was based upon shifts to higher frequency of the NC stretching vibration in the NCS moiety for the crossover to low spin.[11] This shift of ~40 cm^{-1} to higher frequency was interpreted as indicative of a stronger NC bond and hence a weaker Fe-N(NCS) bond and was attributed to the decreased availability of t_2 electrons in the low-spin state. If less metal t_2 electrons are available, back-donation into the π^* orbitals of NCS or NCSe would be reduced resulting in the Fe-NCS bond becoming weaker and the NC bond stronger which in turn implies an increased ionic character to the Fe-NCS bond.[21] Crystallographic data indicate that the angle formed by a nitrogen of NCS and a nitrogen in the plane of the bipy ring system (N(bipy)-Fe-N(NCS)) changes from 102° at 295°K to 93° at 100°K.[20] Thus the Fe-NCS bond is less bent at 100°K and the NC stretching frequency should be greater. However, this interpretation requires a shorter NC bond in going from the bent to the linear configuration[21] whereas the X-ray data show that the NC bond distance in the NCS moiety is lengthened by 0.08 Å in going from 295 to 100°K.

Therefore, based on the X-ray and low-frequency ir data, it would appear in this case that the NC stretching frequency is not a good diagnostic tool for determining the nature of the Fe-N(NCS) bond. Recently, a similar conclusion was reached concerning the bonding in nitrosyl complexes.[22] It was concluded that the NO stretching frequency was not a good structural diagnostic for the nature of nitrosyl bonding. For example, different complexes exist which have both the bent and linear configurations and still have comparable values of the NO stretch.

Our spectral evidence indicates stronger bonds in both the low-spin Fe-N(bipy or phen) and Fe-N(NCS and NCSe) cases. This bond strengthening may be attributed basically to the changes in the Fe-N bond strength which accompany changes in the ground-state electronic configuration. Whether or not π bonding is a significant factor in the low-spin complex is difficult to determine from vibrational spectroscopy.

Registry No. $Fe(phen)_2(NCS)_2$, 14692-67-2; $Fe(phen)_2(NCSe)_2$, 15744-97-5; $Fe(bipy)_2(NCS)_2$, 37843-42-8; $Fe(bipy)_2(CN)_2$, 14841-10-2.

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An Improved Synthesis of Biscarborane and Its Precursor Ethynylcarborane

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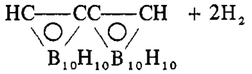
Biscarborane, 1-[1′-1′,2′-dicarba-*closo*-dodecaborane(12)]-1,2-dicarba-*closo*-dodecaborane(12), I, has been found to act as a novel chelating agent with transition metal ions, forming remarkably stable complexes in which the biscarborane ligand is bound *via* metal-carbon σ bonds.[2,3] Previously the preparation of I[4,5] involved two reactions, the preparation and isolation of ethynylcarborane, II, in 35% yield, and reaction of II with additional bis(acetonitrile)decaborane.

We now wish to report an improved, one-step synthesis of I in which the compound was prepared in yields of 55-60% based on $B_{10}H_{14}$. One key feature of the synthesis was the substitution of $B_{10}H_{12}\cdot 2S(CH_2CH_3)_2$[6] for $B_{10}H_{12}\cdot 2CH_3CN$. The second feature of the new method incorporated the use of reduced temperatures (−25°) during the initial phase of the reaction to minimize the loss of diacetylene. One mole of diacetylene was added to 2 mol of $B_{10}H_{12}\cdot 2S(CH_2CH_3)_2$ at reduced temperature; subsequent heating produced I; no II was detected.

$$B_{10}H_{14} + 2S(CH_2CH_3)_2 \xrightarrow[\substack{1.\ 40^\circ \\ 2.\ 60^\circ}]{\text{toluene}} B_{10}H_{12}\cdot 2S(CH_2CH_3)_2 + H_2$$

$$2B_{10}H_{12}\cdot 2S(CH_2CH_3)_2 + HC{\equiv}CC{\equiv}CH \xrightarrow[\substack{1.\ -25^\circ \\ 2.\ \ 80^\circ}]{\text{toluene}}$$



$$\underset{B_{10}H_{10}}{HC\!-\!C}C\underset{B_{10}H_{10}}{\!-\!CH} + 2H_2$$

I

The use of reduced temperatures was also applied to the method of preparation of II. Increased yields of II (65-70%) were obtained from the previously described synthesis[4,5] if the acetonitrile solution of diacetylene was added to the $B_{10}H_{12}\cdot 2CH_3CN$ slurry at room temperature and subsequently slowly heated to the reflux temperature.

