Unusual rearrangement of [.alpha.-(silylalkyl)alkoxycarbene]tungsten complexes: x-ray crystal structure of (E)-(CO)5W[C(N(CH3)2)CH2CH2CH:C(OCH3)Si(CH3)3]

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Unusual Rearrangement of [(α-(Silyl)alkyl)alkoxycarbene]tungsten Complexes: X-ray Crystal Structure of (*E*)-$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH{=}C(OCH_3)Si(CH_3)_3]$

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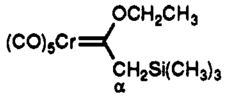
Treatment of the α-lithio carbene anions $(CO)_5W[C(XR)CH_2]Li$ (**3**; XR = OCH_3, $N(CH_3)_2$) with the α,β-unsaturated carbene complexes $(CO)_5W[C(OCH_3)C(SiR'_3){=}CH_2]$ (**4**; R′ = CH_3, C_6H_5) followed by quenching the reaction with the appropriate electrophilic reagent EX (EX = $(CH_3)_3SiCl$, CF_3CO_2H, CH_3CO_2H) afforded the α-silylated vinyl ether complexes $(CO)_5W[C(XR)CH_2CH_2CH{=}C(OCH_3)SiR'_3]$ (**5**) in yields ranging from 23 to 89%. For complexes **5** only the isomers having the *E* configuration about the carbon–carbon double bond of the α-silylated vinyl ether groups were obtained. Treatment of **3b** (XR = $N(CH_3)_2$) with **4a** (R′ = CH_3) followed by only column chromatography afforded **5b** (XR = $N(CH_3)_2$, R′ = CH_3) in 10% yield as well as the (μ-bis(carbene))ditungsten complex $(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(OCH_3)]W(CO)_5$ (**6**) in 58% yield. On the other hand, treatment of **3b** (XR = $N(CH_3)_2$) with **4b** (R′ = C_6H_5) followed by HCl at −78 °C produced the (μ-bis[(α-(triphenylsilyl)alkyl)carbene])ditungsten complex $(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH(Si(C_6H_5)_3)C(OCH_3)]W(CO)_5$ (**7d**). Complex **7d** underwent clean rearrangement in C_6H_6 solution at 25 °C to give **5d** (XR = $N(CH_3)_2$, R′ = C_6H_5) and $W(CO)_6$. Acidic hydrolysis of the α-trimethylsilylated vinyl ether group in complexes **5a** (XR = OCH_3, R′ = CH_3) and **5b** (XR = $N(CH_3)_2$, R′ = CH_3) resulted in good yields of the corresponding acylsilanes $(CO)_5W[C(XR)CH_2CH_2CH_2C(O)Si(CH_3)_3]$ (**10**). Complex **5b** (XR = $N(CH_3)_2$, R′ = CH_3) was also characterized by single-crystal X-ray diffraction methods. Complex **5b** crystallizes in the centric $P2_1/n$ space group with cell constants (at 20 °C) a = 6.840 (7) Å, b = 22.425 (6) Å, c = 13.721 (9) Å, β = 98.64 (9)°, and D_{calcd} = 1.71 g cm^{-3} for Z = 4. Least-squares refinement based on 2832 independent observed [$F_o \geq 5\sigma(F_o)$] reflections led to a final conventional R value of 0.026.

Introduction

Although "Fischer-type" carbene complexes have been extensively studied over the past 25 years,[1] many subclasses of these interesting compounds remain virtually unexplored. One such subclass, namely [(α-(silyl)alkyl)carbene]metal complexes, has received little attention since the initial report of $(CO)_5Cr[C(OCH_2CH_2)CH_2Si(CH_3)_3]$ (**1**) by Connor and Jones in 1973.[2] Compound **1** was prepared by treating $Cr(CO)_6$ with $(CH_3)_3SiCH_2Li$, followed by exchange of Li^+ for $N(CH_3)_4^+$ in the resulting metal acylate anion and finally alkylation with $(CH_3CH_2)_3O^+BF_4^-$. On the other hand, compound **2**, which was recently used by us in the Peterson reaction to synthesize [(alkenyl)(dimethylamino)carbene]tungsten complexes, was prepared by the C-silylation of $(CO)_5W[C(N(CH_3)_2)CH_2]Li$ (**3b**) with $(CH_3)_3SiCl$.[3] Furthermore, [(α-(trimethylsilyl)alkyl)alkoxycarbene]tungsten complexes may be reactive intermediates in the preparation of [(alkyl)alkoxycarbene]tungsten complexes.[4] This article describes the synthesis of four new α-silylated vinyl ether carbene complexes (**5a–d**), which are proposed to arise from an unusual rearrangement of [(α-(silyl)alkyl)alkoxycarbene]tungsten complexes, as well as the X-ray crystal structure of **5b**.



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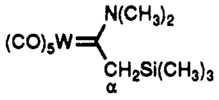

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Results and Discussion

During our investigations on the conjugate addition reactions of α-lithio carbene anions to α,β-unsaturated carbene complexes to synthesize new (μ-bis(carbene))dimetal[5] and (μ-tris(carbene))trimetal[6] complexes we occasionally found that molecules containing both a vinyl ether group and a transition-metal carbene fragment were produced. The formation of these vinyl ether derivatives was dependent upon the reaction conditions and/or the structure of the α,β-unsaturated carbene complex. For example, treatment of the α-lithio carbene anion **3b** with the α-silylated α,β-unsaturated carbene complex **4a** followed by chromatography on silica gel afforded both the α-silylated vinyl ether derivative **5b** (10%) as well as the (μ-bis(carbene))ditungsten complex **6** (58%) (eq 1).

We subsequently found that if chlorotrimethylsilane was used to quench the reaction (eq 1) prior to chromatography

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† Present address: 3M Company, St. Paul, MN 55144-1000.

