(1971); A. H. Norbury and A. I. P. Sinha, *Inorg. Nucl. Chem. Lett.*, **4**, 617 (1968).
(13) A. L. Crumbliss and P. L. Gaus, *Inorg. Nucl. Chem. Lett.*, **10**, 485 (1974), and references therein.
(14) A. V. Ablov and G. P. Syrtsova, *Russ. J. Inorg. Chem. (Engl. Trans.)*, **10**, 1079 (1965).
(15) A sample of Co(dmgH)$_2$(SCN)(py) will undergo a solid-state isomerization over a period of a few months to give Co(dmgH)$_2$(NCS)(py).[16]
(16) R. L. Hassel and J. L. Burmeister, *Chem. Commun.*, 568 (1971).

Contribution from the Department of Chemistry,
P. M. Gross Chemical Laboratory, Duke University, Durham,
North Carolina 27706

Carbon-13 Nuclear Magnetic Resonance Spectra of Cyanocobaloximes Containing Carbon-13-Labeled Cyanide

Paul L. Gaus and Alvin L. Crumbliss*

Received September 9, 1975 AIC50668G

We wish to report on the ^{13}C NMR spectra of the ^{13}C-labeled cyanide ligand in selected cyanocobaloxime and cyano-bridged dicobaloxime complexes listed in Tables I and II.[1] These results bear a close relationship to those reported by Doddrell et al.[2] and Needham[3] et al. for the cyano- and dicyanocobalamins and -cobinamides. They are also of immediate interst due to the techniques employed in obtaining the data of Tables I and II.

Methods and Results

The compounds listed in Tables I and II were prepared according to published procedures[4–6] using 90% ^{13}C-enriched K^{13}CN (Merk Sharp and Dohme, Ltd.). Samples used in this study were characterized by elemental analysis and infrared and ^{1}H NMR spectra.

The data of Tables I and II were obtained at 298 K on a Bruker HFX-10 spectrometer (22.6 MHz) equipped with a Nicolet NIC-80 data processor, by using a pulse-wait Fourier transform method. Magnetic field stabilization was provided by locking on the ^{19}F signal from a 3-mm coaxial insert of hexafluorobenzene in 10-mm sample tubes. Chemical shifts were measured by reference to the center resonance of DMSO and then converted to values relative to TMS. Positive numbers indicate a chemical shift downfield from TMS.

The ^{13}C NMR spectra were obtained according to the methods described below on saturated solutions (ca. 10^{-2}–10^{-4} M) of the monomeric cyanocobaloximes in DMSO-d_6. The spectra of the cyano-bridged dicobaloximes RCo(dmgH)$_2$–NC–Co(dmgH)$_2$B (R = CH$_3$, CF$_3$; B = py, pip) and RCo(dmgH)$_2$–CN–Co(dmgH)$_2$R' (R, R' = CH$_3$, C$_2$H$_5$) were obtained by adding an excess of the complex Co(dmgH)$_2$(R)(H$_2$O)[7] to solutions containing the appropriate monomeric cyanocobaloximes Co(dmgH)$_2$(CN)(B) (10^{-3} M) (see Table I) and [AsPh$_4$][Co(dmgH)$_2$(R)(CN)] (10^{-2} M) (see Table II).

The generally low solubility of the cyanocobaloximes in DMSO necessitated the accumulation of up to 60000 spectra per sample, prior to Fourier transformation. It was the buildup of the DMSO signal which often placed an upper limit on the number of spectral scans obtained for a particular sample. This problem was overcome by obtaining spectra without proton decoupling. This prevented a nuclear Overhauser enhancement of the signals due to carbons bound to protons and resulted in a decrease in the intensity of the DMSO carbon resonance relative to that of the cyanide carbon, as compared with the same spectrum obtained with broad-band proton decoupling. Assignment of the coordinated cyanide resonance, in addition to observing an increase in intensity upon using compounds synthesized from 90%-enriched ^{13}C cyanide, was made by identifying that resonance which did not suffer a diminution in intensity or a change in multiplicity in the absence of proton decoupling. When proton decoupling was used, resonances for ligands other than cyanide (such as those due to the dimethylglyoximato ligands) were observed. These data are comparable to those reported previously for dimethylglyoxime bound to cobalt(III).[8]

