mmol) and $LiAlH_4$ (0.1757 g, 4.360 mmol) in the molar ratio 10.67:1.00 was heated to 148°. A very vigorous reaction which was complete in a few seconds took place. The only volatile material recovered was pure AsH_3 [39.3 mg, 0.504 mmol, 10.9% yield; mol wt, 78.5 (calcd 77.93); confirmed by infrared[7] and mass spectra].

Preparation of SbH_3.—A mixture of Sb_2O_3 (15.363 g, 52.707 mmol) and $LiAlH_4$ (0.1983 g, 5.225 mmol) in the molar ratio 9.08:1.00 was heated to 165° at which temperature a rapid reaction, which was complete in few a seconds, took place. The only volatile material recovered was pure SbH_3 (approximately 1 mg, 0.008 mmol, 0.2% yield; identified by infrared[8] and mass spectra).

Reaction with Miscellaneous Oxides and Oxide Mixtures.—When $LiAlH_4$ was heated with the following oxides, no volatile hydride species were obtained: SnO_2, B_2O_3, TiO_2. When $LiAlH_4$ was heated with a mixture of B_2O_3 and SiO_2, only SiH_4 was evolved. On heating a mixture of SiO_2 and GeO_2 with $LiAlH_4$, no species such as SiH_3GeH_3[9] was formed. Only SiH_4 and the expected mixture of germanes were obtained. When $LiAlH_4$ was heated with a mixture of GeO_2 and As_2O_3, only germanes and AsH_3 were evolved. No species such as GeH_3AsH_2[10] was formed.

Acknowledgment.—The GeO_2 used in this investigation was kindly donated by the Germanium Information Center, Midwest Research Institute, Kansas City 10, Mo.

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Metalloboranes. II.[1] Transition Metal Complexes of $B_{10}H_{12}^{2-}$

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Initial studies suggest a substantial scope and chemistry for metalloboranes based on the $B_{10}H_{12}^{2-}$ ligand and transition metal ions. Three types of complexes have been established: (A) $M(B_{10}H_{12})_2^{2-}$ with M representing cobalt, nickel, palladium, and platinum; (B) $M(B_{10}H_{12})L_2$ for palladium or platinum with L representing triorganophosphines; (C) $M(B_{10}H_{12})L_3^-$ for cobalt, rhodium, and iridium with carbon monoxide and phosphine ligands. It is proposed that the $B_{10}H_{12}^{2-}$ moiety interacts with the transition metal atom primarily as a bidentate ligand to form an 11-atom icosahedral fragment. The two extra hydrogen atoms bridge edges of the open pentagonal face of the icosahedral fragment. Spectral and diffraction data fully support this ligand–metal interaction for all three types of complexes.

Introduction

Metalloborane chemistry is extensive and quite large in scope.[2] The transition metal chemistry of $B_{10}H_{12}^{2-}$ is the subject of this report. This borane anion has been reportedly isolated in the form of the sodium salt by Wilks and Carter[3] from the prolonged reaction of decaborane with sodium hydride. In addition, Greenwood and Travers reported that the reaction of zinc and cadmium dialkyls with decaborane in ether yields $M(B_{10}H_{12})(ether)_2$ derivatives.[4-7] Upon dissolution of the $M(B_{10}H_{12})(ether)_2$ derivatives in water, $M(B_{10}H_{12})_2^{2-}$ complexes of zinc and cadmium are obtained. An analogous mercury complex has also been reported.[7] Greenwood and Travers proposed tetrahedral coordination of the metal atom through direct metal–boron bonds with the 6,9 boron atoms of an unrearranged decaborane cage[4-7] in both types of $B_{10}H_{12}^{2-}$ complexes.

We report here the synthesis and characterization of transition metal complexes of the $B_{10}H_{12}^{2-}$ ligand of the types: $M(B_{10}H_{12})_2^{2-}$, where M = Co, Ni, Pd, Pt; $M(B_{10}H_{12})L_2$, where M = Pd, Pt; L = triorganophosphines; and $M(B_{10}H_{12})L_3^-$, where M = Co, Rh, Ir; L = CO and $P(C_6H_5)_3$.

Discussion

Synthesis.—The most general synthesis of $B_{10}H_{12}^{2-}$ metalloboranes is the reaction of excess $B_{10}H_{13}^-$ ion with transition metal halide complexes. The $B_{10}H_{13}^-$ reagent gives $M(B_{10}H_{12})_2^{2-}$ compounds with cobalt, nickel, palladium, and platinum halide complexes. In addition, phosphine and carbonyl complexes of cobalt, rhodium, and iridium give $M(B_{10}H_{12})L_3^-$ anions as illustrated with Vaska's iridium compound. Initial metal complexation of $B_{10}H_{13}^-$ may enhance[8] the proton release either directly by capture with relatively weak bases such as $B_{10}H_{13}^-$, $Co(CO)_4^-$, and R_3P, or by hydrogen transfer to the metal.

$$4B_{10}H_{13}^- + [(C_6H_5)_3P]_2NiCl_2 \longrightarrow Ni(B_{10}H_{12})_2^{2-} + 2B_{10}H_{14} + 2(C_6H_5)_3P + 2Cl^- \quad (1)$$

$$2B_{10}H_{13}^- + [(C_2H_5)_3P]_2PtCl_2 \longrightarrow Pt(B_{10}H_{12})[P(C_2H_5)_3]_2 + B_{10}H_{14} + 2Cl^- \quad (2)$$

$$2B_{10}H_{13}^- + [(C_6H_5)_3P]_2Ir(CO)Cl \longrightarrow Ir(B_{10}H_{12})(CO)[P(C_6H_5)_3]_2^- + B_{10}H_{14} + Cl^- \quad (3)$$

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[1] Paper I: F. Klanberg, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, in press.

[2] References to the pertinent reviews and recent literature were presented in the first paper of this series.[1]

[3] P. H. Wilks and J. C. Carter, *J. Am. Chem. Soc.*, **88**, 3441 (1966).

