# Organoboranes. 45. An Exploration of the Effectiveness of Representative Homologating Agents with Various Organoborane Derivatives: $R_3B$, $R_2BOR'$, and $RB(OR')_2$

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An exploratory study was undertaken to establish the effectiveness of representative homologating agents for trialkylboranes ($R_3B$) and borinic ($R_2BOR'$) and boronic esters ($RB(OR')_2$). Numerous reactions which work well with $R_3B$ fail with $RB(OR')_2$. Only $LiCHCl_2$ has been shown previously to react well with all three classes of boron compounds. The one-carbon homologation of tri-*n*-butylborane and *B*-methoxyborinane is achieved by treatment with (chloro(trimethylsilyl)methyl)lithium, followed by the desilylation of the boron intermediates to obtain dibutylpentylborane and *B*-methylborepane in high yields. Interestingly, the homologation using (methoxy(phenylthio)methyl)lithium works efficiently for tri-*n*-butylborane without the addition of mercury(II) chloride to facilitate the transfer reaction, while the homologation of *B*-methoxyborinane using the same reagent requires the addition of mercury(II) chloride to afford *B*-methoxy-2-methoxyborepane in high yield. Since the homologation of boronic esters has been previously demonstrated, there are now available three different reagents, $LiCHCl_2$, $LiCHClSiMe_3$, and $LiCH(OMe)SPh$, which are generally applicable to $R_3B$, $R_2BOR'$, and $RB(OR')_2$.

In the initial phases of the development of organoborane reactions, it was observed that many reagents react readily with trialkylboranes to achieve transfer reactions[1] (eq 1–9).

$$R_3B + CO + LiAlH(OCH_3)_3 \rightarrow \rightarrow RCH_2OH \quad (1)$$

$$R_3B + HCCl_3 + 2LiOCEt_3 \rightarrow \rightarrow R_3COH \quad (2)$$

$$R_3B + HCClF_2 + 2LiOCEt_3 \rightarrow \rightarrow R_3COH \quad (3)$$

$$R_3B + HCCl_2OMe + LiOCEt_3 \rightarrow \rightarrow R_3COH \quad (4)$$

$$R_3B + BrCH_2CO_2Et + t\text{-BuOH} \rightarrow RCH_2CO_2Et \quad (5)$$

$$R_3B + BrCH_2COPh + t\text{-BuOK} \rightarrow RCH_2COPh \quad (6)$$

$$R_3B + ClCH_2CN + t\text{-BuOK} \rightarrow RCH_2CN \quad (7)$$

$$R_3B + N_2CHCO_2Et \rightarrow RCH_2CO_2Et \quad (8)$$

$$R_3B + NaCN + (CF_3CO)_2O \rightarrow \rightarrow R_3COH \quad (9)$$

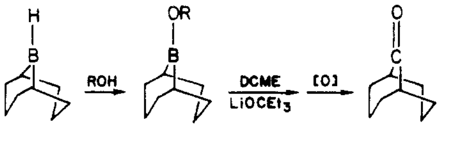
However, with one exception, these reagents have failed to react with either borinic esters or boronic esters[2] (eq 10 and 11).

$$R_2BOR' + CO \rightarrow \text{no reaction} \quad (10)$$

$$RB(OR')_2 + CO \rightarrow \text{no reaction} \quad (11)$$

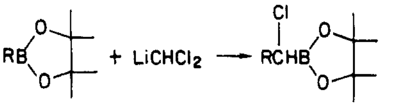
Only in the case of $\alpha,\alpha'$-dichloromethyl methyl ether (DCME) did we achieve a facile reaction with borinic esters in the presence of 2 equiv of lithium triethylcarboxide, making possible the convenient synthesis of ketones[3] (eq 12). For example, the reaction of *B*-alkoxy-9-borabicyclo[3.3.1]nonane with the above reagent provided an elegant synthesis of bicyclo[3.3.1]nonan-9-one[1] (eq 13).

$$R_2BOR' + HCCl_2OMe + 2LiCOEt_3 \rightarrow \rightarrow RCOR \quad (12)$$



(13)

Recently, Matteson and his co-workers established that (dichloromethyl)lithium and (chloro(trimethylsilyl)methyl)lithium[4-6] could react with boronic esters to provide the corresponding homologated boronic esters (eq 14 and 15).



