are obtained from high-yield syntheses,[5-8] and B_4H_{10} and B_5H_{11} are routinely prepared in 20- and 10-mmol quantities, respectively, in the time frames cited above. Scaleup to larger quantities is practical.

Traditionally, B_4H_{10} and B_5H_{11} have been prepared by hot–cold reactor techniques[9,10] and more recently from the protonation of $B_3H_8^-$ salts.[11-13] In addition, B_5H_{11} has been prepared[6] from the protonation of $B_5H_{12}^-$. The procedures outlined here are much safer and simpler than the classical hot–cold reactor techniques.[9,10]

Also requirements for product purification are minimal for the present method compared to the hot–cold reactor methods[9,10] and the method of protonation of $B_3H_8^-$ salts.[11-13] When carried out under conditions indicated, the presence of volatile impurities (trace quantities of B_2H_6 and B_5H_9 from reaction 2 and trace quantities of *n*-B_9H_{15} from reaction 3) present no problems in purifying B_4H_{10} and B_5H_{11}. Our present method for preparing B_5H_{11} is also superior to the earlier reported[6] protonation of $B_5H_{12}^-$, since it gives comparable yields but requires one less step in the preparative procedure.

Reaction 1 can be viewed as hydride abstraction from BH_4^- ions to give BH_3 units which combine to form B_2H_6. This reaction differs from the traditional syntheses of B_2H_6 in which diborane(6) is generated through hydride–halide exchange in reactions of metal borohydrides with group 3 halides in ethereal solvents.[14-16]

For reactions 2 and 3 hydride abstraction would yield the boranes B_3H_7 and B_4H_8, respectively. In view of the products obtained, it is reasonable to assume that subsequent reactions involve, effectively, transfer of BH_3 from one B_3H_7 to another B_3H_7 to produce B_4H_{10} and transfer of BH_3 from one B_4H_8 to another B_4H_8 to produce B_5H_{11}. Viewing reactions 2 and 3 in this light suggests the following stoichiometries.

$$B_3H_8^- + BBr_3 \rightarrow {}^1/_2B_4H_{10} + HBBr_3^- + (1/x)(BH_2)_x \qquad (2')$$

$$B_4H_9^- + BCl_3 \rightarrow {}^1/_2B_5H_{11} + HBCl_3^- + (1/2x)(B_3H_5)_x \qquad (3')$$

In these reactions 67% of the available boron in $B_3H_8^-$ is converted to B_4H_{10} and 63% of the available boron in $B_4H_9^-$ is converted to B_5H_{11}. The close correspondence of experimental yields to these proposed stoichiometries (eq 2′ and 3′) suggests that within experimental error reactions 2 and 3 are quantitative with respect to yields of B_4H_{10} and B_5H_{11}. Residues of empirical compositions $(BH_2)_x$ and $(B_3H_5)_x$ decompose at room temperature to give small amounts of B_5H_9 and *n*-B_9H_{15}, respectively.

Treatment of 20 mmol of $[N(n\text{-}C_4H_9)_4][B_3H_7Br]$[17] with an equal amount of BBr_3 in 10 mL of CH_2Cl_2 at −78 °C for 12 h results in the formation of equal amounts of 2-BrB_4H_9 and B_4H_{10}, 2 mmol each. Although the yield of 2-BrB_4H_9 is relatively low, this preparation is an attractive alternative to an earlier procedure in which 10–15% yields of 2-BrB_4H_9 were obtained from the reaction of excess B_4H_{10} with Br_2 over an 18-h period at −15 °C.[18]

The systematic nature of this procedure was further demonstrated in an extension of reactions 2 and 3. Treatment of $[N(CH_3)_4]B_9H_{14}$ with BCl_3 gave $B_{10}H_{14}$ in a yield of 50% based on $B_9H_{14}^-$ (reaction 4).

$$[N(CH_3)_4][B_9H_{14}] + BCl_3 \xrightarrow[\substack{6\ h,\\ \text{followed by}\\ \text{sublimation of}\\ B_{10}H_{14}\text{ at }90\ ^\circ C}]{\text{room temperature}} B_{10}H_{14} + [N(CH_3)_4][HBCl_3] + H_2 + \text{solid BH residue} \qquad (4)$$

A reaction stoichiometry analogous to 2′ and 3′ is suggested (reaction 4′). In this stoichiometry 56% of the boron in $B_9H_{14}^-$

$$B_9H_{14}^- + BCl_3 \rightarrow {}^1/_2B_{10}H_{14} + HBCl_3^- + {}^1/_2H_2 + (1/2x)(B_8H_{10})_x \qquad (4')$$

is converted to $B_{10}H_{14}$, which corresponds well with our results and is consistent with reaction 4 being close to quantitative.

