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Migration of 1-Alkenyl Groups from Zirconium to Boron Compounds

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Summary: The reaction of dicyclopentadienylzirconium alkenyl chloride with a boron chloride or bromide results in the exchange of the halogen and alkenyl group, forming the alkenylborane. We report here a systematic investigation of the transmetalation of the 1-hexenyl group from zirconium to a variety of boron compounds. This group undergoes facile migration to a variety of boron compounds, yielding structurally different types of alkenylboranes in good to high yields. These results suggest that one can combine the unique reactivity and selectivity of hydrozirconation for the preparation of alkenylboranes.

The hydrozirconation of alkynes has been shown to be useful for the preparation of alkenylzirconium compounds.[1] Unfortunately, these dicyclopentadienylzirconium alkenyl chlorides do not generally undergo carbon–carbon bond-forming reactions. To overcome this limitation, transmetalation to other metals whose ability to form carbon–carbon bonds such as aluminum,[2–4] copper,[5] palladium,[5] mercury,[6] tin,[7] and zinc[7] has been explored. In principle, transmetalation should proceed to a more electronegative metal than zirconium. As such, one would expect that organic groups would migrate from zirconium to boron.

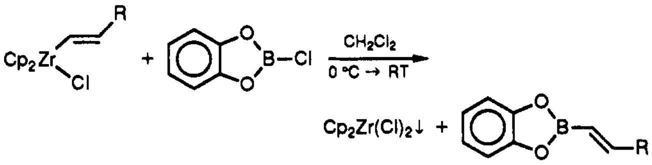
Organoboranes are one of the most versatile intermediates and one of the most intensely studied of the organometallics.[8,9] The variety of products that can be prepared via organoboranes is essentially only limited by the types of organic groups that can be placed on boron. There are obvious advantages in combining the unique reactivity and selectivity of organotransition metals with the versatility of organoboranes for organic synthesis. In this preliminary note, we report the systematic investigation of the migration of the 1-hexenyl group, as a representative 1-alkenyl group, from zirconium to various boron compounds.

Until recently, this potentially useful reaction remained unexplored. Caulton first reported the migration of the methyl groups from the related dimethylzirconocene Cp_2ZrMe_2 to $BH_3{\cdot}THF$, forming a mixture of methylboranes.[10] More recently, two other groups have reported the migration of alkenyl groups from zirconium to boron. Fagan and co-workers published a novel synthesis of substituted boroles from the corresponding substituted zirconium metallocycles.[11] Fryzuk has used the selectivity of the hydrozirconation of 1,3-enynes followed by transmetalation to diphenylbromoborane to form substituted dienes.[12]

Results and Discussion

In this study we used the 1-hexenyl group as a representative 1-alkenyl system. The 1-hexenylzirconium complex was prepared from the hydrozirconation of 1-hexyne by using freshly prepared Schwartz's reagent, $Cp_2ZrH(Cl)$.[13,14] The hydrozirconation reaction is similar in many respects to the hydroboration reaction. Both reactions proceed via cis addition with a high degree of regioselectivity, placing the zirconium or boron on the terminal carbon.[15] The addition of 5 mmol of the 1-hexenylzirconium complex in methylene chloride to 5 mmol of boron trichloride in hexane at 0 °C rapidly formed an off-white precipitate. Analysis of the reaction mixture by ^{11}B NMR revealed a new signal at +52.7 ppm, which is consistent with the migration of the vinyl group. Since trivinylborane and all vinylchloroboranes have similar chemical shifts, ca. +55 ppm, the reaction mixture was methanolyzed with an excess of methanol, forming the readily distinguishable derivatives. In this reaction a new major peak was observed at +27.4 ppm, which corresponded to the vinyl boronic ester, and only small amounts of materials were seen at +18.4 ppm ($B(OMe)_3$ from unreacted BCl_3) and at +47.6 ppm (divinyl borinic ester). The ^{11}B NMR spectra indicated an approximately 90% conversion to 1-hexenyldichloroborane. This suggested selective migration of the 1-hexenyl group to form the monovinylborane. The 1-hexenyldimethoxyborane was isolated and analyzed by both ^1H and ^{13}C NMR. Analysis of the chemical shifts and coupling constants confirmed a pure trans stereochemical assignment of the 1-hexenyl group within the limits of detection by NMR (<3%).[16] In contrast, tribromoborane gave significant amounts of the divinylborane under the same conditions. However, boron trifluoride etherate did not afford any transmetalated products on reaction with the 1-hexenylzirconium complex, even after reflux for 48 h.

