the 2-CH$_3$bzimH complex but behaves bathochromically in the 80.0–100.0% DMF range for the dmapy and 5,6-CH$_3$bzimH complexes. The hypsochromic effect on the 2-CH$_3$bzimH complex in the 80.0–100.0% range follows the order CH$_3$CN (21, 5.3) >> Me$_2$SO (8, 2.0) > DMF (5, 1.3) $\gtrsim$ C$_2$H$_5$OH (4, 1.0) > CH$_3$OH (0, 0.0). Values in parentheses refer to the shifts at 80% solvent in nm and normalized shifts based on C$_2$H$_5$OH as a standard, respectively. Thus CH$_3$CN shifts 5.3 times more hypsochromically for a given enrichment in H$_2$O within the 80.0–100.0% solvent range, and a net shift of −21 nm is observed at 80.0% CH$_3$CN.

The outcome of these studies is that "pure solvents", which contain only the most minimal H$_2$O that cannot be removed by drying procedures, appear to provide data that are meaningful measurements of E_{LMCT} in these solvents. The presence of H$_2$O in larger abundance, in synthetic mixtures in the 80.0–100.0% solvent range, produces shifts of a few nanometers per percent solvent change. These data show the existence of preferential solvation of H$_2$O for all except the (CN)$_5$Fe(2-CH$_3$bzimH)$^{2-}$ complex. Since this complex is the only one to be sterically hindered in the vicinity of the pyrrole N–H and pyrrole lone-pair region, it is tempting to assign the effect of the hypsochromic shift to changes in solvation of the hindered NH and lone pair. However, further studies are necessary to confirm this conjecture. That the tabulated values of $\lambda_{\max}$ of the LMCT transition follow E_{T} and Z linearly with E_{LMCT} to within a maximum deviation of any slope of ±9.5% supports the conclusion that the "pure solvent" data are not plagued by artifacts introduced by preferential solvation of trace water. These studies lend further support to the assignment of the transitions observed for (CN)$_5$FeL^{2-} complexes (L = imidazoles, pyrazoles, and electron-releasing substituted pyridines) as LMCT transitions.[1] Although neutral complexes of the type Fe$^{\mathrm{II}}$(bpy)$_2$(CN)$_2$[11] M^0(bpy)(CO)$_4$ (M = Mo, W),[12,18] and M$^{\mathrm{II}}$(bpy)X$_2$ (M = Pt; X = halide ion)[13] have been shown previously to follow the Reichardt–Dimroth and Kosower scales for their solvatochromic behavior, the present study is the first to be carried out on anionic transition-metal complexes having LMCT excitations.

Experimental Section

Solvents. DMF, CH$_3$OH, and C$_2$H$_5$OH were J. T. Baker Spectral/Analytical grade. These solvents were distilled under N$_2$ and dried over molecular sieves for 1 week prior to preparation of solutions used to obtain spectral data. Purified Me$_2$SO, CH$_3$CN, and propylene carbonate were gifts from Professor J. Coetzee.[10] These solvents had been rigorously purified in Coetzee's laboratory by spinning-band distillations. Karl Fischer analysis estimated the H$_2$O content at less than 3 mM. Transfers to containers were carried out in a dry glovebox to avoid contamination with atmospheric moisture. H$_2$O was the department distilled and laboratory ion exchanged water.

Na$_2$[Fe(CN)$_5$L] Complexes. Preparations of the complexes were reported previously.[2,5,9c,14] Spectra were obtained by dissolving freshly weighed samples in an appropriate solvent. Spectra were obtained on a Varian-Cary 118C spectrophotometer at room temperature (ca. 22 °C) in quartz cells.

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Registry No. DMF, 68-12-2; PC, 108-32-7; H$_2$O, 7732-18-5; CH$_3$OH, 67-56-1; C$_2$H$_5$OH, 64-17-5; Me$_2$SO, 67-68-5; CH$_3$CN, 75-05-8; (CN)$_5$Fe(imH)$^{2-}$, 61332-60-3; (CN)$_5$Fe(bzimH)$^{2-}$, 91209-20-0; (CN)$_5$Fe(2-CH$_3$bzimH)$^{2-}$, 91209-21-1; (CN)$_5$Fe(5,6-CH$_3$bzimH)$^{2-}$, 91209-25-5; (CN)$_5$Fe(dmapy)$^{2-}$, 91209-30-2.

