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Ligand redistribution reactions of tris(3,5-dimethylpyrazolyl)hydroboratomagnesium alkyl derivatives: crystal structure of $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$

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Abstract

Tris(pyrazolyl)hydroboratomagnesium alkyl derivatives $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}$-MgR ($3,5\text{-Me}_2\text{pz} = 3,5\text{-C}_3\text{N}_2\text{Me}_2\text{H}$; $R = CH_3$, CH_2CH_3, $(CH_2)_3CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$, $CH{=}CH_2$, C_6H_5) undergo ligand redistribution reactions, analogous to the Schlenk equilibrium, to give the bis complex $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$. In contrast, magnesium alkyl derivatives of the more sterically demanding tris(3-t-butylpyrazolyl)hydroborato ligand, $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{MgR}$ ($3\text{-Bu}^t\text{pz} = 3\text{-C}_3\text{N}_2\text{Bu}^t\text{H}_2$), are stable with respect to the formation of $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}_2\text{Mg}$.

We have recently reported the synthesis and reactivity of tris(3-t-butylpyrazolyl)hydroborato magnesium alkyl derivatives, $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{MgR}$ ($3\text{-Bu}^t\text{pz} = 3\text{-C}_3\text{N}_2\text{Bu}^t\text{H}_2$; $R = CH_3$, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$), in which the $\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3$ ligand provides a well defined coordination environment for the study of a series monomeric, solvent-free magnesium alkyl derivatives [1]. In view of the fact that Grignard reagents exist in solution as a complex mixture of species as a result of facile ligand redistribution reactions, e.g. the Schlenk equilibrium (eq. 1) [2*],

$$2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2 \qquad (1)$$

we have investigated the possibility of similar ligand redistribution reactions for the tris(pyrazolyl)hydroborato magnesium alkyl derivatives, $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{MgR}$ and $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgR}$ ($3,5\text{-Me}_2\text{pz} = 3,5\text{-C}_3\text{N}_2(\text{CH}_3)_2\text{H}$). The results demonstrate that, whereas tris(3-t-butylpyrazolyl)hydroborato derivatives are stable with respect to ligand redistribution, the less sterically demanding tris(3,5-dimethyl-

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* Reference number with asterisk indicates a note in the list of references.

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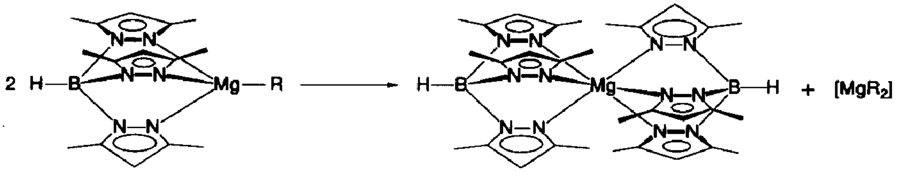
pyrazolyl)hydroborato derivatives are readily converted to the bis complex, $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$.

The alkyl derivatives $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgR}$ ($\text{R} = \text{CH}_3$, CH_2CH_3, $(\text{CH}_2)_3\text{CH}_3$, $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$, CH=CH_2, C_6H_5) [3*] [†] may be prepared by an analogous procedure to that described for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{MgR}$ [1]. Although solutions of the complexes $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgR}$ in benzene are stable at room temperature, a clean transformation to the bis complex $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$ occurs at 80–120 °C (eq. 2).



(2)

($\text{R} = \text{CH}_3$, CH_2CH_3, $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$, CH=CH_2, C_6H_5)

The structure of $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$ has been determined by X-ray diffraction, as shown in Fig. 1 [††]. The two tris(pyrazolyl)hydroborato ligands adopt a mutually staggered conformation and the overall coordination geometry about the centrosymmetric magnesium center is trigonally distorted octahedral. Furthermore, the molecule is distorted from ideal D_{3d} symmetry as a result of rotation of the pyrazolyl planes about their respective N–N axes. As a consequence, the Mg center is not coplanar with any of the pyrazolyl rings and is displaced 0.020, 0.165 and 0.376 Å from the least squares planes of the rings N(11)–N(12), N(21)–N(22) and N(31)–N(32), respectively [4*].

[†] Selected ^{1}H NMR data in C_6D_6:

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgCH}_3$: δ 2.11 and 2.20 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.47 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], −0.25 [s, $\text{MgC}\mathit{H}_3$]

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgCH}_2\text{CH}_3$: δ 2.11 and 2.20 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.46 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], 0.57 [q, $^3J(\text{H–H}) = 8.3$, $\text{MgC}\mathit{H}_2\text{CH}_3$}, 2.14 [t, $^3J(\text{H–H}) = 8.3$, $\text{MgCH}_2\text{C}\mathit{H}_3$].