The addition of 5 mmol of the 1-hexenylzirconium complex to an equal molar solution of *B*-chlorocatecholborane in methylene chloride at 0 °C yielded the slow formation of an off-white precipitate within 0.25 h.



The proton NMR of this isolated solid material was identified as the zirconocene dichloride. The ^{11}B NMR of the reaction mixture showed the disappearance of the starting material at +28.5 ppm and the formation of a new signal at +30.9 ppm. Similar results were obtained by using *B*-bromocatecholborane. Both reactions indicate

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clean formation of the *B*-1-hexenylcatecholborane with conversions of greater than 90%, as measured by the ratio of boron species in the ^{11}B NMR. This boronic ester was isolated from the *B*-chlorocatecholborane in a 57% yield. Careful examination by ^{1}H and ^{13}C NMR did not detect any (<3%) regioisomeric or stereoisomeric products, indicating excellent product purity.[17,18] Although these vinyl boronic esters can be formed from the hydroboration of alkynes[19-21] with catecholborane or dihaloboranes, transmetalation may offer significant advantages over hydroboration. The hydrozirconation and transmetalation reaction offers a more rational route to 1-alkenyl and di-1-alkenylboranes, avoiding potential limitations in the hydroboration of 1-alkynes.[22] This unique migration suggests other potentially important groups that may transfer from zirconium to boron, expanding the number and types of organoboranes that can be readily prepared.

Other *B*-halodialkoxyboranes did not undergo transmetalation of the 1-hexenyl group in high yields. 2-Chloro-1,3,2-dioxaborinane afforded approximately 70% conversion to the transmetalated vinyl boronic ester within 10 min at 0 °C. The reaction did not proceed further after extended periods of time in which the product was isolated in 41% yield. *B*-Chlorodiisopropoxyborane, which can be prepared from the redistribution of boron trichloride and triisopropoxyborane in a 1:2 molar ratio, resulted in formation of approximately 40% alkenyldiisopropoxyborane over 24 h. These reactions show a complete and fast disappearance of the B-chlorodialkoxyborane and simultaneous appearance of a new signal at +17.8 ppm. It appears that this new signal is due to a novel complex formed with either the 2-chloro-1,3,2-dioxaborinane or *B*-chlorodiisopropoxyborane and the vinyl boronic ester. In a separate experiment, the addition of *B*-chlorodiisopropoxyborane and *B*-1-hexenyldiisopropoxyborane yielded a complex with the same chemical shift as formed in the transmetalation reaction. *B*-Chlorodimethoxyborane did not appear to form the expected vinyl boronic ester in any significant amounts within 24 h at room temperature.

The 1-hexenyl group can also be transferred to organohaloboranes. *B*-Bromo-9-BBN rapidly accepts the 1-hexenyl group within 5 min at 0 °C, forming the known *B*-1-hexenyl-9-BBN in 84% isolated yield. The sterically hindered dicyclohexylchloroborane also reacted cleanly within an hour to give the previously reported 1-hexenyldicyclohexylborane[23] in a 64% isolated yield. The reaction of *B*-chlorothexylhexylborane is somewhat slower, with an essentially quantitative yield of the thexylhexylhexenylborane after 2 h at room temperature. The reaction of the more sterically hindered *B*-chlorodiisopinocampheylborane does not go to completion within 24 h at room temperature but yields approximately 50% of the migrated vinyl product. Thus, it appears that almost any alkyl-substituted chloro- or bromoborane is capable of accepting a 1-hexenyl group from zirconium to give the 1-alkenylborane product.

In addition to the above halogens, we have found that *B*-methoxy groups can also exchange with a 1-hexenylzirconium complex. Unlike the chloro and bromo derivatives, these reactions do not proceed to completion even in the presence of 100% excess of the zirconium complex at room temperature within 24 h. Trimethoxyborane rapidly formed small amounts (less than 15%) of the exchanged product but did not proceed further over a period of 24 h. *B*-Methoxy-9-BBN was only slightly more effective, forming approximately 25% of the *B*-1-hexenyl-9-BBN after refluxing for 44 h. The more sterically hindered triisoporpoxyborane did not form any detectable amounts of transmetalated product. The results of these transmetalation reactions and product ratios are summarized in Table I.