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Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706,
Department of Pure and Applied Chemistry,
Univeristy of Strathclyde, Glasgow G1 1XL, United Kingdom,
and Department of Chemistry, University of Edinburgh,
Edinburgh EH9 3JJ, United Kingdom

Solvent Effects on the ^{11}B and ^{1}H NMR Spectra of Decaborane(14), B$_{10}$H$_{14}$

Donald F. Gaines,*[1a] Caterina K. Nelson,[1a] Joan C. Kunz,[1a] John H. Morris,[1b] and David Reed[1c]

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In the past it has been commonly presumed that the ^{11}B NMR chemical shifts of boron hydrides (boranes) and their derivatives are for the most part independent of the nature of the solvent. While this may be true of many boranes, we have recently found that several of the ^{11}B resonances of decaborane(14), B$_{10}$H$_{14}$, exhibit substantial chemical shift differences as a function of the nature of the solvent. In addition we have recorded the resolved ^{11}B–^{11}B coupling in B$_{10}$H$_{14}$, obtained via line narrowing, and have observed that the nature of the solvent and the temperature influences the resolution of such fine structure. Solvent effects on the ^{1}H NMR chemical shifts of B$_{10}$H$_{14}$ are also illustrated.

Experimental Section

B$_{10}$H$_{14}$ was sublimed prior to use. Most solvents were used as received. C$_6$D$_6$ and C$_6$F$_6$ were dried over LiAlH$_4$ and distilled prior to use. THF was dried over potassium and distilled prior to use. All solutions were saturated in B$_{10}$H$_{14}$ unless specified otherwise and were contained in 5-mm o.d. thin-walled Pyrex NMR tubes.

The instruments used were a Bruker 270-MHz (86.6 MHz ^{11}B) NMR spectrometer, an IBM 270-MHz (86.6 MHz ^{11}B) NMR spectrometer, and a Bruker 360-MHz (115.5 MHz ^{11}B) NMR spectrometer. Line narrowing and data refinements were performed with each instrument's accompanying software.

Results and Discussion

Solvent–Chemical Shift Effects. Figure 1 shows the structure and atom numbering for B$_{10}$H$_{14}$. In the ^{11}B NMR spectra of B$_{10}$H$_{14}$, the most dramatic solvent effects are associated with the B(1,3) and B(6,9) resonances at the lowest field positions (Table I). The spectral appearances can be conveniently grouped into three categories on the basis of the solvent polarizabilities. The largest chemical shift differences, between the B(1,3) and B(6,9) resonances, occur in the least polarizable solvents such as butane and *n*-pentane. In addition, the fine structure associated with the B(6,9) resonance is most readily resolved in these solvents (vide infra). Somewhat more polarizable solvents such as benzene and dichloromethane give rise to intermediate shift differences, which in solvents having a permanent dipole such as acetone and acetonitrile the B(1,3) and B(6,9) resonances are coincident. These shift differences in the three classes of solvents are illustrated in Figure 2 for the solvents pentane, benzene-d_6, tetrahydrofuran, and acetonitrile-d_3. While the B(5,7,8,10) and B(2,4) resonances also shift as a function of solvent polarizability, as shown in Table I, these shifts are not as visually dramatic. The largest and most discontinuous shift is that of the B(6,9) resonance in the Lewis base solvents acetone, tetrahydrofuran, and acetonitrile. All three solvents give rise to B(6,9) resonance shifts of over 1.00 ppm to lower field, while the B(1,3) resonance shifts to higher field and is coincident with the B(6,9) resonance in acetone and acetonitrile. In THF the resonances are very nearly coincident, but a slight shoulder can be discerned on the high-field member of the doublet. The B(5,7,8,10) reso-

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[1] (a) University of Wisconsin—Madison. (b) University of Strathclyde. (c) University of Edinburgh.

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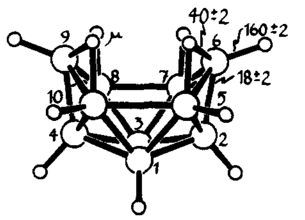

Figure 1. Structure and numbering of $B_{10}H_{14}$. Hydrogen positions take the number of the boron atom to which they are bonded. Bridging hydrogen atoms are denoted by μ. Measured coupling constants at the B(6,9) position (Hz): $J_{B(6)-H(6)} = 160 \pm 2$; $J_{B(6)-H(\mu)} = 40 \pm 2$; $J_{B(2)-B(6)} = 18 \pm 2$.

