halogen p_π and the metal orbitals, thus confirming the original predictions of Fenske and DeKock.

These results stress the importance of using molecular orbital calculations as an aid when assigning photoelectron ionizations. Furthermore, it is evident that the calculational procedure used must adhere closely to the set of criteria previously described.[14] Two specific points must be appreciated. First, eigenvalues are sensitive to any selection of parameters or approximations. If a parameter selection must be made across a series of molecules, the guidelines for this selection must be strongly consistent within the framework of the method used and must not be simply reflecting an expected behavior. Otherwise any predictive or correlative ability of the method will contain substantial uncertainty, as has been noted earlier regarding the SCCC calculation. Second, if a method uses parameters or approximations that adjust calculated eigenvalues to the binding energies found in pes, then this method is of questionable value when used for interpretation of the electronic structure and related properties of the ground state of the molecule. As discussed, a large portion of these adjustments necessarily reflects factors concerned with the state of the excited ion and ionization process and not with the electronic structure of the ground state of the molecule. These excitation effects may only be accounted for as adjustments subsequent to the results of the ground-state calculation and not in the ground-state calculation itself. This study is evidence for the value of our parameter-free molecular orbital calculations as a separate and distinct aid in the assignment and prediction of photoelectron spectra for a series of related molecules.

Registry No. $BrMn(CO)_5$, 14516-54-2; $ClMn(CO)_5$, 14100-30-2; $IMn(CO)_5$, 14879-42-6; *cis*-$BrMn(CO)_4(CNCH_3)$, 37474-14-9.

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Low-Frequency Infrared Spectra of Complexes Which Exhibit Magnetic Crossover. I. Iron(II) Complexes of 1,10-Phenanthroline and 2,2'-Bipyridine

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Transition metal complexes which exhibit magnetic spin crossover have been the subject of much recent experimental and theoretical investigation.[2-8] Previous investigators have made extensive studies of the unusual magnetic properties of the complexes $[Fe(phen)_2(NCS)_2]$, $[Fe(phen)_2(NCSe)_2]$, and $[Fe(bipy)_2(NCS)_2]$ (phen = 1,10-phenanthroline; bipy = 2,2'= bipyridine) and concluded that the temperature dependence of the magnetic moment is best explained in terms of a spin-state crossover between the high-spin ($^5T_2$) and low-spin ($^1A_1$) states.[9-11] In a previous communication, we have shown that in the case of $[Fe(phen)_2(NCS)_2]$, the Fe-N(phen) and Fe-N(NCS) stretching vibrations are highly dependent on the spin state of Fe.[12] In the present paper, we have investigated the low-frequency spectra (600-100 cm^{-1}) of $[Fe(bipy)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ at 298 and ~100°K and $[Fe(bipy)_2(CN)_2]$ at 298°K. Because of the complexity of the spectra in this region, the metal isotope technique was employed to assign the Fe-N(bipy) and Fe-N(NCS) stretching vibrations.[13-15] Using this technique, it was possible to assign the Fe-N(bipy) and Fe-N(NCS) stretching vibrations in both the high-spin (298°K) and low-spin (~100°K) states.

Experimental Section

All the compounds were prepared by methods given in the literature. $[Fe(phen)_2(NCSe)_2]$ was prepared by method (a) of Konig and Madeja.[9] Polymorph II of $[Fe(bipy)_2(NCS)_2]$ was prepared as described by Konig, *et al.*[10] $[Fe(bipy)_2(CN)_2]$ was prepared by the method of Schilt.[16] Isotopic Fe_2O_3 (purchased from Oak Ridge National Laboratory) was reduced to metallic Fe by passing hydrogen gas over the oxide at 400°. The isotopic Fe metal was dissolved in a minimum amount of 6 *N* sulfuric acid. phen or bipy was added to the resulting $FeSO_4$ solution in a 3:1 mole ratio. The resulting complexes were then treated in the same manner as the natural-abundance complexes described previously.

The infrared spectra were recorded on Beckman IR-12 (4000-400 cm^{-1}) and Hitachi Perkin-Elmer FIS-3 (400-100 cm^{-1}) spectrophotometers. All samples were recorded as Nujol mulls on CsI (4000-400 cm^{-1}) and polyethylene (400-100 cm^{-1}) plates. The spectra were recorded at a scanning speed of 1-4 cm^{-1}/min. Reproducibility was checked by multiple scans over the desired frequency range; the average error in frequency was ±0.3 cm^{-1}. The low-temperature spectra in the 600-400-cm^{-1} region were recorded using a cold cell of standard design with liquid nitrogen as a coolant. The low-temperature spectra in the 400-100-cm^{-1} region were recorded using a standard cold cell slightly modified to fit the evacuated sample chamber of the FIS-3. Liquid nitrogen was again used as a coolant.

