$(MeCp)_2$ appear at 41 250 and 24 390 cm^{-1}, respectively.[29,49] Both $^2A_1$ and $^2E_2$ ground states lead to allowed transitions.[45]) The most probable vibrational mode for the progression of such an allowed transition is the a_{1g} symmetric Cp–Re–Cp stretching mode, ν'_4.

On irradiation into this absorption, a laser-excited fluorescence (LEF) spectrum is obtained, which allows us to identify the (0, 0) transition and ν''_4. This appears to be the first observation of a LEF spectrum of a metallocene, although emission from ferrocene has been detected previously.[28] The most remarkable feature of the LEF spectra is the occurrence of bands between 20 140 and 20 370 cm^{-1}, which are to short wavelength of the first absorption maximum and must therefore be assigned to $1' \rightarrow 0''$ transitions. Their presence and the absence of higher frequency bands implies that $v' > 2$ to $v' = 1$ relaxation is much faster than the fluorescence lifetime, τ_f, but that relaxation from $v' = 1$ to $v' = 0$ occurs on a time scale comparable to that of τ_f. Since vibrational relaxation of polyatomic molecules is usually rapid, this observation suggests that τ_f may be in the picosecond–nanosecond range. It follows from this assignment that the intense bands between 19 500–20 040 cm^{-1} are the $0' \rightarrow 1''$ and $0' \rightarrow 0''$ transitions. The $0' \rightarrow 0''$ transitions of the three progressions are then 20 026 (C), 19 919 (D), and 19 860 cm^{-1} (E), compared with a value of 200 80 cm^{-1} for the first absorption band. The small discrepancies are probably associated with the site selectivity of the laser and the variations in phonon coupling. The three progressions may represent three different matrix sites. The presence of the zero phonon lines in the LEF spectrum with 465.8-nm excitation gives a value of 330 ± 2 cm^{-1} for the $\nu'_4 = 1$ to $\nu'_4 = 0$ separation, compared with a value of 332 ± 5 cm^{-1} derived from the first two members of the absorption progressions. Using the average value for the $0' \rightarrow 0''$ and $0' \rightarrow 1''$ transitions from all three emission progressions, we obtain a value of $\nu''_4 = 327$ cm^{-1}, indicating a minimal change from ν'_4.

The information about ν_4 allows some conclusions concerning the other skeletal modes of $ReCp_2$. Surprisingly, $\nu_4(a_{1g})$ exceeds both antisymmetric modes (ν_{11} and ν_{21}) observed in the IR spectrum. In order to avoid an excessive interaction force constant,[50] it is most reasonable to assign the low-frequency IR spectrum as $\nu_{11}(a_{2u}) = 316$ cm^{-1} and $\nu_{21}(e_{1u}) = 289$ cm^{-1}. Comparisons with IR spectra of other metallocenes in matrices will be made elsewhere.[23]

Conclusions

The matrix studies on **1** demonstrate that this metal hydride exhibits a remarkable photochemistry with two competing pathways, hydrogen loss and ring slip with ligand gain. The first reaction leads to the new metallocene **4**, which shows structured visible-absorption and laser-excited emission spectra. The second leads in solid CO to a monocarbonyl that is the first intermediate en route to **3**. Photolysis of **2** leads to coordinatively unsaturated **7**, which may then be identified as one of the products of **3**. Competing with reversible cyclopentadiene loss to form **7**, the complex **3** undergoes one-step oxidative hydrogen transfer to **10** before losing CO in two steps to return to **1**. The monocarbonyl intermediate **5** is identical with the CO-gain product of **1**. Solution reactions of **1** lead to **3** with both photochemical and thermal activation, suggesting that **5** and **10** are also intermediates in solution. As in the matrix, photochemical loss of cyclopentadiene from **3** in CO-saturated solution leads to **2** via a dissociative mechanism. In future studies we will attempt to exploit the synthetic potential of the solution photochemistry of **1** and search for further solution intermediates.

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Registry No. **1**, 1271-32-5; **2**, 12079-73-1; **3**, 79471-01-5; **4**, 56261-86-0; **5**, 56261-86-0; **6**, 85283-44-9; **7**, 85283-45-0; **8**, 36543-62-1; **10**, 85283-46-1.

Supplementary Material Available: Table I, showing IR frequencies of the precursors **1**, **2**, **3**, and cyclopentadiene (2 pages). Ordering information is given on any current masthead page.

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(49) Gordon, K. R.; Warren, K. D. *Inorg. Chem.* **1978**, *17*, 987.

