

the ^{14}N NQR results are complicated by the well-known tendency toward bridging halide structures in adducts of mercuric halides.¹⁷⁻¹⁹ 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 σ 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.²⁰

Registry No. Zn(EDP)Cl₂, 65045-56-9; Zn(EDP)Br₂, 65045-55-8; Zn(EDP)(NO₃)₂, 49626-99-5; Zn(EDP)(NO₂)₂, 49626-97-3; Cd(EDP)Cl₂, 65045-54-7; Cd(EDP)Br₂, 65045-53-6; Cd(EDP)I₂, 65045-52-5; Hg(EDP)Cl₂, 65045-51-4; Hg(EDP)Br₂, 65045-59-2; (EDPH₂)(ClO₄)₂, 65045-39-8; EDP, 1932-04-3; NO₃⁻, 14797-55-8; NO₂⁻, 14797-65-0.

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Oxidative Addition of Halopentaboranes to *trans*-IrCl(CO)(PMe₃)₂

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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 σ -metalloboranes.¹ Boron-hydrogen bonds are capable of similar reactions. Inter- and intramolecular insertion of transition-metal complexes into the B-H bonds of carboranes² and carboranylphosphines,^{2,3} 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.⁴ Earlier, in preliminary form, we reported that 1- and 2-BrB₅H₈ inserted *trans*-IrCl(CO)(PMe₃)₂ 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.⁵ 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 CH₂Cl₂, which was distilled from P₄O₁₀. 1-BrB₅H₈,⁶ 2-BrB₅H₈,⁶ 1-ClB₅H₈,⁷ 2-ClB₅H₈,^{7b} and 1-CH₃-B₅H₈⁸ 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.⁹

Manipulations throughout were performed in vacuo or under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ¹H, 40.5-MHz ³¹P, and 32.1-MHz ¹¹B NMR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, and AEI MS-9 spectrometers. ³¹P and ¹¹B NMR chemical shifts are relative to external 85% phosphoric acid and BF₃·(C₂H₅)₂O, 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-[IrBr₂(CO)(PMe₃)₂]B₅H₈, **2. (1) From 1-BrB₅H₈. To a 10-mm tube equipped with a magnetic stirring bar and stopcock was charged 250 mg (0.62 mmol) of *trans*-IrCl(CO)(PMe₃)₂ (**1**). The vessel was evacuated, 4.5 g of 1-BrB₅H₈ 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, ν_{BH}), 2554 (m, ν_{BH}), 2024 (s, ν_{CO}), and 945 cm⁻¹ (s, σ -apical BH); mp 148 °C (dec); ¹H{¹¹B} NMR (CD₂Cl₂) τ 11.4 (s, 2, μ -BH), 10.0 (s, 2, BH), 8.6 (s, 1, B₁H), and 7.4 (5, 18, PCH₃, $J_{\text{PCH}} = 4.2$ Hz); ³¹P{¹H} NMR (CH₂Cl₂) 45.2 ppm; ¹¹B{¹H} NMR (CH₂Cl₂) 11.3 (B₂), 14.4 (B_{3,5}), 17.3 (B₄), and 50.2 ppm (B₁).**

Anal. Calcd for C₇H₂₆B₅Br₂IrOP: 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-BrB₅H₈. In a similar manner, 2.0 g of 2-BrB₅H₈ 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)(PMe₃)₂]B₅H₈, **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-ClB₅H₈ (1.82 mmol) and 0.3 mL of toluene at -196 °C. The mixture was warmed to -22 °C (CCl₄ 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: ¹H{¹¹B} NMR (toluene-*d*₆) τ 17.79 (t, 1, IrH, $J_{\text{IrH}} = 18$ Hz), 11.8 (s, 2, μ -BH), 9.6 (s, 2, μ -BH), 8.37 (t, 18, PCH₃, $J_{\text{PCH}} = 4.2$ Hz), 7.3 (s, 2, B_{3,5}H), 6.20 (s, 1, B₄H); ³¹P{¹H} NMR (toluene-*d*₆) 42.6 ppm; ¹¹B{¹H} NMR (toluene-*d*₆) 27.9 (s, 1, B₁), 17.7 ppm (broad and unresolved, basal resonances).**

The thermal instability of the compound precluded elemental analysis.

