both THF and THF-d_8 serving as the solvent. Freshly distilled samples of THF and THF-d_8 were added to separate evacuated glass bulbs, each containing freshly distilled sodium–potassium alloy. Both solvents were stored, with intermittent agitation, in these evacuated bulbs for 24 h to several days prior to use. Exactly 1.0 mL of the solvents was then distilled directly into graduated tubes on the separate all glass apparatuses. Each apparatus contained a sealed capillary tube charged with 4–5 mG of naphthalene and freshly distilled sodium mirror. These apparatuses were then sealed from the vacuum system and agitated so as to break the capillary tubes and expose the resulting naphthalene solutions to the metal mirrors. Identical experiments were carried out with two different samples of THF-d_8 (99% isotopic purity) that were purchased on different dates from Cambridge Isotope Laboratories. The THF was purchased from Aldrich Chemical Co.

The presence of a salt in the deuteriated solvent that is not present in the protiated solvent could result in the observation of a smaller value for A_{Na} in the isotopically heavy solvent. However, a salt impurity could not distill with solvent, and since both appratuses were identical and charged with identical materials, the lower A_{Na} for the THF-d_8 solutions could not have arisen from this origin.

The EPR spectra were recorded with a Bruker ER-200 EPR spectrometer with a 9-in. magnet and a dual cavity system. A sample in THF was placed into the back cavity and a sample in THF-d_8 in the front cavity. Both spectra were then recorded several times, after which the samples were interchanged and the spectra recorded again. After a recording of the complete spectra to demonstrate that the species being observed was indeed the naphthalene anion radical (Figure 1), the first two lines of each spectra were recorded using a 1.2 or 1.4 G sweep width. After correcting for the cavity bias, this small scan range allowed the accurate determination of the sodium splitting. A cavity bias in our spectrometer system of 1.90 mG was found. That is, splittings in the back cavity were found to be 1.90 mG larger than those in the front cavity for identical samples, but the distance between the first two lines of the THF samples was found to be larger than that for the THF-d_8 for all recordings regardless of the relative sample positions.

For the experiments carried out with the Gaussmeter (a Bruker NMR Gaussmeter Model ER 035 M), the magnetic field was recorded when the recorder pen was in the center (at the point it crossed the base line) of each of the four ($m = -3/2$ and $m = -1/2$ for the samples in THF and THF-d_8) first derivative lines. The scan was stopped at these four positions, and the field as indicated by the Gaussmeter was recorded.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE-9011801) and the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this work.

Chiral Heterocyclic Ligands. 7. Syntheses of Some Chiral 2,6-Di-*N*-pyrazolylpyridines

Andrew A. Watson, Donald A. House, and Peter J. Steel*

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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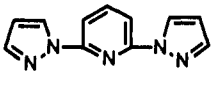
2,2′-Bipyridine (bpy)[1] and 2,2′:6′,2″-terpyridine (terpy)[2] have long been extensively employed as bidentate and tridentate chelating ligands in both preparative and analytical coordination chemistry. More recently, many related ligands have been synthesized in which one or both of the pyridine rings of bpy are replaced by other five- or six-membered aromatic nitrogen heterocycles.[3] Such replacements can significantly modify the properties of the resulting complexes, and it is now possible to tune, in a predictable manner, the ground- and excited-state properties of complexes such as the well-studied $Ru(bpy)_3^{2+}$ complex by replacing one or more of the bpy ligands with other biheteroaromatics.[3,4]

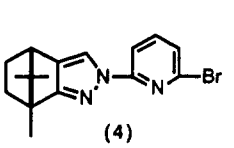
Planar tridentate terheteroaromatic analogues of terpy are less common. Very recently, however, the syntheses of 2,6-di-*N*-pyrazolylpyridine (1) and a number of sub-



