ORGANOMETALLICS

Stereospecific synthesis of the B-(Z)-1-alkenyl-9-borabicyclo[3.3.1]nonanes not available via hydroboration

Herbert C. Brown, N. G. Bhat, and Shyamala. Rajagopalan

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photochemical properties. The enthalpy of reaction can be related to $D(\text{Mn–Mn})$ by

$$\Delta H_r = \phi_{-M}[D(\text{Mn–Mn}) + 2\Delta H_{coord}(\text{Mn(CO)}_5)] + \phi_{-CO}[D(\text{Mn–CO}) + \Delta H_{coord}(\text{Mn}_2(\text{CO})_9)]$$

where ϕ_{-M} is the quantum yield for Mn–Mn bond cleavage, ϕ_{-CO} is the quantum yield for Mn–CO bond cleavage, $D(\text{Mn–CO})$ is the bond enthalpy of the Mn–CO bond, $D(\text{Mn–Mn})$ is the enthalpy of the metal–metal bond, $\Delta H_{coord}(\text{Mn(CO)}_5)$ is the coordination energy of the Mn(CO)_5 fragment, and $\Delta H_{coord}(\text{Mn}_2(\text{CO})_9)$ is the coordination energy of the $\text{Mn}_2(\text{CO})_9$ fragment. Recent reports place the Mn–CO bond enthalpy at 36 ± 2 kcal/mol.[16]

As the present experiments are performed in solution, the enthalpy of coordination to the solvent of the photoproducts must be considered. Reliable estimates for these values are not available. For the solvents employed, $\Delta H_{coord}(\text{Mn(CO)}_5)$ is expected to be small and therefore should contribute little to the overall enthalpy of reaction. However, $\Delta H_{coord}[\text{Mn}_2(\text{CO})_9]$ should be more substantial, perhaps ranging from 5 to 25 kcal/mol. However, the small quantum yield, 0.1, for CO dissociation[22,24] suggests that the contribution to ΔH_r from the ligand loss pathway, $\phi_{-CO}[D(\text{Mn–CO}) + \Delta H_{coord}\text{Mn}_2(\text{CO})_9]$ leads to values ranging from 1.1 to 3.1 kcal/mol. This conclusion is supported by the small range in ΔH_r values observed for both weakly and strongly coordinating solvents.

With use of the enthalpies of reaction reported herein, the literature quantum yields,[22] a value of 36 kcal/mol for $D(\text{Mn–CO})$, and a range of 5–15 kcal/mol for $\Delta H_{coord}[\text{Mn}_2(\text{CO})_9]$ in hexane, the value obtained for $D(\text{Mn–Mn})$ is 38.0 ± 5 kcal/mol in hydrocarbon solvents. The indicated errors is $D(\text{Mn–Mn})$ come only from the precision of the ΔH_r measurement and do not reflect errors in other values used in the calculation.

The determination of the $D(\text{Mn–Mn})$ is dependent on accurate photochemical quantum yields. The quantum yields of 0.3 and 0.1 for the homolysis and ligand loss, respectively, yield a reasonable value for $D(\text{Mn–Mn})$.[22–24] Total quantum yield measurements reporting a higher value[26] are inconsistent with our results. Were the total quantum yield greater than 0.6, values of less than 20 kcal/mol would be calculated for $D(\text{Mn–Mn})$ from our measurements. Such a low value for the metal bond dissociation energy is inconsistent with chemical evidence,[27] and we therefore favor the lower literature values.

Acknowledgment. This work was supported by the NSF (CHE-8418611) and by a grant from the National Institutes of Health. K.S.P. and V.V. acknowledge support from the Alfred P. Sloan Foundation and the Henry and Camille Dreyfus Foundation for teacher–scholar grant. J.L.G. acknowledges generous support from an NIH postdoctoral fellowship.

Registry No. $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; CO, 630-08-0; Mn, 7439-96-5.

(22) The quantum yields for photodissociation,[23] $\phi_{-M} = 0.3$, and the quantum yields for decarbonylation,[24] $\phi_{-CO} = 0.1$, have been determined in a number of solvents. The yields appear relatively insensitive to solvent, and consequently the values chosen are average values.

