

Heteroleptic Metallacyclic Potassium Organodiamido Zincate Complex. Synthesis and Structure of Polymeric $\{[K(thf)][MeZn(Bu^tNCH=CHNBu^t)]\}_n$

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The reaction of the C–C coupled dimer of two neutral organozinc radicals, $[MeZn\{Bu^tN=CHCH(NBu^t)CH(NBu^t)CH=NBu^t\}ZnMe]$ **1**, with potassium in tetrahydrofuran affords the metallacyclic heteroleptic potassium organodiamido zincate $K[MeZn(Bu^tNCH=CHNBu^t)]$ **2** quantitatively, which exists in the solid state (X-ray crystallography) as a linear polymer formed by alternating potassium cations and organodiamidozincate anions.

The intramolecular group-transfer reaction of dialkylzinc compounds R_2Zn with 1,4-disubstituted 1,4-diaza-1,3-butadienes ($R^tN=CHCH=NR$) leads to a regioselective alkylation reaction at either the imine carbon or the imine nitrogen atom of the NCCN skeleton.¹ Two possible mechanisms for this alkylation reaction have been put forward, *i.e.* a radical and a polar mechanism. In the latter mechanism diorganozinc radical anionic intermediates, $[R_2Zn(R^tNCHCHNR^t)]^-$, have been suggested to play an important role.^{2,3} Recently we succeeded in the separate preparation of representative examples of such diorganozinc radical anions, which appeared to be thermally unstable.⁴ They readily undergo an intermolecular single electron transfer (SET) resulting in the formation of a mixture of products in which the heteroleptic metallacyclic organodiamido zincate anions **A** and **B** could be detected (Scheme 1). This unexpected observation prompted us to try to prepare such unique metallacyclic heteroleptic zincate complexes separately to enable a study of their structural features.

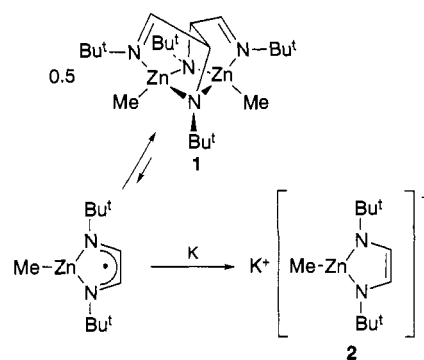
Several homoleptic organozincate complexes have been reported, which have the composition $M[ZnR_3]$ ⁵ ($M = Na, K; R = \text{alkyl}$), $M_2[ZnR_4]$ ^{6,7} ($M = Li, K; R = \text{alkyl}$) or $M[ZnR_3]_2$ ⁸ ($M = Mg; R = \text{alkyl}$). However, very little is known of heteroleptic organozincate complexes^{6,7,9} or heteroleptic zincate complexes of the composition $M[R_2ZnX]$ or $M[RZnX_2]$ ($R = \text{alkyl}; X = \text{alkoxide, halogen}$), in which one or two organic ligands are replaced by more electronegative ligands. The only prior reports of this type of zincate complexes have been a single-crystal X-ray diffraction study of $K[Et_2Zn(OBu^t)]$, derived from $ZnEt_2$ and $KOBu^t$,¹⁰ and the NMR characterization of $Li[(Me_3Si)_3CZnBr_2]$ prepared from $ZnBr_2$ and $LiC(SiMe_3)_3$.⁹

We here report on the independent synthesis, isolation and structural characterization of $K[MeZn(Bu^tNCH=CHNBu^t)]$ **2**, the first metallacyclic heteroleptic organodiamido zincate. Compound **2**, containing zincate anions of type **A** (Scheme 1), is readily obtained as the only reaction product when the

C–C coupled dimer of two neutral organozinc radicals, $[MeZn\{Bu^tN=CHCH(NBu^t)CH(NBu^t)CH=NBu^t\}ZnMe]$,¹¹ is treated with potassium in tetrahydrofuran (Scheme 2).[‡]

The X-ray structure analysis of **2**·thf in the solid state[§] reveals a linear polymer with potassium cations sandwiched between organodiamidozincate anions (Fig. 1).

