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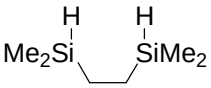
SUPPORTING INFORMATION

Title: Hydrosilanes Are Not Always Reducing Agents for Carbonyl Compounds but Can Also Induce Dehydration: A Ruthenium-Catalyzed Conversion of Primary Amides to Nitriles
Author(s): Shiori Hanada, Yukihiro Motoyama, Hideo Nagashima*
Ref. No.: O200800523

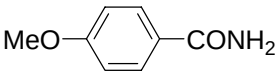
***General*:** All reactions were carried out under a nitrogen atmosphere. Ether and tetraglyme was dried over $CaCl_2$. Dimethoxyethane (DME) was distilled under nitrogen from CaH_2 prior to use. *p*-Toluamide **2a**, lauramide **2h**, 2-phenylacetamide **2i**, *p*-chlorobenzoyl chloride, *p*-methoxybenzoyl chloride, β-naphthoyl chloride, thionyl chloride and triethylsilane were purchased from Tokyo Chemical Industry Co., Ltd. α-Naphthoyl chloride and citronellic acid were purchased from Alfa Aesar. *o*-Toluic acid, ethyl chloroformate, triethylamine, H_2PtCl_6, and aqueous ammonia were purchased from Kanto Chemical Co., Ltd. Polymethylhydrosiloxane (PMHS), tetramethyldisiloxane, diethoxymethylsilane and bis(chlorodimethylsilyl)ethane were purchased from Gelest Inc., and used as received. Pentamethyldisiloxane was purchased from FluoroChem. Octyldimethylsilyl chloride was purchased from Chisso. Ru/C (5 wt%) was purchased from Aldrich Chemical Co. Pd/C (5 wt%) was purchased from Kishida Chemical Co., Ltd. $Pd(OAc)_2$ was purchased from Wako Pure Chemical Ind., Ltd. $Co_2(CO)_8$ was purchased from STREM Chemicals. ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on JEOL GSX-270 (270 MHz), ECA 400 (396 MHz) and ECA 600 (600 MHz) spectrometers. Chemical shifts for ^1H NMR were described in parts per million downfield from tetramethylsilane as an internal standard (δ = 0) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.1), unless otherwise noted. Chemical shifts for ^{29}Si NMR were described in parts per million downfield from tetramethylsilane as an external standard. IR spectra were measured on a JASCO FT/IR-4200 spectrometer. Analytical thin-layer chromatography (TLC) was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F_{254}, layer thickness 0.25 mm, respectively). Visualization was accomplished by UV light (254 nm), iodine, and phosphomolybdic acid. MS (FAB) analysis was performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. (μ_3,η^2,η^3,η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**)[1] and 1,2- $(HMe_2Si)_2C_6H_4$[2] were prepared by the method reported previously. $Ru_3(CO)_{12}$,[3a] $[RuCl_2(CO)_3]_2$,[3b] $RhCl(PPh_3)_3$,[4a] $RhH(CO)(PPh_3)_3$,[4b] $IrCl(CO)(PPh_3)_2$,[4c] $NiCl_2(PPh_3)_2$,[4d] $Pd_2(dba)_3{\cdot}CHCl_3$,[4e] $Pt(dba)_2$,[4f] (η^5-C_5H_5)$RuCl(PPh_3)_2$,[4g] [(η^6-C_6Me_6)$RuCl_2$]$_2$,[4h] were prepared by the literature methods.

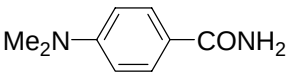
***Synthesis of Hydrosilanes*:**

1,2-Bis(dimethylsilyl)ethane (BDMSE).[5]  To a suspension of lithium aluminum hydride (3 g, large excess) in tetraglyme (30 mL) was slowly added 1,2-bis(chlorodimethylsilyl)ethane (10 g, 23.2 mmol) at 0 °C, then the mixture was stirred at 50 °C for 3 h. Purification by direct distillation from the resultant suspension under reduced pressure (64 °C/90 Torr) gave 1,2-bis(dimethylsilyl)ethane (BDMSE) in 81% yield (5.5 g). Colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.07 (d, *J* = 3.6 Hz, 12H), 0.53 (t, *J* = 1.7 Hz, 4H), 3.84 (t of sept. *J* = 1.7, 3.6 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = -4.7, 7.2; IR (neat): ν_{Si-H} = 2116 cm^{-1}.