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{Mg}(\text{CH}_2)_3\text{CH}_3$: δ 2.11 and 2.21 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.46 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], 0.6 [m, $\text{MgC}\mathit{H}_2\text{CH}_2\text{CH}_2\text{CH}_3$], 2.35 [m, $\text{MgCH}_2\text{C}\mathit{H}_2\text{CH}_2\text{CH}_3$], 1.91 [m, $\text{MgCH}_2\text{CH}_2\text{C}\mathit{H}_2\text{CH}_3$], 1.32 [t, $^3J(\text{H–H}) = 7.2$, $\text{MgCH}_2\text{CH}_2\text{CH}_2\text{C}\mathit{H}_3$].

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgCH}(\text{CH}_3)_2$: δ 2.11 and 2.21 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.45 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], −0.82 [septet, $^3J(\text{H–H}) = 7.8$, $\text{MgC}\mathit{H}(\text{CH}_3)_2$], 2.12 [d, $^3J(\text{H–H}) = 7.8$, $\text{MgCH}(\text{C}\mathit{H}_3)_2$].

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pc})_3\}\text{MgC}(\text{CH}_3)_3$: δ 2.11 and 2.22 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.47 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], 1.77 [s, $\text{MgC}(\text{C}\mathit{H}_3)_3$].

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgCH=CH}_2$: δ 2.11 and 2.24 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.46 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], 7.78 [dd, ^3J (H–H(*trans*)) = 23.2 and ^3J(H–H(*cis*)) = 17.2, $\text{MgC}\mathit{H}\text{=CH}_2$], 7.33 [dd, ^3J(H–H(*cis*)) = 17.2 and $^2J(\text{H–H}) = 7.2$, $\text{MgCH=C}\mathit{H}_2$(*cis*)], 6.64 [dd, ^3J(H–H(*trans*)) = 23.2 and $^2J(\text{H–H}) = 7.2$, $\text{MgCH=C}\mathit{H}_2$(*trans*)].

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{MgC}_6\text{H}_5$: δ 2.12 and 2.17 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H})_2\}_3$], 5.46 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$], 8.38 [m, 2H (*ortho*), $\text{MgC}_6\mathit{H}_5$], 7.72 [m, 2H (*meta*), $\text{MgC}_6\mathit{H}_5$], 7.52 [m, 1H (*para*), $\text{MgC}_6\mathit{H}_5$].

$\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$: δ 1.65 and 2.29 [s, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{C}\mathit{H}_3)_2\}_3$], 5.66 [s, $\text{HB}\{\text{C}_3\text{N}_2\mathit{H}(\text{CH}_3)_2\}_3$].

[††] Crystal data for $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Mg}$: triclinic, $P\bar{1}$(No. 2), $a = 8.837(3)$ Å, $b = 10.223(3)$ Å, $c = 10.773(2)$ Å, $\alpha = 63.92(3)°$, $\beta = 85.24(2)°$, $\gamma = 79.87(2)$, $V = 860.4(4)$ Å^3, $Z = 1$, ρ(calcd.) = 1.19 g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 1.0$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å (graphite monochromator); 6225 unique reflections with $3° < 2\theta < 65°$ were collected of which 2483 reflections with $F_o > 6\sigma(F_o)$ were used in refinement; $R = 5.79\%$, $R_w = 7.65\%$, GOF = 1.63.

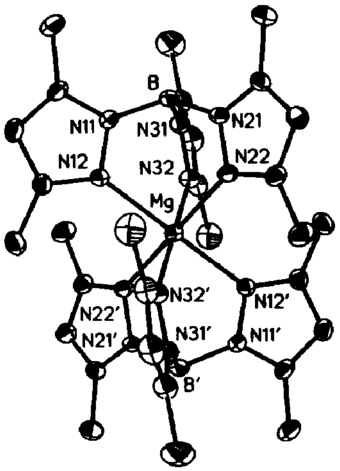


Fig. 1. ORTEP diagram of $\{\eta^3\text{-HB(3,5Me}_2\text{pz)}_3\}_2\text{Mg}$. For clarity, thermal ellipsoids are shown at 20% probability. Selected bond distances (Å) and angles (°): Mg–N(12) = 2.192(2), Mg–N(22) = 2.169(2), Mg–N(32) = 2.197(3); N(12)–Mg–N(2) = 85.6(1), N(12)–Mg–N(32) = 87.0(1), N(22)–Mg–N(32) = 85.6(1), N(12)–Mg–N(12′) = 180.0, N(22)–Mg–N(22′) = 180.0, N(32)–Mg–N(32′) = 180.0, N(12)–Mg–N(22′) = 94.4(1), N(12)–Mg–N(32′) = 93.0(1), N(22)–Mg–N(12′) = 94.4(1), N(22)–Mg–N(32′) = 94.4(1), N(32)–Mg–N(12′) = 93.0(1), N(32)–Mg–N(22′) = 94.4(1).