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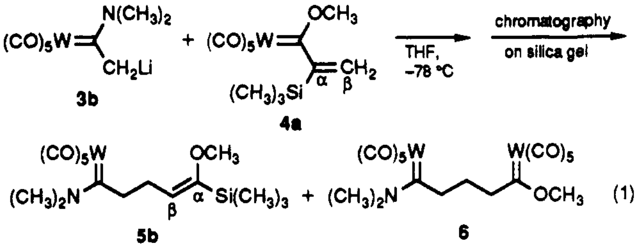
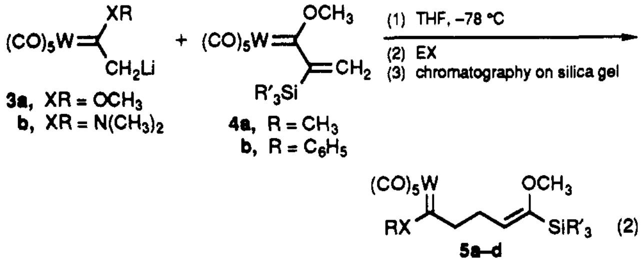


on silica gel, only complex **5b** was produced (eq 2).



Moreover, the other α-silylated vinyl ether derivatives **5a,c,d** could be prepared by reacting anions **3** with α-silylated α,β-unsaturated carbene complexes **4**, in different combinations, followed by the appropriate electrophilic quenching agents EX (eq 2). In all cases the reaction conditions for workup, which are listed in Table I, were optimized to give the highest yields of complexes **5**.

The structures of **5a–d** were easily established through spectroscopic (^{1}H and ^{13}C NMR) as well as analytical methods. For example, the ^{1}H and ^{13}C NMR chemical shift values associated with the (methoxycarbene)tungsten and ((dimethylamino)carbene)tungsten fragments for **5a,c** and **5b,d**, respectively, are consistent with their assigned structures and are similar to those of other Fischer-type tungsten carbene complexes.[3,5b,6] Furthermore, the ^{1}H and ^{13}C NMR chemical shift values associated with the α-silylated vinyl ether fragments of **5a–d** are also consistent with their assigned structures.[6,7] Because complexes **5a–d** contain a trisubstituted alkene group, two possible structural isomers are possible. For each compound (**5a–d**), however, only one isomer was isolated. For complex **5b**, the *E* configuration was unambiguously assigned to the carbon–carbon double bond on the basis of an X-ray crystal structure (vide infra). Moreover, the close similarities of the ^{1}H and ^{13}C NMR chemical shift values of the α-silylated vinyl ether group in compounds **5a,c,d** with **5b** suggest that the double bond in these compounds also has the *E* configuration.

The molecular structure and atom-labeling scheme for complex **5b** are shown in Figure 1, whereas bond distances and angles are presented in Table II. The overall structure of **5b** contains an octahedrally disposed (aminocarbene)tungsten pentacarbonyl fragment connected through two methylene groups to an α-trimethylsilylated vinyl ether group. The W–C(carbene) (W–C(6)) distance of 2.252 (5) Å, and bond angles about the carbene carbon W–C(6)–N (129.7 (4)°), W–C(6)–C(7) (116.7 (3)°), and N–C(6)–C(7) (113.6 (5)°) are typical of other (aminocarbene)tungsten complexes.[3] Likewise, the bond distances and angles associated with the α-trimethylsilylated vinyl ether group in **5b** are similar to the structural parameters reported for both organic[8] and organometallic[9] molecules containing this group.

Table I. Yields and Reaction Conditions for the Preparation of Complexes 5

compd	XR	R′	EX/temp, °C	% yield
5a	OCH_3	CH_3	$(CH_3)_3SiCl/-10$	53
5b	$N(CH_3)_2$	CH_3	$(CH_3)_3SiCl/-10$	89
5c	OCH_3	C_6H_5	$CF_3CO_2H/-78$	23
5d	$N(CH_3)_2$	C_6H_5	$CH_3CO_2H/-40$	56

Table II. Bond Distances (Å) and Angles (deg) for Compound 5b

	Bond Distances		
W–C(1)	1.998 (6)	W–C(2)	2.024 (6)
W–C(3)	2.008 (6)	W–C(4)	2.019 (6)
W–C(5)	2.042 (6)	W–C(6)	2.252 (5)
Si–C(10)	1.891 (5)	Si–C(13)	1.860 (6)
Si–C(14)	1.856 (6)	Si–C(15)	1.857 (6)
O(1)–C(1)	1.150 (6)	O(2)–C(2)	1.146 (6)
O(3)–C(3)	1.165 (6)	O(4)–C(4)	1.154 (6)
O(5)–C(5)	1.135 (6)	O(6)–C(10)	1.387 (6)
O(6)–C(16)	1.396 (7)	N–C(6)	1.306 (6)
N–C(11)	1.474 (6)	N–C(12)	1.477 (7)
C(6)–C(7)	1.530 (7)	C(7)–C(8)	1.537 (7)
C(8)–C(9)	1.500 (7)	C(9)–C(10)	1.318 (7)
	Bond Angles		
C(1)–W–C(2)	85.6 (2)	C(1)–W–C(3)	92.0 (2)
C(2)–W–C(3)	89.4 (2)	C(1)–W–C(4)	85.7 (2)
C(2)–W–C(4)	171.2 (2)	C(3)–W–C(4)	90.1 (2)
C(1)–W–C(5)	91.4 (2)	C(2)–W–C(5)	91.0 (2)
C(3)–W–C(5)	176.6 (2)	C(4)–W–C(5)	90.1 (2)
C(1)–W–C(6)	176.3 (2)	C(2)–W–C(6)	92.7 (2)
C(3)–W–C(6)	84.7 (2)	C(4)–W–C(6)	96.0 (2)
C(5)–W–C(6)	92.0 (2)	C(10)–Si–C(13)	109.9 (3)
C(10)–Si–C(14)	107.9 (3)	C(13)–Si–C(14)	109.2 (3)
C(10)–Si–C(15)	111.1 (3)	C(13)–Si–C(15)	111.1 (3)
C(14)–Si–C(15)	107.6 (4)	C(10)–O(6)–C(16)	120.3 (5)
C(6)–N–C(11)	122.6 (5)	C(6)–N–C(12)	126.5 (5)
C(11)–N–C(12)	110.8 (5)	W–C(1)–O(1)	178.9 (5)
W–C(2)–O(2)	175.5 (5)	W–C(3)–O(3)	177.6 (5)
W–C(4)–O(4)	176.3 (5)	W–C(5)–O(5)	178.9 (5)
W–C(6)–N	129.7 (4)	W–C(6)–C(7)	116.7 (3)
N–C(6)–C(7)	113.6 (5)	C(6)–C(7)–C(8)	111.0 (4)
C(7)–C(8)–C(9)	111.4 (5)	C(8)–C(9)–C(10)	125.0 (5)
Si–C(10)–O(6)	123.6 (4)	Si–C(10)–C(9)	122.6 (4)
O(6)–C(10)–C(9)	113.5 (5)		

