

the fragment ion  $C_3F_5^+$  is unperturbed by the infrared radiation despite the availability of a decay channel whose threshold is  $\sim 72$  kcal/mol: J. L. Beauchamp and B. S. Freiser, *J. Am. Chem. Soc.*, **96**, 6260 (1974). The presence of an ion whose concentration is unaffected by the laser radiation establishes that operation of the ICR cell is not perturbed by the infrared beam.

- (25) D. S. Bomse, R. L. Woodin, and J. L. Beauchamp, unpublished work.  
 (26) R. V. Ambartzumian, *Proc. Nordfjord Conf.*, 1976, 150 (1976).  
 (27) The short coherence time of the laser ( $\sim 10^{-8}$  s) indicates that even conventional incoherent infrared sources in conjunction with a monochromator or band pass filter should make it possible to observe slow multiphoton dissociation through the entire infrared spectral range. A 300-W commercially available blackbody source provides 0.29 W of radiation at  $1000\text{ cm}^{-1}$  ( $25\text{-cm}^{-1}$  band) and 1.1 W at  $3000\text{ cm}^{-1}$  (also over a  $25\text{-cm}^{-1}$  band). These powers should be adequate to effect photodissociation in view of the present experiments.  
 (28) NSF Predoctoral Fellow.

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Contribution No. 5728

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Received January 25, 1978

### Synthesis of $BC_4H_5Fe(CO)_3$ . An Example of the Conversion of an Organometallic Compound into a Metallocarborane

Sir:

Traditionally, organometallic compounds are viewed as polyhaptic-ligand metal complexes and it was only recently that Wade pointed out that such compounds can also be viewed as cage systems in which the metal acts as a single atomic member of the cage.<sup>1</sup> In such a model, organometallic compounds are related to boranes, compounds for which cage geometry is related in a simple way to the number of valence electrons assigned to the framework.<sup>2</sup> If this model is more than an academic extrapolation, then organometallic compounds should exhibit some cagelike chemical or physical characteristics. In terms of the electronic states of the cations, we have already demonstrated similarities between  $B_5H_9$ ,  $B_4H_8Fe(CO)_3$ , and  $C_4H_4Fe(CO)_3$ <sup>3</sup> and, in addition, have shown that in one way the photochemical behavior of  $B_4H_8Fe(CO)_3$  is similar to that of  $C_4H_4Fe(CO)_3$ .<sup>4</sup> Herein is reported the preparation and characterization of  $BC_4H_5Fe(CO)_3$  from the short-time photolysis of  $C_4H_4Fe(CO)_3$  in the presence of  $B_3H_9$ . This observation both demonstrates the conversion of an organometallic compound into a metallocarborane<sup>5</sup> and supports the usefulness of the cage analogy in areas outside of borane chemistry.

Irradiation at 360 nm of a light yellow solution of 2.1 mmol of  $C_4H_4Fe(CO)_3$  and 2.3 mmol of  $B_3H_9$  in 3.5 mL of diethyl ether<sup>6</sup> for 15 to 30 min in a Rayonet photochemical reactor resulted in a dark brown solution and the production of 0.05 mmol of noncondensables. The reaction mixture was fractionated and 1.8 mmol of  $C_4H_4Fe(CO)_3$  was recovered along with a few milligrams of a new compound.<sup>7</sup> The new compound is more volatile than  $C_4H_4Fe(CO)_3$  but less volatile than  $B_3H_9$ , and purification was achieved by repeated fractionation on a vacuum line.

The new compound has an empirical formula  $FeBC_7O_3H_5$  ( $^{56}Fe^{11}B^{12}C_7^{16}O_3^1H_5^+$ , calcd 203.9682 amu, obsd 203.9684 amu;  $^{56}Fe^{10}B^{12}C_7^{16}O_3^1H_5^+$ , calcd 202.9716 amu, obsd 202.9718 amu). The parent ion in the mass spectrum fragments by the sequential loss of three CO molecules, and the envelopes of the parent ion and first three fragment ion clusters are consistent with a molecule containing a single boron atom. The gas phase infrared spectrum exhibits bands at 2930 (m, CH), 2550 (m, BH), 2080 (s, CO), and 2030 (vs, CO)  $cm^{-1}$ .<sup>8</sup> The 25.2-MHz  $^{11}B$  FT NMR spectrum in  $CD_2Cl_2$  contains