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Stereospecific Synthesis of the *B*-(*Z*)-1-Alkenyl-9-borabicyclo[3.3.1]nonanes Not Available via Hydroboration

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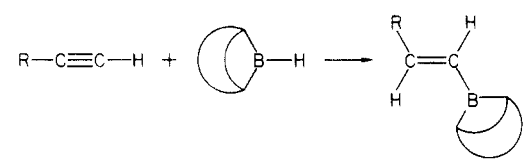
Summary: The reaction of (*Z*)-1-lithio-1-alkenes with *B*-methoxy-9-borabicyclo[3.3.1]nonane proceeds to form lithium (*Z*)-1-alkenyl-*B*-methoxy-9-borabicyclo[3.3.1]nonanes. Treatment of the "ate" complexes with boron trifluoride–diethyl etherate affords the unknown *B*-(*Z*)-1-alkenyl-9-borabicyclo[3.3.1]nonanes in good yields. These undergo smooth reaction with benzaldehyde and methyl vinyl ketone, providing the corresponding allylic alcohols and 4-alkenyl-2-butanones, respectively, with the corresponding stereochemistry.

The *B*-(*E*)-1-alkenyl-9-borabicyclo[3.3.1]nonanes (*B*-(*E*)-1-alkenyl-9-BBN) exhibit exceptional stereospecific reactivity, not exhibited by other boron derivatives.[2] These *B*-(*E*)-1-alkenyl-9-BBN reagents are readily prepared via the regio- and stereospecific monohydroboration of 1-alkynes with 9-BBN in high yields (eq 1).[3] Unfortunately,



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tunately, the lack of a convenient procedure for the clean preparation of the corresponding stereoisomeric *B*-(*Z*)-1-alkenyl-9-BBN derivatives has severely limited the general application of syntheses based on these derivatives.

In the past, two routes have been investigated for the stereospecific synthesis of the *B*-(*Z*)-1-alkenyl-9-BBN reagents. The first effort involves hydroboration of 1-halo-1-alkynes with 9-BBN, followed by treatment with *tert*-butyllithium.[4] Unfortunately, this procedure afforded a mixture of two products due to indiscriminate migration of both the hydride and the cyclooctyl ring.

In the second effort, the controlled catalytic hydrogenation of *B*-1-alkynyl-9-BBN reagents under a variety of experimental conditions resulted in a complex mixture of products containing the desired alkenylborane in <50% yields.[5]

In view of the fact that alkyl-[6] and *B*-1-alkynyl-9-BBN[7] reagents are readily prepared via reaction of the corresponding lithium reagents with *B*-methoxy-9-BBN, it seemed possible that a similar reaction using (*Z*)-1-

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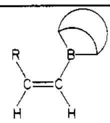
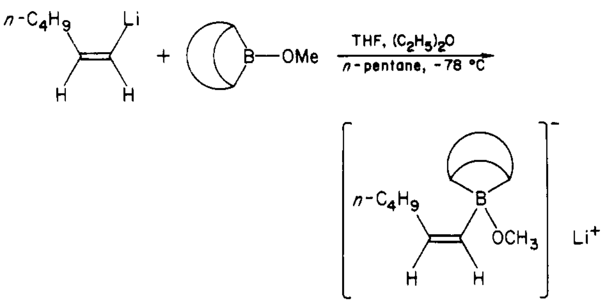
Table I. Preparation of *B*-(*Z*)-1-Alkenyl-9-borabicyclo[3.3.1]nonanes

	isolated yield,[a] %	bp, °C (*p*, torr)	IR[b] $\bar{\nu}$(C=C), cm^{-1}	^{11}B NMR[c] δ	^{1}H NMR data[c] δ
n-C_4H_9	75	80–82 (0.1)	1601	80.4	6.0–6.6 (m, 2 H), 1.1–2.6 (m, 20 H), 0.8–1.0 (distorted t, 3 H)
n-C_5H_{11}	70	104–106 (0.5)	1601	81.0	6.0–6.6 (m, 2 H), 1.1–2.6 (m, 22 H), 0.8–1.0 (distorted t, 3 H)
i-C_3H_7	72	54–56 (0.3)	1601	81.3	6.0–6.4 (m, 2 H), 1.10–3.0 (m, 15 H), 1.0 (d, J = 6.0 Hz, 6 H)
c-C_6H_{11}	74	88–90 (0.03)	1598	81.7	6.0–6.4 (m, 2 H), 1.2–2.6 (m, 25 H)
t-C_4H_9	70	60–62 (0.2)	1615	85.2	5.7–5.9 (m, 2 H, 1.6–2.0 (m, 14 H), 0.9 (s, 9 H)

[a] Yields of pure products isolated by distillation based on (*Z*)-1-iodo-1-alkenes. [b] IR spectra were taken with solutions of samples dissolved in $CDCl_3$. [c] Chemical shift values, all in $CDCl_3$, are given in parts per million (δ) relative to $BF_3 \cdot O(C_2H_5)_2$ in ^{11}B NMR and relative to $(CH_3)_4Si$ in ^{1}H NMR.