Table I. ^{13}C NMR Spectra of the Cyanide Ligand in Inert Cyanocobaloximes^a

Compd	Line width,^{b} Hz	δ-(*CN,)^c ppm
[Co(dmgH)$_2$(SCN)(*CN)]$^-$ ^{d}	95	118.2
Co(dmgH)$_2$(*CN)(py-3-Cl)	65	114.7
Co(dmgH)$_2$(*CN)(py)	65	115.3
Co(dmgH)$_2$(*CN)(pip)	65	118.3
CH$_3$Co(dmgH)$_2$-NC*-Co(dmgH)$_2$py^e	35	122.4
CH$_3$Co(dmgH)$_2$-NC*-Co(dmgH)$_2$pip^e	25	125.4
CF$_3$Co(dmgH)$_2$-NC*-Co(dmgH)$_2$pip^e	30	128.6
Na*CN	10	166.6

^{a} Solvent DMSO-d_6. ^{b} Peak width at half-peak-height. ^{c} Relative to TMS. ^{d} Tetraphenylarsonium salt. ^{e} Ref 16.

Table II. ^{13}C NMR Spectra of the Cyanide Ligand in Labile Cyanocobaloximes^a

Compd	Line width,^{b} Hz	δ(*CN),^{c} ppm
[Co(dmgH)$_2$(CH$_3$)(*CN)]$^-$	10	146.9
[Co(dmgH)$_2$(C$_2$H$_5$)(*CN)]$^-$	10	147.9
[CH$_3$Co(dmgH)$_2$-NC*-Co(dmgH)$_2$-CH$_3$]$^-$	10	156.0
[CH$_3$Co(dmgH)$_2$-NC*-Co(dmgH)$_2$-C$_2$H$_5$]$^-$	10	156.2^d
[C$_2$H$_5$Co(dmgH)$_2$-NC*-Co(dmgH)$_2$-CH$_3$]$^-$	10	157.0^d
Na*CN	10	166.6

^{a} As the tetraphenylarsonium salt in DMSO-d_6. ^{b} Peak width at half-peak-height. ^{c} Relative to TMS. ^{d} The facile isomerization noted in ref 5 implies that this resonance may be due to an equilibrium mixture of cyano-bridged isomers.

A second factor which facilitated the observation of the cyanide carbon resonances in these dilute solutions was the observation that the carbon nuclei (especially that of the cyanide ligand) were efficiently relaxed as a result of the interaction with the quadrupole moment on cobalt. This allowed the use of a full 90° pulse width, with a high repetition rate which was limited only by the acquisition time necessary for obtaining a 5000-Hz spectrum width. This resulted in an effective enhancement of the cyanide carbon resonance relative to the resonance due to DMSO (which was less efficiently relaxed), and it allowed the accumulation of more spectra prior to computer memory overflow due to the DMSO signal than would have been possible using, for example, a 30° pulse width.

The dipole–quadrupole interaction also accounts for the fact that all cyanide carbon resonances listed in Tables I and II were observed as single lines; i.e., no spin–spin coupling was observed between ^{59}Co($I = {}^7/_2$) and ^{13}C($I = {}^1/_2$). The rapid nuclear relaxation caused by this dipole–quadrupole interaction is responsible (through $1/T_2$, the spin–spin relaxation rate[9]) for the broadness of the signals listed in Tables I and II.

This latter line width effect is further modulated by chemical exchange of the cyanide between the tightly coordinated environment and the cyanide ion, free in solution. The compounds of Table I are known to be kinetically inert[4] toward substitution, and as such, these complexes represent the limit of slow chemical exchange with respect to the cyanide ligand. In contrast, the alkylcobaloximes of Table II are known to be labile[10] toward substitution reactions, and as such, these complexes may approach the limit of fast exchange with respect to the cyanide ligand. This difference between the two types of complexes listed separately in Tables I and II may be responsible for the fact that the cyanide carbon resonances were observed in two distinct chemical shift ranges, with differing line widths, the more labile complexes of Table II behaving more like ionic cyanide than the inert complexes of Table I. Within each type of complex, however, the trends in the chemical shifts of the cyanide carbon can be given the same interpretation.