[4] N. N. Greenwood and N. F. Travers, *Inorg. Nucl. Chem. Letters*, **2**, 169 (1966).

[5] N. N. Greenwood and N. F. Travers, *J. Chem. Soc., A*, 880 (1967).

[6] N. N. Greenwood and N. F. Travers, *ibid.*, 15 (1968).

[7] N. N. Greenwood and N. F. Travers, *Chem. Commun.*, 216 (1967).

[8] The isolated $B_{10}H_{13}^-$ ion requires strong bases, metal alkyls, or hydrides for $B_{10}H_{12}^{2-}$ formation.[3]

In the Ni, Pd, and Pt triad, the nature of the product is strongly dependent on the metal halide complex used as starting material. Nickel halides and their aquo and phosphine complexes react with $B_{10}H_{13}^-$ to give $Ni(B_{10}H_{12})_2^{2-}$ salts. The anhydrous palladium and platinum dichlorides are reduced to the free metal by $B_{10}H_{13}^-$. However, complexes of these halides with dienes react smoothly to give the $M(B_{10}H_{12})_2^{2-}$ complexes. Trialkylphosphine ligands are displaced from palladium to give $Pd(B_{10}H_{12})_2^{2-}$ but triphenylphosphine is stable to displacement and the product is $Pd(B_{10}H_{12})[P(C_6H_5)_3]_2$. In the platinum series both types of phosphines are not displaced and the products are $Pt(B_{10}H_{12})(PR_3)_2$.

The $B_{10}H_{12}^{2-}$ ligand is transferred intact from the labile $Zn(B_{10}H_{12})(C_4H_8O)_2$ complex[4] to Co^{2+} to give $Co(B_{10}H_{12})_2^{2-}$ and this is the preferred synthesis for this compound. Also, decaborane may react directly with transition metal hydrides to give $B_{10}H_{12}^{2-}$ metalloboranes as in

$$B_{10}H_{14} + 2[(C_2H_5)_3P]_2PtHCl \longrightarrow 2H_2 + Pt(B_{10}H_{12})[P(C_2H_5)_3]_2 + [(C_2H_5)_3P]_2PtCl_2 \quad (4)$$

Properties.—The cesium salts of the $M(B_{10}H_{12})_2^{2-}$ ions proved surprisingly water soluble. Accordingly, these anions were isolated and purified by crystallization from water as tetraalkylammonium salts. The latter have a very low solubility in water, a higher solubility in alcohols, and a very high solubility in solvents such as acetonitrile, acetone, and dimethylformamide. The conductivity studies (Table I) indicate that the tetraalkylammonium salts behave as 2:1 electrolytes in acetonitrile. Salts of the cobalt complex are burgundy red, the nickel complex is orange, and the palladium and platinum compounds are yellow.

TABLE I
CONDUCTANCE OF $[(CH_3)_4N]_2[M(B_{10}H_{12})_2]$ COMPLEXES IN ACETONITRILE

Species	Molar concn $\times 10^3$	$10^4 \times$ conductance, mhos
Complex		
Co	1.02	3.79
Ni	1.01	3.87
Pd	0.98	3.49
Pt	1.02	3.31
Zn	1.00	4.08
$[(CH_3)_4N]_2[B_{20}H_{18}]$	1.03	3.96
CH_3CN	. . .	0.015

A significant variation is manifest in the thermal stability of the tetramethylammonium salts of $M(B_{10}H_{12})_2^{2-}$ complexes. For nickel and cobalt, decomposition occurs below 180° in a nitrogen atmosphere, for palladium about 240°, and for platinum above 300°. The nickel complex is completely air stable, but the other analogs degrade visibly on exposure to the atmosphere. All of the anions have modest hydrolytic stability in neutral or acidic media at ambient conditions. For example, $Ni(B_{10}H_{12})_2^{2-}$ underwent little degradation in a period of 2 days in aqueous solution of pH 7. In aqueous base, all of the anions rapidly degrade with the formation of metal hydroxides and the $B_9H_{14}^-$ ion. A qualitative ordering of hydrolytic stability in the dianion series is $Pt > Pd > Ni \gg Co$.

The neutral platinum and palladium complexes, $M(B_{10}H_{12})(PR_3)_2$, are soluble in polar solvents, especially methylene chloride and acetone, but insoluble in nonpolar solvents. Compounds of this class are stable under atmospheric conditions and, like those of the dianion class, resist attack by aqueous acids but are rapidly degraded by base. Members of the third class of compounds of the type $M(B_{10}H_{12})L_3^-$ are slightly more unstable in air and water than those of the other two classes.

Structure.—The structure first proposed for zinc, cadmium, and mercury derivatives of $B_{10}H_{12}^{2-}$ retained the decaborane skeleton for the ligand.[4-7] Specifically, metal bonds to the 6 and 9 boron atom positions were proposed to give a tetrahedral coordination about the metal atom and over-all D_{2d} symmetry in the $M(B_{10}H_{12})_2^{2-}$ complexes. Our spectral evidence discounts this suggestion, and, on the basis of an alternative structure[9,10] of $B_{10}H_{12}^{2-}$ (Figure 1), we propose incorporation of the metal atom into an open face of $B_{10}H_{12}^{2-}$ to give a $B_{10}M$ 11-atom icosahedral fragment. The extra hydrogen atoms bridge edge positions of the open pentagonal face as in $B_{11}H_{13}^{2-}$.[11] The complexed metal is nearest neighbor to four boron atoms (5, 6, 9, 10) of the $B_{10}H_{12}^{2-}$ cage. We further tender the formal characterization of $B_{10}H_{12}^{2-}$ as a bidentate ligand with electron density primarily at the 5,6 and 9,10 positions (*vide infra* for spectra and inferential evidence). The $B_{10}H_{12}^{2-}$ ligand is qualitatively distinct in an electronic and structural sense from $B_9C_2H_{11}^{2-}$, $B_{10}CH_{11}^{3-}$, and $B_{10}SH_{10}^{2-}$, which form closed icosahedral metalloboranes[2] with formal six-electron ligand donation and the metal atom in a close, nearly equivalent approach to *five* atoms of the ligand skeleton.

