countered β-C-8 stereochemistry[3a] while the complementary stereochemistry found, for example, in isabelin was expected to arise from a halohydrin-based epoxidation. The preparation of this enone proved, however, to be eventful in that introduction of unsaturation into the readily available photoadduct **4**[1a,10f] (Scheme II) could not be efficiently effected through the use of various conventional procedures, including dehydrobromination of **5**[11] and oxidative elimination based on seleno ketone **6**. However, the complications[12] encountered in these eliminations based on the simultaneous trigonalization of two sp^3 centers of an already strained ring system were effectively circumvented through the use of a sequential trigonalization strategy. Thus, ketone **4** was converted to its silyl enol ether which was smoothly oxidized with palladium(II) acetate[13] to provide the desired enone (**3**) in 84% overall yield.

The aforenoted preference for β-face reagent addition to enone **3** was revealed at this point in both its direct epoxidation with sodium hypochlorite/water/pyridine,[14] which gave epoxides **7** and **8** in the ratio 1:20, and its reaction with chlorine-saturated water[15] followed by treatment of the crude chlorohydrins with potassium carbonate/acetone, which served to stereoselectively provide the epoxide required for isabelin (**7**:**8** = 4.5:1). Alternatively, epoxide **7** could be obtained in a completely stereocontrolled fashion[16] and in an overall yield of greater than 70% via the sequence **3** → **9** → **10** → **7**. The efficient sodium borohydride/cerium(III) chloride[17] reduction of enone **3** in this sequence is noteworthy since the use of sodium borohydride alone gave largely a lactone product arising from 1,4- followed by 1,2-hydride addition.

Reductive cleavage of epoxy ketone **7** with dimethylcopper lithium[18] followed by addition of allyl iodide gave the product of exclusive β-face alkylation, ketone **11**, and unalkylated reduction product **12** in the ratio of ca. 3:4.5, respectively (combined yield ca. 70–80%). While repeated efforts to suppress the proton-transfer process leading to **12** were unsuccessful, the quantitative recycling of this compound placed the adjusted yield of **11**[19] at >50%. Reductive lactonization of ketone **11** provided the hydroxy lactone **13** (85%) which, upon ozonolysis, was converted to a mixture of unstable lactol **14** and its open-chain isomer, hydroxyaldehyde **15**. Oxidation of this mixture with Fetizon's reagent[20] afforded the highly crystalline dilactone **16** in 88% overall yield from hydroxy lactone **13**. Methylenation[21a] of dilactone **16** gave photoisobelin (**2**, 40%) along with a comparable amount of bis[(dimethylamino)methyl] product.[21b] The photoisabelin thus obtained proved to be identical with an authentic sample independently prepared by irradiation of natural isabelin according to the procedure of Yoshioka, Mabry, and Higo.[8c] Finally, pyrolysis of **2** gave, in quantitative yield, a mixture of (±)-isabelin (**1**) and (±)-pyroisabelin (**17**) in a ratio (1:2, respectively) which is similar to that obtained previously in the pyrolysis of dehydrophotoisabelin.[8c,22]

In summary, the described chemistry allows for the synthesis of (±)-isabelin (**1**) with complete control over the C-6, C-7, and C-8 stereocenters in a 13-operation sequence. This strategy, the less selective but shorter (10 operations) chlorohydrin sequence, and the availability of the complementary epoxides **7** and **8** should prove useful in establishing a general approach to germacradiene synthesis and in extending the metathesis concept to other natural and nonnatural objectives.

Acknowledgment. We thank P. R. Neuman and T. J. Mabry for a sample of natural isabelin. This investigation was supported by Grant CA 21136, awarded by the National Cancer Institute, DHEW.