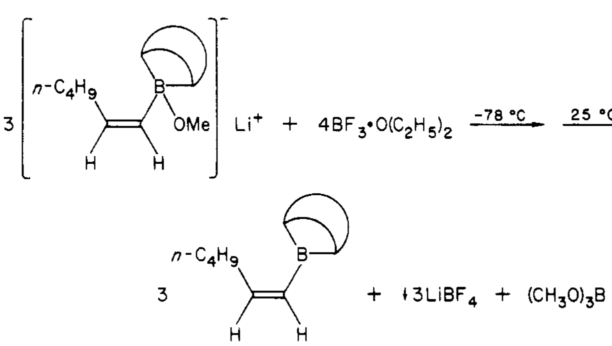
lithio-1-alkenes[8] might provide access to the corresponding *B*-(*Z*)-1-alkenyl-9-BBN derivatives.

In a representative experiment, a solution of (*Z*)-1-lithio-1-hexene in diethyl ether–*n*-pentane mixture at −78 °C was treated with a solution of *B*-methoxy-9-BBN in THF. The ^{11}B NMR analysis showed a single upfield absorption (δ −1.7), indicative of a simple 1:1 adduct shown in eq 2. Treatment of this "ate" complex with 1.33 equiv



(2)

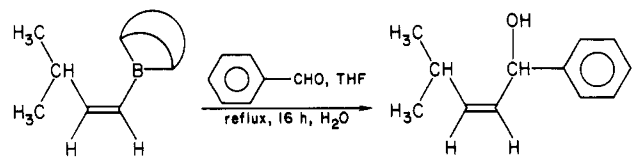
of boron trifluoride–diethyl etherate at −78 °C, followed by warming, resulted in the formation of the desired *B*-(*Z*)-1-hexenyl-9-BBN in good yield (eq 3; ^{11}B NMR δ +80.40 ($CDCl_3$)). A representative selection of *B*-(*Z*)-1-



(3)

alkenyl-9-BBN derivatives were prepared by this procedure in high yields and excellent purities (Table I). The stereochemical purity of these *B*-(*Z*)-1-alkenyl-9-BBN reagents was established by comparison of the ^{1}H NMR data with those of the corresponding *E* isomers obtained by the reaction of 1-alkynes with 9-BBN which exhibited an entirely different pattern in the olefinic region. For example, the ^{1}H NMR spectrum of *B*-(*Z*)-1-hexenyl-9-BBN consists of unresolved multiplet between δ 6.0 and 6.6, while that of the corresponding *E* isomer exhibits well-resolved absorptions centered at δ 6.8 (dt, J = 5.9 and 17.2 Hz) and 6.3 (d, J = 17.2 Hz).[3]

Additional evidence for the stereochemical purity of the *B*-(*Z*)-1-alkenyl-9-BBN compounds prepared in this study was gathered by utilizing them in reactions known for the *E*-isomers.[2a,b] Thus, treatment of *B*-(*Z*)-(3-methyl-1-butenyl)-9-BBN with benzaldehyde afforded the corresponding *Z* allylic alcohol in >99% isomeric purity, as revealed by GLC and ^{13}C NMR analyses (eq 4). Similarly, reaction of *B*-(*Z*)-1-hexenyl-9-BBN with methyl vinyl ketone proceeded stereospecifically (eq 5).



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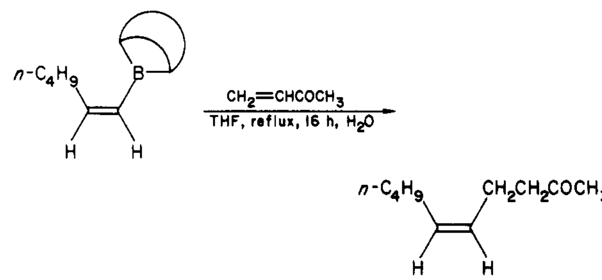

(5)

In conclusion, we have developed a general, stereospecific procedure for the preparation of *B*-(*Z*)-1-alkenyl-9-BBN reagents, adding these derivatives to the previously known *B*-(*E*)-1-alkenyl-9-BBN compounds for synthetic application.

