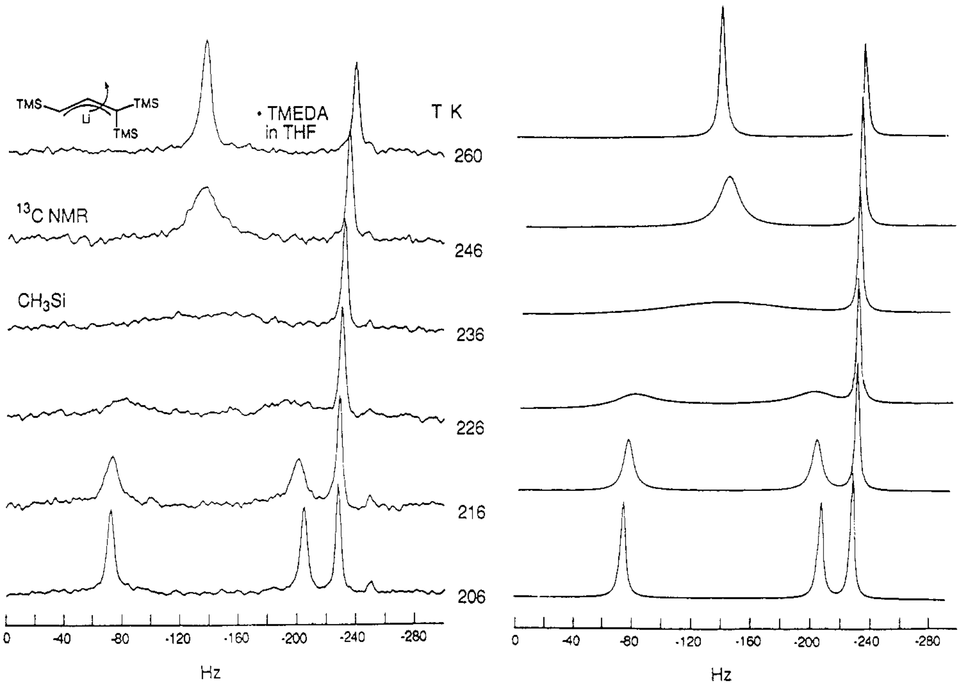

Figure 2. Left: observed ^{13}C NMR line shapes of CH$_3$Si groups of **3** (see Figure 1 caption), at different temperatures (kelvin). Right: calculated line shapes.

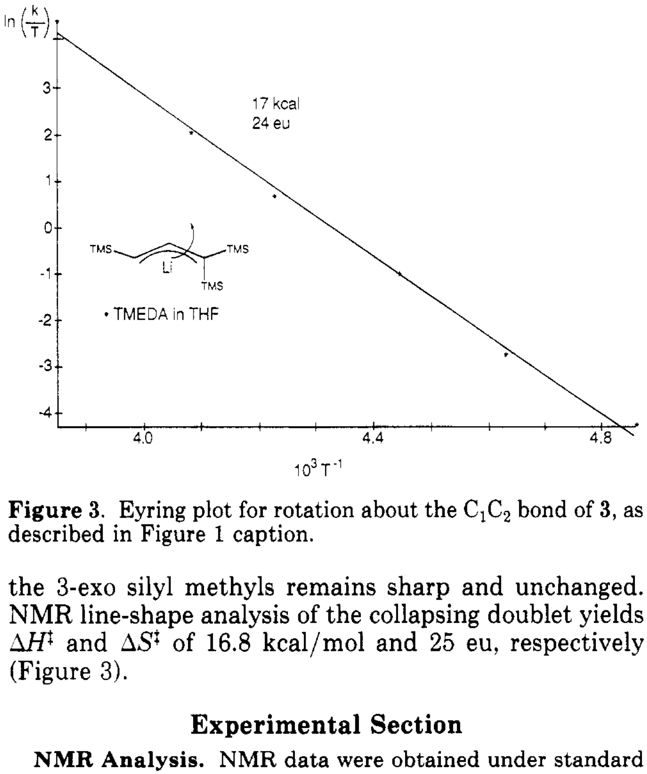

Figure 3. Eyring plot for rotation about the C$_1$C$_2$ bond of **3**, as described in Figure 1 caption.

the 3-exo silyl methyls remains sharp and unchanged. NMR line-shape analysis of the collapsing doublet yields $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 16.8 kcal/mol and 25 eu, respectively (Figure 3).