To demonstrate the utility of this facile transmetalation, we prepared 5,7-tetradecadiene from (1-bromo-1-hexenyl)-1-octenylbromoborane, using a previously reported method for the selective coupling of divinylboranes to form the pure *trans,trans*-1,3-dienes. This unsymmetrical divinylborane was prepared from the migration of the 1-octenyl group from zirconium to (1-bromo-1-hexenyl)dibromoborane. The (1-bromo-1-hexenyl)dibromoborane was prepared by the hydroboration of 1-bromohexyne[24] and dibromoborane on a 24-mmol scale. In a separate reaction flask, 1-octyne (25 mmol) was hydrozirconated with Schwartz's reagent and then transmetalated to (1-bromo-1-hexenyl)-dibromoborane. The two alkenyl groups were then coupled as reported by others, using sodium methoxide, followed by protonation with isobutyric acid.[25] The crude product was isolated after distillation in a 49% yield. Analysis by GC–MS and ^{1}H NMR spectroscopy confirmed the formation of the expected product, *trans,trans*-5,7-tetradecadiene. The FT-IR spectrum showed only one expected stretching frequency at 990 cm^{-1} due to the trans,trans isomer and a complete absence of those stretching frequencies attributed to either the cis,-trans or the cis,cis isomeric material as expected at ca. 982, 948, and 1020 cm^{-1}. The above data are in agreement with previously reported spectral data for this isomeric diene[26] and indicate pure isomeric product within the limits of detectability for the trans,trans product.

Conclusion

In this note we have demonstrated that the simple 1-hexenyl group readily transmetalates to a variety of structurally different boranes. This reaction appears to be general for chloro- and bromoboranes. The reaction is essentially complete in nonpolar solvents within 2 h at room temperature to give the regio- and stereochemically pure 1-alkenylboranes. The methoxy group also undergoes migration, although in much lower yields, and at this point does not appear to be useful. These results suggest potentially new important applications of the organozirconium complexes to form new types of organoboranes. We are currently investigating the transmetalation of other organic groups from zirconium to boron compounds.

Experimental Section

General Comments. All glassware was dried at 130 °C for at least 4 h, assembled hot, and cooled under a stream of nitrogen. All reactions were carried out under a static pressure of nitrogen. $Cp_2ZrH(Cl)$, Schwartz's reagent, was prepared as previously reported by Buchwald.[14] The boron trihalides, *B*-chlorocatecholborane, *B*-bromo-9-BBN, *B*-chlorodiisopinocampheylborane, trimethoxyborane, triisopropoxyborane, and 1-hexyne were obtained from commercial sources (Aldrich). The following reagents were prepared according to literature procedures: *B*-methoxy-

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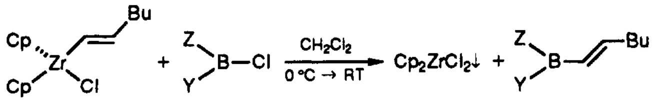
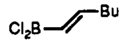
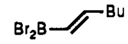
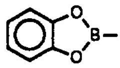
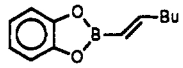
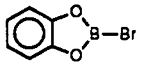
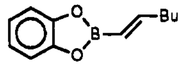
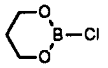
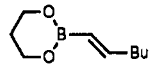
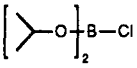
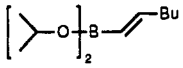
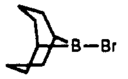
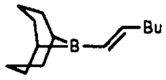
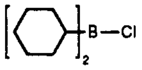
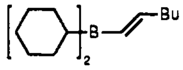
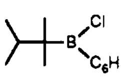
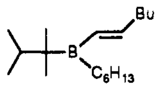
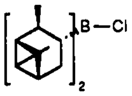
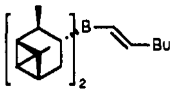
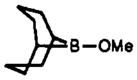
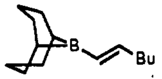
Table I. Migration of 1-Hexenyl Groups from Zirconium to Various Boron Compounds



