18 H, C(CH₃)₃). ¹³C NMR (MeOH-*d*₄): δ 132.7 (NCHN), 121.2 (NCHCHN), 61.1 (C(CH₃)₃), 29.4 (C(CH₃)₃). Anal. Calcd for C₁₂H₂₁F₃N₃O₃S: C, 43.63; H, 6.41; N, 8.48. Found: C, 43.46; H, 6.34; N, 8.35. Mp: 164 °C.

X-ray Structure Determination and Refinement of **2, **3**·thf, and **5**·thf.** Crystal data and details of the structure determinations are given in Table 1.

Crystals of the three compounds were glued on glass fibers (inert-oil technique) and transferred to an Enraf-Nonius CAD-4T diffractometer (rotating anode, graphite-monochromated Mo Kα radiation) for data collection at 150 K. Unit cell parameters were determined from least-squares treatment of SET4 setting angles and were checked for the presence of higher lattice symmetry.⁸ All data were collected in the ω scan mode with θ_{max} = 25° (**2**) and 27.5° (**3**·thf and **5**·thf). Data were corrected for Lp effects and for the observed linear decay of the intensity control reflections; redundant data were merged into unique data sets (2750 with R_{int} = 0.088 for **2**, 7232 with R_{int} = 0.040 for **3**·thf, and 9474 with R_{int} = 0.0342 for **5**·thf). No corrections for absorption or extinction were applied. The structures were solved with

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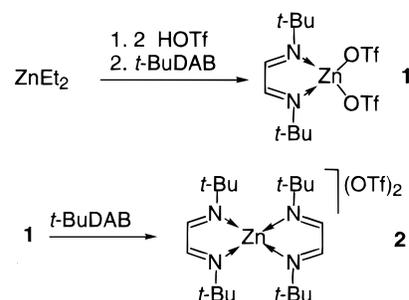
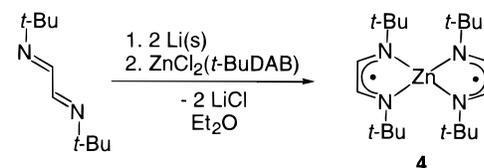
Table 1. Crystallographic Data and Details of the Structure Determination for **2**, **3**·thf, and **5**·thf

	2	3 ·thf	5 ·thf
formula	C ₂₂ H ₄₀ F ₆ S ₂ N ₄ O ₆ Zn	C ₂₅ H ₄₈ F ₃ N ₄ O ₃ SZn	C ₃₆ H ₇₂ KN ₄ O ₃ Zn
fw	700.09	623.13	729.48
crystal system	monoclinic	orthorhombic	triclinic
space group	C2/c (No. 15)	P2 ₁ 2 ₁ 2 ₁ (No. 19)	P1̄ (No. 2)
a, Å	18.015(6)	10.3077(6)	10.8702(10)
b, Å	9.257(6)	17.1974(6)	11.5175(9)
c, Å	20.012(5)	17.8241(13)	18.2815(13)
α, deg	90	90	73.795(6)
β, deg	109.63(3)	90	74.227(6)
γ, deg	90	90	75.736(7)
V, Å ³	3143(2)	3159.6(3)	2078.8(3)
Z	4	4	2
ρ _{calc} , g·cm ⁻³	1.479	1.310	1.165
μ(Mo Kα), cm ⁻¹	10.2	9.0	7.3
T, °C	-123	-123	-123
radiation λ, Å	0.710 73	0.710 73	0.710 73
R1, ^a wR2, ^b S	0.0680, 0.1783, 1.013	0.0483, 0.1063, 1.040	0.0586, 0.1395, 1.022

$${}^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

Patterson methods (DIRDIF96⁹ for **2** and **3**·thf and SHELXS86¹⁰ for **5**·thf) followed by subsequent difference Fourier syntheses. Refinement on F^2 using all unique reflections was carried out by full-matrix least-squares techniques. The *tert*-butyl groups of **2** are disordered around the N–C bond in a 0.530(9):0.470(9) ratio; the thf solvate molecule in **5**·thf shows 0.54(3):0.46(3) disorder as well. The unit cell of **2** contains two cavities of 503 Å³ at *x*, *y*, 0 and *x*, *y*, 0.5, each containing four severely disordered CF₃SO₃ anions. These trifluoromethanesulfonate ions could not be located from difference Fourier maps unambiguously and were taken into account in the structure factor and refinement calculations by Fourier transformation of the diffuse electron density in the cavity (BYPASS procedure¹¹ as implemented in PLATON¹⁴). A total of 289 electrons were recovered from the difference map per cavity, which is close to the number 296 to be expected for four CF₃SO₃ anions. The hydrogen atoms of the three complexes were introduced in calculated positions and included in the refinement riding on their carrier atoms with isotropic thermal parameters related to the U_{eq} of the carrier atoms. All non-hydrogen atoms (with the exception of the disordered atoms in **5**·thf) were refined with anisotropic thermal parameters. Neutral-atom scattering factors and anomalous dispersion factors were taken from ref 12. All calculations were performed with SHELXL96¹³ and the PLATON package¹⁴ (geometrical calculations and illustrations) on a DEC-5000 cluster.