Experimental Section

NMR Analysis. NMR data were obtained under standard conditions by using Bruker AM 250, AM 500, and MSL 300 NMR spectrometers as previously described.[8]

[1,1,3-Tris(trimethylsilyl)allyl]lithium. The alkene, under argon, (*E*)-1,3,3-tris(trimethylsilyl)-1-propene (1.0 g, 3.87 mmol) was weighed into an oven-dried vial, then dissolved in 25 mL of pentane, and transferred to a Schlenk tube. Then, TMEDA at room temperature (0.75 mL, 4 mmol) was added to the solution, and finally *n*-butyllithium[^{6}Li] in pentane (1 mL, 4.4M, 4.4 mmol). This solution was stirred for 24 h at room temperature, by which time it had turned slightly red. Solvent was removed in vacuo, leaving a red black oil. After 1 week crystals were noticed. These were separated with a spatula and carefully washed with a drop of pentane and then dried in vacuo. After drying, they were dissolved in THF-d_8, to ca. 1 M and investigated with NMR methods.

[1,1,3,3-Tetrakis(trimethylsilyl)allyl]lithium. A solution of *n*-butyllithium[^{6}Li] in pentane (5 mL, 2.6 M, 13 mmol) was diluted with 15 mL more of pentane and 13 mmol (1 equiv) of TMEDA. To this solution at room temperature was added (*E*)-1,3,3-tris(trimethylsilyl)-1-propene (2.0 g, 7.7 mmol), and the resulting mixture was stirred at room temperature for 24 h. The resulting reaction mixture was treated with chlorotrimethylsilane (0.85 g, 7.8 mmol) and worked up in the usual way. After evacuation of volatile constituents the residue was vacuum distilled twice, bp 66–67 °C/0.4 Torr, yielding 1 g of a colorless oil; ^{13}C NMR (CDCl$_3$) δ 127.66 (C$_1$), 145.27 (C$_2$), 31.65 (C$_3$) 2.79, 1.04, and 0.19 (1:1:1, CH$_3$Si at C$_1$, C$_1$, and C$_3$, respectively); ^{1}H NMR δ 6.586 (H$_2$), 1.820 (H$_3$), 0.07, 0.075, and 0.14 (1:1:1, CH$_3$Si at C$_3$, C$_3$, and C$_1$, respectively, ^3J(H$_2$,H$_3$) = 13.3 Hz).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation, Grant No. CHE 8304636, and in part by the Goodyear Tire and Rubber Company. Grants from the National Science Foundation also helped finance acquisition of two high-field NMR spectrometers. We thank Dr. Charles Cottrell, Campus Chemical Instrumentation Center, for helpful technical advice.

Oxidation of Organoboranes with Sodium Percarbonate

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Summary: Sodium percarbonate, a readily available, inexpensive, and easily handled reagent, efficiently oxidizes a variety of organoboranes. The product yields compare favorably with those obtained by use of the standard sodium hydroxide/hydrogen peroxide oxidation procedure.

Table I. Comparison of the Efficiencies of Sodium Percarbonate and Hydrogen Peroxide Oxidation Procedures for Simple Trialkylboranes[a,b]

		rel amt, %[c]		total yield, %[d]	
alkene	alcohol products[b]	sodium percarbonate	hydrogen peroxide	sodium percarbonate	hydrogen peroxide
1-hexene	1-hexanol	94	94	100	100
	2-hexanol	6	6		
1-octene	1-octanol	94	94	98	98
	2-octanol	6	6		
2-methyl-1-pentene	2-methyl-1-pentanol			99	99
trans-3-hexene	3-hexanol			99	99
cyclohexene	cyclohexanol			97	98
norbornene	*exo*-norborneol			96	98
styrene	2-phenylethanol	85	85	100	100
	1-phenylethanol	15	15		
1-methylcyclopentene	*trans*-2-methylcyclopentanol	$>99^{e}$	$>99^{e}$	100	100

[a] The trialkylboranes were prepared via hydroboration of the corresponding alkenes with BH_3·THF. [b] All products exhibited physical properties and spectral characteristics in acoord with the literature values. [c] By GLC analysis. [d] By GLC analysis with use of an internal standard. [e] <1% cis isomer.