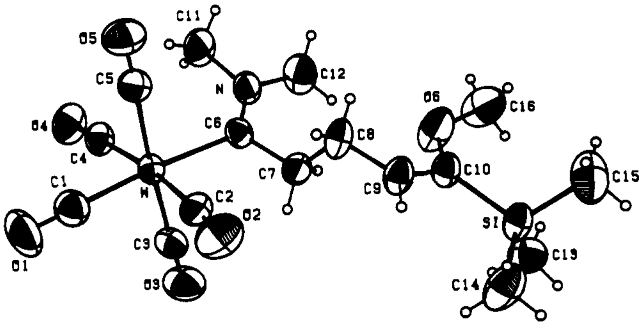


Figure 1. Molecular structure and atom-labeling scheme for **5b** with the atoms represented by their 50% probability ellipsoids for thermal motion.

At this stage of the investigation we postulated that the immediate precursors to complexes **5a–d** were the (μ-bis[(α-(silyl)alkyl)carbene])ditungsten complexes $(CO)_5W[C(XR)CH_2CH_2CH(SiR'_3)C(OCH_3)]W(CO)_5$ (**7**; vide infra) which, in turn, arise from the protonation of the α-lithio

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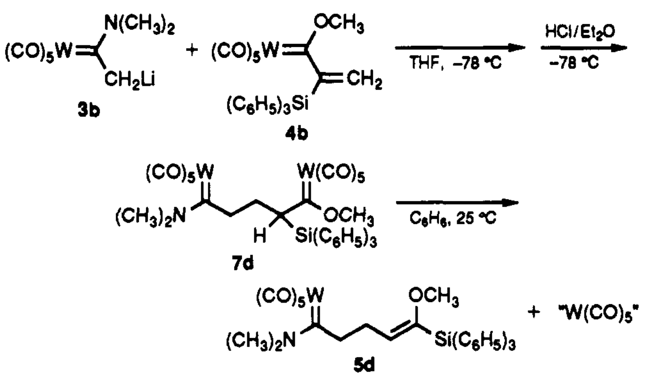
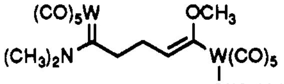
Scheme I



(μ-bis(carbene))ditungsten anions $\{(CO)_5W[C(XR)CH_2CH_2C(SiR'_3)C(OCH_3)]W(CO)_5\}Li$. These α-lithio (μ-bis(carbene))ditungsten anions, which have previously been shown to readily react with various electrophiles to afford (μ-bis(carbene))ditungsten complexes,[5] are produced by the conjugate addition of anions **3** to the α,β-unsaturated carbene complexes **4**. At no time during the preparation of complexes **5a–d**, according to eq 2, did we isolate or detect the proposed intermediates **7**. Furthermore, complex **6** (eq 1) most likely arises by the photodesilylation[2-4] of $(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH(Si(CH_3)_3)C(OCH_3)]W(CO)_5$ (**7b**).

It was subsequently found that by changing the reaction conditions and isolation techniques described in eq 1 we were able to isolate one of these elusive (μ-bis[(α-(silyl)alkyl)carbene])ditungsten complexes namely **7d** (Scheme I). Thus, treatment of **4b** with **3b** followed by quenching the reaction with HCl (−78 °C), and then low-temperature chromatography, afforded **7d** as a yellow oil. The structure of complex **7d** was established through a combination of ^1H and ^{13}C NMR spectroscopy. The characteristic resonances for the magnetically different (aminocarbene)tungsten and (alkoxycarbene)tungsten fragments were readily observed. For example, the ^1H NMR ($CDCl_3$) spectrum of **7d** exhibited resonances at δ 3.64 and 2.78 [$W{=}C(N(CH_3)_2)$] and 4.55 ($W{=}C(OCH_3)$), whereas the ^{13}C NMR ($CDCl_3$) spectrum exhibited resonances at δ 258.17 [$W{=}C(N(CH_3)_2)$] and δ 338.81 ($W{=}C(OCH_3)$). Furthermore, the proton attached to the asymmetric α-(triphenylsilyl)alkyl carbon [$CH(Si(C_6H_5)_3)$] appeared at δ 4.83 as a doublet of doublets (J = 10, 3 Hz; ABC pattern)[10] in the ^1H NMR spectrum. It is interesting to note that, unlike **7b**, complex **7d** did not undergo protodesilylation to **6** upon silica gel chromatography. This may be due to the greater hydrolytic stability of the $C{-}Si(C_6H_5)_3$ bond in complex **7d** over the $C{-}Si(CH_3)_3$ bond in complex **7b**.[11,12]