(50) This argument assumes a linear triatomic model for $ReCp_2$ (cf. ref 27).

Notes

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Synthesis and Studies of Poly(aminoborane), $(H_2NBH_2)_x$

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Even though a substance believed to be polymeric H_2NBH_2 was first reported over 40 years ago[3] and more information on its preparation and properties appeared over the following two decades,[4–7] a detailed characterization was lacking until Shore and co-workers demonstrated that two distinct types of materials exhibit the composition BNH_4.[8,9] Crystalline $(H_2NBH_2)_n$ (n = 2–5) cycloborazane molecules are formed in the reaction of $NaNH_2$ with $BH_2(NH_3)_2{}^+BH_4{}^-$ in liquid NH_3[8] while the reaction of $LiNH_2$ with B_2H_6 in $(C_2H_5)_2O$ affords nonunique amorphous materials[7,9] apparently containing 3-5 NH_2BH_2 units solvated in an undetermined manner. A direct synthesis of $(H_2NBH_2)_3$ from borazine was reported by Dahl and Schaeffer.[10]

Another reported preparation of poly(aminoborane) involved subjecting borazine vapor to a radio-frequency discharge, forming monomeric H_2NBH_2 (among numerous other prod-

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(1) University of Houston.

(2) Los Alamos National Laboratory.

(3) Schlesinger, H. I.; Ritter, D. M.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 2297.

(4) Wiberg, E.; Hertwig, K.; Bolz, A. *Z. Anorg. Allg. Chem.* **1948**, *256*, 177.

(5) Wiberg, E.; Boltz, A.; Buchheit, P. *Z. Anorg. Allg. Chem.* **1948**, *256*, 285.

(6) Schaeffer, G. W.; Basile, L. J. *J. Am. Chem. Soc.* **1955**, *77*, 331.

(7) Schaeffer, G. W.; Adams, M. D.; Koenig, F. J. *J. Am. Chem. Soc.* **1956**, *78*, 725.

(8) Böddeker, K. W.; Shore, S. G.; Bunting, R. K. *J. Am. Chem. Soc.* **1966**, *88*, 4396.

(9) Denton, D. L.; Johnson II, H. D.; Hickam, C. W., Jr.; Bunting, R. K.; Shore, S. G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1037.

(10) Dahl, G. H.; Schaeffer, R. *J. Am. Chem. Soc.* **1961**, *83*, 3032.

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Table I. Infrared Spectral Bands of Poly(aminoboranes)[a]

band,[b] cm⁻¹	intens	band,[c] cm⁻¹	intens	band,[d] cm⁻¹	intens
3300	m, s	3280	m, s	3320–3220	br
2340	m, s	2380	m, br	2380–2280	br
2300	w, sh				
2230	w, sh				
1600	w, br	1560	m, s	1575	
1380	m, s	1390	w, br	1405	
1160	m, s	1180	m, br		
1040	m, br	1090, 1060	w, br		
		970	w, br		
850	vw, br	840	m, br		
780	vw				
725	vw, br				

[a] Recorded on an NaCl plate with a Perkin-Elmer Model 457 infrared spectrophotometer. [b] This work. [c] Band positions and intensities estimated from spectra reproduction in ref 11. [d] Reference 9.

ucts), which polymerized spontaneously between −196 and −155 °C.[11] The product, an "inert white solid", was believed to be $(H_2NBH_2)_x$ although only its infrared spectrum was reported. A subsequent report from the same laboratory[12] described the formation of, presumably, the same product by the vapor-phase pyrolysis of $H_3N{\cdot}BH_3$, but no experimental details of the preparation were given. The TGA and DTA curves of the product were presented, but an attempted molecular mass measurement failed because of low solubility, and no elemental analyses were reported.

We wish to report an improved synthesis and additional characterization of a crystalline poly(aminoborane) that may be identidcal with the "inert white solid" reported earlier.[12]

Experimental Section

Commercial ammonia–borane (Callery) was sublimed before use. Samples used to make polymeric H_2NBH_2 had a melting range of 115–116 °C. In the preparation of the polymer, measured amounts (0.02–0.10 g) of $H_3N{\cdot}BH_3$ were placed in the bottom section of a commercial glass vacuum sublimer that had been modified by the addition of a 1 in. (diameter) × 6 in. test tube to the bottom of the apparatus directly below the cold finger. The apparatus was evacuated to 1×10^{-3} torr or less and back-filled with dry nitrogen to a pressure of 2–3 torr. The nitrogen was necessary to prevent rapid sublimation of $H_3N{\cdot}BH_3$ and facilitate its thermal decomposition.