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(11) All new compounds reported were homogeneous by TLC and gave satisfactory IR and NMR spectra and exact mass or combustion analyses. Partial analytical data for selected intermediates are as follows. Enone **3**: NMR ($CDCl_3$) δ 6.97 (ddd, J = 2.9, 6.1, 10.2 Hz, 1 H), 6.13 (dd, J = 2.8, 10.2 Hz, 1 H), 3.06 (brs, 1 H); IR (film) 1720, 1670 cm^{-1}. Lactone **9**: mp 60–61 °C; NMR ($CDCl_3$) δ 5.72–6.10 (m, 2 H), 4.88 (dd, J = 1.7, 9.2 Hz, 1 H), 2.72 (d, J = 9.2 Hz, 1 H); IR (CCl_4) 1760, 1665 cm^{-1}. Bromohydrin **10**: mp 141–142 °C; NMR ($CDCl_3$) δ 4.99 (brd, J = 9.5 Hz, 1 H), 4.38 (m, 2 H), 2.88 (d, J = 9.5 Hz, 1 H); IR (KBr) 1740 cm^{-1}. Epoxy ketone **7**: mp 76–77 °C; NMR ($CDCl_3$) δ 3.58 (m, 1 H), 3.38 (dd, J = 1.0, 4.5 Hz, 1 H), 2.78 (d, J = 1.0 Hz, 1 H). Keto ester **11**: NMR δ 3.84 (br m, 1 H), 2.83 (s, 1 H); IR (film) 3400, 3050, 1720, 1690, 1640 cm^{-1}. Hydroxy lactone **13**: mp 94.5–95.5 °C; NMR ($CDCl_3$) δ 4.57 (d, J = 8.7 Hz, 1 H), 3.81 (m, 1 H), 2.67 (d, J = 8.7 Hz, 1 H); IR (KBr) 3400, 3050, 1735, 1640 cm^{-1}. Lactol **14**/aldehyde **15**: NMR ($CDCl_3$) δ 9.78 (s), 5.59 (m, 1 H), 4.66 (dd, J = 8.8 17.5 Hz), 4.49 (dd, J = 1.6, 8.7 Hz, 1 H); IR (CH_2Cl_2) 3600, 1760, 1750, 1720 cm^{-1}. Dilactone **16**: mp 180 °C; NMR ($CDCl_3$) δ 4.70 (t, J = 9 Hz, 1 H), 3.97 (ddd, J = 6, 6, 12 Hz, 1 H), 2.73 (d, J = 9.4 Hz, 1 H); IR ($CHCl_3$) 1780, 1760 cm^{-1}. Pyroisabelin **17**: NMR ($CDCl_3$) δ 6.96 (d, J = 1.8 Hz, 1 H), 6.37 (d, J = 3.6 Hz, 1 H), 5.90 (d, J = 3.3 Hz, 1 H), 4.16 (dt, J = 3.5, 10.6 Hz, 1 H); IR ($CHCl_3$) 1760, 1665 cm^{-1}.

(12) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

(13) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 496.

(14) For studies on the utility of this epoxidation method, see: Jakubowski, A. A.; Guziec, F. S.; Tishler, M. *Tetrahedron Lett.* **1977**, *2399*. Wellman, G. R.; Lam, B.; Anderson, E. L.; White, E. *Synthesis* **1976**, 547.

(15) Hendickson, J. B.; Bogard, T. L. *J. Chem. Soc.* **1962**, 1678. We thank Professor Hendrickson for a discussion of this earlier publication.

(16) In the transformation **9** → **10** an allylic bromide byproduct was obtained in 8%.

(17) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226. Luche, J.-L.; Rodriguez-Hahn, L.; Crabbē, P. *J. Chem. Soc., Chem. Commun.* **1978**, 601.

(18) Szajewski, R. P. *J. Org. Chem.* **1978**, *43*, 1819.

(19) The results of an alternative means for effecting this alkylation based on the reaction of enolonium ion equivalents with a nucleophilic C-7 appendage will be disclosed in due course.

(20) Fetizon, M.; Golfier, M.; Louis, J.-M. *Tetrahedron* **1975**, *31*, 171.

(21) (a) Danishefsky, S.; Schuda, P. F.; Kitihara, T.; Etheredge, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 6066. (b) The formation of a bis adduct is a problem which is, for the most part, peculiar to small-scale reactions.

(22) When compared with our previous studies (ref 10a,f,g) and the mechanistic work cited therein, this result is synthetically and mechanistically noteworthy in that only medium-ring Cope isomers are formed, and direct entry into the *E*,*E* series can be realized, presumably due to the influence of the C-7, C-8 lactone on the relative energies for the pro-*E*,*E* (boatlike) and pro-*E*,*Z* (chairlike) transition states required for fragmentation.

(23) Fellow of the Alfred P. Sloan Foundation, 1979–1981.

(24) National Science Foundation Fellow, 1975–1978.