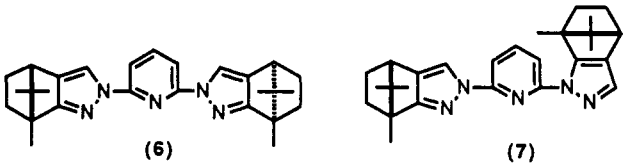
(1) (2)

stituted derivatives were described.[5-7] We had also prepared a number of these ligands and confirm the physical and spectroscopic properties reported by Jameson and Goldsby.[5] In addition, we have prepared a number of chiral derivatives of 1 for potential use as chiral auxiliaries in asymmetric catalysis. As part of ongoing studies of new chiral heterocyclic ligands[8] and of pyrazole-containing ligands,[9] we now report the syntheses and properties of these new ligands that were prepared from the homochiral camphor-derived pyrazole 2.[8,10]

Reaction of 2,6-dibromopyridine (3) with 4 equiv of the sodium salt of the anion of 2 in refluxing THF gave a mixture of four products that were separated by radial chromatography and identified as the two isomeric monosubstituted products 4 and 5 and the two disubstituted



(4) (5)



(6) (7)

products 6 and 7. The two isomers 4 and 5 were distinguished by NMR spectroscopy, which has previously[8] been used to differentiate between the products of alkylation of each of the two nonequivalent nitrogens of 2. This was also used to identify the symmetrical product 6, which, like the major monosubstituted product 4, results from preferential reaction of the less hindered nitrogen. The C_2

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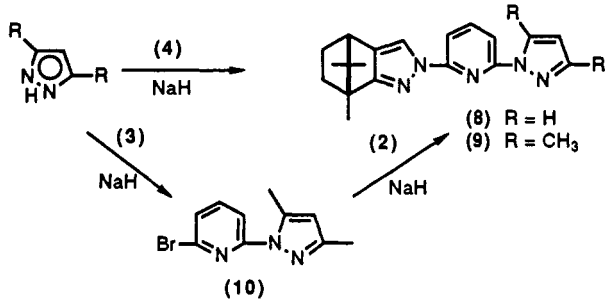
symmetry present in **6** is likely to be advantageous for applications in asymmetric catalysis.[11,12] The structure of **7** followed from the lack of symmetry in its ^1H and ^{13}C NMR spectra, which were both able to be completely assigned by comparison with the spectra of the other ligands.[13] Significantly better yields of the singly and doubly substituted products **4** and **6** were obtained by reaction of **3** with 1 and 4 equiv, respectively, of the potassium salt of **2** in diglyme at 125 °C.

Unsymmetrical disubstituted products were prepared in a manner analogous to that reported by Jameson and Goldsby[5] by reaction of monosubstituted products with a second, but different, pyrazolate anion. Thus, reaction of **4** with sodium pyrazolate and sodium 3,5-dimethylpyrazolate in refluxing THF gave the disubstituted products **8** and **9**, respectively. Alternatively, **9** was prepared as the major product by initial reaction with sodium 3,5-dimethylpyrazolate to give the monosubstituted product **10** (along with a small amount of the previously reported[5] disubstituted 2,6-bis(3,5-dimethyl-*N*-pyrazolyl)pyridine (**11**)) followed by reaction with the anion of **2**. Again, better yields were obtained for the introduction of a second pyrazole by using the potassium salt in hot diglyme.



In order to assess the coordinating ability of these new ligands, copper(II) complexes were prepared by reaction of an equimolar mixture of the ligand and copper perchlorate followed by addition of sodium thiocyanate. The ligands **7**, **9**, and **11** gave green crystalline solids analyzing for a $[CuL(NCS)](ClO_4)$ formulation, whose infrared spectra indicated the presence of coordinated thiocyanate and noncoordinated perchlorate. With **6**, an orange crystalline solid was obtained that analyzed for a $[CuL(NCS)_2]$ formulation, analogous to the complexes previously reported for 2,6-bis(*N*-pyrazolylmethyl)pyridines.[8d] Further details of the properties of these and other complexes will be reported elsewhere.

Experimental Section

General Methods. NMR spectra were recorded with a Varian XL-300 for $CDCl_3$ solutions. Infrared spectra were recorded on a Shimadzu IR27G or Pye Unicam SP3-300 spectrophotometer. Mass spectra were recorded with a Kratos MS80RFA spectrometer. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck Type 60 P.F.$_{254}$ silica gel. Solvents were dried and distilled before use.