X-ray Structure Determination and Refinement of 7. Crystal data for **7**: C₁₂H₂₁F₃N₂O₃S, $M_r = 330.37$, colorless block-shaped crystal (0.10 × 0.20 × 0.25 mm), orthorhombic, space group *Pbca*, with $a = 14.4086(8)$ Å, $b = 12.0293(8)$ Å, $c = 18.6985(12)$ Å, $V = 3240.9(3)$ Å³, $Z = 8$, $\rho_{calc} = 1.354$ g cm⁻³, $F(000) = 1392$, $\mu(\text{Mo K}\alpha) = 2.4$ cm⁻¹; 5718 reflections ($1.09 < \theta < 25.00^\circ$; ω scan; $T = -123$ °C) measured on an Enraf-Nonius CAD-4T diffractometer (rotating anode, graphite-monochromated Mo Kα radiation ($\lambda = 0.710 73$ Å)). Data were corrected for Lp effects and for linear decay (0.1%) of the intensity control reflections and merged into a data set of 2859 unique reflections ($R_{int} = 0.0996$). No corrections for absorption or extinction were applied. The structure was solved with direct methods (SHELXS96) and difference Fourier techniques. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms were refined on F^2 (SHELXL96)¹³ using all 2859

Scheme 1**Scheme 2**

unique reflections, with anisotropic thermal parameters. Convergence was reached at $R1 = 0.0557$ for 1432 reflections with $I > 2.0\sigma(I)$ and 205 parameters; $wR2 = 0.1082$, $S = 0.979$ for all 2859 reflections; $w = 1/[\sigma^2(F_o^2) + (0.0248P)^2]$. A final difference Fourier map showed residual densities between -0.31 and $+0.24$ e/Å³.

Results and Discussion

The reaction of Zn(OTf)₂, *in situ* prepared from ZnEt₂ and 2 equiv of HOTf, with *t*-BuNCHCHN-*t*-Bu in a 1:1 molar ratio in Et₂O gave the 1:1 coordination complex Zn(OTf)₂(*t*-BuNCHCHN-*t*-Bu) (**1**). Interestingly, unsolvated **1** was isolated quantitatively, even when its synthesis was performed in MeCN. This indicates significant interactions between the zinc cation and the OTf anions in **1**, although these anions are known for their low coordinating ability and lack of nucleophilic character. However, the reaction of **1** with a second equivalent of *t*-BuNCHCHN-*t*-Bu gave the new dicationic complex [Zn(*t*-BuNCHCHN-*t*-Bu)₂](OTf)₂ (**2**) quantitatively; see Scheme 1.

The neutral complex Zn(*t*-BuNCHCHN-*t*-Bu)₂ (**4**) was prepared by transmetalation of *in situ* prepared ZnCl₂(*t*-BuNCHCHN-*t*-Bu) with *in situ* generated Li₂(*t*-BuNCHCHN-*t*-Bu)(Et₂O)₄¹⁵ (see Scheme 2). This procedure for the preparation of **4**, which

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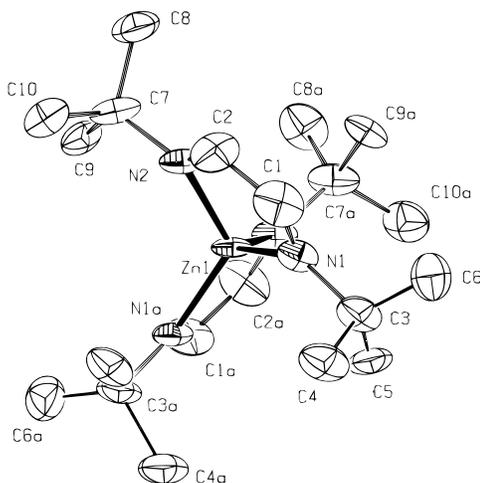


Figure 1. Thermal motion ellipsoid plot (ORTEP, 40% probability) of the major disorder component of **2** together with the adopted numbering scheme. The hydrogen atoms have been omitted for clarity.

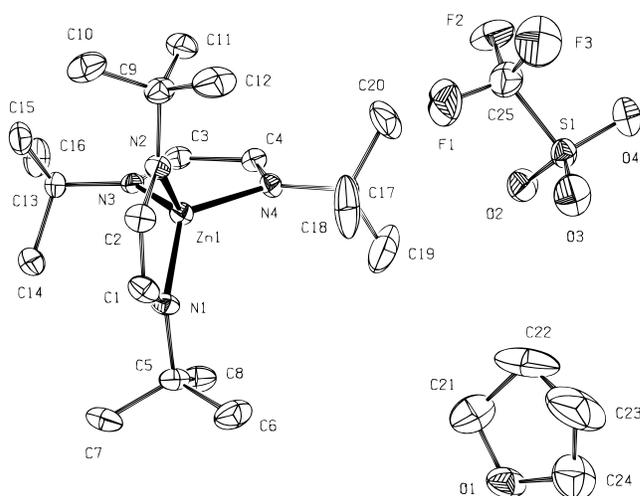


Figure 2. Thermal motion ellipsoid plot (ORTEP, 50% probability) of **3**·thf together with the adopted numbering scheme. The hydrogen atoms have been omitted for clarity.