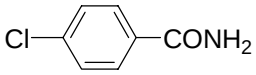
***n*-Octyldimethylsilane.** To a suspension of lithium aluminum hydride (1.5 g, 3.0 equiv.) in ether (40 mL) was slowly added *n*-ocytldimethysilyl chloride (11.3 mL, 43. 5 mmol) at 0 °C. After it was stirred at 40 °C for 2 h, the resultant mixture was quenched with saturated Na_2SO_4 at 0 °C. Purification by vacuum distillation (72 °C/10 Torr) gave *n*-octyldimethylsilane in 96% yield (7.2 g). Colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.06 (d, *J* = 3.6 Hz, 6H), 0.58 (m, 2H), 0.89 (t, *J* = 6.9 H, 3H), 1.23-1.37 (m, 12H), 3.84 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = -4.3, 14.2, 14.3, 22.8, 24.5, 29.4, 29.5, 32.1, 33.4; IR (neat): ν_{Si-H} = 2116 cm^{-1}.

***Synthesis of Primary Carboxamides*:**

***p*-Methoxybenzamide (2b).** Prepared from *p*-methoxybenzoyl chloride (2.4 mL, 17.6 mmol)  and gaseous ammonia, which was obtained from aqueous ammonia by heating. Purification by recrystallization from ethanol gave *p*-methoxybenzamide **2b** in 98% yield (2.6 g). Colorless crystal. m.p. 165.5-166.0 ^{o}C (lit.[6] 166-167 °C); ^{1}H NMR (600 MHz, $CDCl_3$-[D_6]DMSO): δ = 3.53 (s, 3H), 6.07 (bs, 1H), 6.60 (d, *J* = 8.8 Hz, 2H), 7.03 (bs, 1H), 7.56 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$-[D_6]DMSO): δ = 54.7, 112.8, 125.5, 128.9, 161.5, 168.3; IR (KBr): ν = 1616, 1649, 3168, 3387 cm^{-1}.

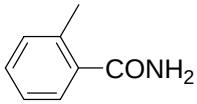
***p*-Dimethylaminobenzamide (2c).** Prepared from *p*-dimethylaminobenzoyl chloride (2.6 g,  14.2 mmol) and gaseous ammonia. Purification by precipitation from ethanol gave *p*-dimethylaminobenzamide **2c** in 62% yield (1.4 g). Yellow powder. m.p. 207-208 ^{o}C (lit.[6] 209-210 °C); ^{1}H NMR (600 MHz, $CDCl_3$-[D_6]DMSO): δ = 2.67 (s, 6H), 5.79 (bs, 1H), 6.31 (d, *J* = 8.8 Hz, 2H), 6.77 (bs, 1H), 7.43 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$-[D_6]DMSO): δ = 39.3, 110.1, 119.8, 128.5, 151.7, 168.6; IR (KBr): ν = 1603, 1642, 1674, 3150, 3341 cm^{-1}.

***p*-Chlorobenzamide (2d).** Prepared from *p*-chlorobenzoyl chloride (2.2 mL, 17.1 mmol) and

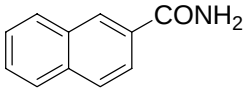


gaseous ammonia. Purification by recrystallization from ethanol gave *p*-chlorobenzamide **2d** in 80% yield (2.1 g). Colorless crystal. m.p. 178.5-189.0 ^{o}C (lit.[6] 178-179 °C); ^{1}H NMR (600 MHz, $CDCl_3$-[D_6]DMSO): δ = 6.35 (bs, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 7.32 (bs, 1H), 7.56 (d, *J* = 8.8 H, 2H); ^{13}C NMR (150 MHz, $CDCl_3$-[D_6]DMSO): δ = 127.7, 128.6, 131.8, 136.7, 167.6; IR (KBr): ν = 1623, 1656, 3183, 3368 cm^{-1}.