borane	chem shift	product	chem shift	chem shift after methanolysis	^{11}B NMR prod ratios, %
BCl_3	41.9		53.0	27.4	>90
BBr_3	38.5		52.1	27.4	53
	28.5		30.9	27.2	>90
	26.9		30.5	27.2	>90
	23.5		25.8		~70
	22.8		26.0		~40
	83.6			-1.7[a]	>90
	76.2		73.4		~90
	79.0		76.5	76.5	>90
	74.2		73.8	73.8	~50
$B(OMe)_3$	18.2		27.0		~15
	56.4		76.4		~25

[a] Pyridine added in place of methanol to form the pyridine complex.

9-BBN;[27] thexylhexylchloroborane;[28] *B*-chlorodiisopropoxyborane; *B*-chloro-1,3,2-dioxaborinane;[29] *B*-chlorodicyclohexylborane.[30,31] Solvents used were ACS grade and were dried prior to use. Manipulation of borane reagents was done under nitgrogen atmosphere by using hypodermic and double-ended needles and solids were handled in a glovebag.[32] The ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded with a Chemagnetics 200-MHz spectrometer. Chemical shift values are given in parts per million (δ) relative to Me_4Si for ^{1}H and ^{13}C NMR and relative to $BF_3 \cdot OEt_2$ in ^{11}B NMR. GC-MS was performed on a Finnigan 3000 GC/MS + 6110 MS data system.

Preparation of Dicyclopentadienyl-1-hexenylzirconium Chloride.[1] To a 50-mL flask was a septum-covered side arm, equipped with a magnetic stirring bar and adapter, was added 20 mmol of Schwartz's reagent, $Cp_2ZrH(Cl)$ (5.16 g), suspended in 15 mL of methylene chloride. The mixture was cooled to 0 °C and 22 mmol 1-hexyne (1.81 g, 2.50 mL) was slowly added, followed by an additional 2.50 mL of methylene chloride to give an approximate 1 M solution. After 15–30 min, the solid disappeared to give a clear yellow solution: ^{1}H NMR ($CDCl_3$) δ 6.80 (dt, 1 H, J = 18 Hz), 6.22 (s, 10 H), 5.76 (d, 1 H, J = 18 Hz), 1.93 (q, 2 H), 1.32 (m, 4 H), 0.89 (t, 3 H).

General Procedure for the Transmetalation from Zirconium to Boron. To a 25-mL flask with a septum-covered side arm, equipped with a magnetic stirring bar and adapter, was added ca. 5 mmol of the borane in 5 mL of methylene chloride. The solution was cooled to 0 °C and a stoichiometric amount of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added. The reaction forms an off-white precipitate, generally within 15–30 min. The extent of reaction can be estimated by using the ratio of peak areas in the ^{11}B NMR. This method appears to give satisfactory results for boron-containing species with similar peak widths. The comparison of this method with weighted mixtures of the pure authentic boron products agreed within ±3%. This procedure has also been used to estimate the concentration of organolithiums by reacting with trialkoxyboranes and analyzing by ^{11}B NMR.[33] Nöth and Wrackmeyer have also reported using this method to determine ratios of boron products in equilibrium mixtures.[34] To distinguish between borane products that have similar chemical shifts, the reactions mixtures were analyzed both before and after methanolysis or complexation with a suitable base such as pyridine. Table I summarizes the results of these reactions. Products were isolated by first separating the solids from the reaction mixture and the solvent was removed under reduced pressure. The residue was extracted with

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4 × 5 mL of pentane followed by removal of the pentane from the combined extracts to yield pure product, as indicated by NMR.

