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Trimethylsilyl Esters: Protection of Carboxylic Acids during Hydroboration Reactions

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Trimethylsilyl esters of carboxylic acids are inert to a variety of hydroborating agents and provide a convenient method for protecting the acid functionality during organoborane transformations.

Introduction

The hydroboration reaction has proven to be the most convenient route to the synthetically important organoboranes.[1] One of the most significant features of the hydroboration reaction is the fact that a large number of functional groups are tolerated by the various hydroborating reagents.[1a,2] Consequently, organoboranes are rather unique synthetic intermediates in that functionality can be introduced rather early in a multistep synthetic sequence

$$H_2C{=}CH(CH_2)_xCH_2Y \xrightarrow{>B\text{-}H} {>}BCH_2CH_2(CH_2)_xCH_2Y$$

where Y may be CO_2R, C≡N, halogen, etc.

Carboxylic acids are among the more useful functional groups of interest to synthetic chemists. However, boron hydrides generally reduce carboxylic acids to the corresponding alcohols.[3] The only exception appears to be the hindered hydroborating agents disiamylborane and dicyclohexylborane which react with acids to generate boryl esters that do not readily undergo further reduction, presumably because the steric bulk of these agents hinder further attack by the borane.[4,5a–e]

We have been interested in the synthesis of functionalized carboxylic acid derivatives for use as synthetic intermediates. In general, we have protected carboxylic acids by converting them to boryl ester derivatives prior to hydroboration.[5] In the case of the dialkylborinic esters, the reaction requires careful monitoring and the desired products are frequently contaminated with the alcohol resulting from reduction of the carboxylic acid.

$$H_2C{=}CH(CH_2)_8COOH \xrightarrow{DCxBH} Cx_2BCH_2CH_2(CH_2)_8COOBCx_2$$

As part of a project involving the synthesis of unsaturated amino acids, we required a convenient method to protect the carboxylic acid functionality during a hydroboration reaction. Interestingly, in a study focused on the reduction of silyl esters of carboxylic acids by a variety of reducing agents, it was reported that these esters were not reduced by borane under hydroboration conditions.[6] We felt that a trimethylsilyl group would be an ideal protecting group for our application, due to the ease of preparing trimethylsilyl esters and their subsequent removal.[7]

We wish to report that silyl esters of carboxylic acids are stable to a variety of hydroborating agents. These readily available carboxylic acid derivatives can be utilized to prepare a number of mixed trialkylboranes that can then be converted to functionalized carboxylic acids via well-known organoborane transformations.

$$H_2C{=}CH(CH_2)_8CO_2Si(CH_3)_3 \xrightarrow{>B\text{-}H} {>}BCH_2CH_2(CH_2)_8CO_2Si(CH_3)_3$$

Results and Discussion

In initial experiments, we found that trimethylsilyl hexanoate reacted only slowly with BH_3·THF below −30 °C, but as the reaction temperature increased, the rate of ester reduction also increased. Since reaction temperature can be an important factor in hydroboration reactions, we examined the reaction of borane with trimethylsilyl hexanoate in detail.

In an NMR experment, 2 mmol of trimethylsilyl hexanoate was treated with 2 mmol of BH_3·THF at −78 °C and the progress of the reaction monitored by ^{11}B NMR. At −78 → 50 °C, only a single sharp peak at −0.5 ppm was evident, corresponding to BH_3·THF. As the temperature was raised to −30 °C, a peak at 26 ppm developed. As the reaction mixture was warmed to −18 °C, a second peak at 17 ppm appeared. A further increase in temperature led to the gradual disappearance of the peak at 26 ppm, while the peak at 17 ppm increased in size. Quenching the reaction (hydrolysis) followed by workup of the reaction mixture gave a quantitative yield of 1-hexanol. Although the products giving rise to the resonances at 17 and 26 ppm have not been identified, the boronate esters resulting from reduction of the carboxylic acid derivatives would be expected to give rise to resonances in the 10–30 ppm region of their ^{11}B NMR. A similar temperature dependence has been noted in the reduction of trimethylsilyl esters with various aluminum hydride reagents.[6]

Fortunately, the rates of hydroboration reactions are generally quite fast. We have found that silyl esters can be successfully hydroborated with excess BH_3·THF as long as the temperature is maintained at or below −30 °C. The hydroboration of unsaturated silyl esters with BH_3·THF proceeds at a reduced rate unless an excess of the hydroborating agent is utilized. For example, the hydroboration of 5 mmol of trimethylsilyl 10-undecenoate with 1.67 mmol

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Table I. Hydroboration of Trimethylsilyl 10-Undecenoate and Conversion to 11-Hydroxyundecanoic Acid

reagent	ratio borane:alkene	% yield[a]
BH_3·THF	1:1	91[b]
BH_3·THF	2:1	91[b]
BH_3·DMS	1:1	76[b]
BH_3·DMS	2:1	96[b]
dicyclohexylborane	1:1	93[c]
disiamylborane	1:1	96[c]
9-borabicyclo[3.3.1]nonane	1:1	95[c]
catecholborane	1.35:1	71[d]
thexylborane	1:1	98[b]

