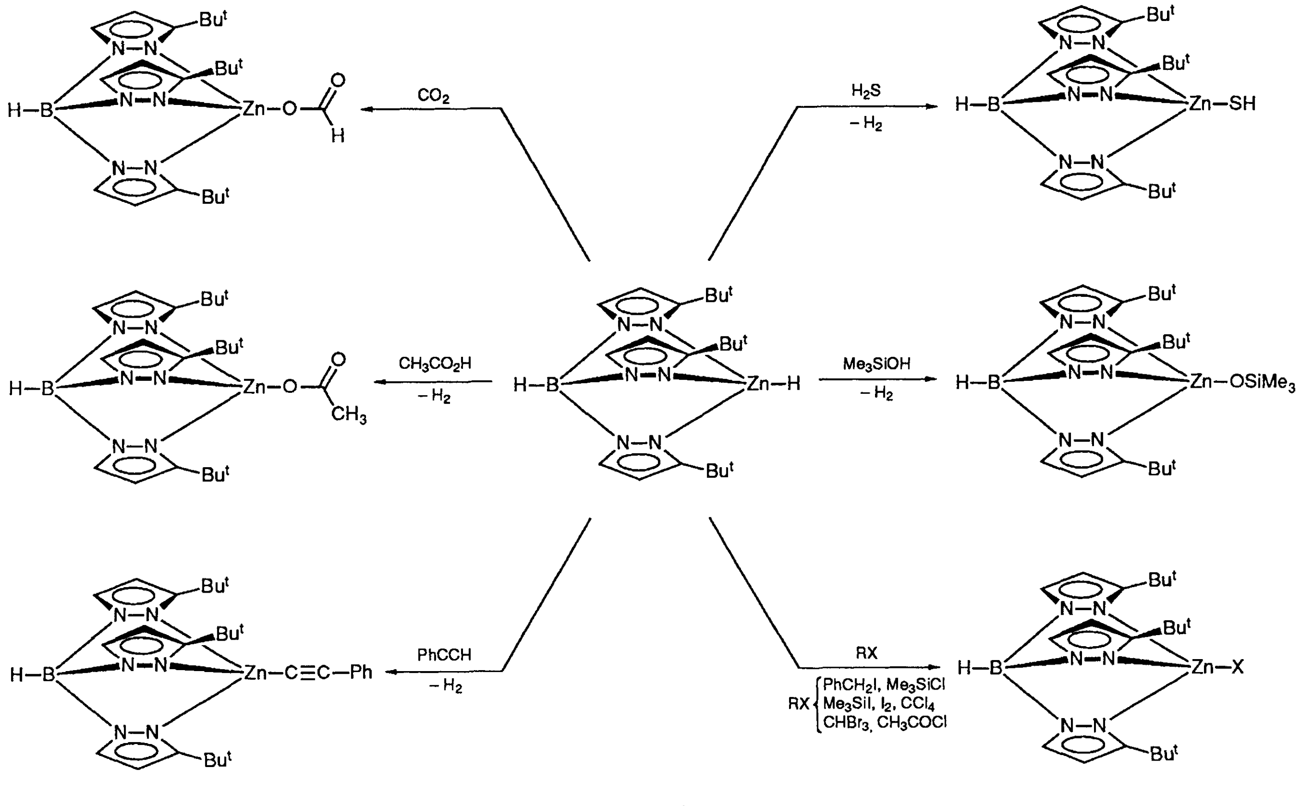
Tris(3-*tert*-butylpyrazolyl)hydroborato Zinc Hydride: Synthesis, Structure and Reactivity of a Monomeric Zinc Hydride Derivative

Runyu Han, Ian B. Gorrell, Adrian G. Looney and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027, USA

The monomeric zinc hydride derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH has been synthesized by the reaction of ZnH_2 with Tl$\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ and its reactivity investigated.