Preparation of (*E*)-1-Hexenyldichloroborane.[35] The preparation was conducted as in the general procedure by adding 5 mmol of the dicyclopentadienyl-1-hexenylzirconium chloride solution to boron trichloride in methylene chloride (5 mmol, 5 mL): ^{11}B NMR (CH_2Cl_2) +53.0 ppm, after methanolysis +27.4 ppm, >90% product ratio based on ^{11}B NMR. In order to assign the stereochemistry of the vinyl group, the (*E*)-1-hexenyldichloroborane was isolated from the reaction mixture and converted into the corresponding methyl ester and analyzed by NMR spectroscopy for retention of the trans stereochemistry as reported by Brown.[36] Spectroscopic data are in agreement with reported values, indicating retention of the 1-alkenyl group. ^{1}H NMR ($CDCl_3$) δ 6.52 (dt, 1 H, *J* = 18 Hz), 5.42 (d, 1 H, *J* = 18 Hz), 2.13 (m, 2 H), 1.30 (m, 4 H), 0.90 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 152.00, 50.89, 35.30, 30.57, 22.30, 13.97.

Preparation of (*E*)-1-Hexenyldibromoborane.[37] As in the general procedure, 5 mmol of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added to boron tribromide in methylene chloride (5 mmol, 5 mL): ^{11}B NMR (CH_2Cl_2) δ +52.1 ppm, after methanolysis +27.4 ppm, 53% ratio of boron containing materials.

Preparation of *B*-(*E*)-1-Hexenyl-1,3,2-dioxaborazole.[20] The preparation was conducted as in the general procedure by adding 9.9 mmol of the dicyclopentadienyl-1-hexenylzirconium chloride solution to 9.9 mmol of *B*-chlorocatecholborane (1.529 g) in 10 mL of methylene chloride. The same experiment was also conducted by using 10 mmol of *B*-bromocatecholborane (0.994 g) in methylene chloride and the product characterized by ^{11}B: ^{11}B NMR (CH_2Cl_2) δ +30.5 (Br), +30.9 ppm (Cl), after methanolysis +27.2 ppm, >90% product ratio for both reactions. The *B*-chlorocatecholborane derivative was isolated as in the general procedure to yield 1.133 g or 57% *B*-(*E*)-1-hexenyl-1,3,2-dioxaborazole. Spectroscopic data are in agreement with expected and reported values:[18,38] ^{11}B NMR ($CDCl_3$) δ 31.1; ^{1}H NMR ($CDCl_3$) δ 7.24–7.06 (m, 5 H), 5.73 (d, 1 H, *J* = 18.0 Hz), 2.19 (q, 2 H, *J* = 6.4 Hz), 1.5–1.2 (m, 4 H), 0.88 (t, 3 H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 157.58, 148.36, 122.24, 115.58, 112.09, 35.63, 30.25, 22.19, 13.70; IR (neat) 3063, 2959, 2929, 2860, 1640, 1474, 1402, 1375, 1334, 997, 810, 741 cm^{-1}. EI mass spectrum: *m*/*z* (relative intensity) 202 (M^+, 46), 173 (20), 160 (71), 159 (34), 146 (100), 145 (39), 120 (40), 67 (31), 65 (39).

Preparation of (*E*)-1-Hexenyl-9-BBN[39] from *B*-Bromo-9-BBN. Ten millimoles of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added to *B*-bromo-9-BBN in methylene chloride (10 mmol, 10 mL). To distinguish between starting material and the vinyl-9-BBN product, 5 mmol of pyridine was added, forming the borane amine complexes: ^{11}B NMR (CH_2Cl_2) δ −1.70 ppm, >90% ratio of boron-containing materials. Isolation of the compound afforded 1.71 g or 84% yield of (*E*)-1-hexenyl-9-BBN. Spectroscopic data are in agreement with expected and reported values.[39] ^{11}B NMR ($CDCl_3$) δ 77.4; ^{1}H NMR ($CDCl_3$) δ 6.84 (dt, 1 H, *J* = 6.4, 17.5 Hz), 6.22 (d, 1 H, *J* = 17.3 Hz), 2.26 (q, 2 H, *J* = 6.9 Hz), 2.00–1.65 (m, 12 H), 1.60–1.15 (m, 6 H), 0.95 (t, 3 H, *J* = 7.6 Hz); ^{13}C NMR (CH_2Cl_2) δ 156.38, 36.12, 34.08, 31.02, 28.87, 22.69, 14.04; IR (neat) 2927, 1635, 1613, 1468, 1447, 1381, 1333, 999 cm^{-1}. EI mass spectrum, *m*/*z* (relative intensity) 206 (M^+, 27), 148 (22), 147 (20), 134 (43), 133 (37), 120 (72), 119 (52), 108 (26), 106 (41), 105 (40), 93 (54), 92 (89).