2-[IrCl₂(CO)(PMe₃)₂]B₅H₈, **4. Quantities of 170 mg of **1** (0.42 mmol) and 90 mg of 1-ClB₅H₈ (0.92 mmol) were stirred in toluene**

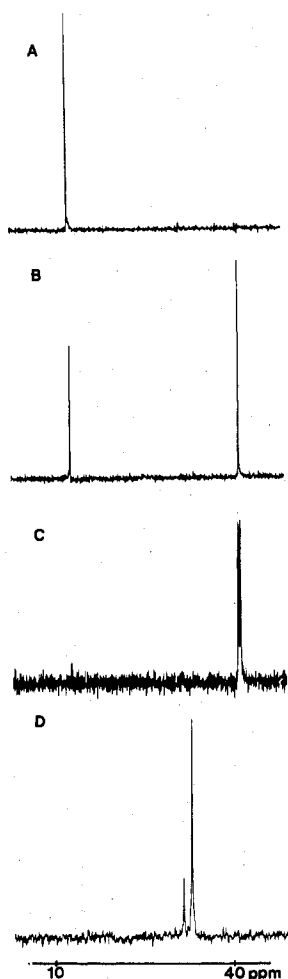


Figure 1. ^{31}P NMR spectra (toluene- d_8) of *trans*- $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$ and excess 1- ClB_5H_8 : (A) prior to reaction (-50°C , proton decoupled); (B) after 1 h at -20°C (proton decoupled); (C) after complete conversion to 1-Cl-2- $[\text{IrHCl}(\text{CO})(\text{PMe}_3)_2]\text{B}_5\text{H}_7$ (-20°C , proton coupled); (D) as final products (30°C , proton decoupled), the minor product at 32.0 ppm being $\text{IrHCl}_2(\text{CO})(\text{PMe}_3)_2$.

at -22°C for 1.5 h, as in the preparation of **3**, and then stirred for 2 h at 25°C . The workup employed in the preparation of **2** afforded 60 mg (0.12 mmol) of **4**: $^1\text{H}\{^{11}\text{B}\}$ NMR (toluene- d_8) τ 12.3 (s, 2, μ -BH), 10.8 (s, 2, μ -BH), 8.42 (t, 18, PCH_3 , $J_{\text{PCH}} = 4.0$ Hz), 7.4 (s, 2 H, $\text{B}_{3,5}\text{H}$), 6.6 (s, 2 H, B_4H); B_1H is obscured by the methyl resonances; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) 33.2 ppm; ^{11}B NMR (toluene- d_8) 50.0 (d, 1, B_1 , $J_{\text{BH}} = 160$ Hz), 15.4 ppm (broad and unresolved, basal resonances).

Anal. Calcd for $\text{C}_7\text{H}_{26}\text{B}_5\text{Cl}_2\text{IrOP}_2$: C, 16.64; H, 5.19; B, 10.70. Found: C, 16.18; H, 4.93; B, 10.92.

Reaction of 2- ClB_5H_8 with *trans*- $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$. Excess 2- ClB_5H_8 was condensed onto 315 mg of **1** in a 10-mm tube at -196°C . While being stirred, the mixture was warmed to 25°C for 10 min and then to 40°C for an additional 10 min. The volatile components were removed in vacuo and the reaction worked up as in the preparation of **2**. Recrystallization from toluene-hexane afforded 180 mg (0.41 mmol, 53%) of $\text{IrCl}_2\text{H}(\text{CO})(\text{PMe}_3)_2$; IR (Nujol mull) 2182 (m, ν_{IrH}) and 2024 cm^{-1} (s, ν_{CO}); ^1H NMR (CD_2Cl_2) τ 26.63 (t, $J_{\text{PIrH}} = 14.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) 32.0 ppm (s).

