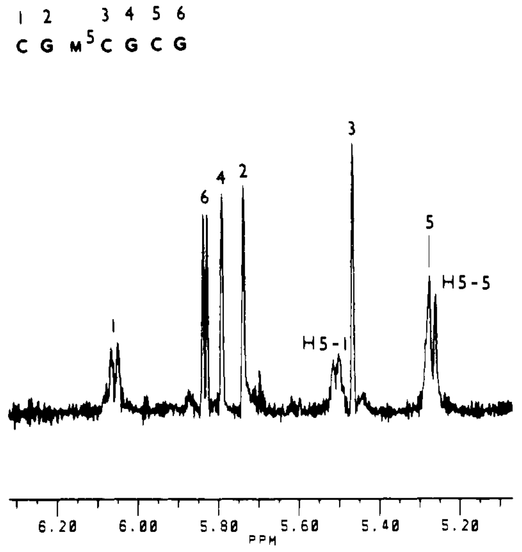

Figure 4. ^1H NMR (500-MHz) spectrum (resolution enhanced) of H1′ and H5 protons of r(CGm^{5}CGCG) (2 mM, pH 6.9, 0.1 M NaCl, 5 mM $PO_4{}^{2-}$) in aqueous solution recorded at 28 °C. Assignment was performed by studying two-dimensional NOE (Nuclear Overhauser effect) spectra. The two cytosine H5 signals are labeled H5-1 and H5-5.

probably via a hydrophobic effect—a distortion of the phosphate backbone which leads to a dramatic change in the sugar pucker of the terminal residues and weakens the corresponding hydrogen-bonded base pairing; however, the four internal residues are found in an A-like conformation. If the temperature is lowered below 28 °C, the first duplex is in slow exchange at the NMR time scale with another duplex whose phosphate backbone organization is close to that observed for r(CGCGCG) and r-(CGUAm^{5}CG).

Further information concerning the kinetics, thermodynamics, molecular process relative to r(CGm^{5}CGCG), as well as studies of other RNA sequences, will be reported in future publications.

Isolation and X-ray Crystal Structure of the Boron Methylidenide Ion $[Mes_2BCH_2]^-$ (Mes = $2,4,6\text{-}Me_3C_6H_2$): A Boron–Carbon Double Bonded Alkene Analogue

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A recent report from this laboratory gave details of the structure of the boron-stabilized carbanion $[CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}BMes_2)]^-$, **1**,[2] which possesses a B–C bond length of 1.522 (10) Å (B–C bond order ~ 1.5). it was obtained by the deprotonation of a carbon center remote from the boron site and was stabilized by conjugation through the aromatic ring. However, there are a number of literature reports dealing with spectroscopically characterized boron-stabilized carbanions arising from deprotonation of a carbon α to the boron center.[3] The facile generation and stabilization of these interesting species are made possible through the use of bulky substituents on boron. In this regard it has been known for some time that two or more mesityl substituents can impart considerable kinetic stability toward reactions at a boron center.[4] This fact led to the isolation and characterization by X-ray crystallography of the stable radical anion $BMes_3{}^{\bullet-}$[5] and the ion **1**.[2] Additionally, Wilson,[6] Pelter,[7] and co-workers have shown that the in situ deprotonation of Mes_2BMe, **2**, with LiMes or $LiN(C_6H_{11})_2$ affords solutions of the anion $[CH_2BMes_2]^-$, **3**, and this anion displays many of the characteristics of ylides.[7] We now report the structure of this anion and show that it has a short B–C bond length of ca. 1.44 Å consistent with a boron–carbon double bond formulation.