General Procedure for the Preparation of *B*-(*Z*)-1-Alkenyl-9-BBN Derivatives. To a 100-mL flask[9] containing a solution of (*Z*)-1-iodo-1-alkene[10] (10 mmol) in diethyl ether (10 mL) cooled to −78 °C was added a solution of *tert*-butyllithium in *n*-pentane (20 mmol). The resultant slurry containing the (*Z*)-1-alkenyllithium[8] reagent was stirred at −78 °C for 3 h. Next, *B*-methoxy-9-BBN in THF (10 mmol) was added, and the reaction solution was stirred at −78 °C for 1 h. Then boron trifluoride etherate (13.30 mmol) was added, and stirring was continued for 30 min at −78 °C. The reaction flask was then removed from the cold bath and allowed to warm to room temperature. Following removal of solvents, *n*-pentane (10 mL) was added to the remaining slurry and the mixture stirred to permit the solid to settle. The supernatant liquid was then decanted. The solid was wahsed with *n*-pentane (2 × 10 mL) and the extracts combined. The pentane was removed and the residual liquid distilled to afford chemically and isomerically pure *B*-(*Z*)-1-alkenyl-9-BBN. The preparative data are summarized in Table I.

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The procedure for the reeaction of benzaldehyde with *B*-(*Z*)-3-methyl-1-butenyl-9-BBN follows that for the *E* isomer.[2b] 4-Methyl-1-phenylpent-2-en-1-ol was obtained in 60% yield: bp 108–110 °C (1.0 torr); n^{22}_D 1.5170; ^{1}H NMR ($CDCl_3$) δ 7.4 (s, 5 H), 5.4–5.8 (m, 3 H), 2.6–3.0 (m, 1 H), 2.0 (br s, 1 H), 1.0 (two overlapping doublets, *J* = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 22.90, 23.20, 27.0, 69.80, 126.0, 127.30, 128.40, 129.70, 139.10, 144.0; IR (meat) ν̄ 3346 (OH), 1685 cm^{-1} (C=C); MS, *m/e* 176 (M^+); GLC analysis on a 50-M methyl silicone glass capillary column showed >99% isomeric purity.

The procedure for the reaction of methyl vinyl ketone with *B*-(*Z*)-1-hexenyl-9-BBN follows that for the *E* isomer.[2a] (*Z*)-5-Decen-2-one was obtained in 67% yield: bp 70–72 °C (2.50 torr); n^{20}_D 1.4433; ^{1}H NMR ($CDCl_3$) δ 5.6–5.3 (m, 2 H), 2.6–2.4 (m, 6 H), 2.20 (s, 3 H), 1.6–1.0 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 13.75, 21.60, 22.20, 26.74, 29.60, 31.72, 43.41, 127.62, 130.98, 204.51; IR (neat) ν̄ 1715 (>C=O), 1658 cm^{-1} (C=C); MS, *m/e* 154 (M^+); GLC analysis on 50-M methyl silicone capillary glass column showed >98% isomeric purity.

Registry No. *B*-(*Z*)-1-Hexenyl-9-BBN, 67826-85-1; *B*-(*Z*)-1-heptenyl-9-BBN, 100839-97-2; *B*-(*Z*)-3-methyl-1-butenyl-9-BBN, 100839-98-3; *B*-(*Z*)-2-cyclohexylethenyl-9-BBN, 100839-99-4; *B*-(*Z*)-3,3-dimethyl-1-butenyl-9-BBN, 100840-00-4; (*Z*)-4-methyl-1-phenylpent-2-en-1-ol, 100840-01-5; (*Z*)-5-decen-2-one, 100840-02-6; (*Z*)-1-iodo-1-hexene, 16538-47-9; (*Z*)-1-iodo-1-heptene, 63318-29-6; (*Z*)-1-iodo-3-methyl-1-butene, 64245-25-6; (*Z*)-2-cyclohexyl-1-iodo-1-ethene, 67404-69-7; (*Z*)-3,3-dimethyl-1-iodo-1-butene, 64245-24-5; *B*-methoxy-9-BBN, 38050-71-4.