We next observed that a purified sample of **7d** rearranged cleanly in C_6D_6 solution and at 25 °C to its α-triphenylsilyl vinyl ether derivative **5d** (Scheme I). The other organometallic product from this rearrangement was determined by ^{13}C NMR spectroscopy to be $W(CO)_6$ (δ 191.14), which, no doubt, arises from dismutation of $W(CO)_5$. A proposed first step in this unusual rearrangement (i.e. **7d** to **5d**) would be a 1,3-shift of the triphenylsilyl group to produce the transient intermediate **8**. A closely related organic analogue of this proposed 1,3-shift is the β-keto silane to siloxyalkene rearrangement.[14] It has also been observed that several different unstable alkylcarbene complexes undergo a similar rearrangement in which an intramolecular hydrogen shift ultimately produces metal–alkene complexes.[15,16] Reductive elimination of **8** would then result in the formation of **5d** and a $W(CO)_5$ fragment. This last step is the same as the proposed final step in the mechanism of hydrosilylation of alkynes.[17] It is also possible that the unobserved $(CO)_5W$–alkene complex[16] **9** is produced as an intermediate after reductive elimination of **8** and then leads to the observed product **7d** by dissociation of the $(CO)_5W$ fragment. Moreover, the two-step proposed mechanism outlined above is consistent with the observed E stereochemistry associated with the α-triphenylsilylated vinyl ether group in **5d**. Although only the rearrangement of **7d** to **5d** has been observed, we feel this is strong evidence to suggest that the other α-silylated vinyl ether complexes **5a–c** arise similarly from **7a–c**, respectively. It should also be noted that to the best of our knowledge the two closely related mononuclear [(α-(silyl)alkyl)carbene]metal complexes **1**[2] and **2**[3] do not undergo this rearrangement. The reason for the reactivity differences of **1** and **2** as compared to the (μ-bis(carbene))ditungsten complexes **7** remains to be elucidated.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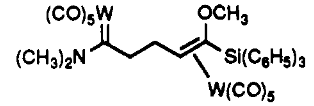
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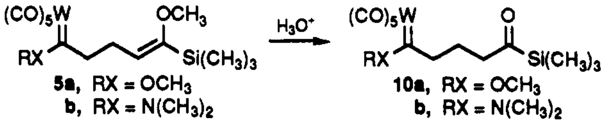
Acidic hydrolysis[7d-f] of the α-trimethylsilylated vinyl ether group in complexes **5a,b** resulted in good yields of the corresponding acylsilanes **10a,b**, respectively (eq 3).



(3)

The characteristic downfield chemical shifts associated with the carbonyl carbon of the acylsilane group in **10a** (δ 246.81) and **10b** (δ 247.81) in the ^{13}C NMR spectra are similar to those of other organic acylsilanes.[7d] The overall process of converting [(α-(silyl)alkyl)alkoxycarbene]tungsten complexes (i.e. **7**) to acylsilanes (i.e. **10**) represents a new method of preparation for acylsilanes, which are finding increasing use in organic synthesis.[18]

Experimental Section

General Data. All reactions were conducted under an inert argon or nitrogen atmosphere. Hexane, pentane, methylene chloride, and chlorotrimethylsilane were distilled from calcium hydride under nitrogen. Diethyl ether and tetrahydrofuran were

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Table III. Crystal Data and Summary of Intensity Data Collection and Refinement of Compound 5b

formula	$C_{16}H_{23}NO_6SiW$
color/shape	yellow/parallelepiped
mol wt	537.3
space group	$P2_1/n$
temp, °C	20
cell constants[a]	
a, Å	6.840 (7)
b, Å	22.425 (6)
c, Å	13.721 (9)
β, deg	98.64 (9)
cell vol, $Å^3$	2081
formula units/unit cell	4
D(calcd), g cm^{-3}	1.71
μ(calcd), cm^{-1}	53.8
diffractometer/scan	Enraf-Nonius CAD-4/θ–2θ
range of relative transmissn factors, %	50–100
radiatn, graphite monochromator	Mo Kα (λ = 0.710 73 Å)
max cryst dimens, mm	0.15 × 0.38 × 0.55
scan width, deg	0.80 + 0.35 tan θ
std reflns	400; 0,18,0; 0,0,12
decay of stds, %	±2
no. of reflns measd	4048
2θ range, deg	$2 \leq 2\theta \leq 50$
range of *hkl*	+8, +26, ±16
no. of rflns obsd $[F_o \geq 5\sigma(F_o)]$[b]	2832
computer programs[c]	SHELX[26]
structure soln	heavy-atom techniques
no. of params varied	244
weights	$[\sigma(F_o)^2 + 0.00008F_o^2]^{-1}$
GOF	0.8
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.026
R_w	0.026
largest feature in final diff map, e $Å^{-3}$	0.5

[a] Least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections, θ > 20°. [b] Corrections: Lorentz–polarization and absorption (empirical, ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 27.

distilled from sodium benzophenone ketyl under nitrogen. Trifluoroacetic acid, chlorotriphenylsilane, and vinylmagnesium bromide were purchased from Aldrich Chemical Co. and used without further purification. The starting (alkylcarbene)tungsten and (alkenylcarbene)tungsten complexes $(CO)_5W[C(OCH_3)CH_3]$,[19] $(CO)_5W[C(N(CH_3)_2)CH_3]$,[3] and $(CO)_5W[C(OCH_3)C(Si(CH_3)_3){=}CH_2]$ (**4a**)[20] were prepared according to literature procedures. Flash chromatography[21] was conducted on E. Merck silica gel 60 (40–63 μm). Low-temperature flash chromatography was conducted under nitrogen on silica gel with use of a modified low-temperature[22] air-sensitive flash chromatography apparatus.[23]

^1H and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument operating at 400.1 and 100.6 MHz, respectively. ^1H NMR data are reported as follows: chemical shift in parts per million referenced to TMS or residual solvent proton resonance (multiplicity, coupling constant(s) in hertz, number of protons). ^{13}C NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent carbon resonance. Low-resolution mass spectra were acquired on a Finnigan 4000 instrument, and spectral data are listed as *m/e* (intensity of base peak) for only the tungsten-184 isotope. Elemental analyses were performed by Microlytics, South Deerfield, MA.