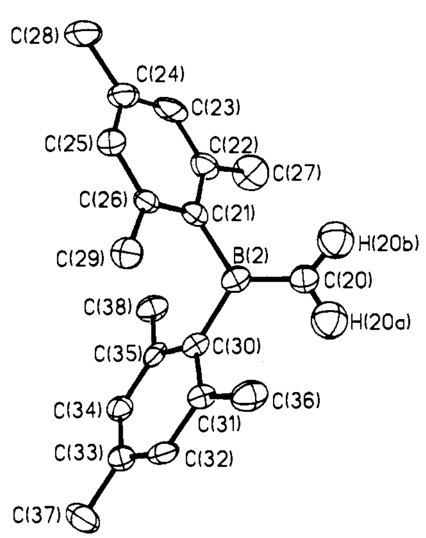

Figure 1. Computer-generated drawing of an $[Mes_2BCH_2]^-$ anion. Important bond distances (Å) and angles (deg), with values for the other crystallographically independent ion in brackets, are as follows: B(2)C(20) = 1.438 (9) {1.450 (7)}, B(2)C(21) = 1.618 (7) {1.627 (7)}, B(2)C(30) = 1.614 (7) {1.610 (8)}, C(20)H(20a) = 1.00 (5), C(20)H(20b) = 1.05 (6) {C(1)H(1a) = 1.04 (5), C(1)H(16) = 0.95 (5)}, C(20)B(2)C(21) = 122.0 (4) {121.0 (5)}, C(20)B(2)C(30) = 121.6 (4) {120.7 (5)}, C(21)B(2)C(30) = 116.4 (5) {118.3 (4)}, H(20a)C(20)H(20b) = 112 (5) {112 (4)}, H(20a)C(20)B(2) = 121 (4) {122 (3)}, H(20b)C(20)B(2) = 128 (6) {126 (3)}. Dihedral angles of the rings C(21) and C(30) with respect to the central core are 53.3 {56.1} and 59.2 {52.9}.

The title anion **3** can be crystallized in ca. 40% yield as colorless parallelepipeds (mp 112–114 °C) when 2 equiv of 12-crown-4 are added to the THF solution of its lithium salt.[5,8] The latter may be generated by the literature methods.[6,7] The structure of **3** is illustrated in Figure 1.[9] The compound crystallizes as two crystallographically independent but chemically equivalent ion pairs. The most notable feature of the molecule is the short B–CH_2 bond, which has the values 1.438 (9) and 1.450 (7) Å for an

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[9] Crystal data for $[Li(12\text{-crown-}4)_2][Mes_2BCH_2]\cdot 0.75THF$ at 130 K with Mo $K\alpha$ radiation: $a = 46.251$ (24) Å, $b = 15.290$ (6) Å, $c = 23.816$ (13) Å, $\beta = 114.70$ (3)°, monoclinic, space group $C2/c$, $Z = 16$, 7279 unique reflections with $I > 2\sigma(I)$, $R = 0.082$.

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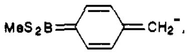
Table I. Summary of B–C Bond Lengths (Å) and C–B–C Bond Angles (deg) in Selected Mes_2BX Species[a]

	B–C(Mes)	B–C	C(Mes)–B–C(Mes)	C(Mes)–B–C	ref
$Mes_2BCH_2^-$, **3**	1.617 (7)	1.444 (8)	117.3 (5)	121.3 (5)	this work
 , **1**	1.609 (2)	1.522 (10)	111.6 (6)	124.2 (7)	2
$Mes_3B^{\cdot -}$	1.597 (4)		120.0 (2)		5
Mes_2BCH_3, **2**	1.586 (3)	1.562 (3)	119.5 (2)	120.2 (2)	*b*
Mes_3B	1.579 (2)		120.0 (2)		5

[a] Average values are given where applicable. [b] P. P. Power and R. A. Bartlett, unpublished results.

