

- (7) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).  
 (8) (a) G. Emschwiller, *C. R. Hebd. Seances Acad. Sci.*, **238**, 341 (1954); (b) *ibid.*, **239** 1213 (1954); (c) *ibid.*, **259**, 4281 (1964); (d) *ibid.*, **260**, 4333 (1965); (e) *C. R. Hebd. Seances Acad. Sci., Ser. C*, **265**, 281 (1967); (f) *ibid.*, **268**, 692 (1969).  
 (9) C. T. Bahner and L. L. Norton, *J. Am. Chem. Soc.*, **72**, 2881 (1950).  
 (10) Microanalyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn.  
 (11) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed, Academic Press, New York, N.Y., 1965, p 1511.  
 (12) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

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### <sup>14</sup>N Nuclear Quadrupole Resonance Spectra of Coordinated 1,2-Dipiperidinoethane<sup>1a</sup>

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With the advent of double resonance methods for the determination of <sup>14</sup>N nuclear quadrupole resonance (NQR) spectra,<sup>2</sup> it has become possible to study in unprecedented detail changes in electronic charge distribution which accompany coordination of nitrogen to diamagnetic Lewis acid sites. We have previously reported on the <sup>14</sup>N NQR spectra of coordinated glyoximes, pyridine, and phenanthroline.<sup>3-5</sup> We have developed a coordination model, based on modification of the Townes-Dailey model, which accounts very well for changes in the electric field gradient (efg) parameters of the pyridine nitrogen upon coordination.<sup>4</sup> This model is applicable also to the <sup>14</sup>N NQR data for coordinated phenanthroline.<sup>5</sup> With slight modifications a similar coordination model is applicable to coordination of other planar, aromatic nitrogen systems such as imidazole.<sup>6</sup>

The coordination model provides, with a minimum of parameterization, a measure of the relative degree of charge transfer from nitrogen to the Lewis acid. A similar model should be applicable to aliphatic nitrogen ligands. However, very few systematic NQR data are available for complexes containing such ligands. We report the <sup>14</sup>N NQR spectra of several complexes of 1,2-dipiperidinoethane, C<sub>5</sub>H<sub>10</sub>NCH<sub>2</sub>CH<sub>2</sub>NC<sub>5</sub>H<sub>10</sub> (EDP), a bidentate chelating ligand.

#### Experimental Section

**Materials.** 1,2-Dipiperidinoethane (EDP) was obtained from the Reilly Tar and Chemical Co. with a stated purity of 98%. The compound was also prepared by condensing 1,2-dichloroethane and piperidine in refluxing benzene.<sup>7,8</sup> EDP was distilled through a 10-cm Vigreux column at 98 °C and 10 mmHg. Satisfactory analyses were obtained for the ligand and for all complexes whose preparations are described below.

**Zn(EDP)Cl<sub>2</sub> and Zn(EDP)Br<sub>2</sub>.** When EDP was added in slight excess to a 2,2-dimethoxypropane solution of either ZnCl<sub>2</sub>·6H<sub>2</sub>O or ZnBr<sub>2</sub>·6H<sub>2</sub>O, the corresponding Zn(EDP)X<sub>2</sub> complex precipitated.<sup>9</sup>

**Zn(EDP)(NO<sub>3</sub>)<sub>2</sub> and Zn(EDP)(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O** in 2,2-dimethoxypropane reacted with EDP to form Zn(EDP)(NO<sub>3</sub>)<sub>2</sub>. When treated with NaNO<sub>2</sub> in a cold bath before EDP was added, the product was Zn(EDP)(NO<sub>2</sub>)<sub>2</sub>.

**Cd(EDP)Cl<sub>2</sub>.** CdCl<sub>2</sub> (1.65 g, 10 mmol) was dissolved in H<sub>2</sub>O; a precipitate formed when a slight excess of EDP was added. The precipitate was washed with small portions of H<sub>2</sub>O and ether and then Soxhlet-extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed with a rotary evaporator to give 1.25 g of Cd(EDP)Cl<sub>2</sub>.

**Cd(EDP)Br<sub>2</sub>.** CdBr<sub>2</sub>·4H<sub>2</sub>O (3.5 g, 10 mmol) was dissolved in H<sub>2</sub>O and reacted with EDP as described for the corresponding chloro complex, to yield 2.3 of Cd(EDP)Br<sub>2</sub>.