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Two-Dimensional Coordination Polymers of Rhodium(1+) with Rigid Collinear Diisocyanide Bridges and Stacked Layers Arrangement

Sir:

Interaction of the coordination sphere of metals with stereochemically rigid nonchelating bidentate ligands should in theory provide a mechanism for template polymerization. For instance, the application of rigid bidentate ligands, capable of forming collinear bridges between metal nuclei, to the coordination symmetries $D_{\infty h}$, D_{4h}, and O_h is a conceivable route to well-defined one-, two-, and three-dimensional coordination polymers of the type $[M(\text{bridge})_m]_n$, where m = 1, 2, and 3, respectively. Conceptually, terminally coordinated[1] rigid diisocyano bridging ligands constitute an excellent model system on which to examine the effects of template polymerization. The rigid bridging geometries of such bidentate ligands can conveniently be divided into three main categories, considering metal to isocyanide bonds as vectors: (i) collinear (e.g., 1,4-diisocyanobenzene), (ii) bent (e.g., 1,3-diisocyanobenzene), and (iii) parallel (e.g., 1,5-diisocyanonaphthalene), depending on the relationship between the vectors of the bridging units. In the current communication, we exemplify the concept of template polymerization by reporting the formation of some novel coordination polymers of rhodium(1+) with certain collinear diisocyano linkages.

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(1) Review articles covering the coordination properties of isocyanides: L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, London, 1969; P. M. Treichel, *Adv. Organomet. Chem.*, **11**, 21 (1973); F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, **9**, 95 (1974).

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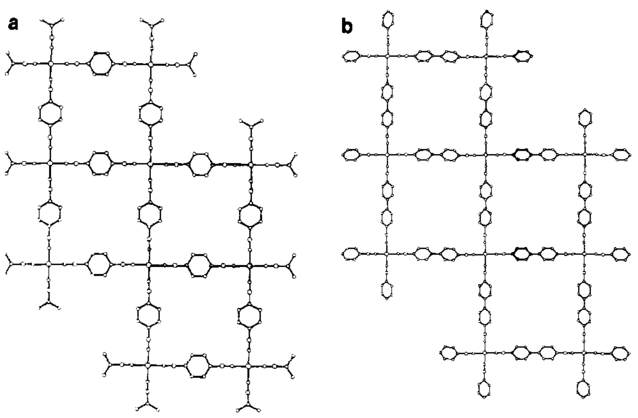

Figure 1. Two-dimensional models of the $[Rh(bridge)_2]_n$ network in polymers A (a) and B (b).

Table I. X-ray Powder Diffraction Angles [θ (deg)], Interplanary Spacings [d (Å)], and Assigned Indices (hkl) for the New Polymers A and B

polymer A[a]		polymer B[b]		assigned[c] indices		
θ, deg (RI[d])	d, Å	θ, deg (RI[d])	d, Å	h	k	l
3.85 (vs)	11.47	2.91 (vs)	15.15	1	0	0
5.30 (vs)	8.34	4.12 (w)	10.72	1	1	0
7.80 (vs)	5.67	5.84 (vs)	7.58	2	0	0
		8.77 (s)	5.05	3	0	0
		11.73 (w)	3.78	4	0	0
13.48 (s)	3.31			0	0	1

[a] Space group $P4$; cell dimensions, $a = 11.47$ (8) Å, $c = 3.31$ Å. [b] Space group $P4$; cell dimensions, $a = 15.15$ (6) Å, c not available. [c] Indices were assigned with the aid of the $\sin^2 \theta$ values according to conventional procedures.[7] [d] Relative intensities (RI): vs = very strong, s = strong, w = weak.

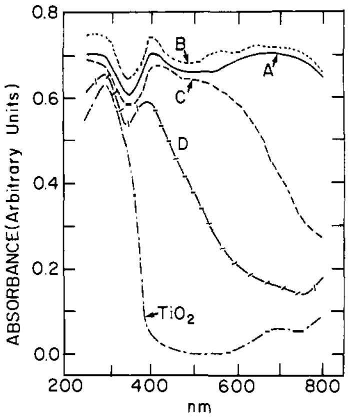

Figure 2. Diffuse reflectance spectra of polymers A, B, C, D, and TiO_2.

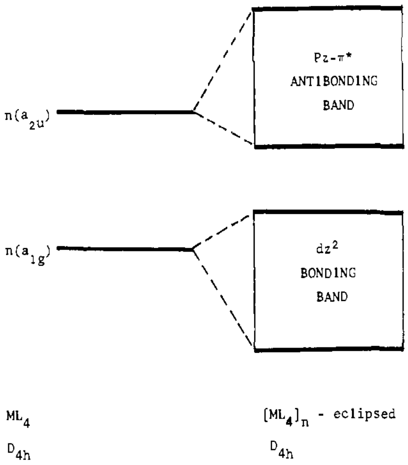

Figure 3. Proposed relative energy band diagram for polymers A and B.