X-ray Data Collection, Structure Determination, and Refinement for Compound 5b. A yellow single crystal of the title compound was mounted in a thin-walled glass capillary and transferred to the goniometer. The space group was determined to be the centric $P2_1/n$ from the systematic absences. A summary of data collection parameters is given in Table III.

Table IV. Final Fractional Coordinates for Compound 5b

atom	*x/a*	*y/b*	*z/c*	*B*(eqv),[a] $Å^2$
W	0.20956 (3)	0.38957 (1)	0.07934 (1)	2.22
Si	0.9099 (2)	0.10298 (7)	0.1224 (1)	2.98
O(1)	0.1591 (8)	0.5043 (2)	0.2054 (3)	5.37
O(2)	0.6415 (7)	0.3869 (2)	0.2008 (3)	4.65
O(3)	0.0711 (7)	0.3042 (2)	0.2403 (3)	4.79
O(4)	−0.2363 (6)	0.4141 (2)	−0.0137 (3)	4.22
O(5)	0.3532 (6)	0.4674 (2)	−0.0900 (3)	4.02
O(6)	0.5985 (7)	0.1411 (2)	−0.0321 (3)	4.84
N	0.1609 (7)	0.2855 (2)	−0.0870 (3)	2.98
C(1)	0.1783 (9)	0.4627 (3)	0.1586 (4)	3.41
C(2)	0.4880 (9)	0.3864 (3)	0.1540 (4)	2.88
C(3)	0.1196 (8)	0.3366 (3)	0.1819 (4)	3.04
C(4)	−0.0746 (8)	0.4033 (2)	0.0187 (4)	2.78
C(5)	0.3026 (8)	0.4391 (3)	−0.0299 (4)	2.72
C(6)	0.2478 (7)	0.3037 (2)	−0.0008 (3)	2.36
C(7)	0.3893 (8)	0.2578 (2)	0.0536 (4)	2.81
C(8)	0.5905 (8)	0.2591 (2)	0.0166 (4)	3.09
C(9)	0.7310 (8)	0.2145 (2)	0.0701 (4)	2.97
C(10)	0.7397 (8)	0.1577 (2)	0.0466 (4)	2.77
C(11)	0.0245 (9)	0.3235 (3)	−0.1533 (4)	3.96
C(12)	0.173 (1)	0.2252 (3)	−0.1290 (5)	4.26
C(13)	0.765 (1)	0.0381 (3)	0.1568 (4)	4.11
C(14)	1.025 (1)	0.1418 (3)	0.2361 (5)	4.56
C(15)	1.112 (1)	0.0785 (3)	0.0551 (6)	5.51
C(16)	0.622 (1)	0.0889 (3)	−0.0846 (5)	5.52

[a] $B(\text{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Least-squares refinement with isotropic thermal parameters led to *R* = 0.051. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 $Å^2$. The methyl hydrogen atoms were refined as rigid groups with C–H fixed at 0.95 Å and *B* fixed at 5.5 $Å^2$, but with rotational freedom. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of *R* = 0.026 and R_w = 0.026. The final values of the positional parameters are given in Table IV.

(Triphenylsilyl)ethylene. The title compound was prepared according to a procedure developed for (trimethylsilyl)ethylene[24] as follows: chlorotriphenylsilane (5.00 g, 17.0 mmol) was dissolved in THF (100 mL), and 1.0 M vinylmagnesium bromide in THF (18.7 mL, 18.7 mmol) was added dropwise through a cannula. After the addition was complete, the reaction mixture was refluxed for 24 h, cooled to 25 °C, and then hydrolyzed with water. The resulting solution was exhaustively extracted with methylene chloride, and the combined organic extracts were washed with 3 N HCl (25 mL), followed by two times with water (25 mL). The organic extracts were dried over anhydrous magnesium sulfate and then filtered. Removal of the solvent under vacuum afforded 4.87 g (100%) of (triphenylsilyl)ethylene.

1-Bromo-1-(triphenylsilyl)ethylene. The title compound was prepared according to the literature procedure[25] from (triphenylsilyl)ethylene.

$(CO)_5W[C(OCH_3)C(Si(C_6H_5)_3){=}CH_2]$ (4b). To a stirred solution of 1-bromo-1-(triphenylsilyl)ethylene (3.30 g, 9.0 mmol) in 50 mL of diethyl ether, which was cooled to −24 °C, was added 2.5 M *n*-BuLi (4.20 mL, 10.5 mmol) via a syringe. The resulting white suspension was stirred at −24 °C for 1.5 h and then transferred through a cannula to a suspension of tungsten hexacarbonyl (3.17 g, 9.0 mmol) in 250 mL of diethyl ether at 25 °C. The resulting clear red reaction mixture was stirred at 25 °C for 3 h, and then the solvent was removed under vacuum. The resulting yellow-orange residue was then taken up in 10 mL of nitrogen-saturated water. To this aqueous solution was added trimethyloxonium tetrafluoroborate (1.60 g, 10.2 mmol) in small portions. The resulting carbene complex was extracted into methylene chloride, and the combined organic extracts were washed twice with 25 mL of water and then dried over anhydrous

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magnesium sulfate. The solvent was removed under vacuum, and the resulting orange-red residue was taken up in a minimum of methylene chloride and then transferred to a column of silica gel. Elution of the column with 10% methylene chloride/90% hexane, collection of all the red fractions, and removal of the solvent under vacuum afforded **4b** (4.00 g, 68%): red-brown crystals; mp 108–109 °C; ^{1}H NMR ($CDCl_3$) δ 7.55–7.31 (m, 15 H), 6.44 (s, 1 H), 5.87 (s, 1 H), 4.19 (s, 3 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 332.37, 203.29, 197.36, 166.70, 136.03, 135.83, 133.05, 129.83, 127.87, 68.65. Anal. Calcd for $C_{27}H_{20}O_6SiW$: C, 49.55; H, 3.08. Found: C, 49.37; H, 3.11.