We have recently described the use of the sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand[1] to provide a well-defined coordination environment that has allowed an investigation of the synthesis and reactivity of the monomeric zinc[2] and magnesium[3] alkyl derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$MR (3-Bu^{t}pz = 3-$C_3N_2Bu^tH_2$; M = Zn, Mg). Here we report that the tris(3-*tert*-butylpyrazolyl)hydroborato ligand also allows isolation of the monomeric zinc hydride



Scheme 1

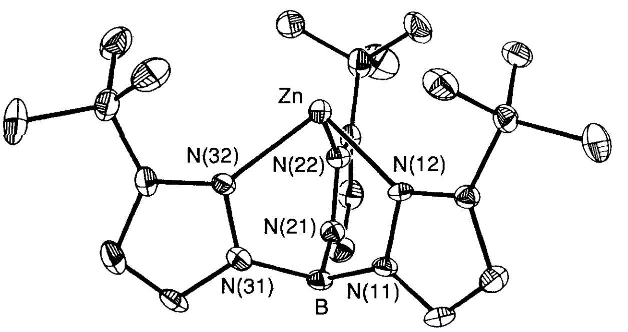


Fig. 1 ORTEP diagram of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH. Selected bond distances (Å) and angles (°): Zn–N(12) 2.078(5), Zn–N(22) 2.089(6), Zn–N(32) 2.079(5); N(12)–Zn–N(22) 90.2(2), N(12)–Zn–N(32) 91.72, N(22)–Zn–N(32) 92.3(2).

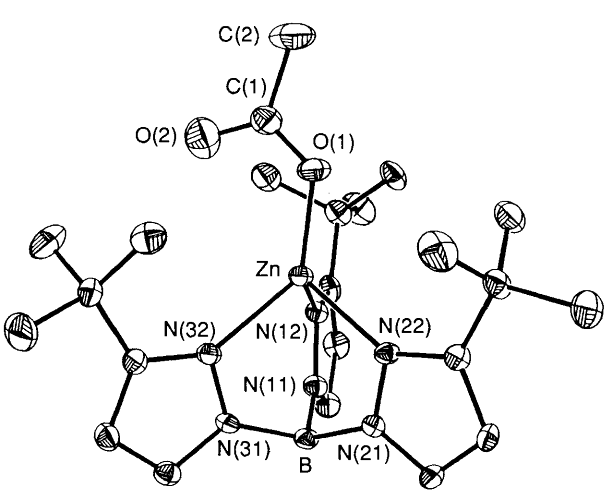


Fig. 2 ORTEP diagram of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn}(\eta^2\text{-O}_2\text{CCH}_3)$. Selected bond distances (Å) and angles (°): Zn–N(12) 2.061(5), Zn–N(22) 2.075(5), Zn–N(32) 2.108(6); Zn–O(1) 1.859(6); N(12)–Zn–N(22) 92.1(2), N(12)–Zn–N(32) 97.0(3), N(22)–Zn–N(32) 91.4(3), N(12)–Zn–O(1) 122.1(3), N(22)–Zn–O(1) 115.6(3), N(32)–Zn–O(1) 129.2(2).

derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH, which has been structurally characterized by X-ray diffraction studies.

The zinc hydride complex $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH is readily prepared by metathesis of ZnH_2[4] with $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ [eqn. (1)].

$$\text{ZnH}_2 \xrightarrow[\text{THF}]{\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{ZnH} \quad (1)$$