**Cd(EDP)I<sub>2</sub>.** CdI<sub>2</sub> (3.65 g, 10 mmol) (Baker) was dissolved in CH<sub>3</sub>OH and reacted with EDP. The resulting precipitate was washed with small portions of CH<sub>3</sub>OH and ether and then extracted in a

**Table I.** <sup>14</sup>N Quadrupole Resonance Transitions (kHz) and Calculated Electric Field Gradient Parameters in EDP Compounds at 77 K

Compd	$\nu_+$	$e^2Qq/h$	$\eta$
Zn(EDP)Cl <sub>2</sub>	2583	3444	0
Zn(EDP)Br <sub>2</sub>	2543	3391	0
Zn(EDP)(NO <sub>3</sub> ) <sub>2</sub>	2476	3301	0
(NO <sub>3</sub> ) <sup>-</sup> group	552	695	0.178
	( $\nu_- = 490$ )		
Zn(EDP)(NO <sub>2</sub> ) <sub>2</sub>	2580	3440	0
(NO <sub>2</sub> ) <sup>-</sup> group	550		
	( $\nu_-$ not seen)		
Cd(EDP)Cl <sub>2</sub>	2676	3568	0
Cd(EDP)Br <sub>2</sub>	2652	3538	0
Cd(EDP)I <sub>2</sub>	2627	3503	0
Hg(EDP)Cl <sub>2</sub>	2505	3340	0
Hg(EDP)Br <sub>2</sub>	2490	3320	0
(EDPH <sub>2</sub> ) <sup>2+</sup> (ClO <sub>4</sub> ) <sub>2</sub>	850	1133	0

Soxhlet extractor using CH<sub>2</sub>Cl<sub>2</sub>, to yield 4.80 g of Cd(EDP)I<sub>2</sub>.

**Hg(EDP)Cl<sub>2</sub>.** HgCl<sub>2</sub> (2.6 g, 9.5 mmol) was dissolved in CH<sub>3</sub>CH<sub>2</sub>OH; a white precipitate formed when EDP was added. The precipitate was filtered and washed with small portions of CH<sub>3</sub>CH<sub>2</sub>OH and ether and then Soxhlet extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed with a rotary evaporator to give 1.95 g of Hg(EDP)Cl<sub>2</sub>.

**Hg(EDP)Br<sub>2</sub>.** HgBr<sub>2</sub> (5.4 g, 15 mmol) was dissolved in CH<sub>3</sub>OH. Synthesis proceeded as for the corresponding iodide complex, except that CH<sub>3</sub>OH replaced CH<sub>3</sub>CH<sub>2</sub>OH; yield 4.5 g of Hg(EDP)Br<sub>2</sub>.

**(EDPH<sub>2</sub>)<sup>2+</sup>(ClO<sub>4</sub>)<sub>2</sub>.** EDP (2.6 mL, 12 mmol) was mixed with 15 mL of CH<sub>3</sub>OH; 2 mL (24 mmol) of 70% HClO<sub>4</sub> was added drop by drop with stirring. The solution was filtered after several hours. The precipitate was washed with several small portions of CH<sub>3</sub>OH and ether. The product was dried under vacuum to give 3.9 g of (EDPH<sub>2</sub>)<sup>2+</sup>(ClO<sub>4</sub>)<sub>2</sub>.

**NQR Spectra.** The <sup>14</sup>N NQR spectra were obtained as described elsewhere.<sup>3,4</sup>

#### Results and Discussion

The measured <sup>14</sup>N quadrupole resonance transitions, in kilohertz, for all of the complexes studied are listed in Table I. In every instance, only one transition ascribable to coordinated EDP was observed. The electronic environment about each nitrogen in EDP should possess approximate axial symmetry, since there are three nearly equivalent N-C bonds involved. It is noteworthy that for *N*-methylpiperidine  $\eta = 0.036$ .<sup>10</sup> From inspection of a molecular model it appears that the five-membered ring formed upon coordination of EDP to a metal ion is relatively free of strain. The M-N internuclear vector should lie roughly along the pseudo-threefold axis through the nitrogen. Thus, it is reasonable to expect that  $\eta$  should be near 0 in the complexes formed by EDP. In keeping with this, as noted above, only one transition ascribable to the coordinated nitrogen was observed in each complex. The calculated quadrupole coupling constant based on the assumption that  $\eta = 0$  is listed in Table I for each compound.

