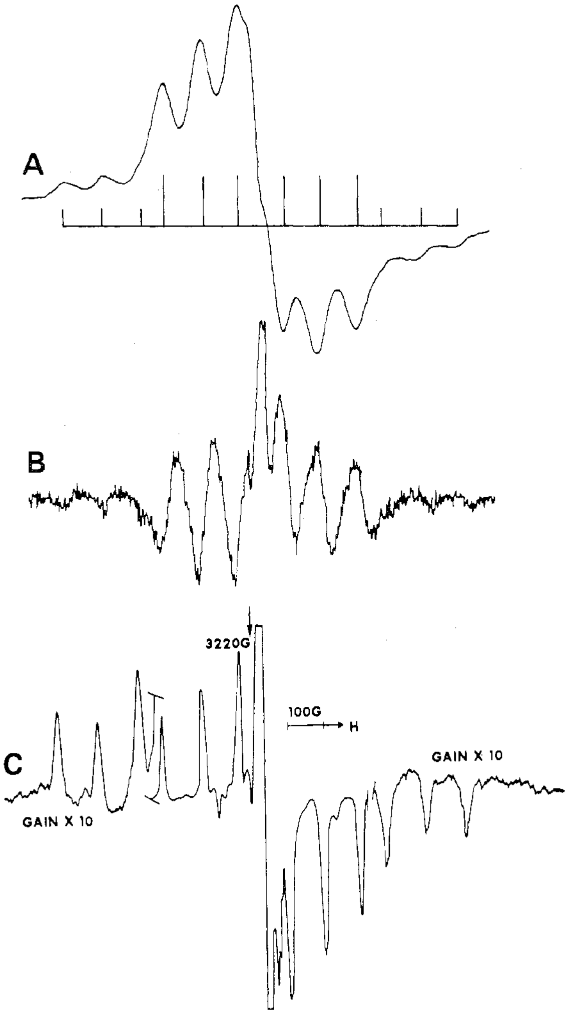

Figure 1. ESR spectra of the $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ radical cation obtained by UV photolysis of NF_3–F_2–BF_3 at −196 °C: trace A, first derivative; trace B, second derivative. For comparison, the known[4] first-derivative spectrum of $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ obtained by γ irradiation of polycrystalline $\mathrm{NF}_4\mathrm{SbF}_6$ at −196 °C is given as trace C.

ments. The observation of hyperfine splittings for the free $\mathrm{AsF}_6\cdot$ or $\mathrm{BF}_4\cdot$ radical at temperatures above several Kelvins is not likely because they would be in orbitally degenerate states which could cause rapid spin relaxation resulting in a strongly temperature-dependent line width. Furthermore, if we assume the existence of an $\mathrm{AsF}_6\cdot$ or $\mathrm{BF}_4\cdot$ radical in an ionic lattice, rapid electron exchange between the radicals and the corresponding anions is possible which would destroy hyperfine structure. The line width of the resulting signal would depend on the rate of exchange. Finally, in our experiments we were dealing with polymeric solid AsF_5 or BF_3 phases which on combination with a fluorine radical are not likely to result in an isolated $\mathrm{AsF}_6\cdot$ or $\mathrm{BF}_4\cdot$ radical. In our experiments, several ESR signals were observed in addition to $\dot{\mathrm{N}}\mathrm{F}_3{}^+$. However, in the absence of observable hyperfine structure we prefer not to make any assignments.

On the basis of our results, the following conclusions can be reached concerning the formation mechanism of $\mathrm{NF}_4{}^+$ salts. (i) The $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ radical cation is indeed an important intermediate. (ii) The requirement of UV activation and of both F_2 and a Lewis acid for the synthesis of $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ is in agreement with steps 1 and 2 of the given mechanism. (iii) The strength of the Lewis acid determines the thermal stability and lifetime of the intermediate $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ salt formed. This can account for the low-temperature conditions required for the synthesis of the $\mathrm{NF}_4{}^+$ salts of weaker Lewis acids. (iv) In the absence of UV irradiation, the $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ salts do not spontaneously react with the large excess of liquid F_2 present. This indicates that in the absence of an activation energy source the thermodynamically feasible[2] chain-propagation step $\dot{\mathrm{N}}\mathrm{F}_3{}^+\mathrm{AsF}_6{}^- + \mathrm{F}_2 \rightarrow \mathrm{NF}_4{}^+\mathrm{AsF}_6{}^- + \mathrm{F}\cdot$ does not play an important role. Possibly, the conversion of $\dot{\mathrm{N}}\mathrm{F}_3{}^+\mathrm{AsF}_6{}^-$ to $\mathrm{NF}_4{}^+\mathrm{AsF}_6{}^-$ may require $\mathrm{F}\cdot$ atoms according to

$$\dot{\mathrm{N}}\mathrm{F}_3{}^+\mathrm{AsF}_6{}^- + \mathrm{F}\cdot \rightarrow \mathrm{NF}_4{}^+\mathrm{AsF}_6{}^- \qquad (5)$$

Since the intermediate $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ salt is an ionic solid, its reaction with a fluorine atom might well be a heterogeneous diffusion-controlled reaction and step 5 might be the rate-determining step in the mechanism. It was shown that at temperatures above −196 °C, where a given $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ salt is still stable in the absence of light, UV irradiation causes a rapid decay of the $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ ESR signal. However, it was not possible to distinguish whether this decay was caused by photodecomposition of the intermediate $\dot{\mathrm{N}}\mathrm{F}_3{}^+$ salt or by the reaction of the latter with the generated F atoms according to step 5.