[a] Isolated product. [b] HB reaction carried out at −10 °C (−30 °C for BH_3·THF) for 0.5–3 h; water was added to hydrolyze any remaining hydride and then the mixture oxidized with H_2O_2/NaOH. [c] HB reactions carried out at −10 °C and then warmed to room temperature for 4–12 h; the mixture was then oxidized with H_2O_2/NaOH. [d] Catecholborane reaction carried out in absence of solvent at 70 °C for 24 h.[12]

of BH_3·THF yielded 3 mmol of 11-hydroxyundecanoic acid (after oxidative workup) and 2 mmol of starting olefin after 12 days at −5 °C (initial mixing temperature −78 °C). In a parallel experiment utilizing equimolar quantities of alkene and hydride, ^{11}B NMR analysis revealed that the peak at 17 ppm began to appear as the temperature rose above 0 °C; oxidative workup after 24 h at room temperature yielded 60% hydroxy acid and 32% of a mixture of unreacted alkene and diol. In contrast, an experiment in which 5 mmol of the protected alkene was treated with 5 mmol of BH_3·THF yielded 4.6 mmol of the expected hydroxy acid after 2 h at −30 °C.

The borane–dimethyl sulfide (BMS) complex appears to hydroborate unsaturated silyl esters more effectively than the THF complex. Furthermore, control experiments revealed that no reduction of the ester group occurs as long as the reaction temperature is kept at or below 0 °C. For example, when 2 mmol of trimethylsilyl hexanoate was mixed with 2 mmol of BMS at −78 °C and the reaction monitored by ^{11}B NMR at −50 °C, only a sharp peak at 0.1 ppm was observed as the reaction temperature was increased to 0 °C.[8] At 10 °C a small peak appeared at 48 ppm, but even when the reaction was left at 10 °C for 1 h, this peak did not increase significantly. As the temperature rose to 20 °C, the peak at 48 ppm became larger and a new peak at 38.6 ppm began to appear. When the reaction was allowed to come to probe temperature (37 °C), the peak at 48 ppm disappeared at the expense of the peak at 38.6 ppm. Quenching the reaction (hydrolysis) produced a quantitative yield of 1-hexanol. Thus, the critical temperature for avoiding reduction with BH_3·THF appears to be −30 °C, whereas 0 °C is the maximum temperature when BMS is utilized. BMS reactions involving equivalent quantities of hydride and olefin also proceed rather slowly at the reduced temperatures but, unlike BH_3·THF, will go to completion. Thus the reaction of 1.67 mmol of BMS with 5 mmol of the TMS ester of 10-undecenoic acid afforded, after 4 days at 0 °C (mixing temperature −78 °C), 4.9 mmol of the expected hydroxy acid after oxidation. The same yield could be obtained in a matter of hours when excess BMS was used at −5 °C.

We then examined the reaction of the silyl ester of 10-undecenoic acid with a number of common hydroborating agents. Our results are summarized in Table I. It is readily apparent that the trimethylsilyl moiety effectively protects the carboxylic acid functionality during hydroboration reactions.

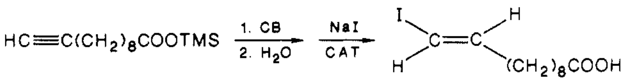
Table II. Hydroboration of Various Unsaturated Trimethylsilyl Esters with 9-BBN, Dicyclohexylborane, and BMS

TMS ester	borane	borane: alkene	% yield[a]
TMS oleate	9-BBN	1:1	47[b]
TMS oleate	BMS	1:1	73[b,c]
TMS oleate	DCxBH	1:1	56[b,c]
TMS 10-undecenoate	9-BBN	1:1	83
TMS 10-undecenoate	BMS	1:1	76
TMS 4-pentenoate	9-BBN	1:1	78
TMS 3-cyclohexene-1-carboxylate	9-BBN	1:1	0
TMS 3-cyclohexene-1-carboxylate	BMS	2:1	51[d]

[a] Isolated yield of hydroxy acid. [b] Remaining mass balance was recovered as unreacted olefinic acid. [c] A mixture of the 9- and 10-hydroxy adducts were obtained. [d] A complex mixture of hydroxy-acids was obtained.

A series of olefinic esters was then hydroborated with 9-BBN, dicyclohexylborane, and BMS, and these results are presented in Table II. In the hydroboration of trimethylsilyl 3-cyclohexene-1-carboxylate with 9-BBN, only 3-cyclohexene-1-carboxylic acid was recovered, presumably due to the reduced reactivity of 9-BBN at lower temperatures with internal double bonds.[9] No reduction of the ester funtionality was observed. However, when the hydroboration was carried out at elevated temperatures (refluxing THF), competitive reduction of the ester functionality was observed. In an effort to determine whether reduction of trimethylsilyl esters with 9-BBN at elevated temperatures was a general reaction or simply an artifact of the 3-cyclohexene-1-carboxylate system, treatment of trimethylsilyl hexanoate with 9-BBN in refluxing THF for 1 h gave a near quantitative yield of unreduced hexanoic acid. Thus, it appears that ester reduction by 9-BBN is not a general reaction but becomes competitive with hydroboration only with hindered internal double bonds or when proximal ester functionality can affect the normal course of the hyroboration reaction.[10] Hydroboration with BMS was more successful; no reduction of the ester group occurred. However, a mixture of hydroxy acid products were obtained from the hydroboration of trimethylsilyl 3-cyclohexene-1-carboxylate with BMS. Although the regiochemical outcome was not determined, these findings are in accord with results obtained by Klein and co-workers[11] who obtained a complex mixture of alcohols in the hydroboration of 3-cyclohexene-1-carboxylates with diborane.