The hydroboration/oxidation sequence represents a very convenient procedure for the anti-Markovnikov hydration of carbon–carbon multiple bonds.[1-4] The traditional method for oxidizing organoboranes involves heating the borane reagent with 30% hydrogen peroxide and 3 N sodium hydroxide at 50 °C.[5,6] Other reagents have also been employed for the oxidation of organoboranes to the corresponding alcohols; these include perbenzoic acid,[7] amine *N*-oxides,[8,9] sodium hypochlorite,[10] and sodium perborate.[11]

Sodium percarbonate is an inexpensive, stable, and easily handled reagent that has an excellent shelf life. It is extensively used in the detergent industry as a bleaching agent.[12] The reagent is an addition compound of hydrogen peroxide and sodium carbonate (soda ash) (Na_2CO_3·$^3/_2H_2O_2$).[13-16] The crystal structure has been reported; the carbonate ions are hydrogen-bonded to the peroxide molecules.[17] Surprisingly, there has been very little study of the possible applications of sodium percarbonate to organic syntheses.[18,19]

We recently reported that sodium percarbonate can be utilized to oxidize simple trialkylboranes.[20] This newly developed, inexpensive, and operationally simple oxidation procedure has now been evaluated with use of a variety of organoboranes.

Scheme I

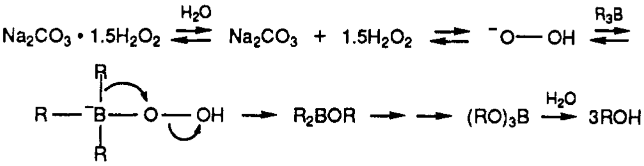
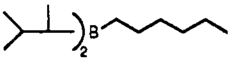
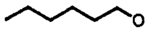
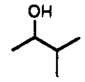
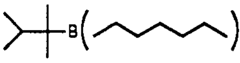
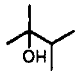
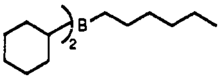
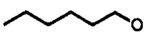
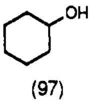
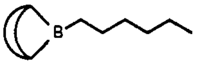
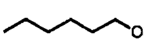
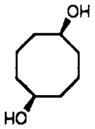
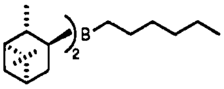
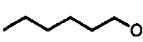
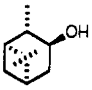
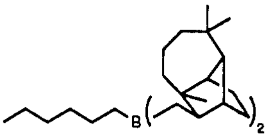
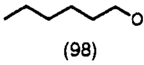
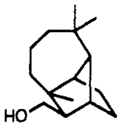


Table II. Oxidation of Mixed Organoboranes with Sodium Percarbonate

organoboranes	products (yield, %)[a]	
	 (98)	 (98)
	 (93)	 (97)
	 (99)	 (97)
	 (98)	 (96)
	 (99)	 (96)
	 (98)	 $(81)^{b}$

[a] By GLC analysis with use of an internal standard. [b] Isolated yield.

Results and Discussion

A series of representative alkenes was hydroborated with the borane–tetrahydrofuran complex (BH_3·THF), and the organoboranes formed were oxidized to the corresponding alcohols with use of sodium percarbonate as the oxidizing

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Table III. Oxidation of Trihexylborane (3 mmol), Prepared with Use of Borane–Methyl Sulfide in the Absence and Presence of Added Base (Sodium Hydroxide), with Sodium Percarbonate[a]

entry no.	amt of sodium percarbonate,[b] mmol	yield[c] of 1- and 2-hexanol, %
1	6 (9)	75
2	12 (18)	84
3	15 (22.5)	97
4	6 (9)[d]	99

[a] Trihexylborane was prepared via hydroboration of 1-hexene (9 mmol) with BMS (3 mmol) in THF. [b] Values in parentheses are the amounts (in mmol) of hydrogen peroxide released from sodium percarbonate. [c] By GLC analysis with use of an internal standard. [d] 3 mmol of NaOH added.

agent. Since 1 equiv of trialkylborane reacts with 3 equiv of hydrogen peroxide and 1 equiv of sodium percarbonate releases 1.5 equiv of hydrogen peroxide,[14,16] 2 equiv of sodium percarbonate was utilized. The results summarized in Table I indicate that oxidation with sodium percarbonate produces essentially quantitative yields of alcohols from the corresponding trialkylboranes. A comparative study was performed with use of the standard sodium hydroxide/hydrogen peroxide oxidation procedure, and the results are also included in Table I. In nearly every instance, the yields of alcohols obtained with use of the sodium percarbonate procedure were as high as those obtained with use of the standard sodium hydroxide/hydrogen peroxide oxidation procedure.