As can be seen from the data of Tables I and II, the coordination of the cyanide anion to form the complexes $\mathrm{Co(dmgH)_2(CN)(B)}$ (B = py, py-3-Cl, pip), $\mathrm{[AsPh_4][Co(dmgH)_2(CN)(SCN)]}$, and $\mathrm{[AsPh_4][Co(dmgH)_2(R)(CN)]}$ (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$) results in an upfield shift (less positive chemical shift) of the cyanide resonance, relative to ionic cyanide. Within the two types of complexes reported here, the chemical shifts of the cyanide carbon resonances parallel changes in the σ-electron donor strength of the trans ligands R and B. The cyanide carbon resonance is found at the highest field (least positive chemical shift) for the weakest trans donor (B = py-3-Cl) in the complexes $\mathrm{Co(dmgH)_2(CN)(B)}$ and the weakest trans donor (R = $\mathrm{CH_3}$) in the complexes $\mathrm{[AsPh_4][Co(dmgH)_2(R)(CN)]}$. Similar observations can be made for the cyano-bridged complexes $\mathrm{RCo(dmgH)_2{-}NC{-}Co(dmgH)_2B}$ (R = $\mathrm{CH_3}$, $\mathrm{CF_3}$; B = py, pip) and $\mathrm{[AsPh_4][RCo(dmgH)_2{-}NC{-}Co(dmgH)_2R']}$ (R, R′ = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$); the weakest donor ligand trans to the carbon bonded cyanide yields the highest field carbon resonance.

Discussion

Although the cobalt(III) ion may have an appreciable anisotropic influence on the observed ^{13}C chemical shifts for coordinated cyanide, the chemical shifts in Tables I and II can be shown to parallel cyanide carbon electronegativity changes predicted by molecular orbital calculations.[11] These calculations[11] predict that one direct consequence of the coordination of the cyanide anion to non-π-bonding Lewis acids[12] is an increase in the electronegativity of the CN group carbon. This is reflected by a polarization of electron density in the π_x and π_y cyanide molecular orbitals toward the carbon. Such a polarization of π-electron density in the cyanide ligand coincides with the increased shielding of the cyanide carbon upon forming the complexes $\mathrm{Co(dmgH)_2(CN)(B)}$ and $\mathrm{[AsPh_4][Co(dmgH)_2(R)(CN)]}$ from ionic cyanide. This electronegativity change also parallels the upfield trend in chemical shift for the complexes $\mathrm{Co(dmgH)_2(CN)(B)}$ when B is changed from pip to py to py-3-Cl, as shown in Table I. The weakest trans σ-electron donor (B = py-3-Cl) provides the strongest Lewis acid cobalt center for coordination by the cyanide, which in turn causes the greatest enhancement of the cyanide carbon electronegativity with concomitant polarization of the CN π-electron cloud. It is this complex (B = py-3-Cl) that exhibits the greatest shielding of the cyanide carbon within the series. Similar parallel trends are observed for the upfield chemical shift listed in Table II and the predicted polarization of the CN π-electron cloud upon substituting R = $\mathrm{CH_3}$ for R = $\mathrm{C_2H_5}$ in $\mathrm{[Co(dmgH)_2(R)(CN)]^-}$. These trends are opposite to those which would be expected if the chemical shift of the cyanide carbon resonance was determined by the degree of electron density placed at the cobalt by the ligands B or R. A similar effect has been observed for substituted metal carbonyls, in that electron-donating ligands cause a deshielding of the carbonyl carbon.[14] This does not require, however, that the origin of these trends in chemical shift be the same for the carbonyl complexes and the cyanocobaloximes reported here.

A similar but opposite polarization of the CN group π_x and π_y molecular orbitals is expected upon forming the cyano-bridged dicobaloximes in Tables I and II from the corresponding monocyanocobaloximes. Here, coordination of the nitrogen of the cyanide ligand in the complexes $\mathrm{Co(dmgH)_2(CN)(B)}$ and $\mathrm{[Co(dmgH)_2(R)(CN)]^-}$ to form the bridged complexes $\mathrm{RCo(dmgH)_2{-}NC{-}Co(dmgH)_2B}$ and $\mathrm{[RCo(dmgH)_2{-}CN{-}Co(dmgH)_2R']^-}$, respectively, should result in an increase in the CN group nitrogen atom electronegativity.[11] This would cause a polarization of the π-electron density away from the CN group carbon (relative to the corresponding terminal cyanocobaloxime). The cyano-bridged dicobaloximes exhibit ^{13}C cyanide resonances downfield from the corresponding terminal cyanocobaloxime. In addition, the weaker the σ-electron donor strength of the ligand R at the cobalt coordinated to the CN group nitrogen, the more should the CN group π-electron density be polarized away from the carbon. This coincides with the downfield trend in chemical shifts shown in Table I for the complexes $\mathrm{RCo(dmgH)_2{-}NC{-}Co(dmgH)_2pip}$ where the ligand with R = $\mathrm{CF_3}$ provides a less shielded CN carbon nucleus than that with R = $\mathrm{CH_3}$. The data of Table II also show this trend.

