Dimerization–Double Silylation of 1,3-Dienes Using Organodisilanes Catalyzed by a Palladium Complex

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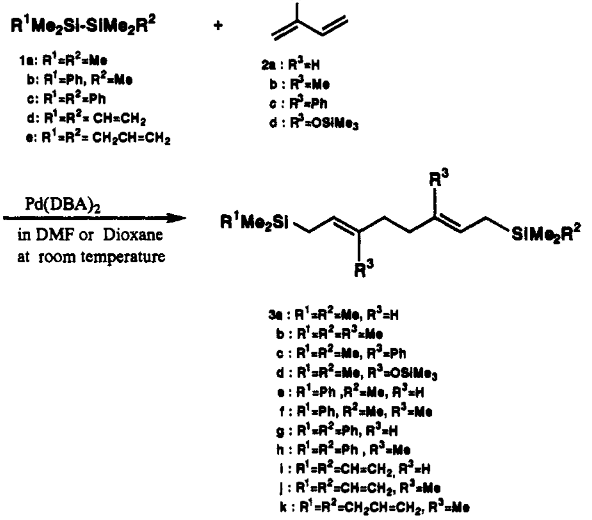
Received January 8, 1993

*Summary: Disilanes (**1a–e**) react with 1,3-dienes (**2a–d**) in the presence of a palladium catalyst to give dimerization–double silylation products (**3a–k**) regio- and stereoselectively in high yields. $Pd(DBA)_2$ shows high catalytic activity in DMF or dioxane as the solvent at room temperature. No crossover silylations occur.*

Transition-metal-catalyzed insertions of unsaturated hydrocarbons into σ-bonds between group 14 atoms such as Si–Si,[1–4] Si–Sn,[5] and Sn–Sn[6] are of current interest, since the reactions provide facile synthetic methods for useful functionalized compounds containing the group 14 elements.[7] In particular, the reaction of the Si–Si bonds are well-studied, in which 1,3-dienes,[1] acetylenes,[2] allenes,[3] and olefins[4] are disilylated in the presence of a transition-metal catalyst. We have recently developed 1,4-disilylation,[1a] 1,4-silylstannation,[5a] and dimerization–double stannation[6a] of 1,3-dienes, where cleavages of Si–Si, Si–Sn, and Sn–Sn σ-bonds are involved. During the course of these studies, we have found a highly active catalyst system for dimerization–double silylation of 1,3-dienes at room temperature using disilanes. Concerning the dimerization–double silylation of 1,3-dienes, Sakurai and coworkers have reported the reaction at elevated temperatures (120 or 90 °C) catalyzed by $Pd(OAc)_2$ or $PdCl_2(ArCN)_2$.[8a] They claimed the reaction should be carried out without solvent; the reaction performed with the solvent, such as benzene or THF, reduced the yields dramatically to 0–6%. Low yield dimerization–double silylation of isoprene with cyclic octaethyltetrasilane at 120 °C has been reported by West *et al.*[8b]

In this paper, we wish to report the highly regio- and stereoselective dimerization–double silylation of 1,3-dienes using disilanes in various media (eq 1). The reaction proceeds readily at room temperature in high yield in the presence of a catalytic amount of $Pd(DBA)_2$[9] (DBA = dibenzylideneacetone). Several unsaturated hydrocarbon substituents on the silicon atom are tolerated in the reaction.



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Results and Discussion

The results are summarized in Table I. When hexamethyldisilane (**1a**) was allowed to react with 1,3-butadiene (**2a**) in the presence of catalytic amount (5 mol %) of $Pd(DBA)_2$ in DMF or dioxane as the solvent, the single dimerization–double silylation product (**3a**) was isolated in high yields (entries 1 and 2). The reaction is highly regio- and stereoselective, and only the α,ω-disilylated *E*-1,4 dimer is obtained exclusively. The reaction also proceeds with isoprene (**2b**) to give the *E*-1,4 head to head dimer regio- and stereoselectively, and no other isomers were detected. The reaction can be carried out in various media. The yields with **2b** in some representative solvents are as follows: DMF, 99% (entry 3); dioxane, 91% (entry