The oxidizing ability of the reagent is presumably due to hydrogen peroxide arising from the dissolution of sodium percarbonate in water. The hydroperoxide anion is generated in the alkaline medium, which then coordinates with the electron-deficient boron (Scheme I).

Since sterically hindered boranes are becoming increasingly important in stereoselective and regioselective synthetic applications, the utility of sodium percarbonate as an oxidant for typical mixed hydroboration products was investigated. The results are summarized in Table II. The data reveal that sodium percarbonate effectively oxidizes a wide variety of alkyl groups.

Borane–methyl sulfide (BMS) has emerged as a valuable reagent for the hydroboration of alkenes.[21] 1-Hexene was hydroborated with BMS, and the resulting trihexylborane solution, in tetrahydrofuran containing dimethyl sulfide, was oxidized with use of a stoichiometric quantity of sodium percarbonate (Table III). A 75% yield of hexanol was obtained. A 100% excess of sodium percarbonate also failed to provide a quantitative yield of hexanol. However, the use of 2.5 equiv of sodium percarbonate resulted in an essentially complete conversion to hexanol. The lower yield of alcohol from the oxidation of an organoborane in the presence of dimethyl sulfide is presumably due to the simultaneous oxidation of dimethyl sulfide by hydrogen peroxide in the weakly basic medium.[22] Since this reaction is suppressed at higher pH, 1 equiv of sodium hydroxide was added to the reaction mixture. The results indicate (Table III, entry 4) that the organoborane was selectively and quantitatively oxidized to the corresponding alcohol in the presence of dimethyl sulfide. Therefore, in the oxidation of organoborane solutions containing dimethyl sulfide with a stoichiometric quantity of sodium percarbonate, addition of an equivalent quantity of a strong base such as aqueous sodium hydroxide (3 N) is recommended.

The synthetic utility of this new oxidation procedure was further demonstrated by oxidizing organoboranes prepared from functionally substituted alkenes. The results are presented in Table IV. Only the major products are reported in Table IV; isomeric alcohols are also formed due to the mesomeric and inductive effects of the functional substituent during hydroboration.[23] The product yields were as good as or better than those for the standard sodium hydroxide/hydrogen peroxide oxidation procedure.

We next investigated the usefulness of sodium percarbonate for the oxidation of vinylorganoboranes. Our results are summarized in Table V. Representative terminal and internal alkynes were hydroborated with disiamylborane and the resultant vinylorganoboranes successfully oxidized to the corresponding carbonyl derivatives at room temperature. Triphenylboron was oxidized to phenol. The product yields compare favorably with those realized with use of the standard sodium hydroxide/hydrogen peroxide oxidation procedure.

Conclusions

Sodium percarbonate is a valuable reagent for efficiently oxidizing a variety of organoboranes. Its stability, low cost, and ease of handling should make sodium percarbonate a popular reagent for these transformations.