In conclusion, it should be noted that the results reported here are similar to those obtained for the cyanocobalamins and -cobinamides, for which the cobaloximes are often cited as models.[15] Data obtained by Needham et al.[2] in $\mathrm{D_2O}$ at 32 °C show cyanide ligand carbon chemical shifts for both isomers of cyanocobinamide at 109.2 and 110.3 ppm (relative to TMS) and for methylcyanocobinamide, dicyanocobinamide, and dicyanocobalamin at 161.6, 138.0, and 137.5 ppm (relative to TMS), respectively. As is reported in this work, the weaker σ-electron donor trans ligand produces a more shielded cyano carbon than the stronger σ-electron donor trans ligand (e.g., trans $\mathrm{H_2O}$ in cyanocobinamide vs. trans $\mathrm{CH_3}$ in methylcyanocobinamide; trans CN in dicyanocobinamide vs. trans $\mathrm{CH_3}$ in methylcyanocobinamide).

Acknowledgment. We wish to thank Dr. C. H. Lochmüller for helpful discussions. Financial support through a Frederick Gardner Cottrell grant from the Research Corp., the Duke University Research Council, and a Biomedical Sciences Support Grant administered by Duke University is gratefully acknowledged.

Registry No. $\mathrm{[Co(dmgH)_2(SCN)(*CN)]^-}$, 57774-47-7; $\mathrm{Co(dmgH)_2(*CN)(py\text{-}3\text{-}Cl)}$, 57821-05-3; $\mathrm{Co(dmgH)_2(*CN)(py)}$, 57774-64-8; $\mathrm{Co(dmgH)_2(*CN)(pip)}$, 57774-65-9; $\mathrm{CH_3Co(dmgH)_2{-}NC*{-}Co(dmgH)_2py}$, 57819-07-5; $\mathrm{CH_3Co(dmgH)_2{-}NC*{-}Co(dmgH)_2pip}$, 57819-08-6; $\mathrm{CF_3Co(dmgH)_2{-}NC*{-}Co(dmgH)_2pip}$, 57821-07-5; $\mathrm{[Co(dmgH)_2(CH_3)(*CN)]^-}$, 57774-60-4; $\mathrm{[Co(dmgH)_2(C_2H_5)(*CN)]^-}$, 57774-61-5; $\mathrm{[CH_3Co(dmgH)_2{-}NC*{-}Co(dmgH)_2CH_3]^-}$, 57819-06-4; $\mathrm{[CH_3Co(dmgH)_2{-}NC*{-}Co(dmgH)_2C_2H_5]^-}$, 57774-62-6; $\mathrm{[C_2H_5Co(dmgH)_2{-}NC*{-}Co(dmgH)_2CH_3]^-}$, 57774-63-7; ^{13}C, 14762-74-4.

References and Notes

(1) The term cobaloxime is used to denote complexes containing the bis(dimethylglyoximato)cobalt(III) moiety. All such complexes reported here are known to be in the trans configuration. Abbreviations: dmgH = dimethylglyoximato anion, $\mathrm{[CH_3C({=}NOH)C({=}NO)CH_3]^-}$; py = pyridine; py-3-Cl = 3-chloropyridine; pip = piperidine.

(2) D. Doddrell and A. Allerhand, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 1083 (1971).

(3) T. E. Needham, N. A. Matwiyoff, T. E. Walker, and H. P. C. Hogenkamp, *J. Am. Chem. Soc.*, **95**, 5019 (1973).

(4) A. L. Crumbliss and P. L. Gaus, *Inorg. Chem.*, preceding paper in this issue.

(5) D. Dodd and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, 1218 (1973).

(6) A. L. Crumbliss and P. L. Gaus, *Inorg. Nucl. Chem. Lett.*, **10**, 485 (1974).

(7) G. N. Schrauzer, *Inorg. Synth.*, **11**, 61 (1968).

(8) C. Bied-Charreton, B. Septe, and A. Gaudemer, *Org. Magn. Reson.*, **7**, 116 (1975).