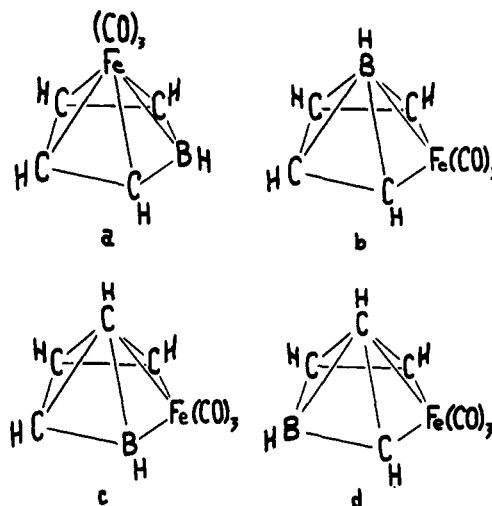


Figure 1. Possible structures for  $BC_4H_5Fe(CO)_3$ .

a single doublet with chemical shift of 11.8 ppm ( $J = 140$  Hz) downfield relative to  $BF_3 \cdot O(C_2H_5)_2$ . The 100-MHz  $^1H$  FT NMR spectrum in  $C_6D_6$  consists of two multiplets (14-Hz fwhm) at  $\delta$  4.62 and 0.95 having relative areas of  $\sim 1:3$ .<sup>9</sup> On  $^{11}B$  decoupling a broad peak (40-Hz fwhm) appeared at  $\delta$  2.57 with relative area 1. Under probe conditions<sup>10</sup> the signals attributed to the new compound decay with a half-life of  $\sim 1$  h.

The new compound is formulated as  $BC_4H_5Fe(CO)_3$ , and it is isoelectronic with the known compounds  $B_5H_9Fe(CO)_3$ <sup>11</sup> and  $B_3C_2H_7Fe(CO)_3$ .<sup>12</sup> Four likely structures for this compound are shown in Figure 1. All four structures are nido frameworks in agreement with the presence of 16 skeletal electrons (2 from  $Fe(CO)_3$ , 2 from BH, and 3 from each CH) in a six-atom cage.<sup>2</sup> Structure a is that of the ligand borole bound to  $Fe(CO)_3$ , substituted derivatives of which have been reported recently.<sup>13</sup> This structure is ruled out on the basis of the proton spectra. Structure b is ruled out for the same reason and also because the  $^{11}B$  chemical shift suggests a boron in the environment of a basal position rather than an apical position.<sup>14</sup> Neither structure c nor d can be ruled out on the basis of the available data. However, structure c is preferred as it is easier to rationalize the nearly equal chemical shifts of three CH protons.<sup>15</sup> It is interesting that the new compound has a basal  $Fe(CO)_3$  group like  $B_5H_9Fe(CO)_3$  rather than an apical  $Fe(CO)_3$  like  $B_3C_2H_7Fe(CO)_3$ .

The mechanism for the formation of  $BC_4H_5Fe(CO)_3$  is unknown and undoubtedly complex. Other products are formed in the reaction but those partially identified thus far do nothing to illuminate the situation. It is intriguing to note, however, that here the insertion of boron into the carbon ring takes place with the metal carbonyl fragment being retained in the product, whereas in the case of insertion of carbon into a metal bound borane cage the metal carbonyl fragment was lost.<sup>4,16</sup> Although the particular reaction reported here is poor in terms of yield, it does suggest a new approach to the preparation of unusual metallocarboranes.

**Acknowledgement.** The support of the National Science Foundation through Grant CHE75-10938 is gratefully acknowledged as are helpful discussions with Dr. Jay Labinger.

### References and Notes

- (1) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976), and references therein.
- (2) Reference 1 and R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, **18**, 67 (1976), and R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).
- (3) J. A. Ullman, E. L. Andersen, and T. P. Fehlner, *J. Am. Chem. Soc.*, **100**, 456 (1978).