Experimental Section

Toluene was distilled from CaH_2, diethyl sulfide was distilled from Linde molecular sieves (Type 5A), and acetonitrile was distilled from CaH_2, P_2O_5, and finally CaH_2 prior to use. *p*-Dioxane was distilled from CaH_2 prior to use, and decaborane,[7] $B_{10}H_{14}$, was freshly sublimed. Distilled H_2O and all other solvents were used without further purification. Where applicable, reactions were performed under anhydrous conditions and all reactions were performed in a nitrogen atmosphere. Basic alumina, activity I, was supplied by EM reagents.

Preparation of Biscarborane, I. Decaborane, 24.5 g (0.2 mol), diethyl sulfide, 36.0 g (0.41 mol), and toluene (100 ml) were combined in a 250-ml, three-necked flask equipped with a mechanical stirrer, Dry Ice condenser, and thermometer. Prior to the addition of reagents, the system was flushed with a stream of nitrogen. The solution was maintained at 40° for 3 hr and then at 60° for 2 hr and finally was cooled to room temperature.

In a 500-ml, three-necked flask equipped with a mechanical stirrer, pressure equalizing addition funnel, and Friedrichs condenser were placed 167 ml of H_2O, 10 ml of *p*-dioxane, and 24.5 g of KOH. The condenser (cooled by circulating ice water) was connected to a series of two scrubbing towers, each of which contained 200 ml of 10% aqueous KOH. The second scrubbing tower was connected to a $CaCl_2$ drying tower (60 cm × 10 mm) and the drying tower was connected to an inlet tube.

After all solutions had been added to this reaction train, the entire system was flushed with a stream of nitrogen for 0.5 hr. The thermometer in the flask containing the $B_{10}H_{12}\cdot 2(CH_2CH_3)_2$ was removed and replaced by the inlet tube which connected to the drying tower, and the toluene solution of $B_{10}H_{12}\cdot 2S(CH_2CH_3)_2$ was cooled

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(1) National Defense Education Act Title IV Predoctoral Fellow, 1967-1969, 1972.

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(4) J. A. Dupont and M. F. Hawthorne, U. S. Patents 3,228,986 and 3,228,987 (1966).

(5) J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 86, 1643 (1964).

(6) M. F. Hawthorne, *et al.*, *Inorg. Syn.*, 10, 91 (1967).

(7) M. F. Hawthorne, *et al.*, *Inorg. Syn.*, 10, 94 (1967).

to –25° in a Dry Ice–2-propanol bath. The KOH–dioxane solution was heated to the reflux temperature and 41.0 g (0.334 mol) of 1,4-dichloro-2-butyne was added to the solution at a rate of 2–3 drops/sec. The diacetylene gas produced (a yield of 55% based on 1,4-dichloro-2-butyne was assumed) was carried by a slow stream of nitrogen through the scrubbing towers and condensed into the cold solution of $B_{10}H_{12}{\cdot}2S(CH_2CH_3)_2$. After diacetylene production was complete, the short section of Tygon tubing connecting the inlet tube to the drying tower was clamped shut and the Dry Ice condenser was allowed to warm to room temperature. In this manner, any diacetylene that was condensed on the cold finger was allowed to return to the reaction flask. The reaction solution was slowly warmed to 80° and stirred for 12 hr. The solution was cooled and stripped on a rotary evaporator by a water aspirator to an oily solid. This solid and 500 ml of methanol, which destroyed any unreacted boranes,[8] were added to a 1-l. round-bottom flask equipped with a Friedrichs condenser. The solution was slowly heated over a steam bath to the reflux temperature and maintained at this temperature until hydrogen evolution terminated. A 3–5-ml amount of 50% aqueous HCl was cautiously added and the solution again was slowly warmed to the reflux temperature. When hydrogen evolution had terminated, the condenser was replaced by a distillation head and Liebig condenser. Ethanol was added to increase the boiling point of the solution and the alcohol–diethyl sulfide solution codistilled until all diethyl sulfide was removed (more ethanol was periodically added). The solvent was removed by a rotary evaporator and a water aspirator and the resulting solid dissolved in 1 l. of benzene. The solution was cooled to 5°, 1 l. of cold 10% aqueous NaOH was added, and the mixture was vigorously stirred for 15 min. The aqueous and organic phases were separated; the aqueous phase was washed once with 250 ml of benzene and the aqueous phase discarded. The combined organic phases were washed two times with 500-ml portions of H_2O and dried over anhydrous $MgSO_4$. The dry benzene solution was filtered through a bed of basic alumina (500 ml dry volume) and the solvent was removed with a rotary evaporator and water aspirator to afford 16.7 g of crystalline I (58.3% based on $B_{10}H_{14}$).