The X-ray structure of $\{\eta\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH† (Fig. 1) clearly identifies its monomeric nature. The only other structurally characterized zinc hydride derivative, that we are aware of, is that of dimeric $[\text{HZnN(Me)CH}_2\text{CH}_2\text{NMe}_2]_2$.[5] Several other oligomeric zinc hydride derivatives[4,6] have been reported including $[\text{HZnOC(CH}_3)_3]_4$,[7] $[\text{HZnO(CH}_2)_2\text{NMe}_2]_2$,[8] and $[\text{RZnH(C}_5\text{H}_5\text{N)}]_3$ (R = CH_2CH_3, C_6H_5).[9] Although the hydrogen atom bound to zinc could not be located by the X-ray diffraction study, good evidence for the presence of a Zn–H bond is provided by NMR and IR spectroscopic studies. Thus, the hydride resonance is observed at δ 5.36 in the ^{1}H NMR spectrum, and has been confirmed by the ^{2}H NMR spectrum of the isotopomer $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnD. Similarly, ν(Zn–H) is observed as a strong absorption at 1770 cm^{-1} in the IR spectrum, which shifts to 1270 cm^{-1} ($\nu_\text{H}/\nu_\text{D}$ = 1.39) upon deuterium substitution. The expected axial location of the hydride ligand is clearly suggested by the trigonal coordination of the tris(3-*tert*-butylpyrazolyl)hydroborato ligand illustrated in Fig. 1.

The reactivity of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH is shown in Scheme 1. Protic reagents (HX = H_2S, Me_3SiOH, $\text{CH}_3\text{CO}_2\text{H}$, PhC≡CH) react at the Zn–H bond to give $\{\eta^3\text{-HB-(3-Bu}^t\text{pz)}_3\}$ZnX and H_2. The Zn–H bond also undergoes metathesis with a variety of halide derivatives, *e.g.* CCl_4, CHBr_3, PhCH_2I, CH_3COCl, I_2 and Me_3SiCl, to give $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnX (X = Cl, Br, I). Although $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH does not insert ethylene into the Zn–H bond to give the ethyl derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{ZnCH}_2\text{CH}_3$ (at 120 °C and 1 atm.), a clean insertion of CO_2 is observed at 50 °C to give the η^1-formato derivative, $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn}(\eta^1\text{-O}_2\text{CH})$. The complex is characterized as an η^1-rather than η^2-formato derivative on the basis of the absorptions due to $\nu_\text{asym}(\text{CO}_2)$ [1655 cm^{-1}] and $\nu_\text{sym}(\text{CO}_2)$ [1290 cm^{-1}] in the IR spectrum. These absorptions have been identified by the shifts observed for the isotopomers $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn}(\eta^1\text{-O}_2{}^{13}\text{CH})$ and $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn}(\eta^1\text{-O}_2\text{CD})$. Most notably, the large difference between $\nu_\text{sym}(\text{CO}_2)$ and $\nu_\text{asym}(\text{CO}_2)$ (Δν = 365 cm^{-1}) is very diagnostic of η^1-coordination.‡ In support of these results, the molecular structure of the related η^1-acetato complex $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\text{Zn}(\eta^1\text{-O}_2\text{CCH}_3)$ has been determined by X-ray diffraction as shown in Fig. 2.§ The observation of unidentate rather than bidentate coordination of the formato and acetato ligands in $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn}(\eta^1\text{-O}_2\text{CR})$ (R = H, CH_3) is undoubtably a consequence of the sterically demanding

---

† *Crystal data* for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ZnH: $\text{C}_{21}\text{H}_{35}\text{N}_6\text{BZn}$, M = 447.74, monoclinic, Pn (No. 7), a = 8.262(1), b = 15.465(2), c = 9.696(2) Å, β = 100.76(2)°, V = 1217.2(4) Å^3, Z = 2, ρ (calcd.) = 1.22 g cm^{-3}, μ(Mo-Kα) = 10.6 cm^{-1} (graphite monochromator), F(000) = 476 electrons, T = 295 K, crystal dimensions 0.36 × 0.48 × 0.60 mm. Intensity data were collected on a Nicolet R3m diffractometer using monochromated Mo-Kα X-radiation (λ = 0.71073 Å) and were corrected for Lorentz, polarization and absorption effects. A total of 3464 unique reflections with 3° < 2θ < 45° were collected of which 2100 with $F > 6\sigma(F)$ were used in refinement. 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_CH = 0.96 Å; $U_\text{iso}(\text{H}) = 1.2U_\text{iso}(\text{C})$]. Block-diagonal least-squares refinement converged to R = 0.0410, R_w = 0.0589, GOF = 1.548.