- (4) The photolysis of  $B_4H_8Fe(CO)_3$  and  $C_4H_4Fe(CO)_3$  in the presence of acetylenes yields carboranes and benzenes, respectively: T. P. Fehlner, *J. Am. Chem. Soc.*, **99**, 8355 (1977), and J. S. Ward and R. Petit, *ibid.*, **93**, 262 (1971).
- (5) The synthesis of a metallocarborane from something other than a carborane is rare. There are five reported instances: the formation of  $(B_{10}H_{10}COH)M(CO)_4^-$  from  $B_{10}H_{13}^-$  and  $M(CO)_8$  ( $M = Cr, Mo, W$ ), P. A. Wegner, L. J. Guggenberger, and E. L. Muettterties, *J. Am. Chem. Soc.*, **92**, 3473 (1970); the formation of  $CpCoC_2B_3H_7$  from  $C_2H_2$  and 2-CpCoB<sub>4</sub>H<sub>8</sub>, R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974), and R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.*, in press; the formation of  $\mu-C_3H_4(C_5H_5)_2Co_2C_2B_3H_3$  from  $B_2H_8$ ,  $CoCl_2$ , and  $C_3H_5$ , V. R. Miller, R. Weiss, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 5646 (1977); the formation of the metal bound hydridoborate ion from  $Cp_2Co$  and  $RBX_2$ , G. E. Herberich, G. Greiss, and H. F. Hell, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970); and the formation of metallocarboranes from metal atom reactions, G. J. Zimmerman, R. Wilczynski, L. W. Hall, and L. G. Sneddon, Abstracts of the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977, INORG 165.
- (6) Pentane has also been used as a solvent; however, the yields are smaller.
- (7) Longer irradiations did not result in an increased yield of this product. Sufficient quantity for characterization was obtained by repetitive photolysis and fractionation.
- (8) The carbonyl bands for  $C_4H_4Fe(CO)_3$  were observed at 2065 (s) and 1995 (vs)  $cm^{-1}$ .
- (9) The  $^1H$  spectrum of  $C_4H_4Fe(CO)_3$  was a single sharp line (2-Hz fwhm) at  $\delta$  3.23 under these conditions.
- (10) Temperature of 30 °C.
- (11) T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Am. Chem. Soc.*, **98**, 7085 (1976).
- (12) R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971); D. A. Franz, V. R. Miller, and R. N. Grimes, *ibid.*, **94**, 412 (1972); and J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2266 (1973).
- (13) G. E. Herberich, J. Hengesbach, V. Kölle, and W. Oschmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 42 (1977).
- (14) In the  $^{11}B$  spectrum of a closely related compound, 2,3,4,5- $C_4B_2H_6$ , the apical boron appears at  $-60.8$  ppm ( $J = 202$  Hz), while the basal boron appears at 10.4 ppm ( $J = 144$  Hz).
- (15) This is a somewhat unusual structure in that it has a carbon atom in an apical position, i.e. a position of high coordination number. There is precedence for this in carborane chemistry in that  $B_3C_2H_7$  has both apical and basal CH units as demonstrated by the  $^1H$  NMR ( $\delta$  0.79 and 1.8). It is interesting to note that 1,2- $B_3C_2H_7$  is also unstable in solution. D. A. Franz and R. N. Grimes, *J. Am. Chem. Soc.*, **92**, 1438 (1970).
- (16) Note, however, in the case of the thermal reaction of  $C_2H_2$  with 2-CpCoB<sub>4</sub>H<sub>8</sub> the metal is retained in the product metallocarborane. See ref 5.

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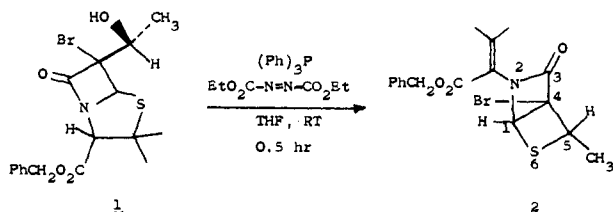
Received January 6, 1978

### 3-Oxo-6-thia-2-azabicyclo[2.2.0]hexanes: Novel $\beta$ -Lactams Derived from Penams

Sir:

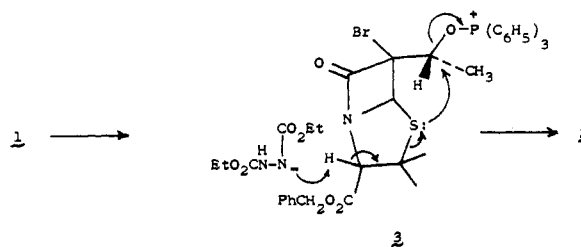
The combination of triphenylphosphine and azodicarboxylate esters has been utilized as an efficient method of in situ hydroxyl activation for nucleophilic displacement reactions.<sup>1</sup> It is of interest to note that, in systems possessing an appropriately situated internal nucleophile, the "DEADCAT" reaction<sup>1f</sup> facilitates an intramolecular cyclization process.<sup>1b,c,e</sup> We report herein another example of such a reaction in which a penicillin derivative has been transformed into the first reported example of a 4,4-ring system of the type  $C_3N-C_3S$ .<sup>2,3</sup>