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Table I. Dimerization–Double Silylation of 1,3-Dienes Using Disilanes[a]

entry	disilane	diene	solvent	product	yield, %[b]
1	**1a**	**2a**	DMF	**3a**	71
2	**1a**	**2a**	dioxane	**3a**	62
3	**1a**	**2b**	DMF	**3b**	(99) 85
4	**1a**	**2b**	dioxane	**3b**	(91)
5	**1a**	**2c**	DMF	**3c**	82
6	**1a**	**2d**	DMF	**3d**	63
7	**1b**	**2a**	dioxane	**3e**	92
8	**1b**	**2b**	DMF	**3f**	80
9	**1c**	**2a**	dioxane	**3g**	84
10	**1c**	**2b**	dioxane	**3h**	86
11	**1d**	**2a**	dioxane	**3i**	64
12	**1d**	**2b**	dioxane	**3j**	86
13	**1e**	**2b**	DMF	**3k**	41

[a] Conditions: disilane (**1**; 0.50 mmol), diene (**2**; 3.0 mmol), Pd(DBA)$_2$ (0.025 mmol), DMF (2.0 mL), for 40 h, at room temperature. [b] Isolated yields. Numbers in parentheses show GLC yields determined by the internal standard method with naphthalene.

Table II. Effect of Catalyst Precursor and Solvent[a]

entry	catalyst precursor	yield, %[b] in DMF	yield, %[b] in benzene
14	Pd(DBA)$_2$	99	63
15	Pd(PPh$_3$)$_4$	0	54
16	PdCl$_2$(PhCN)$_2$	64	10
17	[Pd(η^3-C$_3$H$_5$)(COD)]BF$_4$	70	*c*
18	[PdCl(η^3-C$_3$H$_5$)]$_2$	45	39

[a] Conditions: Me$_3$SiSiMe$_3$ (**1a**; 0.50 mmol), isoprene (**2b**; 3.0 mmol), catalyst precursor (0.025 mmol), solvent (2.0 mL), at room temperature, for 40 h. [b] Yield of **3b** by GLC. [c] The catalyst precursor was not dissolved.

4); benzene, 63%; toluene, 61%; THF, 55%; HMPA, 47%; dichloromethane, 19%. In the precedent study,[8a] the quite low reactivity associated with the reaction using a solvent (vide supra) was attributed to the weaker coordination ability of the Si–Si bonds toward the catalyst center than to that of solvents. Hence, it is notable that in the present study the reaction proceeds efficiently even in coordinating DMF as the solvent. The nature of the catalyst precursor affects the reaction markedly. The results are shown in Table II. Pd(DBA)$_2$, a naked palladium(0) complex without coordinating ligands, shows the highest catalytic activity (entry 14). Pd(PPh$_3$)$_4$, PdCl$_2$(PhCN)$_2$, [Pd(η^3-C$_3$H$_5$)(COD)]BF$_4$, and [PdCl(η^3-C$_3$H$_5$)]$_2$ also realize fair to good catalytic activity at room temperature (entries 15–18). In these cases, the combination of the catalyst precursor and the solvent is crucial. The coordinating solvent may suppress the catalytic activity by saturating the catalyst center (entry 15) or enhance the activity via ligation (entry 16). Other selected low valent transition-metal complexes such as Pt(DBA)$_2$, PtCl$_2$(PhCN)$_2$, Ru(COD)(COT), and [RhCl(COD)]$_2$ do not show any catalytic activity at all.

2-Phenyl-1,3-butadiene (**2c**) and 2-[(trimethylsilyl)oxy]-1,3-butadiene (**2d**) also readily give the corresponding dimerization–double silylation products (entries 5 and 6; Table I). In contrast, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-cyclohexadiene were totally inert under the same reaction conditions, as well as even at 100 °C. The steric bulk of the 1,3-dienes seems to affect the reaction significantly.