General Reaction Procedures. Method A. To a suspension of NaH (50% dispersion in oil) in dry THF was added the appropriate pyrazole, and the resulting mixture was stirred at room temperature for 1 h. The bromopyridine was then added and the resulting solution stirred and refluxed overnight. After addition of water, the product was extracted with ether. The organic extract was dried (Na_2SO_4) and evaporated under reduced pressure to give a product mixture, a sample of which was absorbed onto a 2-mm silica radial chromatography plate. Elution with pentane/ether (20:1) gave the pure products described in the following text.

Method B.[14] Equimolar quantities of the appropriate pyrazole and potassium metal were reacted at 70 °C in anhydrous 2-methoxyethyl ether until the metal dissolved. An equimolar quantity of the bromopyridine was then added, and the mixture was stirred at 120–130 °C for 3–4 days. The solvent was removed under reduced pressure to give a crude product mixture that was purified as described previously.

Method C.[14] The same as Method B, except that a 4:1 ratio of potassium pyrazolate/bromopyridine was used.

2-Bromo-6-[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl]pyridine (4): yield method A, 60%, method B, 78%; mp 107.5–108.5 °C; ν_{max} (KBr) 2900, 1580, 1450, 1300, 1120, 1040, 920, 780 cm^{-1}; ^1H NMR (300 MHz) δ_H 0.70 (s, 3 H, *syn*-8′-CH_3), 0.99 (s, 3 H, *anti*-8′-CH_3), 1.25 (m, 1 H, *endo*-H5′), 1.33 (s, 3 H, 7′-CH_3), 1.41 (m, 1 H, *endo*-H6′), 1.89 (m 1 H, *exo*-H6′), 2.11(m, 1 H, *exo*-H5′), 2.82 (d, 1 H, H4′), 7.18 (d, 1 H, H3), 7.54 (t, 1 H, H4), 7.77 (d, 1 H, H5), 8.05 (s, 1 H, H3′); ^{13}C NMR δ_C 10.5 (7′-CH_3), 18.9 (*anti*-8′-CH_3), 20.6 (*syn*-8′-CH_3), 27.4 (C5′), 33.6 (C6′), 46.9 (C4′), 50.3 (C8′), 59.9 (C7′), 110.2 (C5), 119.0 (C3′), 123.0 (C3), 129.8 (C3a′), 139.6 (C2), 140.2 (C4), 170.6 (C7a′). Anal. Calcd for $C_{16}H_{18}BrN_3$: C, 57.8; H, 5.5, N, 12.7. Found: C, 57.2; H, 5.3; N, 12.6.

2-Bromo-6-[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1-indazolyl]pyridine (5): yield method A, 10%, method B, 8% (oil); ^1H NMR (300 MHz) δ_H 0.80 (s, 3 H, *syn*-8′-CH_3), 0.95 (s, 3 H, *anti*-8′-CH_3), 1.09 (m, 1 H, *endo*-H5′), 1.38 (m, 1 H, *endo*-H6′), 1.56 (s, 3 H, 7′-CH_3), 1.89 (m, 1 H, *exo*-H6′), 2.08 (m, 1 H, *exo*-H5′), 2.79 (d, 1 H, H4′), 7.30 (d, 1 H, H3), 7.38 (s, 1 H, H3′), 7.61 (t, 1 H, H4), 7.85 (d, 1 H, H5); ^{13}C NMR δ_C 13.8 (7′-CH_3), 20.0 (*anti*-8′-CH_3), 20.4 (*syn*-8′-CH_3), 27.5 (C5′), 33.1 (C6′), 47.1 (C4′), 55.5 (C8′), 63.2 (C7′), 112.7 (C5), 124.6 (C3), 132.8 (C3a′), 134.8 (C3′), 139.2 (C2), 140.2 (C4), 154.5 (C7a′); HRMS calcd for $C_{16}H_{18}{}^{81}BrN_3$ $M^{\bullet+}$ 333.0665, found $M^{\bullet+}$ 333.0665.