Unfortunately, all attempts to obtain the NQR spectrum for the free EDP ligand were unsuccessful, because the proton  $T_1$  and  $T_{1d}$  are too short at 77 K. Apparently, some low-frequency motion persists in the solid at this temperature, providing a relatively facile pathway for relaxation. However, from the observed  $e^2Qq/h$  values of 5.01 and 4.99 MHz for triethylamine<sup>11</sup> and *N*-methylpiperidine,<sup>10</sup> respectively, we can assume a value of  $e^2Qq/h = 5.00$  MHz for the free EDP ligand.

Assuming threefold symmetry at the nitrogen, the nitrogen 2p orbitals in free EDP are involved in three equivalent carbon-nitrogen bonds and one lone pair orbital. We designate the effective occupancy of the nitrogen orbital in the N-C  $\sigma$  bonds as  $\delta_0$ , and denote the lone pair orbital occupancy as  $\sigma$ . In the free ligand  $\sigma = \sigma_0 = 2.00$ . Upon coordination the occupancy of the lone pair orbital decreases. Correspondingly, the occupation number of the three equivalent orbitals involved

Table II. Calculated  $\sigma$  and  $\delta$  Parameters

Compd	$\sigma$	$\delta$
EDP (uncomplexed)	2.000	1.259
Zn(EDP)Cl <sub>2</sub>	1.80	1.29
Zn(EDP)Br <sub>2</sub>	1.79	1.29
Zn(EDP)(NO <sub>3</sub> ) <sub>2</sub>	1.78	1.29
Zn(EDP)(NO <sub>3</sub> ) <sub>2</sub>	1.80	1.29
Cd(EDP)Cl <sub>2</sub>	1.81	1.29
Cd(EDP)Br <sub>2</sub>	1.81	1.29
Cd(EDP)I <sub>2</sub>	1.81	1.29
Hg(EDP)Cl <sub>2</sub>	1.78	1.29
Hg(EDP)Br <sub>2</sub>	1.78	1.29
(EDPH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1.53	1.33
(EDPH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1.18	1.38

in the bonds to carbon increases, through inductive effects.

The Townes-Dailey model<sup>12</sup> provides a means of relating the observed quadrupole coupling constants to orbital occupation numbers. Assuming an angle  $\alpha$  between the direction of the lone pair orbital and the direction of the N-C  $\sigma$  bonds, the observed quadrupole coupling constant is related to the quadrupole coupling constant generated by a single 2p electron,  $e^2Qq_0/h$ , as in eq 1. The angle  $\alpha$  in trimethylamine is

$$\frac{e^2Qq}{h} = \frac{e^2Qq_0}{h} \left( \frac{-3 \cos \alpha}{1 - \cos \alpha} \right) (\sigma - \delta) \quad (1)$$

108.7°;<sup>13</sup> it seems reasonable to assume the tetrahedral angle of 109.5° for  $\alpha$  in EDP and its complexes. With this assumption we obtain eq 2. For free EDP, assuming  $e^2Qq/h$

$$\frac{e^2Qq}{h} = \frac{3}{4} \left( \frac{e^2Qq_0}{h} \right) (\sigma - \delta) \quad (2)$$

= 5.00 MHz,  $e^2Qq_0/h = 9.0$  MHz, and  $\sigma_0 = 2.00$ , then  $\delta_0 = 1.259$ .

Upon coordination of EDP to a Lewis acid, the value for  $\sigma$  decreases, because the ligand donates electronic charge to the Lewis acid. The total charge loss from the nitrogen is  $2 - \sigma$ . Through an inductive effect this results in an increase in the population of the nitrogen orbitals directed toward carbon. Since the NQR data provide only one observable for each complex, there is no way in which both  $\sigma$  and  $\delta$  can be determined. However, we can assume that the increase in orbital occupancy in the nitrogen N-C bonds is proportional to the extent of electronic charge withdrawal from the donor orbital. Thus, we can write  $\delta = \delta_0 + \beta(2 - \sigma)$ , where  $3\beta$  = the fractional increase in occupancy of the three nitrogen N-C orbitals in response to the unit charge withdrawal from the donor orbital. The proportionality constant  $\beta$  must be estimated. In pyridine, in which a similar model was applied,<sup>4</sup> the charge loss upon coordination is partially offset by increases in the occupancies of two nitrogen N-C  $\sigma$  orbitals and one  $p_\pi$  nitrogen orbital. It was estimated that the total fractional charge replacement in pyridine is 0.62.<sup>4</sup> It is reasonable to assume a value somewhat less than this for the aliphatic nitrogen ligand, since the more polarizable  $\pi$  system is not present. Thus, we assume  $\beta = 0.15$ . Thus, for coordinated EDP the occupancy of the nitrogen N-C orbitals is given by  $\delta = 1.259 + 0.15(2 - \sigma)$ .

