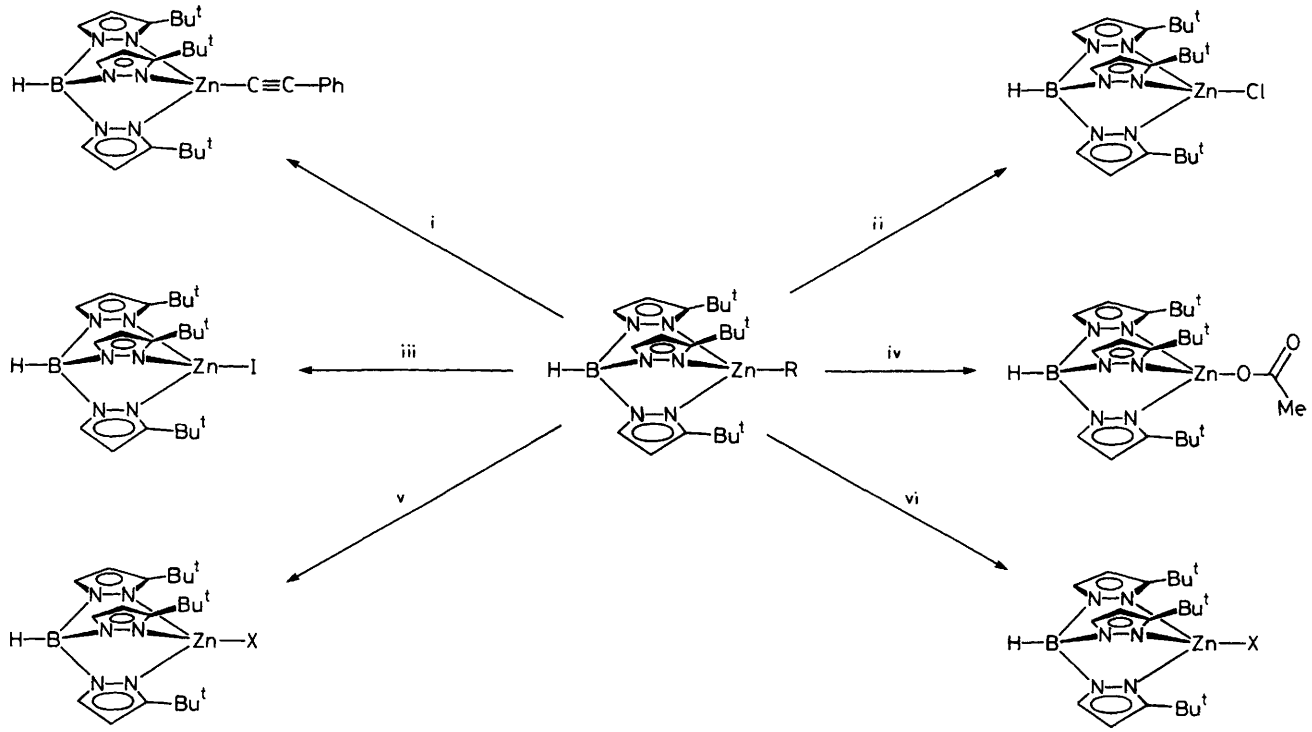
Tris(pyrazolyl)hydroboratozinc Alkyl Derivatives: Direct Comparison of the Reactivity of Zn–C and Mg–C Bonds

Ian B. Gorrell, Adrian Looney, and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027, U.S.A.

The monoalkyl zinc derivatives $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnR}$ (3-Bu^{t}pz = 3-$C_3N_2Bu^tH_2$; R = Me, Et) have been prepared by metathesis of R_2Zn with $Tl[HB(3\text{-Bu}^t\text{pz})_3]$, and their reactivity compared with that of the isostructural magnesium alkyl derivatives.

Organozinc and organomagnesium derivatives are invaluable reagents in organic synthesis.[1] More recently, R_2M (M = Mg, Zn) derivatives have been used successfully for the asymmetric alkylation of aldehydes in the presence of chiral amino alcohols.[2] In order to be able to control the selectivity and reactivity of such organic transformations by the use of different organomagnesium or organozinc derivatives, it is essential to understand the detailed nature of the reactivity of the M–C bonds in such complexes. Previous studies have demonstrated that magnesium alkyl derivatives are often more reactive than the corresponding zinc derivatives.[3] However, in order to make quantitative comparisons between



Scheme 1. *Reagents*: i, PhCCH, −RH; ii, HCl, −RH; iii, RI (R = Me, $PhCH_2$); iv, $MeCO_2H$, −RH; v, Me_3SiX/H_2O (X = I, Br, Cl, CN, N_3, NCS), −RH; vi, X_2 (X_2 = Cl_2, Br_2, I_2), −RX.