Finally, we carried out a series of standard organoborane transformations; these results are summarized in Table III. The successful hydroboration of trimethylsilyl 10-undecynoate with catecholborane is a most promising result, as it offers a more direct route of preparing iodovinyl fatty acids.[5a,6]



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(8) Control experiments reveal that BMS and BMS/THF solutions exhibit boron-11 resonances near −20 ppm at −50 °C. However, the boron-11 resonance immediately shifts from −20 to 0.1 ppm upon addition of a carboxylic acid ester. Presumably a complexation occurs between BMS and the oxygen atoms of the ester; such a complex would also account for the upfield shifts observed for the reduction products.

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Table III. Organoborane Transformations Utilizing Trimethylsilyl Esters

substrate	reagents	product	% yield[a]
TMS 10-undecenoate	DCxBH/NaI, CAT	11-iodoundecanoic acid	88
TMS 10-undecenoate	BMS/HOAc	undecanoic acid	82
TMS 10-undecenoate	DCxBH/NaOH, H_2O_2	11-hydroxyundecanoic acid	93
TMS 4-pentenoate	DCxBH/ICl	5-iodopentanoic acid	76
TMS 10-undecynoate	CB/H_2O	10-undecenylboronic acid	87

[a] Isolated yield.

Experimental Section

The ^1H, ^{13}C, ^{29}Si NMR spectra were obtained on a JEOL-FX90Q spectrometer in $CDCl_3$ or DMSO-d_6 solutions using tetramethylsilane as an internal standard. The ^1H NMR spectra were referenced using tetramethylsilane, TMS, as an internal standard ($\delta = 0.0$ ppm). The ^{13}C NMR spectra were referenced to either $CDCl_3$ ($\delta = 77.1$ ppm) or dimethyl sulfoxide-d_6 ($\delta = 39.5$ ppm). The ^{11}B NMR spectra were referenced to boron trifluoride etherate ($\delta = 0.0$ ppm) by use of a sealed capillary external reference. The ^{29}Si NMR spectra were referenced to tetramethylsilane ($\delta = 0.0$ ppm). Low-temperature NMR experiments were carried out in nitrogen- or argon-flushed 10-mm NMR tubes with septum caps using a JEOL NMR VTS variable-temperature controller equipped with a liquid-nitrogen Dewar attachment to the NMR probe. Infrared spectra were obtained on a Perkin-Elmer Model 1330 spectrometer. Melting points were recorded by using a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Dicyclohexylborane, disiamylborane, and thexylborane were prepared according to the known procedures.[1a] Commercially available samples of 10-undecenoic acid (Aldrich), 4-pentenoic acid (Aldrich), oleic acid (Aldrich), 3-cyclohexene-1-carboxylic acid (ICN Biomedicals), 2-methyl-2-butene (Aldrich), 2,3-dimethyl-2-butene (Aldrich), BH_3·THF (Aldrich), BMS (Aldrich), catecholborane (Aldrich), and 9-BBN (Aldrich) were used as received. Hexanoic acid (Fisher) and cyclohexene (Aldrich) were distilled prior to use. Chlorotrimethylsilane (Aldrich) was distilled from calcium hydride prior to use and stored under argon. Triethylamine (Fisher) was distilled from potassium hydroxide prior to use and stored under argon. Tetrahydrofuran was distilled from sodium/benzophenone prior to use. All glassware and equipment were oven-dried and flushed with argon prior to use.

Preparation of Trimethylsilyl Esters. General Procedure. The preparation of trimethylsilyl 10-undecenoate is representative. A 500-mL round-bottomed flask fitted with a septum inlet was equipped with a magnetic stirring bar, addition funnel, and gas outlet to a mercury bubbler. Placed in the flask by cannula was 10-undecenoic acid (200 mmol, 36.86 g), followed by anhydrous THF (200 mL) and triethylamine (200 mmol, 27.9 mL). The reaction flask was cooled to 0 °C, and then trimethylsilyl chloride (200 mmol, 25.4 mL) was added dropwise (exothermic!). After the addition was complete, the reaction mixture was stirred at room temperature for 1 h.