The repeating unit in the polymer consists of two $MeZn(Bu^tNCH=CHNBu^t)$ anions each located on a mirror plane, two



Scheme 2

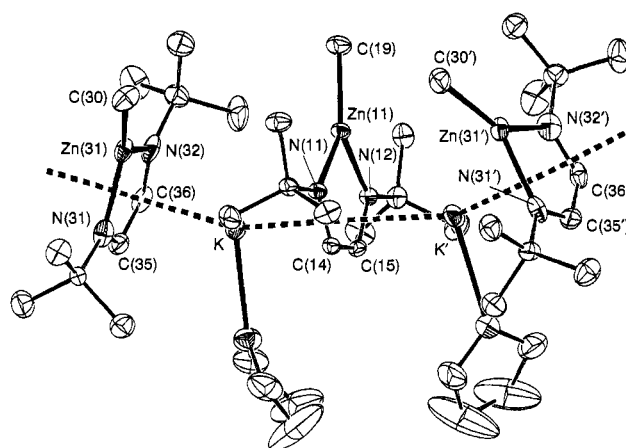
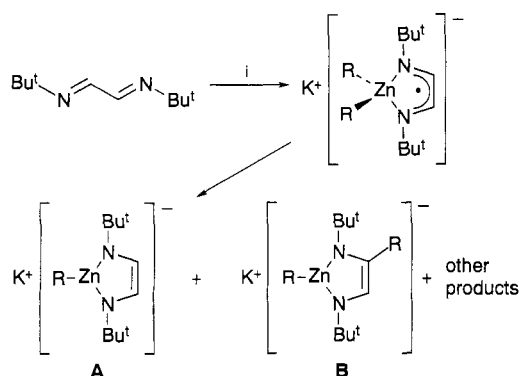


Fig. 1 ORTEP drawing at 30% probability level of the polymer **2**·thf. Hydrogen atoms have been omitted for clarity. Selected atomic distances (Å) and angles (°): K–N(11) 3.1421(16), K–N(12) 3.1895(18), K–C(14) 2.9210(15), K–C(15) 2.9519(16), K–N(31) 3.023(19), K–N(32) 3.05(2), K–C(35) 2.986(7), K–C(36) 3.040(7), Zn(11)–C(19) 1.951(5), Zn(31)–C(30) 1.956(7), Zn(11)–N(11) 1.956(3), Zn(11)–N(12) 1.951(3), Zn(31)–N(31) 2.03(2), Zn(31)–N(32) 2.018(17), N(11)–C(14) 1.388(6), N(12)–C(15) 1.391(5), N(31)–C(35) 1.291(19), N(32)–C(36) 1.31(2), C(14)–C(15) 1.357(6), C(35)–C(36) 1.380(12), N(11)–Zn(11)–C(19) 136.81(17), N(12)–Zn(11)–C(19) 138.15(17), N(31)–Zn(31)–C(30) 139.7(5), N(32)–Zn(31)–C(30) 138.0(6), N(11)–Zn(11)–N(12) 85.05(14), N(31)–Zn(31)–N(32) 82.0(7).



Scheme 1 Reagents and conditions: i, K then ZnR_2

MeZn(Bu^tNCH=CHNBu^t) anions each located on an inversion centre and four bridging potassium cations. The differences in K–N and K–C distances between two MeZn(Bu^tNCH=CHNBu^t) moieties, ranging from 3.023(19) to 3.1895(18) Å and from 2.9210(15) to 3.103(8) Å, respectively, suggest that each potassium cation in the chain is $\eta^2 + \eta^4$ coordinated to the six π -electrons of the MeZn(Bu^tNCH=CHNBu^t) moieties. In addition, one molecule of tetrahydrofuran completes the coordination sphere around potassium.