Anal. Calcd for $\text{C}_7\text{H}_{19}\text{Cl}_2\text{IrOP}_2$: C, 18.92; H, 4.31; Cl, 15.96. Found: C, 19.36; H, 4.40; Cl, 15.57.

Preparation of 2- $[\text{IrClH}(\text{CO})(\text{PMe}_3)_2]\text{B}_5\text{H}_8$, **6.** To a vacuum-line filtration assembly was charged 244 mg (0.57 mmol) of **1**. The apparatus was evacuated and cooled to -196°C , and 2 mL of B_5H_9 was condensed onto the solid. Stirring to 25°C for several minutes gave a colorless solution, which was cooled to -45°C and into which ca. 10 mL of hexane was slowly distilled. The resulting precipitate was collected by filtration at -78°C , washed with 2×4 ml each of hexane and pentane, and dried in vacuo at -78°C to yield 206 mg

(77%) of a microcrystalline white powder: IR (Kel-F and Nujol mulls) 2573 (m, ν_{BH}), 2555 (m, ν_{BH}), 2082 (s, ν_{CO}), 1978 (s, ν_{IrH}), and 945 cm^{-1} (s, δ -apical BH); mp 64°C (dec); $^1\text{H}\{^{11}\text{B}\}$ NMR (-30°C , CD_2Cl_2) τ 16.10 (t, 1, IrH, $J_{\text{PIrH}} = 20$ Hz), 11.4 (s, 2, μ -BH), 9.9 (s, 2, μ -BH), 8.6 (s, 1, B_1H), 7.20 (t, 18, PCH_3 , $J_{\text{PCH}} = 4.2$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (-30°C , CH_2Cl_2) 42.2 ppm.

Anal. Calcd for $\text{C}_7\text{H}_{27}\text{B}_5\text{ClIrOP}_2$: C, 17.85; H, 5.79; Cl, 7.53. Found: C, 17.14; H, 5.71; Cl, 7.89.

In a similar reaction *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ was quantitatively recovered after stirring with B_5H_9 for 3 days at 25°C .

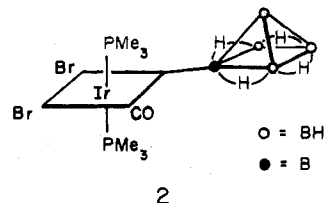
Pyrolysis of **6.** To a small sublimation apparatus was charged 60 mg (0.13 mmol) of **6**; the solid was covered with a plug of glass wool. The apparatus was sealed to the vacuum line and heated to 150°C for 6 h while cooling the sublimation probe to 0°C and pumping the evolved gases through a -196°C trap. The major product was a nonvolatile brown solid. Pure B_5H_9 (0.048 mmol, 38%) was recovered from the -196°C trap (identified by comparison of its IR and mass spectrum with that of an authentic sample). A small amount of yellow sublimate on the 0°C probe was identified as **1** by IR spectroscopy.

NMR Monitoring Experiments. A 12-mm NMR tube was charged with a measured amount of iridium complex. The tube was evacuated and cooled to -196°C , and a measured amount of the appropriate derivatized pentaborane was condensed onto the solid. CD_2Cl_2 or toluene- d_8 was distilled in and the vessel sealed in vacuo. The frozen tube was inserted into the probe of the spectrometer and warmed to the appropriate temperature, and then spectral accumulation was begun.

Infrared Monitoring Experiments. In a typical experiment, 50 mg of **1** was charged to a 25 mL flask equipped with a magnetic stirring bar and a side arm. The side arm was stoppered, the vessel was evacuated and cooled to -196°C , and a large excess of 1- BrB_5H_8 and 3.0 mL of CH_2Cl_2 was condensed onto the solid **1**. Under a nitrogen atmosphere the stopper was replaced with a serum cap and the flask warmed to 0°C with stirring. After the solution decolorized (which occurred within seconds), aliquots were withdrawn with a syringe and infrared spectra in the region 2200–1900 cm^{-1} recorded immediately.

