for the coupled spin systems.

The first two points of this list can be rationalized by the recognition that hfs splitting cannot be resolved unless the electron hopping between rings is eliminated (or considerably diminished). The results discussed here will remove the third anomaly and provide some insight into point 4.

The preparation of electrolyzed samples under inert-atmosphere conditions has been described previously.[4,9] Spectra were determined with an IBM ESR instrument for the complexes in dimethyl sulfoxide (DMSO) solvent and N,N-dimethylformamide (DMF) solvent in some cases. The high temperatures were obtained by using a nitrogen gas variable-temperature apparatus adapted to the IBM cavity system. The voltammetry of the complexes (approximately millimolar concentration) in DMSO is similar to that in DMF, and electrolysis potentials were determined from the voltammograms. The first- and second-derivative ESR spectra for $[Ru(bpy^-)_3]^-$ determined at 75 °C in DMSO are shown in Figure 1. The spectra at 24 °C are anisotropic, similar to that found for other electrolytic solvents near their freezing point. As the temperature is increased the signal becomes isotropic, consistent with rapid tumbling. At temperatures greater than 60 °C and up to 160 °C, the signal-to-noise ratio decreases due to the heating of the cavity and the consequent detuning of the spectrometer. Cycling of the temperature between room temperature and 160 °C does not result in any decomposition in DMSO. While DMF has been the solvent of choice for the prior ESR measurements, DMF does decompose at high temperature and the ESR signal is lost. The ESR spectra of the $[Ru(bpz^-)_3]^-$ species was also obtained at high temperature in DMSO and hfs was measured although the spectra here are not as well resolved as that of $[Ru(bpy^-)_3]^-$. The $[Ru(COOetbpy^-)_3]^-$ complex does not give hfs at high temperature in DMSO because of the very weak signal intensity. The spectra of the two-electron-reduction product $[Ru(bpy^-)_2bpy]^0$ was determined in DMSO and only a broad $S = {}^1/_2$ line could be determined with no hfs observed at any temperature.

The appearance of the hfs at high temperature and the anisotropic spectra just above the solvent melting point indicate that the inability to resolve the hfs is due, in part, to a small amount of **g** and/or **A** tensor anisotropy. Further, the absence of high-temperature (60 °C) resolution for $[Ru(bpy^-)_3]^-$ in DMF implies that the DMSO may provide a minor perturbation upon the coupling constant, producing a favorable spectral density. The possibility that the three-electron species is a localized orbital system with a coupling of two spins to give a doublet state remains and could be the origin of some of the loss in ESR intensity for the three-electron relative to the one-electron species. However, for most complexes, the $n = 3$ spectrum is much less intense than the $n = 1$ spectrum rather than having comparable intensity to the spectrum of the one-electron species. Further, the two-electron species are all paramagnetic with intensities comparable to or less than that of the $n = 1$ species.

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A Novel Route for Macroscale Preparation of the Unsubstituted C_2B_4 Carborane 2,3-Dicarba-*nido*-hexaborane(8)

Sir:

Recent dramatic development in the chemistry of C-substituted derivatives of 2,3-dicarba-*nido*-hexaborane(8) has been partly due to availability of improved synthetic procedures for these C-substituted *nido*-carboranes.[1,2] These new preparative routes are significantly better than the conventional ones[3] in terms of safety, yield, and practicality. However, none of these improved procedures gives the parent C_2B_4 carborane, even in trace quantities. The only available route to the parent carborane has been the method of Onak and co-workers.[3e] This method produces in low yield a complex mixture of *nido*-$C_2B_4H_8$ and several other unwanted carboranes. Therefore, an investigation of alternative routes for the synthesis of 2,3-dicarba-*nido*-hexaborane(8) is warranted.

We have recently reported that *nido*-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_6$ (I) is produced in multigram quantities (12-13 g/batch; over 73% yield) from a reaction between B_5H_9 and $Me_3SiC\equiv CSiMe_3$ at elevated temperature.[2a,b] We have also shown that one of the C(cage)-Si bonds in I could be cleaved effectively to produce *nido*-2-(Me_3Si)-2,3-$C_2B_4H_7$ (II), in 90% yields.[2c] During the course of our investigation in this area, we sought to examine the reactivity of both the C(cage)-Si bonds in I toward gaseous HCl at elevated temperatures and at different molar ratios of these reactants.