Although $B_9H_{14}^-$ is generally prepared through the degradation of $B_{10}H_{14}$ by base,[19] it is also possible to prepare this ion through the thermal decomposition of $B_5H_8^-$ which is generated by deprotonating B_5H_9. However, the yields of $B_9H_{14}^-$ prepared this way from B_5H_9 do not exceed 60%.[20-23] By allowing $B_5H_8^-$ to react with an equimolar amount of B_5H_9 in THF at room temperature, we have been able to obtain good quality $B_9H_{14}^-$ in 90% yield.[24] This is achieved by treating B_5H_9 with an alkali metal hydride (KH or NaH) in a 2:1 molar ratio. This preparation of $B_9H_{14}^-$ from B_5H_9 coupled with reaction 4 provides a practical route to $B_{10}H_{14}$ from B_5H_9, employing a single reactor for the entire procedure.

In a typical preparation of $B_{10}H_{14}$ from B_5H_9, 21.6 mmol of NaH, 43.2 mmol of B_5H_9, and 22 mmol of $[N(CH_3)_4]Cl$ are stirred for 12 h in 16 mL of THF at room temperature. Hydrogen gas and THF are pumped away, leaving behind a dry solid which is good quality $[N(CH_3)_4][B_9H_{14}]$ and NaCl. Then 22 mmol of BCl_3 is condensed onto the solid reaction products, and this mixture is stirred vigorously for 6 h at 25 °C. The $B_{10}H_{14}$ is then sublimed from the flask under dynamic vacuum. A 9.57-mmol quantity of $B_{10}H_{14}$ representing a 45% conversion of B_5H_9 to $B_{10}H_{14}$ is obtained. This percent conversion of starting material to $B_{10}H_{14}$ is comparable to that reported for the conversion of $NaBH_4$ to $B_{10}H_{14}$ by a nonpyrolytic method.[25] The present procedure, however, requires fewer steps and it, also, can be scaledup.

Work is continuing on the further development of this systematic approach to boron hydride syntheses and the further development of the preparation of $B_{10}H_{14}$ from B_5H_9.

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Preparation and Reactivity of the (Cyclohexadiene)manganese Tricarbonyl Anion. Potentially Useful Methods of Arene and C–H Bond Activation

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It is well established that arenes complexed to transition metals are often activated toward nucleophilic attack. Nucleophilic

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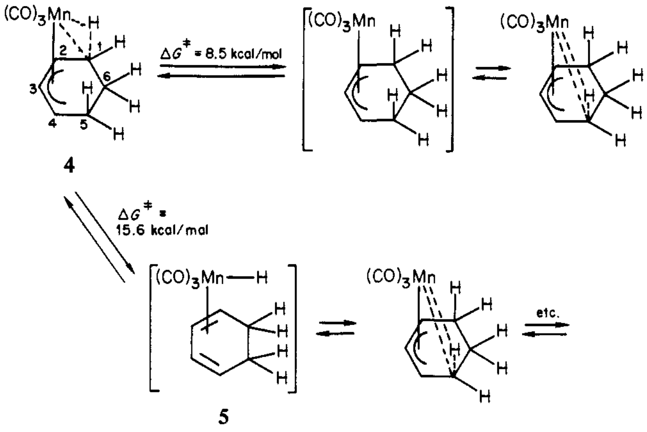
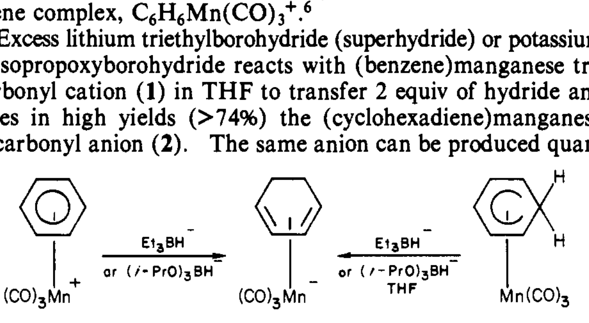
Scheme I