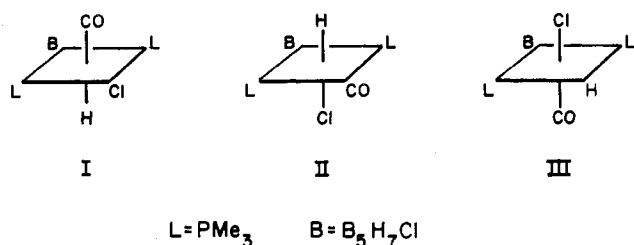
Results and Discussion

trans- $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$ (**1**) reacts rapidly with excess 1- or 2- BrB_5H_8 , affording 2- $[\text{IrBr}_2(\text{CO})(\text{PMe}_3)_2]\text{B}_5\text{H}_8$ (**2**) in both



cases.⁵ By crystallographic methods, **2** has been shown to have the structure indicated.^{5,10} Infrared monitoring experiments at ca. 0°C revealed rapid disappearance of **1** (ν_{CO} 1950 cm^{-1}) accompanied by the appearance of **2** (ν_{CO} 2024 cm^{-1}) and an iridium carbonyl hydride (ν_{CO} 2085, ν_{IrH} 1985 cm^{-1}). The hydride bands rapidly decayed with simultaneous growth of the carbonyl absorption of **2**. More detailed investigations by this method were hampered by the speed of the reaction.

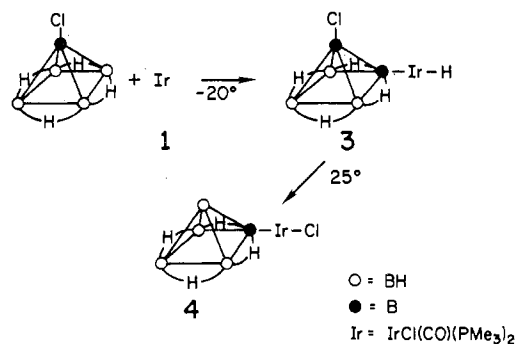
Subsequently, ^{31}P NMR monitoring experiments of the reaction of **1** with an excess or a stoichiometric amount of 1- ClB_5H_8 revealed quantitative conversion of **1** (13.5 ppm) to an iridium hydride (42.6 ppm) at -20°C (Figure 1). A preparative-scale reaction under these conditions allowed the isolation of this complex as a colorless crystalline solid. Although the thermal instability of the compound precluded elemental analysis, the spectral data are consistent only with the formulation 1-Cl-2- $[\text{IrHCl}(\text{CO})(\text{PMe}_3)_2]\text{B}_5\text{H}_7$ (**3**). The NMR data, requiring mutually *trans* trimethylphosphine ligands, do not distinguish between the remaining three isomers. I and II are formally derived by *cis* addition and III is derived by *trans* addition. Metal-hydrogen stretching frequencies for the isomers of $\text{IrHCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2$ indicate that the band for a hydride *trans* to the carbonyl occurs 200



cm^{-1} lower than that for a hydride cis to the carbonyl.^{11,12} Further, $IrHCl_2(CO)(PMe_3)_2$ (in which H and CO are cis¹¹) exhibits ν_{IrH} at 2182 cm^{-1} . Thus, the value of 1985 cm^{-1} observed for **3** (and for **6**; vide infra) is consistent with I. A similar argument can be based on the chemical shifts of the metal hydride.¹¹

Inasmuch as the bridge hydrogens of pentaborane and its derivatives are the most acidic,¹³ insertion into the B-H-B bridge bond to give a μ -Ir precursor to **3** is plausible. Complexes containing three-center boron-metal-boron bonds and derived from $B_5H_8^{-13e,14}$ and related species^{14c,15} are well-known. The bridge-terminal isomerization, which would be required for subsequent formation of **3** from a μ -Ir intermediate, has been observed for silyl- and germyl-substituted pentaboranes^{13e,14b,16} and related carborane derivatives.^{15d,e} However, if the bridge-bonded species is present, its concentration is too low to detect by ^{31}P NMR; i.e., isomerization to terminally bonded **3** must be rapid. Since bridge-terminal isomerization is generally slow in the absence of Lewis bases,^{13e,15d,17} formation of **3** by direct insertion into the basal B-H bond is likely. As further support for direct insertion, we note $B_{10}H_{14}$ exchanges only terminal hydrogens with deuterium in the presence of $(PPh_3)_3RuHCl$.⁴