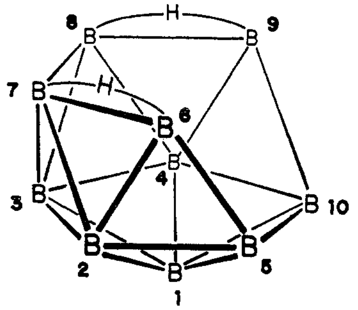

Figure 1.—A possible structure of the $B_{10}H_{12}^{2-}$ ion.

For the d^7 and d^8 $M(B_{10}H_{12})_2^{2-}$ class our proposal leads to a structure of two 11-atom fragments fused through a central metal atom with an over-all C_{2h} symmetry (Figure 2). The extra hydrogen atoms are present as symmetrically bridged hydrogens in the open

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(9) See ref 3 for a different structural proposal for the $B_{10}H_{12}^{2-}$ ion. There is the possibility that the $Na_2B_{10}H_{12}$ species isolated by Wilks and Carter may be $Na^+[NaB_{10}H_{12}]^-$ with a sodium ion complexed to $B_{10}H_{12}^{2-}$.

(10) The $B_{10}H_{12}^{2-}$ ion is numbered in accord with the normal numbering system of decaborane as in Figure 1.

(11) C. J. Fritchie, *Inorg. Chem.*, **6**, 1199 (1967).

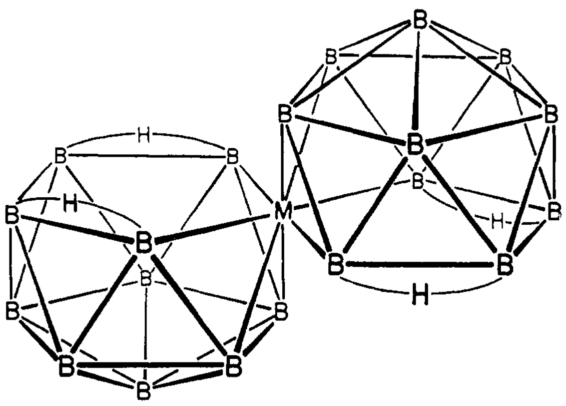

Figure 2.—The proposed heavy-atom structure for the transition metal $M(B_{10}H_{12})_2^{2-}$ ions.

B_4M five-membered face of the icosahedral fragment. A single-crystal X-ray diffraction study by Guggenberger[12] has confirmed this heavy-atom arrangement for $[(CH_3)_4N]_2[Ni(B_{15}H_{12})_2]$, and the analogous cobalt complex is isomorphous.

All of the spectral data available for the platinum, palladium, nickel, and cobalt examples of the $M(B_{10}H_{12})_2^{2-}$ ions are consistent with the structure presented in Figure 2. The infrared spectra (Nujol) of common salts of the anions show essentially complete correspondence in band shape and intensity and only slight differences in absorption positions within the region 4000–700 cm^{-1}. In addition, the ^{11}B nmr spectra of the diamagnetic derivatives are clearly related (Figure 3). Although the spectra cannot be conclusively interpreted, they can be rationalized in terms of the C_{2h} structure for the $M(B_{10}H_{12})_2^{2-}$ complexes.[13]

Six-coordinate platinum or palladium(II) derivatives are not beyond reason but the chemistry of these d^8 ions is dominated by square-planar four-coordination and occasionally relieved by five-coordination as in $Pt(SnCl_3)_5^{3-}$.[14] This background inferentially supports the primarily bidentate functionality proposed for $B_{10}H_{12}^{2-}$. The low-spin (μ = 2.08 BM) character of $Co(B_{10}H_{12})_2^{2-}$ is consistent with a square-planar coordination although in C_{2h} symmetry a low-spin six-coordinate cobalt(II) is feasible. Similar arguments apply to the diamagnetic $Ni(B_{10}H_{12})_2^{2-}$. However, the esr data for the cobalt complex are so strikingly similar to the square-planar bis-dithiolato derivatives of cobalt(II) as to make the proposed formalistic bonding thesis for $B_{10}H_{12}^{2-}$ an almost inescapable conclusion. This thesis leads to a structural characterization of post-transition metal derivatives of $B_{10}H_{12}^{2-}$ consonant with spectral data (*vide infra*).

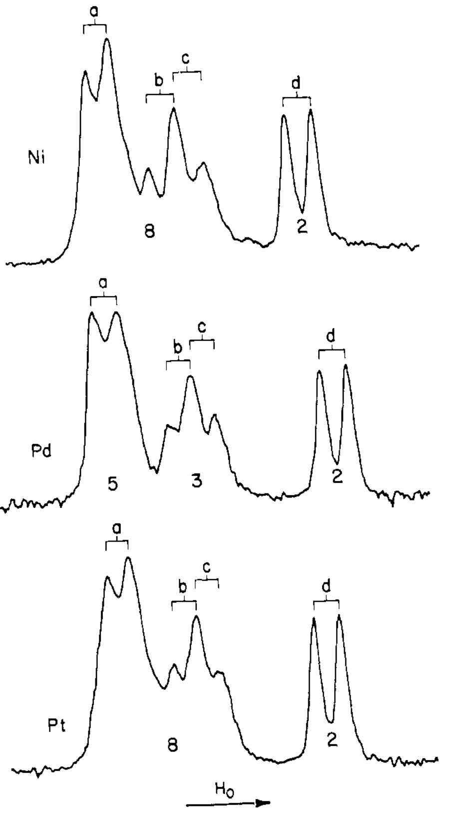

Figure 3.—The 32-MHz ^{11}B nmr spectra of the tetramethylammonium salts of the nickel, palladium, and platinum derivatives of $M(B_{10}H_{12})_2^{2-}$ in acetonitrile. The chemical shift values for these spectra are listed in the Experimental Section.