(*E*)-$(CO)_5W[C(OCH_3)CH_2CH_2CH{=}C(OCH_3)Si(CH_3)_3]$ (5a). To a stirred solution of $(CO)_5W[C(OCH_3)CH_3]$ (0.50 g, 1.3 mmol) in 30 mL of THF at −78 °C was added (2.5 M) *n*-BuLi/hexane (0.63 mL, 1.6 mmol). After the resulting solution of **3a** was stirred for 30 min at −78 °C, a solution of **4a** (0.61 g, 1.3 mmol) in 30 mL of THF was introduced through a cannula. The temperature of the solution was brought slowly to −10 °C over the course of 3 h, and then chlorotrimethylsilane (0.83 mL, 6.5 mmol) was added and the mixture stirred at −10 °C for an additional 5 min. The solution was warmed to 25 °C, the solvent was then removed under vacuum, and the resulting residue was transferred, with a minimum amount of methylene chloride, to a silica gel column. Elution of the column with 15% methylene chloride/85% hexane, collection of all the yellow fractions, and removal of the solvent under vacuum gave **5a** (0.36 g, 53%): ^{1}H NMR ($CDCl_3$) δ 4.95 (t, *J* = 7.0 Hz, 1 H), 4.61 (s, 3 H), 3.60 (s, 3 H), 3.25 (t, *J* = 7.3 Hz, 2 H), 2.35 (q, *J* = 7.4 Hz, 2 H), 0.17 (s, 9 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 336.80, 203.33, 197.27, 163.28, 122.27, 70.35, 64.26, 58.71, 22.07, −0.47; MS (15.9 eV) *m/e* 524 (M^+, 8%), 496 (2), 468 (6), 440 (30), 384 (25). Anal. Calcd for $C_{15}H_{20}O_7SiW$: C, 34.37; H, 3.85. Found: C, 34.50; H, 3.93. Besides **5a**, a small amount of the (μ-bis(carbene))ditungsten complex $(CO)_5W[C(OCH_3)CH_2CH_2CH_2C(OCH_3)]W(CO)_5$,[5] which is less polar than **5a**, was also isolated.

(*E*)-$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH{=}C(OCH_3)Si(CH_3)_3]$ (5b). To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.95 g, 2.4 mmol) in 50 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (1.2 mL, 2.9 mmol). After the resulting solution of **3b** was stirred for 30 min at −78 °C, a solution of **4a** (1.12 g, 2.4 mmol) in 50 mL of THF was introduced through a cannula. The temperature of the solution was brought slowly to −10 °C over the course of 3 h, and then chlorotrimethylsilane (1.52 mL, 12.0 mmol) was added. The solution was warmed to 25 °C, the solvent was removed under vacuum, and the resulting residue was transferred, with a minimum amount of methylene chloride, to a column of silica gel. Elution of the column with 20% methylene/80% hexane, collection of all the yellow fractions, and removal of the solvent under vacuum gave **5b** (1.15 g, 89%): yellow needles; mp 123–124 °C; ^{1}H NMR ($CDCl_3$) δ 5.06 (t, *J* = 7.1 Hz, 1 H), 3.78 (s, 3 H), 3.61 (s, 3 H), 3.35 (s, 3 H), 3.14 (t, *J* = 8.5 Hz, 2 H), 2.24 (m, 2 H), 0.14 (s, 9 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 259.01, 203.14, 199.03, 163.98, 121.73, 58.15, 55.95, 53.57, 40.92, 17.36, −0.33; MS (11.2 eV) *m/e* 537 (M^+, 98%), 509 (62), 481 (61), 453 (100), 425 (1), 397 (14). Anal. Calcd for $C_{16}H_{23}NO_6SiW$: C, 35.77; H, 4.31; N, 2.61. Found: C, 35.73; H, 4.14; N, 2.57.

(*E*)-$(CO)_5W[C(OCH_3)CH_2CH_2CH{=}C(OCH_3)Si(C_6H_5)_3]$ (5c). To a stirred solution of $(CO)_5W[C(OCH_3)CH_3]$ (0.50 g, 1.3 mmol) in 30 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (0.63 mL, 1.6 mmol). After stirring the resulting solution of **3a** was stirred for 30 min at −78 °C, a solution of **4b** (0.84 g, 1.3 mmol) in 30 mL of THF was introduced through a cannula. After the reaction mixture was stirred for 2 h at −78 °C, trifluoroacetic acid (0.20 mL, 2.6 mmol) was added with continued stirring for 5 min. The solution was warmed to 25 °C, the solvent was removed under vacuum, and the resulting residue was transferred, with a minimum amount of methylene chloride, to a column of silica gel. Elution of the column with 10% methylene chloride/90% hexane, collection of all the fractions from the second yellow band, and removal of the solvent under vacuum gave **5c** (0.21 g, 23%): yellow-orange oily crystals; mp 84 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.62–7.35 (m, 15 H), 5.06 (t, *J* = 7.2 Hz, 1 H), 4.50 (s, 3 H), 3.40 (s, 3 H), 3.27 (t, *J* = 7.3 Hz, 2 H), 2.47 (q, *J* = 7.3 Hz, 2 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 335.97, 203.19, 197.22, 158.95, 136.07, 133.96, 129.73, 129.13, 127.92, 70.33, 64.13, 59.76, 22.45. Anal. Calcd for $C_{29}H_{26}O_7SiW$: C, 50.71; H, 3.69. Found: C, 51.54; H, 3.89. Repeated attempts to obtain a carbon analysis within the acceptable ±0.4 limits by a combination of recrystallization and chromatography were unsuccessful.