1,4-Diisocyanobenzene[2] and 4,4′-diisocyanobiphenyl[2] are rigid collinear bridging ligands capable of separating metal nuclei by approximately 12 and 16 Å, respectively. These "road-like" ligands undergo a facile reaction with $[Rh(CO)_2Cl]_2$, in various organic solvents at ambient temperature, to afford dark green polycrystalline polymers of the type $[Rh(bridge)_2{}^+Cl^-]_n$ in quantitative yields. The new polymers neither melt nor decompose below 300 °C and are virtually insoluble in either aqueous or organic media. Polymers A (bridge = 1,4-diisocyanobenzene) and B (bridge = 4,4′-diisocyanobiphenyl) readily absorb water when exposed to air, and thus, unless rigorously dried [80–100 °C (0.1 torr)], these materials are best formulated as $[Rh(bridge)_2{}^+Cl^-\cdot xH_2O]_n$ (x = 0–10).[3] Infrared spectra of A and B, taken as KBr pellets, exhibit one strong ν(NC) frequency at 2140 and 2135 cm^{-1}, respectively, and this feature suggests an ordered polymeric network. The specific conductivity (ac; 10^3 Hz) measured[4] across the compressed powder pellets of the polymers A and B at 300 K was found to be on the order of 10^{-6} Ω^{-1} cm^{-1}.

Two-dimensional models of A (Figure 1a) and B (Figure 1b), showing a rigid $[Rh(bridge)_2]_n$ network, were constructed by using idealized bond angles and bond distances similar to those reported[5,6] for $[Rh_2(CNAr)_8]^{2+}$. In these models, the phenyl rings in A assume a coplanar orientation, and the perpendicularly oriented phenyl rings of the biphenyl polymer B intercept the molecular plane with a 45° angle. Calculated cell dimensions for the tetragonal models are a = 11.81 Å for A and a = 16.07 Å for B. In the absence of suitable single crystals, the powder X-ray diffractometric traces of the new polymers were obtained on a Phillips diffractometer with filtered Cu radiation. Interpretation of the powder diffraction data[7] (Table I), in terms of intense reflections[8] coming from rhodium-containing sets of planes, appears to be consistent with structures resulting from the stacking of the two-dimensional models in an eclipsed fashion. Experimentally determined cell dimensions (Table I) are some 3–6% shorter compared with the respective model-calculated terms. However, this can be rationalized by the nonidealized bond angles expected in the polymers. The relatively strong 001 reflection found for A reveals an intermetallic distance of 3.31 Å. This distance appears only slightly longer than those reported for the dinuclear cations $[Rh_2(CNAr)_8]^{2+}$ [Ar = Ph (3.19 Å),[5] 4-fluorophenyl (3.21 Å),[6] and 4-nitrophenyl (3.25 Å)[6]], or certain chloro-bridged neutral complexes such as $[RhCl(CO)(PMe_2Ph)]_2$ (3.17 Å)[9] and $[Rh(CO)_2Cl]_2$ (3.12 Å).[10]

The diffuse reflectance spectra of polymers A and B are shown, among others, in Figure 2. These spectra consist of absorptions

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(2) I. Ugi, "Isonitrile Chemistry", Academic Press, New York, 1971, and pertinent references therein.

(3) Typical elemental composition data of the water-free polymers. *Polymer A*. Found (Calcd): C, 48.33 (48.68); H, 2.4 (2.03); N, 14.38 (14.20); Cl, 9.45 (8.99); Rh, 25.70 (26.09). *Polymer B*. Found (Calcd): C, 62.05 (61.48); H, 2.96 (2.93); N, 9.57 (10.25); Cl, 6.80 (6.49); Rh, 19.34 (18.84).

(4) The method used was similar to that reported by L. Atkinson, P. Day, and R. J. P. Williams, *Nature (London)*, **218**, 668 (1968). Standards were used in the range of the actual measurements. Preliminary results of a temperature-dependent conductivity study have suggested semiconductor behavior for these polymers.

(5) K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray, and J. G. Gordon II, *Inorg. Chem.*, **17**, 828 (1978).

(6) H. Endres, N. Gottstein, H. J. Keller, and R. Martin, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **34B**, 827 (1979).