magnesium and zinc alkyl derivatives, and thus determine the intrinsic reactivity of Mg–C *vs.* Zn–C bonds, it is important to examine isostructural alkyl derivatives. Thus, comparisons between R_2Zn, a molecular species containing two-co-ordinate zinc, and $(R_2Mg)_n$, a polymeric solid, would not be expected to give a true indication of the relative intrinsic reactivities of the Zn–C and Mg–C bonds. Similarly, comparisons between the RMX (M = Mg, Zn) derivatives would not be straightforward as a result of the complex nature of these species in solution. We have recently described the syntheses and reactivity of the magnesium alkyl derivatives [η^3-HB(3-Bu^{t}pz)$_3$]MgR (3-Bu^{t}pz = 3-$C_3N_2Bu^tH_2$; R = Me, Et), in which the tris(pyrazolyl)hydroborato ligand provides a well-defined environment about the magnesium centre.[4] Here we describe the syntheses and reactivity of the monoalkyl zinc derivatives [η^3-HB(3-Bu^{t}pz)$_3$]ZnR (R = Me, Et) so that direct comparisons between the reactivity of the Zn–C and Mg–C bonds may be made.

$$R_2Zn \xrightarrow[THF]{Tl[HB(3\text{-}Bu^tpz)_3]} [\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnR \quad (1)$$

The zinc alkyl complexes [η^3-HB(3-Bu^{t}pz)$_3$]ZnR† are readily prepared by metathesis of R_2Zn with Tl[HB(3-Bu^{t}pz)$_3$] (equation 1, where THF = tetrahydrofuran).

The molecular structure of [η^3-HB(3-Bu^{t}pz)$_3$]ZnMe has been determined by single-crystal *X*-ray diffraction studies (Figure 1), which confirm both the monomeric nature of the complex and the η^3-co-ordination mode of the [η^3-tris(pyrazolyl)hydroborato] ligand.‡ The Zn–C bond length [1.890(10) Å] is noticeably shorter than the Mg–C bond length [2.118(11) Å] in the isostructural derivative, [η^3-HB(3-Bu^{t}pz)$_3$]MgMe.[4] For comparison, the Zn–C bond length [1.957(5) Å] in the diethyl derivative, (18-crown-6)$ZnEt_2$ is also shorter than the Mg–C bond length [2.104(2) Å] in the related complex, (18-crown-6)$MgEt_2$.[5]

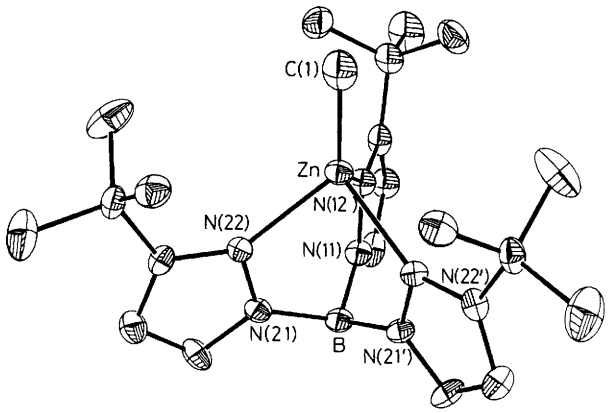


Figure 1. ORTEP diagram of [η^3-HB(3-Bu^{t}pz)$_3$]ZnMe. For clarity, thermal ellipsoids are shown at 20% probability. Selected bond distances (Å) and angles (°): Zn–C(1) 1.890(10), Zn–N(12) 2.121(9), Zn–N(22) 2.117(6), N(11)–N(12) 1.374(13), N(21)–N(22) 1.368(8), B–N(11) 1.530(17), B–N(21) 1.555(10); N(12)–Zn–N(22) 90.5(2), N(22)–Zn–N(22') 90.1(3), N(11)–B–N(21) 109.8(7), N(21)–B–N(21') 108.5(9), C(1)–Zn–N(12) 123.8(4), C(1)–Zn–N(22) 125.6(2).

The complexes [η^3-HB(3-Bu^{t}pz)$_3$]ZnR represent the first examples of zinc alkyl derivatives stabilized by a [η^3-tris(pyrazolyl)hydroborato] ligand. The stabilizing influence of the [η^3-tris(pyrazolyl)hydroborato] ligand upon the Zn–C bond is clearly indicated the remarkable stability of [η^3-HB(3-Bu^{t}pz)$_3$]ZnR (R = Me, Et) towards oxygen, both in the solid state and in solution over a period of days.

