

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 ($R'N=CHCH=NR$) 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, $[R_2Zn(R'NCHCHNR')]^-$, 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.

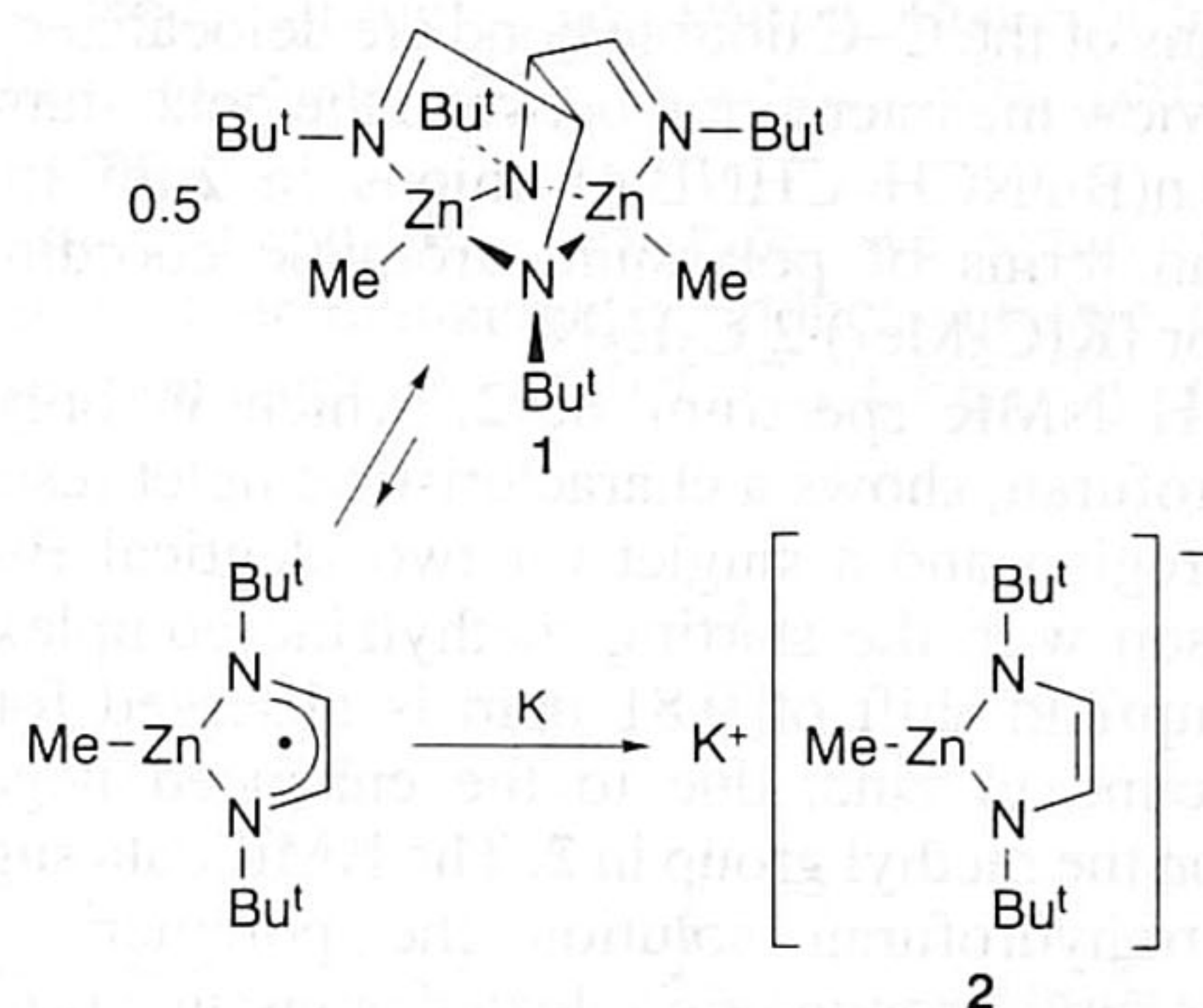
Several homoleptic organozincate complexes have been reported, which have the composition $M[ZnR_3]^5$ ($M = Na, K; R = \text{alkyl}$), $M_2[ZnR_4]^6,7$ ($M = Li, K; R = \text{alkyl}$) or $M[ZnR_3]_2^8$ ($M = Mg; R = \text{alkyl}$). However, very little is known of heteroleptic organozincate complexes^{6,7,9} 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

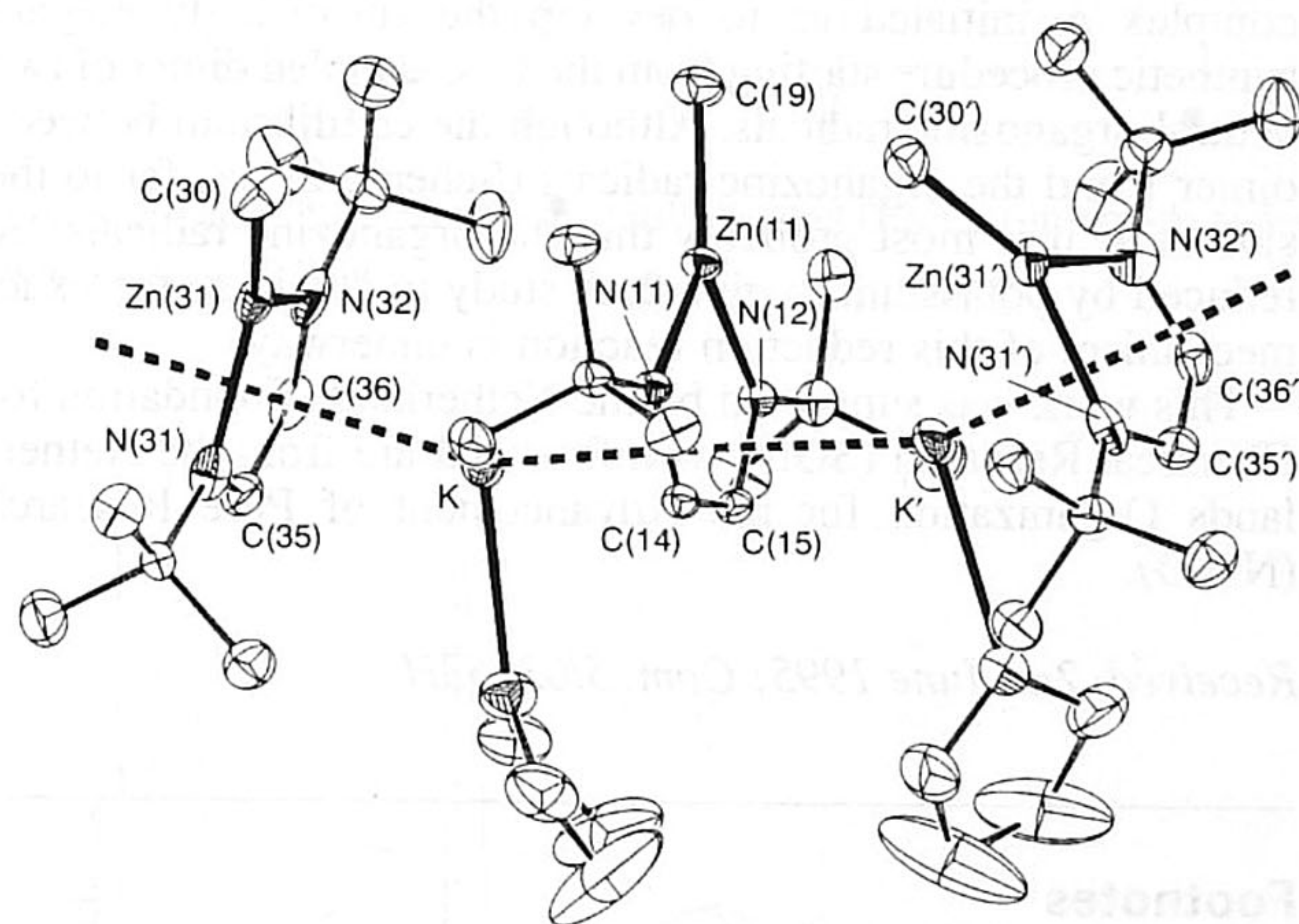
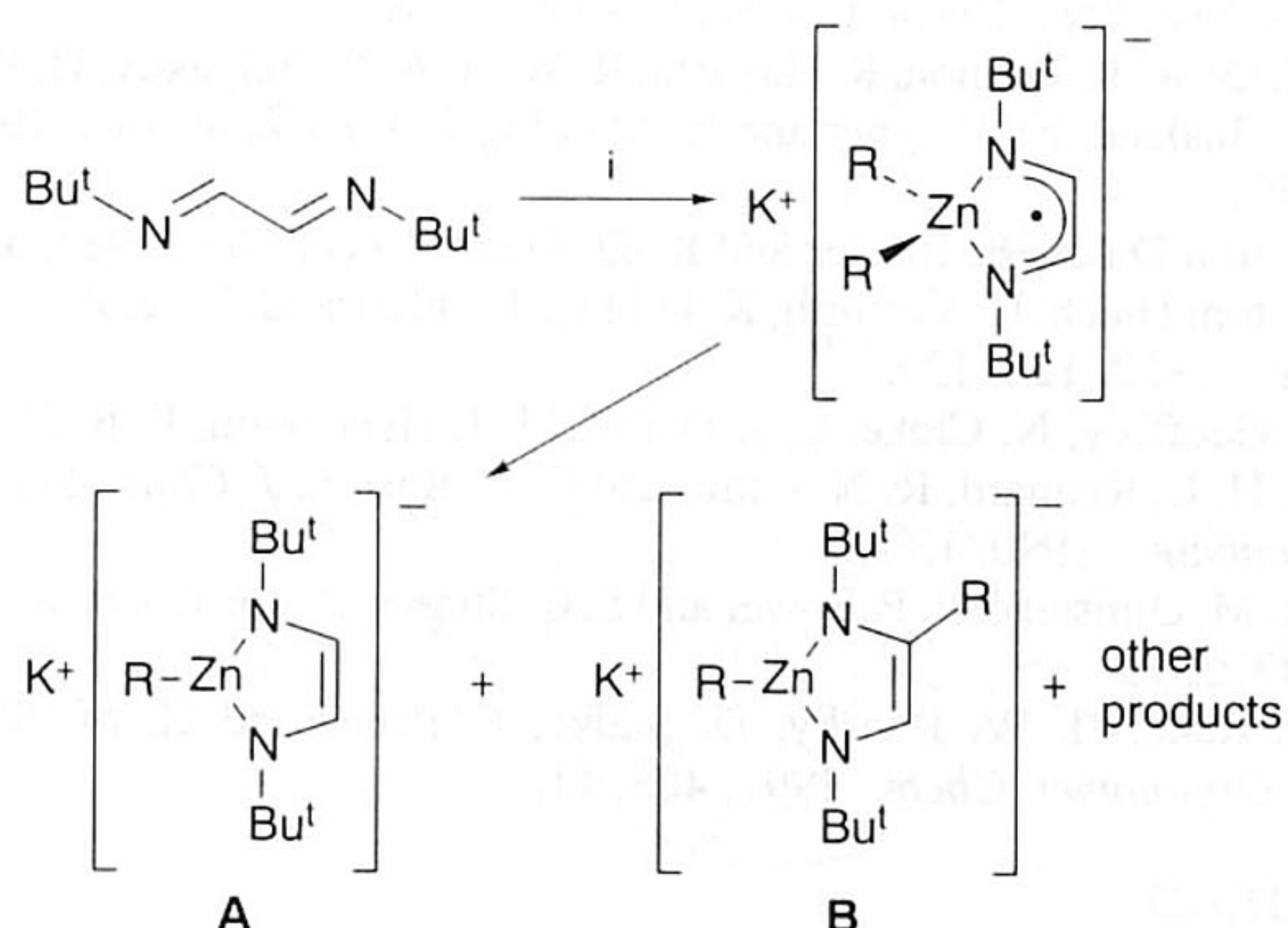


Fig. 1 ORTEP drawing at 30% probability level of the polymer **2**·thf. Hydrogen atoms have been omitted for clarity. Selected atomic distances (Å) and angles (°): K–N(11) 3.1421(16), K–N(12) 3.1895(18), K–C(14) 2.9210(15), K–C(15) 2.9519(16), K–N(31) 3.023(19), K–N(32) 3.05(2), K–C(35) 2.986(7), K–C(36) 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)·2 C₅H₅N].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 < θ < 14°. 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}, μ (Mo-K α) = 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 –2 θ scans). Data were corrected for *Lp* 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.