Synthesis and Transition Metal Complexation of an Enantiomerically Pure Tris(pyrazolyl)hydroborate Ligand

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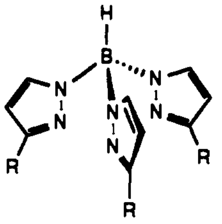
Received September 11, 1992

Tris(pyrazolyl)hydroborate ligands (**1**) are well-known to be useful for the preparation of a wide range of complexes of metal ions from throughout the periodic table.[1] Particularly reactive species important in organometallic,[2] inorganic,[3] and bioinorganic chemistry[4] have been stabilized by using sterically hindered ligand variants derived from pyrazoles containing simple alkyl or aryl substituents at the 3-position.[5] The "fence" enclosing the remaining binding site(s) on metal ions coordinated to these bulky ligands attenuates the complexes' nuclearity, geometry, spectroscopic properties, and reactivity. We reasoned that if optically active centers were affixed to the ligand frame at the pyrazolyl rings' 3-position, a novel C_3-symmetric *chiral* cavity useful for effecting asymmetric metal-mediated reactions would result.[6-8] In this communication we report a practical synthesis of such a ligand and demonstrate its versatile metal ion binding properties via the isolation and characterization of its complexes with Zn(II), Ni(II), Cu(II), and Co(II).



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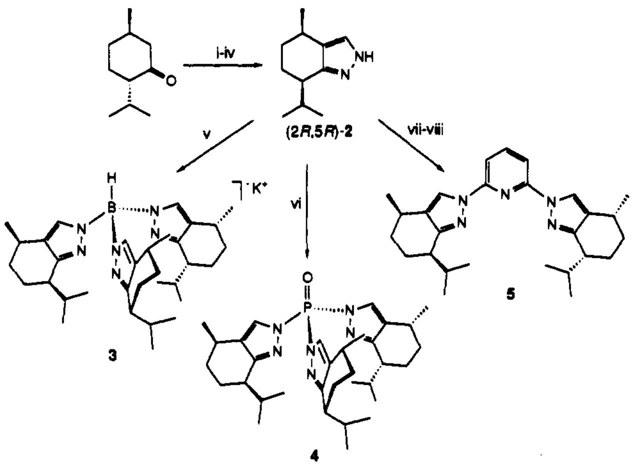
R = H, alkyl, aryl

Scheme I[a]



[a] Reagents and Conditions: (i) NaOMe, HCO_2Et; (ii) N_2H_4, MeOH, Δ; (iii) H_2SO_4, Et_2O, fractional crystallization; (iv) aqueous $NaHCO_3$; (v) KBH_4, DMAC, anisole, Δ; (vi) $POCl_3$, NEt_3, PhH, Δ; (vii) K, diglyme, Δ; (viii) 2,6-dibromopyridine.

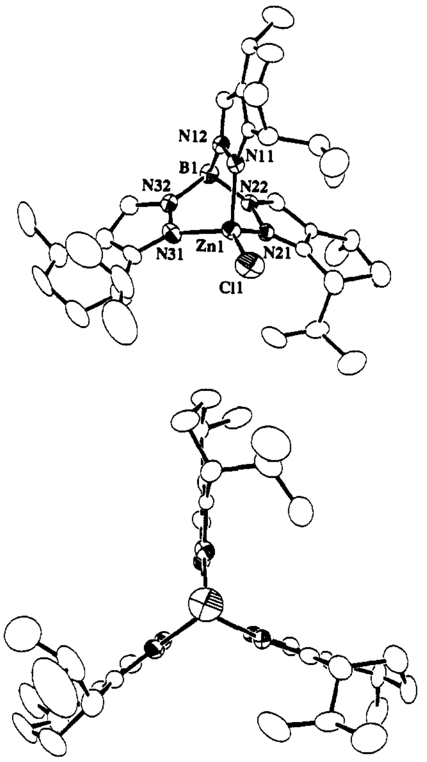


Figure 1. Top: ORTEP drawing of **6** showing 60% probability thermal ellipsoids and atom labels for all non-hydrogen atoms (hydrogen atoms and labels for carbon atoms omitted for clarity). Bottom: View down Cl1-Zn1 bond (atom labels omitted for clarity). Selected interatomic distances (Å) and angles (deg) are as follows: Zn1-Cl1, 2.168(2); Zn1-N11, 2.026(5); Zn1-N21, 2.047(5); Zn1-N31, 2.037(6); Cl1-Zn1-N11, 118.1(2); Cl1-Zn1-N21, 124.6(2); Cl1-Zn1-N31, 126.2(2); N11-Zn1-N21, 91.0(2); N11-Zn1-N31, 96.0(2); N21-Zn1-N31, 92.2(2).