‡ Monomeric carboxylato complexes with Δ values greater than 200 cm^{-1} invariably have unidentate coordination. G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.

§ *Crystal data* for $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn}(\eta^1\text{-O}_2\text{CCH}_3)\cdot(\text{C}_6\text{H}_6)$: $\text{C}_{29}\text{H}_{43}\text{N}_6\text{BO}_2\text{Zn}$, M = 583.90, orthorhombic, $P2_1cn$ (No. 33), a = 10.433(1), b = 15.832(2), c = 19.292(3) Å, V = 3186.4(8) Å^3, Z = 4, ρ (calcd.) = 1.22 g cm^{-3}, μ(Mo-Kα) = 8.3 cm^{-1} (graphite monochromator), F(000) = 1240 electrons, T = 295 K, crystal dimensions 0.42 × 0.60 × 0.66 mm. Intensity data were collected on a Nicolet R3m diffractometer using monochromated Mo-Kα X-radiation (λ = 0.71073 Å) and were corrected for Lorentz, polarization and absorption effects. A total of 3208 unique reflections with 3° < 2θ < 52° were collected of which 2081 with $F > 6\sigma(F)$ were used in refinement. 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_CH = 0.96 Å; $U_\text{iso}(\text{H}) = 1.2U_\text{iso}(\text{C})$]. Block-diagonal least-squares refinement converged to R = 0.0456, R_w = 0.0548, GOF = 1.380. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

environment provided by the tris(3-*tert*-butylpyrazolyl)hydroborato ligand. Interestingly, the related nitrato complex of the slightly less sterically demanding tris(3-phenylpyrazolyl)-hydroborato ligand $\{\eta^3\text{-HB(3-Phpz)}_3\}\text{Zn(NO}_3)$ has recently been structurally characterized by Vahrenkamp *et al.*[10] and found to possess a nitrato ligand which is intermediate between monodentate and bidentate coordination. In particular, the Zn–O bond distances of 1.95 and 2.47 Å in $\{\eta^3\text{-HB(3-Phpz)}_3\}\text{Zn(NO}_3)$ may be compared with the more disparate Zn–O bond distances of 1.86 and 2.95 Å in $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{Zn(}\eta^1\text{-O}_2\text{CCH}_3)$.

In summary, the sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand has allowed isolation of the monomeric zinc hydride derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{ZnH}$, which has been characterized structurally, spectroscopically and chemically.

Acknowledgment is made to the National Science Foundation (Grant CHE 90-07512) and to the donors of the Petroleum Research Fund, administered by the ACS, for support of this research.

Received, 10th January 1991; Com. 1/00115I

References

1 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507.

2 I. B. Gorrell, A. Looney and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1990, 220.

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

4 A. J. De Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **186**, 159.

5 (*a*) N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1968, 823; (*b*) N. A. Bell, P. T. Moseley, H. M. M. Shearer and C. B. Spencer, *J. Chem. Soc., Chem. Commun.*, 1980, 359; (c) N. A. Bell, P. T. Moseley, H. M. M. Shearer and C. B. Spencer, *Acta Crystallogr., Sect. B.*, 1980, **36**, 2950.

6 (*a*) A. J. De Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **195**, 1; (*b*) E. C. Ashby and A. B. Goel, *Inorg. Chem.*, 1981, **20**, 1096; (*c*) A. J. De Koning, J. Boersma and G. J. M. van der Kerk, *Tetrahedron Lett.* 1977, 2547.

7 T. L. Neils and J. M. Burlitch, *Inorg. Chem.*, 1989, **28**, 1607.

8 G. V. Goeden and K. G. Caulton, *J. Am. Chem. Soc.*, 1981, **103**, 7354.

9 A. J. De Koning, J. Boersma and G. J. M. van der Ker, *J. Organomet. Chem.*, 1978, **155**, C5.

10 R. Alsfasser, A. K. Powell and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 898.