From the observed value of  $e^2Qq/h$  in each case it is possible to calculate the corresponding value for  $\sigma$  and  $\delta$ , as listed in Table II;  $e^2Qq/h$  varies as a function of the donor orbital occupancy as shown in Figure 1. As shown in Figure 1,  $e^2Qq/h = 0$  in the limiting case that  $\sigma = \delta$ . When  $\sigma > \delta$ , the quadrupole coupling constant is negative. Thus two sets of values for  $\sigma$  and  $\delta$  are possible, depending on their relative values. In all cases except (EDPH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, we have assumed that  $\sigma > \delta$ . Both sets of values are listed for (EDPH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> in Table II and shown in Figure 1. Because the electro-

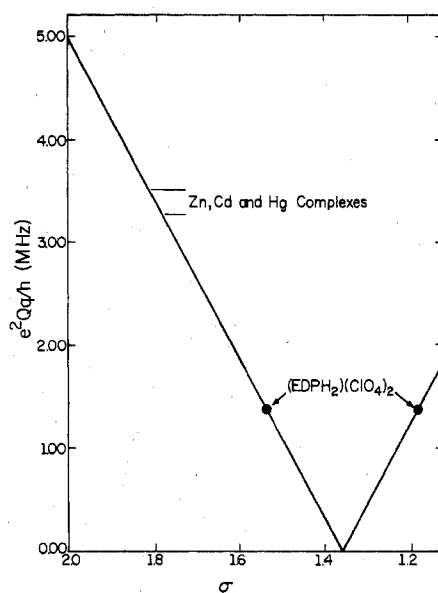


Figure 1. Quadrupole coupling constant,  $e^2Qq/h$  (MHz), vs. donor orbital occupancy,  $\sigma$ , for coordinated 1,2-dipiperidinoethane.

Table III. Comparison of the  $\sigma$  Parameter for Analogous EDP and Pyridine Complexes

Compd	$\sigma$ for (x) <sub>2</sub> = EDP	$\sigma$ for x = pyridine <sup>4</sup>
Zn(x) <sub>2</sub> Cl <sub>2</sub>	1.80	1.76, 1.79
Zn(x) <sub>2</sub> Br <sub>2</sub>	1.79	1.79, 1.78
Zn(x) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	1.78	1.76, 1.77
Cd(x) <sub>2</sub> Cl <sub>2</sub>	1.81	1.87
(EDPH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1.53	
HpyNO <sub>3</sub>		1.38

negativities of hydrogen and alkyl groups are nearly the same,<sup>14</sup> it is not feasible to decide on the relative values of  $\sigma$  and  $\delta$  on the basis of relative electronegativities. However, in two studies of the <sup>14</sup>N NQR spectra of amines<sup>15</sup> and ammonium salts<sup>16</sup> the data could be satisfactorily interpreted only by assuming that  $\sigma_{NH} > \delta_{NC}$ . For example, in H<sub>3</sub>N<sup>+</sup>-CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>, the nitrogen N-H and N-C bond orbital populations are estimated to be 1.41 and 1.25, respectively.<sup>16</sup> Thus it would appear that in EDPH<sub>2</sub><sup>2+</sup> the appropriate value for  $\sigma$  is 1.53.