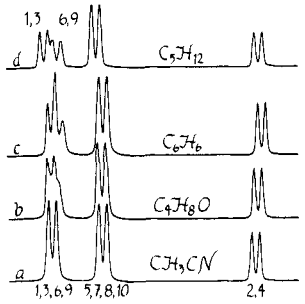

Figure 2. 86.6-MHz ^{11}B NMR of $B_{10}H_{14}$ in selected solvents: (a) acetonitrile; (b) tetrahydrofuran; (c) benzene; (d) *n*-pentane. All solutions are saturated in $B_{10}H_{14}$.

Table I. ^{11}B NMR Data (86.6 MHz) for $B_{10}H_{14}$

	atom positions			
solvent	B(1,3)	B(6,9)	B(5,7,8,10)	B(2,4)
n-butane	13.0[a] (151)[b]	10.0 (165)[b] [39][c] {18}[d]	0.96 (161)	−35.9 (160)
n-pentane	13.0 (150)	10.2 (169) [39][c] {18}[d]	1.1 (161)	−35.8 (159)
n-hexane	13.5 (151)	10.7 (166)	1.6 (161)	−35.2 (156)
octane	12.7 (142)	10.0 (162)	0.84 (161)	−36.0 (156)
Me_4Si	12.8 (161)	10.1 (169)	0.93 (156)	−35.9 (161)
cyclohexane	12.6 (156)	9.8 (159) (40)[b]	0.68 (156)	−36.1 (159)
CD_2Cl_2	11.9 (140)	9.9 (144)	0.23 (161)	−36.2 (155)
benzene-d_6	11.7 (150)	9.7 (171)	0.28 (159)	−36.5 (154)
C_6F_6	11.7 (156)	9.3 (160)	0.17 (160)	−37.4 (156)
CS_2	12.3 (155)	10.1 (180)	0.71 (157)	−35.8 (157)

	atom positions		
solvent	B(1,3,6,9)	B(5,7,8,10)	B(2,4)
acetone-d_6	11.5 (146)	−0.2 (156)	−35.3 (155)
THF	11.3 (~140)[e]	−0.45 (158)	−35.9 (155)
CD_3CN	11.2 (150)	−0.90 (156)	−35.3 (156)

[a] Chemical shift in ppm from external $BF_3 \cdot OEt_2$ reference. [b] $^{11}B-^{1}H_t$ coupling in Hz. [c] $^{11}B-^{1}H_b$ coupling in Hz. [d] $^{11}B-^{11}B$ coupling in Hz. [e] Approximate due to incomplete B(1,3)–B(6,9) peak overlap.

nance generally shifts to higher field as the solvent polarizability increases, while the B(2,4) resonance stays relatively constant except in acetone and acetonitrile solutions where a downfield shift of ~0.5 ppm is observed and in C_6F_6 where an upfield shift of over 1.0 ppm is observed.

In order to assess some aspects of the solvent effects on the NMR shifts of $B_{10}H_{14}$, several variations of the solutions were examined. First, while the solutions were generally saturated in $B_{10}H_{14}$, we determined that chemical shifts in *n*-pentane remained unchanged as the solution was diluted to 0.33 of the saturated solution. Second, using a standard solution of $B_{10}H_{14}$ in *n*-pentane, we observed that the addition of even 0.10 mol of CH_3CN/mol of $B_{10}H_{14}$ caused a substantial shift in the B(6,9) resonance and addition of 0.20 mol of CH_3CN/mol of $B_{10}H_{14}$ caused further collapse. These results, shown in Figure 3, indicate that the lifetime of the $(CH_3CN)_x$–$B_{10}H_{14}$ solvate is short on the NMR time scale but that the chemical shift effect is substantial.

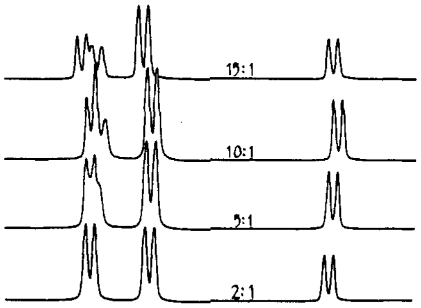

Figure 3. Influence of acetonitrile on the ^{11}B NMR spectra of $B_{10}H_{14}$ in a standard (0.22 M) solution in pentane. The ratios given represent mol of $B_{10}H_{14}$/mol of CH_3CN.