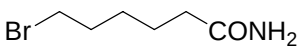
***o*-Toluamide (2e).** Prepared from *o*-toluoyl chloride, which was obtained by the reaction of *o*-toluic acid (3.0 g, 22.0 mmol) and $SOCl_2$ (8 mL, 5.0 equiv.), and gaseous ammonia. Purification by recrystallization from ethanol gave *o*-toluamide **2e** in 62% yield (1.9 g). Colorless crystal. m.p. 139.5-140.5 ^{o}C (lit.[7] 142 °C); ^{1}H NMR (600 MHz, $CDCl_3$-[D_6]DMSO): δ = 2.32 (s, 3H), 6.17 (bs, 1H), 6.57 (bs, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$-[D_6]DMSO): δ = 19.6, 125.3, 126.8, 129.6, 130.6, 135.66, 135.72, 171.9; IR (KBr): ν = 1622, 1656, 3181, 3367 cm^{-1}.



α-Naphthamide (2f). Prepared from α-naphthoyl chloride (3.34 g, 17.5 mmol) and gaseous ammonia. Purification by recrystallization from ethanol gave α-naphthamide **2f** in 87% yield (2.6 g). Colorless crystal. m.p. 205.5-206.5 °C (lit.[8] 206.0 °C); ^{1}H NMR (600 MHz, $CDCl_3$-[D_6]DMSO): δ = 6.37 (bs, 1H), 7.00 (bs, 1H), 7.23-7.33 (m, 3H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 8.2 H,z 1H); ^{13}C NMR (150 MHz, $CDCl_3$-[D_6]DMSO): δ = 124.2, 124.9, 125.2, 125.8, 126.4, 127.7, 129.6, 130.0, 133.1, 133.6, 171.2; IR (KBr): ν = 1616, 1629, 1662, 3170, 3341 cm^{-1}.



β-Naphthamide (2g). Prepared from β-naphthoyl chloride (3.34 g, 17.5 mmol) and gaseous ammonia. Purification by recrystallization from ethanol gave α-naphthamide **2g** in 77% yield (2.3 g). Colorless crystal. m.p. 194.5-195.0 ^{o}C (lit.[9] 191-192 °C); ^{1}H NMR (600 MHz, $CDCl_3$-[D_6]DMSO): δ = 6.12 (bs, 1H), 7.13 (bs, 1H), 7.39-7.44 (m, 2H), 7.73-7.76 (m, 2H), 7.79-7.81 (m, 2H), 8.29 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$-[D_6]DMSO): δ = 123.7, 125.9, 126.96, 127.01, 127.4, 127.6, 128.3, 130.6, 131.9, 134.0, 168.7; IR (KBr): ν = 1616, 1656, 3195, 3374 cm^{-1}.



6-Bromohexanamide (2j). Prepared from 6–bromohexanoyl chloride (4.0 mL, 26.1 mmol) and gaseous ammonia. Purification by recrystallization from ethanol gave 6-bromohexanamide **2j** in 81% yield (2.9 g). Colorless crystal. m.p. 106.5-107.5 °C (lit.[10] 107-109 °C); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.50 (m, 2H), 1.68 (m, 2H), 1.89 (tt, *J* = 6.9, 7.6 Hz, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 3.41 (t,

J = 6.6 Hz, 2H), 5.44 (bs, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$-[D_6]DMSO): δ = 24.2, 27.3, 32.1, 33.4, 35.1, 175.1; IR (KBr): ν = 1630, 1662, 3189, 3363 cm^{-1}.

Citronellamide (2k). Prepared from citronellic acid (3.8 mL, 20.6 mmol), triethylamine (4.3 mL, 1.5 equiv.), and ethyl chloroformate (2.0 mL, 1.0 equiv.) followed by addition of gaseous ammonia. Purification by silica gel column chromatography (hexane/acetone = 1:1) gave citronellamide **2k** in 61% yield (2.1 g). White powder. m.p. 72.0-74.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.3 Hz, 3H), 1.15-1.45 (m, 2H), 1.60 (s, 3H), 1.68 (s, 3H), 1.89-2.05 (m, 4H), 2.24 (m, 1H), 5.09 (m, 1H), 5.42 (s, 1H), 5.46 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 17.7, 19.6, 25.5, 25.8, 30.4, 36.9, 43.7, 124.2, 131.4, 175.5; IR (KBr): ν = 1630, 1662, 3189, 3370 cm^{-1}.