Because the choices of certain model parameters are somewhat arbitrary, it is the relative values of  $\sigma$  in a series of related EDP complexes that are of principal interest. Nevertheless values obtained for donor orbital occupancies in the EDP complexes compare fairly well with the  $\sigma$  values obtained in analogous pyridine complexes, as illustrated in Table III. The comparative results are slightly dependent on the value chosen for  $\beta$  in each case, but the sensitivity is not great. For example, if  $\beta$  is increased from 0.15 to 0.20, the calculated  $\sigma$  for Zn(EDP)Cl<sub>2</sub> increases by only 0.008. Since the aliphatic amine is a stronger base toward proton than pyridine, as measured by pK<sub>b</sub> in aqueous medium, one might have expected that  $\sigma$  would be smaller in EDPH<sub>2</sub><sup>2+</sup> than in pyH<sup>+</sup>. However, the degree of charge withdrawal from nitrogen in the N-H bond is not necessarily related directly to pK<sub>b</sub> values. The lower value for  $\sigma$  in pyH<sup>+</sup> may be a result of the greater polarizability of the overall charge distribution in the pyridine molecule.

Although the differences are small, the NQR data are quite consistent in showing that  $\sigma$  decreases in the order Cd(II) > Zn(II) > Hg(II). On the basis of electrostatic factors one would have expected  $\sigma$  to vary in the order of the relative ionic radii, i.e., in the order Hg(II) > Cd(II) > Zn(II). Thus the NQR data provide evidence of a substantially larger covalent interaction between nitrogen and mercury. Comparisons of

the  $^{14}\text{N}$  NQR results are complicated by the well-known tendency toward bridging halide structures in adducts of mercuric halides.<sup>17-19</sup> Thus, the coordination number about Hg(II) in the two compounds listed in Table 1 may be six rather than four. However, an increase in coordination number would be expected to lower the electron demand made by the metal on any one ligand. Thus, even though the structures are not known, the relatively low  $\sigma$  values for the Hg(II) complexes are a valid indication of the greater importance of covalent interaction as compared with the Zn(II) and Cd(II) complexes.<sup>20</sup>

**Registry No.** Zn(EDP)Cl<sub>2</sub>, 65045-56-9; Zn(EDP)Br<sub>2</sub>, 65045-55-8; Zn(EDP)(NO<sub>3</sub>)<sub>2</sub>, 49626-99-5; Zn(EDP)(NO<sub>2</sub>)<sub>2</sub>, 49626-97-3; Cd(EDP)Cl<sub>2</sub>, 65045-54-7; Cd(EDP)Br<sub>2</sub>, 65045-53-6; Cd(EDP)I<sub>2</sub>, 65045-52-5; Hg(EDP)Cl<sub>2</sub>, 65045-51-4; Hg(EDP)Br<sub>2</sub>, 65045-59-2; (EDPH<sub>2</sub>)(ClO<sub>4</sub>)<sub>2</sub>, 65045-39-8; EDP, 1932-04-3; NO<sub>3</sub><sup>-</sup>, 14797-55-8; NO<sub>2</sub><sup>-</sup>, 14797-65-0.

## References and Notes

- (1) (a) This research was supported by Research Grant NSF CHE 76-17570 from the National Science Foundation. (b) Based on a thesis submitted in partial fulfillment of requirements for the B. S. degree with distinction, University of Illinois—Urbana.
- (2) D. T. Edmonds, *Phys. Rep.*, **29**, 233 (1977).
- (3) Y. N. Hsieh, P. S. Ireland, and T. L. Brown, *J. Magn. Reson.*, **21**, 445 (1976).
- (4) Y. N. Hsieh, G. V. Rubenacker, C. P. Cheng, and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 1384 (1977).
- (5) C. P. Cheng, B. Plankey, J. V. Rund, and T. L. Brown, *J. Am. Chem. Soc.*, in press.
- (6) C. I. H. Ashby, C. P. Cheng, and T. L. Brown, submitted for publication.
- (7) A. Gero, *J. Am. Chem. Soc.*, **76**, 5158 (1954).
- (8) A. L. Lott, II, *Inorg. Chem.*, **13**, 667 (1974).
- (9) A. L. Lott, II, and P. G. Rasmussen, *J. Inorg. Nucl. Chem.*, **32**, 101 (1970).
- (10) E. Schempp and P. J. Bray, *Bull. Am. Phys. Soc.*, **13**, 957 (1968).
- (11) E. Schempp and P. J. Bray in "Physical Chemistry, an Advanced Treatise", Vol. IV, D. Henderson, Ed., Academic Press, New York, N.Y., 1970, Chapter 11.
- (12) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).
- (13) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958).
- (14) J. Hinze, M. A. Whitehead, and H. H. Jaffe, *J. Am. Chem. Soc.*, **85**, 148 (1963).
- (15) S. Onda, H. Harada, D. Nakamura, and M. Kubo, *J. Magn. Reson.*, **8**, 238 (1972).
- (16) R. A. Marino and T. Oja, *J. Chem. Phys.*, **56**, 5453 (1972).
- (17) (a) A. T. McPhail and G. A. Sim, *Chem. Commun.*, 21 (1966); (b) R. S. McEwen and G. A. Sim, *J. Chem. Soc.*, 271 (1967).
- (18) C. I. Brändén, *Ark. Kemi*, **22**, 495, 561 (1964).
- (19) A. F. Wells, "Structural Inorganic Chemistry", 4th ed, Clarendon Press, Oxford, England, 1975, pp 920-923.
- (20) K. J. Fisher and R. S. Drago, *Inorg. Chem.*, **14**, 2805 (1975).