is a simplification of the procedure published by Raston *et al.*,^{1a} made this valuable precursor for the preparation of a homologous series of monocationic and mono- and dianionic zinc bis-(1,4-disubstituted 1,4-diaza-1,3-butadiene) complexes easily available. Moreover, it opened the way to the preparation of unsymmetrically substituted $Zn(R^1NCR^2CR^2NR^1)(R^3NCR^4CR^4-NR^3)$ complexes.¹⁶

The reduction of **4** with an excess of potassium metal in thf at ambient temperature resulted in the formation of the dianionic zinc complex $K_2(thf)_2[Zn(t-BuNCHCHN-t-Bu)_2]$ (**6**). In thf solution, **6** has a deep red color, which changes to bright yellow upon evaporation of the solvent. Complex **6** was further used as a starting material for the preparation of its monoanionic analog (see Scheme 3).

The radical-monoanionic complex $K(thf)_3[Zn(t-BuNCHCHN-t-Bu)_2]$ (**5**) was prepared *via* the one-electron reduction of **4** with exactly 1 equiv of potassium metal. Alternatively, **5** was obtained quantitatively by the reaction of the biradical species **4** with the dianionic species **6** in a 1:1 molar ratio in Et_2O or thf. This second route, which might be described as a comproportionation reaction, is based on the reversible nature

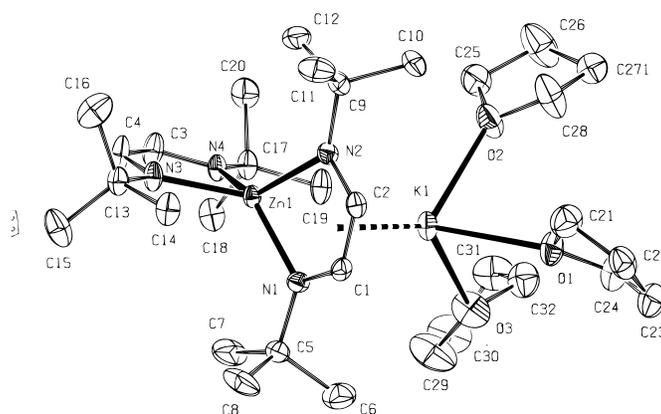


Figure 3. Thermal motion ellipsoid plot (ORTEP, 40% probability) of the major disorder component of **5**·thf together with the adopted numbering scheme. The hydrogen atoms and the disordered thf solvate molecule have been omitted for clarity.

Scheme 3

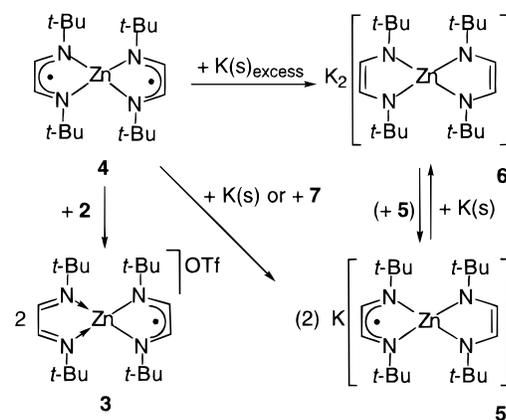


Table 2. Selected Bond Lengths and Bond Angles for **2**^a

Bond Lengths (Å)			
Zn(1)–N(1)	2.015(4)	N(1)–C(1)	1.253(8)
Zn(1)–N(2)	2.020(4)	N(2)–C(2)	1.241(7)
C(1)–C(2)	1.465(11)		
Bond Angles (deg)			
N(1)–Zn(1)–N(2)	83.17(16)	N(1)–C(1)–C(2)	119.5(6)
Zn(1)–N(1)–C(1)	108.9(4)	N(2)–C(2)–C(1)	118.6(6)
Zn(1)–N(2)–C(2)	109.7(4)		

^a The estimated standard deviations of the last significant digits are shown in parentheses.

of the redox system involving **4**, **5**, and **6**. In analogy, the one-electron-oxidation reaction of **4** with a stoichiometric amount of **2** in Et_2O resulted in the formation of the new radical-monocationic zinc complex $[Zn(t-BuNCHCHN-t-Bu)_2]Otf$ (**3**). Both yellow-green complexes **3** and **5** are only soluble in thf. Up to now, complexes **3** and **5** had only been detected by EPR spectroscopy in solution.^{1a,d}

Solid-State Structures of 2, 3, and 5. The structural features of the various species, which all have the $[Zn(t-BuNCHCHN-t-Bu)_2]$ unit in common but differ in the number of electrons, were studied in the solid state in order to establish the effect of the formal oxidation states of these complexes on the ligands and their interactions with the zinc atom. X-ray diffraction studies were carried out on $[Zn(t-BuNCHCHN-t-Bu)_2](Otf)_2$ (**2**), $[Zn(t-BuNCHCHN-t-Bu)_2]Otf$ (**3**), and $K(thf)_3[Zn(t-BuNCHCHN-t-Bu)_2]$ (**5**). Unfortunately, up to now attempts to obtain suitable crystals of $K_2(thf)_2[Zn(t-BuNCHCHN-t-Bu)_2]$ (**6**) failed. Thermal motion ellipsoid plots of the molecular

(16) Richter, B.; Rijnberg, E.; Veldman, N.; Spek, A. L.; van Koten, G.; Thiele, K.-H. To be published.