When benzyl 6 $\alpha$ -bromo-6 $\beta$ -(1-hydroxyethyl)penicillanate (**1**)<sup>4</sup> was subjected to the DEADCAT reaction (2.5 equiv of  $(Ph)_3P$ , 2.2 equiv of  $EtO_2CN=NCO_2Et$ , THF, 25 °C), the novel bicyclic  $\beta$ -lactam **2** was obtained in yields of 20–30%.<sup>5</sup>



The structure of **2** was deduced from an examination of its spectral properties. The IR spectrum ( $CHCl_3$ ) exhibited carbonyl frequencies at 1770 and 1724  $cm^{-1}$ , which were attributed to the  $\beta$ -lactam and ester moieties, respectively. The mass spectrum (MS) showed parent ions at  $m/e$  397 and 395 (FD-MS: calcd for  $C_{17}H_{18}NO_3SBr$ , 395.0188; found, 395.0187)<sup>6</sup> and fragmentation peaks at  $m/e$  337 and 335, corresponding to the loss of thioacetaldehyde generated by a cycloreversion process typical of thietanes.<sup>7</sup> The loss of bromine from the latter fragment and the parent ion was also evident by peaks at  $m/e$  256 and 316, respectively. Aside from the base peak,  $m/e$  91 [ $CH_2Ph$ ]<sup>+</sup>, the next most intense peaks were found at  $m/e$  166 and 164, which correspond to a molecular ion for  $\alpha$ -bromothiocrotonaldehyde or its cyclic equivalent, 3-bromo-2-methyl-2H-thiete, another expected reverse cycloaddition fragment. The complementary fragment at  $m/e$  231 was also present. The 300-MHz NMR spectrum ( $CDCl_3$ ) exhibited resonances at  $\delta$  1.64 (d,  $J = 7$  Hz,  $CH_3$ ), 2.14 (s,  $CH_3$ ), 2.3 (s,  $CH_3$ ), 3.94 (qd,  $J = 0.8$  and 7.0 Hz, H-5), 5.17 and 5.23 (dd,  $J = 12$  Hz,  $CO_2CH_2Ph$ ), 5.28 (d,  $J = 0.8$  Hz, H-1), and 7.39 (s, ArH).

The configuration at C-5 was assigned on the basis of mechanistic considerations and nuclear Overhauser effects. In conformity with the observed stereospecificity<sup>1</sup> of nucleophilic displacement reactions of alcohols mediated by triphenylphosphine and diethyl azodicarboxylate, back-side attack by the sulfur atom in phosphonium ion intermediate **3**



followed by proton abstraction would generate **2** having the *S* configuration at C-5. In support of this postulation was an observed positive effect on H-1 (13.3%) upon irradiation of the C-5 methyl doublet.

To further substantiate the assigned structure, compound **2** was degraded as outlined in Scheme I. Reductive debromination with zinc-silver couple<sup>8</sup> (MeOH, 3 equiv HOAc, room temperature) provided **4** (60%): IR ( $CHCl_3$ ) 1754 and 1718  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  1.64 (d,  $J = 6.5$  Hz,  $CH_3$ ), 2.17 (s,  $CH_3$ ), 2.28 (s,  $CH_3$ ), 3.84 (m,  $SCHCH_3$ ), 3.96 (app t,  $J = 3$  and 4 Hz, H-4), 5.12 (dd,  $J = 1.5$  and 4 Hz, H-1), 5.16 and 5.24 (dd,  $J = 12$  Hz,  $CO_2CH_2Ph$ ), and 7.38 (s, ArH);  $m/e$  317 ( $M^+$ ).<sup>6</sup> Compound **4** was desulfurized with Raney nickel (absolute EtOH, 60 °C) to yield 1-(1-benzyloxycarbonyl-2-methylprop-1-enyl)-3 $\beta$ -ethylazetidin-2-one (**5**): IR ( $CHCl_3$ ) 1733 and 1709  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  0.95 (t,  $J = 6$  Hz,  $CH_3$ ), 1.68 (m,  $-CH_2CH_3$ ), 1.94 (s,  $CH_3$ ), 2.22 (s,  $CH_3$ ), 3.15 (m,  $H_A$  and  $H_C$ ), 3.52 (app t,  $J = 5$  Hz,  $H_B$ ), 5.18 (s,  $CO_2CH_2Ph$ ), and 7.26 (s, ArH);  $m/e$  287 ( $M^+$ ). Owing to the coincident chemical shifts of  $H_A$  and  $H_C$  of azetidinone **5**, a complete assignment of coupling constants for the ring protons was not discernible from the 300-MHz  $^1H$  NMR spectra recorded in either  $CDCl_3$ ,  $C_6D_6$ , or 1:1  $C_6D_6-CDCl_3$ . However,

Scheme I