Preparation of 1-Hexenyldicyclohexylborane.[23] The dicyclohexylchloroborane was prepared by the procedure reported by Brown[30] or from the addition of anhydrous hydrogen chloride to dicylohexylborane using the procedure of Zweifel.[31] By use of the general procedure, 10 mmol of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added to the dialkylcholorborane. The product was isolated in a 64% isolated yield (1.66 g). Spectroscopic data are in agreement with expected and previously reported values.[23] ^{11}B NMR ($CDCl_3$) δ 73; ^{1}H NMR ($CDCl_3$) δ 6.72 (dt, 1 H, *J* = 17.6, 6.3 Hz), 6.20 (d, 1 H, *J* = 17.5 Hz), 2.21 (q, 2 H, *J* = 6.7 Hz), 1.72 (m, 10 H), 1.46–1.26 (m, 16 H), 0.91 (t, 3 H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 154.11, 133.65, 36.11, 34.44, 30.90, 27.83, 27.67, 27.24, 22.41, 13.92; IR (neat) 3078, 2958, 2921, 2847, 1612, 1447, 1371, 1145, 997 cm^{-1}.

Preparation of *B*-(*E*)-1-Hexenyl-1,3,2-dioxaborinane.[16] The dioxaborinane (10 mmol) was prepared by the procedure reported by Finch, redistributing boron trichloride in methylene chloride (3.35 mmol, 3.35 mL) with 6.6 mmol of trimethylene borate (1.624 g, 1.4 mL).[29] Using the general procedure, 10 mmol of the dicyclopentadienyl-1-hexenylzirconium chloride solution was added to the freshly prepared *B*-chloro-1,3,2-dioxaborinane: ^{11}B NMR (CH_2Cl_2) +25.8 ppm, in an approximate 70% product ratio. The product was obtained in a 41% isolated yield (0.652 g). Spectroscopic data are in agreement with expected and reported values.[16] ^{11}B NMR ($CDCl_3$) δ 26.97; ^{1}H NMR ($CDCl_3$) δ 6.47 (dt, 1 H, *J* = 6.3, 17.8 Hz), 5.32 (d, 1 H, *J* = 17.8 Hz), 3.98 (t, 4 H, *J* = 5.6 Hz), 2.10 (q, 2 H, *J* = 7.1 Hz), 1.92 (p, 2 H), 1.55–1.20 (m, 4 H), 0.88 (t, 3 H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 150.78, 123.32, 61.20, 34.82, 30.41, 27.24, 21.87, 13.43; IR (neat) 2957, 2873, 1640, 1484, 1421, 1326, 1000, 911, 735 cm^{-1}; EI mass spectrum, *m*/*z* (relative intensity) 168 (M^+, 10), 153 (10), 140 (34), 139 (44), 126 (100), 125 (58), 111 (58), 97 (51), 86 (86).

Preparation of 1-Bromo-1-hexyne.[24] To a 250-mL flask with a septum-covered side arm, equipped with a magnetic stirring bar and adapted, was added 18 g (300 mmol) of potassium hydroxide and 100 mL of water was added to dissolve the alkali. The mixture was cooled to 0 °C and 50 mmol of bromine (2.75 mL) was added dropwise over 15 min. Fifty millimoles of 1-hexyne (4.1 g, 5.75 mL) was added to this mixture at 0 °C and the solution was allowed to stir and come to room temperature overnight. The aqueous layer was extracted with ether (3 × 25 mL). The ether extracts were dried over anhydrous magnesium sulfate; then, after removal of the solvent, the product was isolated by distillation. Isolated yield: 4.51 g (56%) of 1-bromo-1-hexyne, bp 44–47 °C (18 mmHg): ^{1}H NMR ($CDCl_3$) δ 2.20 (t, 2 H), 1.46 (m, 4 H), 0.91 (t, 3 H), EI mass spectrum, *m*/*z* (relative intensity) 160 (M^+, 100), 162 ($M + 2^+$, 99), 147 (30), 145 (34), 119 (100), 117 (100), 115 (90), 81 (100), 79 (100).