Although definitive structural evidence for the other two classes of $B_{10}H_{12}^{2-}$ complexes is lacking, it seems unlikely that the metal–ligand interaction will be different. Thus $B_{10}H_{12}^{2-}$ probably acts as a bidentate ligand to form pseudo-square-planar coordination about the platinum or palladium atom of the $M(B_{10}H_{12})(PR_3)_2$ derivatives. This reasoning leads to an over-all structure similar to that in Figure 2 except that two phosphines have replaced a $B_{10}H_{12}^{2-}$ ligand. Because the ^{11}B nmr spectra of these derivatives are poorly resolved, supporting spectral evidence is not available.

In the case of the $M(B_{10}H_{12})L_3^-$ compounds, the ^{11}B nmr spectral data for the cobalt derivative are very informative while those of the rhodium and iridium derivatives are not, because of poor resolution. The ^{11}B nmr spectrum of $Co(B_{10}H_{12})(CO)_3^-$ is shown in Figure 4. The spectrum clearly can be interpreted as the 2:2:2:2:1:1 pattern required for the 11-atom icosahedral fragment.[15] The spectral data are thus completely consistent with a structure in which $B_{10}H_{12}^{2-}$ occupies two coordination positions about a cobalt(I) atom. The iridium and rhodium derivatives of the series probably have an analogous structure.

The ^{11}B nmr spectrum of $[(CH_3)_4N]_2[Zn(B_{10}H_{12})_2]$ (Figure 5) is clearly not similar to those of the analogous palladium, nickel, and platinum derivatives (Figure 3). In contrast to the very close congruence for infrared

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[12] L. J. Guggenberger, to be submitted for publication.

[13] The C_{2h} structure requires the ^{11}B nmr spectrum to consist of six doublets of relative intensities 2:2:2:2:1:1. The most highly resolved spectrum, that of $Pd(B_{10}H_{12})_2^{2-}$, can easily be interpreted in terms of this pattern. The high-field area is clearly a doublet of intensity 2, the central triplet is derived from two overlapping doublets of relative intensities 2:1, and thus the multiplet of intensity 5 results from the near coincidence of resonances from boron environments of relative intensities 2:2:1.

[14] R. D. Cramer, H. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

[15] The high-field doublet has intensity 2, the low-field doublet has intensity 1, and the triplet of intensity 4 is likely two overlapping doublets of intensity 2, while the unresolved resonance of intensity 3 likely is two overlapping doublets of intensities 1 and 2. Although other interpretations of the spectrum are feasible, they lead to improbable structures containing numerous BH_2 groups and/or borons having no terminal hydrogens.

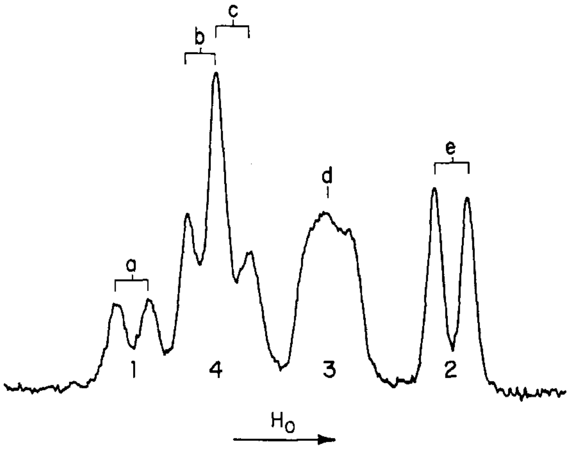

Figure 4.—The 32-MHz ^{11}B nmr spectrum of $[(CH_3)_4N]$-$[Co(B_{10}H_{12})(CO)_3]$ in acetonitrile ($BF_3O(C_2H_5)_2$ = 0) δ, ppm (*J*, Hz): a, −11.9 (115); b, −2.47 (130); c, 1.50 (123); d, 14.9; e, 30.2 (147).

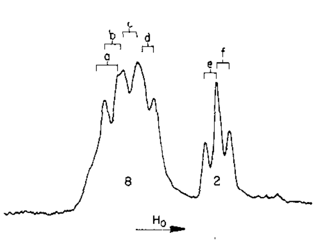

Figure 5.—The 32-MHz ^{11}B nmr spectrum of $[(CH_3)_4N]_2$-$[Zn(B_{10}H_{12})_2]$ in acetonitrile ($BF_3O(C_2H_5)_2$ = 0) δ, ppm (*J*, Hz): a, −5.63 (130); b, −3.10 (139); c, 3.04 (142); d, 9.00 (115); e, 29.5 (130); f, 33.6 (126).

spectra of common salts of the d^7 and d^8 transition metal $M(B_{10}H_{12})_2^{2-}$ anions, the infrared spectrum of the zinc complex with a similar cation is completely different. Thus, it is unlikely that the zinc complex is isostructural with the transition metal complexes. However, the ^{11}B spectrum (Figure 5) consists of a minimum of five, more likely six, doublets, and, most importantly, the high-field resonance must be two overlapping doublets of intensity 1.[16] The D_{2d} structure proposed by Greenwood and Travers for $Zn(B_{10}H_{12})_2^{2-}$ allows only boron resonances of intensities 2 and 4 and is thus completely incompatible with these spectral data. An alternative structure for $Zn(B_{10}H_{12})_2^{2-}$ is shown in Figure 6. The tetrahedrally coordinated zinc atom is the fusion point between two 11-atom icosahedral fragments with an over-all symmetry of C_i as opposed to C_{2h} for the transition metal derivatives. The interaction of $B_{10}H_{12}^{2-}$ with a metal to form an icosahedral fragment is probably similar in both the zinc and the transition metal derivatives, but the tetrahedral coordination requirements of zinc as opposed to the possibility of square coordination in the transition metal derivatives lead to the spectral differences between the compositionally analogous derivatives.

Experimental Section

Decaborane was purchased from the Callery Chemical Co. and used as received. Tetrahydrofuran and diethyl ether were distilled from lithium aluminum hydride immediately prior to use. Acetonitrile was dried over molecular sieve. All reactions were run under a nitrogen atmosphere. Transition metal complexes used as starting reagents were obtained by standard literature procedures.

