Acknowledgments. The authors wish to thank Professor J. W. Cobble for his helpful suggestions and discussions. They also are grateful to Mr. Gary L. Hatch of this department for making analyzed samples of crystalline potassium perbromate available for these studies. The authors also thank Dr. E. H. Appelman for the use of a preprint of his work[2] before publication. This research was supported in part by a grant from the Faculty Research Committee of Kansas State Teachers College.

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(11) To whom correspondence should be addressed.

John R. Brand,[11] Steven A. Bunck
Department of Chemistry, Kansas State Teachers College
Emporia, Kansas 66801

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A Paramagnetic Complex of Palladium(II)[1]

Sir:

While the chemistry of Pd(II) deals almost exclusively with square-planar, diamagnetic species, there are reports in the literature of other coordination geometries. To our knowledge, there are no substantiated reports of a tetrahedral species of Pd(II). In this communication we wish to report a paramagnetic complex of Pd(II) which we believe to be tetrahedral.

The ligand N,N-ethylenedimorpholine (EDM), $C_{10}H_{20}N_2O_2$ (Figure 1), has been shown to force tetrahedral coordination geometry with divalent first-row transition metal halides.[2] The reaction of EDM with palladium halides does not lead to such simple results. The reaction of $PdCl_2$ with EDM in acetone gives a yellow complex with the stoichiometry $PdCl_2EDM$ (**1**). The complex is insoluble in an extremely wide variety of solvents and is diamagnetic.[3] Similar results are obtained with $PdBr_2$, prepared through the reaction of $PdCl_2$ with KBr. The insolubility of these complexes is attributed to a polymeric structure with the nitrogens of the EDM moiety bridging adjacent palladiums.

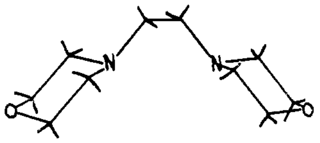


Figure 1.

The reaction of PdI_2 with EDM in acetone leads to no apparent reaction. However, the reaction of K_2PdI_4 (prepared by the reaction of $PdCl_2$ with excess KI) with a 50-fold molar excess of EDM in acetone produces a red solution. Evaporation of the acetone and trituration of the resulting solid with ether gives a product with the approximate stoichiometry PdI_2EDM (**2**). The solid is diamagnetic. When dissolved in acetone **2** originally gives a light red solution (**3**) which darkens over a period of 2 hr to give **4**. Upon addition of a large excess of EDM to **4**, the solution again reverts to a light red color (**5**). Solutions **3** and **4** are diamagnetic while solution **5** is paramagnetic. The magnetic moment is 3.4 ± 0.1 BM at 305°K.

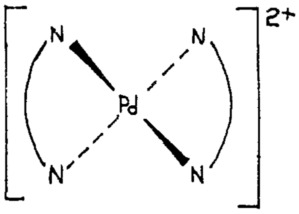
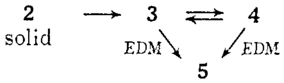


Figure 2.

Conductivity studies show the solutions **4** and **5** are 2:1 electrolytes while solution **3** is a nonelectrolyte. Upon the conversion of **4** to **5** a band grows into the electronic spectrum at 19,200 cm^{-1} (ϵ 200). Kinetic studies on the conversion of **3** to **4** show that the two species are in equilibrium; **3** ⇄ **4**. The equilibrium constant is 25 ± 5 at 298°K. Addition of a large amount of EDM to either **3** or **4** leads to the appearance of a paramagnetic species in the time required to make the susceptibility measurement, about 2 min. These results lead to the following reaction scheme.



The species **2**–**5** can be assigned reasonable structures on the basis of the above data and a knowledge of the steric requirements of the ligand. **2** and **3** most probably are square-planar monomeric species. Species **4** can reasonably be assigned a dimeric structure with bridging iodides. Since the paramagnetic species **5** is only formed in the presence of a large excess of EDM, it is reasonable to assign a structure to **5** which contains more EDM than the solid **2**. The observed paramagnetism does not, *a priori*, rule out a square-planar structure[4] but makes it unlikely. The steric requirements of the ligand tend to rule out an octahedral structure.[5] On the basis of the above and the conductivity studies on **5**, a tetrahedral species is postulated (Figure 2). If this is the case a band in the electronic spectrum between 8,000 and 10,000 cm^{-1} might be expected. No band, however, was observed in this region. Upon evaporation of the solvent and trituration with ether, **5** yields **2**. Complex **5** has not been isolated in the solid state at this time, but work on the system is continuing.

The difference in behavior between the chloride and bromide complexes, on the one hand, and the iodide complex, on the other, can be rationalized on the basis of the coordinating power of the species involved and the size of the anion present. Chloride and bromide are better coordinating ligands than iodide. As a result of this the nitrogens of the EDM moiety are better able to compete with the halide ions for the available coordination sites in the case of iodide. The size of the anion is also a factor. With the large iodide ion the

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(1) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14–18, 1969.

(2) A. L. Lott and P. G. Rasmussen, *J. Inorg. Nucl. Chem.*, in press.

(3) Magnetic moments on solid complexes were determined by the Gouy method. Magnetic moments of solutions were determined by nmr techniques; for details see B. N. Figgis and J. Lewis in "Techniques of Inorganic Chemistry," Vol. IV, H. B. Jonassen and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1965, Chapter IV.

(4) (a) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); (b) *ibid.*, **29**, 162, 1129 (1959); (c) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, **81**, 538 (1959).

(5) W. R. Scheidt, J. C. Hanson, and P. G. Rasmussen, *Inorg. Chem.*, 8, 2398 (1969).

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.

Antone L. Lott, Paul G. Rasmussen
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104
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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).

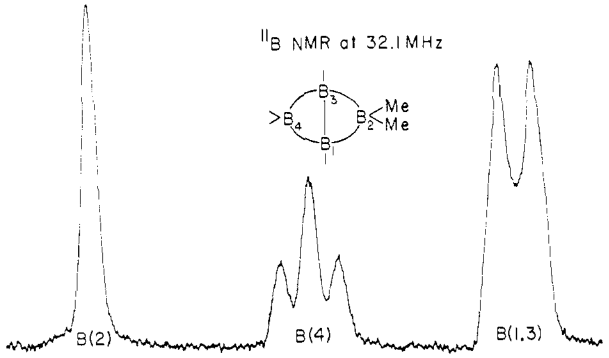

Figure 1. The ^{11}B nmr spectrum of 2,2-$(CH_3)_2B_4H_8$ at 32.1 MHz. Chemical shifts from $BF_3 \cdot O(C_2H_5)_2$ ± 0.5 ppm (and coupling constants ± 5 Hz) for the resonances are: B(2), −21.1; B(4), +9.3 (126); B(1,3), 37.9 (150).

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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(5) W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Am. Chem. Soc.*, **80**, 1828 (1958).

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