2,6-Bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl]pyridine (6): yield method A, 12%, method C, 70%; mp 212–213 °C; ^1H NMR (300 MHz) δ_H 0.73 (s, 6 H, *syn*-8′-CH_3), 0.99 (s, 6 H, *anti*-8′-CH_3), 1.27 (m, 2 H, *endo*-H5′), 1.35 (s, 6 H, 7′-CH_3), 1.43 (m, 2 H, *endo*-H6′), 1.89 (m, 2 H, *exo*-H6′), 2.12 (m, 2 H, *exo*-H5′), 2.83 (d, 2 H, H4′), 7.57 (d, 2 H, H3 and H5), 7.75 (t, 1 H, H4), 8.10 (s, 2 H, H3′); ^{13}C NMR δ_C 10.6 (7′-CH_3), 19.0 (*anti*-8′-CH_3), 20.7 (*syn*-8′-CH_3), 27.6 (C5′), 33.7 (C6′), 47.0 (C4′), 50.3 (C8′), 60.0 (C7′), 106.8 (C3/5), 118.5 (C3′), 129.2, (C3a′), 140.5 (C4), 150.8 (C2/6), 169.9 (C7a′); HRMS calcd for $C_{27}H_{33}N_5$ $M^{\bullet+}$ 427.2736, found $M^{\bullet+}$ 427.2739.

2-[(4*S*,7*R*)-7,8,8-Trimethyl-4,5,6,7-tetrahydro-4,7-methano-1-indazolyl]-6-[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl]pyridine (7): yield method A, 8%, method C, 10% (oil); ^1H NMR (300 MHz) δ_H 0.74 (s, 3 H, *syn*-8″-CH_3), 0.80 (s, 3 H, *syn*-8′-CH_3), 0.95 (s, 3 H, *anti*-8′-CH_3), 1.00 (s, 3 H, *anti*-8″-CH_3), 1.35 (s, 3 H, 7″-CH_3), 1.42 (s, 3 H, 7′-CH_3), 2.82 (d, 1 H, H4′), 2.85 (d, 1 H, H4″), 7.38 (s, 1 H, H3′), 7.53 (dd, 1 H, H5), 7.80 (m, 2 H, H4 and H3), 8.02 (s, 1 H, H3″); ^{13}C NMR δ_C 10.6 (7″-CH_3), 13.0 (C7′-CH_3), 19.0 (*anti*-8″-CH_3), 19.9 (*anti*-8′-CH_3), 20.4 (*syn*-8′-CH_3), 20.7 (syn-8″-CH_3), 27.5, (C5″), 27.8 (C5′), 32.8 (C6′), 33.7 (C6″), 47.1 (C4′/C4″), 50.3 (C8″), 54.5 (C8′), 60.0 (C7″), 63.6 (C7′), 109.3 (C5), 111.5 (C3), 118.7 (C3″), 129.5 (C3a″), 131.9 (C3a′), 134.0 (C3′) 140.4 (C4) 151.0 (C2/6) 153.9 (C7a′) 170.0 (C7a″); HRMS calcd for $C_{27}H_{33}N_5$ $M^{\bullet+}$ 427.2736, found $M^{\bullet+}$ 427.2745.

2-*N*-Pyrazolyl-6-[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl]pyridine (8): yield method A, 52% (oil); ^1H NMR (300 MHz) δ_H 0.74 (s, 3 H, *syn*-8″-CH_3), 1.00 (s, 3 H, *anti*-8″-CH_3), 1.28 (m, 1 H, *endo*-H5″), 1.35 (s, 3 H, 7″-CH_3), 1.44 (m, 1 H, *endo*-H6″), 1.90 (m, 1 H, *exo*-H6″), 2.14 (m, 1 H, *exo*-H5″), 2.85 (d, 1 H, H4″), 6.47 (dd, 1 H, H4′) 7.71 (m, 3 H, H3′, H3, and H5), 7.84 (dd, 1 H, H4), 8.11 (s, 1 H, H3″), 8.55 (d, 1 H, H5′); ^{13}C NMR δ_C 10.6 (7″-CH_3), 19.0 (*anti*-8″-CH_3), 20.7 (*syn*-8″-CH_3), 27.5 (C5″), 33.7 (C6″) 47.0 (C4″), 50.3 (C8″),

(11) For a review on C_2 symmetry and asymmetric induction, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

(12) For asymmetric catalysis by C_2-symmetrical chiral 2,6-di-2-oxazolinylpyridines, see: Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846.