(7) H. Lipson and H. Steeple, "Interpretation of X-Ray Powder Diffraction Patterns", Macmillan, London, 1970.

(8) The diffractometric trace technique is limited by the scan speed [1° (2θ) min^{-1}] to relatively intense reflections. Powder diffraction photographs of these polymers will be obtained in order to gain further structural information.

(9) J. J. Bonnet, Y. Jeaning, P. Kalck, A. Maisonnat, and R. Poilblanc, *Inorg. Chem.*, **14**, 743 (1975).

(10) L. F. Dahl, C. Martell, and D. J. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

at ~410 nm and extended absorption envelopes centered at ~660 nm. The electronic spectral properties of these polymers may be understood in terms of the band diagram, shown in Figure 3, derived by the *n*-way splitting of the monomeric [ML_4 (D_{4h})], HOMO (a_{1g}), and LUMO (a_{2u}) of a supposedly isolated linear chain section ($[ML_4]_n$ eclipsed) of the polymers.[11] Both the bonding (d_{z^2}) and antibonding (p_z–π^*) bands are comprised of *n*-filled (2*n* electrons) and empty levels, respectively. The high-energy absorptions in the spectra of the polymers have been assigned as either top-to-top or bottom-to-bottom band transitions. These transitions should be similar in energy to the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition in the monomer $Rh(CNPh)_4BPh_4$ (411 nm).[5] The low-energy broad absorptions in the polymers have been assigned as a multitude of transitions occurring between the upper region of the bonding and the lower region of the antibonding bands. In view of their origin, these low-energy absorptions should be greatly affected by the breaking of intermetallic interactions in the polymers. Manifestation of this effect is found in the spectra of certain oxidized polymers such as those derived by the iodination (C) and photobleaching (D)[12] of polymer B (see Figure 2). Finally, we call attention to the overall ability of the new polymers A and B to extensively absorb light, especially in the visible region, which is illustrated in Figure 2 by comparison with the spectrum of TiO_2, a known photosemiconductor.

The new coordination polymers reported herein, and others containing different transition elements and various rigid linkages, are currently under intensive investigation in our laboratory. These polymers are being developed in the context of unconventional materials having both fundamentally interesting and useful chemical and/or physical properties. Special emphasis in this program is placed on the study of new surfaces for catalysis and photocatalysis.

Acknowledgment. This research program was supported by generous funds received from KFA, NCRD, and Minerva.

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[11] This approach represents an extension of the treatment proposed for oligomers by Gray et al.[5] A somewhat similar band diagram was suggested by A. E. Underhill in "Low-Dimensional Cooperative Phenomena—The Possibility of High-Temperature Superconductivity", H. J. Keller, Ed., Plenum Press, New York and London, 1974, p 288.

[12] The yellow photobleached polymer D was obtained by irradiating the suspended polymer B in a 12 N HCl solution. The infrared spectra of the fully oxidized polymers (e.g., C and D) show one strong ν(NC) band at a frequency 40–50 cm^{-1} higher than those found in the starting polymers. Partially oxidized polymers, which can be obtained, for instance, by controlled halogenation, show ν(NC) bands in both Rh(1+) and Rh(3+) regions.

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Boron Analogues of the α-Amino Acids. Synthesis, X-ray Crystal Structure, and Biological Activity of Ammonia–Carboxyborane, the Boron Analogue of Glycine

Sir:

Glycine, $H_2NCH_2CO_2H$ or $H_3N^+CH_2CO_2^-$, may be considered the simplest α-amino acid and was the first to be discovered. We now report the synthesis and characterization of its isoelectronic and isosteric (protonated) boron analogue, ammonia–carboxyborane, $H_3N{\cdot}BH_2CO_2H$ (**1**), which may be viewed as the parent of a novel class of boron analogues of the common α-amino acids. Although we have previously reported the synthesis of other amine–carboxyboranes, e.g., $Me_3N{\cdot}BH_2CO_2H$, the boron analogue of betaine,[1] all previous examples did not contain hydrogen bonded directly to nitrogen. An extremely important feature of the present example, like its glycine counterpart, is its potential to form peptide linkages and to be incorporated into proteins. The structure of **1** has been unequivocally established by single-crystal X-ray analysis, and its stability in several media has been investigated. Preliminary testing of **1** in animal model studies has demonstrated biological activity, in particular, significant antihyperlipidemic activity.