Table 3. Selected Bond Lengths and Bond Angles for **3**·thf^a

Bond Lengths (Å)			
Zn(1)–N(1)	1.973(3)	Zn(1)–N(3)	2.063(3)
Zn(1)–N(2)	1.975(2)	Zn(1)–N(4)	2.051(2)
N(1)–C(1)	1.326(5)	N(3)–C(3)	1.272(4)
N(2)–C(2)	1.323(4)	N(4)–C(4)	1.270(4)
C(1)–C(2)	1.406(6)	C(3)–C(4)	1.474(5)
Bond Angles (deg)			
N(1)–Zn(1)–N(2)	86.41(2)	N(3)–Zn(1)–N(4)	81.57(10)
Zn(1)–N(1)–C(1)	107.4(2)	Zn(1)–N(3)–C(3)	110.2(2)
Zn(1)–N(2)–C(2)	107.4(2)	Zn(1)–N(4)–C(4)	110.9(2)
N(1)–C(1)–C(2)	119.3(3)	N(3)–C(3)–C(4)	118.7(3)
N(2)–C(2)–C(1)	119.3(3)	N(4)–C(4)–C(3)	118.3(3)

^a The estimated standard deviations of the last significant digits are shown in parentheses.

Table 4. Selected Bond Lengths and Bond Angles for **5**·thf^a

Bond Lengths (Å)			
Zn(1)–N(1)	1.979(3)	Zn(1)–N(3)	2.079(3)
Zn(1)–N(2)	1.984(2)	Zn(1)–N(4)	2.043(3)
N(1)–C(1)	1.399(4)	N(3)–C(4)	1.317(5)
N(2)–C(2)	1.391(5)	N(4)–C(3)	1.322(5)
C(1)–C(2)	1.355(5)	C(3)–C(4)	1.398(5)
K(1)–N(1)	2.990(3)	K(1)–N(2)	2.962(4)
K(1)–C(1)	2.894(4)	K(1)–C(2)	2.876(4)
Bond Angles (deg)			
N(1)–Zn(1)–N(2)	85.67(12)	N(3)–Zn(1)–N(4)	82.16(12)
Zn(1)–N(1)–C(1)	105.8(2)	Zn(1)–N(3)–C(4)	108.9(3)
Zn(1)–N(2)–C(2)	105.7(2)	Zn(1)–N(4)–C(3)	109.3(2)
C(1)–C(2)–N(2)	118.9(3)	C(3)–C(4)–N(3)	119.2(4)
C(2)–C(1)–N(1)	118.4(3)	C(4)–C(3)–N(4)	120.3(3)

^a The estimated standard deviations of the last significant digits are shown in parentheses.

structures together with the adopted numbering schemes are shown in Figures 1–3. Selected bond lengths and bond angles are collected in Tables 2–4. Crystallization of **3** and **5** gave crystals that turned out to be **3**·thf and **5**·thf, respectively.

Complexes **2**–**5** all contain a four-coordinate zinc center which is bonded to four nitrogen atoms. The zinc atoms have a distorted tetrahedral geometry with rather acute bite angles of the two chelate bonded *t*-BuNCHCHN-*t*-Bu ligands (81.57–86.41°).

The [Zn(*t*-BuNCHCHN-*t*-Bu)₂] units in di- and monocationic **2** and **3**·thf, respectively, are completely separated from the monoanionic OTf anions. The two *t*-BuNCHCHN-*t*-Bu ligands in **2** are equivalent and symmetry related. The N–C and C–C bond lengths of 1.25(1) Å (mean) and 1.465(11) Å, respectively, are comparable to those found in the neutral complexes [ZnMe(OTf)(*t*-BuNCHCHN-*t*-Bu)] and [ZnMe₂(*t*-BuNCHCHN-*t*-Bu)].^{3,16} However, the Zn–N distances of 2.02(1) Å (mean) in dicationic **2** are significantly shorter than those found in the latter complexes. The bond lengths and angles of **2** correspond with the formal description of [Zn(*t*-BuNCHCHN-*t*-Bu)₂] as a dicationic unit.