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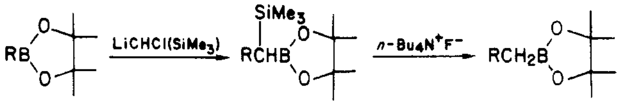
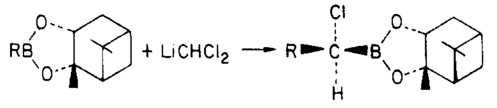


(15)

Indeed, they successfully utilized (dichloromethyl)lithium for the preparation of chiral boronic esters. Thus, the homologation of chiral pinanediol alkylboronates with the above reagent yields chiral boronic esters in very high enantiomeric excess[7] (eq 16).



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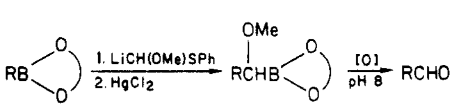
Similarly, we recently reported another carbanionic reagent, (methoxy(phenylthio)methyl)lithium, which reacts with boronic esters to provide homologated boronic esters, oxidized easily into aldehydes[8] (eq 17).



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(1) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

(2) Brown, H. C., unpublished results.

(3) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6878.

(4) The reagent was first generated in situ by Larson and his coworkers. (a) Rosario, O.; Oliva, A.; Larson, G. L. *J. Organomet. Chem.* **1978**, *146*, C8. (b) Larson, G. L.; Arguelles, R.; Rosario, O.; Sandoval, S. *Ibid.* **1980**, *198*, 15. (c) Rosario, O.; Sandoval, S.; Larson, G. L. *Synth. Commun.* **1980**, *10*, 813.

(5) (a) Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (b) *Organometallics* **1983**, *2*, 1529.

(6) (a) Matteson, D. S.; Majumdar, D. *J. Organomet. Chem.* **1980**, *184*, C41. (b) Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236.

(7) (a) Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7590. (b) Matteson, D. S.; Ray, R.; Rocks, R. R.; Tsai, D. J. *Organometallics* **1983**, *2*, 1536.

(8) Brown, H. C.; Imai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6285.

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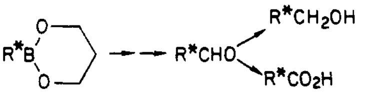
**Table I. Reactions of Organoboranes with a Variety of Reagents[a]**

| reagent | $R_3B$ | $R_2BOR'$ | $RB(OR')_2$ |
|---|---|---|---|
| CO | +[b] | − | − |
| $HCCl_3/LiOCEt_3$ | + | | |
| $LiCCl_3$ | +[c] | | |
| $HCClF_2/LiOCEt_3$ | + | | |
| $BrCH_2CO_2Et$/*t*-BuOK | + | | |
| $BrCH_2CN$/*t*-BuOK | + | | |
| $N_2CHCO_2Et$ | +[d] | | |
| $HCCl_2OMe/LiOCEt_3$ | + | + | |
| $LiCHCl_2$ | + | + | + |
| $LiCHCl(SiMe_3)$ | | | + |
| LiCH(OMe)SPh | | | + |

[a] The positive (+) sign indicates reactions that worked while the negative (−) sign is indicative of the reactions that did not work. [b] Reference 17. [c] Reference 10. [d] Reference 18.

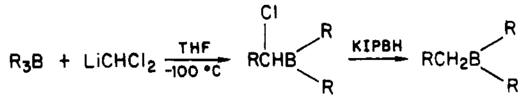
The above reaction has proven exceptionally valuable for the synthesis of optically active aldehydes, alcohols, and carboxylic acids. Thus, the homologation of chiral boronic esters with the above reagent provides the above products in essentially 100% ee[9] (eq 18).



(18)

Thus, we had numerous reactions known to be applicable to triorganylboranes, three reactions known to be applicable to boronic esters, but only one reaction (DCME) known to be applicable to borinic esters (Table I).

Recently, we demonstrated that the reaction of (dichloromethyl)lithium with trialkylboranes and borinic and boronic esters at −100 °C, followed by the reduction of the boron intermediates with potassium triisopropoxyborohydride (KIPBH), provided one-carbon homologated organoboranes in excellent yields[11] (eq 19–21).