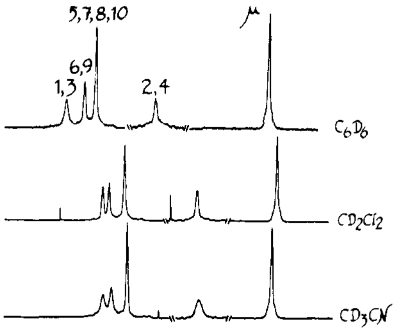

Figure 4. $^{1}H\{^{11}B\}$ NMR spectra of $B_{10}H_{14}$ at 270 MHz in selected solvents.

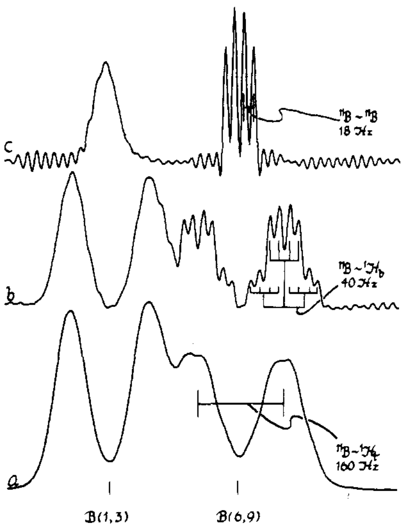

Figure 5. 86.6-MHz ^{11}B NMR of $B_{10}H_{14}$ in saturated *n*-pentane solution showing the B(1,3) and B(6,9) resonances only: (a) normal spectrum ($J_{B(6,9)-H(6,9)} = 160$ Hz); (b) coupled, line-narrowed spectrum ($J_{B(6,9)-H_b} = 40$ Hz); (c) ^{1}H-decoupled, line-narrowed spectrum ($J_{B(6,9)-B(2,4)} = 18$ Hz).

Solvent-induced ^{1}H NMR shifts for $B_{10}H_{14}$ have not been as extensively studied[2,3] as have ^{11}B NMR shifts. Representative examples indicate substantial shifts of the bridge hydrogens (denoted as H_b or H_μ) in the most polar solvents, but minimal changes in the other hydrogen shifts. In intermediate and low-polarity solvents there is a wider range of

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Table II. ^1H NMR of $B_{10}H_{14}$ in Various Solvents

	atom positions				
solvent	H(1,3)	H(6,9)	H(5,7,8,10)	H(2,4)	H(μ)
C_6D_6	4.12[a] (141)[b]	3.51 (157)	3.10 (158)	1.05 (157)	−1.21
CD_2Cl_2	3.87[c]	3.64[c]	3.11[c]	0.63 (157)	−2.07
THF-d_8	3.76[c]	3.58[c]	3.03[c]	0.58 (155)	−1.73
$(CD_3)_2CO$	3.83[c]	3.57[c]	3.03[c]	0.58 (154)	−1.55
CD_3CN	3.82[c]	3.53[c]	2.99[c]	0.55 (155)	−1.92

[a] Chemical shift in δ from Me_4Si. [b] ^1H_t–^{11}B coupling in Hz. [c] Coupling constant values were not determined due to overlap of hydrogen resonances, but they are on the same order of magnitude as those determined in C_6D_6 solution.

variations for other hydrogen resonance positions, as shown in Table II and Figure 4.

B(2,4)–B(6,9) Coupling. In low-polarity low molecular weight solvents such as *n*-butane and *n*-pentane, the ^{11}B NMR spectra of $B_{10}H_{14}$ display evidence of substantial fine structure in the B(6,9) resonance (Figure 5). Upon line narrowing, each half of the B(6,9) resonance exhibits eight clean resonances. In the line-narrowed $^{11}B\{^1H\}$ NMR spectrum the B(6,9) resonance is a 1:1:1:1 quartet with $J_{B(2,4)-B(6,9)} = 18 \pm 1$ Hz. The B(6,9) resonance is then a doublet of triplets of quartets, with coupling constants of 160 ± 2 (^{11}B–H_t), 40 ± 2 (^{11}B–H_b), and 18 ± 2 (^{11}B–^{11}B), respectively, identified in Figure 1.