Several unsaturated hydrocarbon functionalities on the silicon atom of the disilanes are tolerated in the reaction. Thus, pentamethylphenyldisilane (**1b**), tetramethyl-1,2-diphenyldisilane (**1c**), tetramethyl-1,2-divinyldisilane (**1d**), and 1,2-diallyltetramethyldisilane (**1e**) afford the corresponding dimerization–double silylation products (**3e–k**) in fair to excellent yields (entries 7–13). In all the cases, the reaction is highly regio- and stereoselective, affording the single isomer. In palladium-catalyzed 1,4-disilylation of 1,3-dienes using disilanes, electronegative substituents such as F or Cl on the silicon atom were found indispensable for obtaining high reactivity. Similar effects of electronegative substituents were also evident in the disilylation of acetylenes[2c–f] and olefins[4b] using disilanes. However, in the present reaction, the disilanes with electronegative substituents such as 1,2-difluorotetramethyldisilane[1b,2b,4b] and 1,2-dichlorotetramethyldisilane[1c,2d,4b,8a] did not afford any dimerization–double silylation products under standard reaction conditions. Octamethyltrisilane (Me$_3$SiMe$_2$SiSiMe$_3$) reacted with **2a** at room temperature regio- and stereoselectively to give [Me$_3$Si(CH$_2$CH=CHCH$_2$)$_2$]$_2$SiMe$_2$ (**4**) having an all *E* configuration in 32% isolated yield.

It is noteworthy that in the reaction of **1b** with butadiene (**2a**) or isoprene (**2b**) (entries 7 and 8), none of crossover-silylation products (*i.e.*, **3a**, **3b**, **3g**, or **3h**) were obtained at all. In order to confirm the lack of crossover silylation in the present reaction, an equimolar mixture of two different disilanes was subjected to the reaction with **2b** (eqs 2 and 3). The reaction of an equimolar mixture of **1a** and **1c** with **2b** afforded **3b** and **3h** in 91% total isolated yield with a 51:49 molar ratio (eq 2). No trace of the crossover-silylation product **3l** was detected in the reaction mixture. The same result was obtained with an equimolar mixture of **1a** and **1d**. The reaction afforded **3b** and **3j** in 78% total isolated yield with a 54:46 molar ratio (eq 3), where the crossover-silylation product (**3m**) was not afforded at all. Thus, the 1,3-dienes are apparently inserted into the Si–Si bonds of the parent disilanes and no crossover-silylation reaction occurs.

Throughout the present study, no trace of the 1,4-disilylation products,[1] which would be formed by insertion of one diene unit into the Si–Si bonds, appeared. Furthermore, higher telomers are not detected, either. Hence, the first step in the present catalytic reaction might be dimerization of the dienes within the palladium coordination sphere followed by the disilylation. A template effect[10] of the palladium center can bring about the selective formation of the dimer products, possibly via a bis(π-allyl)palladium intermediate which has been postulated in many low valent palladium-catalyzed dimerizations or telomerizations of 1,3-dienes.[11]

Experimental Section

Materials. The reagents and the solvents were dried and purified before use by the usual procedures.[12] Hexamethyldisilane (**1a**) was purchased from Aldrich. 1,2-Difluorotetramethyldisilane,[13a] chloropentamethyldisilane,[13b] and 1,2-dichlorotetramethyldisilane[13b] were prepared by the methods reported by Kumada. Octamethyltrisilane was synthesized by the published method.[13c] Other disilanes were prepared from chloropentamethyldisilane or dichlorotetramethyldisilane by the reactions with corresponding organolithium or organomagnesium