Synthesis and Carbon Monoxide Insertion Reactions of (η^5-Cycloheptadienyl)Fe(CO)L(CH_3) (L = CO, P(OPh)$_3$)

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Summary: The first pentadienyl analogues of CpFe(CO)LCH_3 have been prepared from (η^5-C_7H_9)FeL(CO)I (L = CO, P(OPh)$_3$). The structure of (η^5-C_7H_9)Fe(CO)(P(OPh)$_3$)CH_3 is presented. The reactions of (η^5-C_7H_9)Fe(CO)$_2$$CH_3$ with CO and PPh_3 are described. These insertion reactions occur much more readily than do those of the isoelectronic analogue (C_5H_5)Fe(CO)$_2$$CH_3$. The difference in reactivity is ascribed to a facile η^5–η^3 ring slip for the pentadienyl complex.

The η^5-pentadienyl ligand has received significant attention in recent years because of its potential as a substrate for carbon–carbon bond-forming reactions[1] and because multiple coordination modes for the pentadienyl ligand make its complexes attractive candidates for new homogeneous catalysts.[2] The versatility of the dienyl ligand coupled with the wealth of chemistry known for complexes of its isoelectronic counterpart, cyclopentadienyl (Cp), prompted us to initiate studies of the chemical reactivity patterns of (η^5-dienyl)metal complexes. In this paper we report the synthesis of (η^5-C_7H_9)FeL(CO)CH_3 (L = CO, P(OPh)$_3$), the first examples of pentadienyl iron alkyl complexes that have direct cyclopentadienyl counterparts.[3] We also discuss the CO insertion reactions of the dicarbonyl species; acetyl-substituted (diene)Fe(CO)$_2$L complexes are produced.

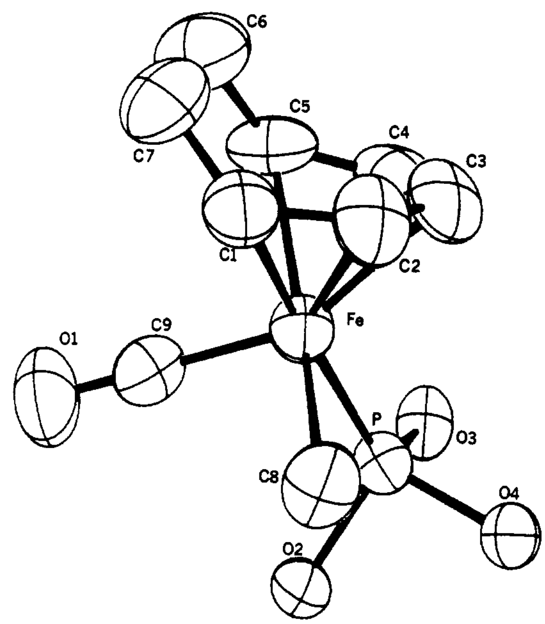
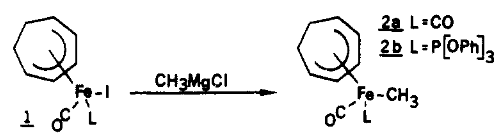


Figure 1. ORTEP illustration of (η^5-C_7H_9)Fe(CO)(P(OPh)$_3$)CH_3 (**2b**). Phenyl rings are omitted for clarity.

Each of the iron methyl complexes can be prepared by treating the corresponding iodoiron dienyl **1**[4] with CH_3MgCl (eq 1). In contrast with its Cp counterpart, **2a** is



(1)

a very sensitive compound. It must be removed from reaction byproducts by filtration through silica gel at low temperature. Removal of solvent (−30 °C) and sublimation (25 °C (10^{-5} torr)) provides **2a** as a waxy yellow-orange solid in 95% yield. Once purified, **2a** can be stored for several days under an inert atmosphere at −25 °C with only minor decomposition. Consistent with the known chemistry of the Cp series, substitution of P(OPh)$_3$ for CO results in increased stability of the complex. Hence, **2b** is an orange crystalline solid which may be handled briefly in air.

Complex **2b** was characterized by X-ray crystallography; the ORTEP is shown in Figure 1. The pentadienyl fragment is distorted from planarity to a somewhat larger degree than is commonly observed for this ligand.[2,5] Thus, C4 is 0.069 Å below the least-squares plane of the five dienyl

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