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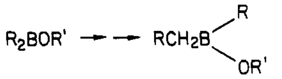

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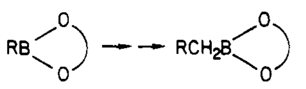
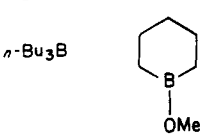


(21)

It was of interest to see if the other two reagents, (chloro(trimethylsilyl)methyl)lithium and (methoxy(phenylthio)methyl)lithium, recently established for the homologation of boronic esters, could be applicable to trialkylboranes and borinic esters. We also explored the possibility that those reactions which are known to work well with $R_3B$ (Table I) could be applied to $RB(OR')_2$.

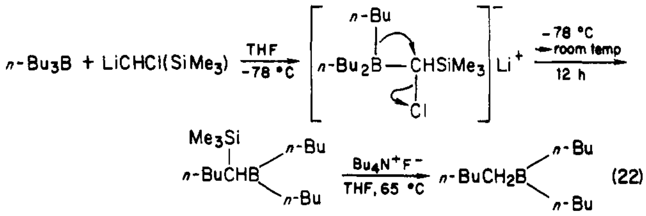
Accordingly, we chose tri-*n*-butylborane and *B*-methoxyborinane[12] as a representative trialkylborane and borinic ester respectively for the study of the applicability of the above two reagents to achieve homologation.



We were gratified to find that both (chloro(trimethylsilyl)methyl)lithium[4] and (methoxy(phenylthio)methyl)lithium work efficiently with both tri-*n*-butylborane and *B*-methoxyborinane and provide the corresponding homologated products in excellent yields.

## Results and Discussion

Homologation of tri-*n*-butylborane utilizing (chloro(trimethylsilyl)methyl)lithium[4] and (methoxy(phenylthio)methyl)lithium[13,14] was first studied. To a mixture of (chloromethyl)trimethylsilane in tetrahydrofuran (THF) was added *sec*-butyllithium in cyclohexane dropwise at −78 °C, followed by the addition of tetramethylethylenediamine (TMED). After being stirred for 45 min, the reaction mixture was warmed to −55 °C and tri-*n*-butylborane in THF added to the reaction mixture. Following the addition, the contents were cooled to −78 °C and allowed to reach room temperature slowly as the bath warmed over a period of 12 h. The $^{11}B$ NMR spectrum of the reaction mixture revealed the formation of dibutyl(1-(trimethylsilyl)pentyl)borane (δ +83). The product was isolated from the reaction mixture by pumping off the solvents and extracting the residue with *n*-pentane. The crude dibutyl(1-(trimethylsilyl)pentyl)borane thus obtained was desilylated with tetrabutylammonium fluoride in THF at 65 °C to provide dibutylpentylborane in excellent yield (eq 22). We determined the yield and purity of dibutylpentylborane by oxidation and GC identification and analysis of 1-pentanol.



(22)

We then explored the homologation of tri-*n*-butylborane with the second reagent, (methoxy(phenylthio)methyl)lithium.[13] Thus, *sec*-butyllithium was added dropwise to a mixture of methoxymethyl phenyl sulfide in THF at −55 °C. Following the addition, the reaction mixture was stirred for 1 h and then cooled to −78 °C. Tri-*n*-butylborane in THF was added to the reaction mixture. After 30 min, the $^{11}B$ NMR spectrum of an aliquot of the reaction mixture showed the formation of two borate complexes A (δ −18) and B (δ −0.2). The peak at δ −0.2 can be attributed to the complex B resulting from the migration of the *n*-butyl group to the carbon bearing the methoxy group, with the latter acting as a leaving group in the borate complex A. As the reaction proceeds, the peak at δ −18 decreases with the concurrent increase of the peak at δ −0.2. Finally, it completely disappears as the reaction mixture was brought from −78 °C to room temperature over 4 h. The homologated boron intermediate obtained was oxidized with hydrogen peroxide in the presence of phosphate buffer (pH 8) to afford 1-pentanal in high yield, analyzed by GC as 1-pentanol following reduction with borane–dimethyl sulfide (eq 23).