(13) The isomer with C_2 symmetry that results from double arylation at the more hindered nitrogen was not observed.

(14) We thank Mr. I. G. Phillips for performing some experiments.

60.0 (C7″), 107.3, (C4′), 107.6 (C5), 108.8 (C3), 118.5 (C3″), 126.8 (C5′), 129.6 (C3a″), 140.9 (C4), 142.1 (C3′), 170.2 (C7a″); HRMS calcd for $C_{19}H_{21}N_5$ $M^{\bullet+}$ 319.1797, found $M^{\bullet+}$ 319.1800.

2-(3,5-Dimethyl-*N*-pyrazolyl)-6-[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl]pyridine (9): yield method A, 11%, method C, 60%; mp 132.5–134 °C; ν_{max} (KBr) 2900, 1590, 1440, 1360, 1290, 940, 780 cm^{-1}; ^1H NMR (300 MHz) δ_H 0.73 (s, 3 H, *syn*-8″-CH_3), 1.00 (s, 3 H, *anti*-8″-CH_3), 1.24 (m, 1 H, *endo*-H5″), 1.35 (s, 3 H, 7″-CH_3), 1.43 (m, 1 H, *endo*-H6″), 1.90 (m, 1 H, *exo*-H6″), 2.13 (m, 1 H, *exo*-H5″), 2.31 (s, 3 H, 3′-CH_3), 2.74 (s, 3 H, 5′-CH_3), 2.83 (d, 1 H, H4″), 6.01 (s, 1 H, H4′), 7.62 (dd, 1 H), 7.68 (dd, 1 H, H3 and H5) 7.80 (dd, 1 H, H4), 7.98 (s, 1 H, H3″); ^{13}C NMR δ_C 10.6 (7″-CH_3), 13.6 (3′-CH_3), 15.1 (5′-CH_3), 19.0 (*anti*-8″-CH_3), 20.7 (*syn*-8″-CH_3), 27.5 (C5″), 33.7 (C6″), 47.1 (C4″), 50.3 (C8″), 60.0 (C7″), 107.8 (C5), 109.2 (C4′), 110.4 (C3), 118.6 (C3″), 129.4 (C3a″), 140.5 (C4), 141.2 (C5′), 149.8 (C3′), 170.0 (C7a″). Anal. Calcd for $C_{21}H_{25}N_5$: C, 72.6; H, 7.3; N, 20.2. Found: C, 72.0; H, 7.3; N, 19.9.

2-Bromo-6-(3,5-dimethyl-*N*-pyrazolyl)pyridine (10): yield method A, 52%; mp 75.5–76.5 °C ν_{max} (KBr) 1570, 1420, 1400, 1110, 970, 780, 710 cm^{-1}; ^1H NMR (300 MHz) δ_H 2.28 (s, 3 H, 3′-CH_3), 2.65 (s, 3 H, 5′-CH_3), 5.99 (s, 1 H, H4′), 7.29 (d, 1 H, H3), 7.60 (t, 1 H, H4), 7.84 (d, 1 H, H5); ^{13}C NMR δ_C 13.6 (3′-CH_3), 14.7 (5′-CH_3), 109.7 (C4′), 113.5 (C5), 124.2 (C3), 138.8 (C2), 140.2 (C4), 142.2 (C5′), 150.5 (C3′). Anal. Calcd for $C_{10}H_{10}BrN_3$: C, 47.6; H, 4.0; N, 16.7. Found: C, 47.8; H, 3.8; N, 16.9.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of all new ligands. Preparations, elemental analyses and IR spectra of the copper complexes of the ligands (15 pages). Ordering information is given on any current masthead page.