To begin the decomposition, the sublimer was closed and the tip containing $H_3N{\cdot}BH_3$ immersed in a stirred oil bath at 130–140 °C. Liquid nitrogen was placed in the cold finger of the sublimer as heating was begun. Within 60–90 s, a rapid frothing decomposition of the fused $H_3N{\cdot}BH_3$ commenced, releasing noncondensible gas, presumably H_2, and depositing a white coating on the cold finger. In some runs an NaCl plate was attached to the cold finger with which the infrared spectral bands of the coating were recorded (Table I).

The white solid product was allowed to form for up to 5 min, during which time hydrogen was pumped away periodically, and then the heating bath was removed and the closed sublimer allowed to equilibrate thermally. The product was collected by opening the sublimer in air and scraping the solid off the cold finger. The white solid was not apparently air sensitive or hygroscopic. A typical yield was 24.2 mg from 84.8 mg of $H_3N{\cdot}BH_3$. The crystallinity of the solid is demonstrated by the *d* spacings in its X-ray powder pattern (Table II).

The solid exhibited very low solubility in common organic solvents and in water but hydrolyzed in aqueous acid. Attempts to determine its molecular weight cryoscopically in dimethyl sulfoxide and in tetramethylene sulfone gave inconsistent results owing probably to low solubility. A solution of 17 mg of the product in 10 mL of dry dimethyl sulfoxide exhibited a very broad unsymmetrical triplet in its ^{11}B FT NMR spectrum with peaks visible at δ −45.9, −50.1, and −54 (referenced to $BF_3{\cdot}O(C_2H_5)_2$).

Table II. X-ray Powder Diffraction Data for Poly(aminoborane)[a]

d, Å	intens	*d*, Å	intens	*d*, Å	intens
8.66	vvw	2.62	w	1.90	w
5.59	vvw	2.20	m	1.36	vvw
3.76	vvs	1.99	w		

[a] Pattern obtained with use of a Debye-Scherrer camera using Cu Kα radiation. Intensities are visual estimates.

The hydrolyzable hydrogen content of the product was determined by hydrolysis with aqueous HCl at 120 °C for 2 weeks[13] followed by measurement of the hydrogen in a calibrated Toepler system.[6] The boron content was determined by Parr peroxide fusion followed by titration of the mannitol complex. Anal. Calcd for BNH_4: B, 37.6; H (hydridic) 7.00. Found: B, 37.9; H, 6.97.

The physical characteristics of the product were investigated by attaching a polystyrene film to the cold finger onto which the solid was deposited. The resulting bilayer was mounted on a copper screen and carefully positioned on the surface of toluene in a Petri dish. After dissolution of the polystyrene, the product remained on the screen in the form of fragments of a brittle opaque film. Segments as large as about 10 mm square were isolated, but the film ruptured easily and tended to curl.

Results and Discussion

The thermal decomposition of ammonia–borane is a complex process, the products of which markedly depend on the conditions employed.[14] When the solid is heated above its melting temperature (115–116 °C), a rapid frothing hydrogen evolution begins immediately, eventually leaving an oily, intractable residue. Traces of diborane(6) and borazine are produced, and a white solid condenses in cool regions of the pyrolysis vessel. According to its infrared spectrum, the latter contains some (sublimed) $H_3N{\cdot}BH_3$ along with at least one other compound. A report[12] that vapor-phase pyrolysis of $H_3N{\cdot}BH_3$ produces poly(aminoborane) led us to examine the solid pyrolysis reaction further in seeking more convenient means to obtain pure $(H_2NBH_2)_x$.

An apparatus was designed with a pyrolysis tube attached to a commerical sublimer, which permitted us to collect the desired product without $H_3N{\cdot}BH_3$ contamination. A few torricelli of N_2 pressure is maintained in the system to help initiate the decomposition after which volatiles are pumped over the cold finger held near −196 °C. The white solid condensate was then allowed to warm slowly to ambient temperature under a dynamic vacuum before isolation. Typical conversion yields of about 30% were obtained.

An earlier investigation[11] of H_2NBH_2, prepared from borazine, indicated that a polymerization of that species resulted when the monomer was condensed at −196 °C and simply allowed to warm to −155 °C (eq 1). Thus, we presume that

$$xH_2NBH_2 \rightarrow (H_2NBH_2)_x \qquad (1)$$

some free H_2NBH_2 is released in the pyrolysis reaction and the white product obtained in our study is the same as that reported earlier.[11] That product was not convincingly characterized, however, and therefore a more thorough characterization was undertaken.

