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Hydrotris(3-neopentylpyrazol-1-yl)borates: A New Type of Sterically Hindered Poly(pyrazolyl)borate

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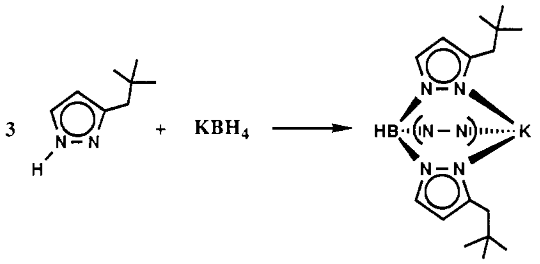
The new ligand hydrotris(3-neopentylpyrazol-1-yl)borate (=L*) was synthesized and found useful in preparing heteroleptic L*ML compounds, by the reaction of its stable L*MCl derivatives with L^-. Examples of L included pseudohalides, in which case L*ML complexes were tetrahedral, various tris(pyrazolyl)borates, which led to octahedral complexes of C_{3v} symmetry, and $H_2B(3,5\text{-}Me_2pz)_2$, which yielded complexes containing five N-bonds to the metal, plus an agostic B–H–M bond. L^*_2M complexes (M = Co, Ni, Fe) were also obtained, as were the complexes $L^*Mo(CO)_2(\pi\text{-methallyl})$ and $L^*Rh(CO)_2$. Structures of the compounds Co[HB(3-neopentylpyrazol-1-yl)$_3$]NCO and Ni[HB(3-neopentylpyrazol-1-yl)$_3$]$_2$ were established by X-ray crystallography. The former complex, $CoON_7C_{25}BH_{40}$, crystallizes in the monoclinic space group $P2_1/n$ (No. 14), with four molecules per unit cell of dimensions a = 12.240 (2) Å, b = 10.496 (2) Å, c = 23.103 (6) Å, and β = 94.52 (2)°, at −70 °C. Least-squares refinement of 316 variables led to a value of the conventional R index (on F) of 0.053 and a value of R_w = 0.051 for 3591 reflections with $I > 3.0\sigma(I)$. The Co(II) ion is coordinated to three pyrazolyl nitrogens of L* and one nitrogen of the linear NCO ligand. The L^*_2Ni complex, $NiCl_2N_{12}C_{49}B_2H_{82}$, crystallizes on the triclinic space group $P\bar{1}$ (No. 2), with one molecule per unit cell of dimensions a = 10.211 (2) Å, b = 12.327 (4) Å, c = 12.932 (2) Å, α = 107.55°, β = 101.49 (1)°, and γ = 106.80 (2)°, at −70 °C. Least-squares refinement of 304 variables led to a value of the conventional R index (on F) of 0.068 and a value of R_w = 0.065 for 3831 reflections with $I > 3.0\sigma(I)$. The Ni(II) ion is coordinated to six pyrazolyl nitrogens of two L* ligands. This complex is five-coordinate in solution, while L^*_2Co is five-coordinate in the solid state but tetrahedral in solution. Both compounds rearrange on heating to high-melting, octahedral complexes containing the mixed ligand HB(3-neopentyl-pz)$_2$(5-neopentyl-pz).

Introduction

It has been shown recently[1] that the complexes [HB(3Pr^{i}4Br-pz)$_3$]MCl are convenient precursors for the synthesis of heteroleptic poly(pyrazolyl)borate compounds [HB(3Pr^{i}4Br-pz)$_3$]ML,[2] where L can be a β-diketonate, dithiocarbamate, tropolonate, oxalate, or any other bidentate ligand; in addition, L can be another poly(pyrazolyl)borate ligand, in which case the [HB(3Pr^{i}4Br-pz)$_3$]ML complexes are either octahedral of C_{3v} symmetry (when L is HB(pz)$_3$, HB(3,5Me$_2$pz)$_3$, or HB(3-(2-thienyl)pz)$_3$)[3] or pseudooctahedral with five pyrazolyl groups and one agostic B–H coordinating to the metal when L is H$_2$B(pz)$_2$, H$_2$B(3,5Mepz)$_2$, or HB(3Phpz)$_3$. While being useful starting materials for these various heteroleptic compounds, the [HB(3Pr^{i}4Br-pz)$_3$]MCl complexes have a potential drawback in the presence of the 4-Br substituent, which might introduce complications in the course of attempted reactions at the metal with Grignard reagents or with organolithium compounds.

To eliminate this potential problem, we sought a halogen-free tris(pyrazolyl)borate ligand which would behave like HB(3Pr^i-4Br-pz)$_3$ in forming reasonably stable, yet reactive, L*MCl complexes. The ligand chosen was hydrotris(3-neopentylpyrazol-1-yl)borate (=L*), which was prepared from 3-neopentylpyrazole with KBH$_4$:



Unlike the case of HB(3Pr^{i}4Br-pz)$_3$, where the isopropyl methyl groups symmetrically straddle the pyrazolyl planes, regardless of whether pointing toward the metal, as in tetrahedral [HB(3Pr^i-4Br-pz)$_3$]CoCl,[4] or away from it, as in octahedral [HB(3Pr^i-4Br-pz)$_3$]Ni[(3,5-Me$_2$pz)$_3$BH],[5] the neopentyl groups in L* must be asymmetric with respect to the pyrazolyl planes. Symmetrical disposition of the neopentyl groups ought to be unfavorable, due to steric interactions of the Bu^t groups either with the pyrazolyl 4-H's or with the metal. Unstrained geometry for the neopentyl groups in L* would place the Bu^t groups roughly at right angles with respect to the pyrazolyl planes, with all Bu^t groups pointing either clockwise or counterclockwise around the B–M axis. This raises the intriguing possibility that if the barrier to rotation of a neopentyl group around the pz–CH$_2$ hinge were high enough (which might require additional blocking substitution at the 4-position or at the metal), one might be able to isolate optically active isomers.

The L* ligand was synthesized, and its coordinative behavior toward a variety of transition metals was investigated and compared with those of HB(3Pr^{i}4Br-pz)$_3$ and of other hindered poly(pyrazolyl)borate ligands. We did not explore the optical activity aspect.