A separate apparatus consisting of a 250-mL round-bottomed flask equipped with a septum inlet, magnetic stirring bar, and a sintered glass fritted funnel with septum was assembled while hot, flame-dried, and flushed with argon. The reaction mixture was then filtered under argon through the filtering funnel by transferring it into the fritted funnel using a 12 ga. double-ended needle. After washing the precipitate ($Et_3NH^+Cl^-$) with anhydrous THF, the solvent was removed from the filtrate by slow distillation under argon. Bulb-to-bulb distillation under reduced pressure yielded 45.31 g (82%) of trimethylsilyl 10-undecenoate as a pale yellow oil: bp 112 °C (116 Torr) (lit.[13] bp 96–100 °C (2 Torr)]; ^1H NMR ($CDCl_3$) δ 6.05–5.5 (m, 1 H, $J_{ab} = 6.6$ Hz, $H_2C{=}CH_aCH_bR$), 5.1–4.75 (m, 2 H, $J_{trans} = 17.1$ Hz, $J_{cis} = 9.2$ Hz, $H_2C{=}CHCH_2R$), 2.29 (t, 2 H, $J = 7.0$ Hz, $CH_2COOTMS$), 2.15–1.85 (m, 2 H, $H_2C{=}CHCH_2R$), 1.75–1.1 (broad envelope, 12 H), 0.27 (s, 9 H, $(CH_3)_3Si$)); ^{13}C NMR ($CDCl_3$) δ 174.45 (COOTMS), 139.05 ($H_2C{=}CHR$), 114.16 ($H_2C{=}CHR$), 35.90, 33.98, 33.82, 29.26, 29.07, 28.91, 24.96, 24.71, −0.23 ($(CH_3)_3Si$); ^{29}Si NMR ($CDCl_3$) δ 22.77.

Trimethylsilyl 4-Pentenoate. Reaction of 4-pentenoic acid (108.1 mmol, 10.82 g) with triethylamine (108.1 mmol, 10.94 g, 15.1 mL) and chlorotrimethylsilane (108.1 mmol, 11.74 g, 13.72 mL) in anhydrous THF (100 mL) according to the general procedure gave 14.8 g (80%) of trimethylsilyl 4-pentenoate as a colorless oil after bulb-to-bulb distillation: bp 66 °C (14 Torr) (lit.[14] bp 70–72 °C (8 Torr)); ^1H NMR ($CDCl_3$) δ 6.0–5.6 (m, 1 H, $H_2C{=}CHR$), 5.1–4.9 (m, 2 H, $J_{trans} = 17.5$ Hz, $J_{cis} = 11$ Hz, $H_2C{=}CHR$), 2.5–2.1 (m, 4 H, CH_2CH_2), 0.28 (s, 9 H, $Si(CH_3)_3$)); ^{13}C NMR ($CDCl_3$) δ 173.56 (COOTMS), 136.83 ($H_2C{=}CHR$), 115.29 ($H_2C{=}CHR$), 35.12 ($CH_2COOTMS$), 29.02 ($H_2C{=}CHCH_2$), −0.26 ($(CH_3)_3Si$); ^{29}Si NMR ($CDCl_3$) δ 23.69.

Trimethylsilyl Hexanoate. Reaction of hexanoic acid (195.76 mmol, 22.74 g) with triethylamine (210 mmol, 21.25 g, 29.3 mL) and chlorotrimethylsilane (210 mmol, 22.81 g, 26.65 mL) in anhydrous THF (100 mL) according to the general procedure gave 32.25 g (87%) of trimethylsilyl hexanoate as a colorless oil after bulb-to-bulb distillation: bp 44 °C (0.2 Torr); ^1H NMR ($CDCl_3$) δ 2.30 (t, 2 H, $J = 7.0$ Hz, $CH_2COOTMS$), 1.8–1.2 (m, 6 H), 0.90 (t, 3 H, $J = 6.1$ Hz), 0.28 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 174.56 (COOTMS), 35.96 ($CH_2COOTMS$), 31.35, 24.74, 22.41, 13.94 (CH_3); ^{29}Si NMR ($CDCl_3$) δ 23.50.

Trimethylsilyl (*Z*)-9-Octadecenoate. Reaction of oleic acid (100 mmol, 28.25 g) with triethylamine (105 mmol, 10.62 g, 14.6 mL) and chlorotrimethylsilane (105 mmol, 11.41 g, 13.33 mL) in anhydrous THF (100 mL) according to the general procedure gave 29.81 g (84%) of trimethylsilyl (*Z*)-9-octadecenoate as a colorless oil after bulb-to-bulb distillation: bp 166 °C (0.9 Torr); 5.45–5.2 (m, 2 H, $RHC{=}CHR'$), 2.29 (t, 2 H, $CH_2COOTMS$), 2.15–1.85 (m, 4 H), 1.75–1.1 (broad envelope, 22 H), 0.88 (t, 3 H, CH_3), 0.27 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 174.56 (COOTMS), 130.03 ($RCH{=}CHR'$), 129.81 ($RCH{=}CHR'$), 36.01 ($RCH_2COOTMS$), 32.70, 32.65, 32.01, 29.67, 29.59, 29.43, 29.26, 29.16, 29.05, 25.06 ($RCH_2CH_2COOTMS$), 22.76, 14.18 (CH_3), −0.14 ($Si(CH_3)_3$); ^{29}SiNMR ($CDCl_3$) δ 22.77.