As outlined in Scheme I, commercially available (2*S*,5*R*)-menthone (95%) was formylated[9] and then heated with hydrazine to form pyrazole **2** as a 9:1 mixture of diastereomers.[10] Pure

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[7] A tris(pyrazolyl)hydroborate with stereogenic centers three bonds removed from the pyrazolyl rings[7a] and an optically active tetrakis(camphorpyrazolyl)borate[7b] have been isolated: (a) Scheck, T. Ph.D. Thesis, Universität Regensburg, Regensburg, Germany, 1991. (b) Brunner, H.; Singh, U. P.; Boeck, T.; Altmann, S.; Scheck, T.; Wrackmeyer, B., submitted for publication.

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[9] Contrary to a previous report (Potapov, V. M.; Kiryushkina, G. V.; Talebarovskaya, I. K.; Shapet'ko, N. N.; Radushnova, I. L. *Zh. Org. Khim.* **1973**, *9*, 2134-2140), the major diastereomer formed upon formylation of menthone has syn (2*R*,5*R*) stereochemistry.

0002-7863/93/1515-1153$04.00/0

(2*R*,5*R*)-**2** (>97% by ^{1}H NMR) was isolated by fractional crystallization of the bisulfate salts followed by release of the free base [21 g, 31% yield from menthone, $[\alpha]^{23}_{D} = +43.3°$ (*c* 2.5, $CHCl_3$)]. Thermolysis of (2*R*,5*R*)-**2** in the presence of KBH_4 (0.33 equiv, 1.5 h in dimethylacetamide, 6.5 h in anisole) yielded the desired ligand K[HB((2*R*,5*R*)-menthylpz)$_3$] [**3**; 46% based on (2*R*,5*R*)-**2**] contaminated by unreacted (2*R*,5*R*)-**2**. Isolation of pure **3** proved difficult, so the crude ligand was used directly to precipitate the complexes [HB((2*R*,5*R*)-menthylpz)$_3$]MCl [M = Zn (**6**) or Ni (**7**)] by adding the appropriate metal(II) halide in MeOH. Additional complexes [HB((2*R*,5*R*)-menthylpz)$_3$]MX [X = Cl, M = Cu (**8**) or Co (**9**); X = OAc, M = Cu (**10**) or Ni (**11**); X = NO_3, M = Cu (**12**) or Ni (**13**)] were prepared by metal exchange with **6** or by coligand metathesis reactions. We have also synthesized other potentially useful multidentate optically active ligands from (2*R*,5*R*)-**2**, including phospine oxide **4** (a neutral analog of **3**) and pyridine **5** (a C_2-symmetric meridianal binder).[11]

Similarities among the properties of the complexes of **3**[10] and those of known analogs containing hindered achiral tris(pyrazolyl)hydroborate ligands[4c,5a,12] support assignment of tetrahedral geometries to **7–9** and square pyramidal structures to **10–13**.[13] The absolute configuration of the ligand was obtained, and its tridentate C_3-symmetric coordination mode was confirmed by an X-ray crystal structure analysis of **6** (Figure 1).[14] The propellor of alternating isopropyl groups and hydrogen atoms fixed at the periphery of the metal-centered ligand cavity in **6** provides a unique and highly directed asymmetric environment which contrasts with the topology of complexes of previously reported camphorpyrazole ligands in which the alternating array of dimethylmethano and ethano moieties forms a torus well-removed from incoming substrates.[6,7a]

The practical synthesis of (2*R*,5*R*)-**2**, its elaboration into ligands **3–5**, and the isolation and characterization of a series of first-row transition metal complexes of **3** represent significant first steps in the development of a new class of chiral, C_3-symmetric catalysts and metal-centered templates for stereoselective molecular recognition. In view of the prevalence of tris(pyrazolyl)hydroborate complexes in the contemporary organometallic and inorganic chemical literature,[1-5] the recent successes in the use of optically active N-donor ligands in asymmetric synthesis,[15] and the ready accessibility and novel structural features of **3** (e.g., fixed, convergent, and highly sterically differentiated C_3 array of stereogenic centers), we believe that there exists a wide range of promising options for future enantioselective reactivity studies of its complexes.