Preparation of Ethynylcarborane, II. Bis(acetonitrile)decaborane, $B_{10}H_{12}{\cdot}2CH_3CN$, was prepared by the method of Schaeffer[9] from 45.2 g (0.37 mol) of decaborane. As described above, 67.0 g (0.54 mol) of 1,4-dichloro-2-butyne was added dropwise to a solution of 500 ml of H_2O, 55 ml of *p*-dioxane, and 73.2 g of KOH at the reflux temperature. Again the diacetylene was scrubbed with a 10% aqueous KOH solution and dried. The dry gas was condensed into a preweighed 100-ml, three-necked flask equipped with a Dry Ice condenser maintained at –80°, an inlet tube which connected to the diacetylene generation train, and a glass stopper. The flask contained 40 ml of acetonitrile cooled to –35° in a Dry Ice–2-propanol bath. After diacetylene generation was complete, the flask was warmed to room temperature, the inlet tube was replaced by a glass stopper, and the flask was reweighed to determine the yield of diacetylene (15 g, 0.37 mol).

The acetonitrile solution of diacetylene was added to the addition funnel under a stream of nitrogen and the diacetylene solution was added to the stirring suspension of $B_{10}H_{12}{\cdot}2CH_3CN$ over a 45-min period. The reactants were stirred for 4 hr, then slowly warmed to 40° and stirred for 12 hr, and finally heated to the reflux temperature for 2 hr. The solution was cooled to room temperature and using the purification methods previously described,[4,5] 3 g (3.3%) of I and 35.3 g of II (70% based on $B_{10}H_{14}$) were obtained.

Registry No. $B_{10}H_{12}{\cdot}2Et_2S$, 32124-79-1; HCCCCH, 460-12-8; $[1\text{-}(1'\text{-}1',2'\text{-}B_{10}C_2H_{11})\text{-}1,2\text{-}B_{10}C_2H_{11}]$, 12075-02-4; $B_{10}H_{12}{\cdot}2CH_3CN$, 28377-97-1; $HCCC_2B_{10}H_{11}$, 23883-21-8.

Acknowledgment. The authors wish to thank the Office of Naval Research for its generous support of this research.

[8] There is an induction period for the decomposition reaction which is an exothermic process, and therefore while heating or adding reagents to this solution, caution should be employed.

[9] R. O. Schaeffer, *J. Amer. Chem. Soc.*, 79, 1006 (1957).

Correspondence

A Topological Approach to Boron Hydride Reactivities. Electrophilic and Nucleophilic Substitution.

Sir:

The topological approach is perhaps the simplest, yet potentially one of the most powerful methods which can be applied to the study of electron-deficient molecules. No parameters, experimental or theoretical, need be introduced. No equations are solved. The entire conceptual apparatus of the method consists of a few simple counting rules, which may be summarized as (1) conservation of topology, (2) conservation of electrons, and (3) conservation of orbitals.

In a recent paper,[1] we showed how the Dickerson-Lipscomb approach[2] could be simplified and extended by incorporating certain results from self-consistent field (SCF) and localized molecular orbital (LMO) calculations. Elimination of open three-center boron framework bonds[3] from our topological picture made possible the rapid evaluation of possible boron hydride frameworks. Our results were in agreement with the hypothesis that topologies which give rise to at least one, but preferably many, allowable valence structures are found in stable boron hydrides, while topologies with few or no such structures do not give rise to stable molecular frameworks. With this hypothesis as a starting point, one can use the topological method to predict the stability of proposed boron hydrides or to suggest likely structures for new species.

The synthetic chemistry of electron-deficient molecules is experiencing a remarkable growth. The plethora of new compounds has made clear the need for a generally applicable scheme for systematizing boron chemistry to a degree approaching that of carbon chemistry.[4] Some progress in this direction has been made by employing purely geometric considerations.[5] Although the geometrical approach is a profitable one when applied to structural questions, we believe that the complementary topological method can be equally useful in predicting structures and more fruitful in the study of reactions. In this correspondence we show how topological notions may be employed to predict the course of ionic substitution reactions in the boron hydrides.

The Topological Approach to Reactivity. Given that one

[1] I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, 10, 1921 (1971). Several errors appear in the counting rules given in this reference. In rule (4) the number of B–B bonds should be $s - q/2$, not $(s - q)/2$. In footnote 14 there should be $s - q/2 - 3l/2$ two-center and $p - s + l$ three-center bonds. The undefined parameter y should not appear in footnote 14.

[2] R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, 27, 212 (1957).

[3] Further localized orbital calculations (D. S. Marynick, I. R. Epstein, and W. N. Lipscomb, submitted for publication) have given evidence for the existence of an open three-center *boron–carbon–boron* bond in at least one carborane. However, these calculations also confirm the absence of open B–B–B bonds in either the carboranes or the boron hydrides.

[4] One possible scheme has been suggested by R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, 81, 3554 (1959).

[5] R. E. Williams, *Inorg. Chem.*, 10, 210 (1971).