(*E*)-$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH{=}C(OCH_3)Si(C_6H_5)_3]$ (5d). To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.30 g, 0.76 mmol) in 30 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (0.36 mL, 0.9 mmol). After the resulting solution of **3b** was stirred for 30 min at −78 °C, a solution of **4b** (0.50 g, 0.76 mmol) in 30 mL of THF was transferred through a cannula. The temperature of the solution was brought slowly to −40 °C over the course of 3 h, glacial acetic acid (0.21 mL, 3.7 mmol) was then added, and the mixture was stirred at −40 °C for an additional 10 min. Next, the solution was warmed to 25 °C, the solvent was removed under vacuum, and the resulting residue was transferred, with a minimum amount of methylene chloride, to a column of silica gel. Elution of the column with 20% methylene chloride/80% hexane, collection of all the yellow fractions, and removal of the solvent under vacuum gave **5d** (0.31 g, 56%): small yellow crystals; mp 123 °C; ^{1}H NMR ($CDCl_3$) δ 7.63–7.36 (m, 15 H), 5.17 (t, *J* = 7.1 Hz, 1 H), 3.72 (s, 3 H), 3.40 (s, 3 H), 3.26 (s, 3 H), 3.15 (t, *J* = 8.3 Hz, 2 H), 2.40 (m, 2 H); ^{1}H NMR (C_6D_6) δ 7.76 (m, 6 H), 7.19 (m, 9 H), 5.31 (t, *J* = 7.0 Hz, 1 H), 3.33 (s, 3 H), 2.88 (br s, 5 H), 2.32 (m, 2 H), 2.01 (s, 3 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 258.21, 203.08, 198.91, 159.45, 135.00, 133.80, 129.74, 128.29, 127.96, 59.68, 55.90, 53.07, 40.94, 21.74; $^{13}C\{^{1}H\}$ NMR (C_6D_6) δ 257.40, 203.09, 199.54, 159.99, 136.43, 134.43, 130.13, 128.56, 128.37, 59.65, 55.24, 53.14, 39.88, 21.72. Anal. Calcd for $C_{30}H_{29}NO_6SiW$: C, 51.32; H, 4.03; N, 1.93. Found: C, 51.38; H, 4.07; N, 1.79.

Preparation of (*E*)-$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH{=}C(OCH_3)Si(CH_3)_3]$ (5b) and $(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(OCH_3)]W(CO)_5$ (6). To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.50 g, 1.3 mmol) in 50 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol). After the mixture was stirred for 30 min, a solution of **4a** (0.60 g, 1.3 mmol) in 50 mL of THF was introduced slowly through a cannula. The deep red color of **4a** was immediately discharged upon its addition to the solution of anion **3b**. The resulting mixture was stirred at −78 °C for 30 min and warmed to 25 °C, and the solvent was removed under high vacuum to give a yellow-brown residue. This residue was taken up in 30 mL of anhydrous THF and passed through a short column of silica gel with continued elution of the column with methylene chloride. All the yellow fractions were collected, and the solvent was removed under vacuum. The resulting residue was taken up in a minimum amount of methylene chloride and the solution transferred to a column of silica gel. Elution of the column with 20% methylene chloride/80% hexane, collection of the first yellow-orange band, and removal of the solvent under vacuum afforded **6**[5] (0.58 g, 58%). Continued elution of the column with 20% methylene chloride/80% hexane, collection of all the yellow fractions, and removal of the solvent under vacuum afforded **5b** (0.07 g, 10%).

Preparation of $(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH(Si(C_6H_5)_3)C(OCH_3)]W(CO)_5$ (7d) and Its Rearrangement to 5d. To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.10 g, 0.25 mmol) in 10 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (0.12 mL, 0.30 mmol). After the resulting solution of **3b** was stirred for 30 min at −78 °C, a solution of **4b** (0.17 g, 0.26 mmol) in 10 mL of THF was added through a cannula. After the reaction mixture was stirred for 1.5 h at −78 °C, a 1 M solution of HCl in anhydrous diethyl ether (0.25 mL, 0.25 mmol) was added and stirring was continued for 0.5 h at −78 °C. The reaction mixture was warmed to 0 °C and the solvent removed under vacuum at this temperature; the resulting residue was transferred, with a minimum amount of anhydrous methylene chloride, to a column of silica gel at −30 °C. Elution of the column (at −30 °C) with 20% methylene chloride/80% hexane produced a red band, which upon removal of the solvent under vacuum afforded recovered **4b** (30 mg). The column was eluted further with 20% methylene chloride/80% hexane, and the resulting yellow fractions were collected under nitrogen at 0 °C. The solvent was removed under vacuum at 0 °C to afford **7d** (ca. 0.1 g): ^{1}H NMR ($CDCl_3$) δ 7.62–7.34 (m, 15 H), 4.83 (dd, *J* = 10, 3 Hz, 1 H), 4.55 (s, 3 H), 3.64 (s, 3 H), 3.47 (m, 1 H), 2.97 (m, 1 H), 2.78 (s, 3 H), 2.46 (m, 1 H), 1.52 (m, 1 H); ^{1}H NMR (C_6D_6) δ 7.76–7.01 (m, 15 H), 5.02 (dd, *J* = 10.6, 2.8 Hz, 1 H), 4.12 (s, 3 H), 3.51 (m, 1 H), 2.88 (m, 1 H), 2.71 (s, 3 H), 2.58 (m, 1 H), 1.81 (s, 3 H), 1.51 (m, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 338.81, 258.17, 202.61, 198.94, 198.67, 197.40, 136.36, 130.24, 128.10, 128.01, 69.70, 69.58, 55.95, 55.39, 40.09, 27.95.