Results and Discussion

High-Spin Spectra. Figure 1 shows the low-frequency spectra of $[Fe(bipy)_2(NCS)_2]$, $[Fe(phen)_2(NCS)_2]$, and $[Fe(phen)_2(NCSe)_2]$ from 400 to 100 cm^{-1} at 298°K.

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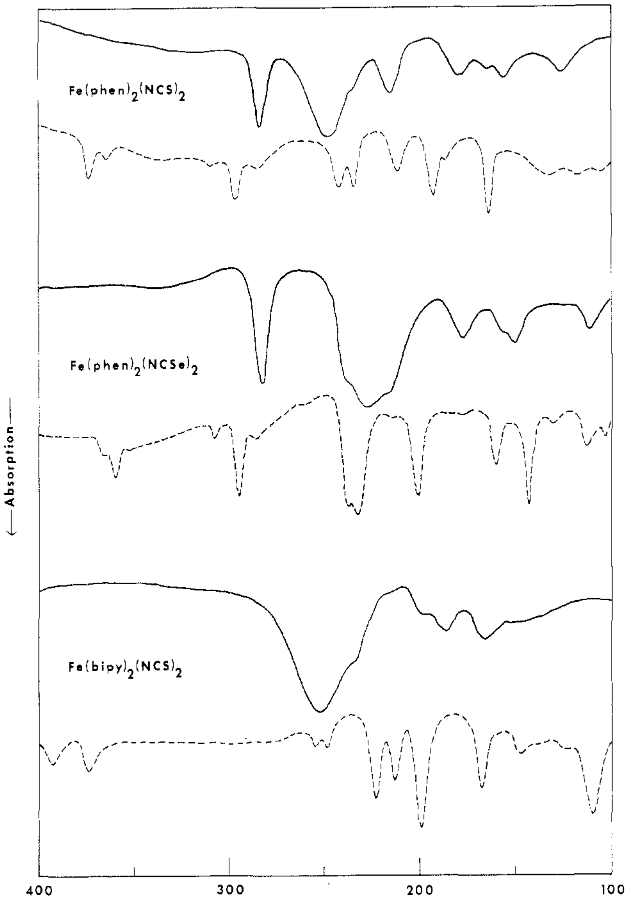

Figure 1. Low-frequency infrared spectra of [Fe(phen)$_2$(NCS)$_2$], [Fe(phen)$_2$(NCSe)$_2$], and [Fe(bipy)$_2$(NCS)$_2$] at a 298°K (full line) and ~100°K (broken line).

Table I lists the observed frequencies and isotopic shifts for the 600-100-cm^{-1} region. [Fe(bipy)$_2$(NCS)$_2$] has been assigned the cis configuration[7] and therefore belongs to C_2 symmetry. Under C_2 symmetry two infrared-active (A + B) Fe-N(NCS) stretching vibrations should be observed. As can be seen from Figure 1, only one strong, broad band is observed which is isotope sensitive. The broadness of this band would allow several band maxima within the band envelope which could not be resolved. The strong, isotope sensitive band at 253.0 cm^{-1} in the spectrum of [Fe(bipy)$_2$(NCS)$_2$] (Table I) is assigned to the Fe-N(NCS) stretching vibration. The isotope-sensitive band at 252.0 cm^{-1} in the spectrum of [Fe(phen)$_2$(NCS)$_2$] has been previously assigned to the Fe-N(NCS) stretching vibration.[12] A small shift to lower frequencies is observed when NCSe is substituted for NCS with the Fe-N(NCSe) stretch occuring at 228 cm^{-1} (Table I).

The isotope-sensitive band at 220.0 cm^{-1} in [Fe(phen)$_2$(NCS)$_2$] has been assigned to the Fe-N(phen) stretching vibration.[12] The change from [Fe(phen)$_2$(NCS)$_2$] to [Fe(phen)$_2$(NCSe)$_2$] should cause only slight effects on the Fe-N(phen) band. Therefore, the shoulder at 218 cm^{-1} (Figure 1) can be assigned to the Fe-N(phen) stretching vibration. In the case of [Fe(bipy)$_2$(NCS)$_2$], the Fe-N(NCS) stretching vibration is quite strong and broad as can be seen from Figure 1. The Fe-N(bipy) stretching vibration occurs at a slightly higher frequency (235 cm^{-1}) than the Fe-N(phen) stretch. It is, however, overlapped by the neighboring Fe-N(NCS) band. Therefore, it was not possible to obtain isotopic shift data.