In a procedure[2c] identical with that employed in the preparation of *nido*-2-(Me_3Si)-2,3-$C_2B_4H_7$ (II), *nido*-carborane I (9.38 g, 42.7 mmol) was allowed to react with pure anhydrous HCl gas (141 mmol) in a molar ratio of 1:3.3 at 160-170 °C for 4 days in a high-vacuum stainless-steel cylinder. This reaction produced II (1.97 g, 13.34 mmol; 31% yield based on I consumed), a mixture of Me_3SiCl and *nido*-2,3-$C_2B_4H_8$ (III) (9.92 g), and *closo*-$C_2B_4H_2Cl_4$ (IV) (0.81 g, 3.82 mmol; 8.9% yield based on I consumed), which were collected in traps held at -45, -95, and -196 °C, respectively. A substantial quantity of H_2 gas (19.42 mmol) produced in the reaction was pumped out. Since the parent C_2B_4 carborane (III) is highly miscible in Me_3SiCl, separation of III from Me_3SiCl by vacuum fractionation was unsuccessful. Therefore, a new separation procedure was used by condensing the mixture of Me_3SiCl and III at -196 °C into a Pyrex-glass reactor of 0.5-L capacity that had been previously charged with anhydrous $LiAlH_4$ (3.95 g, 104.0 mmol) and a magnetic stirring bar. After stirring of this heterogeneous mixture at -78 °C for 12 h and then at room temperature for 36 h, the volatiles were fractionated to collect Me_3SiH (5.11 g, 69.05 mmol) and parent C_2B_4 carborane (III) (0.89 g, 11.71 mmol; 27% yield based on I consumed) in traps held at -196 and -95 °C, respectively. A noncondensable gas, identified as H_2 (22.3 mmol), produced during this reduction process was pumped out. A substantial quantity (0.33 g, 1.34 mmol) of transparent crystals was collected in trap held at -78 °C, and these crystals were identified by spectroscopy as unsolvated $(Me_3Si)_3Al$.[4] Scheme I represents the reaction pathways during the production of III.

The reaction of II with HCl in a molar ratio of 1:1.5 under similar conditions produced III and IV in 30% and 15% yields, respectively. When the molar ratio of I to HCl was 1:10, under similar conditions the reaction shown in Scheme I produced IV in 91% yield as the sole carborane product. When the molar ratio

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Scheme I

$\bigcirc$ = B $\bullet$ = C   o = H
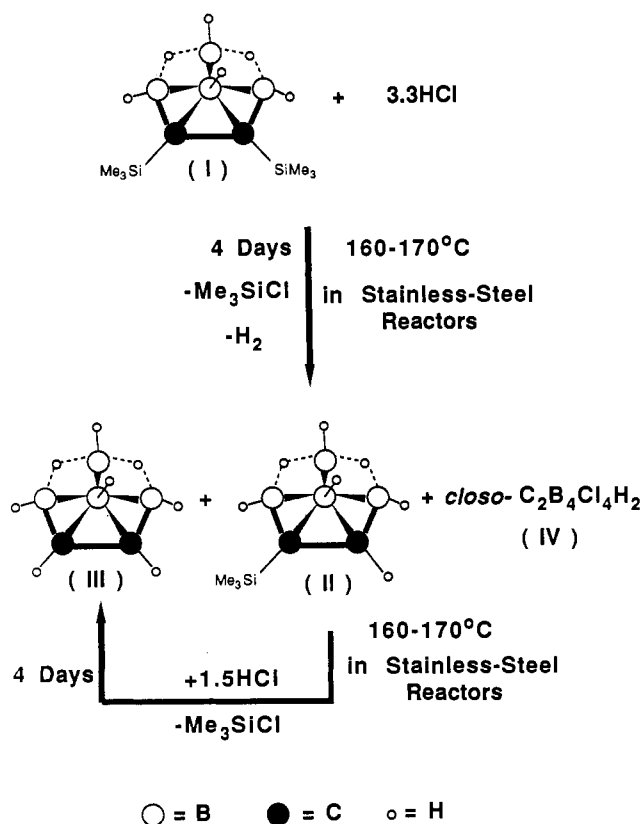
of I to HCl was 1:0.9, compound II was produced in 80% yield in addition to Me₃SiCl and H₂.