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† Contribution No. 6014.

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Experimental Section

All the chemicals were reagent grade and were used as received. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. Diamagnetic compounds were studied with typical conditions of 16K data points, a sweep width of 3000–4000 Hz, 90° pulse angles, and a recycle time of 4–5 s. Paramagnetic compounds were studied with 64K data points, a sweep width of 100 kHz, 45° pulse angles, and a recycle time of 1.2 s.

3-Neopentylpyrazole. To 52 g (0.96 mol) of dry sodium methoxide stirred in 1 L of toluene was added in one portion a mixture of 100 g (0.88 mol) of methyl neopentyl ketone and 300 mL of ethyl formate. After a short induction period, the solution turned yellow and became a thick paste. This was stirred mechanically with 2 L of hexane, 1 L of water, and 300 mL of isopropyl alcohol, whereupon the solid went into the aqueous phase. The aqueous phase was separated from the mixture and was treated with 44 g (0.88 mol) of hydrazine hydrate and 50 mL of acetic acid. The product was extracted with methylene chloride, and the extracts were stripped of solvent and distilled in vacuo after addition of 10 mL of hydrazine hydrate. Rough distillation afforded material boiling at 110–115 °C/3 Torr, which was redistilled, producing a pure fraction boiling at 101–102 °C/0.7 Torr (lit.[6a] bp 88–91 °C/3 Torr) in 69.4 g (57.3%) yield. Anal. Calc for $C_8H_{14}N_2$: C, 69.6; H, 10.1; N, 20.3. Found: C, 70.0; H, 9.98; N, 20.6. NMR: broad NH peak around 12, d 7.50, d 6.7, s 2.58, and s 0.94 ppm in 1:1:1:2:9 ratio.

Potassium and Thallium Hydrotris(3-neopentylpyrazol-1-yl)borates (KL* and TlL*). A mixture of 230 g (1.67 mol) of 3-neopentylpyrazole and 18.5 g (0.34 mol) of potassium tetrahydroborate was stirred in a 500-mL round-bottom flask and heated in an oil bath, ultimately at 214 °C, until about 26 L of hydrogen, as measured by a wet-test meter, was evolved. The temperature was lowered somewhat, and excess 3-neopentylpyrazole was distilled out at 1 Torr (72 g was recovered in this fashion), leaving a pasty residue, which was recrystallized from heptane. Filtration, washing with hexane, and air-drying yielded 135 g (85.9%) of KL* which could be used directly to prepare the L* complexes.

A sample of KL* was dissolved in THF, and the solution was stirred with excess aqueous thallium nitrate. The product was extracted with methylene chloride, and the extracts were stripped to dryness. Stirring of the residue with methanol produced a white solid, which was filtered off, washed with methanol, and dried, yielding crystals, mp 117–118 °C, after additional recrystallization from methanol. TlL* is very soluble in aliphatic hydrocarbons. IR: BH peaks at 2470, 2440, and 2410 cm^{-1}. ^{1}H NMR: broad peaks at 7.57, 5.95, 2.57, and s 0.90 ppm in 1:1:2:9 ratio. ^{13}C NMR (proton decoupled): d (J = 60.7 Hz) 150.86 (3-C), d (J = 14.5 Hz) 135.62 (5-C), d (J = 29.3 Hz) 105.04 (4-C), d (J = 61.4 Hz) 42.33 (CH_2), s 31.37 ($\mathit{C}(CH_3)_3$), d (J = 57.03 Hz) 29.68 ppm ($\mathit{C}H_3$). Anal. Calc for $C_{24}H_{40}BN_6Tl$: C, 45.9; H, 6.38; N, 13.4. Found: C, 46.2; H, 6.54; N, 13.4.

From the filtrate was isolated a small amount of another Tl salt, which differed from the first crop in the IR spectrum (BH peaks at 2440, 2450, and 2470 cm^{-1}, plus a sharp peak at 950 cm^{-1}, absent in L*Tl). It also had additional peaks in the NMR spectrum (besides those present in L*Tl) at 7.40, 5.92, 2.84, and 0.93 ppm. The ratio of these new peaks to those of L*Tl was about 1:3. This second crop is probably a mixture of L*Tl and [HB(3-neopentyl-pz)$_2$(5-neopentyl-pz)]Tl, since it reacts with MCl_2, producing the [HB(3-neopentyl-pz)$_2$(5-neopentyl-pz)]$_2$M complexes directly.

L*MCl Complexes (M = Co, Ni, Zn). A 0.1 M solution of TlL* in ether was stirred rapidly at room temperature with an aqueous solution of MCl_2 plus 2 M KCl (excess chloride ion suppressed L*$_2$M formation). The color of the tetrahedral L*MCl appeared rapidly and migrated into the ether layer as TlCl precipitated. After 2 h, the layers were separated, and the ether layer was filtered through a 2-cm bed of alumina. Evaporation of the solvent yielded the crude L*MCl complexes (60–80%), which were recrystallized from heptane.

M = Co: deep blue needles, mp 170–171 °C. IR: 2495 cm^{-1}. ^{1}H NMR: 85.1 (5-H), 42.5 (4-H), 21.5 (CH_2), 18.8 (CH_3), –27.2 ppm (broad) (BH) in 3:3:6:27:1 ratio. Anal. Calc for $C_{24}H_{40}BClCoN_6$: C, 55.7; H, 7.73; N, 16.2. Found: C, 55.7; H, 7.91; N, 16.4.

M = Ni: red needles, mp 175–176 °C. IR: 2495 cm^{-1}. Anal. Calc for $C_{24}H_{40}BClN_6Ni$: C, 55.7; H, 7.73; N, 16.2. Found: C, 55.8; H, 7.89; N, 16.5.

M = Zn: white crystals, mp 155–156 °C. IR: 2495 cm^{-1}. ^{1}H NMR: d 7.57 (5-H), d 5.97 (4-H), s 2.72 (CH_2), s 0.93 ppm (CH_3) in 3:3:6:27 ratio. Anal. Calc for $C_{24}H_{40}BClN_6Zn$: C, 55.0; H, 7.63; N, 16.0. Found: C, 55.0; H, 7.39; N, 15.9.