Table I. Low-Frequency Infrared Spectra in the 600-100-Cm^{-1} Region at 298°K

[^{54}Fe(bipy)$_2$-(NCS)$_2$]	$\Delta\nu$(^{54}Fe-^{57}Fe)	[Fe(phen)$_2$-(NCSe)$_2$]
478.0 m	−0.3	512.0 w
431.0 vw	*b*	499.0 w
411.0 s	−0.5	434.0 m
253.0 s, br	*3.0*^{c}	427.0 w
235 sh	*a*	419.0 m
197.4 w	0.4	283.6 s
187.0 m	0.3	239 sh
167.0 m	0.0	*228.0* s, br
		218 sh
		177.2 m
		157 sh
		151.0 m
		112.5 w

^{a} Overlapped by neighboring band. ^{b} Too weak to get accurate shift data on an isotopic scale. ^{c} Italic frequencies are assigned to Fe-N stretches.

Low-Spin Spectra. It has been shown that upon cooling, [Fe(phen)$_2$(NCS)$_2$], [Fe(phen)$_2$(NCSe)$_2$], and [Fe(bipy)$_2$(NCS)$_2$] exhibit large decreases in magnetic moment over narrow temperature ranges.[9,10] These sharp decreases in magnetic moment, which correspond to changes in spin state of Fe(II), occur at 174, 232, and 215°K, respectively. Thus the spectra recorded at liquid nitrogen temperatures (~100°K) should be characteristic of complexes in the low-spin state.

Figure 1 shows the spectra of [Fe(bipy)$_2$(NCS)$_2$], [Fe(phen)$_2$(NCS)$_2$], and [Fe(phen)$_2$(NCSe)$_2$] at ~100°K in the 400-100-cm^{-1} region and Table II lists the observed frequencies and isotopic shifts in the 600-100-cm^{-1} region. [^{54}Fe(bipy)$_2$(NCS)$_2$] shows two isotope-sensitive bands at 393.0 and 374.7 cm^{-1} which are absent in the corresponding high-spin complexes. The low-spin complexes [Fe(bipy)$_3$]$^{2+}$ and [Fe(phen)$_3$]$^{2+}$ have two isotope-sensitive Fe-N stretching vibrations (Table II) in the same region.[17] We therefore assign these bands to the Fe-N(bipy) stretches. The Fe-N(phen) stretch in [Fe(phen)$_2$(NCS)$_2$] has been assigned at 379.0 and 371.0 cm^{-1}.[12] Based on the above data, the [Fe(phen)$_2$(NCSe)$_2$] complex shows two bands at 366 and 360 cm^{-1} which are assigned to the Fe-N(phen) stretching vibrations. No bands below 350 cm^{-1} are observed to be isotope sensitive.

As can be seen from Table II, [Fe(bipy)$_2$(NCS)$_2$] has two bands at 498.3 and 492.0 cm^{-1} which are isotope sensitive. These bands, which are absent in the respective high-spin spectra are assigned to the Fe-N(NCS) stretching vibrations. The [Fe(phen)$_2$(NCSe)$_2$] complex shows two bands at 530.5 and 527.0 cm^{-1} which may be assigned to the Fe-N(NCSe) stretching vibrations. This is similar to the assignment for the Fe-N(NCS) stretch in [Fe(phen)$_2$(NCS)$_2$].[12]

Comparison of High-Spin and Low-Spin Spectra. Previous infrared spectroscopic investigations have led to the conclusion that upon spin crossover to low spin, the Fe-N(phen or bipy) bond would be strengthened due to extensive delocalization of t_{2g} electrons of Fe(II) into vacant π^* orbitals of phen and a decreased Fe-N(NCS or NCSe) bond strength due to a reduction in back-donation of Fe(II) into π^* orbitals of NCS or NCSe.[10,11] It has also been proposed that high-spin Fe-N(phen) stretching vibrations are in the region below 200 cm^{-1}.[7] Although no indication of a Fe-N(diamine) stretching vibration was given for the range studied (4000-300 cm^{-1}), it was postulated that the