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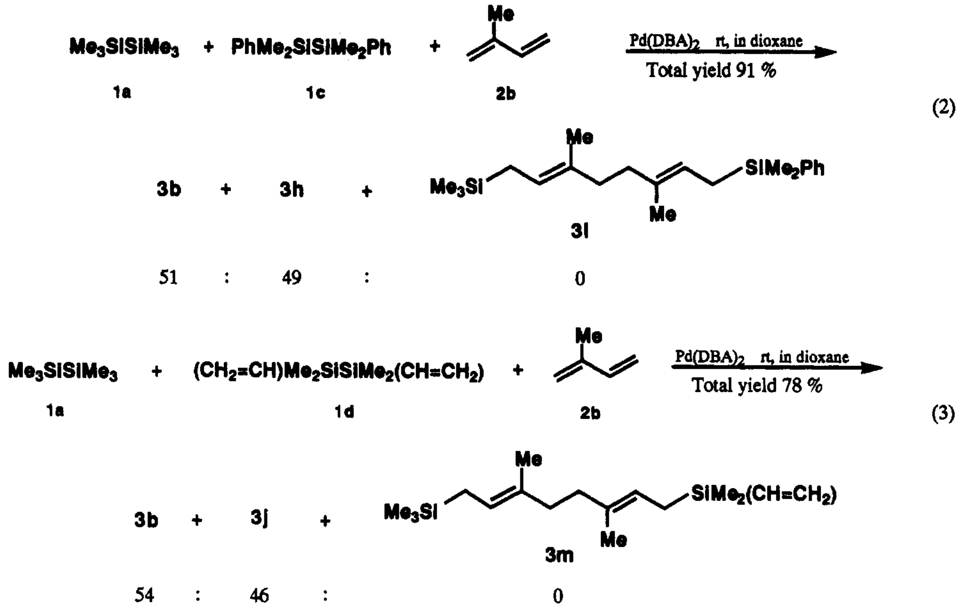
Scheme I



reagents. The following substrates and catalyst precursors were prepared by the published methods: Pd(DBA)$_2$,[9] Pd(PPh$_3$)$_4$,[14a] PdCl$_2$(PhCN)$_2$,[14b] [Pd(η^3-C$_3$H$_5$)(COD)]BF$_4$,[14c] [PdCl(η^3-C$_3$H$_5$)]$_2$,[14d] Pt(DBA)$_2$,[14e] PtCl$_2$(PhCN)$_2$,[14b] Ru(COD)(COT),[14f] [RhCl(COD)]$_2$,[14g] **2c**,[15a] and **2d**.[15b]

General Procedure. A typical reaction procedure is described for the synthesis of **3b**. A mixture of isoprene (**2b**; 204 mg, 3.0 mmol), hexamethyldisilane (**1a**; 73 mg, 0.5 mmol), Pd(DBA)$_2$ (14 mg, 0.025 mmol), and DMF (2.0 mL) was placed under an argon flow in a 20-mL flask and stirred for 40 h at room temperature. Then, the mixture was passed through a short Florisil column (8-mm i.d. × 50 mm) to give a clear colorless solution. GLC analysis (Apiezon Grease L) with naphthalene as an internal standard showed **3b** was formed in 99% yield. The product was isolated by medium-pressure chromatography (silica gel: Wakogel 300, 45–75 μm; hexane as an eluent) followed by Kugelrohr distillation in 85% yield (90 °C (pot)/0.3 mmHg; 120 mg).

The identification of the products was made by ^{1}H- and ^{13}C-NMR and GC/MS spectra. Spectral data for **3a** and **3b** were consistent with reported values.[8a] The NMR spectra were recorded with a JEOL GX-270 spectrometer. Samples were dissolved in CDCl$_3$, and the chemical shift values were expressed relative to Me$_4$Si as an internal standard. The mass spectra were measured on Shimadzu QP-1000 (GC/MS) and Shimadzu 9020-DF (HRMS) equipped with a PAC 1100S computer system. The GLC analysis was made on a Shimadzu GC-8APF equipped with an integrator (C-R6A) with a column (3-mm i.d. × 3 m) packed with Apiezon Grease L (5% on Uniport HP, 60/80 mesh) or Silicon OV-17 (2% on Uniport HP, 60/80 mesh). Elemental analyses were performed at the Microanalytical Center of Kyoto University. The analytical data for the products are as follows.

3c: colorless liquid; 115 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.01 (s, 18H), 1.44 (d, J = 8 Hz, 4H), 2.39 (s, 4H), 5.47 (t, J = 8 Hz, 2H), 7.13–7.48 (m, 10H); ^{13}C-NMR δ −1.62 (q), 19.21 (t), 38.48 (t), 122.9 (d), 126.0 (d), 128.0 (d), 128.9 (d), 138.9 (s), 141.6 (s); MS (EI) m/e 406 (M$^+$, 5.6), 391 (M$^+$ − Me, 0.84), 260 (16), 203 (52), 129 (56), 115 (51), 91 (30), 73 (100). HRMS (EI) calcd for C$_{26}$H$_{38}$Si$_2$: 406.2512. Found: 406.2497. NOE difference measurement: Irradiation at the methylene proton resonance at δ 2.39 (=C(C$_6$H$_5$)—CH_2–) caused enhancement of the olefin proton resonance at δ 5.47, while no NOE was observed at the methylene proton resonance at δ 1.44 (Me$_3$Si—CH_2–).