Warming solutions of **3** to $25^\circ C$ results in the decay of the ^{31}P NMR signal from **3** and the formation of $2-[IrCl_2(CO)(PMe_3)_2]B_5H_8$ (**4**) together with a small amount of a



product whose ^{31}P and 1H NMR spectra are identical with those of an authentic sample of $IrHCl_2(CO)(PMe_3)_2$ (Figure 1). No detectable intermediates are observable in the conversion of **3** to **4**.

trans- $IrBr(CO)(PMe_3)_2$ and $1-BrB_5H_8$ react similarly, although more rapidly. Thus, ^{31}P NMR spectra show quantitative conversion of the starting material (20.1 ppm) to an iridium hydride (49.1 ppm, $J_{PH} = 18.8\text{ Hz}$) at $-40^\circ C$. Warming to $25^\circ C$ affords **2** and a small amount of a product having ^{31}P and 1H NMR spectra identical with those of $IrHBr_2(CO)(PMe_3)_2$.

If **1** is treated with an excess of $1-BrB_5H_8$, the formation of **2** is accompanied by isomerization of the haloborane to a mixture of 1- and $2-BrB_5H_8$ (ca. 1:1 by GLC analysis¹⁸). The chloride from **1** is found as $2-ClB_5H_8$. Product **2** is formed irreversibly as pyrolysis does not regenerate bromopentaborane and heating **2** with $1-ClB_5H_8$ leaves **2** unchanged; no bromopentaborane or **4** is formed. The halide exchange exhibited in conversion of **1** to **2** must occur prior to the irreversible formation of **2**. A control experiment established that **2** does

not catalyze the isomerization of $1-BrB_5H_8$. Isomerization may result from undetectable (by NMR) amounts of liberated trimethylphosphine, which control experiments show to be an efficient catalyst.

The mechanism of migration of the halogen from the apical boron in **3** to iridium in **4** remains unclarified. 1H and ^{31}P NMR monitoring experiments gave no evidence for a 1-metalated intermediate. $1-ClB_5H_8$ has been shown to give $2-[M(CO)_5]B_5H_8$ ($M = Mn, Re$) on treatment with alkali metal salts of $M(CO)_5^-$ in ethereal solvents.¹⁹ In this instance, however, the Lewis base solvent is capable of catalyzing 1-2 isomerizations of derivitized pentaboranes.^{13e}

At $-60^\circ C$ 1 equiv each of $2-ClB_5H_8$ and **1** cleanly give an unstable iridium hydride. This compound was too unstable to isolate, but the ^{31}P , ^{11}B , and 1H NMR data from material prepared in situ are consistent only with $2-Cl-4-[IrHCl(CO)(PMe_3)_2]B_5H_7$ (**5**). Warming to $25^\circ C$ results in exclusive conversion to $IrHCl_2(CO)(PMe_3)_2$, in contrast to the conversion of **3** to **4**. $2-BrB_5H_8$ and *trans*- $IrBr(CO)(PMe_3)_2$ react similarly, initially forming an iridium hydride (detected by ^{31}P NMR, 48.9 ppm). However, warming affords **4** contaminated with $IrHBr_2(CO)(PMe_3)_2$. That is, in all cases, warming the iridium hydride intermediates yields $IrHX_2(CO)(PMe_3)_2$. For 1-halo- and 2-bromopentaboranes, this is a minor product. The major product is **2** or **4**. The intermediate derived from $2-ClB_5H_8$, however, gives the HCl adduct of **1** quantitatively.