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Table II. Low-Frequency Infrared Spectra in the 600-100-Cm^{-1} Region at ~100°K

$[^{54}\mathrm{Fe(bipy)_2}$-$(\mathrm{NCS})_2]$	$\Delta\nu(^{54}\mathrm{Fe}-^{57}\mathrm{Fe})$	$[\mathrm{Fe(bipy)_3}]$-$(\mathrm{ClO_4})_2$[d]
498.3 s	*1.5*	
492.0 w	*1.2*	
482.0 s	0.5	
473.0 w	0.0	
460.5 w	0.5	
446.0 w	0.3	
434.0 w	0.3	
418.0 s	−0.4	418 s
393.0 w	*6.0*[c]	*381* m
374.7 m	*4.7*	*374* m
369.0 m	*b*	283 vw
255.0 w	0.0	237 w
249.0 w	0.0	203 w
223.2 m	0.2	190 w
214.0 m	0.0	163 vw
200.0 s	0.0	
168.2 s	0.2	
148 vw	*a*	
124 vw	*a*	
110.0 s	0.3	

$[\mathrm{Fe(phen)_2(NCSe)_2}]$	$[\mathrm{Fe(phen)_3}](\mathrm{ClO_4})_2$[d]
560.0 w	
530.5 s	
527.0 m	
511.5 m	
502.5 w	438 w
450.0 m	428 w
441.0 m	*374* w
432.0 s	*359* m
415.7 w	296 s
366.0 w	289 sh
360.0 w	250 sh
308.0 w	244 s
295.5 s	216 s
286.0 w	212 sh
238.5 s	192 m
233.0 s	176 m
202.0 s	
160.5 m	
143.5 s	
130.0 w	
112.5 w	
102.5 w	

[a] Too weak to get accurate shift data on an isotopic scale. [b] Split in the case of ^{54}Fe. Perhaps due to a slight crystal modification (different polymorph). [c] Underlined frequencies are assigned to Fe-N stretches. [d] Data taken from ref 18 at 298°K.

365-375-cm^{-1} region could contain the Fe-N(phen) stretches for the low-spin complex.[7] Recent far-infrared studies on $[\mathrm{M(bipy)_3}]^{n+}$ (M = first-row transition metal) complexes have shown the metal-nitrogen stretching frequencies to be highly sensitive to the electronic configuration of the central metal atom.[18] $[\mathrm{Cr(bipy)_3}]^{2+}$ and $[\mathrm{Fe(bipy)_3}]^{2+}$ are both low-spin complexes and have M-N(bipy) stretches at 343, 351 and 376, 386 cm^{-1}, respectively. In contrast, $[\mathrm{Mn(bipy)_3}]^{2+}$ is a high-spin complex and shows Mn-N(bipy) stretches at 224 and 191 cm^{-1}. $[\mathrm{Fe(bipy)_3}]^{3+}$ (low-spin) is isoelectronic with $[\mathrm{Mn(bipy)_3}]^{2+}$ (d^5) but shows Fe-N(bipy) stretches at 367 and 384 cm^{-1}. We would then expect a shift of about 150 cm^{-1} on spin-state change based on the $[\mathrm{M(bipy)_3}]^{n+}$ data.

A comparison of the spectra at the two temperatures given in Figure 1 shows that the low-frequency spectra are highly dependent on the spin-state of Fe(II). Furthermore, both Fe-N(phen or bipy) and Fe-N(NCS or NCSe) stretching vibrations are highly dependent on spin state. In the case of $[\mathrm{Fe(bipy)_2(NCS)_2}]$, a frequency shift from 235 to 393.0 and 374.7 cm^{-1} accompanies the spin crossover. It is interesting to note that high-spin $[\mathrm{Fe(bipy)_2(NCS)_2}]$ shows Fe-N(bipy) stretches in the same region as $[\mathrm{Mn(bipy)_3}]^{2+}$ (235 and 224, 191 cm^{-1} respectively).

