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Infrared Spectroelectrochemistry of Boron–Hydrogen Stretches: A Tool for Diagnosis of Delocalization in Mixed-Valent Metallacarborane Complexes

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We report that the infrared spectroelectrochemistry of B–H stretching bands is a powerful tool for the study of mixed valency (MV) effects in polynuclear metal carborane complexes. Polydecker sandwiches and staircase oligomers incorporating planar C_2B_3 ring units have been prepared, with a view, in part, to studying metal–metal interactions over extended arrays.[1,2] Despite the large number of electrochemical studies of metallacarboranes[3,4] and the well-established ability of carborane ligands to stabilize unusual metal oxidation states,[3,5,6] few in-depth studies of delocalization in MV ions have been possible, owing primarily to the lack of diagnostic spectroscopic probes for the characterization of oxidation states of metallacarboranes in solution.[4b] This situation arises in part from rapid electronic relaxations, inherent to radicals with quasi-degenerate ground states,[7] which broaden ESR absorptions in fluid media, often beyond the point of detectability. A similar problem bedevils investigations of ferrocenium-containing multinuclear complexes in fluid solutions.[8]

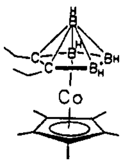
IR spectroscopy is arguably the most definitive probe of intrinsic delocalization in MV ions, owing in part to the short observation time scale.[9] We now show that (a) large shifts in BH stretching frequencies, $\bar{\nu}$(BH), accompany stepwise one-electron transfer reactions of small metallacarboranes and (b) these shifts may be diagnostic of either trapped valency or intrinsic delocalization in formally MV complexes.

The complexes $(\eta^5\text{-}C_5H_5)Co^{III}(Et_2C_2B_4H_4)$,[10] **1**, and $(\eta^6\text{-}C_{10}H_{12})Fe^{II}(Et_2C_2B_4H_4)$,[11] **2**, were investigated by transmission-mode IR spectroelectrochemistry in an OTTLE cell at subambient temperatures.[12] Clean spectra of the Co^{IV}, Co^{III}, Co^{II}, Fe^{III}, and Fe^{II} species were obtained between 2800 and 2350 cm^{-1}, the expected range for terminal $\bar{\nu}$(BH) stretching energies.[13] All electrolyses were reversible: starting materials were recovered in good yields by back-electrolyses. The data collected in Table 1 show that $\bar{\nu}$(BH) shifts to lower frequency by 58–73 cm^{-1} for each electron added to the mononuclear complexes.

Table 1

compd	M oxidn state	$\bar{\nu}$(BH),[a]	$\Delta\bar{\nu}$(BH),[b]	$E°'$ V vs Fc[c]
1$^+$	+4	2617		
			65	1.02
1	+3	2552		
			73 (av)[e]	−2.24
1$^-$	+2	2494, 2465[d]		
2$^+$	+3	2590		
			58	0.34
2	+2	2532		
				−2.64
2$^-$	+1	[f]		
3	+3, +3	2556		
			41	−2.06
3$^-$	+2.5, +2.5	2515		
			38 (av)[e]	−2.52
3^{2-}	+2, +2	2491, 2464[d]		
4^{2+}	+3, +3	2612		
			79 (from **4**)	0.84
4$^+$	+3, +2	2610, 2540[g]		
				0.55
4	+2, +2	2533		

[a] Frequency of maximum intensity of BH stretching band. [b] Shift in BH band between complexes in adjacent formal oxidation states. [c] Formal potential between complexes in adjacent oxidation states. [d] Split band. [e] Average taken from frequencies of split band in lower oxidation state. [f] Not obtained, owing to instability of monoanion. [g] The spectrum was an approximate composite of bands of **4** and **4**$^{2+}$.



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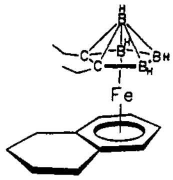

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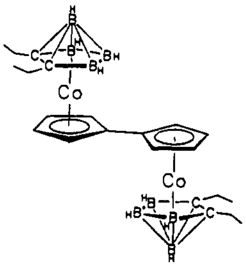

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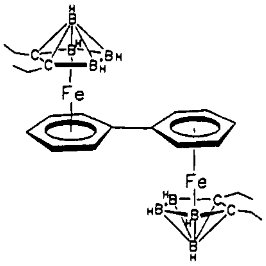

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The band contours of the spectra are typically complex, owing to the fact that several BH modes are contained in each absorption band.[14] The split band observed for **1**$^-$ (Figure 1) has precedence and may arise from different apical and equatorial BH frequencies.[15]

The relevance of the results for **1** and **2** to the study of charge distributions between redox sites is seen when similar experiments