In this procedure addition of mercury(II) chloride was unnecessary since the methoxy group served spontaneously as the leaving group.

We next applied these two carbanionic reagents to the homologation of *B*-methoxyborinane. (Chloro(tri-

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[9] Brown, H. C.; Imai, T.; Desai, M. C.; Singaram, B. *J. Am. Chem. Soc.*, in press.

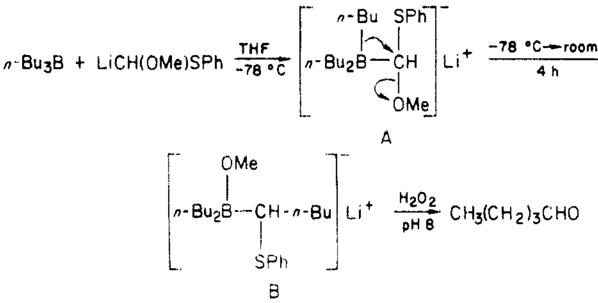
[10] Brown, H. C.; Singh, S. M., unpublished results.

[11] Brown, H. C.; Naik, R. G.; Singaram, B.; Pyun, C. *Organometallics*, in press.

[12] (a) Brown, H. C.; Pai, G. G. *J. Organomet. Chem.* **1983**, *250*, 13. (b) Brown, H. C.; Zaidlewicz, M. *J. Am. Chem. Soc.* **1976**, *98*, 4917.

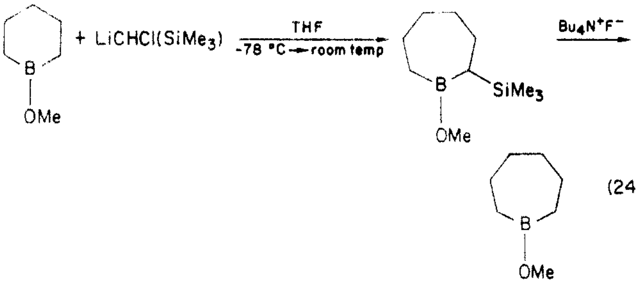
[13] 1,6-Hexanediol thus obtained was silylated with bis(trimethylsilyl)acetamide (BSA) prior to use for GC analysis. Silylated 1,6-hexanediol was identified by GC coinjection with an authentic sample.

[14] Brown, H. C.; Imai, T. *J. Org. Chem.* **1984**, *49*, 892.



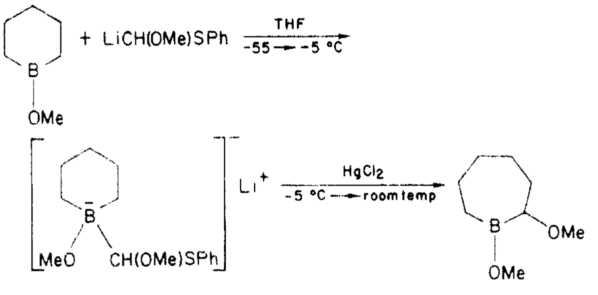
(23)

methylsilyl)methyl)lithium, prepared as described above, was treated with *B*-methoxyborinane at −78 °C. Following the addition, the contents were allowed to warm to room temperature over a period of 12 h. The $^{11}$B NMR analysis of the reaction mixture revealed the formation of *B*-methoxy-2-(trimethylsilyl)borepane ($\delta$ +54), which was desilylated with tetrabutylammonium fluoride to furnish *B*-methoxyborepane in high yield (eq 24). *B*-Methoxyborepane was characterized and identified by the oxidation and GC analysis of the silylated 1,6-hexanediol.[15]



(24)

We then turned our attention to examine the reaction of *B*-methoxyborinane with (methoxy(phenylthio)-methyl)lithium. To a mixture of (methoxy(phenylthio)-methyl)lithium in THF was added *B*-methoxyborinane in THF. Following the addition, the reaction mixture was stirred for 2 h at −55 to −5 °C. The $^{11}$B NMR spectrum of the reaction mixture showed the formation of borate complex ($\delta$ −1). The alkyl migration was induced by the addition of mercury(II) chloride, stirring the reaction mixture over a period of 12 h from −5 °C to room temperature, as indicated by the $^{11}$B NMR spectrum ($\delta$ +53). Oxidation of the reaction mixture with hydrogen peroxide in the presence of phosphate buffer (pH 8) gave 6-hydroxyhexanal, reduced with borane–dimethyl sulfide to provide 1,6-hexanediol in good yield (eq 25).



