palladium can less readily accommodate two halides and an EDM moiety in a square-planar configuration than in the case of the smaller halides. Palladium would still prefer a square-planar environment, but the steric requirements of the ligand prevent this. We are currently investigating the reactions of this unusual species.

It is interesting to note that no characterizable complexes could be isolated from the reaction of EDM with Pt(II) halides under a variety of conditions.

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Boron Insertion Reactions. Preparation of 1,1-Dimethyldiborane(6) and 2,2-Dimethyltetraborane(10)

Sir:

We wish to report two boron insertion reactions that appear to be the simplest examples of a previously unrecognized class of insertion reactions in boron hydride chemistry.[1] The inserting agent used was dimethylboron chloride, $(CH_3)_2BCl$, which was found to react with sodium tetrahydroborate, $NaBH_4$, and with sodium octahydrotriborate, NaB_3H_8, to produce 1,1-dimethyldiborane(6), 1,1-$(CH_3)_2B_2H_4$, and the new 2,2-dimethyltetraborane(10), 2,2-$(CH_3)_2B_4H_8$, respectively. Thus these reactions may be considered as explicit examples of insertion of a formal $(CH_3)_2B^+$ moiety into a borane anion *via* two bridge hydrogen bonds without loss of hydrogen. A plausible but tenuous analogy may be drawn between the reactions described here and reactions of BH_4^- and $B_3H_8^-$ with several types of transition metal complexes to produce compounds in which the transition metal is bonded to the borane moiety through double bridge hydrogen bonds.[2] Previous studies of the synthesis of B_4H_{10} having a specific boron label in the 2 position involved formal addition of BH_3 to the intermediate B_3H_7.[3]

Long and Wallbridge have postulated that the high-temperature reaction of $(CH_3)_3B$ and $NaBH_4$ or $LiBH_4$ in the presence of HCl to produce mixed methylated diboranes proceeds through the intermediate formation of $(CH_3)_2BCl$ and subsequent reaction of this with the BH_4^- salt.[4] In view of our observations this postulate appears to be quite reasonable, but the differences in reaction conditions do not allow definitive conclusions.

In a typical preparation of 2,2-$(CH_3)_2B_4H_8$, ether-free NaB_3H_8[5] (from 16.56 mmoles of B_2H_6 and excess 0.6% Na–Hg, theoretical yield 8.28 mmoles) was slurried with 10.0 mmoles of $(CH_3)_2BCl$ for 40 min at −30°. The volatile materials were then separated by fractional distillation in the vacuum line. The 2,2-$(CH_3)_2B_4H_8$ slowly distils through a −78° trap and is almost completely condensed in a −95° trap (yield 4.06 mmoles, 49%). Decomposition of 2,2-$(CH_3)_2B_4H_8$ occurs fairly rapidly at room temperature even in the gas phase. Thus vapor pressures and gas density data are at best only marginally reliable criteria for determining purity. Observed vapor pressures are 5.8 mm at −30.4°, 9.4 mm at −23.7°, and 36.5 mm at 0.0°. Extrapolation of these data gives a normal boiling point of about 72°. The vapor density molecular weight was found to be 82.8; calcd 81.4. The mass spectrum of 2,2-$(CH_3)_2B_4H_8$ (MS-902 spectrometer) at 70 V cuts off at *m/e* 78, which corresponds to the parent ion less four hydrogen atoms: calcd for $^{12}C_2{}^{11}B_4H_{10}$, 78.1155; found 78.1162. The *m/e* 77 peak also arises from a single species of the same empirical composition as the *m/e* 78 peak but containing a ^{10}B in place of a ^{11}B: calcd for $^{12}C_2{}^{10}B^{11}B_3H_{10}$, 77.1191; found, 77.1197. The ^{11}B nmr spectrum of 2,2-$(CH_3)_2B_4H_8$ is shown in Figure 1. The chemical shifts of the triplet and doublet differ very little from the corresponding shifts for B_4H_{10},[6] but there is a conspicuous absence of resolved long-range coupling, as has also been noted in the spectrum of 2-BrB_4H_9.[7] The ^1H nmr spectrum (100 MHz) of 2,2-$(CH_3)_2B_4H_8$ is somewhat complex owing to bad overlap, but the general features are in agreement with the other spectral evidence. The gas-phase infrared spectrum of 2,2-$(CH_3)_2B_4H_8$ (10-mm pressure, 10-cm cell) contains bands (in cm^{-1}) characteristic of C–H at 2970 (m), 2925 (w, sh), and 2850 (vw); B–H at 2575 (vs) and 2500 (s); and B–H–B at 2250 (s) and 2095 (m); as well as a fairly complex fingerprint region having bands at 1440 (w), 1325 (s), 1155 (m), 1100 (m), 1035 (s), 990 (w, sh), 940 (m), 885 (w), 840 (m), 795 (m), and 670 (w).

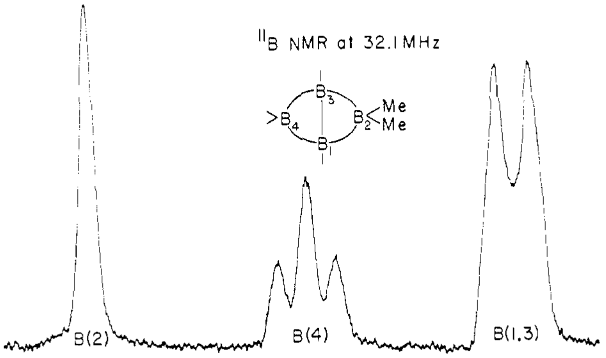

Figure 1. The ^{11}B nmr spectrum of 2,2-$(CH_3)_2B_4H_8$ at 32.1 MHz. Chemical shifts from $BF_3 \cdot O(C_2H_5)_2$ ± 0.5 ppm (and coupling constants ± 5 Hz) for the resonances are: B(2), −21.1; B(4), +9.3 (126); B(1,3), 37.9 (150).