average of 1.444 Å. The C_2BCH_2 core of the molecule is also planar with an essentially zero twist angle. This is in contrast to **1** which has a 25° twist angle between the planes at boron and carbon.[2] The BCH_2 bond length in the title compound is significantly shorter than the multiple bond in the ion **1** and also the ca. 1.5-Å distance found in the aromatic 2π-electron [cyclobutadiene]$^{2+}$ analogue[10] $\mathrm{Me_2N\overline{B{-}C(\mathit{t}\text{-}Bu){-}B(NMe_2){-}C}(\mathit{t}\text{-}Bu)}$.[11] If a B–C double bond is assumed to be ca. 10% shorter than a B–C single bond, a value of 1.42–1.45 Å may be predicted for the B=C moiety, assuming a typical B–C single bond length (for three-coordinate boron) to be in the range 1.58–1.62 Å. The average distance of 1.444 Å in **3** is therefore consistent with a double bond formulation and in agreement with theoretical calculations.[12] Further supporting evidence for double bonding comes from the lowered CBC and HCH angles, which average 117° and 112°, respectively. A similar effect is seen in the structures of alkenes[13] (>C=C<), which, of course, are isoelectronic with the moiety $[>B{=}C<]^-$.[14] Trends in bonding are further illustrated in Table I where it can be seen that increasing bond order in one of the B–C bonds causes a regular decrease in the bond order of the remaining B–C bonds. The boron–carbon double bond in **3** may also be compared with that recently found by Nöth and co-workers in the compound tmpB=fluorenyl, **4**.[15] In **4** the B–C distance, 1.414 (3) Å, is slightly shorter than that in **3**. This is to be expected due to the two-coordinate nature of boron in **4**.

Finally, we draw attention to the trend in ^{11}B NMR chemical shifts on the deprotonation of Mes_2BMe to give **3**. A THF solution of Mes_2BMe displays a broad singlet at +83.6 ppm. The addition of 1 equiv of $LiN(C_6H_{11})_2$ in THF affords a new signal at +40.4 ppm due, presumably, to the solvated ions $[Li^+][Mes_2BCH_2]$. The addition of 2.2 equiv of 12-crown-4 to this solution results in a small upfield shift to +35.0 ppm. The upfield shifts[16] indicate increased electron density at boron due to the formation of the double bond. In addition the small (but significant) shift seen upon addition of 12-crown-4 seems to indicate that the $[Li]^+$ and $[Mes_2BCH_2]^-$ ions are associated in some way in THF solution in the absence of 12-crown-4. Further studies on the structures of related B–C double bonded species are in progress.

Acknowledgment. We thank Rasika Dias for experimental assistance and the National Science Foundation for financial support.

Supplementary Material Available: Details of data collection and refinement, and tables of atom coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (15 pages). Ordering information is given on any current masthead page.

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(15) tmp = 2,2,6,6-tetramethylpiperidine. Glaser, B.; Nöth, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 416. This reference contains the spectroscopic characterization of this compound. We are grateful to Professor Nöth for providing us with some details of his recent structural determination of this interesting species. Nöth, H. "Symposium on Multiple Bonding Involving the Heavier Main Group Elements", 192nd National Meeting of the American Chemical Society, Anaheim, Sept 7–12, 1986; American Chemical Society: Washington, DC.

(16) Similar upfield shifts were seen in the ^{11}B NMR spectra of $[Mes_2BPR]^-$ (R = Ph, C_6H_{11}, or Mes) relative to their neutral Mes_2BPHR precursors. However, little change was observed except a broadening of the peaks when 12-crown-4 was added. Likewise their ^{31}P NMR spectra showed considerable downfield shifts when metalated and further downfield shifts when 12-crown-4 was added. See also: Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817.

Asymmetric Induction in the Formal Iron-Catalyzed [4 + 4] Ene Reaction: The Highly Diastereoselective Cross-Coupling of 1,3-Dienes to Chiral Cyclic Acetals

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The design of new transition-metal catalysts for asymmetric organic synthesis has proven to be a challenging but nonetheless exceptionally powerful approach to the problem of controlling absolute stereochemistry.[1-3] We have recently reported the chemo- and regioselective formal [4 + 4] ene and 1,4-hydrovinylation reactions of 1,3-dienes with allyl benzyl ether catalyzed by soluble iron(0) complexes, L·Fe(0).[4] We now wish to report the first examples in which a remote stereocenter, specifically a remote acetal substituent, is used to direct the stereochemical course of the carbon–carbon bond construction in an L·Fe(0)-catalyzed [4 + 4] ene reaction.

Homochiral five- and six-membered-ring acetal subunits have been widely used as removable chiral auxiliaries to direct diastereoselective carbon–carbon bond-forming reactions.[5] While the

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