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## Oxidative Addition of Halopentaboranes to *trans*-IrCl(CO)(PMe<sub>3</sub>)<sub>2</sub>

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Oxidative addition of boron-halogen bonds in organoboron halides and boron trihalides to low-valent transition-metal complexes has been utilized as a synthetic method for the preparation of  $\sigma$ -metalloboranes.<sup>1</sup> Boron-hydrogen bonds are capable of similar reactions. Inter- and intramolecular insertion of transition-metal complexes into the B-H bonds of carboranes<sup>2</sup> and carboranylphosphines,<sup>2,3</sup> respectively, has been observed to result in stable adducts and, in some cases, catalytic

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exchange of deuterium with the terminal boron hydrogens.<sup>4</sup> Earlier, in preliminary form, we reported that 1- and 2-BrB<sub>5</sub>H<sub>8</sub> inserted *trans*-IrCl(CO)(PMe<sub>3</sub>)<sub>2</sub> into the B-Br bonds, affording the 2-metalated adduct. Pentaborane(9) itself was shown to undergo a similar addition of the basal B-H bond. Infrared evidence that a hydridic intermediate was present in the addition of halopentaboranes was cited.<sup>5</sup> Since this system is sufficiently simple to directly test for selectivity in the site of intermolecular B-H addition and to determine the relative reactivities of boron-halogen and boron-hydrogen bonds, we report herein extension of these studies with particular attention directed to the course of these reactions.

## Experimental Section

Solvents were purified by distillation from sodium benzophenone ketyl except CH<sub>2</sub>Cl<sub>2</sub>, which was distilled from P<sub>4</sub>O<sub>10</sub>. 1-BrB<sub>5</sub>H<sub>8</sub>,<sup>6</sup> 2-BrB<sub>5</sub>H<sub>8</sub>,<sup>6</sup> 1-ClB<sub>5</sub>H<sub>8</sub>,<sup>7</sup> 2-ClB<sub>5</sub>H<sub>8</sub>,<sup>7b</sup> and 1-CH<sub>3</sub>-B<sub>5</sub>H<sub>8</sub><sup>8</sup> were prepared by literature methods. *trans*-Chlorocarbonylbis(trimethylphosphine)iridium was sublimed three times before use. *trans*-Bromocarbonylbis(trimethylphosphine) was prepared by metathesis with anhydrous LiBr in refluxing THF, similar to the procedure described by Halpern et al.<sup>9</sup>

Manipulations throughout were performed in vacuo or under an atmosphere of prepurified nitrogen. Infrared, 100-MHz <sup>1</sup>H, 40.5-MHz <sup>31</sup>P, and 32.1-MHz <sup>11</sup>B NMR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, and AEI MS-9 spectrometers. <sup>31</sup>P and <sup>11</sup>B NMR chemical shifts are relative to external 85% phosphoric acid and BF<sub>3</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, respectively. GLC analyses were performed on an F & M 720 gas chromatograph with a 1/4 in. × 8 ft, 10% Apiezon L column.

Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn., or the Analytical Center, University of Massachusetts, Amherst, Mass.

### Preparation of 2-[IrBr<sub>2</sub>(CO)(PMe<sub>3</sub>)<sub>2</sub>]B<sub>5</sub>H<sub>8</sub>, **2**. (1) From 1-BrB<sub>5</sub>H<sub>8</sub>.