L*MNCO Complexes (M = Co, Ni, Cu, Zn). The above complexes were synthesized by the same procedure as used for L*MCl, except that the aqueous layer contained excess $M(NO_3)_2$ plus 4 equiv of KNCO. An alternative procedure to prepare L*M(pseudohalide) complexes consists of rapidly stirring an L*MCl slurry in a mixture of ethyl acetate and acetonitrile with a large excess of powdered potassium or sodium pseudohalide salt. After several hours, all L*MCl is converted to L*M-(pseudohalide), which can be isolated by filtration of the slurry and evaporation of the solvent.

M = Co: deep blue crystals, mp 198–200 °C. IR: 2495 (BH), 2220 (NCO) cm^{-1}. ^{1}H NMR: 72.3 (5-H), 42.3 (4-H), 6.60 (CH_3), 2.7 (CH_2), –19.0 ppm (BH) in 3:3:27:6:1 ratio. Anal. Calc for $C_{25}H_{40}BCoN_7O$: C, 57.3; H, 7.63; N, 18.8. Found: C, 57.3: h, 8.01; N, 18.5.

M = Ni: burgundy-red needles, mp 202–204 °C. IR: 2495, 2220 cm^{-1}. Calc for $C_{25}H_{40}BN_7NiO$: C, 57.3; H, 7.63; N, 18.8. Found: C, 57.1; H, 7.89; N, 18.5.

M = Cu: brown crystals, mp 162–163 °C. IR: 2490, 2220 cm^{-1}. Anal. Calc for $C_{25}H_{40}BCuN_7O$: C, 56.7; H, 7.56; N, 18.5. Found: C, 56.4; H. 7.73; N, 18.5.

M = Zn: white crystals, mp 200–202 °C. IR: 2495, 2240 cm^{-1}. ^{1}H NMR: d, 7.57 (5-H), d 5.98 (4-H), s 2.63 (CH_2), s 0.92 ppm (CH_3) in 1:1:2:9 ratio. Anal. Calc for $C_{25}H_{40}BN_7OZn$: C, 56.6; H, 7.55; N, 18.5. Found: C, 56.5; H, 7.67; N, 18.3.

L*MNCS Complexes (M = Co, Ni, Zn). These complexes were synthesized by the same method used for their NCO analogs, except that KNCO was replaced with KNCS.

M = Co: blue crystals, mp 198–199 °C. IR: 2515 (BH), 2080 (NCS) cm^{-1}. ^{1}H NMR: 74.5 (5-H), 41.3 (4-H), 7.31 (CH_3), 2.4 (CH_3), –16.5 ppm (BH) in 3:3:27:6:1 ratio. Anal. Calc for $C_{25}H_{40}BCoN_7S$: C, 55.6; H, 7.41; N, 18.2. Found: C, 55.8; H, 7.55; N, 18.0.

M = Ni: burgundy-red crystals, mp 197–199 °C. IR: 2515, 2070 cm^{-1}. Anal. Calc for $C_{25}H_{40}BN_7NiS$: C, 55.6; H, 7.41; N, 18.2. Found: C, 55.3; H, 7.63; N, 18.4.

M = Zn: white crystals, mp 194–196 °C. IR: 2515, 2090 cm^{-1}. ^{1}H NMR: d 7.57, d 6.00, s 2.61, s 0.94 ppm in 1:1:2:9 ratio. Anal. Calc for $C_{25}H_{40}BN_7Zn$: C, 54.9; H, 7.32; N, 17.9. Found: C, 54.8; H, 7.44; N, 17.6.

L*MN$_3$ Complexes (M = Co, Ni, Zn). These complexes were synthesized by the same procedure used for their NCO analogs, except that KNCO was replaced with NaN_3.

M = Co: blue crystals, mp 196–198 °C. IR: 2490, 2080 cm^{-1}. ^{1}H NMR: 72 (5-H), 42 (4-H), 5.0 (CH_3), 0.0 (CH_2), –18 (BH) ppm in 3:3:27:61 ratio. Anal. Calc for $C_{25}H_{40}BCoN_9$: C, 57.2; H, 7.63; N, 24.0. Found: C, 56.9; H, 7.46; N, 23.8.

M = Ni: maroon crystals, mp 182–184 °C. IR: 2495, 2090 cm^{-1}. Anal. Calc for $C_{25}H_{40}BN_9Ni$: C, 57.2; H, 7.63; N, 24.0. Found: C, 57.1: H, 7.59; N, 23.8.

M = Zn: white crystals, mp 196–198 °C. IR: 2495, 2095 cm^{-1}. ^{1}H NMR: d 7.58, d 5.98, s 2.72, s 0.92 ppm in 1:1:2:9 ratio. Anal. Calc for $C_{24}H_{40}BN_9$: C, 54.3; H, 7.54; N, 23.8. Found: C, 54.1; H, 7.59; N, 23.4.

L*CoL Complexes (L = Other Poly(pyrazolyl)borates). These complexes were prepared by stirring equimolar quantities of L*CoCl and the appropriate KL or TlL salt in methylene chloride until precipitation of KCl or TlCl was complete and the solution color changed from blue to yellow. The mixtures were filtered through a bed of Celite, and the filtrates were evaporated to give 60–80% yield of the crude complexes, which were purified by recrystallization from toluene or heptane.

L = HB(pz)$_3$: yellow crystals, mp 211–212 °C. IR: 2470, 2450 cm^{-1} (each a narrow doublet). ^{1}H NMR: 115 (BH), 112 (BH), 92 (5H), 82 (5H′), 46 (4H), 43 (4H′), –21 (CH_3), –102 ppm (CH_2) in 1:1:3:3:3:3:27:6 ratio. Anal. Calc for $C_{33}H_{50}B_2CoN_{12}$: C, 57.0; H, 7.19; N, 24.2. Found: C, 57.3; H, 7.35; N, 24.1.

L = HB(3,5Me$_2$pz)$_3$: yellow crystals, mp 254–256 °C. IR: 2520, 2475, 2450 cm^{-1}. ^{1}H NMR: 107 (BH + BH′), 80 (5-H), 49 (4-H), 47 (4-H′), 43 (5-Me), –18 (Bu^{t}), –76 (3-Me), –99 ppm (CH_2) in [2 (1 + 1)]:#:3:3:9:27:9:6 ratio. Anal. Calc for $C_{39}H_{62}B_2CoN_{12}$: C, 60.1; H, 7.96; N, 21.6. Found: C, 60.0; H, 8.15; N, 21.8.