Elemental analyses confirmed the empirical formula as BNH_4, but our attempts to determine the molecular mass by cryoscopic means gave inconsistent results perhaps owing to the very low solubility of the poly(aminoborane) in appropriate solvents.[15] All the major bands in the infrared spectrum of our product match bands in the spectrum of $(H_2NBH_2)_x$ reported earlier (Table I). Its ^{11}B FT NMR spectrum in dilute dimethyl sulfoxide solution consists of a very broad triplet (δ

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[11] Kwon, C. T.; McGee, H. A. Jr. *Inorg. Chem.* **1970**, *9*, 2458.

[12] Pusatcioglu, S. Y.; McGee, H. A., Jr.; Fricke, A. L.; Hassler, J. C. *J. App. Polym. Sci.* **1977**, *21*, 1561.

[13] Shore, S. G.; Hickam, C. W. *Inorg. Chem.* **1963**, *2*, 638.

[14] Hu, M. G.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1978**, *23*, 249.

[15] Earlier investigators[12] experienced the same problem when attempting to use light scattering to determine the molecular weight of $(H_2NBH_2)_x$.

$\sim$-50, $J \cong 130$ Hz). While the general appearance of the spectrum is consistent with BH_2 groups in a polymeric structure, the chemical shift is at higher field than that of any other comparable species known to us. For comparison, the ^{11}B resonance of the cyclic $(H_2BNH_2)_3$ occurs at δ -11.[8,16]

The X-ray powder diffraction pattern of our $(H_2NBH_2)_x$ product (Table II) confirms its crystallinity, but the pattern clearly does not match those reported for the cyclic $(H_2NBH_2)_x$ (x = 2-5) oligomers.[8,13] The most intense band (3.76 Å) is similar to intense bands from 3.71 to 3.93 Å which appear in the patterns of the cyclic oligomers. Thus, the new product is distinct from both the known amorphous and crystalline forms of poly(aminoborane). The very low solubility of the product is consistent with either a cyclic or a linear polymer of relatively high molecular weight.[8] The evidence currently available does not permit a clear choice between these possibilities.

Some observations of the physical characteristics of the poly(aminoborane) were carried out by forming the substance on a polystyrene film and then dissolving the latter in toluene. The thin pieces of material thus formed were quite brittle and seemed to lack characteristics expected for high polymers.

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Registry No. $H_3N{\cdot}BH_3$, 13774-81-7; $(H_2NBH_2)_n$, 42208-67-3.

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(16) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1963**, *85*, 3592.

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Novel Iron Tetracarbonyl Fluorophosphine Complexes

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Fluorophosphine derivatives of iron carbonyl have been known for a number of years and have been prepared by several methods: direct substitution into iron pentacarbonyl,[1] cleavage of diiron enneacarbonyl by a fluorophosphine or reaction of a coordinated fluorophosphine with HCl or a nucleophile, which yielded a number of iron tetracarbonyl difluorophosphine derivatives containing a halogen or pseudohalogen on the phosphorus.[2] Interest in these compounds arises because of the possibility of fluxionality of the product. Clark showed that $(CO)_4FePF_3$ exists as a mixture of the axially and equatorially substituted isomers by infrared spectroscopy, although he was not able to confirm their presence by low-temperature NMR experiments nor was he able to separate them by chromatography. He concluded that the complex was fluxional. This behavior was also found for the other halofluorophosphine and pseudohalofluorophosphine complexes, $(CO)_4FeL$, where L = F_2PCl, $FPCl_2$, F_2PN_3, F_2PNCS, and $FP(NCS)_2$.[2]

On the other hand, if methoxy, dialkylamino, or phenyl groups are substituted for fluorine in the fluorophosphine complex $(CO)_4FeL$, where L = F_2POCH_3, $FP(OCH_3)_2$, $P(OCH_3)_3$,[3] $[(CH_3)_2N]_2PF$, $(CH_3)NCH_2CH_2N(CH_3)PF$,[4] $PhPF_2$,[2] and PPh_3,[5] only the axial isomers are observed.