(25)

We also attempted to achieve the successful reaction of boronic esters with the reagents that work so well with trialkylboranes (Table I), but the reagents studied, $HCCl_3/LiOCEt_3$, $LiCCl_3$, $HCClF_2/LiOCEt_3$, $BrCH_2CO_2Et/t$-BuOK, $BrCH_2CN/t$-BuOK, $N_2CHCO_2Et$, and $HCCl_2OMe/LiOCEt_3$, failed to undergo successful reaction with boronic esters (Table II). We did not explore with borinic esters reagents that failed to undergo satisfactory reaction with the boronic esters.

**Table II. Homologation of Organoboranes with the Various Reagents**[a]

| reagent | $R_3B$ | $R_2BOR'$ | $RB(OR')_2$ |
|---|---|---|---|
| CO | +[b] | − | − |
| $HCCl_3/LiOCEt_3$ | + | | −[e] |
| $LiCCl_3$ | +[c] | | −[e,f] |
| $HCClF_2/LiOCEt_3$ | + | | −[g] |
| $BrCH_2CO_2Et/t$-BuOK | + | | −[g] |
| $BrCH_2CN/t$-BuOK | + | | −[g] |
| $N_2CHCO_2Et$ | +[d] | | −[g] |
| $HCCl_2OMe/LiOCEt_3$ | + | + | −[e] |
| $LiCHCl_2$ | + | + | + |
| $LiCHCl(SiMe_3)$ | + | + | + |
| LiCH(OMe)SPh | + | + | + |

[a] The positive (+) sign is indicative of reactions that work satisfactorily while the negative (−) sign indicates reactions that did not work. [b] Reference 17. [c] Reference 10. [d] Reference 12. [e] Brown, H. C.; Singh, S. M., unpublished results. [f] Reaction of the thioboronic esters with (trichloromethyl)lithium gave homologated carboxylic acid in high yield.[13] [g] Brown, H. C.; Imai, T., unpublished results.

Thus, the present study establishes two more valuable reagents capable of achieving the homologation of all three types of organoboranes. We now have numerous reagents that operate satisfactorily for trialkylboranes (Table I), four reagents which can be successfully utilized for borinic esters and three reagents applicable to boronic esters (Table II).

## Experimental Section

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[1] $^1$H NMR spectra were recorded on a Varian T-60 (60-MHz) spectrometer. $^{11}$B NMR spectra were recorded on a Varian FT-80A instrument. The GC analyses were carried out on a Varian 1200 research chromatograph equipped with a flame ionization detector (columns 12 ft × $^1/_8$ in. packed with 5% Carbowax 20M on Chromosorb W and 5% SE-30 on Chromosorb W AW DMCS).

**Materials.** Tetrahydrofuran (THF) was freshly distilled prior to use. Methoxymethyl phenyl sulfide was prepared by adding chloromethyl methyl ether to a solution of lithium thiophenolate in THF: 82% yield; bp 112–113 °C (18 torr) [lit.[16] bp 108 °C (12 torr)]. *B*-Methoxyborinane was prepared by the action of methanol to a solution of borinane in THF. Tri-*n*-butylborane in THF and (chloromethyl)trimethylsilane were purchased from Aldrich Chemical Co. A phosphate buffer solution was prepared by alternate addition of $NaH_2PO_4$ and $K_2HPO_4$ into distilled water to bring the solution to pH 8 (pH meter). The solution was ca. 2.5 M in total phosphate concentration.