Trimethylsilyl 3-Cyclohexene-1-carboxylate. Reaction of 3-cyclohexene-1-carboxylic acid (78.31 mmol, 9.88 g) with triethylamine (78.3 mmol, 7.92 g, 10.9 mL) and chlorotrimethylsilane (78.3 mmol, 8.50 g, 9.94 mL) in anhydrous THF (100 mL) according to the general procedure gave 11.32 g (73%) of trimethylsilyl 3-cyclohexene-1-carboxylate as a colorless oil after bulb-to-bulb distillation: bp 67 °C (2.1 Torr); ^1H NMR ($CDCl_3$) δ 5.67 (s, 2 H, $RHC{=}CHR'$), 2.7–1.6 (m, 7 H), 0.28 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 176.40 (COOTMS), 126.64 ($RCH{=}CHR'$), 125.34 ($RCH{=}CHR'$), 40.58 ($R'C{=}CHCH_2CH(COOTMS)R$), 27.50 ($RCH_2C{=}CR'$), 25.09, 24.47, −0.23 ($Si(CH_3)_3$).

Trimethylsilyl 10-Undecynoate. Reaction of 10-undecynoic acid (20 mmol, 3.64 g) with triethylamine (20 mmol, 2.02 g, 2.78 mL) and chlorotrimethylsilane (20 mmol, 2.17 g, 2.54 mL) in anhydrous THF (50 mL) according to the general procedure gave 4.14 g (82%) of trimethylsilyl 10-undecynoate as a colorless oil after bulb-to-bulb distillation: bp 150–155 °C (0.1–0.12 Torr); ^1H NMR ($CDCl_3$) δ 2.4–2.05 (m, 4 H, $HC{\equiv}CCH_2R$, $CH_2COOTMS$), 1.92 (t, 1 H, $J = 2.6$ Hz, $HC{\equiv}CR$, 1.7–1.2 (m, 12 H), 0.26 (s, 9 H, $COOSi(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 174.42 (COOTMS), 84.58 ($HC{\equiv}CR$), 68.13 ($HC{\equiv}CR$), 35.85 ($CH_2CH_2COOTMS$), 29.13, 28.99, 28.91, 28.64, 28.42, 24.90 ($CH_2CH_2COOTMS$), 18.35, ($HC{\equiv}CCH_2R$), −0.26 ($Si(CH_3)_3$). Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30; Si, 11.04. Found: C, 66.28; H, 10.49; Si, 8.80.

Hydroboration of Trimethylsilyl 10-Undecenoate with Dialkylboranes. General Procedure. The hydroboration with 9-BBN is representative. A 50-mL round-bottomed flask fitted

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with a septum inlet, a magnetic stirring bar, and gas outlet (mercury bubbler) was flame-dried, purged with argon, and allowed to cool under a stream of argon. Trimethylsilyl 10-undecenoate (5 mmol) in 5 mL of THF was added to the flask by syringe, and the mixture was cooled to −10 °C (salt–ice bath). A cooled solution (0 °C) of 9-BBN (5 mmol) was introduced slowly over a 10-min period and the reaction mixture gradually allowed to come to room temperature over a 4-h period. The flask was cooled to 0 °C, and then sodium hydroxide (3 M, 1.67 mL) and hydrogen peroxide (30%, 1.5 mL) were added sequentially. The mixture was heated for 1 h at 50 °C and then cooled to room temperature. The pH was adjusted to 10, and the mixture was washed with ether (3 × 25 mL). The aqueous layer was acidified (pH 2) with 1 N HCl and saturated with NaCl, and the product was extracted into ether (3 × 25 mL). The combined ethereal layers were dried (Na_2SO_4) and filtered, and the solvent was removed to give 0.96 g (95%) of 11-hydroxyundecanoic acid, which was essentially pure. Recrystallization from ether–petroleum ether afforded 0.94 g (83%) of a white powder: mp 68–69 °c (lit.[15] 70 °C); ^{1}H NMR ($CDCl_3$) δ 6.55 (s, 2 H, OH), 3.64 (t, 2 H, *J* = 6.6 Hz, RCH_2OH), 2.33 (t, 2 H, *J* = 7.0 Hz, RCH_2COOH), 1.8–1.1 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 179.33 (COOH), 63.01 (RCH_2OH), 34.11, 32.62, 29.51, 29.37, 29.21, 29.07, 25.74, 24.77.