(9) J. R. Lyenla and G. C. Levy, *Top. Carbon-13 NMR Spectrosc.*, **1**, 79 (1974).

(10) See for example ref 5 and L. M. Ludwick and T. L. Brown, *J. Am. Chem. Soc.*, **91**, 5188 (1969); A. L. Crumbliss and W. K. Wilmarth, *ibid.*, **92**, 2593 (1970); T. Sakurai, J. P. Fox, and L. L. Ingraham, *Inorg. Chem.*, **10**, 1105 (1971); K. L. Brown and R. G. Kallen, *J. Am. Chem. Soc.*, **94**, 1894 (1972).

(11) K. F. Purcell, *J. Am. Chem. Soc.*, **89**, 247, 6139 (1967); **91**, 3487 (1969).

(12) See ref 13 for a discussion of the lack of evidence to support metal to cyanide π bonding in cobalt(III) complexes.

(13) J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem.*, **12**, 375 (1969).

(14) See for example: L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974), and references therein; G. M. Border and L. J. Todd, *Inorg. Chem.*, **13**, 360 (1974).

(15) See for example: G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968), and references therein; H. A. O. Hill, *Inorg. Biochem.*, **2**, 1067 (1973), and references therein.

(16) Cyano bridge linkage isomer established as written: A. L. Crumbliss and P. L. Gaus, submitted for publication in *Inorg. Chem.*

Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

A Comparative Study of Methylamine Adducts of Triborane(7)

Alan R. Dodds and Goji Kodama*

Received September 18, 1975 AIC506957

Although the complete series of methylamine adducts of borane(3) has been known,[1] the corresponding series of triborane(7) adducts was not complete. Monomethylamine- and dimethylamine–triborane(7) were missing in the series. Therefore, the preparation of these two adducts was undertaken so that a comparative study of the complete series of compounds, $(CH_3)_nNH_{3-n}\cdot B_3H_7$ (n = 0–3), would become possible. The preparation and characterization of the two new adducts and observations on NMR spectra of the series of compounds are described in this paper.

Results and Discussion

Monomethylamine and dimethylamine adducts of triborane(7), $CH_3NH_2\cdot B_3H_7$ and $(CH_3)_2NH\cdot B_3H_7$, were prepared by a method similar to that reported for $NH_3\cdot B_3H_7$ preparation:[2] tetraborane(10), B_4H_{10}, was first converted to tetrahydrofuran–triborane(7) and a base-exchange reaction was then performed on the tetrahydrofuran adduct in various solvents

$$B_4H_{10} + THF \rightarrow THF\cdot B_3H_7 + {}^1/_2B_2H_6$$

$$THF\cdot B_3H_7 + \text{amine} \rightarrow \text{amine}\cdot B_3H_7 + THF$$

Like ammonia[3] and unlike trimethylamine,[4] neither monomethylamine nor dimethylamine produces the triborane adduct in its direct reaction with B_4H_{10}.[5] The two new adducts were characterized by elemental analysis and infrared, mass, and NMR spectra with reference to the known adducts, trimethylamine- and ammonia–triborane(7). Monomethylamine–triborane(7) is a colorless liquid at room temperature (25 °C) melting at a temperature around 20 °C. Dimethylamine–triborane(7) is a white solid which melts near 30 °C. Melting points of these compounds are lowered sharply by the presence of a small amount of impurity in the sample. These low melting points contrast with those of $NH_3\cdot B_3H_7$ (73–75 °C)[2] and $(CH_3)_3N\cdot B_3H_7$ (above 200 °C).[4] A similar contrast is observed for the series of methylamine adducts of borane(3): 112–114 (dec),[6] 56, 36, and 94 °C,[1] for $NH_3\cdot BH_3$, $CH_3NH_2\cdot BH_3$, $(CH_3)_2NH\cdot BH_3$, and $(CH_3)_3N\cdot BH_3$, respectively. The newly prepared adducts are stable in dry air and resistant to complete hydrolysis in 6 N HCl. These are comparable to the properties of $NH_3\cdot B_3H_7$[2] and $(CH_3)_3N\cdot B_3H_7$.[4]

Listed in Table I are the ^{11}B and ^1H NMR data obtained in this study for the four triborane(7) adducts. The results are, in general, in agreement with those previously reported for $NH_3\cdot B_3H_7$[7] and $(CH_3)_3N\cdot B_3H_7$[8] and with those expected for the other two methylamine adducts. However, this study, by virtue of complete coverage of the series of compounds, revealed new aspects of the spectral properties which are described below.