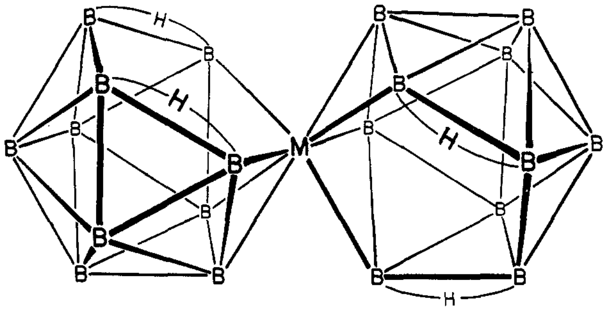

Figure 6.—The proposed heavy-atom structure of $Zn(B_{10}H_{12})_2^{2-}$.

$[(CH_3)_4N]_2[Ni(B_{10}H_{12})_2]$.—A filtered 125-ml tetrahydrofuran solution of $NaB_{10}H_{13}$, prepared from 4.88 g (0.04 mol) of $B_{10}H_{14}$ and 2.8 g (0.065 mol of NaH) of a 56% emulsion of NaH in mineral oil, was added rapidly under nitrogen to 7.43 g (0.01 mol) of bis(triphenylphosphine)nickel(II) bromide in 100 ml of acetonitrile. The resulting orange-red reaction mixture was stirred for 30 min and then filtered. The precipitate was discarded and the filtrate was condensed to *ca.* 75 ml and then diluted with 250 ml of water. The mixture was extracted twice with 125 ml of toluene and once with 100 ml of petroleum ether (bp 30–60°). The extracts were discarded, while the aqueous layer was filtered through Filter-Aid into excess aqueous tetramethylammonium chloride. The orange-red precipitate was collected and dried giving 3.4 g (76%) of crude complex. The crude product was recrystallized from ethanol–acetonitrile (60:40), mp 180° dec.

Anal. Calcd for $[(CH_3)_4N]_2[Ni(B_{10}H_{12})_2]$: C, 21.5; H, 10.8; B, 48.4; N, 6.3; Ni, 13.1; mol wt, 447.32. Found: C, 21.9; H, 10.8; B, 48.3; N, 5.8; Ni, 12.09; mol wt (CH_3CN, osmometer), 432. Uv and visible spectral maxima (CH_3CN): 447 (ε 4520), 310 (ε 24,600), and 222 mμ (ε 15,200); ir spectrum includes absorptions at (Nujol): 2500 (B–H) and 1940 cm^{-1} (BHB bridge); ^1H nmr (CD_3CN): τ 6.87 (s, $(CH_3)_4N$); 32-MHz ^{11}B nmr ($B_3FO(C_2H_5)_2$ = 0) (CH_3CN) δ ppm (*J* Hz): a, −9.30 (120); b, −0.06 (136); c, 3.78 (130); d, 22.0 (134).

$[(CH_3)_4N]_2[Pd(B_{10}H_{12})_2]$.—The palladium derivative was prepared from 1,5-cyclooctadienepalladium(II) chloride and $B_{10}H_{13}^-$ in essentially the same way as the nickel complex using 4.88 g of $B_{10}H_{14}$ (0.94 mol), 2.8 g of a 56% dispersion of NaH in mineral oil, 0.065 mol of NaH, and 2.88 g of 1,5-cyclooctadienepalladium(II) chloride (0.01 mol). The yield of the air-sensitive yellow $[(CH_3)_4N]_2[Pd(B_{10}H_{12})_2]$ complex was 4.62 g (95%). The product was recrystallized from ethanol–acetonitrile (60:40), mp 240° dec.

Anal. Calcd for $[(CH_3)_4N]_2[Pd(B_{10}H_{12})_2]$: C, 19.4; H, 9.76; B, 43.7; N, 5.66; Pd, 21.5; mol wt, 495.00. Found: C, 19.43; H, 9.72; B, 42.3; N, 6.21; Pd, 21.3; mol wt (CH_3CN, osmometer), 466. Uv and visible spectral maxima (CH_3CN): 365 (ε 4230), 306 (ε 26,900), and 212 mμ (ε 15,200); ir spectrum includes absorptions at (Nujol): 2505 (B–H) and 1950 cm^{-1} (BHB bridge); ^1H nmr (CD_3CN): τ 6.88 (s, $(CH_3)_4N$); 32-MHz ^{11}B nmr ($BF_3O(C_2H_5)_2$ = 0) (CH_3CN) δ, ppm (*J*, Hz): a, −10.2 (119); b, 1.03 (127); c, 4.60 (115); d, 24.5 (128).

$[(C_4H_9)_3PH]_2[Pd(B_{10}H_{12})_2]$.—A mixture of 2.3 g (0.004 mol) of $[(C_4H_9)_3P]_2PdCl_2$ and 0.0057 mol of $NaB_{10}H_{13}$ in 100 ml of ether was stirred for 30 min. The precipitating solid was filtered off and washed with ether until the runoff was colorless. The residue (1.5 g) was first recrystallized from ether–tetrahydrofuran (30 ml) and subsequently from tetrahydrofuran to give 0.6 g of yellow crystals of poorly defined habit, mp 158–161° dec.

Anal. Calcd for $[(C_4H_9)_3PH]_2[Pd(B_{10}H_{12})_2]$: C, 38.3; H, 10.7; P, 8.2; B, 28.7; Pd, 14.1. Found: C, 38.1; H, 10.6; P,

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[16] The ^{11}B nmr spectrum of the zinc complex at 19.3 MHz eliminates the possibility that the high-field area is a triplet of intensity 2.

8.1; B, 31.4; Pd, 13.9. Ir spectrum (Nujol): 2500 (B–H), 2300 (P–H), and 1950 cm^{-1} (BHB bridge).