Experimental Section

General Comments. All glassware was predried at 140 °C for at least 4 h, assembled hot, and cooled under a stream of prepurified nitrogen. All transformations of boron reagents were conducted under a nitrogen atmosphere by using extensively the techniques outlined in chapter 9 of ref 24. Borane–tetrahydrofuran solution (1.0 M) and 9-borabicyclo[3.3.1]nonane (9-BBN) were purchased from Aldrich Chemical Co. Borane–methyl sulfide (10 M) was obtained from Aldrich Chemical Co. and diluted to a 1 M solution in tetrahydrofuran, and the solution concentration was estimated according to the standard procedure.[24] Tetrahydrofuran was distilled over benzophenone ketyl and stored under a nitrogen atmosphere. The olefins were all commercially available and were distilled from lithium aluminum hydride before use. Safrole, 5-benzoxy-1-hexene, and 3-chloro-2-methylpropene were passed through neutral alumina and distilled over calcium hydride. Alkynes used were commercial samples, which were distilled under nitrogen from a small amount of calcium hydride. Triphenylboron was purchased from Aldrich Chemical Co. Thexylborane, disiamylborane, dicyclohexylborane, diisopinocampheylborane, and dilongifolylborane were prepared by the known procedures.[1] Sodium percarbonate (practical grade) was purchased from Fluka. The available oxygen content of the sample, determined by titration with standard potassium permanganate, was found to be 13%. Proton NMR spectra were recorded on a JEOL FX90Q spectrometer. All chemical shifts are reported in parts per million downfield from tetramethylsilane. Boiling points reported are uncorrected. The gas chromatography analyses were performed on a Varian Model 3700 chromatograph. The following columns were used: 5% SE-30 on Chromosorb W, 10 ft × 0.25 in.; 10% Carbowax 20 M on Chromosorb W, 10 ft × 0.25 in.

Hydroborations. Alkenes. The hydroborations were carried out with use of standard procedures.[5] The alkene (30 mmol) was added to a dry, nitrogen-flushed, 50-mL three-necked flask equipped with a nitrogen inlet tube, a gas outlet tube connected to a mercury bubbler, a thermometer, and a magnetic stirring bar and maintained under a positive pressure of nitrogen. The flask was cooled to 0 °C (ice bath), and hydroboration was initiated by dropwise addition of a 1.0 M solution of BH_3·THF (10 mmol,

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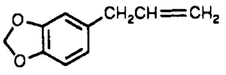
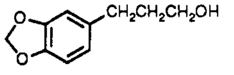
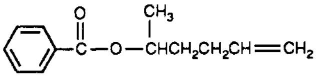
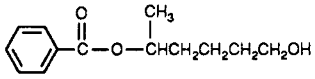
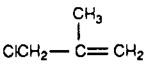
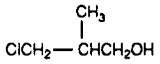
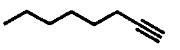
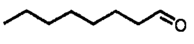
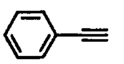
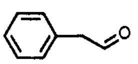
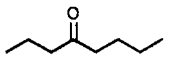
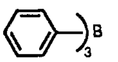
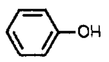
Table IV. Comparison of the Efficiencies of Sodium Percarbonate and Hydrogen Peroxide Oxidation Procedures for Functionally Substituted Organoboranes[a]

alkene	product[b]	yield, %[c] sodium percarbonate	yield, %[c] hydrogen peroxide
		81 (83)	78
		84 (78)	86
 $ClCH_2C(CH_3)=CH_2$	 $ClCH_2CH(CH_3)CH_2OH$	88 (76)[d]	62[d]

[a] The organoboranes were formed via the hydroboration of alkenes listed in the table with BH_3·THF. [b] Only the major product is indicated. [c] By GLC analysis with use of an internal standard. Values in parentheses are isolated yields of isomer mixtures. [d] The oxidation was carried out at room temperature for 2 h.

Table V. Comparison of the Efficiencies of Sodium Percarbonate and Hydrogen Peroxide Oxidation Procedures for Vinylorganoboranes[a]

reagent	product	yield, %[b] sodium percarbonate	yield, %[b] hydrogen peroxide
		97 (82)	96
		97 (86)	96
		100 (85)	100
		77[c]	76[c]

[a] The vinylorganoboranes were formed via hydroboration of the alkynes with use of disiamylborane. [b] By GLC analysis with use of an internal standard. Values in parentheses are isolated yields. [c] The oxidation was carried out at 50 °C for 1 h.

10 mL). The mixture was stirred at room temperature for 2 h.

Alkynes. Disiamylborane solution (20 mmol, 20 mL of a 1.0 M solution) was added to a dry, nitrogen-flushed, 50-mL three-necked flask equipped with a nitrogen inlet tube, a gas outlet tube connected to a mercury bubbler, a thermometer, and a magnetic stirring bar and maintained under a positive pressure of nitrogen. The flask was cooled to 0 °C (ice bath), and the alkyne (10 mmol) was added to the disiamylborane solution while the temperature was maintained below 5 °C. The mixture was stirred at 0 °C for 15 min and then at room temperature for 1 h to complete the hydroboration.