**Homologation of Tri-*n*-butylborane with (Chloro(trimethylsilyl)methyl)lithium.** To a mixture of (chloromethyl)trimethylsilane (0.92 mL, 6.6 mmol) in THF (6 mL) was added *sec*-butyllithium (4.2 mL, 5.5 mmol) in cyclohexqane dropwise at −78 °C, followed by addition of tetramethylethylenediamine (0.9 mL, 6 mmol). After being stirred for 45 min, the reaction mixture was warmed to −55 °C and tri-*n*-butylborane (5 mL, 5 mmol) was added. Following the addition, the contents were cooled to −78 °C and then allowed to come to room temperature slowly over a period of 12 h. *n*-Hexadecane (0.5 mL, 1.7068 mmol) was added to the reaction mixture to serve as an internal standard. The $^{11}$B NMR of an aliquot showed the formation of dibutyl(1-(trimethylsilyl)pentyl)borane ($\delta$ +83). The solvent was removed under water aspirator, and the residue thus obtained was extracted with *n*-pentane (5 × 25 mL). *n*-Pentane was removed at 12 torr to give the crude dibutyl(1-(trimethylsilyl)pentyl)borane. The crude product in THF was desilylated with tetrabutylammonium fluoride (5.5 mL, 5 mmol) at 65 °C in 5 h to afford the dibutylpentylborane. The yield and purity of the dibutylpentylborane was determined by oxidation and GC

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[15] (a) Trost, B. M.; Miller, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 7182. (b) de Groot, Ae.; Jensen, B. J. M. *Tetrahedron Lett.* **1981**, *22*, 887.

[16] de Lattre, J. *Bull. Soc. Chim. Belg.* **1912**, *26*, 323.

[17] Hillman, M. E. D. *J. Am. Chem. Soc.* **1962**, *84*, 4715.

[18] Hooz, J.; Gunn, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 6195.

analysis of both 1-butanol and 1-pentanol (80%).

**Homologation of *B*-Methoxyborinane with (Chloro(trimethylsilyl)methyl)lithium.** (Chloro(trimethylsilyl)methyl)lithium (5.5 mmol) was prepared as described above for the homologation of tri-*n*-butylborane and treated with *B*-methoxyborinane (4 mL, 5 mmol) at −78 °C. Following the addition, the reaction mixture was stirred for 12 h as the temperature was slowly raised from −78 to 25 °C. *n*-Hexadecane (0.5 mL, 1.7068 mmol) was added into the reaction mixture to serve as the internal standard. The $^{11}B$ NMR of the reaction mixture revealed the formation of *B*-methoxy-2-(trimethylsilyl)borepane ($\delta$ +54). The solvent was removed under water aspirator, and the residue thus obtained was extracted with *n*-pentane (5 × 25 mL). *n*-Pentane was removed at reduced pressure, and the crude *B*-methoxy-2-(trimethylsilyl)borepane thus obtained was dissolved in THF (6 mL). Tetrabutylammonium fluoride (5.5 mL, 5.5 mmol) was added to the above reaction mixture. Following the addition, the contents were refluxed for 5 h and oxidized with alkaline $H_2O_2$ to provide 1,6-hexanediol in 75% GC yield.[15]

**Homologation of Tri-*n*-butylborane with (Methoxy(phenylthio)methyl)lithium.** *sec*-Butyllithium (4.2 mL, 5.5 mmol) was added dropwise to a mixture of methoxymethyl phenyl sulfide (0.85 mL, 6 mmol) in THF (10 mL) at −55 °C. Following the addition, the reaction mixture was stirred for 1 h and then cooled to −78 °C. Tri-*n*-butylborane (5 mL, 5 mmol) was added to the reaction mixture and the cold bath allowed to reach room temperature in 4 h. *n*-Hexadecane (0.5 mL, 1.7068 mmol) was added to the reaction mixture. The $^{11}B$ NMR spectrum of the reaction mixture showed the formation of borate complex ($\delta$ −0.2). Oxidation of the borate complex with hydrogen peroxide (15 mL) at pH 8 (phosphate buffer, 2.5 mL) gave 1-pentanal, which was reduced with borane–dimethyl sulfide to afford 1-pentanol in 81% GC yield.

**Homologation of *B*-Methoxyborinane with (Methoxy(phenylthio)methyl)lithium.** (Methoxy(phenylthio)methyl)lithium (5.5 mmol) was prepared as described above and treated with *B*-methoxyborinane (4 mL, 5 mmol) at −55 °C. The reaction mixture was allowed to reach −5 °C in 2 h. The $^{11}B$ NMR spectrum of the reaction mixture showed the formation of borate complex ($\delta$ −7). Finely powdered mercury(II) chloride (1.49 g, 5.5 mmol) was added all at once with vigorous stirring. The migration was complete as the temperature was raised from −5 °C to room temperature over 12 h, as indicated by the $^{11}B$ NMR spectrum ($\delta$ +54). The reaction mixture was oxidized as described above to afford the crude 6-hydroxyhexanal, reduced with borane–dimethyl sulfide to yield 1,6-hexanediol (76% by GC).[15]

**Acknowledgment.** The financial support from the National Science Foundation (Grant CHE 8514171) is gratefully acknowledged.