$[(CH_3)_4N]_2[Pt(B_{10}H_{12})_2]$.—The complex was prepared from norbornadieneplatinum(II) chloride and $NaB_{10}H_{13}$ by the procedure reported for the analogous nickel complex using 5.7 g (0.016 mol) of $(C_7H_8)PtCl_2$, 7.8 g (0.064 mol) of $B_{10}H_{14}$, and 4.2 g (0.096 mol of NaH) of a 56% dispersion of NaH in mineral oil. The yield of crude, air-sensitive $[(CH_3)_4N]_2[Pt(B_{10}H_{12})_2]$ was 9.0 g (96%). The crude yellow material was recrystallized from acetonitrile–ethanol (60:40), mp 310° dec.

Anal. Calcd for $[(CH_3)_4N]_2[Pt(B_{10}H_{12})_2]$: C, 16.5; H, 8.29; B, 37.2; N, 4.70; Pt, 33.5; mol wt, 583.69. Found: C, 16.11; H, 8.28; B, 3.49; N, 4.79; Pt, 33.6; mol wt (CH_3CN, osmometer), 583. Uv and visible spectral maxima (CH_3CN): 375 (ϵ 7810) and 275 mμ (ϵ 23,600); ir spectrum contains absorptions at (Nujol): 2150 (B–H) and 1948 cm^{-1} (BHB bridge); ^{1}H nmr (CD_3CN): τ 6.88 (s, $(CH_3)_4N$); 32-MHz ^{11}B nmr ($BF_3O(C_2H_5)_2$ = 0) (CH_3CN) δ, ppm (J, cps): a, −4.65 (100); b, 2.22 (142); c, 6.44 (128); d, 24.5 (133).

$[(CH_3)_4N]_2[Co(B_{10}H_{12})_2]$.—A solution of 1.30 g (0.01 mol) of anhydrous $CoCl_2$ in 150 ml of acetone was added dropwise to 6.6 g of $Zn(B_{10}H_{12})(C_4H_8O)_2$ in 20 ml of acetone. The resulting red solution was diluted with 300 ml of tetrahydrofuran to give a red precipitate which was collected. The red precipitate was dissolved in water and immediately filtered into aqueous tetramethylammonium chloride. The red solid which formed was collected and dried. The crude product was recrystallized from acetone–toluene to give 1.6 g (36%) of red needles, dec pt 140°, without melting.

Anal. Calcd for $[(CH_3)_4N]_2[Co(B_{10}H_{12})_2]$: C, 21.4; H, 10.8; B, 48.4; N, 6.3; Co, 13.1; mol wt, 447.53. Found: C, 22.5; H, 11.0; B, 47.6; N, 5.3; Co, 13.6; mol wt (CH_3CN, osmometer), 439. Uv and visible spectral maxima (CH_3CN): 507 (ϵ 3260), 405 (sh) (ϵ 2680), 325 (ϵ 14,100), 280 (ϵ 15,000), and 220 mμ (ϵ 19,900): ir spectrum contains absorptions at (Nujol): 2500 (B–H) and 1950 cm^{-1} (BHB bridge).

$[(CH_3)_4N]_2[Zn(B_{10}H_{12})_2]$.—A solution of 3.6 g (0.02 mol) of $Zn(NCS)_2$ in 100 ml of tetrahydrofuran was added to a solution of 0.04 mol of $NaB_{10}H_{13}$ in diethyl ether. The mixture was filtered and the golden yellow filtrate was evaporated. The residue was chromatographed on alumina using acetonitrile as the eluent. A fast-moving yellow fraction was collected and evaporated. This residue was dissolved in water, and addition of excess tetramethylammonium chloride gave a yellow precipitate. The crude salt was recrystallized from methanol–acetone (2:1) to give 0.6 g (14%) of yellow needles, dec pt 300°, without melting.

Anal. Calcd for $[(CH_3)_4N]_2[Zn(B_{10}H_{12})_2]$: C, 21.2; H, 10.7; N, 6.2; Zn, 14.4; B, 47.6. Found: C, 21.7; H, 10.8; N, 6.1; Zn, 14.1; B, 48.1. Uv and visible spectral maxima (CH_3CN): 345 (ϵ 4000), 228 (ϵ 15,300), and 275 mμ (ϵ 15,200). The infrared spectrum was identical with that reported in the literature.[5]

$[(CH_3)_4N][Co(B_{10}H_{12})(CO)_3]$.—A solution of 9.3 g (0.027 mol) of $Co_2(CO)_8$ in 150 ml of tetrahydrofuran was stirred with 0.054 mol of $NaB_{10}H_{13}$ in 100 ml of diethyl ether. Gas evolution occurred and the solution became red. Evaporation of the solvent gave a red oil which yielded a solid on addition of 700 ml of aqueous tetramethylammonium chloride solution. The resulting precipitate (a mixture of $(CH_3)_4NCo(CO)_4$ and product) was collected, dried, and chromatographed on alumina using CH_2Cl_2 as the eluent. A fast-moving yellow fraction was collected and evaporated. The residue was recrystallized from 50 ml of benzene–dichloromethane (4:1) to give 4.8 g (55%) of yellow plates, dec pt 117°, without melting.

Anal. Calcd for $[(CH_3)_4N][Co(B_{10}H_{12})(CO)_3]$: C, 24.9; H, 7.2; B, 32.1; N, 4.2; O, 14.2; Co, 17.5; mol wt, 337. Found: C, 24.9; H, 7.3; B, 32.5; N, 4.0; O, 13.9; Co, 17.1; mol wt (CH_2Cl_2, osmometer), 354. Uv and visible spectral maxima (CH_3CN): 385 (ϵ 182), 313 (ϵ 3400), and 235 mμ (ϵ 15,600); ir $(CH_2Cl)_2$: 2508 (B–H), 2082 (s), 2024 (s), and 2002 (s) cm^{-1} (CO); H^1 nmr (CD_3CN): τ 7.16 (s, $(CH_3)_3N$).