Pentaborane(9) reacts directly with **1** by insertion into the basal B-H bond, yielding $2-[IrHCl(CO)(PMe_3)_2]B_5H_8$ (**6**). In contrast to **2** and **4**, formation of **6** is reversible to some degree, as pyrolysis liberates B_5H_9 in moderate yield.

trans- $Ir(CO)Cl(PPh_3)_2$ could be recovered quantitatively after treatment with pentaborane or halopentaboranes. $1-CH_3B_5H_8$ reacted extremely slowly with **1**, as determined by ^{31}P NMR monitoring experiments.

In summary, the kinetic product derived by treatment of 1- or 2-halopentaboranes with **1** is that formed by insertion into a basal B-H bond, the site predicted to be most susceptible to nucleophilic substitution from charge and frontier orbital criteria derived from SCF calculations.^{20,21} Qualitatively, the relative order of reactivity is $2-BrB_5H_8 \approx 2-ClB_5H_8 > 1-BrB_5H_8 > 1-ClB_5H_8 \approx B_5H_9 \gg 1-(CH_3)B_5H_8$. The initially formed iridium hydride, except **5**, isomerizes, formally exchanging hydrogen bound to iridium for halogen bound to boron. No apically metalated intermediates were detected.

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Registry No. **1**, 21209-86-9; **2**, 53221-42-4; **3**, 65016-06-0; **4**, 65016-05-9; **5**, 65016-04-8; **6**, 65016-03-7; $1-BrB_5H_8$, 23753-67-5; $2-BrB_5H_8$, 23753-64-2; $1-ClB_5H_8$, 19469-13-7; $2-ClB_5H_8$, 19469-14-8; *trans*- $IrBr(CO)(PMe_3)_2$, 65016-02-6; $1-CH_3B_5H_8$, 19495-55-7; B_5H_9 , 19624-22-7.

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 (17) Additionally, μ -Me₃MC₂B₄H₇ (M = Sn, Pb) fail to undergo isomerization¹⁶ as do μ transition-metal derivatives of C₂B₄H₈.
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 (21) Ruthenium-catalyzed exchange of deuterium with hydrogen bound to boron in 1,2- or 1,7-C₂B₁₀H₁₂ also occurs preferentially at the sites regarded as most prone to nucleophilic attack.⁴

Contribution from Rocketdyne,

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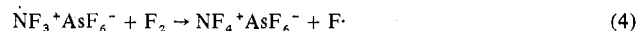
Canoga Park, California 91304, and from the Science Center,
 Rockwell International, Thousand Oaks, California 91360

Electron Spin Resonance Evidence for the Formation of the NF₃⁺ Radical Cation as an Intermediate in the Syntheses of NF₄⁺ Salts by Low-Temperature Ultraviolet Photolysis

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The mechanism of the formation of NF₄⁺ salts is of significant practical and theoretical interest. From a practical point of view, a better understanding of this mechanism would permit optimization of the reaction conditions for the direct syntheses of NF₄⁺ salts, such as NF₄BF₄, NF₄PF₆, or NF₄GeF₅.¹ From a theoretical point of view, the formation of the NF₄⁺ cation is intriguing² because its parent molecule NF₅ does not exist as a stable species. Since under the conditions used for most of the syntheses of NF₄⁺ salts an F⁺ cation should be extremely difficult, if not impossible, to prepare by chemical means, the following mechanism has previously been proposed² for the formation of NF₄AsF₆:



In good agreement with the known experimental facts,² this mechanism requires only a moderate activation energy ($D^\circ(\text{F}_2) = 36.8 \text{ kcal mol}^{-1}$).³ The two critical intermediates are the AsF₆[·] radical and the NF₃[·] radical cation. Whereas the AsF₆[·] radical is unknown, the NF₃[·] radical cation was shown⁴ to form during γ irradiation of NF₄⁺ salts at -196 °C. Although

this observation of the NF₃[·] cation demonstrated its possible existence at low temperature, it remained to be shown that the NF₃[·] radical cation is indeed formed as an intermediate in the syntheses of NF₄⁺ salts. We have now succeeded in observing experimentally the NF₃[·] radical cation by ESR spectroscopy as an intermediate in the low-temperature UV photolyses of both the NF₃-F₂-AsF₅ and the NF₃-F₂-BF₃ systems. The results and implications derived from the observations are given in this paper.