Preparation of 5,7-Tetradecadiene.[26] 1-Bromo-1-hexyne was hydroborated at 0 °C with 1.0 M dibromoborane–methyl sulfide in methylene chloride (24 mmol, 24 mL). Dicyclopentadienyl-1-octenylzirconium chloride (25 mmol) was prepared in the same manner as previously reported for hydrozirconation reactions. The zirconocene complex was added at 0 °C to the dibromoalkenylborane and after 15 min an off-white precipitate appeared. After removal of the precipitate, the dialkenylbromoborane was isolated by evaporation of the solvent under reduced pressure. The borane was then dissolved in 50 mL of THF and 3.89 g (72 mmol) of sodium methoxide in 72 mL of methanol was added at −25 °C. The cold bath was removed after 5 min and stirring was continued for 1 h at room temperature. The solvents were removed under reduced pressure. The flask was fitted with a reflux condenser and the vinylborane was protonated by using 25 mL of isobutyric acid under reflux conditions for 3 h. The reaction was cooled and added to 100 mL of water and extracted with diethyl ether (6 × 25 mL). The ether extract was washed with a saturated aqueous solution of sodium carbonate to remove isobutyric acid and then oxidized with 8.5 mL of 3 M NaOH and 8.5 mL of 30% H_2O_2 to remove boron-containing materials. The aqueous layer was extracted again with diethyl ether and the combined ether layers were dried over magnesium sulfate. The solvent was removed at reduced pressure and the product was distilled to give 2.27 g (49%) of the *trans*,*trans*-5,7-tetradecadiene, bp 65–70 °C (0.5 mmHg). Spectroscopic data are in agreement with expected and reported values:[26] ^{1}H NMR ($CDCl_3$) δ 6.0 (d, 2 H, *J* = 14.6 Hz), 5.56 (dt, 2 H, *J* = 14.6 Hz), 2.05 (q, 4 H), 1.30 (m, 12 H), 0.89 (t, 6 H); IR (neat) 3015, 2959, 2928, 2857, 1626, 1467, 990, 906 cm^{-1}; EI mass spectrum, *m*/*z* (relative intensity) 194 (M^+, 16), 123 (15), 110 (46), 109 (29), 96 (38), 95 (62), 82 (71), 81 (100).

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Registry No. $Cp_2ZrH(Cl)$, 37342-97-5; BCl_3, 10294-34-5; BBr_3, 10294-33-4; $B(OMe)_3$, 121-43-7; *B*-bromo-9-BBN, 22086-45-9; *B*-methoxy-9-BBN, 38050-71-4; *B*-(*E*)-1-hexenyl-9-BBN pyridine complex, 136115-27-0; *B*-(*E*)-1-hexenyl-9-BBN, 69322-45-8; 1-hexyne, 693-02-7; bis(cyclopentadienyl)-1-hexenylzirconium chloride, 79083-22-0; bis(cyclopentadienyl)-1-octenylzirconium chloride, 63175-90-6; *B*-chlorocatecholborane, 55718-76-8; *B*-bromocatecholborane, 51901-85-0; *B*-chloro-1,3,2-dioxaborinane, 1003-43-6; *B*-chlorodiisopropoxyborane, 66009-09-4; dicyclohexylchloroborane, 36140-19-9; *B*-chlorohexylhexylborane, 88817-20-3; *B*-chlorodiisopinocamphenylborane, 85116-37-6; (*E*)-1-hexenyldichloroborane, 51207-21-7; (*E*)-1-hexenyldibromoborane, 72228-55-8; *B*-(*E*)-1-hexenyl-1,3,2-benzodioxaborole, 37490-22-5; *B*-(*E*)-1-hexenyl-1,3,2-dioxaborinane, 91083-28-2; (*E*)-1-hexenyldiisopropoxyborane, 91083-27-1; (*E*)-1-hexenyldicyclohexylborane, 37609-12-4; thexylhexyl-(*E*)-1-hexenylborane, 136089-08-2; *B*-(*E*)-1-hexenyldiisopinocamphenylborane, 70179-28-1; (*E*)-1-hexenyldimethoxyborane, 91083-26-0; 1-bromo-1-hexyne, 1119-64-8; dibromoborane–methyl sulfide, 55671-55-1; (1-bromo-1-hexenyl)dibromoborane, 136089-09-3; (1-bromo-1-hexenyl)-1-octenylbromoborane, 136089-10-6; isobutyric acid, 79-31-2; *trans,trans*-5,7-tetradecadiene, 73349-16-3.