$[(CH_3)_4N][Rh(B_{10}H_{12})(CO)[P(C_6H_5)_3]_2]$.—A mixture of 3.5 g (0.005 mol) of $[P(C_6H_5)_3]_2Rh(CO)Cl$ and 0.020 mol of $NaB_{10}H_{13}$ in 250 ml of ether–tetrahydrofuran (1:1) was stirred for 30 min and filtered. The filtrate was added to aqueous tetramethylammonium chloride (1 l.) and the resulting precipitate was collected. The yellow precipitate was washed with diethyl ether and recrystallized from acetone–acetonitrile (7:2). A yield of 1.5 g (35%) of the yellow crystals, dec 152° pt, was obtained in two crops.

Anal. Calcd for $[(CH_3)_4N][Rh(B_{10}H_{12})(CO)[P(C_6H_5)_3]_2]$: C, 57.9; H, 6.4; N, 1.7; O, 1.9; P, 7.3; B, 12.7; Rh, 12.1. Found: C, 57.4; H, 6.4; N, 1.6; O, 2.0; P, 7.0; B, 11.7; Rh, 12.0. Uv and visible spectral maxima (CH_3CN): 267 (ϵ 18,100) and 225 mμ (ϵ 52,000); ir (Nujol): 2525 (B–H) and 1984 cm^{-1} (CO); ^{1}H nmr (CD_3CN): τ 3.04 (m, 30, $P(C_6H_5)_3$) and 7.25 (s, 12, $(CH_3)_4N$).

$[(CH_3)_4N][Ir(B_{10}H_{12})(CO)[P(C_6H_5)_3]_2]$.—A solution of 0.024 mol of $NaB_{10}H_{13}$ in 100 ml of diethyl ether was added to a suspension of 7.8 g (0.010 mol) of $[(C_6H_5)_3P]_2Ir(CO)Cl$ in 150 ml of acetonitrile–tetrahydrofuran (1:1). The mixture was stirred for 3 hr and filtered. The filtrate was concentrated to remove the ether and was then poured into 500 ml of aqueous tetramethylammonium chloride solution. The yellow precipitate which resulted was collected, washed with ether, and recrystallized from 250 ml of hot acetonitrile. Concentration and chilling of the solution gave two crops of 1.7 and 0.8 g (29%) of yellow microcrystals, dec pt 218°, without melting.

Anal. Calcd for $[(CH_3)_4N][Ir(B_{10}H_{12})(CO)[P(C_6H_5)_3]_2]$: C, 52.4; H, 5.8; N, 1.5; O, 1.7; P, 6.6; B, 11.6. Found: C, 52.4; H, 5.9; N, 1.6; O, 1.7; P, 6.5; B, 10.8. Uv and visible spectral maxima (CH_3CN): 305 (ϵ 1010) and 265 mμ (ϵ 15,550); ir (Nujol): 2500 (B–H) and 1960 cm^{-1} (CO); 19.3-MHz ^{11}B nmr ($BF_3O(C_2H_5)_2$ = 0): δ 12.9 ppm (broad, unstructured).

$Pd(B_{10}H_{12})[P(C_6H_5)_3]_2$.—A solution of 0.01 mol of $NaB_{10}H_{13}$ was stirred with a suspension of 3.5 g (0.005 mol) of $[(C_6H_5)_3P]_2PdCl_2$ in 100 ml of acetonitrile–tetrahydrofuran (1:1) for 3 hr. The mixture was filtered and the filtrate was concentrated to about half-volume, whereupon a yellow solid (1.1 g) precipitated. The solid was recrystallized from 175 ml of acetonitrile to give 0.6 g of yellow needles, dec pt 140°.

Anal. Calcd for $Pd(B_{10}H_{12})[P(C_6H_5)_3]_2$: C, 57.6; H, 5.6; P, 8.3; B, 14.4; Pd, 14.2. Found: C, 57.7; H, 5.8; P, 8.4; B, 14.4; Pd, 14.0. Uv and visible spectral maxima (CH_3CN): 288 (ϵ 20,200), 276 (ϵ 20,400), and 230 mμ (ϵ 51,000); ir (Nujol): 2550 (B–H) and 680, 740, and 750 cm^{-1} (phenyl); the ^{11}B nmr spectrum was broad and unstructured.

$Pt(B_{10}H_{12})[P(C_6H_5)_3]_2$.—A tetrahydrofuran solution of $NaB_{10}H_{13}$ (0.01 mol) was added to a suspension of 4.0 g (0.005 mol) of $[(C_6H_5)_3P]_2PtCl_2$ in 100 ml of tetrahydrofuran. The mixture was stirred for 3 hr and filtered. The filtrate was evaporated and the residue was washed with cyclohexane. Recrystallization from acetone gave 1.3 g of $Pt(B_{10}H_{12})[P(C_6H_5)_3]_2$. A further 0.87 g was obtained from the precipitate by extraction with hot acetone and then cooling the solution. The total yield of yellow product, dec pt 200°, without melting, was 2.17 g (52%).

Anal. Calcd for $Pt(B_{10}H_{12})[P(C_6H_5)_3]_2$: C, 51.48; H, 5.04; B, 12.86; P, 7.38. Found: C, 51.19; H, 5.16; B, 12.77; P, 7.32. Ir spectrum (Nujol): 2525 (B–H) and 685, 696, 735, and 746 cm^{-1} (phenyl).

$Pt(B_{10}H_{12})[P(C_2H_5)_3]_2$.—(A) A solution of 1.22 g (0.01 mol) of $B_{10}H_{14}$ and 4.68 g (0.01 mol) of $[(C_2H_5)_3P]_2PtHCl$ in 25 ml of benzene was heated at 70° for 3 hr. Gas was evolved and the solution became yellow. The reaction mixture was cooled and pale yellow crystals formed. The yield was 0.45 g (9%). The crude product was recrystallized from acetone to give yellow flakes whose ir spectrum was identical with those of the product from part B (see below). Some *cis*-$[(C_2H_5)_3P]_2PtCl_2$, mp 190–192°, was isolated from the reaction solution.