To a 10-mm tube equipped with a magnetic stirring bar and stopcock was charged 250 mg (0.62 mmol) of *trans*-IrCl(CO)(PMe<sub>3</sub>)<sub>2</sub> (**1**). The vessel was evacuated, 4.5 g of 1-BrB<sub>5</sub>H<sub>8</sub> condensed in at -196 °C, and the vessel warmed to ca. 45 °C. After the mixture was stirred for 45 min, removal of the volatile components in vacuo left a yellow oil. Repeated extractions with hexane gave a solid which was dissolved in 10 mL of toluene and chromatographed on an acetylated polyamide (Machery, Nagel, and Co.) column (2 × 20 cm, toluene eluent). The pale yellow band was collected and evaporated to dryness, and the residue crystallized from toluene-hexane (slow cooling) to give three crops of nearly colorless crystals (209 mg, 62%): IR (KBr and Nujol mulls) 2573 (m,  $\nu_{\text{BH}}$ ), 2554 (m,  $\nu_{\text{BH}}$ ), 2024 (s,  $\nu_{\text{CO}}$ ), and 945 cm<sup>-1</sup> (s,  $\sigma$ -apical BH); mp 148 °C (dec); <sup>1</sup>H{<sup>11</sup>B} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\tau$  11.4 (s, 2,  $\mu$ -BH), 10.0 (s, 2, BH), 8.6 (s, 1, B<sub>1</sub>H), and 7.4 (5, 18, PCH<sub>3</sub>,  $J_{\text{PCH}} = 4.2$  Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) 45.2 ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) 11.3 (B<sub>2</sub>), 14.4 (B<sub>3,5</sub>), 17.3 (B<sub>4</sub>), and 50.2 ppm (B<sub>1</sub>).

Anal. Calcd for C<sub>7</sub>H<sub>28</sub>B<sub>5</sub>Br<sub>2</sub>IrOP: C, 14.15; H, 4.42; Br, 9.09; Ir, 26.89; P, 32.34; O, 10.42. Found: C, 14.09; H, 4.39; Br, 8.84; Ir, 26.88; P, 35.45; O, 10.50.

(2) From 2-BrB<sub>5</sub>H<sub>8</sub>. In a similar manner, 2.0 g of 2-BrB<sub>5</sub>H<sub>8</sub> was reacted with 200 mg (0.53 mmol) of **1**. The reaction was complete within several minutes at 25 °C. Removal of the volatile components in vacuo and recrystallization of the residue from toluene-hexane gave a material having an IR spectrum identical with that of **2**.

1-Cl-2-[IrCH(CO)(PMe<sub>3</sub>)<sub>2</sub>]B<sub>5</sub>H<sub>8</sub>, **3**. To 200 mg of **1** (0.49 mmol) in a 10-mm tube equipped with a side arm and magnetic stirring bar were added 178 mg of 1-ClB<sub>5</sub>H<sub>8</sub> (1.82 mmol) and 0.3 mL of toluene at -196 °C. The mixture was warmed to -22 °C (CCl<sub>4</sub> slush) and stirred for 1.5 h. During this period, **1** dissolved and white crystals were deposited. After cooling of the system to -78 °C, 5 mL of hexane was added and the supernatant decanted with a syringe. The resulting **3** was washed with 3 × 5 mL of hexane while being maintained at -78 °C and then dried in vacuo at -22 °C: <sup>1</sup>H{<sup>11</sup>B} NMR (toluene-*d*<sub>6</sub>)  $\tau$  17.79 (t, 1, IrH,  $J_{\text{IrH}} = 18$  Hz), 11.8 (s, 2,  $\mu$ -BH), 9.6 (s, 2,  $\mu$ -BH), 8.37 (t, 18, PCH<sub>3</sub>,  $J_{\text{PCH}} = 4.2$  Hz), 7.3 (s, 2, B<sub>3,5</sub>H), 6.20 (s, 1, B<sub>4</sub>H); <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>6</sub>) 42.6 ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (toluene-*d*<sub>6</sub>) 27.9 (s, 1, B<sub>1</sub>), 17.7 ppm (broad and unresolved, basal resonances).

The thermal instability of the compound precluded elemental analysis.

2-[IrCl<sub>2</sub>(CO)(PMe<sub>3</sub>)<sub>2</sub>]B<sub>5</sub>H<sub>8</sub>, **4**. Quantities of 170 mg of **1** (0.42 mmol) and 90 mg of 1-ClB<sub>5</sub>H<sub>8</sub> (0.92 mmol) were stirred in toluene