Hydroboration of Trimethylsilyl 10-Undecenoate with Excess BH_3·THF. General Procedure. A 50-mL round-bottomed flask fitted with a septum inlet, a magnetic stirring bar, and gas outlet (mercury bubbler) was flame-dried, purged with argon, and allowed to cool under a stream of argon. Trimethylsilyl 10-undecenoate (5 mmol, 1.28 g, 1.47 mL) in THF (5 mL) was added to the flask by syringe and cooled to −30 °C (bromobenzene–dry ice bath). A cooled solution (−30 °C) of BH_3·THF (1 M, 5 mmol) was introduced slowly over a 10-min period and the reaction mixture stirred at −30 °C for 2 h. At −30 °C, the reaction was quenched by adding acetone (5 mL) and then water (5 mL). Aqueous sodium hyroxide (3 M, 1.67 mL) and hydrogen peroxide (30%, 1.5 mL) were added sequentially, and the contents were heated for 1 h at 50 °C and then cooled to room temperature. The acetone was removed under reduced pressure, the pH was adjusted to 10 with 1 N NaOH, and the mixture was washed with ether (3 × 25 mL). The aqueous layer was acidified (pH 2) with 1 N HCl and saturated with NaCl, and the product was extracted into ether (3 × 25 mL). The combined ethereal layers were dried (Na_2SO_4) and filtered, and the solvent was removed to give 0.92 g (91%) of 11-hydroxyundecanoic acid, which was essentially pure. Recrystallization from ether–petroleum ether afforded 0.80 g (80%) of a white powder, mp 69–70 °C (lit.[15] mp 70 °C).

Hydroboration of Trimethylsilyl 10-Undecenoate with BH_3·DMS. General Procedure. A 50-mL round-bottomed flask fitted with a septum inlet, a magnetic stirring bar, and gas outlet (mercury bubbler) was flame-dried, purged with argon, and allowed to cool under a stream of argon. Trimethylsilyl 10-undecenoate (5 mmol, 1.28 g, 1.47 mL) in THF (5 mL) was added to the flask by syringe and cooled to −5 °C (ice–salt bath). A cooled solution (0 °C) of BMS (10 M, 5 mmol, 500 μL) was introduced slowly over a 10-min period and the reaction mixture stirred at −5 °C for 0.5 h. At −5 °C, the reaction was quenched by adding acetone (5 mL) and then water (5 mL). Aqueous sodium hydroxide (3 M, 1.67 mL) and hydrogen peroxide (30%, 1.5 mL) were added sequentially, and the contents were heated for 1 h at 50 °C and then cooled to room temperature. The acetone was removed under reduced pressure, the pH adjusted to 10 with 1 N NaOH, and the mixture washed with ether (3 × 25 mL). The aqueous layer (ice was added to hinder esterification) was acidified (pH 2) with 1 N HCl, upon which a white precipitate formed. Filtration of the precipitate followed by washing with petroleum ether and drying afforded 0.80 g (80%) of the crude product, which was essentially pure. Recrystallizaton from ether–petroleum ether afforded 0.76 g (76%) of 11-hydroxyundecanoic acid as a white powder, mp 69–70 °C (lit.[15] mp 70 °C).

Hydroboration of Trimethylsilyl 10-Undecenoate with Catecholborane. A 50-mL round-bottomed flask fitted with a septum inlet, a magnetic stirring bar, reflux condenser, and gas outlet (mercury bubbler) was flame-dried, purged with argon, and allowed to cool under a stream of argon. Trimethylsilyl 10-undecenoate (5.0 mmol, 1.28 g, 1.47 mL) was introduced by syringe, catecholborane (6.78 mmol, 0.89 g, 0.69 mL) slowly added at room temperature, and the mixture heated to 70 °C for 24 h. The reaction mixture was cooled to 0 °C, aqueous sodium hydroxide (3 *M*, 6.78 mmol) and hydrogen peroxide (30%, 5 mmol) were added sequentially, and then the mixture was heated to 70 °C for 24 h. The reaction mixture was made basic (pH 10) with 1 N NaOH and extracted with ether (3 × 25 mL). The aqueous layer was separated, acidified (pH 2) with 1 N HCl, and saturated with NaCl, and the product was extracted into ether (3 × 25 mL). The combined ether layers were washed with ice water (10 × 100 mL) to remove any remaining catechol. The ether layer was then dried (Na_2SO_4) and filtered, and the solvent was removed to give 0.72 g (71%) of 11-hydroxyundecanoic acid. Recrystallization from ether–petroleum ether afforded 0.61 g (60%) of the hydroxyacid as a white powder, mp 70–71 °C.

11-Iodoundecanoic Acid. A 100-mL round-bottomed flask fitted with a septum inlet, a magnetic stirring bar, and gas outlet (mercury bubbler) was flame-dried, purged with argon, and allowed to cool under a stream of argon. Cyclohexene (10 mmol, 0.82 g) and THF (10 mL) were introduced by syringe, and the contents of the flask were cooled to −10 °C (ice–acetone bath). BH_3·DMS (5 mmol, 10 M, 500 μL) was added slowly and the resulting mixture stirred for 3 h at 0 °C (dicyclohexylborane precipitates from solution). Trimethylsilyl 10-undecenoate (5.0 mmol, 1.28 g, 1.47 mL) was slowly added and stirred at 0 °C for 4 h, then allowed to gradually come to room temperature, and stirred for an additional 7 h. The reaction mixture was cooled to 0 °C, and methanolic sodium acetate (1 M, 10 mmol), aqueous sodium iodide (1 M, 5 mmol), and methanolic chloramine T (0.5 M, 10 mmol) were sequentially added. The contents were stirred for 1 min and quenched by addition of sodium thiosulfate (1 M, 5 mL), and 1.2 N HCl (5 mL). Water (20 mL) and petroleum ether (20 mL) were added, and the organic layer was separated. The aqueous layer was extracted twice more with petroleum ether (20-mL portions), and the combined organic layer was dried ($MgSO_4$). Filtration followed by removal of the solvent under reduced pressure gave the crude product as a white solid. Purification by column chromatography (silica gel, 10%, then 15% ethyl acetate–petroleum ether) afforded 11-iodoundecanoic acid, 1.38 g, (88%), as a colorless oil, which solidified upon standing; mp 48–50 °C (lit.[5a] mp 47–50 °C); ^{1}H NMR ($CDCl_3$) δ 10.50 (COOH), 3.18 (t, 2 H, *J* = 7.0 Hz, CH_2I), 2.35 (t, 2 H, *J* = 6.5 Hz, CH_2COOH), 2.05–1.1 (broad envelope, 16 H); ^{13}C NMR ($CDCl_3$) δ 180.30 (COOH), 34.08, 33.54, 30.48, 29.29, 29.15, 29.02, 28.48, 24.63, 7.24 (CH_2I).