The reactivity of [η^3-HB(3-Bu^{t}pz)$_3$]ZnR is illustrated in Scheme 1.§ The Zn–C bond is readily cleaved by protic reagents to eliminate RH. Thus, the reactions of [η^3-HB(3-Bu^{t}pz)$_3$]ZnR with hydrogen chloride, acetic acid and phenylacetylene give [η^3-HB(3-Bu^{t}pz)$_3$]ZnCl,† [η^3-HB(3-

† All complexes have been characterized by elemental analysis, mass spectrometry, NMR and IR spectroscopies. *Selected NMR data* for [η^3-HB(3-Bu^{t}pz)$_3$]ZnMe: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.41 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}, 0.54 [3H, s, $ZnCH_3$]; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 30.7 {q, $^1J_{C-H}$ 126 Hz, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}, 32.0 {s, η^3-HB($C_3N_2H_2CMe_3)_3$}, −2.8 [q, $^1J_{C-H}$ 118 Hz, $ZnCH_3$]. For [η^3-HB(3-Bu^{t}pz)$_3$]ZnEt: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.41 {9H, s, η^3-HB-[$C_3N_2H_2C(CH_3)_3]_3$}, 1.31 [2H, q, $^3J_{H-H}$ 8.0 Hz, $ZnCH_2CH_3$], 1.96 [3H, t, $^3J_{H-H}$ 8.0 Hz, $ZnCH_2CH_3$]; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 30.9 {q, $^1J_{C-H}$ 126 Hz, η^3-HB[$C_3N_2H_2C$-$(CH_3)_3]_3$}, 32.0 [s, η^3-HB($C_3N_2H_2CMe_3)_3$], 7.3 [t, $^1J_{C-H}$ 116 Hz, $ZnCH_2CH_3$], 13.9 [q, $^1J_{C-H}$ 123 Hz, $ZnCH_2CH_3$]. For [η^3-HB(3-Bu^{t}pz)$_3$]ZnCl: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.51 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 30.7 {q, $^1J_{C-H}$ = 126 Hz, η^3-HB[$C_3N_2H_2C$-$(CH_3)_3]_3$}, 32.2 (s, η^3-HB[$C_3N_2H_2CMe_3)_3$). For [η^3-HB(3-Bu^{t}pz)$_3$]ZnBr: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.53 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 31.0 {q, $^1J_{C-H}$ 126 Hz, η^3-HB[$C_3N_2H_2C$-$(CH_3)_3]_3$}, 32.3 (s, η^3-HB[$C_3N_2H_2CMe_3)_3$). For [η^3-HB(3-Bu^{t}pz)$_3$]ZnI: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.55 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}; ^{13}C NMR ([^{2}H]$CHCl_3$, room temp., 100.6 MHz) δ 31.5 {q, $^1J_{C-H}$ 127 Hz, η^3-HB[$C_3N_2H_2C$-$(CH_3)_3]_3$}, 32.2 [s, η^3-HB($C_3N_2H_2CMe_3)_3$]. For [η^3-HB(3-Bu^{t}pz)$_3$]ZnCN: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.46 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 30.9 {q, $^1J_{C-H}$ 126 Hz, η^3-HB[$C_3N_2H_2C$-$(CH_3)_3]_3$}, 32.2 [s, η^3-HB($C_3N_2H_2CMe_3)_3$], 137.6 [s, $ZnCN$]. For [η^3-HB(3-Bu^{t}pz)$_3$]ZnC_2Ph: ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.50 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]$}; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 30.9 {q, $^1J_{C-H}$ 126 Hz, η^3-HB[$C_3N_2H_2C(CH_3)_3]$}, 32.3 [s, η^3-HB($C_3N_2H_2CMe_3)_3$]. For [η^3-HB(3-Bu^{t}pz)$_3$]Zn(η^1-O_2CMe): ^{1}H NMR ([$^2H_6$]C_6H_6, room temp., 200 MHz) δ 1.47 {9H, s, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}, 2.25 [3H, s, O_2CCH_3]; ^{13}C NMR ([$^2H_6$]C_6H_6, room temp., 100.6 MHz) δ 30.5 {q, $^1J_{C-H}$ 126 Hz, η^3-HB[$C_3N_2H_2C(CH_3)_3]_3$}, 32.1 [s, η^3-HB($C_3N_2H_2CMe_3)_3$], 23.1 [q, $^1J_{C-H}$ 126 Hz, O_2CCH_3], 177.0 [s, O_2CMe].