L = HB(3-(2-thienyl)pz)$_3$: yellow crystals, mp 206–208 °C. IR: 2470, 2450 cm^{-1}. ^{1}H NMR: 96 (BH + BH′), 75 (5-H), 71 (5-H′), 53 (4-H), 46 (4-H′), 7.5 (thienyl 5-H), –3 (thienyl 4-H), –17 (CH_3), –35 (thienyl

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3-H), −88 ppm (CH_2) in [2 (1 + 1)]:3:3:3:3:3:3:27:3:6 ratio. Anal. Calc for $C_{45}H_{56}B_2CoN_{12}S_3$: C, 57.4; H, 5.95; N, 17.8. Found: C, 57.7; H, 6.27; N, 17.5.

L = $H_2B(3,5Me_2pz)_2$: wine-red crystals (from heptane), mp 171–172 °C. IR: BH peaks at 2475, 2450, 2310, 2260, and 2220 cm^{-1}. Anal. Calc for $C_{34}H_{56}B_2CoN_{10}$: C, 59.6; H, 8.18; N, 20.4. Found: C, 59.3; H, 7.99; N, 20.8.

L*Ni[$H_2B(3,5Me_2pz)_2$]: pale blue crystals (from octane), mp 178–180 °C. IR: BH peaks at 2475, 2450, 2310, 2260, and 2220 cm^{-1}. Anal. Calc for $C_{34}H_{56}B_2NiN_{10}$: C, 59.6; H, 8.18; N, 20.4. Found: C, 59.4; H, 8.18; N, 20.8.

L*$_2$M. These complexes were prepared by mixing a THF solution of KL* with an aqueous solution of $M(NO_3)_2$. The product was extracted with methylene chloride, and the extracts were purified by chromatography, followed by evaporation of solvent and crystallization from chloroform/hexane.

L*$_2$Co: wine-red solid. This compound becomes a deep purple melt at 133–136 °C; on further heating, the color begins to fade, and a yellow crystalline solid (the rearranged complex) forms in the 255–260 °C range. IR: 2475, 2460, 2450, 2390 (broad) cm^{-1}. Anal. Calc for $C_{32}H_{80}B_2CoN_{10}$: C, 63.6; H, 8.84; N, 18.6. Found: C, 63.3; H, 8.71; N, 18.5.

L*$_2$Ni: pale purplish-blue solid. This compound melts gradually from 190 °C and rapidly at 212–215 °C, becoming a deep green melt; the color begins to fade from 221 °C, as a pale lilac solid (the rearranged complex) separates, which does not melt up to 320 °C. IR: 2480, 2450 cm^{-1}. Anal. Calc for $C_{32}H_{80}B_2NiN_{10}$: C, 63.6; H, 8.84; N, 18.6. Found: C, 63.2; H, 8.60; N, 18.7.

Other L*$_2$M complexes were prepared similarly, but they were characterized by IR only; on the basis of the similarity of its IR spectrum to that of the L*$_2$Ni complex, L*$_2$Fe was assigned an octahedral structure, while the spectrum of L*$_2$Cu resembled that of L*$_2$Co.

Rearranged Complexes [HB(3-neopentyl-pz)$_2$(5-neopentyl-pz)]$_2$M (M = Co, Ni, Fe). These compounds were prepared either by heating the L*$_2$M complexes in the melt to 220–240 °C or by recrystallizing them from *o*-dichlorobenzene, anisole, or xylene. In each case, only the rearranged product crystallized. The rearranged complexes were also isolated as minor byproducts and identified by their characteristic IR spectra, in the course of preparing L*MX complexes. They could also be obtained by the reaction of M(II) salts with the "high-solubility" Tl salt, recovered from the filtrates during the synthesis of L*Tl.

[HB(3-neopentyl-pz)$_2$(5-neopentyl-pz)]$_2$Co: yellow solid, mp 307–309 °C dec. IR: 2490, 2464 cm^{-1}. Anal. Calc for $C_{32}H_{80}B_2CoN_{12}$: C, 63.6; H, 8.84; N, 18.6. Found: C, 63.4; H, 8.75; N, 18.52.

[HB(3-neopentyl-pz)$_2$(5-neopentyl-pz)]$_2$Ni: pale lilac solid, not melting up to 312 °C. IR: 2490, 2460 cm^{-1}. Calc for $C_{32}H_{80}B_2NiN_{12}$: C, 63.6; H, 8.84; N, 18.6. Found: C, 63.7; N, 8.92; N, 18.3.

[HB(3-neopentyl-pz)$_2$(5-neopentyl-pz)]$_2$Fe: This complex was prepared by rearrangement of L*$_2$Fe. It had an IR spectrum almost identical to that of L*$_2$Ni (BH peaks at 2470 and 2440 cm^{-1}) and was thus assumed to be octahedral. After recrystallization from boiling anisole, a cream-colored solid was obtained; mp 283–285 °C dec. IR: 2490, 2460 cm^{-1}. Anal. Calc for $C_{32}H_{80}B_2FeN_{12}$: C, 54.1; H, 11.3; N, 23.7. Found: C, 53.9; H, 11.4; N, 23.5.

L*Rh(CO)$_2$. This complex was prepared by the reaction of L*Tl with $[Rh(CO)_2Cl]_2$ in methylene chloride. After filtration to remove TlCl, the filtrate was concentrated and chromatographed on alumina. The yellow eluate was stripped of solvent, and the residue was recrystallized from heptane/toluene; mp 176–178 °C. IR: 2490, 2056, 1995, 1085 (sh), 1976 cm^{-1}. Anal. Calc for $C_{18}H_{40}BN_6O_2Rh$: C, 44.4; H, 8.23; N, 17.3. Found: C, 44.3; H, 8.32; N, 17.0.