The three-coordinate zinc atoms in the MeZn(Bu^tNCH=CHNBu^t) moieties in the polymer chain have a distorted trigonal-planar geometry. The Zn–C distances, 1.951(5) and 1.956(7) Å, are shorter than those reported for K[Zn(CH₂SiMe₃)₃], where they are in the range of 2.03(1) to 2.06(1) Å.⁶ The C–C bond distances in the NCCN skeletons range from 1.357(6) to 1.380(12) Å, normal values for sp²–sp² C–C bonds. The C–C and C–N distances suggest a σ, σ', N, N' -enediamide bonding mode for the dianionic Bu^tNCH=CHNBu^t ligands. Related organometallic compounds with chelating dianionic enediamide ligands have been reported for germanium,¹² hafnium,¹³ silicon(II),¹⁴ silicon(IV)¹⁵ and aluminum.¹⁶

The five-membered ZnN₂C₂ chelate ring is planar and isostructural with that in Ge^{II}(Bu^tNCH=CHNBu^t)¹² and Si^{II}(Bu^tNCH=CHNBu^t).¹⁴ It may be regarded as a quasi-aromatic system in which the lone pairs of the nitrogen atoms and the two π electrons of the C–C double bond are delocalized.¹⁷ From this point of view the interaction between the potassium cations and the MeZn(Bu^tNCH=CHNBu^t) anions in **2**-thf might be described in terms of potassium–aromatic coordination as reported for [K(C₅Me₅)₂C₅H₅N].¹⁸

The ¹H NMR spectrum of **2**, which is only soluble in tetrahydrofuran, shows a characteristic singlet resonance in the olefinic region and a singlet for two identical Bu^t groups. In comparison with the starting methylzinc complex **1** (Scheme 2)¹¹ an upfield shift of 0.81 ppm is observed for the methyl group bound to zinc, due to the enhanced negative charge density on the methyl group in **2**. The NMR data suggest that for **2** in tetrahydrofuran solution the polymeric structure is dissociated into monomeric solvated potassium organodiamidozincate complexes.

Just counting the π electrons of the target heteroleptic zincate complex **A** initiated us to develop the surprisingly elegant synthetic procedure starting from the C–C coupled dimer of two neutral organozinc radicals. Although the equilibrium between dimer **1** and the organozinc radicals (Scheme 2) lies far to the side of **1**, it is most probably that the organozinc radicals are reduced by potassium to give **2**. A study to elucidate the exact mechanism of this reduction reaction is underway.

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Footnotes

† General correspondence to G. v. K.; correspondence regarding crystallographic work to A. L. S.

‡ Under an inert atmosphere a solution of **1** (prepared as in ref. 11) (2.38 g, 4.8 mmol) in tetrahydrofuran (30 ml) was added to a suspension of finely divided potassium (0.38 g, 9.7 mmol) in tetrahydrofuran (20 ml). After stirring for 16 h at room temperature the solvent was removed *in vacuo*, leaving a yellow-brown residue. The residue was washed with hexanes (2 × 20 ml) and dried *in vacuo*, affording **2** as a yellow powder, isolated yield 2.73 g (99%). Crystals of **2**-thf were obtained by crystallization from

tetrahydrofuran–diethyl ether (1:5) at –30 °C. ¹H NMR (200 MHz, [²H₈]tetrahydrofuran): δ 5.65 (s, 2, NCH=), 1.16 [s, 18, C(CH₃)₃], –0.82 (s, 3, CH₃). ¹³C NMR: δ 114.4 (NCH=); 52.4 [C(CH₃)₃], 33.9 [C(CH₃)₃], –11.3 (CH₃). Mp > 180 °C. Anal. Calc. for C₁₁H₂₃KN₂Zn: C, 45.91; H, 8.06; N, 9.73. Found: C, 46.08; H, 8.01; N, 9.64%.