In contrast, in **3**·thf, two geometrically distinct *t*-BuNCHCHN-*t*-Bu ligand systems are present. The differences in the Zn–N, N–C, and C–C bond lengths of both chelate rings in **3**·thf suggest that one ligand has a somewhat larger negative charge than the other. Accordingly, **3**·thf can be seen as a species having one radical-anionic *t*-BuNCHCHN-*t*-Bu ligand¹⁷ in addition to a neutral *t*-BuNCHCHN-*t*-Bu ligand, so that both are σ, σ' -*N, N'*-bonded to the zinc atom *via* the lone pair on the

Table 5. Comparison of Selected Averaged Bond Lengths (Å) of **2**, **3**·thf, **4**,^a and **5**·thf^b

	2	3 ·thf	4 ^a	5 ·thf
<i>n</i> ^c	+2	+1	0	–1
Zn–N _A ^d	2.02(1)	1.97(1)	2.013(4)	1.98(1)
N _A –C _A	1.25(1)	1.32(1)	1.339(6)	1.39(1)
C _A –C _A	1.465(11)	1.406(6)	1.378(7)	1.355(5)
Zn–N _B ^e	2.02(1)	2.06(1)	1.999(4)	2.06(1)
N _B –C _B	1.25(1)	1.27(1)	1.321(6)	1.32(1)
C _B –C _B	1.465(11)	1.474(5)	1.400(8)	1.398(5)

^a See ref 1a. ^b The estimated standard deviations of the last significant digits are shown in parentheses. ^c Formal charge on the [Zn(*t*-BuNCHCHN-*t*-Bu)₂] unit. ^d The labels A belong to the most reduced chelate ring. ^e The labels B belong to the most oxidized chelate ring.

nitrogen atoms. The fact that the monocationic [Zn(*t*-BuNCHCHN-*t*-Bu)₂]⁺ moiety is isoelectronic with the neutral lithium analog, Li(*t*-BuNCHCHN-*t*-Bu)₂,^{1a} is reflected in the identical trends observed for the M–N, N–C, and C–C bond distances in both chelate rings. The significantly shorter Zn–N bond distances in **3**·thf in comparison with those in the lithium analog, are due to the formal +1 charge of the [Zn(*t*-BuNCHCHN-*t*-Bu)₂] moiety.

The molecular structure of **5**·thf shows a unique associated aggregate consisting of a potassium cation and a [Zn(*t*-BuNCHCHN-*t*-Bu)₂] monoanion. From the differences between the Zn–N, N–C, and C–C bond distances in both chelate rings, it appears that the [Zn(*t*-BuNCHCHN-*t*-Bu)₂] unit in **5**·thf contains two geometrically distinct *t*-BuNCHCHN-*t*-Bu ligands. These distances are indicative of the presence of a radical-anionic ligand and a dianionic enediamide ligand, both σ, σ' -*N, N'*-bonded. The significantly longer Zn–N bond distances in the radical-anionic ligand in **5**·thf compared to those in neutral Zn(*t*-BuNCHCHN-*t*-Bu)₂ (**4**) are in agreement with a formal –1 charge of the former. The N–C and C–C bond distances of the dianionic ligand in **5**·thf are comparable to those found in the two-electron-donating ZnNCCN monoanion in polymeric {K(thf)[ZnMe(*t*-BuNCHCHN-*t*-Bu)]_n}^{4,5}. The [K(thf)₃]⁺ cation in **5**·thf is coordinated to the π electrons of the dianionic *t*-BuNCHCHN-*t*-Bu ligand with K–N bond distances of 2.93 Å (mean) and K–C bond distances of 2.88 Å (mean) between the potassium cation and the [Zn(*t*-BuNCHCHN-*t*-Bu)₂] unit. These distances are significantly shorter than those found in {K(thf)[ZnMe(*t*-BuNCHCHN-*t*-Bu)]_n. The interaction with three molecules of thf completes the coordination sphere around potassium. The Zn···K distance is 3.5660(10) Å, longer than the sum of the individual covalent radii of zinc and potassium (3.28 Å).

The ligand-centered nature of the unpaired electron in the series **2**–**5** is apparent from the comparison of the N–Zn–N angles and the Zn–N, N–C, and C–C bond distances, as summarized in Table 5. The “stepwise” addition of each single-electron in this series is accompanied by structural changes in the *t*-BuNCHCHN-*t*-Bu ligands, such as lengthening of the N–C and shortening of the C–C bond lengths. These distortions are to be expected from a population of the *t*-BuNCHCHN-*t*-Bu π^* orbitals upon the addition of electrons (*i.e.*, reduction), since these orbitals have N–C antibonding and C–C bonding character. These trends in the series **2**–**5** as a function of the formal charge of the [Zn(*t*-BuNCHCHN-*t*-Bu)₂] unit are identical to those observed in the related homologous series of methylzinc derivatives, K[ZnMe(*t*-BuNCHCHN-*t*-Bu)]⁺,¹⁸ and [ZnMe(*t*-BuNCHCHN-*t*-Bu)]⁺.^{3,4,5,17} A comparison of the Zn–N and N–C bond distances in the neutral *t*-BuNCHCHN-*t*-Bu ligands reveals a

(17) Kaupp, M.; Stoll, H.; Preuss, H.; Kaim, W.; Stahl, T.; van Koten, G.; Wissing, E.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5606.

decrease of the Lewis acidity of the zinc center in the series $\mathbf{2} > \mathbf{3} \cdot \text{thf} > \text{ZnMe}(\text{OTf})(t\text{-BuNCHCHN-}t\text{-Bu}) > \text{ZnMe}_2(t\text{-BuNCHCHN-}t\text{-Bu})$. The Zn–N bond lengths in $\mathbf{2}$ – $\mathbf{5}$ differ only slightly (1.973(3)–2.079(3) Å). Since the zinc atoms in these complexes are all four-coordinated, it can be concluded that the Zn–N bond lengths in the $[\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2]$ units are determined by the polarization in these bonds, *i.e.* by the electron density on the $t\text{-BuNCHCHN-}t\text{-Bu}$ ligand.