In the case of the low-spin Fe-N(NCS or NCSe) stretch, an inspection of Table II reveals no bands below 250 cm^{-1} which are isotope sensitive and therefore indicative of a weaker Fe-N(NCS or NCSe) bond. Instead, isotope-sensitive bands are observed in the 490-540-cm^{-1} region. Since no previous assignments for the Fe-X stretch in low-spin $[\mathrm{Fe(phen)_2X_2}]$ or $[\mathrm{Fe(bipy)_2X_2}]$ type complexes have been made and the observed isotopic shifts were rather small, $[\mathrm{Fe(bipy)_2(CN)_2}]$ (low-spin) was investigated to help establish a general frequency range for these low-spin Fe-X stretches. $[\mathrm{Fe(bipy)_2(CN)_2}]$ is prepared by the displacement of bipy from $[\mathrm{Fe(bipy)_3}]^{2+}$ by $\mathrm{CN^-}$ in aqueous solution. Since $\mathrm{CN^-}$ has a stronger ligand field strength than bipy and is much smaller in mass, it is reasonable to expect the Fe-CN stretch at a frequency greater than that observed for the Fe-N(bipy) stretches which as mentioned previously occur in the 370-390-cm^{-1} region. In order to assign the Fe-CN stretching vibration, isotopically substituted $[\mathrm{Fe(bipy)_2(CN_2)}]$ was prepared and the 600-400-cm^{-1} region was examined. A broad band at 525.8 cm^{-1} is observed in the spectrum of $[\mathrm{Fe(bipy)_2(CN)_2}]$ which is absent in the spectrum of $[\mathrm{Fe(bipy)_2(NCS)_2}]$ at ~100°K. Furthermore this band shows a relatively large shift (2.7 cm^{-1} for the ^{54}Fe-^{57}Fe substitution) as compared to the other bands in the 600-400-cm^{-1} region (477.8 (w), 471.0 (w), 447.0 (w), 436.2 (w), and 420.2 (m) cm^{-1}) which show little isotopic sensitivity (shifts of −0.2, 0.2, 0.0, 0.7, and 0.3 cm^{-1}, respectively). The present assignment is reasonable in view of the fact that $[\mathrm{Fe(CN)_6}]^{4-}$ shows the Fe-CN stretch at 585 cm^{-1}.[19] At ~100°K, the ligand field strength of the NCS group is sufficient to cause spin pairing. Thus a shift in frequencies of the Fe-NCS stretch from the high-spin value of 253 cm^{-1} to the 490-500-cm^{-1} region is observed on cooling. As might be expected on the basis of ligand field strength, the frequency of the Fe-NCS stretch (at ~100°K) is somewhat less than that observed for the Fe-CN stretch.

The crystallographic data of Konig and Watson on $[\mathrm{Fe(bipy)_2(NCS)_2}]$ (polymorph II) are also consistent with strengthened Fe-N(bipy) and Fe-N(NCS) bonds upon spin crossover to the low-spin state.[20] The structures at both 295 and 100°K are orthorhombic, space group *Pcnb*, and show no phase change with temperature change. The Fe-N(bipy) bond lengths are shortened by 0.12 and 0.16 Å and the Fe-N(NCS) bond length is shortened by 0.08 Å for the given temperature change. Furthermore, the NC distance in the NCS group is lengthened by 0.08 Å for the same temperature change. These crystallographic data agree with our spectral findings. A decreased bond length is indicative of a stronger bond and these bond changes are reflected in our spectral data by the substantially higher frequency range observed for the low-spin Fe-N(phen, bipy, NCS, or NCSe) stretches as compared to these same Fe-N stretches in the high-spin state.

The original prediction of a weakened Fe-N(NCS) bond

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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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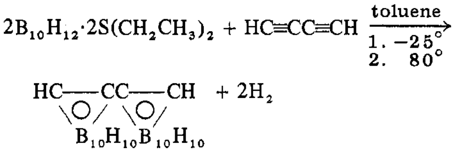
Biscarborane, 1-[1′-1′,2′-dicarba-*closo*-dodecaborane(12)]-1,2-dicarba-*closo*-dodecaborane(12), I, has been found to act as a novel chelating agent with transition metal ions, forming remarkably stable complexes in which the biscarborane ligand is bound *via* metal-carbon σ bonds.[2,3] Previously the 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.

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



$$2B_{10}H_{12}\cdot 2S(CH_2CH_3)_2 + HC{\equiv}CC{\equiv}CH \xrightarrow[\substack{1.\ -25^\circ \\ 2.\ \ 80^\circ}]{\text{toluene}} HC\text{—}CC\text{—}CH\ (B_{10}H_{10}B_{10}H_{10}) + 2H_2$$

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$_2$O$_5$, 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$_2$O 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$_2$O, 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 $B_{10}H_{12}\cdot 2S(CH_2CH_3)_2$ 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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