Oxidation of Trialkylboranes. General Procedure A. Sodium Percarbonate. The organobrane (10 mmol) dissolved in THF (10 mL) was contained in a dry, nitrogen-flushed, 50-mL three-necked flask equipped with a nitrogen inlet tube, a gas outlet tube connected to a mercury bubbler, a thermometer, and a magnetic stirring bar and maintained under a positive pressure of nitrogen. Water (10 mL) was added to the reaction mixture, followed by the addition of sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) in small portions at such a rate that the temperature did not rise above 30 °C. The reaction mixture was then heated to 50 °C for 1 h to ensure the completion of oxidation. When the mixture was cooled, the two phases were separated and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic phase was washed with sodium chloride solution (10 mL) and dried over magnesium sulfate, and the product was analyzed by GLC and isolated by distillation.

General Procedure B. Hydrogen Peroxide. The organoborane (3 mmol), dissolved in THF (3 mL), was contained in a dry, nitrogen-flushed, 25-mL three-necked flask equipped with a nitrogen inlet tube, a gas outlet tube connected to a mercury bubbler, a thermometer, and a magnetic stirring bar and maintained under a positive pressure of nitrogen. Aqueous sodium hydroxide (3 mmol, 1 mL of a 3 N solution) was added followed by the slow addition of hydrogen peroxide (1 mL of a 30% aqueous solution). The reaction mixture was heated to 50 °C for 1 h to ensure completion of the oxidation reaction. The mixture was saturated with potassium carbonate, the two phases were separated, and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic phase was washed with saturated sodium chloride solution (10 mL) and dried over magnesium sulfate, and the product was analyzed by GLC.

3-(3,4-(Methylenedioxy)phenyl)-1-propanol. Safrole (30 mmol, 4.86 g) was hydroborated with BH_3·THF (10 mmol, 10 mL) for 2 h. The resultant organoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) as described in the general procedure. GLC analysis (SE-30) indicated a 81% yield of 3-(3,4-(methylenedioxy)phenyl)-1-propanol; 12% of the secondary isomer was also present. Distillation afforded 4.48 g (83%) of a mixture of alcohols: bp 130–132 °C (3 mmHg) [lit.[8] bp 124–128 °C (2 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.8 (m, 2 H, $-CH_2$), 2.7 (t, J = 7 Hz, 2 H, $ArCH_2$), 3.0 (s, 1 H, -OH), 3.7 (t, J = 6.5 Hz, 2 H, $-CH_2O$), 6.0 (s, 2 H, OCH_2O), 6.8 (s, 3 H, ArH).

5-Benzoxy-1-hexanol. 5-Benzoxy-1-hexene (30 mmol, 6.12 g) was hydroborated with BH_3·THF (10 mmol, 10 mL) for 2 h. The resultant organoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) as described in the general procedure. GLC analysis (SE-30) indicated an 84% yield of 5-benzoxy-1-hexanol; 6% of the secondary isomer was also present. The product was isolated by distillation; 5.20 g (78%) of the mixture of alcohols was obtained: bp 140–142 °C (0.3 mmHg) [lit.[8] bp 121–125 °C (0.05 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.5 (m, 9 H, alkyl), 3.3 (s, 1 H, OH), 3.7 (t, J = 6.5 Hz, 2 H, $-CH_2OH$), 5.2 (m, 1 H, OCH–), 7.6 (m, 3 H, ArH), 8.2 (m, 2 H, ArH).

3-Chloro-2-methyl-1-propanol. 3-Chloro-2-methylpropene (30 mmol, 2.72 g) was hydroborated with BH_3·THF (10 mmol, 10 mL) for 2 h. The resultant organoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) at room temperature (25 °C) for 2 h. GLC analysis (SE-30) indicated an 88% yield of 3-chloro-2-methylpropanol. The product was isolated by distillation; 2.47 g (76%) of the alcohol was obtained: bp 72–74 °C (15 mmHg) [lit.[8] bp 65–66 °C (10 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.9 (d, J = 7 Hz, 3 H, CH_3), 1.9 (m, 1 H, CH), 3.5 (d, J = 6 Hz, 2 H, $-CH_2Cl$), 3.6 (d, J = 5.5 Hz, 2 H, CH_2OH), 4.6 (s, 1 H, OH).