L*Mo(CO)$_2$(η^3-CH$_2$CMeCH$_2$). This complex was obtained by the reaction of L*K or L*Tl with $Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2Cl$[6b] in methylene chloride, followed by filtration and chromatography on alumina, collecting the yellow band. After solvent evaporation, the residue was recrystallized from isopropyl alcohol and was obtained as yellow crystals, mp 171–171 °C, in 60–70% yield. IR: 2495, 2480, 1922, 1822 cm^{-1}. ^1H NMR: d 7.54 (2 H, 5-H), d 7.12 (1 H, 5-H′), d 6.08 (1 H, 4-H′), d 5.95 (2 H, 4-H), s 3.44 (2 H, Bu^t CH$_2$), s 3.40 (1 H), s 3.35 (1 H), s 3.24 (2 H, syn), s 2.62 (1 H), s 2.58 (1 H), s 1.41 (2 H, anti), s 1.11 (9 H, Bu^t), s 0.93 (3 H, methallyl CH$_3$), s 0.76 ppm (18 H, Bu^t). The signals at 3.40, 3.35, 2.62, and 2.58 ppm are for nonidentical neopentyl methylene protons, as was established through a ^1H–^{13}C cross-coupling experiment. ^{13}C NMR: 228.9 (CO), 156.4 and 155.2 (1:2, 3-C), 136.8 and 135.2 (2:1, 5-C), 106.8 and 103.0 (2:1, 4-C), 87.9 (π-allyl central C), 66.2 (π-allyl CH$_2$), 43.4 and 42.7 (1:2, neopentyl CH$_2$), 32.4 and 31.4 (2:1, *C*(CH$_3$)$_3$), 30.2 and 29.2 (1:2, C(*C*H$_3$)$_3$), 18.0 ppm (π-allyl CH$_3$). Anal. Calc: C, 57.1; H, 7.46; N, 13.3. Found: C, 56.8; H, 7.38; N, 13.0.

Table I. Crystal Data for Co[HB(3-neopentyl-pz)$_3$]NCO (I) and Ni[HB(3-neopentyl-pz)$_3$]$_2$ (II)

	I	II
mol formula	$CoON_7C_{25}BH_{40}$	$NiCl_2N_{12}C_{49}B_2H_{82}$
M_r	524.38	990.52
a, Å	12.240 (2)	10.211 (2)
b, Å	10.496 (2)	12.327 (4)
c, Å	23.103 (6)	12.932 (2)
α, deg	90	107.55 (2)
β, deg	94.52 (2)	101.49 (1)
γ, deg	90	106.80 (2)
V, Å^3	2858.8	1410.8
Z	4	1
space group	$P2_1/n$	$P\bar{1}$
radiation	Mo Kα	Mo Kα
temp, °C	−70	−70
abs coeff, cm^{-1}	6.04	4.81
min–max 2θ, deg	1.8–60.0	5.7–52.0
no. of reflns [($I > 3\sigma(I)$]	3594	3831
no. of params	316	304
esd	1.6	2.07
R	0.053	0.068
R_w	0.051	0.065

For comparison, ^{13}C NMR spectra for the related complexes $[HB(pz)_3]Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ and $[HB(3,5Me_2pz)_3]Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ were obtained. The former had peaks at 227.3 (CO), 144.2 (3-C, broad), 135.6 (5-C), 105.6 (4-C), 83.8 (π-allyl central C), 59.3 (CH$_2$), and 18.5 ppm (CH$_3$), and the latter had peaks at 229.0 (CO), 153.5 and 152.4 (1:2, 3-C), 146.0 and 143.4 (2:1, 5-C), 108.2 and 106.2 (2:1, 4-C), 88.7 (π-allyl central C), and 64.5 ppm (CH$_2$) and five methyl peaks at 19.2, 16.6, 15.7, 13.0, and 12.9 ppm, which contained two 2:1 peak pairs. They could not be assigned without ambiguity.

X-ray Data Collection and Structure Solution and Refinement for Co[HB(3-neopentyl-pz)$_3$]NCO (I). Crystals suitable for diffraction were obtained by evaporation of solvent from a heptane solution of the compound. The crystal was encapsulated in a glass capillary that was then placed on an Enraf-Nonius CAD4 diffractometer, which showed a typical peak width at half-height to be ca. 0.14° at −70 °C. The cell parameters were then refined on the basis of 19 reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I. Intensity data were collected by the ω-scan technique and treated for a 6% decrease in intensity over the course of the experiment.

The structure was solved by automated Patterson analysis (PHASE), followed by the usual Fourier methods, yielding one molecule in a general position. The model was refined by full-matrix anisotropic least-squares calculations on F and included hydrogen atoms as fixed atom contributions in ideal positions.[7] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[8] Hydrogen atom positions were calculated with C–H and B–H distances of 0.95 Å. No attempt was made to refine hydrogen atoms, although most hydrogens, including the BH hydrogens were visible on a difference map. Least-squares refinement converged to $R = 0.053$ and $R_w = 0.051$. Attempts to model the high thermal motion of the isocyanate group by several half-atoms were unsuccessful, and the most satisfactory model was that of the normal anisotropic motion. The largest peak in the final difference Fourier map was 0.38 e/Å^3.

The final positional and thermal parameters of the refined atoms and complete distances and angles are available as supplementary material.

X-ray Data Collection and Structure Solution and Refinement for Ni[HB(3-neopentyl-pz)$_3$]$_2$ (II). Crystals suitable for diffraction were obtained by evaporation of solvent from a methylene chloride solution of the compound. The crystal was encapsulated in a glass capillary that was then placed on the Enraf-Nonius CAD4 diffractometer, which showed a typical peak width at half-height to be ca. 0.19° at −70 °C. The cell parameters were then refined on the basis of 25 reflections chosen from diverse regions of reciprocal space. The solution and refinement methods were similar to those described above.

The structure was solved by automatic Patterson analysis, with the asymmetric unit consisting of half the molecule related by an inversion

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(7) All crystallographic calculations were performed on a DEC/CRAY computer network using a system of programs developed by J. C. Calabrese. Plots were made with the ORTEP program (C. K. Johnson, 1971).