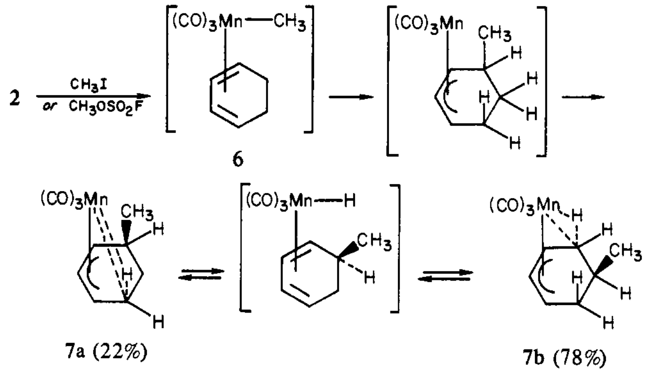
addition to neutral and cationic transition-metal–arene complexes typically yields the corresponding anionic and neutral cyclohexadienyl complexes, respectively. Examples of species which exhibit this behavior include $C_6H_6Cr(CO)_3$[1] and $C_6H_6FeCp^{+}$[2] as well as $C_6H_6Mn(CO)_3^{+}$[3] and their derivatives.[4] Similarly, there is ample precedent for nucleophilic addition to cationic cyclohexadienyl–metal complexes to yield neutral diene complexes,[4,5] for example, the numerous cases of hydride addition to $C_6H_7Fe(CO)_3^{+}$ and its derivatives.[5] We wish to report here the characterization and unusual chemistry of the (cyclohexadiene)manganese tricarbonyl anion generated by an apparently unprecedented addition of 2 equiv of hydride to the cationic arene complex, $C_6H_6Mn(CO)_3^{+}$.[6]

Excess lithium triethylborohydride (superhydride) or potassium triisopropoxyborohydride reacts with (benzene)manganese tricarbonyl cation (**1**) in THF to transfer 2 equiv of hydride and gives in high yields (>74%) the (cyclohexadiene)manganese tricarbonyl anion (**2**). The same anion can be produced quantitatively by hydride reduction of cyclohexadienylmanganese tricarbonyl (**3**) which has been identified by IR as the intermediate in the former reaction. The potassium and sodium salts of anion **2** exhibit strong IR bands at 1930, 1840, and 1789 cm^{-1} for the metal carbonyl groups,[7] while the ^{1}H NMR spectrum in THF-d_8 (identical in band patterns with and similar in chemical shifts to cyclohexadieneiron tricarbonyl) shows resonances at δ 4.37 (m, 2 H), 2.19 (br m, 2 H), and 1.52 (br s, 4 H).[8]



1 2 3

Scheme II



By analogy with $Mn(CO)_5^{-}$, the diene anion (**2**) is expected to be basic and quite nucleophilic, and, indeed, interesting reactions with electrophiles have been observed. Protonation of **2** with water results in quantitative conversion to the unusual cyclohexenyl species **4** possessing an endo hydrogen bridged between carbon and manganese and constituting part of a two-electron, three-center C–H–Mn bonding arrangement as shown in Scheme I.

Although structures of this type are certainly uncommon, a small number of transition-metal complexes possessing bridged C–H bonds have been reported,[9] the closest analogues being the cationic π-allyliron species generated upon protonation of the neutral (diene)FeL_3 complexes.[10,11] Surprisingly, the bridged structure **4** is stable to temperatures greater than 120 °C and exhibits two distinct degenerate modes of isomerization observable by ^{1}H NMR. These modes are illustrated in Scheme I and involve a low-energy process ($\Delta G^{‡} = 8.5$ kcal/mol) which averages $H_{1\text{-endo}}$ with $H_{5\text{-endo}}$, $H_{1\text{-exo}}$ with $H_{5\text{-exo}}$, and H_2 with H_4 and a higher energy process ($\Delta G^{‡} = 15.6$ kcal/mol) (involving the diene hydride (**5**) as an intermediate) which, coupled with the low-energy process, scrambles all three "endo" hydrogens and, separately, all exo and olefinic hydrogens.[12]