3d: colorless liquid; 100 °C/0.3 mmHg; ^{1}H-NMR δ −0.01 (s, 18H), 0.20 (s, 18H), 1.33 (d, J = 8 Hz, 4H), 2.17 (s, 4H), 4.44 (t, J = 8 Hz, 2H); ^{13}C-NMR δ −1.58 (q), 0.90 (q), 15.09 (t), 35.21 (t), 103.2 (d), 148.8 (s); MS m/e 430 (M$^+$). NOE difference measurement: When the olefin proton resonance at δ 4.44 was irradiated, NOE was observed at two methylene proton resonances at δ 1.33 and 2.17. Irradiation at the methylene proton resonances at δ 1.33 (Me$_3$Si—CH_2CH=) caused enhancement of the olefin proton resonance at δ 4.44, while no NOE was observed at the methylene proton resonance at δ 2.17. Anal. Calcd for C$_{20}$H$_{46}$O$_2$Si$_4$: C, 55.75; H, 10.76. Found: C, 55.61; H, 11.00.

3e: colorless liquid; 110 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.01 (s, 9H), 0.27 (s, 6H), 1.41 (d, J = 8 Hz, 2H), 1.67 (d, J = 8 Hz, 2H), 2.01–2.03 (m, 4H), 5.18–5.48 (m, 4H), 7.32–7.36 (m, 3H), 7.48–7.54 (m, 2H); ^{13}C-NMR δ −3.33 (q), −1.92 (q), 21.69 (t), 22.67 (t), 33.39 (t), 33.48 (t), 125.5 (d), 126.2 (d), 127.7 (d), 128.5 (d), 128.9 (d), 129.4 (d), 133.7 (d), 139.2 (s). Anal. Calcd for C$_{19}$H$_{32}$Si$_2$: C, 72.07; H, 10.19. Found: C, 72.29; H, 10.35.

3f: colorless liquid; 120 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.09 (s, 9H), 0.37 (s, 6H), 1.49 (d, J = 8 Hz, 2H), 1.60 (s, 3H), 1.65 (s, 3H), 1.73 (d, J = 8 Hz, 2H), 2.17 (s, 4H), 5.27 (t, J = 8 Hz, 2H), 7.41–7.63 (m, 5H); ^{13}C-NMR δ −3.01 (q), −1.62 (q), 16.12 (q), 17.93 (t), 18.81 (t), 39.20 (t), 119.5 (d), 120.3 (d), 127.8 (d), 129.0 (d), 132.7 (s), 133.6 (s), 133.9 (d), 139.5 (s). Anal. Calcd for C$_{21}$H$_{36}$Si$_2$: C, 73.18; H, 10.53. Found: C, 72.91; H, 10.43.

3g: colorless liquid; 145 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.03 (s, 12H), 1.42 (d, J = 7 Hz, 4H), 1.74–1.78 (m, 4H), 4.97–5.22 (m, 4H), 7.07–7.14 (m, 6H), 7.24–7.30 (m, 4H); ^{13}C-NMR δ −3.33 (q), 21.66 (t), 33.35 (t), 125.6 (d), 127.7 (d), 128.9 (d), 129.3 (d), 133.6 (d), 139.1 (s). Anal. Calcd for C$_{24}$H$_{34}$Si$_2$: C, 76.12; H, 9.05. Found: C, 75.90; H, 9.15.