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Registry No. $\dot{\mathrm{N}}\mathrm{F}_3{}^+$, 54384-83-7; $\mathrm{NF}_4\mathrm{AsF}_6$, 16871-75-3; $\mathrm{NF}_4\mathrm{BF}_4$, 15640-93-4.

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Attachment of 1,2-Dicarbadodecaborane(12) to Polystyrene. Catalysis by a Polymer-Bound Rhodium Complex

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Paxon and Hawthorne[1] reported the preparation of hydridorhodium carboranes and their use as homogeneous hydrogenation and isomerization catalysts. We obtained similar results for a hydridorhodium thiaborane.[2] The attachment of homogeneous rhodium catalysts to polystyrene, their reactions, and their advantages have been studied by Grubbs[3] Collman,[4] and Pittman[5] and their co-workers. Although we have been unable to devise a convenient means to attach a thiaborane to polystyrene, we report here a scheme for the attachment of carborane to polystyrene and its conversion to a polymer-bound rhodium complex which functions as a hydrogenation catalyst.[1]

Experimental Section

Materials and Procedures. The 20% cross-linked macroreticular polystyrene–divinylbenzene copolymer (600 Å pore) was a gift from Dow Chemical Co. The beads were chloromethylated according to the procedure of Brubaker and Grubbs[6] and analyzed for 1.1 mmol of CH_2Cl/g of copolymer (beads). [*Hazardous Procedure. Chloromethyl ethyl ether is a carcinogen.* All procedures involving chloromethyl ethyl ether should be carried out in a system which will contain the substance. Here it was handled in a glovebox placed in a fume hood. The glovebox was maintained under a partial vacuum with an aspirator which drew the exhaust gases through two scrubbers containing 20% NaOH and 6 N H_2SO_4, respectively.] Organolithium reagents were obtained from Alfa. Solvents were transferred by syringe or distilled in vacuo from appropriate drying agents: benzene (Vitride), tetrahydrofuran (lithium aluminum hydride), piperidine (KOH), and ethanol (magnesium). Carborane was obtained from Columbia Chemical and sublimed prior to use.

Air-sensitive materials were handled in a nitrogen-filled glovebox or in Schlenk-type vessels.

Infrared spectra were recorded as KBr disks on a Perkin-Elmer 457. Analyses were performed by Spang Microanalytic Lab, Ann Arbor, Mich., or Galbraith Labs, Knoxville, Tenn.

Carborane-Substituted Copolymer. In a typical preparation 30 g of beads (1.1 mmol of CH_2Cl/g) and 7.5 g of 1,2-$C_2B_{10}H_{12}$ were placed in a 250-mL, three-necked flask fitted with a condenser. Benzene (100 mL) was distilled in, the mixture cooled to 0 °C, and 32 mL (2.0 M in hexane) of *n*-BuLi added by syringe. The mixture was brought to room temperature and stirred for 3–8 days. The excess $Li^+C_2B_{10}H_{11}^-$, LiCl–benzene slurry was then removed by syringe. The beads were then washed with three 50-mL portions of absolute methanol, placed in an extraction thimble, and washed with ethanol for 2 days in a Soxhlet extractor. They were dried at room temperature in vacuo for 2 days. A typical analysis showed 0.8 mmol of $C_2B_{10}H_{12}$/g of polystyrene. The Cl analysis indicated 0.1 mmol of Cl/g of beads after reaction.

Degradation of Polymer-Bound Carborane. Typically, 1.0 g of beads with bound $C_2B_{10}H_{12}$ (0.8 mmol/g) was placed in a flask with 25 mL of dry benzene and 1 mL (17 mmol) of piperidine added by syringe. The reaction mixture was then maintained at reflux for 40 h before removing the liquid with a syringe and washing the solid with five 5-mL portions of benzene. The beads were then successively extracted for 24 h with benzene and 18 h with ethanol before vacuum drying (12 h). The typical analysis gave 0.23 mmol of N/g and 7.7 mmol of B/g.