Acknowledgment. We thank Professor Doyle Britton for his work on the X-ray structure of **6**, Bijan Mossadeghi for the initial synthesis of **5**, and Professor H. Brunner (Universität Regensburg) for a preprint and a copy of the Ph.D. thesis of T. Scheck. Funding for this research was provided by the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant CHE-9207152), the University of Minnesota's Undergraduate Research Opportunities Program (D.D.L.), and the University of Minnesota.

Supplementary Material Available: Preparative procedures and analytical and spectroscopic data for **2-13** and fully labeled ORTEP drawing, fractional coordinates, bond distances, bond angles, and anisotropic thermal parameters for **6** (24 pages); observed and calculated structure factor amplitudes for the X-ray structure of **6** (27 pages). Ordering information is given on any current masthead page.

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[10] Synthetic procedures and analytical and spectroscopic data for all new compounds are reported in the supplementary material.

[11] Camphorpyrazole analogs of **5**: Watson, A. A.; House, D. A.; Steel, P. J. *J. Org. Chem.* **1991**, *56*, 4072–4074.

[12] (a) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452–2456. (b) Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9707–9708. (c) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3210–3212.

[13] A preliminary X-ray structure analysis of **11** confirmed assignment of a square pyramidal geometry to the complex (see supplementary material).

[14] X-ray data for **6** $C_{33}H_{52}N_6BZnCl$, *MW* 644.46, space group $P2_12_12_1$ (No. 19) at −101 °C: $a = 9.658(7)$ Å, $b = 17.777(7)$ Å, $c = 20.058(6)$ Å, $V = 3444(5)$ Å^3, $Z = 4$. For 4055 unique, observed reflections with $I > 2\sigma(I)$ (including Friedel pairs collected to $\theta = 20°$) and 379 variable parameters $R = 0.063$ and $R_w = 0.049$. Refinement using the opposite enantiomer converged to $R = 0.073$ and $R_w = 0.061$. Full tables of positional and thermal parameters, bond lengths and angles, and observed and calculated structure factor amplitudes are reported in supplementary material.

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A [W(CO)$_5$·THF]-Mediated Pauson–Khand Reaction: Cyclizations of 1,6-Enynes via a Batch-Catalytic Protocol

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Received October 13, 1992

The Pauson–Khand cyclization reaction (PKCR) merges alkyne, alkene, and carbon monoxide subunits into a common cyclopentenone ring.[1] The most widely used source of CO for these reactions is (a stoichiometric quantity of) dicobalt octacarbonyl. The only other reported metal carbonyl precursor to effectively cyclize enynes is Fe(CO)$_5$.[2] As part of our study of cyclization reactions of enynes with various Fischer carbene species, we observed the unexpected formation of the bicyclic cyclopentenone **2a** as a minor byproduct from reaction of 1,6-enyne **1a** with a tungsten-containing Fischer carbene [(CO)$_5$W=CMe(OMe)]. We speculated and then demonstrated that tungsten pentacarbonyl was the likely species which mediated that particular reaction.[3] This observation was unprecedented and of sufficient interest that we have studied and now report various aspects including the batch-catalytic nature of this new method of cyclopentenone synthesis.

Enynes **1a–j** were treated with preformed W(CO)$_5$·THF in a THF solution at 65–110 °C for 6–20 h to provide the bicyclo[3.3.0]octenones **2a–j** in the yields stated in Table I. The "parent" allyl propargyl malonate and *gem*-dimethylated substrates **1a** and **1b** cyclize smoothly when reacted with W(CO)$_5$·THF (W-PKCR), producing cyclopentenones **2a** and **2b**.[4] Minor byproducts of reductive cyclization and/or alkyne reduction, presumably via tungsten hydride containing intermediates, were always observed

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