Infrared spectra and ^{1}H, ^{11}B, and ^{13}C NMR spectra of both II and III are identical with their published spectra.[2a,3,5] Compound IV was characterized by its ^{1}H, ^{11}B, ^{13}C, and ^{35}Cl pulse Fourier transform NMR and IR spectra.[6]

It is important to note that the ratio of reactants in Scheme I determines the formation of either one particular carborane or a mixture of several carborane products and their respective yields. Evidently, a large excess of HCl in Scheme I produced IV in that all the B–H bonds are chlorinated, whereas an insufficient quantity of HCl yields mainly mono(trimethylsilyl)-substituted carborane (II). However, for the high-yield preparation of the parent C₂B₄ carborane (III) the ideal molar ratio between I and HCl was found to be 1:3.3.

The new synthetic route described in this investigation is of extreme interest for the following reasons: (i) this is the method of choice over the existing method of preparation of 2,3-dicarba-*nido*-hexaborane(8) (III), which involves the gas-phase pyrolysis of a mixture of HC≡CH and B₅H₉; (ii) the reaction avoids the utilization of large-volume gas bulbs and Lewis bases and the necessity of handling the volatile flammable and explosive pentaborane–acetylene mixture; (iii) it does not result in the formation of a complex mixture of carboranes under specific conditions and hence eliminates the necessity of separating products by gas chromatography; and (iv) it could produce III in gram quantities since its precursor (I) is routinely prepared in multigram quantities.

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(6) FT NMR data (neat liquid): ^{1}H NMR (relative to external Me₄Si) δ 1.65 [s (br), 2 H, cage CH]; ^{11}B NMR (relative to external BF₃·OEt₂) δ 62.76 [s, 4 B, basal B–Cl]; ^{13}C NMR (relative to external Me₄Si) δ 14.88 [d of q (br), cage CH, $^1J(^{13}C-^1H)$ = 181.4 Hz, $^1J(^{13}C-^{11}B)$ = 65 Hz]; ^{35}Cl NMR (relative to external NaCl/D₂O) δ 299.7 [s (br), cage B–Cl]. IR data (gas phase at 40 Torr vapor pressure): 2990 (m, br), 2965 (sh) [ν(C–H)], 1380 (s, br), 1308 (w, s), 1303 (m, s), 1260 (sh), 1200 (w), 1073 (m, br), 1050 (w), 1015 (s, br), 945 (w, br), 905 (m, br), 830 (s, br), 765 (s, br), 625 (sh), 570 (w, br), 529 (s, br) cm⁻¹. Mass spectrum: since the compound IV is extremely sensitive to air and/or moisture even in trace quantity, it decomposed in the mass spectrometer.

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Oxygen Content of Superconducting Perovskites, La₂₋ₓSrₓCuOᵧ and YBa₂Cu₃Oᵧ

Sir:

Since the recent discovery of high superconducting transition temperatures (T_c), first in La₂₋ₓ(Ba,Sr)ₓCuOᵧ ($T_c \simeq$ 30–40 K) and second in YBa₂Cu₃Oᵧ ($T_c \simeq$ 90 K), the superconducting properties of these oxides have been generally considered to be dependent on their oxygen content.[1,2] While acknowledgment has been made of the importance of oxygen stoichiometry, however, most studies of these materials to date have neglected chemical analyses, although articles are now beginning to appear that attempt to correlate analyzed oxygen content with variations in electrical transport properties.[3] The superconducting properties of YBa₂Cu₃Oᵧ are influenced by an additional factor, only recognized very recently, that relates to a tetragonal-to-orthorhombic phase transition near ~700 °C. Either of the two pure phases or a two-phase mixture can be obtained at room temperature, depending on the high-temperature O₂ annealing procedures and the cooling rates.[4] The two phases, each of composition YBa₂Cu₃Oᵧ (but generally with different values of *y*), have considerably different normal-state and superconducting properties: the orthorhombic phase is the ~90 K superconductor, whereas the tetragonal phase is either a semiconductor or at best a lower T_c superconductor. The occurrence of a two-phase mixture thus considerably complicates the correlation of properties with oxygen content.

Since in the composition YBa₂Cu₃Oᵧ Y and Ba have fixed oxidation states of +3 and +2, respectively, a direct relationship exists between the Cu(II):Cu(III) ratio and the oxygen stoichiometry: if the compound contains only Cu(II), *y* = 6.5, whereas if it contains all Cu(III), *y* = 8.0. In classical studies of Cu(III) compounds such as KCuO₂, the Cu(III) content has been determined by iodometry or by hydrogen reduction.[5-7] Hydrogen reduction has thus far been the principal analytical procedure used

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