***Dehydration of 2a with BDMSE Catalyzed by Various Catalysts*:**

To a stirred solution of *p*-toluamide **2a** (0.5 mmol) and the catalyst (2.5 mol%) in dimethoxyethane (0.25 mL) was slowly added 1,2-bis(dimethylsilyl)ethane (1.25 mmol, Si–H = 2.5 equiv. to **2a**), and the mixture was stirred at 70 °C for 7 h. The conversion of **2a** and the chemical yield of *p*-tolunitrile **3a** were determined by ^{1}H NMR analysis with dibenzyl ether as an internal standard.

Table S1.

Catalyst	Yield [%]	Catalyst	Yield [%]	Catalyst	Yield [%]
$Ru_3(CO)_{12}$	19	$[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$	<2	$RhCl(PPh_3)_3$	<2
$[RuCl_2(CO)_3]_2$	51	$(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2$	<2	$NiCl_2(PPh_3)_2$	<2
1	61	$[(\eta^6\text{-}C_6Me_6)RuCl(MeCN)_2]PF_6$	<2	$Pd_2(dba)_3 \cdot CHCl_3$	<2
$Co_2(CO)_8$	<2	Ru/C (5 wt%; Aldrich)	<2	$Pd(OAc)_2$	<2
$RhH(CO)(PPh_3)_3$	<2			Pd/C (5 wt%, Kishida)	<2
$IrCl(CO)(PPh_3)_2$	<2			$Pt(dba)_2$	<10
				H_2PtCl_6	<10

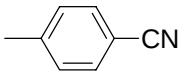
***General Procedure for the Dehydration of Primary Amides (Table 2)*:**

To a stirred solution of primary amide (1.0 mmol) and (μ_3,η^2,η^3,η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**) (16.3 mg, 2.5 mol%) in dimethoxyethane (0.5 mL) was slowly added 1,2-bis(dimethylsilyl)ethane (246 μL, Si–H = 2.5 equiv. to the amide). At this time, evolution of hydrogen gas was observed. After the mixture was stirred at 70 °C for 12–24 h, the cooled reaction mixture was diluted with diethyl ether and quenched by the addition of sodium hydrogen carbonate. After it was stirred at room temperature for 30 min, the resultant mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. Purification by silica gel column chromatography gave the desired nitrile.

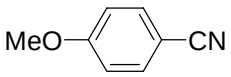
***Spectral Data of Nitriles*:**

All compounds were identified by spectral comparison with samples purchased from commercially sources or literature data.

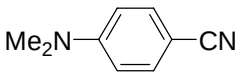
***p*-Tolunitrile (3a).** Colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 21.9, 109.4, 119.2, 129.9, 132.1, 143.7; IR (neat): $\nu_{C\equiv N}$ = 2222 cm^{-1}.



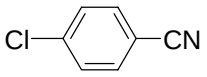
***p*-Anisonitrile (3b).** White powder. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 6.95 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 55.6, 104.1, 114.8, 119.3, 134.1, 162.9; IR (KBr): $\nu_{C\equiv N}$ 2215 cm^{-1}.



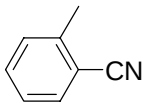
***p*-Dimethylaminobenzonitrile (3c).** White powder. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 3.04 (s, 6H), 6.66 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 40.0, 97.5, 111.5, 120.8, 133.5, 152.5; IR (KBr): $\nu_{C\equiv N}$ 2208 cm^{-1}.



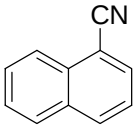
***p*-Chlorobenzonitrile (3d).** White powder. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 110.9, 118.0, 129.8, 133.5, 139.6; IR (KBr): $\nu_{C\equiv N}$ 2228 cm^{-1}.



***o*-Tolunitrile (3e).** Colorless liquid. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 2.54 (s, 3H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 20.5, 112.8, 118.2, 126.3, 130.3, 132.5, 132.7, 142.0; IR (neat): $\nu_{C\equiv N}$ 2253 cm^{-1}.