Undecanoic Acid. A 100-mL round-bottomed flask fitted with a septum inlet, a magnetic stirring bar, reflux condenser, and gas outlet (mercury bubbler) was flame dried, purged with argon, and allowed to cool under a stream of argon. Trimethylsilyl 10-undecenoate (5 mmol, 1.28 g, 1.47 mL) in THF (5 mL) was added to the flask by syringe and the solution cooled to 0 °C (ice salt bath). A cooled solution (0 °C) of BMS (10 M, 1.67 mmol, 170 μL) was introduced slowly, and the contents were stirred for 3 h, during which time the reaction mixture was allowed to warm to 15 °C. The flask was cooled to 0 °C, anhydrous THF (10 mL) and propionic acid (10 mL) were added, and the contents were refluxed at 125 °C (oil bath temperature), for 4 h. The reaction mixture was extracted into ether (4 × 50 mL), and the combined ether layers were washed with 1.2 N HCl (50 mL) and dried over anhydrous $MgSO_4$. Filtration followed by removal of the solvent gave a yellow oil containing the product and propionic acid. Water (100 mL) was added and the precipitated product filtered. The crude product was dissolved in ether, aqueous sodium hydroxide (1 M, 25 mL) added, and the ether layer removed. The separated aqueous layer was acidified with 1.2 N HCl (pH 3) and the product extracted into ether (3 × 25 mL). Filtration followed by removal of the solvent under reduced pressure gave 0.93 g of the crude acid. Recrystallization from methanol–water afforded, after drying under vacuum, undecanoic acid, 0.76 g (82%), as a white solid: mp 28 °C (lit.[16] mp 28.5 °C); ^{1}H NMR ($CDCl_3$) δ 9.06 (br, 1 H, COOH), 2.34 (t, 2 H, *J* = 7.0 Hz, CH_2COOH), 1.8–1.1 (broad

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envelope, 16 H), 0.87 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 180.25 (COOH), 34.16, 31.95, 29.62, 29.51, 29.34, 29.12, 24.74, 22.73, 14.15 (CH_3).

5-Iodopentanoic Acid. Trimethylsilyl 4-pentenoate (2.0 mmol, 0.35 g, 0.44 mL) in THF (2 mL) was slowly added to freshly prepared dicyclohexylborane (2 mmol) and the mixture stirred at 0 °C for 2 h, then gradually allowed to come to room temperature, and stirred for an additional 2 h. The reaction mixture was cooled to 0 °C and shielded from light by wrapping the flask with aluminum foil, and sodium acetate (1 M in anhydrous methanol, 4 mmol) and iodine monochloride (1 M in anhydrous methanol, 2 mmol) were sequentially added. The contents were stirred for 1 min and quenched by addition of sodium thiosulfate (1 M, 5 mL). The reaction mixture was adjusted to pH 10 with 1 N NaOH, water (20 mL) and ether (20 mL) were added, the reaction mixture was saturated with salt, and the organic layer was separated. The aqueous layer was washed twice more with ether (20-mL portions), acidified to pH 3 with 1 N HCl, and extracted with ether (3 × 25 mL). The combined organic layer was then dried over anhydrous magnesium sulfate. Filtration, followed by removal of the solvent under reduced pressure gave the crude product. Purification by column chromatography (silica gel, 10%, then 15%, and then 20% ethyl acetate–petroleum ether) afforded 5-iodopentanoic acid, 0.27 g (76%), as a colorless oil: ^1H NMR ($CDCl_3$) δ 6.2 (br, COOH), 3.19 (t, 2 H, J = 6.6 Hz, CH_2I), 2.39 (t, 2 H, J = 6.6 Hz, CH_2COOH), 2.05–1.5 (m, 4 H); ^{13}C-NMR ($CDCl_3$) δ 178.60 (COOH), 32.87 (CH_2COOH), 32.68 (RCH_2CH_2I), 25.63 (RCH_2CH_2COOH), 5.67 (CH_2I).