Experimental Section

Binary and ternary mixtures of the starting materials were prepared for both the NF₃-F₂-BF₃ and the NF₃-F₂-AsF₅ systems in a stainless-steel Teflon FEP vacuum system. The sample tubes consisted of flamed-out quartz tubes of 4-mm o.d., 30-cm long, with a ballast volume of about 150 mL attached at the top. The starting materials were condensed into these tubes at -210 °C and the tubes were flame sealed. The NF₃ (Rocketdyne) was used without further purification, F₂ (Rocketdyne) was passed through a NaF scrubber for HF removal, and BF₃ (Matheson) and AsF₅ (Ozark Mahoning) were purified by fractional condensation prior to use. About 300 cm³ of gas mixture was used for each sample tube in the following mole ratios: NF₃:F₂ = 1:10; BF₃:F₂ = 1:10; AsF₅:F₂ = 1:10; NF₃:BF₃ = 1:1; NF₃:AsF₅ = 1:1; NF₃:F₂:BF₃ = 1:4:1 and 1:2:1; NF₃:F₂:AsF₅ = 1:4:1.

The ESR spectra were recorded as previously described.^{5,6} Variable-temperature control over the temperature range 4–300 K was achieved with an Air Products liquid-helium-transfer refrigerator, Model LTD110. For the photolyses, an Oriel Model 6240 arc lamp with a 200-W Hg lamp was used. In some of the experiments, the starting materials were condensed at -196 °C into the tip of the ESR tube and were irradiated for 10–30 min while inserted in a liquid-nitrogen-filled unsilvered Dewar. The ESR tube was then quickly transferred to the precooled ESR spectrometer. In other experiments, the sample tubes were irradiated at various temperatures inside the ESR cavity.

Results and Discussion

UV photolysis of both the NF₃-F₂-AsF₅ and the NF₃-F₂-BF₃ systems produced an intensely violet species which exhibited the ESR signal shown in Figure 1, traces A and B. Comparison with the previously published⁴ anisotropic spectrum of the NF₃[·] cation (trace C, Figure 1) establishes beyond doubt the presence of NF₃[·] in our samples. The spectra are assigned on the basis of anisotropic hyperfine coupling to three fluorine atoms ($I = 1/2$) and approximately isotropic hyperfine coupling to one nitrogen atom ($I = 1$). The g matrix is isotropic to within the line width. The spectra thus appear as a quartet of triplets as shown in Figure 1. The broader line widths observed in the spectra of UV-irradiated NF₃-F₂-AsF₅ and NF₃-F₂-BF₃ mixtures than in γ -irradiated NF₄SbF₆ may be the result of exchange or of dipolar interactions of materials on the surfaces of the solid components of the mixtures.

The observation of identical signals for both the BF₃- and the AsF₅-containing system proves that the signal must be due to a species not containing boron or arsenic. By carrying out irradiation experiments of the sample within the ESR cavity at -196 °C, it was shown that the signal strength increased during irradiation but did not decrease when the lamp was turned off. The thermal stability of the signal in the absence of UV radiation depended on the strength of the Lewis acid used. For the stronger Lewis acid AsF₅, the signal did not change significantly up to about -105 °C, whereas for BF₃ decomposition started at about -155 °C. When the sample tubes were warmed to ambient temperature, they contained white stable solids which were identified by Raman spectroscopy as NF₄AsF₆ and NF₄BF₄, respectively.^{1,7,8} Irradiation of all possible binary mixtures, i.e., NF₃-F₂, Lewis acid-F₂, and NF₃-Lewis acid, under comparable conditions did not produce any ESR signal attributable to NF₃[·].

A positive identification of the proposed AsF₆[·] or BF₄[·] radical intermediates was not possible in the above experi-

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