While steric interactions are probably a factor in determining which isomer is formed under some circumstances, they are obviously not important here: trimethyl phosphite with a cone angle of 107° and triphenylphosphine with the larger cone angle of 145° both give the axial isomer whereas PF_3 with a cone angle of 104°[6] gives a mixture of the axial and equatorial isomers. Large cone angles would favor the formation of the equatorial isomer. Thus electronic effects must predominate in these cases. It was, therefore, of interest to prepare iron tetracarbonyl fluorophosphine complexes in which a group that was both bulky and highly electronegative had been substituted for fluorine on the phosphorus. Since $F_2P[OC(CF_3)_2CN]$ had been reported,[7] it was thought that this ligand would fill these requirements. In addition the related ligands $FP[OC(CF_3)_2CN]_2$ and $P[OC(CF_3)_2CN]_3$ were synthesized and used in the preparation of the series of iron tetracarbonyl complexes $(CO)_4FeF_{3-x}P[OC(CF_3)_2CN]_x$ (x = 1, 2, and 3).

Experimental Section

General Methods. A standard Pyrex vacuum system was used for the transfer of volatile materials. Other manipulations of products were carried out under a nitrogen atmosphere. Purification was obtained either through trap to trap fractionation or by distillation with a variety of short-path stills or a Holzmann column.[8] Mercury manometers were covered with Kel F-10 oil. The compounds were prepared in 125-mL heavy-wall Pyrex pressure reactors fitted with Fischer-Porter Teflon valves (pressures were generally below 4 atm). All solid reactants were dried for 2 h on a vacuum line before volatile reactants were added. Since most compounds are moisture and oxygen sensitive, they were handled under vacuum or under a nitrogen atmosphere after preparation.

Materials. All the starting materials were prepared by literature methods; (i.e. $NaOC(CF_3)_2CN$,[7] $Fe_2(CO)_9$, F_2PCl, and $FPCl_2$,[7] $Fe(CO)_4PF_2Cl$ and $Fe(CO)_4PFCl_2$,[2] and $F_2POC(CF_3)_2CN$[7]). Hexafluoroacetone and iron pentacarbonyl were obtained from commercial sources and used without further purification.

Spectral and Analytical Characterization. NMR spectra were recorded on Hitachi Perkin-Elmer R-20 ($Cl_3C^{19}F$ as an internal standard) and Varian HR-100 ($^{31}P_4O_6$ as an external standard) instruments. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 instrument. Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer and calibrated with polystyrene. Analyses were performed at the University of Georgia, Meade Microanalytical Labs, Amherst, MA, and Galbraith Labs, Knoxville, TN.

Preparation of Bis(2-cyanohexafluoroisopropoxy)fluorophosphine, $FP[OC(CF_3)_2CN]_2$. A 4.30-g (0.020-mol) sample of the sodium cyanohydrin salt was placed in a pressure reactor. Pentane, 20.0 mL, and 1.21 g (0.010 mol) of dichlorofluorophosphine were condensed into the reactor. After the reaction mixture was warmed to 25 °C, it was stirred for 6 h. The excess $FPCl_2$ was removed under vacuum, and the residue was extracted with 50 mL of pentane. After the solution was filtered through filter aid, the filtrate was fractionated through traps maintained at -24, -78, and -196 °C. The product was retained in the -24 °C trap. Further purification was accomplished by distillation with a Holzmann column.

Preparation of Tris(2-cyanohexafluoroisopropyl) Phosphite, $P[OC(CF_3)_2CN]_3$. A 6.45-g (0.030-mol) sample of $NaOC(CF_3)_2CN$ was placed in a 300-ml round-bottom flask equipped with a magentic stirring bar. After the flask was flushed with dry nitrogen, 45 mL of pentane and 1.37 g (0.010 mol) of freshly distilled phosphorus trichloride were added. After the mixture was stirred for 6 h, the reaction solution was filtered and the filtrate was concentrated to about 10 mL in vacuo. After fractionation through traps maintained at -24, -78, and -196 °C, the product was obtained in the -24 °C trap.

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(1) R. J. Clark, *Inorg. Chem.*, **8**, 1395 (1969).

(2) W. M. Douglas and J. K. Ruff, *J. Chem. Soc. A*, 3558 (1971).

(3) C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969).

(4) R. G. Montemayor et al., *J. Am. Chem. Soc.*, **100**, 2231 (1978).

(5) P. E. Riley and R. E. Davis, *Inorg. Chem.*, **19**, 159 (1980).

(6) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

(7) M. Lustig, *Inorg. Chem.*, **10**, 2054 (1968).

(8) C. W. Gould, G. Holzman, and C. Nieman, *Anal. Chem.*, **20**, 361 (1948).

0020-1669/83/1322-1686$01.50/0