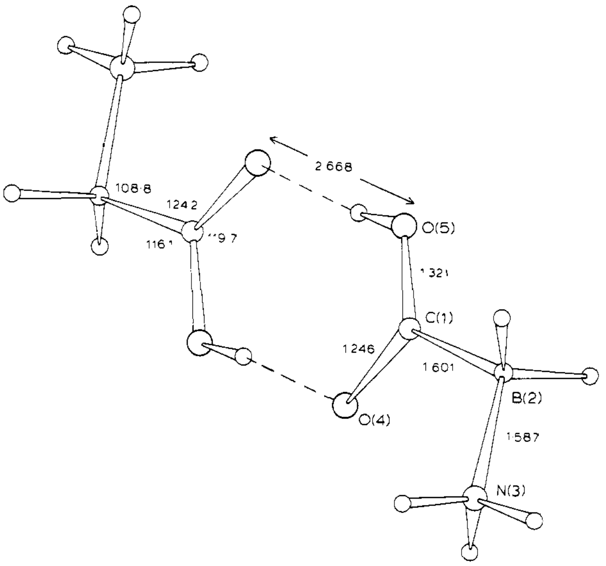

Figure 1. Conformation, interatomic distances (0.002–0.003 Å), and valency angles (0.2°) in the centrosymmetric $(H_3N{\cdot}BH_2CO_2H)_2$ dimer; small circles denote hydrogen atoms.

Preparation of **1** may be achieved by an amine exchange reaction. In a typical preparation, $Me_3N{\cdot}BH_2CO_2H$ was allowed to react with liquid NH_3 (ca. 1:10 w/w) in an evacuated stainless-steel cylinder at room temperature for 3 weeks after which time excess ammonia was allowed to evaporate off and removed finally by pumping out. The residue was transferred to a flask with the aid of dry $CHCl_3$, refluxed for 3–4 h, filtered hot, and washed with hot $CHCl_3$ to give $H_3N{\cdot}BH_2CO_2H$ as an insoluble residue. This procedure led to a yield of crude product in the 50–55% range which remained essentially constant even when the time of reaction was increased from 3 to 6 weeks; a reaction period of 2 weeks gives $H_3N{\cdot}BH_2CO_2H$ in 30% yield.[2] When the crude product is freshly crystallized from cold water, it melts at 116 °C, but this is lowered, with no observable change in spectral characteristics, after storage of the product in screw-capped vials over a period of time in normal laboratory conditions [IR (KBr in cm^{-1}) ν(NH), a broad envelope with peaks at 3330 (s), 3250 (s), 3200 (br, s); ν(OH) 3000 (br); ν(NH···O) 2780 (br, s), 2650 (s); ν(BH) 2400 (s), 2340 (sh), 2250 (sh); ($\delta + \tau$) (NH) 2050 (w), 1840 (br, w), 1760 (br, w); ν(CO) 1640 (s), δ(NH) 1605 (s)]. Anal. Calcd for $H_3N{\cdot}BH_2CO_2H$: C, 16.04; H, 8.02; N, 18.71; B, 14.44. Found: C, 15.83; H, 8.04; N, 18.53; B, 14.31.

Single-crystal X-ray analysis established the structure of **1** unequivocally. Monoclinic crystals of **1** belong to space group $P2_1/c$, with $a = 4.859$ (2), $b = 5.291$ (2), $c = 15.523$ (7) Å, $\beta = 108.42$ (3)°; $V = 378.6$ Å^3; $Z = 4$; $d_{calcd} = 1.313$ g cm^{-3}. The structure was solved by direct methods with the MULTAN program package.[3] Full-matrix least-squares refinement of atomic positional and thermal (anisotropic B, C, N, O; isotropic H) parameters converged to an R[4] value of 0.052 over 598 statistically significant [$I > 2.0\sigma(I)$] reflections measured on an Enraf–Nonius

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[1] B. F. Spielvogel, L. Wojnowich, M. K. Das, A. T. McPhail, and K. D. Hargrave, *J. Am. Chem. Soc.*, **98**, 5703 (1976).

[2] The Me_3N group in $Me_3N{\cdot}BH_2CN$ can also be replaced by NH_3 in a similar manner by reacting it with liquid NH_3 in a steel bomb to give about 20% yield of $H_3N{\cdot}BH_2CN$ in ca. 10 days. The unreacted $Me_3N{\cdot}BH_2CN$ can then be removed by sublimation, leaving $H_3N{\cdot}BH_2CN$ as a residue which may be purified by the usual procedures.

[3] G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27A**, 368 (1971).

[4] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

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