**Registry No.** $ClCH_2(SiMe_3)$, 2344-80-1; $CH_2(OMe)SPh$, 13865-50-4; $HCCl_3$, 67-66-3; $LiOCEt_3$, 32777-93-8; $LiCCl_3$, 2146-66-9; $HCClF_2$, 75-45-6; $BrCH_2CO_2Et$, 105-36-2; $BrCH_2CN$, 590-17-0; $HCCl_2OMe$, 4885-02-3; $LiCHCl_2$, 2146-67-0; $LiCHCl(SiMe_3)$, 63830-85-3; $LiCH(OMe)SPh$, 57788-49-5; tri-*n*-butylborane, 122-56-5; *B*-methoxyborinane, 38050-70-3; dibutylpentylborane, 30101-38-3; 1,6-hexanediol, 629-11-8; 1-pentanol, 71-41-0.

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# Reductive Synthesis and Characterization of the Complexes $CpM(NO)L_2$ (Cp = $\eta^5$-$C_5H_5$; M = Cr, Mo, or W; L = Lewis Base)[1]

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The synthesis of the previously inaccessible complexes $CpM(NO)L_2$ (Cp = $\eta^5$-$C_5H_5$; M = Cr, Mo, or W; L = $P(OMe)_3$, $PMePh_2$, $P(n\text{-}Bu)_3$, $SbPh_3$, or $^1/_2$(dppe)) is described. The new complexes are preparable in moderate to high yields by the reduction of the iodo dimers $[CpM(NO)I_n]_2$ (M = Cr, $n$ = 1; M = Mo or W, $n$ = 2) with sodium amalgam in THF in the presence of the appropriate Lewis base, L. The $CpM(NO)L_2$ compounds have been fully characterized by conventional spectroscopic methods and exhibit metal-dependent trends in $\nu_{NO}$ (Cr ≫ Mo > W), $\delta(^{31}P)$ (Cr > Mo ≫ W), and $^2J_{^{31}P-^{31}P}$ (Cr < Mo < W). Monitoring by IR spectroscopy of the progress of the reductive syntheses of the $CpM(NO)L_2$ complexes when M = Mo reveals the transient formation of intermediate nitrosyl complexes, some of which (i.e., $CpMo(NO)I_2L$ and $[CpMo(NO)IL_2]I$) are isolable from independent stoichiometric reactions. These experimental observations have led to the formulation of a unified mechanism for these reductive syntheses which accounts for the dependence of the yields of $CpM(NO)L_2$ on the nature of M, L, and the solvent employed.

## Introduction

We recently reported[2] that reduction of $[CpMo(NO)I_2]_2$ (Cp = $\eta^5$-$C_5H_5$) with sodium amalgam in the presence of acyclic conjugated dienes in THF results in the formation of novel $\eta^4$-*trans*-diene complexes, i.e., eq 1. However, the

$$[CpMo(NO)I_2]_2 + 4Na/Hg + 2\text{diene} \xrightarrow[20\ ^\circ C]{THF} 2CpMo(NO)(\eta^4\text{-diene}) + 4\ NaI + Hg \quad (1)$$

product organometallic complexes are isolable in only 10% yield, and the congeneric complexes containing chromium or tungsten are not preparable in an analogous manner. We reasoned that these disheartening results reflected either the intrinsically unstable nature of an intermediate species such as solvated "CpM(NO)" (M = Cr, Mo, or W) or the relative inefficiency of the unsaturated organic molecules to function as trapping agents for such an in-

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[1] (a) Organometallic Nitrosyl Chemistry. 27. For part 26 see: Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525. (b) Taken in part from: Hunter, A. D. Ph.D. Dissertation, The University of British Columbia, 1985.

[2] Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

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