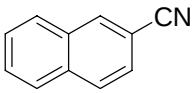


α-Naphthonitrile (3f). Colorless liquid. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 8.2 Hz, 1H), 7.63 (dd, *J* = 7.2, 8.2 Hz, 1H), 7.71 (t, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H),



7.93 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 110.2, 117.9, 124.9, 125.2, 127.6, 128.6, 128.7, 132.4, 132.7, 132.9, 133.3; IR (neat): $\nu_{C\equiv N}$ 2220 cm^{-1}.

β-Naphthonitrile (3g). White powder. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 7.59-7.67 (m, 3H),



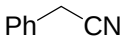
7.89-7.96 (m, 3H), 8.24 (s, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 109.5, 119.3, 126.4, 127.7, 128.1, 128.5, 129.1, 129.3, 132.3, 134.2, 134.7; IR (KBr): $\nu_{C\equiv N}$ 2222 cm^{-1}.

Dodecanenitrile (3h). Colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9

$C_{10}H_{21}CN$

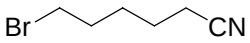
Hz, 3H), 1.21-1.33 (m, 12H), 1.39-1.49 (m, 2H), 1.65 (m, 2H), 2.33 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 9.8, 14.2, 17.2, 22.8, 25.5, 28.8, 29.4, 29.58, 29.63, 32.0, 119.9; IR (neat): $\nu_{C\equiv N}$ 2247 cm^{-1}.

2-Phenylacetnitrile (3i). Colorless liquid. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 3.75 (s, 2H),



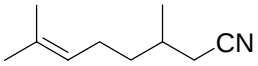
7.31-7.40 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 23.7, 117.9, 128.0, 128.1, 129.2, 130.0; IR (neat): $\nu_{C\equiv N}$ 2228 cm^{-1}.

6-Bromohexanenitrile (3j). Colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.55-1.76



(m, 4H), 1.96 (quint, *J* = 6.9 Hz, 2H), 2.37 (t, *J* = 6.6 Hz, 2H), 3.41 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 17.2, 24.7, 27.3, 31.9, 32.9, 119.5; IR (neat): $\nu_{C\equiv N}$ 2247 cm^{-1}.

Citronellyl nitrile (3k).[11] Colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.08 (d, *J* =



6.6 Hz, 3H), 1.25-1.56 (m, 2H), 1.61 (bs, 3H), 1.69 (bs, 3H), 1.87 (m, 1H), 2.02 (m, 2H), 2.23 (dd, *J* = 6.9, 16.8 Hz, 1H), 2.33 (dd, *J* = 5.9, 16.8 Hz, 1H), 5.07 (bm, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 17.7, 19.4, 24.5, 25.3, 25.7, 30.0, 35.9, 118.9, 123.5, 132.3; IR (neat): $\nu_{C\equiv N}$ 2247 cm^{-1}.

***Preparation of Bis-Silylated Amide Compounds*:**[12]

Reaction of *p*-Toluoyl Chloride with Li(TMS)$_2$. To a stirred solution of LiN(TMS)$_2$ (1.0 M in hexane, 5 mL, 5 mmol) in hexane (10 mL) was added *p*-toluoyl chloride (661 μL, 5 mmol) at room temperature. After it was stirred at that temperature for 1 h, LiCl formed was removed by filtration. Purification by vacuum distillation (67 °C/5 Pa) gave the desired bis-silylated amide in 45 %yield (0.63 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.14 (s, 9H), 0.29 (s, 9H), 2.37 (s, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H).

Reaction of *p*-Toluoyl Chloride with Lithium 2,4-Bis(dimethylsilyl)-1-azacyclopentane. To a stirred solution of lithium 2,4-bis(dimethylsilyl)-1-azacyclopentane, which was obtained by the reaction of 2,4-bis(dimethylsilyl)-1-azacyclopentane (398 μL, 2.1 mmol) and *n*-BuLi in hexane (1.63 *N*, 1.23 mL, 2.0 mmol) at 0 °C for 1 h, was added *p*-toluoyl chloride (264 μL, 2 mmol). After it was stirred at that temperature for 1 h, LiCl formed was removed by filtration and the filtrate was concentrated under reduced pressure to afford the crude product, which was measured by ^{29}Si NMR. ^{29}Si NMR (119.2 MHz, [D_6]benzene) δ = 10.1, 14.0, 15.7, 23.9.