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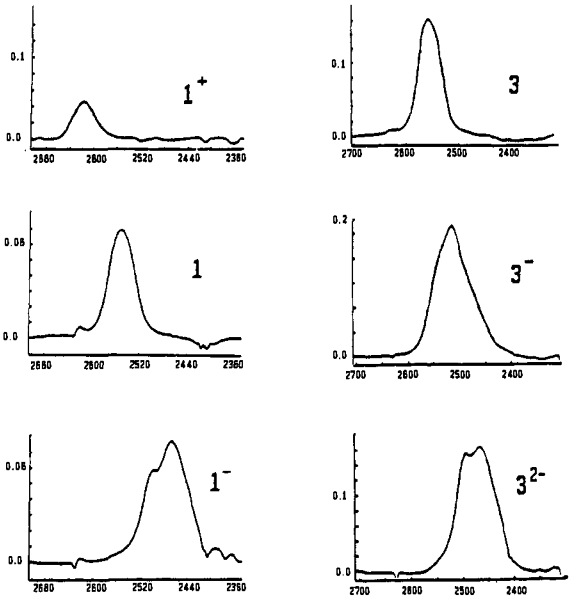

Figure 1. IR spectroelectrochemistry of cobaltacarboranes in different formal oxidation states: absorbance vs energy in cm^{-1}; cell path length 0.5 mm. Left: Spectra (T = 253 K) of 3.3 mM **1** in CH_3CN/0.3 M $[Bu_4N][PF_6]$ and the product $\mathbf{1}^-$ after electrolysis at –2.4 V; $\mathbf{1}^+$ was obtained by electrolysis of 6.6 mM **1** in CH_2Cl_2/0.22 M $[Bu_4N][PF_6]$ at 1.45 V, T = 213 K. Right: Spectra (T = 253 K) of 2.7 mM **3** electrolyzed in CH_3CN/0.3 M $[Bu_4N][PF_6]$ at –2.3 V (producing $\mathbf{3}^-$) and –2.7 V (producing $\mathbf{3}^{2-}$).

are performed on the homodinuclear complexes ($\eta^5,\eta^{5'}$-fulvalene)-$Co_2(Et_2C_2B_4H_4)_2$[16] (**3**) and ($\eta^6,\eta^{6'}$-biphenyl)$Fe_2(Et_2C_2B_4H_4)_2$[17] (**4**). Oxidation of the latter occurs in two one-electron steps with $E°'$ values of 0.55 and 0.84 V vs ferrocene$^{0/+}$.[18] IR anodic spectroelectrochemistry of **4** resulted in smooth conversion from $\bar{\nu}$(BH) = 2533 cm^{-1} in **4** to 2612 cm^{-1} in $\mathbf{4}^{2+}$, the shift of +79 cm^{-1} being consistent with conversion from an Fe^{II}Fe^{II} complex to an Fe^{III}Fe^{III} dication. The spectrum of the 1e intermediate, $\mathbf{4}^+$, has Fe^{II} and Fe^{III} $\bar{\nu}$(BH) bands (Table 1), demonstrating that the MV ion $\mathbf{4}^+$ has *trapped valence* on the IR time scale.

A different conclusion is reached about the fulvalene-bridged MV ion $\mathbf{3}^-$ based on the IR cathodic spectroelectrochemistry of the dicobalt complex **3** in THF. The fully oxidized and reduced complexes, **3** and $\mathbf{3}^{2-}$, respectively, have BH-region spectra virtually identical to those of their mononuclear analogues, **1** and $\mathbf{1}^-$: reduction from Co^{III}Co^{III} to Co^{II}Co^{II} results in a $\bar{\nu}$(BH) shift of –78 cm^{-1}, taking the average of the split band of $\mathbf{3}^{2-}$ as the band center. At the 1e reduction stage, however, a spectrum is obtained which has no features in common with either **3** or $\mathbf{3}^{2-}$. Rather, a single band is observed with a $\bar{\nu}$(BH) shift just *half* (41 cm^{-1}) that of the fully reduced dianion. The implied equivalency of the BH groups on the two carborane rings provides the basis for assignment of the MV ion $\mathbf{3}^-$ as *delocalized* over both metal centers. The difference in delocalization between $\mathbf{4}^+$ and $\mathbf{3}^-$ is most likely due to their different formal electronic configurations (d^5d^6 in $\mathbf{4}^+$, d^6d^7 in $\mathbf{3}^-$). Some M_2–fulvalene ions with the d^6d^7 configuration have shown a higher degree of M–M interaction than that found with analogous structures (e.g., the biferrocenium ion) with a d^5d^6 electronic configuration.[19]

There is a considerable body of literature which shows that BH stretching frequencies of boranes, carboranes, and, to a lesser extent, their metallo derivatives are quite sensitive to electronic effects.[20] Increasing the electron density at boron lowers the BH force constant and, therefore, $\bar{\nu}$(BH). The present data show that changes in BH frequencies are monotonic in a metallacarborane electron transfer series and of sufficient magnitude to provide a powerful diagnostic probe for ligand and metal charge densities in redox-related polynuclear complexes.

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