Remarkably, the complexes $\mathbf{3} \cdot \text{thf}$, $\mathbf{4}$, and $\mathbf{5} \cdot \text{thf}$ containing a radical-anionic $t\text{-BuNCHCHN-}t\text{-Bu}$ ligand are monomers. This is in contrast to the neutral radical complexes $[\text{ZnR}(t\text{-BuNCHCHN-}t\text{-Bu})]^*$, which are isolated in the solid-state as dimers $[\text{ZnR}(t\text{-BuNCHCHN-}t\text{-Bu})_2]$ formed *via* C–C coupling of the radical-anionic ligands of the former.¹⁹

Spectroscopic Studies in Solution. The distribution of the electron(s) over the ligands in the homoleptic series $\text{K}_x[\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2]$, $\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2$, and $\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2(\text{OTf})_x$ ($x = 1, 2$) in solution is detectable by NMR (for diamagnetic $\mathbf{1}$, $\mathbf{2}$, and $\mathbf{6}$) or EPR (for paramagnetic $\mathbf{3}$ and $\mathbf{5}$).

The ^1H and ^{13}C NMR spectra of $\mathbf{1}$ and $\mathbf{2}$ in $\text{MeCN-}d_3$ solution show the characteristic resonance pattern of the bidentate N,N' -coordinating $t\text{-BuNCHCHN-}t\text{-Bu}$ ligands. A comparison of the chemical shifts of $\mathbf{1}$ and $\mathbf{2}$ shows that $\mathbf{2}$ is a cationic species with two chelate-coordinated $t\text{-BuNCHCHN-}t\text{-Bu}$ ligands and excludes a disproportionation equilibrium of $\mathbf{2}$ with $\mathbf{1}$ and free $t\text{-BuNCHCHN-}t\text{-Bu}$ ligand. The enhanced σ donation of electron density from the lone pairs of all four nitrogen atoms to the zinc center causes a low-field shift of 0.45 ppm for the imine hydrogen atoms in $\mathbf{2}$ related to $\mathbf{1}$. In both complexes, the imine hydrogen atoms are shifted considerably to low-field compared to those of the free ligand. The ^{19}F NMR spectra of $\mathbf{1}$ and $\mathbf{2}$ show only one singlet resonance at -78.3 ppm, in accord with the presence of two magnetically equivalent OTf anions. This chemical shift, in the range of -73.0 to -79.5 ppm, is indicative of noncoordinating anions.²⁰

The EPR spectra of paramagnetic $\mathbf{3}$ and $\mathbf{5}$ in thf solutions at room temperature are very similar; see Figure 4. The relatively broad signals hamper the exact determination of the g values. Both spectra show seven hyperfine lines, which is consistent with an unpaired electron being coupled to two magnetically equivalent nitrogen nuclei ($I = 1$) and two magnetically equivalent protons ($I = 1/2$) with nearly identical hyperfine coupling constants a_{H} and a_{N} of approximately 0.54 mT. This points to asymmetric structures with localized mixed-valence $t\text{-BuNCHCHN-}t\text{-Bu}$ ligands for $\mathbf{3}$ and $\mathbf{5}$, respectively, in solution and in the solid state (*vide supra*). Comparison of these experimental spectra with the computer-simulated spectra given by Raston^{1a} and von Zelewsky^{1d} revealed significant deviations from the calculated values for the hyperfine coupling constants a_{H} and a_{N} .

Dianionic $\mathbf{6}$ was studied with variable-temperature ^1H NMR in $\text{thf-}d_8$. The ^1H NMR spectrum of $\mathbf{6}$ at low temperatures (< 273 K) shows one singlet for the olefinic protons and one singlet for the *tert*-butyl substituents in addition to the resonances of coordinated thf. Upon an increase in the temperature to 298 K, a process becomes operative that results in the appearance of two other broad resonances at 6.45 and 4.18 ppm besides

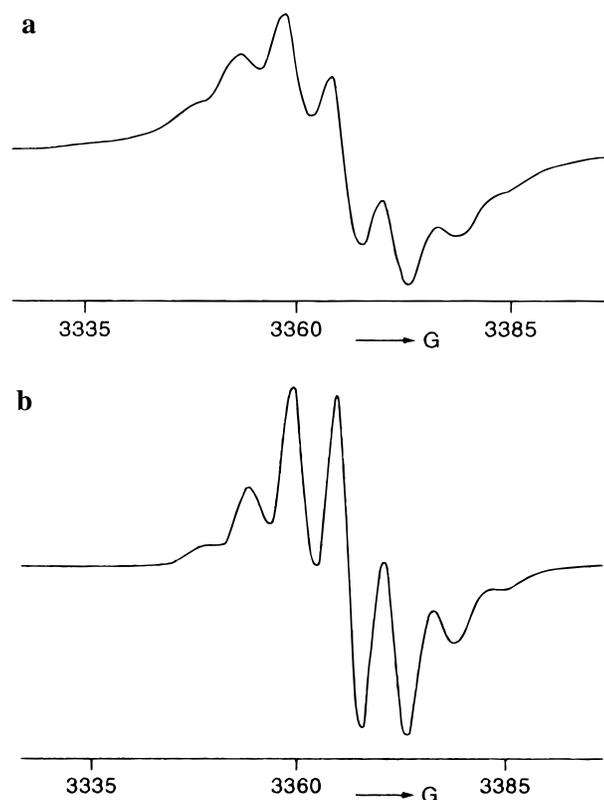


Figure 4. EPR spectra of (a) $\mathbf{3}$ and (b) $\mathbf{5}$ in thf at room temperature (10 G = 1 mT).