10-Undecenylboronic Acid. An oven-dried 250-mL round-bottomed flask fitted with a septum inlet was equipped with a magnetic stirring bar and gas outlet, flame-dried, and purged with nitrogen. Trimethylsilyl 10-undecynoate (4.82 mmol, 1.23 g) was introduced to the flask, followed by the slow addition of catecholborane (4.82 mmol, 0.51 mL), and the contents were stirred at 40 °C for 19 h. Water (150 mL) was added and the mixture stirred overnight to hydrolyze the boronic ester. The aqueous layer was decanted off, the solid boronic acid dissolved in ether and washed with cold water (2 × 50 mL), and the product precipitated by addition of petroleum ether. The product was redissolved in ether and crystallized by the addition of petroleum ether to afford 0.96 g (87%) of 10-undecenylboronic acid as a white powder: ^1H NMR (DMSO-d_6) δ 11.8 (br, COOH), 6.65–6.2 (m, 1 H, $(HO)_2BCH{=}CHR$), 5.45–5.15 (m, 1 H, J_{trans} = 18.0 Hz, $(HO)_2BCH{=}CHR$), 2.3–1.8 (m, 4 H, $(HO)_2BCH{=}CHCH_2R$, CH_2COOH), 1.7–1.1 (broad envelope, 12 H); ^{13}C NMR (DMSO-d_6) δ 174.50 (COOH), 150.01 ($(HO)_2BCH{=}CHR$), 35.08, 33.70, 28.66, 28.12, 24.55; ^{13}C NMR (acetone-d_6) δ 175.74 (COOH), 152.20 ($(HO)_2BCH{=}CHR$), 36.76, 34.79, 30.67, 30.48, 30.4, 29.86, 26.15; ^{11}B NMR (THF) δ 27.3.

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Registry No. ^{29}Si, 14304-87-1; trimethylsilyl 10-undecenoate, 24338-09-8; 10-undecenoic acid, 112-38-9; trimethylsilyl 4-pentenoate, 23523-56-0; 4-pentenoic acid, 591-80-0; trimethylsilyl hexanoate, 14246-15-2; hexanoic acid, 142-62-1; trimethylsilyl (*Z*)-9-octadecenoate, 21556-26-3; oleic acid, 112-80-1; trimethylsilyl 3-cyclohexene-1-carboxylate, 104171-36-0; 3-cyclohexene-1-carboxylic acid, 4771-80-6; trimethylsilyl 10-undecynoate, 118798-27-9; 10-undecynoic acid, 2777-65-3; 11-hydroxyundecanoic acid, 3669-80-5; 11-iodoundecanoic acid, 63632-65-5; undecanoic acid, 112-37-8; propionic acid, 79-09-4; 5-iodopentanoic acid, 19448-36-3; 10-undecenylboronic acid, 118798-28-0.

Synthesis, Characterization, and Reactivity of Alkoxide and Hydroxide Complexes of Rhodium(I) and Iridium(I)[1]

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Bimetallic alkoxide- and hydroxide-bridged complexes of rhodium(I) and iridium(I), $[M(OR)COD]_2$ (M = Rh, Ir; R = H, alkyl or aryl group; COD = 1,5-cyclooctadiene), were prepared and used in the synthesis of four-coordinate alkoxide and hydroxide complexes of rhodium(I) and iridium(I) containing the chelating triphosphine ligands ttp $\{C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2\}$ or Cyttp $\{C_6H_5P[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}$, i.e. M(OR)(ttp) or M(OR)(Cyttp). The basicity of the Rh–OR bond in Rh(OH)(ttp) and $Rh(OC_6H_5)$(ttp) was tested by use of reactions with weak organic acids; consequently, a series of rhodium carboxylates (e.g., $Rh(OC(O)CF_3)$(ttp), $Rh(OC(O)C_6H_4Br)$(ttp), and $Rh(OC(O)C_6H_5)$(ttp)) was formed. Sulfur dioxide insertion reactions led to metal sulfonates and metal sulfonic acids, i.e. $Rh(SO_2OC_6H_5)(ttp){\cdot}SO_2$, $Rh(SO_2OC_6H_5)(Cyttp){\cdot}SO_2$, $Ir(SO_2OC_6H_5)(ttp){\cdot}SO_2$, and $Rh(SO_2OH)(ttp){\cdot}SO_2$. The three olefins ($CH_2{=}CH_2$, $Cl_2C{=}CClH$, and $(CN)_2C{=}C(CN)_2$) failed to react with Rh(OH)(ttp) or $Rh(OC_6H_5)$(ttp) to produce insertion products or simple olefin adducts. All metal complexes were characterized by elemental analysis and infrared and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Although extensive work has been published on alkoxide derivatives of early and inner transition metals and of main-group metals,[3,4] until recently, few investigations of group VIII metal alkoxide complexes have been undertaken. In fact, this topic has been reviewed in the literature only once.[4b] Metal alkoxide intermediates have been postulated in the formation of metal hydrides from alcohols,[5-10] Pd(II)-catalyzed vinyl interchange reactions,[11,12] metal-catalyzed hydroformylation reactions,[13] and the

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