Overlap of the triplet of quartets produces the approximate 1:1:3:3:3:3:1:1 appearance of each half of the line-narrowed resonance. The coupling is clearly visible in the B(6,9) resonance, as the boron atoms in these positions are bonded to only three other boron atoms and the bonding of two of them is via bridging hydrogen atoms. The B(2,4) atoms, on the other hand, are each adjacent to five other boron atoms in the molecule and, as a result, do not exhibit any resolvable fine structure, even upon substantial line narrowing. ^{11}B–^{11}B coupling has been observed in a number of small boron hydrogen clusters and typically exhibits a coupling constant of about 20 Hz.[4a,b,5]

The observation of coupling beyond that due to ^{11}B–^1H_t in $B_{10}H_{14}$ was recorded by Schaeffer[4a] who was able to resolve a doublet of quartets but indicated that this was a complex pattern and did not define it further. Odom and Ellis[4b] reported a $^{11}B(2,4)$–$^{11}B(6,9)$ coupling constant of 18.7 Hz from a $^{11}B\{^1H\}$ 32.1-MHz line-narrowed NMR spectrum in CS_2 solution.

In low-polarity high molecular weight solvents such a *n*-octane and C_6F_6 the ^{11}B–^{11}B coupling appears unresolvable. This suggests that the viscosity of the solvent is affecting the $B_{10}H_{14}$ correlation time, τ_R, such that the coupling cannot be observed on the NMR time scale. A recent study[6] on relaxation times in $B_{10}H_{14}$ in perdeuteriotoluene indicated that T_1 for ^{11}B depends only on τ_R when isotropic tumbling is occurring. It was demonstrated that as the temperature was raised, $T_1(^{11}B)$ also increased (and τ_R decreased). For quadrupolar nuclei that are interacting directly with only a few other nuclei, the effect of an increased T_1 may render fine structure observable. B(6,9), having only one direct ^{11}B–^{11}B interaction with B(2,4), shows the ^{11}B–^{11}B coupling in low-viscosity solvents or at higher temperatures. This temperature effect on the B(6,9) fine structure resolution occurs with a moderate temperature increase from 298 to 333 K for $B_{10}H_{14}$ in C_6D_6. The other boron positions in $B_{10}H_{14}$ interact with a larger number of nuclei in the molecule. These interactions give rise to more complex spin patterns, which are currently unresolved.

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Registry No. $B_{10}H_{14}$, 17702-41-9; Me_4Si, 75-76-3; CD_2Cl_2, 1665-00-5; C_6F_6, 392-56-3; CS_2, 75-15-0; CD_3CN, 2206-26-0; THF, 109-99-9; *n*-butane, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; octane, 111-65-9; cyclohexane, 110-82-7; benzene-d_6, 1076-43-3; acetone-d_6, 666-52-4.

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Contribution from the School of Chemistry,
The University of New South Wales,
Kensington NSW, Australia 2033,
and Department of Chemistry, The University of California,
Santa Barbara, California 93106

Observation of both Bridging and Chelating Modes of the 2-(2-Pyridyl)-1,8-naphthyridine Ligand (pynp) in a Single Dirhodium(II) Complex: X-ray Structure of $[Rh_2(pynp)_3Cl_2][PF_6]_2\cdot CH_3CN$

A. T. Baker,*[1] Wayne R. Tikkanen,[2] William C. Kaska,[2] and Peter C. Ford*[2]

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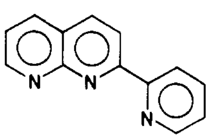
Polydentate ligands have the capacity to bind metals in different modes utilizing some or all of the base sites. For example, 2-2(2-pyridyl)-1,8-naphthyridine (pynp) can act as a bidentate chelating ligand in tris complexes with ruthenium(II)[3] or as a tridentate bridging ligand in mono- and disubstituted derivatives of the rhodium(II) acetate dimer.[4] Here we report the single-crystal X-ray structure of dichlorotris[2-(2-pyridyl)-1,8-naphthyridine]dirhodium(II) hexafluorophosphate acetonitrile solvate, $[Rh_2(pynp)_3Cl_2]$-



pynp

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(1) The University of New South Wales.

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