the broadened singlet at 5.37 ppm, which was originally (*i.e.*, at lower temperatures) ascribed to the olefinic protons, and at least four separate resonances for the *tert*-butyl substituents in the aliphatic region. Finally, at 345 K the resonances in the region of 10.0–3.8 ppm are so broad that they nearly merge with the baseline, while the resonances of thf and the *tert*-butyl substituents are still present. This temperature-dependent process was found to be reversible.

According to the integral ratios in the ^1H NMR spectra, $\text{K}_2\text{-}[\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2]$ is isolated as the bis thf adduct $\mathbf{6}$. This suggests that each potassium cation in $\mathbf{6}$ is η^4 -coordinated to a ZnNCCN chelate ring of the $[\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2]^{2-}$ unit and that in the solid state both chelate rings act as six- π -electron donors. The ^1H NMR spectra of $\mathbf{6}$ in thf solution at 204 K show one singlet for the olefinic protons. This suggests that in thf all $[\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2]^-$ units are completely separated from the solvated potassium cations. The fluxional behavior of $\mathbf{6}$ observed in the ^1H NMR spectra in thf solution at high temperature may be explained by a temperature-dependent process that affects the interactions between the potassium cations and the ZnNCCN chelate rings. A probable explanation is that at higher temperatures the exchange process between potassium-coordinated thf and free thf is in competition with coordination of the $[\text{Zn}(t\text{-BuNCHCHN-}t\text{-Bu})_2]^-$ units. The observation of an asymmetrical resonance pattern points to a situation in which this coordination is asymmetrical. This asymmetry may be caused by η^1 - or η^3 -coordination of the chelate rings donating two or four π electrons, respectively. The situation is further complicated by the presence of two chelate rings in $\mathbf{6}$ that may be inequivalent. The existence of η^2 -, η^3 -, and η^4 -coordination modes of zinc enediamide ZnNCCN chelate rings donating two, four, and six π electrons, respectively, is supported by the recent solid-state studies on $\text{K}[\text{ZnR}(t\text{-BuNCHCHN-}t\text{-Bu})]$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$).^{4,5}

(18) Kaim, W.; Matheis, W. *J. Chem. Soc., Chem. Commun.* **1991**, 597.

(19) (a) Jastrzebski, J. T. B. H.; Klerks, J. M.; van Koten, G. *J. Organomet. Chem.* **1981**, 210, C49. (b) van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem.* **1983**, 250, 49. (c) Wissing, E.; van der Linden, S.; Rijnberg, E.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, 13, 2602.

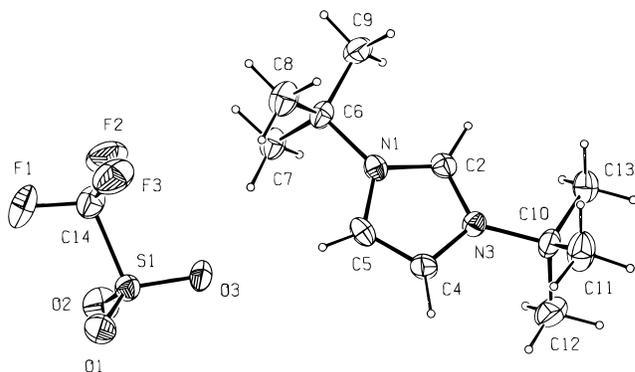
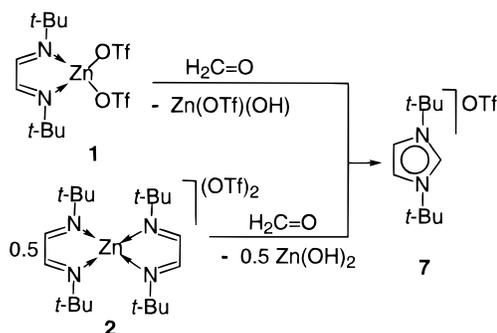


Figure 5. Thermal motion ellipsoid plot (ORTEP, 50% probability) of **7** together with the adopted numbering scheme. The hydrogen atoms have been omitted for clarity.