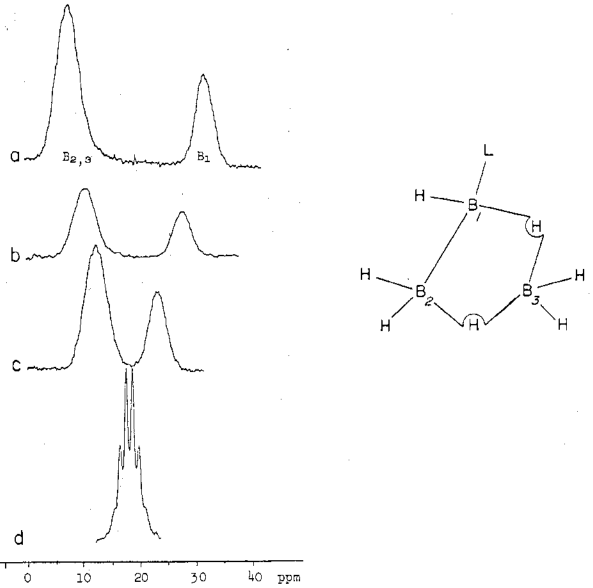

Figure 1. Structure and ^{11}B NMR spectra of methylamine–triboranes(7) in CH_2Cl_2 at 20 °C (32.1 MHz): (a) $NH_3\cdot B_3H_7$, (b) $CH_3NH_2\cdot B_3H_7$, (c) $(CH_3)_2NH\cdot B_3H_7$, (d) $(CH_3)_3N\cdot B_3H_7$. Structure is from the structure of $NH_3\cdot B_3H_7$ (C. E. Nordman and C. Reimann, *J. Am. Chem. Soc.*, **81**, 3538 (1959)); L = amine.

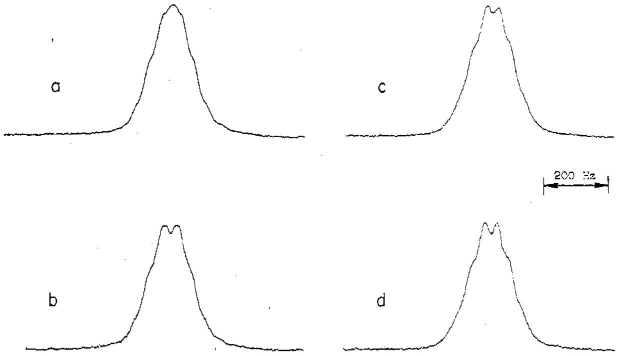

Figure 2. $B_{2,3}$ resonance peaks of $NH_3B_3H_7$ at 20 °C (32.1 MHz): (a) and (b) [CH_2Cl_2 solution], normal and $^{11}B_1$ irradiated spectra, respectively; (c) and (d) [$(C_2H_5)_2O$ solution], normal and $^{11}B_1$ irradiated spectra, respectively.

In going from $NH_3\cdot B_3H_7$ to $(CH_3)_3N\cdot B_3H_7$, the chemical shift for B_1 (amine-attached boron atom) decreases while the $B_{2,3}$ shift increases. (See Figure 1.) The downfield shift trend observed here for the signal of amine-attached boron is consistent with those observed for amine–boranes(3),[9a,c] μ-amino-diboranes(6),[9a] and cycloborazanes.[9b] Shown in Figure 2c is the $B_{2,3}$ resonance peak of $NH_3\cdot B_3H_7$ in diethyl ether solution. The shape of the peak is comparable to that reported previously.[7] A line shape simulation, assuming a Lorentzian curve for each of the component peaks of the multiplet and a value of 35 Hz for the peak separation, revealed that the shape of the multiplet peak is consistent with that of a 1:7:21:35:35:21:7:1 octet and is inconsistent with that of a 1:5:10:10:5:1 sextet. The model in which seven hydrogen atoms are migrating rapidly around the three boron atoms in the $NH_3B_3H_7$ molecule[7] is consistent with this spectrum. The $B_{2,3}$ peak of $NH_3B_3H_7$ in CH_2Cl_2 solution, however, has the appearance of an odd-number multiplet with a hump at the middle (Figure 2a). Upon irradiating the CH_2Cl_2 solution