Three-Center Transition Structures for Alkene Hydroboration and Alkylborane Rearrangement

Nicolaas J. R. van Eikema Hommes and Paul von Ragué Schleyer*

Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Germany

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The mechanistic details of alkene hydroboration,[1] one of the basic reactions in modern organic chemistry,[2] have intrigued both experimental and theoretical chemists for more than three decades.[3-7] Several basic questions remain unanswered, which we will address in this paper using high-level ab initio theory: (1) Is there a π-complex intermediate in the hydroboration reaction? (2) What is the structure of the transition state? Does it have four-center[4-6] or three-center[7] character? (3) Does the alkylborane rearrangement occur intramolecularly, or does it proceed intermolecularly, by Brown's[2] dissociation/recombination mechanism? We also emphasize the importance of including electron correlation in the geometry optimizations.

Prior semiempirical[4] and Hartree Fock ab initio[5,8] calculations on model olefin hydroboration reactions indicate the formation of weakly bound π-complexes, four-center transition states, and activation barriers between 6 and 12 kcal/mol. However, the barriers decrease when electron correlation is taken into account.[6,8] Indeed, for the parent reaction of borane and ethylene, no transition structure

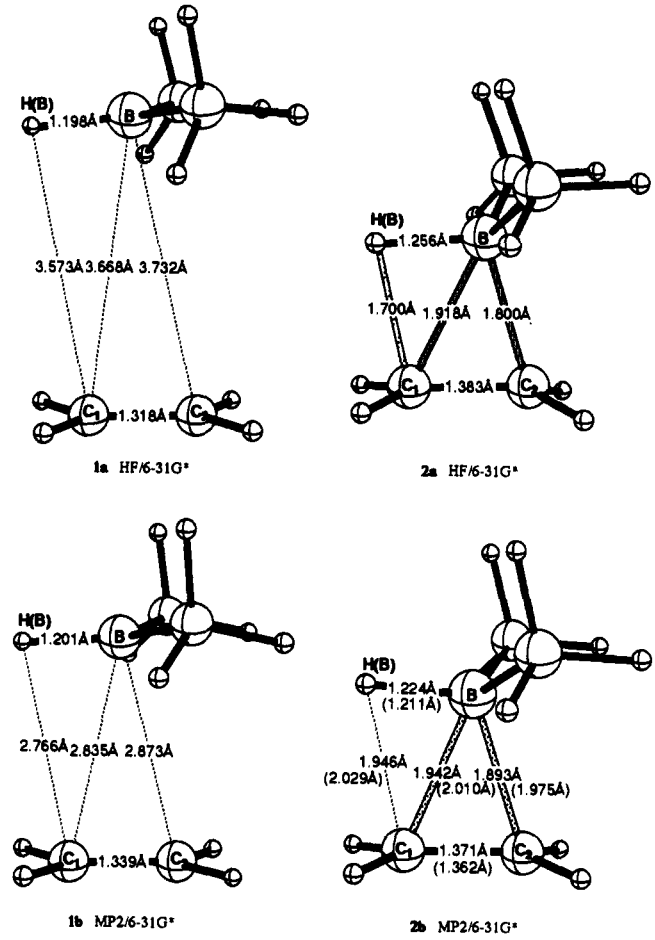

Figure 1. HF/6-31G* and MP2/6-31G* optimized structures for the π-complex of dimethylborane and ethylene and the transition structure for hydroboration.

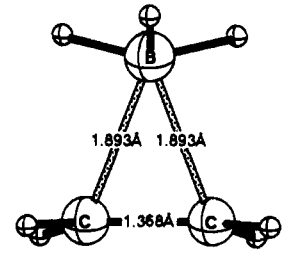

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Figure 2. MP2/6-31G** optimized transition structure for intramolecular rearrangement of ethylborane.

(1) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1959**, *81*, 6423, 6428.
(2) (a) Brown, H. C. *Hydroboration*; W. A. Benjamin: New York, 1962. (b) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.
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