(8) *International Tables of X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

center, in addition to the presence of a partially occupied methylene chloride solvate molecule (occupancy determined by the refinement to be ~0.40). Anisotropic least-squares refinement converged to $R = 0.068$ and $R_w = 0.065$. The largest peak on the final difference map, 1.47 e/Å^3, was near the disordered methylene chloride solvate molecule.

The final positional and thermal parameters of the refined atoms and complete bond distances and angles are available as supplementary material.

Results and Discussion

The reaction of excess 3-neopentylpyrazole (pz*) with KBH_4 proceeded readily to yield the isolable K[HB(pz*)$_3$] salt, characterized as the Tl derivative. NMR data (^{1}H and ^{13}C) indicated regiospecific purity, with all neopentyl groups in the 3-position. The presence of a single peak for both methylene protons was suggestive of a dynamic process making them equivalent. This could be either a full rotation of the neopentyl group around the pz–CH_2 bond or a "windshield-wiper"-type motion around the same bond. In either case, the rotations had to be synchronous for all three neopentyl groups, to avoid "collision" of the *tert*-butyl groups at the rotational midpoint. Strong ^{13}C–^{205}Tl coupling was observed for all carbons ranging from a high of 61.4 Hz for CH_2 and a close second of 60.7 Hz for C-3 to a low of 14.5 Hz for C-5. This is noteworthy, since none of the other known thallium hydrotris(pyrazolyl)borates exhibit a coupling of C-5 to Tl. The coupling for the *tert*-butyl methyls was 57.0 Hz, much lower than in the case of [HB(3Bu^{t}pz)$_3$]Tl[9] (171 Hz) or [HB(3Bu^{t}5Mepz)$_3$]Tl[10] (197.4 Hz), commensurate with the greater distance of these methyls from the Tl atom. ^{1}H–^{205}Tl coupling was indicated by the broadening of the 3-H, 4-H, and CH_2 proton signals.

The intermediates L*MCl, useful as starting materials for the heteroleptic complexes L*ML, were obtained by the reaction of MCl_2 with L*Tl, and they were purified by recrystallization from hydrocarbon solvents or by sublimation. The complexes L*MX (X = NCS, NCO, N_3) could be prepared either directly from L* and MX_2 or indirectly by the phase-transfer reaction of L*MCl in methylene chloride with a concentrated aqueous solution of KX. Their structures were tetrahedral, with end-on M–N bonding, on the basis of IR spectra.[11,12] The main difference, in comparing these L*MX complexes with their [HB(3Pr^{i}4Br-pz)$_3$]MX analogs, was that L*NiNCS was tetrahedral and monomeric, while [HB(3Pr^{i}4Br-pz)$_3$]NiNCS was an NCS-bridged dimer.[10] Five-coordinate, solvated, L*NiNCS complexes could be obtained with various donor solvents and reconverted to the unsolvated L*NiNCS complexes by heating in vacuo.

The structure of L*CoNCO was determined by X-ray crystallography (see Figure 1). The molecule is tetrahedral, with trigonal distortion. The neopentyl groups, which are all in the 3-position, are oriented to yield nearly 3-fold symmetry, in such a way as to minimize steric interactions in the molecule. Two of the neopentyl groups are nearly perpendicular to their corresponding pyrazole rings (both 83.5°), while the third is not (76.4°). The isocyanate group deviates only slightly from linearity (Co–N–C = 161.9°). The Co–N(NCO) distance is 1.892 (4) Å, as compared with 1.911 (3) Å in [HB(3Bu^{t}pz)$_3$]CoNCS and 1.927 (12) Å in [HB(3Pr^{i}4Br-pz)$_3$]CoNCS. From this X-ray structure, it appears that the neopentyl group is capable of free rotation around the pz–CH_2 bond.

To compare the reactivity of L*MCl with that of [HB(3Pr^{i}4Br-pz)$_3$] in forming mixed octahedral poly(pyrazolyl)borates, L*CoCl was converted to L*ML complexes where L was HB(pz)$_3$, HB(3,5Me$_2$pz)$_3$, and HB(3-(2-thienyl)pz)$_3$. These octahedral compounds were characterized by analysis and by their paramagnetic NMR spectra, which showed the presence of each ligand and all neopentyl groups still in the 3-positions. The ease of forming these complexes was comparable to that for [HB(3Pr^{i}4Br-pz)$_3$]CoCl.

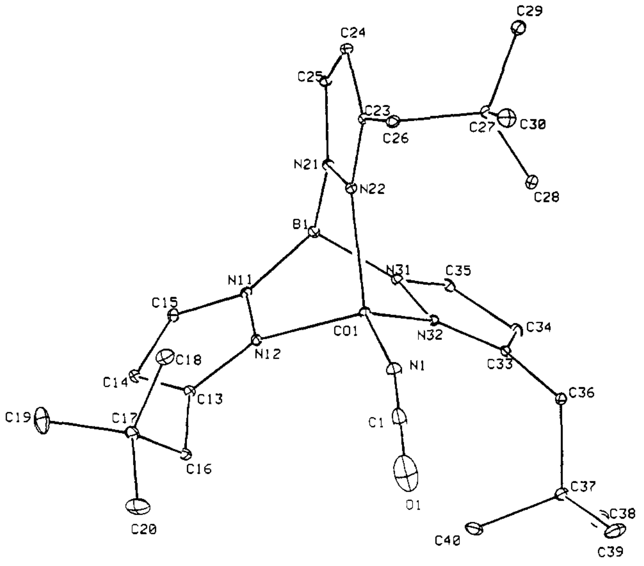

Figure 1. View of Co[HB(3-neopentylpyrazolyl-1-yl)]NCO.

The reaction of L*MCl with [H$_2$B(3,5Me$_2$pz)$_2$]K yielded the complexes L*Co[H$_2$B(3,5Me$_2$pz)$_2$] and L*Ni[H$_2$B(3,5Me$_2$pz)$_2$]. They had identical IR spectra containing two distinct BH patterns: an asymmetric doublet at 2475, 2450 cm^{-1} and a symmetric triplet at 2310, 2260, 2220 cm^{-1}. The Co complex was wine-red and the Ni complex pale blue, again suggesting the presence of five-coordinate structures with one agostic B–H–M bond, similar to those encountered in the HB(3Pr^{i}4Br-pz)$_3$ system.