(B) A 50-ml diethyl ether solution of 0.002 mol of $NaB_{10}H_{13}$ was added to a suspension of 5.0 g (0.001 mol) of *cis*-$[(C_2H_5)_3P]_2PtCl_2$ in 50 ml of acetonitrile. The reaction mixture was stirred for 1 hr and filtered. The filtrate was evaporated to dryness and the residue was washed with hexane and recrystallized from 40 ml of acetonitrile to give 0.3 g (55%) of $Pt(B_{10}H_{12})[P(C_2H_5)_3]_2$, dec pt 180°, without melting.

Anal. Calcd for $Pt(B_{10}H_{12})[P(C_2H_5)_3]_2$: C, 26.1; H, 7.7; B, 19.6; P, 11.2; Pt, 35.4; mol wt, 552. Found: C, 26.1; H, 8.1; B, 19.7; P, 10.7; Pt, 36.1; mol wt (acetone) (ebullioscopic), 537. Ir spectrum (Nujol): 2535 (B–H) and 1940 cm^{-1} (BHB bridge); uv and visible maxima (CH_3CN): 220 (ϵ 21,180) and 245 mμ (ϵ 14,050); the ^{11}B nmr spectrum was broad and unresolved; ^1H nmr ($(CD_3)_2CO$): τ 8.86 (t, 3, CH_3CH_2) and 7.8 (q, 2, CH_3CH_2).

$Pt(B_{10}H_{12})[P(C_4H_9)_3]_2$.—A 50-ml solution of 0.005 mol of $NaB_{10}H_{13}$ was added to a slurry of 3.35 g (0.0025 mol) of *cis*-$[(C_4H_9)_3P]_2PtCl_2$ in tetrahydrofuran. The reaction was stirred for 30 min and filtered and the filtrate was evaporated to a yellow oil. Trituration with hexane gave a yellow solid. The crude product was recrystallized from benzene to give well-formed yellow crystals, mp 182–183°. The yield was 1.0 g (55%).

Anal. Calcd for $Pt(B_{10}H_{12})[P(C_4H_9)_3]_2$: C, 40.02; H, 9.24; B, 15.02. Found: C, 40.25; H, 9.09; B, 14.83. Ir spectrum (Nujol): 2530 (B–H) and 1430 cm^{-1} (BHB bridge); 19.3-MHz ^{11}B nmr ($BF_3O(C_2H_5)_2 = 0$) (acetone): δ −8.1 (b, 8) and 28.1 ppm (d, 2).

$Pd(B_{10}H_{12})[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$.—A suspension of 1.15 g (0.002 mol) of P,P,P′,P′-tetraphenylethylenediphosphine-palladium(II) chloride in 30 ml of tetrahydrofuran was treated with 0.004 mol of $NaB_{10}H_{13}$ in 20 ml of tetrahydrofuran. During a 3-hr period at 25°, the reaction mixture became yellow and then white. The mixture was filtered and the filtrate was evaporated. The off-white solid was recrystallized from acetone as light yellow needles, mp 230–240°.

Anal. Calcd for $Pd(B_{10}H_{12})[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 49.94; H, 5.80. Found: C, 50.53; H, 6.78. Ir spectrum (Nujol): 2535 (B–H) and 1940 cm^{-1} (BHB bridge).

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Hydrolysis of Tris(N-dibutylboryl-4-methyl-2-pyridylamino)borane

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The rate of hydrolysis of tris(N-dibutylboryl-4-methyl-2-pyridylamino)borane was investigated spectrophotometrically in aqueous dioxane. The reaction was affected by the addition of hydrochloric acid and was shown to be first order in the substrate. The hydrolysis proceeded more rapidly in a D_2O–dioxane solution than in a H_2O–dioxane solution by a factor of about 2.5 over a wide range of solvent composition. The rate changed with the solvent composition in a similar way as did the acidity function. The activation energy was obtained as 20.5 kcal/mol and the activation entropy as +18.1 eu at 300°K in 90 vol % aqueous dioxane. On the basis of these experimental results, the hydrolysis mechanism was concluded to be of the A-1 type which involves rapid preequilibrium between the reactants and a conjugate acid followed by a first-order rate-determining reaction of the conjugate acid.

Introduction

A preceding paper[1] has dealt with the mechanism of catalytic hydrolysis of borazine derivatives in aqueous dioxane media in the presence of hydrochloric acid or triethylamine. The present paper describes a kinetic and mechanistic study in which the rates of hydrolysis of tris(N-dibutylboryl-4-methyl-2-pyridylamino)borane [abbreviated hereafter as S] have been determined by measuring the rate of decreasing absorption of its aqueous dioxane solution. As shown in Figure 1, S has three kinds of B–N bonds, one of which is an N→B coordination bond. All of these B–N bonds are broken during the hydrolysis

$$S + 9H_2O \longrightarrow 3CH_3(C_5H_3N)NH_2 + 3C_4H_9B(OH)_2 + B(OH)_3 + 3C_4H_{10}$$

It is an important as well as an interesting point in this study to determine which bond is split at the rate-determining step. In order to clarify the mechanism and to determine the kinetic order, the rate of hydrolysis, the hydrogen isotope effect of solvent, and the activation parameters have been determined.

Experimental Section

Materials.—Dioxane was purified by the method of Fieser.[2] The mixed solvent of 90% dioxane–10% water was prepared by diluting one volume of water with nine volumes of dioxane. (This solvent will be abbreviated as 90% aqueous dioxane throughout this paper.) The catalyst was dissolved in water before mixing, and its concentration was corrected for the volume compression due to mixing. The sample of S was prepared by a method virtually identical with that described earlier using 4-methyl-2-aminopyridine instead of 2-aminopyridine.[3]

Kinetic Measurements.—The hydrolysis experiments were carried out in a glass-stoppered 1-cm quartz cuvette, and the progress of the hydrolysis was followed by reading the decrease in optical density of the sample solution on a Model EPU-2A photoelectric spectrophotometer from Hitachi Co., Ltd., the cell compartment of which was modified[1] so that the desired temperature could be maintained within ±0.02°. The sample gives rise to a strong absorption at 340 mμ and the measurements were

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