An important result of the coordination of the C–H bond in **4** to manganese is that the bridged hydrogen is activated and rendered acidic. Treatment of **4** with a variety of bases (i.e., KH, NaH, *n*-BuLi) results in regeneration of anion **2**. The reaction using KH in tetrahydrofuran proceeds quantitatively (<*20* min, 25 °C) and was the method of choice for spectral characterization and examination of further reactions of the anion.

Reaction of **2**, thus prepared, with methyl iodide or methyl fluorosulfonate results in endo ring methylation and coordination of a *second* endo C–H bond, giving a 22:78 mixture of the monomethylated complexes **7a** and **7b**, respectively, in an overall yield of 79% (Scheme II). Complex **7a** must be the first formed isomer and is thought to arise from initial formation of **6** (or a methyl bridged species) followed by methyl migration to the endo side

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(7) The IR spectrum of the lithium salt of anion **2** in the metal carbonyl region is more complex, exhibiting bands at 1929 (s), 1896 (v), 1853 (v), 1831 (s), 1811 (s), and 1758 (v) cm^{-1}. This is presumably a result of ion pairing with the more highly coordinating lithium cation.

(8) ^{1}H NMR samples of **2** were prepared by deprotonation of **4** with KH in THF-d_8.

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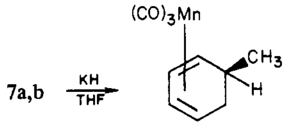
(12) ^{1}H NMR spectrum of **4** at −99 °C exhibits resonances at δ 5.32 (1 H, H_2), 4.98 (1 H, H_3), 3.78 (1 H, H_4), 1.59 (2 H, $H_{1\text{-exo},5\text{-exo}}$), 1.39 (1 H, $H_{5\text{-endo}}$), 0.97 (1 H, $H_{6\text{-endo}}$), 0.44 (1 H, $H_{6\text{-exo}}$), −12.83 (1 H, $H_{1\text{-bridging}}$). Characterization as the C–H bridged structure is supported by the dynamic NMR properties of **4** as well as the X-ray crystal structure of the monomethylated derivative **7b**. Complete structural and spectroscopic details will be described in a full paper. This species may be identical with one previously isolated by Pauson but formulated as a bicyclic π-allylmanganese dihydride based on ^{1}H NMR data. See: Pauson, P. L. *Pure Appl. Chem.* **1977**, *49*, 839–855. Pauson, P. L.; Munro, G. A. M., *Isr. J. Chem.* **1977**, *15*, 258.

of the ring. It is presumed that **7b** arises by isomerization of **7a** through a diene hydride intermediate similar to **5**. Indeed, high-temperature ^1H NMR studies have verified that isomers **7a** and **7b** are in rapid equilibrium.[13] The structure of isomer **7b** has been confirmed by X-ray crystallographic analysis.[14]

Perhaps the most surprising aspect of the mechanism in Scheme II is the proposed metal-to-ring migration of the methyl group upon methylation of diene anion **2**, formally an insertion of an olefin into a metal–alkyl bond. The only other known example of a metal-to-ring alkyl migration of this type is the transfer of the ethyl group of $Cp_2Mo(Et)Cl$ to the endo side of one of the cyclopentadienyl rings upon treatment with phosphines.[15]

The conversion of **4** to **7** is remarkable in that, following methyl migration to the ring, a second endo C–H bond is activated through coordination to manganese. Thus, quantitative deprotonation of **7** by KH gives the monomethylated cyclohexadiene anion (**8**). The ultimate conversion of **2** to **8** represents formally an electrophilic substitution of an endo hydrogen of cyclohexadiene mediated by manganese activation. Preliminary results indicate that the monomethylated anion (8) is also highly nucleophilic and can be alkylated with methyl iodide to produce ring-dialkylated products.