Unlike the HB(3Pr^{i}4Br-pz)$_3$ ligand, HB(3-neopentyl-pz)$_3$ readily formed L*$_2$M (M = Co, Ni, Fe) complexes. They were not isomorphous: the Ni complex had a pale lilac color, characteristic of an octahedral Ni tris(pyrazolyl)borate species, while the Co complex was not yellow, as an octahedral Co tris(pyrazolyl)borate would be, but rather wine-red, which is typical of five-coordinate Co in heteroleptic tris(pyrazolyl)borates.[2] The IR spectra of the Ni and Co complexes were markedly different in the BH and the 800–1100-cm^{-1} regions. The IR spectrum of L*$_2$Fe resembled that of the L*$_2$Ni, and these complexes were assumed to have similar structures. Since we were not sure if six neopentyl groups could be fitted into the equatorial belt of an octahedral L*$_2$M complex and because the "octahedral" color for L*$_2$Ni could also exist in a six-coordinate structure containing agostic B–H–Ni bonds [as was found in the related [HB(3Pr^{i}4Br-pz)$_3$]Co[(3Phpz)$_3$BH] complex], an X-ray structure determination for L*$_2$Ni was undertaken.

Surprisingly, it turned out that L*$_2$Ni is indeed octahedral in the solid state, with six neopentyl groups in the equatorial belt (see Figure 2). They all are turned, propeller-like in one direction, so that the molecule does not have D_{3d} symmetry, but this sideways turn of the *tert*-butyl groups away from the metal more extensive than in the L*CoNCO complex. The H_2C–CMe_3 bond is twisted by about 160°, approaching coplanarity with the pz ring, while in L*CoNCO the average value for this twist is 81°. In both cases, the *tert*-butyl group is pointed away from the metal, which leads to reduction of the equatorial congestion. Clearly, the equatorial zone in L*$_2$Ni can tolerate six neopentyl groups much less than the relatively unstrained metal environment in L*CoNCO.

The average Ni–N distance 2.115 (3) Å is slightly shorter than that found for the HB(3Pr^{i}4Br-pz)$_3$ ligand in the heteroleptic complex [HB(3Pr^{i}4Br-pz)$_3$]Ni[(pz)$_3$BH] (2.15 Å) but longer than that for the HB(pz)$_3$ ligand in the above complex (2.07 Å)[2] or for HB(3,5Me$_2$pz)$_3$ in the mixed complex [HB(3Pr^{i}4Br-pz)$_3$]-

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[9] Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Trofimenko, S. *J. Organomet. Chem.* **1989**, *365*, 19–22.

[10] Trofimenko, S.; Calabrese, J. C.; Kochi, J. K.; Wolowiec, S.; Hulsbergen, F. B.; Reedijk, J. *Inorg. Chem.*, in press.

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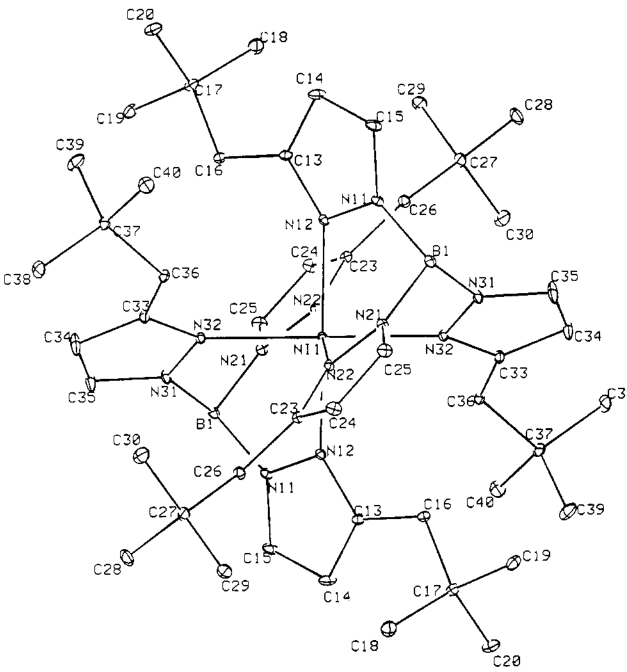

Figure 2. View of $Ni[HB(3\text{-neopentylpyrazol-1-yl})_3]_2$.

$Ni[(3,5Me_2pz)_3BH]$ (2.07 Å).[5] In general, the Ni–N distance increases as one goes from tetrahedral ($[HB(3Bu^t5Mepz)_3]NiNCS$, 2.00 Å), through five-coordinate dimer ($[HB(3Pr^i4Brpz)_3]NiNCS]_2$, 2.07 Å), to octahedral (2.07–2.18 Å). In addition, the substituent location in the $HB(pz)_3$ ligand does play a role in octahedral complexes. Thus in the complex $[HB(3Pr^ipz)_2(5Pr^ipz)]_2Ni$, which contains a rearranged ligand, the Ni–N distance is 2.17 Å when Pr^i is in the 3-position but only 2.10 Å when it is in position 5.

The octahedral structure of $L^*{}_2Ni$, present in the solid state, is not retained in the melt or in solution, where the compound is green, which is typical of five-coordinate Ni. Similarly, the $L^*{}_2Co$ complex, which is probably five-coordinate in the solid state, becomes tetrahedral in solution or in the melt, as manifested by its deep purple color.

The three complexes $L^*{}_2Co$, $L^*{}_2Fe$, and $L^*{}_2Ni$, on heating in the melt or in solution, are transformed into isomorphous, high-melting octahedral complexes, where L* must have undergone rearrangement to $HB(3\text{-neopentyl-pz})_2(5\text{-neopentyl-pz})$, as has been observed earlier for complexes of the $HB(3Pr^i4Xpz)_3$ ligand (X = H, Br). The recrystallized, high-melting materials (Co, 307–309 °C dec; Fe, 283–285 °C dec; Ni, no melting up to 312 °C) had totally superimposable IR spectra. Their low solubility precluded the measurement of NMR spectra.

The same materials were obtained from a second, more soluble, crop of the Tl salt, implying some formation of the asymmetric ligand during the original reaction of KBH_4 with Hpz*.