Reaction of 2a with BDMSE in the Presence of 1. In a 5Φ NMR tube was placed ruthenium complex **1** (3.3 mg, 0.005 mmol, 2.5 mol% to **2a**), *p*-toluamide **2a** (67 mg, 0.5 mmol) and [D_6]benzene (0.3 mL), and the atmosphere was replaced by nitrogen. BDMSE (Si–H = 2.2 equiv. to **2a**) was added to the NMR tube containing **1**, **2a**, and [D_6]benzene, which was heated at 70 °C, by syringe. After it was heated at that temperature for 1 h, the resultant mixture was directly measured by ^{29}Si NMR. ^{29}Si NMR (119.2 MHz, [D_6]benzene) δ = 10.1, 14.0, 15.7, 23.9.

References

[1] a) H. Nagashima, T. Fukahori, K. Aoki, K. Itoh, *J. Am. Chem. Soc*. **1993**, *115*, 10430; b) Y. Motoyama, C. Itonaga, T. Ishida, M. Takasaki, H. Nagashima, *Org. Synth.* **2005**, *82*, 188.

[2] H. Nagashima, K. Takebe, T. Ishibashi, A. Nakaoka, J. Sakakibara, K. Itoh, *Organometallics* **1995**, *14*, 2868.

[3] a) M. I. Bruce, C. M. Jensen, N. L. Jones, *Inorg. Synth*. **1990**, *28* (Reagents Transition Met. Complex Organomet. Synth.), 216, and references cited therein; b) A. Mantovani, S. Cenini, *Inorg. Synth*. **1976**, *16*, 51.

[4] a) J. A. Osborn, G. Wilkinson, *Inorg. Synth.* **1967**, *10*, 67; b) N. Ahmad, J. J. Levison, S. D. Robinson, M. F. Uttley, *Inorg. Synth*. **1974**, *15*, 59; c) J. Chatt, N. P. Johnson, B. L. Shaw, *J. Chem. Soc. A* **1967**, 604; d) L. M. Venanzi, *J. Chem. Soc*. **1958**, 719; e) T. Ukai, H. Kawazura, Y. Ishii, *J. Organomet. Chem*. **1974**, *65*, 253; f) W. J. Cherwinski, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans*. **1974**, 1405; g) M. I. Bruce, N. J. Windsor, *Aust. J. Chem*. **1977**, *30*, 1601; h) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, P. A. Tucker, *Inorg. Chem*. **1980**, *19*, 1014.

[5] P. Pawluc, B. Marciniec, I. Kownacki, H. Maciejewski, *Appl. Organometal. Chem.* **2005**, *19*, 49.

[6] L. Zhang, S. Wang, S. Zhou, G. Yang, E. Sheng, *J. Org. Chem.* **2006**, *71*, 3149.

[7] H. Sharghi, M. H. Sarvari, *J. Chem. Res. (S)* **2005**, 176.

[8] M. Kashiwagi, K. Fuhshuku, T. Sugai, *J. Mol. Catal. B: Enzymatic* **2004**, *29*, 249.

[9] P. Gaspari, T. Benerjee, W. P. Malachowski, A. J. Muller, G. C. Prendergast, J. DuHadaway, S. Bennett, A. D. Donovan, *J. Med. Chem.* **2006**, *49*, 684.

[10] G. Voss, H. Gerlach, *Helv. Chim. Acta* **1983**, *66*, 2294.

[11] a) C. Herschmann, *Helv. Chim. Acta* **1949**, *32*, 2537; b) T. Yamamoto, A. Shimada, T. Ohmoto, H. Matsuda, M. Ogura, T. Kanisawa, *Flavour Fragr. J*. **2004**, *19*, 12.

[12] a) J. Pump, E. G. Rochow, *Chem. Ber*. **1964**, *97*, 627; b) K. Itoh, M. Katsuda, Y. Ishii, *J. Chem. Soc. B* **1970**, 302.