§ X-Ray data were collected on an Enraf-Nonius CAD4T/rotating anode diffractometer for a suitable transparent, cut to size crystal, covered by inert oil, glued on top of a glass fibre and stabilized by a cold dinitrogen stream (150 K). Unit cell dimensions were derived from the SET4 setting angles of 25 reflections in the range of $11 < \theta < 14^\circ$. Crystal data for **2**-thf are: C₁₅H₃₁KN₂OZn, orthorhombic, space group *Pnma*, *a* = 15.6658(7), *b* = 21.5705(11), *c* = 11.3578(9) Å, *Z* = 8, *V* = 3838.0(4) Å³, *D*_c = 1.246 g cm^{–3}, $\mu(\text{Mo-K}\alpha)$ = 15.3 cm^{–1}, λ = 0.710 73 Å, crystal size: 0.13 × 0.38 × 0.50 mm. A total of 6685 reflections were scanned and averaged (*R*_{int} = 0.025) to a unique set of 4526 reflections (θ_{max} = 27.5°, ω – 2θ scans). Data were corrected for *L*_p and absorption (DIFABS). The structure was solved by Patterson techniques (DIRDIF) and refined on *F*² using SHELXL-93. Non-hydrogen atoms were included on calculated positions, riding on and with isotropic displacement parameters derived from their carrier atoms. The crystallographic unit cell contains two [ZnC₁₁H₂₃N₂][–] anions located on a crystallographic mirror plane, two [ZnC₁₁H₂₃N₂][–] located on an inversion centre and four [K-thf]⁺ cations. The anions on the inversion centre are disordered and were refined with a disorder model. Convergence was reached at *R*₁ = 0.0495 [for 2846 reflections with *F* > 4 σ (*F*); *wR*₂ = 0.115; *S* = 1.02; 280 parameters]. No residual density outside the range –0.56 < $\Delta\rho$ < 0.47 e Å^{–3} was observed.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- J. M. Klerks, J. T. B. H. Jastrzebski, G. van Koten and K. Vrieze, *J. Organomet. Chem.*, 1982, **224**, 107; G. van Koten, *Organometallics in Organic Synthesis*, ed. A. de Meijere and H. tom Dieck, Springer-Verlag, Berlin, 1987, p. 277.
- E. Wissing, M. Kaupp, J. Boersma, A. L. Spek and G. van Koten, *Organometallics*, 1994, **13**, 2349.
- M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606.
- E. Rijnberg, J. Boersma, J. T. B. H. Jastrzebski, M. T. Lakin, A. L. Spek and G. van Koten, unpublished work.
- A. P. Purdy and C. F. George, *Organometallics*, 1992, **11**, 1955.
- Powder diffraction studies: E. Weiss and R. Wolfrum, *Chem. Ber.*, 1968, **101**, 35; E. Weiss and H. Plass, *J. Organomet. Chem.*, 1968, **14**, 21.
- H.-O. Frölich, B. Kosan, B. Undeutsch and H. Görls, *J. Organomet. Chem.*, 1994, **72**, 1.
- E. Rijnberg, J. Boersma, J. T. B. H. Jastrzebski, H. Kooijman, A. L. Spek and G. van Koten, submitted.
- M. B. Westerhausen, B. Rademacher, W. Schwartz, J. Weidlein and S. Henkel, *J. Organomet. Chem.*, 1994, **469**, 135.
- R. Fabicon, M. Parvez and H. G. Richey, Jr., *J. Am. Chem. Soc.*, 1991, **113**, 1412.
- E. Wissing, S. van der Linden, E. Rijnberg, J. Boersma, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1994, **13**, 2602.
- W. A. Hermann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1485.
- B. Hessen, J. E. Bol, J. L. de Boer, A. Meetsma and J. H. Teuben, *J. Chem. Soc., Chem. Commun.*, 1989, 1276.
- M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
- H. tom Dieck, B. Bruder and K.-D. Franz, *Chem. Ber.*, 1983, **116**, 136; H. tom Dieck, U. Verfürth, K. Doblitz, J. Ehlers and G. Fendesak, *Chem. Ber.*, 1989, **122**, 129.
- F. Geoffrey, N. Cloke, C. I. Dalby, M. J. Henderson, P. B. Hitchcock, C. H. L. Kennard, R. N. Lamb and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1990, 1394.
- M. M. Olmstead, P. P. Power and S. C. Shoner, *J. Am. Chem. Soc.*, 1991, **113**, 3379.
- G. Rabe, H. W. Roesky, D. Stalke, F. Pauer and G. M. Sheldrick, *J. Organomet. Chem.*, 1991, **403**, 11.