In contrast to the facile formation of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2\text{Mg}$ from $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgR}$, solutions of the tris(3-t-butylpyrazolyl)hydroborato derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR}$ in benzene are thermally stable. For example, solutions of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgCH}_3$ show no evidence of decomposition after 7 days at 120 °C. This marked difference in reactivity of the $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR}$ and $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgR}$ derivatives is undoubtably a consequence of the sterically demanding environment created by the $\eta^3\text{-HB(3-Bu}^t\text{pz)}_3$ ligand that disfavors the formation of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}_2\text{Mg}$. Indeed, the tris(3-t-butylpyrazolyl)hydroborato ligand has been suggested to effectively restrict a metal center to a maximum of four-coordination [5,6*].

Thus, in conclusion, whereas the complexes $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgR}$ undergo transformations that are analogous to the Schlenk equilibrium, the more sterically demanding tris(3-t-butylpyrazolyl)hydroborato derivatives $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{MgR}$ are not subject to such ligand redistribution reactions.

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References and notes

1 (a) R. Han, A. Looney and G. Parkin, J. Am. Chem. Soc., 111 (1989) 7276, (b) R. Han and G. Parkin, J. Am. Chem. Soc., 112 (1990) 3662.

2 The simple model of the Schlenk equilibrium ($2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$) for describing the composition of Grignard reagents is complicated by a variety of factors including (i) the formation of complexes of each component with either solvent, reactant or product, (ii) the formation of dimeric (or higher order) species, and (iii) the presence of ionic species. (a) B.J. Wakefield, Pure Appl. Chem., 1 (1966) 131; (b) M.S. Kharasch and O. Reinmuth, Grignard Reactions of Nonmetallic Substances, Prentice-Hall, New York, 1954; (c) J. Toney and G.D. Stucky, J. Organomet. Chem., 28 (1971) 5; (d) E.C. Ashby and M.B. Smith, J. Am. Chem. Soc., 86 (1964) 4363; (e) E.C. Ashby and W.E. Becker, J. Am. Chem. Soc., 85 (1963) 118.

3 The syntheses of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgR}$ are typically carried out by addition of 1 equivalent of the appropriate dialkylmagnesium to solutions of $\text{K}\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}$ in Et_2O or THF, and the products isolated after filtration and crystallization in 40–70% yield. For example, a solution of $(\text{CH}_3\text{CH}_2)_2\text{Mg}$ (1 ml of 1.5 *M* in Et_2O, 1.5 mmol) was added dropwise to $\text{K}\{\text{HB(3,5-Me}_2\text{pz)}_3\}$ (0.5 g, 1.5 mmol) in Et_2O (80 mL). The mixture was stirred for 30 minutes at room temperature and filtered. The filtrate was concentrated to ca. 20 ml and placed at 0 ° C giving a crop of colorless crystals. The crystals of $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{MgCH}_2\text{CH}_3$ were isolated by filtration and dried in vacuo (0.26 g, 50%). All complexes have been characterized spectroscopically and analytically.

4 Similar distortions have been observed for other tris(pyrazolyl) hydroborato derivatives. See for example (a) M.R. Churchill, K. Gold and C.E. Maw, Jr., Inorg. Chem., 9 (1970) 1597; (b) M.R. Churchill, B.G. DeBoer, F.J. Rotella, O.M. Abu Salah and M.I. Bruce, Inorg. Chem., 14 (1975) 2051.

5 S. Trofimenko, J.C. Calabrese and J.S. Thompson, Inorg. Chem., 26 (1987) 1507.

6 However, note that the novel 5-coordinate superoxo cobalt complex, $\{\eta^3\text{-HB(3,5-Bu}^t\text{Mepz)}_3\}\text{Co}(\eta^2\text{-O}_2)$, has recently been structurally characterized. J.W. Egan, Jr., B.S. Haggerty, A.L. Rheingold, S.C. Sendlinger, K.H. Theopold, J. Am. Chem. Soc., 112 (1990) 2445.