The 1,1-$(CH_3)_2B_2H_4$ was prepared by slowly warming a mixture of excess $NaBH_4$ (barely wet with diethylene glycol dimethyl ether) and $(CH_3)_2BCl$ from −196 to about 0°. The material that passed a trap at −122° consisted entirely of 1,1-$(CH_3)_2B_2H_4$, as shown by exact correspondence comparison of the gas-phase infrared spectrum with that in the literature[8] (yield 71%).

Further studies of boron insertion reactions are in progress and will be reported shortly.

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Temperature Dependence of Photocurrent in γ-Irradiated Alkaline Ice. Location of Energy Levels of Trapped Electrons

Sir:

Strongly alkaline solutions (5–10 *M* NaOH) form transparent glasses when rapidly frozen to 77°K. ^{60}Co γ radiolysis of this alkaline ice produces trapped electrons characterized by an epr singlet and an optical absorption with λ_{max} at 580 nm.[1] In this paper we report observation of photocurrent and its temperature dependence in this system. The photocurrent shows that the trapped electrons can be optically excited to a mobile state. The temperature dependence between 4 and 77°K indicates that the optical transition is from a bound ground state directly to the conduction band, and the temperature dependence above 77°K indicates the presence of shallow traps near the conduction band.

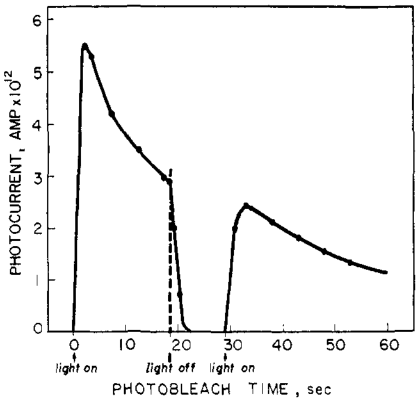

Figure 1. Time-dependent photocurrent in 10 *M* NaOH at 77°K with a radiation dose of 0.03 Mrad and an applied electric field of 4.5 kV/cm. The rise time of the photocurrent is due to the response time of the apparatus.

The alkaline ice sample was contained in a polyvinyl chloride sleeve (4.5-mm i.d.) into which two brass 4-mm diameter mesh electrodes were inserted. After γ irradiation at 77°K, the electrodes were connected to electrometer and voltage supply cables with gold pin connectors, and the sample was placed in an unsilvered dewar without allowing the sample to warm. The electrode distance was 2 mm and a typical applied voltage was 900 V. Light from a 500-W slide projector was passed through a water filter to remove infrared light and through a uv filter, and was directed perpendicular to a line between the electrodes. At 77°K and 0.03 Mrad, a peak photocurrent of 5×10^{-12} A is observed. The photocurrent varies with time as shown in Figure 1. Blanks verified that insignificant photocurrent was seen in unirradiated samples or in irradiated pure ice.

The peak photocurrent is linear with radiation dose from 0.006 to 0.06 Mrad, and is also linear with light intensity. When a monochromator is used, the peak photocurrent varies with wavelength in a manner similar to the known absorption spectrum of the trapped electron. The peak photocurrent is slightly higher at 4°K (liquid helium) than at 77°K (liquid nitrogen). However, between 74 and 111°K the peak photocurrent increases with temperature. A plot of peak photocurrent *vs.* reciprocal temperature is linear and gives an activation energy of 0.4 kcal/mole.

The fact that photocurrent is observed indicates that the trapped electrons in alkaline ice can be optically excited to a mobile state which can be considered as a type of conduction band level. The current is proportional to the number of electrons reaching the conduction band, their mobility, and their average lifetime in the conduction band. By analogy with trapped electrons in alkali halides (F centers), the mobility is expected to have a small negative temperature dependence.[2] The observation of a nearly temperature-independent photocurrent between 4 and 77°K indicates that the optical transition associated with the trapped electrons occurs directly to the conduction band or to a bound state that can cross over to the conduction band upon lattice relaxation.[3] There is no evidence for a strongly bound excited state. The negative temperature dependence of the electron mobility probably accounts for the slightly higher photocurrent at 4°K compared to 77°K. The positive temperature dependence of the photocurrent above 77°K indicates the presence of shallow traps. Above 77°K the electrons can be thermally excited out of these traps to effectively increase their lifetime in the conduction band and thus increase the photocurrent. This model implies that the temperature dependence of the net rate of loss of trapped electrons by optical bleaching will be negative near 77°K, because at higher temperatures there will be an increased probability for retrapping the electron in a deep trap. This negative temperature dependence has recently been confirmed in our laboratory.[4]

A number of calculations of the energy levels for trapped electrons in water and in ice have been made.[1,5–8] Although different approximations and both continuum and structural models have been used, all calculations predict that the first excited state is strongly bound by 1.8–3.0 eV with respect to the conduction band. Our experiments show that this value is much too large, and that the first excited state is probably not bound. Current calculations in our laboratory with a semicontinuum potential[9] appear to give a more weakly bound excited state which is in better agreement with experiment.

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