Preparation of Polymer-Bound $(Ph_3P)_2RhH(C_2B_9H_{11})$. In a typical case 600 mg of the copolymer with attached degraded carborane and 110 mg of $(PPh_3)_3RhCl$ were placed in a flask, 40 cm^3 of EtOH or 1:1 EtOH/C_6H_6 was added, and the mixture was maintained at reflux with magnetic stirring for 30 h. Then the solvent was decanted and the mixture of solids placed in a Soxhlet thimble for extraction with 1:1 C_6H_6/EtOH for 24 h to give yellow beads when wet. The vacuum dried beads (brown) contained typically 0.055 mmol of Rh/g (range 0.04–0.07) and 0.12 mmol of P/g.

Hydrogenation and Isomerization. The copolymer with bound rhodium (1.39 g) was placed in a high-pressure vessel with 20 cm^3 of benzene and 0.3 cm^3 of oct-1-ene. The vessel was pressurized with 100 atm of H_2 and shaken at 25 °C. The reaction was periodically interrupted to remove samples by syringe for GC analysis. The hydrogenation was 90% complete in 4 h at this pressure. The addition of more substrate did not appear to alter the catalyst activity (the turnover number is greater than 540). Hydrogenation at 1 atm and 25 °C is not significant even after 2 days, but 2–3% isomerization of the oct-1-ene to internal olefins was detected.

Results and Discussion

o-Carborane, 1,2-$C_2B_{10}H_{12}$, was readily attached to a rigid matrix by reaction of 1-Li-1,2-$C_2B_{10}H_{11}$ with the chloromethylated copolymer. As observed with a similar attachment

$$\textcircled{P}\text{-}CH_2Cl + Li^+C_2B_{10}H_{11}^- \xrightarrow[C_6H_6]{} \textcircled{P}\text{-}CH_2C_2B_{10}H_{11} + LiCl$$

of cyclopentadiene,[6] not all of the chloromethylated sites react. The IR spectrum of the product showed a B–H stretch, but more extensive analysis was precluded by the predominant polystyrene spectrum. Elemental analyses for B indicated that at least 75% of the chloromethylated sites were substituted to give 0.80 mmol of $C_2B_{10}H_{12}$/g of copolymer. There may be some carborane bound through two C atoms because the Cl analysis was lower than expected for 75% reaction.

Degradation of the polymer-bound carborane to bound $C_2B_9H_{12}^-$ was difficult in alcoholic KOH because the reagents do not diffuse into the polymer appreciably in alcohol. In benzene the copolymer swells more, and therefore, piperidine/benzene[7] proved to be a better means of obtaining polymer-bound 1,2-$C_2B_9H_{12}^-$. The extent of degradation was

$$\textcircled{P}\text{-}CH_2C_2B_{10}H_{11} + 3C_5H_{10}NH \xrightarrow[C_6H_6]{} \textcircled{P}\text{-}CH_2C_2B_9H_{11}^-[C_5H_{10}NH_2]^+ + (C_5H_{10}N)_2BH$$

determined from the N analysis since each polymer-bound $C_2B_9H_{12}^-$ must have a piperidinium ion associated with it. This analysis indicated that ca. 30% of the bound carborane was degraded.

After insertion of Rh with $(PPh_3)_3RhCl$ in ethanol/benzene analysis for P and Rh showed 30% of the bound $C_2B_9H_{12}^-$ moieties were metalated. On the basis of the elemental analysis and the known stoichiometry[1] of the corresponding reaction with free $C_2B_9H_{12}^-$ the Rh complex attached to the copolymer is written $\textcircled{P}$-$CH_2C_2B_9H_{10}Rh(H)[PPh_3]_2$. When the undegraded polymer-bound carborane was treated with $(PPh_3)_3RhCl$ in the same manner as the degraded material, the amount of Rh incorporated was insignificant.

The Rh complex bound to the rigid matrix of the 20% cross-linked copolymer does not hydrogenate alkenes as rapidly as the homogeneous counterpart at 1 atm of H_2; however, at 100 atm oct-1-ene is 90% reduced in 4 h.

Although not all of the copolymer-attached carborane was converted to bound $(PPh_3)_2RhH(C_2B_9H_{11})$ by the scheme used here, the catalyst does retain appreciable activity. A greater conversion and greater activity probably could be realized by employing a copolymer with less cross-linking which presumably would give the reactants greater accessibility to the carborane. The rhodium carborane catalyst has the attractive feature of having the Rh bound to the copolymer through a π-type interaction as opposed to the coordinate phosphine bond used by others.[3-5] Since a phosphine most probably dissociates to induce catalytic activity,[7] the likelihood of Rh leaching is greater for phosphine-bound catalysts. In the carborane-bound counterparts, when a phosphine dissociates, the Rh remains bound.

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Registry No. Polystyrene–divinylbenzene, 9003-70-7; 1-Li-1,2-$C_2B_{10}H_{11}$, 23841-96-5; $(PPh_3)_3RhCl$, 14694-95-2; $(PPh_3)_2RhH(C_2B_9H_{11})$, 53687-46-0.

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