‡ *Crystal data* for [η^3-HB(3-Bu^{t}pz)$_3$]ZnMe: $C_{22}H_{37}N_6BZn$, M = 461.77, orthorhombic, space group *Pnma* (No. 62), a = 16.341(4), b = 15.932(6), c = 9.775(4) Å, U = 2545(2) Å^3, Z = 4, D_c = 1.2 g cm^{-3}, $F(000)$ = 984 electrons, μ(Mo-K_α) = 10.1 cm^{-1}, T = 295 K, crystal dimensions 0.30 mm × 0.36 mm × 0.42 mm. Intensity data were collected on a Nicolet R3m diffractometer using monochromated Mo-K_α *X*-radiation (λ = 0.71073 Å) and were corrected for Lorentz, polarization, and absorption effects. A total of 3498 unique reflections were collected in the range $3 < 2\theta < 58°$, of which 953 with $F_o > 6\sigma(F_o)$ were used in the structure determination. The structure was solved using Patterson and standard difference map techniques. Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions [d_{C-H} = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$]. Block-diagonal least-squares refinement converged to R = 5.47 (R_w = 4.20), with the maximum shift-to-σ ratio of 0.028 for the last cycle. The final difference map showed no significant features, with the highest final peak 0.6 e Å^{-3} near Zn. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Reactions were most conveniently monitored by ^{1}H NMR spectroscopy.

$Bu^tpz)_3]Zn(\eta^1\text{-}O_2CMe)$,† and $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnCCPh$,† respectively. Similarly, halogens cleave the Zn–C bond to eliminate RX and give the halide, $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnX$ (X = Cl, Br, I).† The reactions of $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnR$ with HX (X = Br, Cl, I, CN, N_3, NCS), generated *in situ* by the prior treatment of Me_3SiX with H_2O, provide convenient synthetic procedures for the formation of $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnX$.[6]

The rates of the reactions of $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnR$ are significantly slower than the corresponding reactions of the magnesium derivatives.[4] For example, whereas both $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnEt$ and $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]MgEt$ react with $PhCH_2I$ to give $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]MI$ (M = Zn, Mg), the half-lives under similar conditions at 100 °C are 2.3×10^3 and 0.23 h, respectively, a factor of four orders of magnitude difference in reactivity.¶ Similarly, whereas $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]MgMe$ undergoes insertion of CO_2 into the Mg–C bond at room temperature, no reaction is observed between $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnMe$ and CO_2 at 140 °C, although the expected product, $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]Zn(\eta^1\text{-}O_2CMe)$, has been isolated by the reaction of $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnR$ with $MeCO_2H$.

In conclusion, we have demonstrated that co-ordination of the [η^3-tris(pyrazolyl)hydroborato] ligands to zinc alkyl derivatives results in the formation of 4-co-ordinate monoalkyl complexes that are isostructural with the analogous magnesium derivatives. Comparison of the reactivity of the Zn–C and Mg–C bonds in these complexes provides good evidence for the intrinsic higher reactivity of the Mg–C *vs.* the Zn–C bonds.

We thank the Donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research.

Received, 12th October 1989; Com. 9/03909K

¶ These preliminary kinetic studies are only intended to give an indication of the relative reactivity under similar conditions and the complete rate-law has not yet been determined.

References

1 E. Negishi, 'Organometallics in Organic Synthesis,' vol. 1, Wiley, New York, 1980; B. J. Wakefield, 'Comprehensive Organometallic Chemistry,' vol. 7, Pergamon Press, Oxford, 1982, p. 1; 'New Applications of Organometallic Reagents in Organic Synthesis,' ed. D. Seyferth, Elsevier, Amsterdam, 1976; Y. H. Lai, *Synthesis*, 1981, 585; M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Nonmetallic Substances,' Prentice-Hall, New York, 1954.

2 P. A. Chaloner and S. A. R. Perera, *Tetrahedron Lett.*, 1987, **28**, 3013; K. Soai, M. Nishi, and Y. Ito, *Chem. Lett.*, 1987, 2405; E. J. Corey and F. J. Hannon, *Tetrahedron Lett.*, 1987, **28**, 5233; 5237; R. Noyori, S. Suga, K. Kawai, S. Okada, and M. Kitamura, *Pure Appl. Chem.*, 1988, **60**, 1597; M. Kitamura, S. Okada, S. Suga, and R. Noyori, *J. Am. Chem. Soc.*, 1989, **111**, 4028; M. M. J.-P. Battioni and W. Chodkiewcz, *Bull. Soc. Chim. Fr.*, 1972, 2068.

3 E. G. Rochow, D. T. Hurd, and R. N. Lewis, 'The Chemistry of Organometallic Compounds,' Wiley, New York, 1957.

4 R. Han, A. Looney, and G. Parkin, *J. Am. Chem. Soc.*, 1989, **111**, 7276.

5 A. D. Pajerski, G. L. BergStresser, M. Parvez, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, 1988, **110**, 4844.

6 The complexes $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]ZnX$ (X = N_3, NCS) have been recently reported. S. Trofimenko, J. C. Calabrese, and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507.