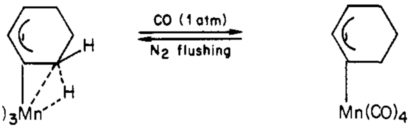


8

ν_{CO} = 1930, 1838, and 1789 cm^{-1}

A result which bears directly on the potential synthetic utility of this system is the rapid oxidative cleavage of the diene from the diene anions by oxygen. Exposure of a THF solution of **2** to 1 atm of oxygen causes immediate precipitation of a brown solid (containing MnO_2) and quantitative formation of free 1,3-cyclohexadiene which can be trapped with tetracyanoethylene and isolated as the Diels–Alder adduct.

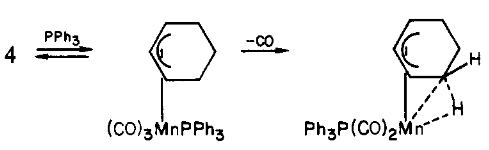
The reactions of the hydrogen-bridged species with external ligands have also been investigated. Reaction of **4** with CO in methylene chloride solution rapidly gives the π-allyl tetracarbonyl complex **9**[16] by simple C–H bond displacement. This reaction has parallels with the behavior of the protonated (diene)iron–L_3 species.[11b–d,17] Interestingly, the addition at 1 atm of CO pressure proceeds to only 25% completion and is readily reversible; flushing a solution of **9** with N_2 results in quantitative regeneration of starting material. Complex **4** reacts with triphenylphosphine in a similar fashion; however, the resulting π-allyltricarbonylmonophosphine complex **10** slowly loses CO to form the C–H bridged dicarbonylmonophosphine complex **11** which exists as a mixture of all three possible isomers.



4 9

ν_{CO} = 2020, 1945, and 1937 cm^{-1}

ν_{CO} = 2055, 1987, 1970, and 1959 cm^{-1}



10 11

Nucleophilic addition to the π-allyl complexes **9** and **10** has not yet been investigated; however, literature precedent suggests conversion to cyclohexene derivatives is likely.[18] Hence, the reactions reported herein should enable a series of manganese-mediated transformations for the stepwise reduction of arenes to 1,3-cyclohexadienes and possibly cyclohexenes with highly varied functionalization. Since all of the reactions leading to ring functionalization proceed exclusively either exo or endo to the metal, control of product stereochemistry is expected. Such a series should prove relatively versatile and has obvious potential synthetic utility.

The chemistry reported illustrates two novel aspects of transition-metal activation of hydrocarbon ligands. First, the activation of arenes toward addition of *2* equiv of nucleophiles to yield coordinated dienes has been demonstrated in the conversion of benzene complex **1** to the cyclohexadiene complex **2**. Secondly, although coordination of C–H bonds to transition metals has been previously observed in a limited number of systems, the transformations reported for the hydrogen-bridged manganese system represent the first clear illustration that such metal–CH interactions can be used to advantage for carrying out electrophilic substitutions at the bridged carbon. This chemistry suggests in a general way how metal-activated C–H bonds may be utilized to achieve functionalization at saturated carbon centers.

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(13) At −10 °C isomer **7a** exhibits a ^1H NMR resonance at *−13.67* ppm (1 H) corresponding to the single endo hydrogen bridged to manganese. In isomer **7b** there are two endo hydrogens capable of bridging to manganese, and at −10 °C these are rapidly exchanging on an NMR time scale resulting in a two proton resonance at −6.49 ppm. Heating a mixture of **7a** and **7b** causes the two isomers to rapidly exchange and results in coalescence of the two high field bridging hydride resonances giving an average resonance at −6.44 ppm at 140 °C.

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Analogues for Acetoacetate as an Enzyme Substrate. Stereochemical Preferences

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The use of conformationally restricted substrate analogues is one of the few experimental options available for determining which of a number of rapidly interconverting conformers of a molecule is the actual substrate for an enzyme.[1] We report here that 2-oxocyclohexanecarboxylate (**1**), as a conformationally constrained analogue for acetoacetate (**2**), is a substrate for two enzymes that catalyze reactions of acetoacetate, acetoacetate decarboxylase (AAD),[2] and 3-hydroxybutyrate dehydrogenase

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