3h: colorless liquid; 150 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.15 (s, 12H), 1.38 (s, 6H), 1.52 (d, J = 8 Hz, 4H), 1.94 (s, 4H), 5.07 (t, J = 8 Hz, 2H), 7.19–7.23 (m, 3H), 7.36–7.41 (m, 2H); ^{13}C-NMR δ −3.17 (q), 15.78 (q), 17.73 (t), 39.0 (t), 119.4 (d), 127.7 (d), 128.9 (d), 133.4 (s), 133.6 (d), 139.3 (s). Anal. Calcd for C$_{26}$H$_{38}$Si$_2$: C, 76.77; H, 9.42. Found: C, 76.48; H, 9.22.

3i: colorless liquid; 100 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.07 (s, 12H), 1.48 (d, J = 7 Hz, 4H), 2.02 (m, 4H), 5.23–5.46 (m, 4H), 5.68 (dd, J = 4 and 20 Hz, 2H), 5.96 (dd, J = 4 and 14 Hz), 6.15 (dd, J = 14 and 20 Hz); ^{13}C-NMR δ −3.70 (q), 21.35 (t), 33.41 (t),

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125.7 (d), 129.1 (d), 131.7 (t), 138.7 (d); MS (EI) *m/e* 278 (M$^+$, 0.24), 251 (M$^+$ − C_2H_3, 1.0), 139 (23), 85 (100), 59 (76). HRMS (EI) calcd for $C_{16}H_{30}Si_2$: 278.1886. Found: 278.1895.

3j: colorless liquid; 105 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.07 (s, 12H), 1.47 (d, J = 8 Hz, 4H), 1.55 (s, 6H), 2.10 (s, 4H), 5.18 (t, J = 8 Hz, 2H), 5.64–5.81 (m, 1H), 5.92–6.04 (m, 1H), 6.10–6.26 (m, 1H); ^{13}C-NMR δ −3.48 (q), 15.88 (q), 17.37 (t), 39.06 (t), 119.5 (d), 131.5 (t), 133.1 (s), 139.0 (d); MS *m/e* 306 (M$^+$, 0.51), 179 (1.7), 167 (1.1), 85 (100), 59 (37). HRMS (EI) calcd for $C_{18}H_{34}Si_2$: 306.2197. Found: 306.2187. NOE difference measurement: Irradiation at the olefin proton resonance at δ 5.18 ($-CH_2-CH=$) enhanced intensities of the two methylene resonances at δ 1.47 and 2.10. Anal. Calcd for $C_{18}H_{34}Si_2$: C, 70.51; H, 11.18. Found: C, 70.06; H, 11.06.

3k: colorless liquid; 110 °C (pot)/0.3 mmHg; ^{1}H-NMR δ 0.07 (s, 12H), 1.47 (d, J = 8 Hz, 4H), 1.52 (d, J = 8 Hz, 4H), 1.55 (s, 6H), 2.08 (s, 4H), 4.83 (d, J = 11 Hz, 2H), 4.84 (d, J = 18 Hz, 2H), 5.16 (t, J = 8 Hz, 2H), 5.79 (ddt, J = 8, 11, and 18 Hz, 2H); ^{13}C-NMR δ −3.81 (q), 15.83 (q), 16.80 (t), 23.15 (t), 38.98 (t), 112.8 (t), 119.6 (d), 133.0 (s), 135.1 (d); MS *m/e* 293 (M$^+$ − C_3H_5). Anal. Calcd for $C_{20}H_{38}Si_2$: C, 71.77; H, 11.44. Found: C, 71.68; H, 11.57.

4: colorless liquid; 140 °C (pot)/0.3 mmHg; ^{1}H-NMR δ −0.038 (s, 6H), −0.030 (s, 18H), 1.38 (d, J = 8 Hz, 4H), 1.43 (d, J = 8 Hz, 4H), 1.98–2.02 (m, 8H), 5.20–5.44 (m, 8H); ^{13}C-NMR δ −3.96 (q), −1.95 (q), 20.82 (t), 22.66 (t), 33.45 (t), 33.49 (t), 125.9 (d), 126.2 (d), 128.5 (d), 128.8 (d); MS (EI) *m/e* 420 (M$^+$, 0.74), 240 (7.5), 165 (24), 151 (16), 97 (12), 73 (100). HRMS (EI) calcd for $C_{24}H_{48}Si_3$: 420.3064. Found: 420.3083.

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