Scheme 4



Reactivity of 1 and 2. Complex **2** reacts with MeOH to give a mixture of products from which 1,3-di-*tert*-butylimidazolium trifluoromethanesulfonate (**7**) crystallized selectively. An investigation of this reaction revealed that the key step in the formation of **7** most probably is the oxidation of MeOH to paraformaldehyde. Indeed, the reaction of (*in situ* prepared) **2** with 2 equiv of paraformaldehyde in MeCN at room temperature gave **7**. Although **7** is formed quantitatively from paraformaldehyde, it was only isolated in 54% yield. This moderate isolated yield is a consequence of its high solubility in MeCN solution at low temperature: only by crystallization from MeCN at 243 K can **7** be separated from the inorganic zinc salt. Alternatively, **7** was obtained selectively in 45% yield (after crystallization) from *in situ* prepared **1** with paraformaldehyde in a 1:1 molar ratio. (See Scheme 4.) In the absence of Zn(OTf)₂, *t*-BuNCHCHN-*t*-Bu is stable toward paraformaldehyde.

Compound **7** was identified by ¹H and ¹³C NMR and by an X-ray structure determination. A thermal motion ellipsoid plot of the molecular structure of **7** with the adopted numbering scheme is shown in Figure 5, and relevant bond lengths and bond angles are presented in Table 6.

The solid-state structure of **7** shows this compound to contain an imidazolium skeleton. The C–C and N–C bond distances in the five-membered heterocyclic ring are in the typical range for sp²–sp² interactions, comparable to those of related 1,3-di-1-adamantylimidazolium tetraphenylborate.²¹ These bond distances in combination with the planarity within 0.011 Å of the

Table 6. Selected Bond Distances and Bond Angles for **7**

Bond Distances (Å)			
N(1)–C(2)	1.336(5)	C(5)–N(1)	1.378(5)
C(2)–N(3)	1.325(5)	C(2)–H(21)	1.01(3)
N(3)–C(4)	1.375(5)	C(4)–H(41)	0.97(2)
C(4)–C(5)	1.345(5)	C(5)–H(51)	0.87(3)
Bond Angles (deg)			
N(1)–C(2)–N(3)	109.8(4)	C(4)–C(5)–N(1)	107.6(4)
C(2)–N(3)–C(4)	107.8(3)	C(5)–N(1)–C(2)	107.3(3)
N(3)–C(4)–C(5)	107.6(4)		

^a The estimated standard deviations of the last significant digits are given in parentheses.

ring system point to an aromatic system. Comparison of the structural features of **7** with its conjugated base, the carbene 1,3-di-*tert*-butylimidazol-2-ylidene,²² reveals the same trends as observed for the series of the 1-adamantyl-substituted derivatives,²¹ *i.e.* significantly shorter N(1,3)–C(2) bond lengths and a larger N(1)–C(2)–N(3) bond angle than in the carbene. The ¹H NMR spectrum of **7** shows characteristic triplet and doublet resonances in the aromatic region and a singlet for the two identical *t*-Bu substituents. The low-field shift of 0.94 ppm of the imidazolium ring protons in comparison to those of its conjugate base supports the complete delocalization of the six π electrons.²³

The mechanism we propose for the formation of **7** involves an intermediate species in which the *t*-BuNCHCHN-*t*-Bu ligand is monodentately coordinated to zinc, resulting in a coordinatively unsaturated zinc center to which paraformaldehyde can coordinate *via* an oxygen lone pair. This renders the carbonyl carbon of the latter susceptible to intramolecular nucleophilic attack of the free nitrogen lone pair of a monodentate coordinated *t*-BuNCHCHN-*t*-Bu ligand. Finally, a rearrangement and a subsequent ring closure afford **7** after elimination of Zn(OTf)(OH) or Zn(OH)₂. Overall, the driving force for the rearrangement to **7** is the formation of a species with a delocalized π-electron system.

The role of the Lewis-acidic zinc center as the active site in this 1- or 2-catalyzed oxidation of MeOH to HCHO is comparable to that of the zinc ion in *alcohol dehydrogenase*, an enzyme that catalyzes the biological redox reaction between acetaldehyde and EtOH. The new procedure for the preparation of **7** presented here provides an interesting alternative to the recently published procedures, which use Brønsted acids.²³

Concluding Remarks

The homologous series of zinc complexes K_x[Zn(*t*-BuNCHCHN-*t*-Bu)₂], Zn(*t*-BuNCHCHN-*t*-Bu)₂, and [Zn(*t*-BuNCHCHN-*t*-Bu)₂](OTf)_x (x = 1, 2) has been prepared by chemical reduction and oxidation reactions. The synthetic methods used for the preparation of **3** and **5** are indirect evidence for the reversible character of these redox processes. The results presented here show that *t*-BuNCHCHN-*t*-Bu ligands are able to stabilize both complexes containing electron-deficient units and complexes containing electron-rich [Zn(*t*-BuNCHCHN-*t*-Bu)₂] units. In a forthcoming paper, we will present an extension of this study to the preparation of monoanionic heteroleptic (di)organozinc complexes containing a single

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t-BuNCHCHN-*t*-Bu ligand, *i.e.* K[ZnR(*t*-BuNCHCHN-*t*-Bu)], K[ZnR(*t*-BuNC(R)CHN-*t*-Bu)], and K[ZnR₂(*t*-BuNCHCHN-*t*-Bu)] (R = Me, Et).^{4,5}

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Supporting Information Available: ¹H, ¹⁹F, and ¹³C NMR spectra of complexes **2** and **6** (4 pages). Four X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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