The rearrangement of **7d** to **5d** was conducted in an NMR tube as follows: a small amount (ca. 30 mg) of complex **7d** was placed in a 5-mm NMR tube. The NMR tube was attached to a vacuum line, and benzene-d_6 (ca. 0.6 mL), which had been dried first with calcium hydride and then over sodium metal, was vacuum-transferred into the NMR tube. The contents of the NMR tube were subjected to several freeze–thaw–pump cycles, and then the tube was flame-sealed under vacuum. The progress of the rearrangement, which was conducted at 25 °C, was monitored by observing a decrease in the intensities of the resonances of **7d** with a concomitant increase in the intensities of the resonances of **5d**. Moreover, the solution changed color from an initial clear yellow to a final opaque brown-black. After 8 h only the NMR resonances for complex **5d** and $W(CO)_6$ were observed. ^1H NMR (C_6D_6): δ 7.77 (m, 6 H), 7.19 (m, 9 H), 5.30 (t, J = 7 Hz, 1 H), 3.33 (s, 3 H), 2.88 (br s, 5 H), 2.33 (m, 2 H), 2.02 (s, 3 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 257.50, 203.07, 199.59, 191.14 ($W(CO)_6$), 160.01, 136.45, 134.44, 130.15, 128.60, 128.44, 59.68, 55.24, 53.19, 39.89, 21.74.

$(CO)_5W[C(OCH_3)CH_2CH_2CH_2C(O)Si(CH_3)_3]$ (10a). Complex **5a** (100 mg, 0.2 mmol) was dissolved in 25 mL of chloroform, and then the solvent was removed under vacuum. The resulting residue was then allowed to stand under nitrogen at 0 °C for 8–10 weeks. After this period, ^1H NMR spectroscopy revealed that quantitative conversion to complex **10a** had occurred. The resulting residue was taken up in a minimum amount of methylene chloride and the solution transferred to a column of silica gel. Elution of the column with 50% methylene chloride/50% hexane, collection of all the yellow fractions, and then removal of the solvent under vacuum afforded **10a**: yellow oil; ^1H NMR ($CDCl_3$) δ 4.61 (s, 3 H), 3.17 (t, J = 7.7 Hz, 2 H), 2.62 (t, J = 7.2 Hz, 2 H), 1.73 (pentet, J = 7.5 Hz, 2 H), 0.20 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 336.20, 246.81, 203.14, 197.19, 70.46, 64.13, 47.03, 18.66, 1.37; MS (14.4 eV) m/e 510 (M^+, 0.6%), 454 (21), 426 (4), 398 (27), 370 (27), 342 (7). Anal. Calcd for $C_{14}H_{18}O_7SiW$: C, 32.95; H, 3.56. Found: C, 34.88; H, 3.89. The carbon analysis exceeded the acceptable limit because purification by distillation led to decomposition.

$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(O)Si(CH_3)_3]$ (10b). Complex **5b** (0.59 g, 1.1 mmol) was dissolved in a solvent mixture of THF (20 mL), methanol (30 mL), and water (5 mL). Then 5 drops of concentrated sulfuric acid was added with stirring for 24 h at 25 °C. The reaction mixture was then extracted several times with 50-mL portions of methylene chloride. The resulting combined organic extracts were washed several times with water, were then dried over anhydrous magnesium sulfate, and were finally filtered. The solvent was removed under vacuum, and the resulting residue was transferred, with a minimum amount of methylene chloride, to a column of silica gel. Elution of the column with 30% methylene chloride/70% hexane, collection of all the yellow fractions, and then removal of the solvent under vacuum afforded **10b** (0.46 g, 80%): orange-yellow oil; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 3.37 (s, 3 H), 2.97 (t, J = 8.8 Hz, 2 H), 2.71 (t, J = 6.2 Hz, 2 H), 1.55 (m, 2 H), 0.14 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 257.88, 247.81, 203.00, 198.90, 55.81, 53.38, 47.08, 41.20, 17.22, 1.31; MS (11.2 eV) m/e 523 (M^+, 0.5%), 495 (4), 467 (2), 439 (0.2). Anal. Calcd for $C_{15}H_{21}NO_6SiW$: C, 34.43; H, 4.05; N, 2.68. Found: C, 34.53; H, 4.04; N, 2.63.

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Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, and least-squares plane results (4 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Selective Hydrogenation of α,β-Unsaturated Aldehydes in Aqueous Organic Two-Phase Solvent Systems Using Ruthenium or Rhodium Complexes of Sulfonated Phosphines

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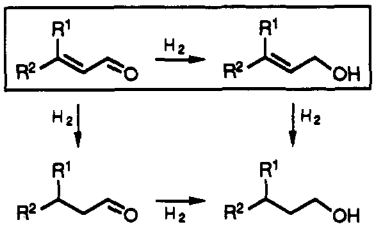
Selective hydrogenation of α,β-unsaturated aldehydes catalyzed by metal–sulfonated phosphine complexes prepared in situ is reported. The regioselectivity in the reduction was found to depend markedly on the nature of the metal used (Ru or Rh). Others factors controlling the activity and selectivity in the case of the ruthenium–sulfonated phosphine system were also investigated. ^{31}P and ^1H NMR experiments were carried out to explain the behavior of the mixture $RuCl_3$/TPPTS (TPPTS = tris(m-sulfophenyl)phosphine trisodium salt) in water. A possible mechanism that could accommodate these results is discussed.

Introduction

α,β-Unsaturated aldehydes are known to be valuable intermediates in the field of fragrance and flavor chemistry,[1] and very often the multistep synthesis to new products involves the selective reduction of the carbonyl function. Hydrogenation of the carbon–carbon double bond is readily achieved under mild conditions with high selectivity[2] whereas catalytic reduction of the aldehyde group remains a challenging problem (Scheme I).

Scheme I



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[1] (a) Bauer, K.; Garbe, D. *Common Fragrance and Flavor Materials*; VCH: New York, 1985. (b) Bauer, K.; Garbe, D. *Ullman Encyclopedia*, 3rd ed.; VCH: New York, 1988; Vol. A11, p 141.

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