Octanal. 1-Octyne (10 mmol, 1.1 g) was hydroborated with disiamylborane (20 mmol, 20 mL of a 1.0 M solution) for 1 h. The resultant vinylorganoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) at room temperature for 2 h. GLC analysis (SE-30) indicated a 97% yield of octanal. Distillation afforded 1.05 g (82%) of octanal: bp 83–85 °C (33 mmHg) [lit.[25] bp 72 °C (20 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 7 Hz, 3 H, CH_3), 1.5 (m, 10 H, CH_2), 2.5 (m, 2 H, CH_2), 9.7 (s, 1 H, CHO).

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(25) *Handbook of Chemistry and Physics*, 59th ed.; CRC Press: Boca Raton, FL, 1978.

Phenylacetaldehyde. Phenylacetylene (10 mmol, 1.02 g) was hydroborated with disiamylborane (20 mmol, 20 mL) for 1 h. The resultant vinylorganoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) at room temperature for 2 h. GLC analysis (SE-30) indicated a 97% yield of phenylacetaldehyde. Distillation afforded 1.03 g (86%) of phenylacetaldehyde: bp 76–78 °C (8 mmHg) [lit.[25] bp 88 °C (18 mmHg)]; ^1H NMR ($CDCl_3$), δ 2.8 (d, J = 7 Hz, 2 H, CH_2), 7.1 (s, 5 H, ArH), 9.8 (s, 1 H, CHO).

4-Octanone. 3-Octyne (10 mmol, 1.1 g) was hydroborated with disiamylborane (20 mmol, 20 mL) for 1 h. The resultant vinylorganoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) at room temperature for 2 h. GLC analysis (SE-30) indicated a 100% yield of 4-octanone. Distillation afforded 1.0 g (85%) of 4-octanone: bp 75–77 °C (40 mmHg) [lit.[25] bp 70 °C (26 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 7 Hz, 6 H, CH_3), 1.5 (m, 6 H, CH_2), 2.5 (t, J = 7 Hz, 4 H, 2 CH_2CO).

Acknowledgment. We thank the Department of Energy (Contract No. DE-FG05-86ER-60434) and NIH (Grant No. GM 39081) for support of this research.

Regioselective Iodine Addition to the Metal–Metal Bond of a Carboxamido Triosmium Cluster

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Summary: The triosmium complex $HOs_3(CO)_{10}(OCNHCHMe_2)I_2$ (**3b**) was isolated as a minor product from the reaction of $HOs_3(CO)_{10}(OCNHCHMe_2)$ (**1**) with I_2. An X-ray characterization of **3b** reveals that the unsymmetrical carboxamido ligand controls the regioselective addition of the iodine molecule onto the M–M bond. The species that result from the cleavage of different M–M bonds exhibit distinctive chemical reactivities. The cleavage of the Os–Os bond neighboring the Os atom with oxygen coordination yields the stable complex **3b**. However, the cleavage of the other nonbridged Os–Os bond gives the isomeric intermediate **3a**, which then reacts with another I_2 to form the dinuclear complex $Os_2(CO)_6(OCNHR)I_3$ (**2-*cis***). The difference between the reactivities of **3b** and **3a** demonstrates the influence of the activating ability of the oxygen atom of the carboxamido ligand.

The addition of an I_2 molecule to $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OCNHCHMe_2)$ (1) causes a cleavage of the trinuclear cluster.[1] The reaction produces two kinetic products, the mononuclear *trans*-$HOs(CO)_4I$ (4-*trans*) and the dinuclear osmium complex *cis*-$(\mu\text{-}I)Os_2(CO)_6(\mu\text{-}OCNHCHMe_2)I_2$ (2-*cis*).[2a] Complex 4-*trans* then transforms to the thermodynamically more stable complex 4-*cis*.[1] Recently we found that 2-*cis* in solution slowly isomerizes to the more stable 2-*trans*.[2b] The production of two kinetic compounds indicates that the reaction should be controlled by an as yet unspecified pathway. Described herein are the results of the spectroscopic observation of an intermediate, which we propose as $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OCNHCHMe_2)I_2$ (**3a**), and the isolation of the minor isomeric complex **3b**. An X-ray characterization of **3b** reveals a regioselective addition of the iodine molecule to the triosmium cluster, controlled by the presence of the unsymmetrical carboxamido ligand,[3] and implies a stereospecific control of two kinetic products.