Synthesis of Cadmium Pentamethylcyclopentadienyl Complexes

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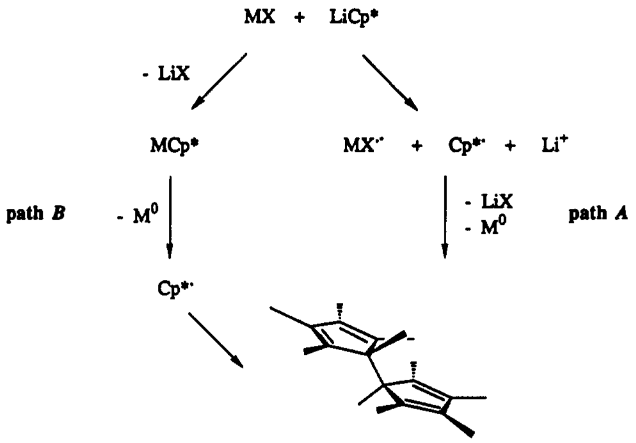
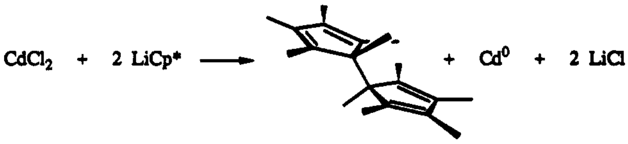
Summary: The preparation of red, light-sensitive cadmium bis(pentamethylcyclopentadienide) has been effected by reaction of $Cd(acac)_2$ with 2 equiv of $LiCp^*$ in the dark. $CdCp^*_2$ forms a weak adduct with 1,2-dimethoxyethane (DME). A Schlenk-type equilibrium exists when $CdCp^*_2$ is mixed with an equimolar amount of $Cd[N(SiMe_3)_2]_2$, giving solutions from which $(CdCp^*[N(SiMe_3)_2])_2$ can be crystallized. Single-crystal X-ray diffraction revealed the dimeric nature of the latter complex, which displays bridging silylamides and terminal Cp* ligands. Bonding of the Cp* ligand to cadmium in this complex is regarded primarily as σ in character, but a weak dative interaction between the diene HOMO and the empty cadmium p_z orbital is plausible in view of structural parameters. The structure determination is believed to be the first on any complex containing either a cadmium amide *or* a cadmium pentamethylcyclopentadienide linkage.

Introduction

Cadmium compounds that contain bulky ligands are currently of interest with respect to the design of molecular precursors to semiconductors such as CdS and CdSe.[1] Alkyl,[1a] thiophenoxide,[1b] and selenophenoxide[1b] complexes are examples that recently have been synthesized with this purpose in mind. The absence of pentamethylcyclopentadienyl (Cp*) complexes in the list is especially surprising, since the Cp* ligand has been useful in stabilizing a wide variety of low-coordinate compounds that contain metals throughout the periodic table.[2] We became interested in preparing Cp* cadmium complexes as part of a project concerned with the synthesis of semiconductor clusters employing ROMP block copolymer technology.[3]

Scheme I





(1)

It is reported in the literature that $CdCl_2$ is efficiently reduced by $LiCp^*$ in tetrahydrofuran (THF) to give colloidal cadmium, LiCl, and $C_{10}Me_{10}$ (eq 1).[4] Although details of this reaction are not known, $C_{10}Me_{10}$ most likely is formed via coupling of C_5Me_5 radicals, which are known to be generated upon oxidation of $C_5Me_5^-$ or upon photolysis of Cp* derivatives (including the parent hydrocarbon, C_5Me_5H) and to combine to give $C_{10}Me_{10}$ at diffusion-controlled rates.[5] Interestingly, Jutzi and Kohl expressed doubt that the original report[6] of $HgCp^*_2$ is correct, since its reported ^{1}H NMR spectrum is virtually identical with that obtained by them for $C_{10}Me_{10}$, which they produced by adding pyridine to $SnCp^*_2I_2$.[7] It also

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