In all the above compounds, the NMR spectra showed only a single proton peak for the neopentyl methylene group, implying either complete rotation or free "windshield-wiper" motion around the pz–CH_2 bond. The only exception was found in the complex $L^*Mo(CO)_2(\pi\text{-methallyl})$. In this complex, the three pyrazolyl groups exhibit a 2:1 pattern due to restricted rotation around the B–Mo axis, as had been found in other reported $[RB(pz^*)_3]Mo(CO)_2(\pi\text{-allyl})$ complexes.[13] The neopentyl methylene protons appear as one singlet (2 H) and two pairs of singlets (1 H each), the identity of which was confirmed by ^1H–^{13}C cross-coupling experiments and by comparison of the ^{13}C spectrum with the ^{13}C spectra of the related $[HB(pz)_3]Mo(CO)_2(\pi\text{-methallyl})$ and $[HB(3,5Me_2pz)_3]Mo(CO)_2(\pi\text{-methallyl})$ complexes. The latter spectrum shows a 2:1 pattern for the pyrazolyl groups based on carbons 3, 4, and 5, while in the $HB(pz)_3Mo(CO)_2(\pi\text{-methallyl})$ spectrum shows that all pz groups are identical, with only a small broadening of the 3-C signal. This is consistent with the room-temperature ^1H spectrum reported earlier.[13] We assume that the single CH_2 peak in $L^*Mo(CO)_2(\pi\text{-methallyl})$ is due to the methylene which fits in the ample space between the carbonyl groups and can rotate, while the unique nonexchangeable protons are on methylenes crowded between the CO and the π-methallyl group.

Conclusions

The easily prepared, halogen-free, new ligand hydrotris(3-neopentylpyrazol-1-yl)borate (=L*) is suitable for the preparation of stable L*MCl precursors for the synthesis of heteroleptic L*ML complexes, particularly those where L is another poly(pyrazolyl)-borate ligand.

It also forms $L^*{}_2M$ complexes with first-row transition metals, the structure of which is metal-dependent. For instance, $L^*{}_2Ni$ is octahedral in the solid state but five-coordinate in the melt or in solution; $L^*{}_2Co$ is five-coordinate in the solid state but tetrahedral in the melt or in solution. Both $L^*{}_2Co$ and $L^*{}_2Ni$ rearrange on heating to the thermally very stable complexes $[HB(3\text{-neopentyl-pz})_2(5\text{-neopentyl-pz})]_2M$, in which one of the neopentyl groups has migrated from the 3- to the 5-position. This underscores the driving force toward octahedral structures in these compounds and the difficulty of maintaining six neopentyl groups in the equatorial belt of $L^*{}_2M$ complexes.

The neopentyl group is capable of free rotation, as manifested by a single peak for the neopentyl $-CH_2-$ protons; only in the sterically crowded $L^*Mo(CO)_2(\pi\text{-methallyl})$ complex are *two* pairs of methylene protons all nonequivalent. It appears that a bulky substituent in the 4-position would be required to prevent rotation of the neopentyl group around the pyrazolyl plane.

The steric effect of neopentyl groups in the 3-positions of a tris(pyrazolyl)borate ligand cannot be uniquely assessed, as compared with the effect of isopropyl groups: in some ways neopentyl is "larger" (the L*NiNCS complex is monomeric, while $[HB(3Pr^i4Br\text{-pz})_3]NiNCS$ is a dimer, involving μ-S bridging) and in some ways "smaller" than isopropyl (octahedral $L^*{}_2Ni$ was isolated, but its 3-isopropyl analog is unknown). For this reason, the 3-neopentyl group cannot be placed exactly in the hierarchy of steric hindrance of $HB(3Rpz)_3$ ligands but may be regarded as roughly equivalent to an isopropyl group: H < 2-thienyl < methyl < phenyl < neopentyl ≈ isopropyl < *tert*-butyl.

Supplementary Material Available: Tables of positional and isotropic thermal parameters and complete bond distances and angles for I and II (12 pages). Ordering information is given on any current masthead page.

Registry No. I, 143493-71-4; II, 143493-81-6; L*, 143493-88-3; KBH_4, 13762-51-1; KL*, 143493-65-6; TlL*, 143493-66-7; $[HB(3\text{-neopentyl-pz})_2(5\text{-neopentyl-pz})]Tl$, 143493-67-8; L*CoCl, 143493-68-9; L*NiCl, 143493-69-0; L*ZnCl, 143493-70-3; L*NiNCO, 143307-31-7; L*CuNCO, 143493-72-5; L*ZnNCO, 143493-73-6; L*CoNCS, 143307-57-7; L*NiNCS, 143307-27-1; L*ZnNCS, 143307-58-8; L*CoN3, 143307-59-9; L*NiN3, 143307-34-0; L*ZnN3, 143307-60-2; $L^*Co[HB(pz)_3]$, 143493-74-7; $L^*Co[HB(3,5\text{-}Me_2pz)_3]$, 143493-75-8; $L^*Co[HB((2\text{-thienyl})pz)_3]$, 143493-76-9; $L^*Co[H_2B(3,5\text{-}Me_2pz)_3]$, 143493-77-0; $L^*Ni[H_2B(3,5\text{-}Me_2pz)_2]$, 143493-78-1; $L^*{}_2Co$, 143493-79-2; $L^*{}_2Fe$, 143493-82-7; $L^*{}_2Cu$, 143493-83-8; $[HB(3\text{-neopentyl-pz})_2(5\text{-neopentyl-pz})]_2Co$, 143493-84-9; $[HB(3\text{-neopentyl-pz})_2(5\text{-neopentyl-pz})]_2Ni$, 143493-85-0; $[HB(3\text{-neopentyl-pz})_2(5\text{-neopentyl-pz})]_2Fe$, 143493-86-1; $L^*Rh(CO)_2$, 143493-87-2; $L^*Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$, 143507-85-1; $[Rh(CO)_2Cl]_2$, 14523-22-9; $Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2Cl$, 97590-30-2; 3-neopentylpyrazole, 29075-47-6; methyl neopentyl ketone, 590-50-1; ethyl formate, 109-94-4; hydrazine, 302-01-2.

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