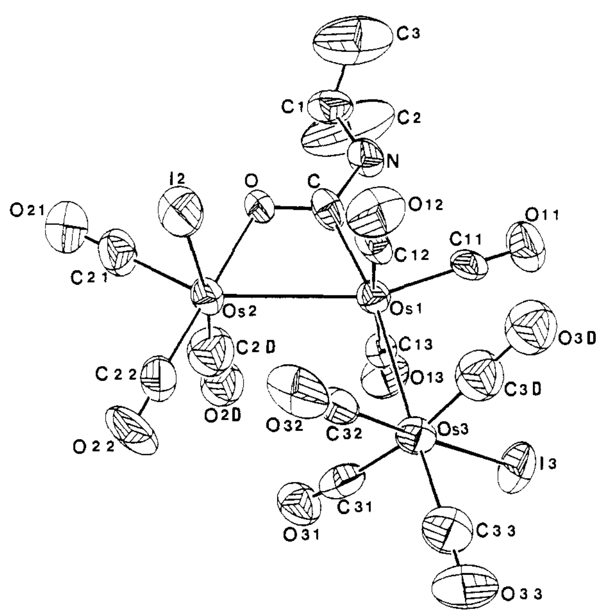

Figure 1. ORTEP disgram of $HOs_3(CO)_{10}(OCNHCHMe_2)i_2$ (**3b**), showing the atom-labeling scheme. Selected bond distances (Å) and bond angles (deg) are as follows: Os(1)–Os(2), 3.1115 (14); Os(1)–Os(3), 2.9545 (16); Os(1)–C, 2.096 (16); O–C, 1.281 (17); C–N, 1.362 (18); N–C(1), 1.484 (21); Os(2)–I(2), 2.7163 (18); Os(2)–O, 2.085 (9); Os(3)–I(3), 2.7343 (25); Os(2)–Os(1)–Os(3), 108.05 (4); Os(1)–Os(3)–I(3), 92.60 (6); Os(2)–Os(1)–C, 62.9 (4); Os(3)–Os(1)–C, 170.9 (4); C–Os(1)–C(11), 96.9 (6); C–Os(1)–C(12), 94.1 (6); C–Os(1)–C(13), 89.8 (6); Os(1)–Os(2)–I(2), 93.60 (5); Os(2)–O–C, 113.6 (9); Os(1)–Os(2)–O, 65.2 (3); Os(1)–C–O, 118.3 (10); Os(1)–C–N, 123.9 (11); O–C–N, 117.7 (14); C–N–C(1), 119.4 (13); I(2)–Os(2)–O, 89.0 (3); N–C(1)–C(2), 106.0 (15); N–C(1)–C(3), 105.2 (14); C(2)–C(1)–C(3), 113.7 (20).

A ^1H NMR examination of the freshly prepared CD_3COCD_3 solution containing complex 1 and 1 equiv of I_2 reveals the presence of four hydride species: 4-*trans*, complex 1, complex **3b**, and intermediate **3a**, at δ −11.8, −13.4, −16.9, and −18.2, respectively. The intensity of the resonance at δ −18.2 increases at first and then, with the simultaneous production of complexes 4-*trans* and 2-*cis*, slowly decreases, disappearing within 2 h. This indicates that the species with the hydride peak at δ −18.2 is the intermediate that leads to complexes 2-*cis* and 4-*trans*. The intermediate is too active to be isolated, and its structure cannot be discerned from the NMR data alone.

The minor complex **3b**, with a resonance at δ −16.9, however, is stable and can be purified by column chromatography and isolated as a microcrystalline solid, with an optimum yield of 15% when carried out at 0 °C. This complex was spectroscopically characterized and has been fully defined by an X-ray diffraction study (Figure 1). Two of the three M–M separations are within 3.12 Å, indicating the existence of two metal–metal bonds. For a noncyclic triosmium system, in which one of the terminal

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(1) Lu, K. L.; Chen, J. L., Lin, Y. C.; Peng, S. M. *Inorg. Chem.* **1988**, *27*, 1726–1730.

(2) (a) The term cis here refers to the disposition of two terminal I ligands with respect to the Os—C=O—Os plane. (b) Lu, K. L.; Lin, Y. C. Submitted for publication.

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