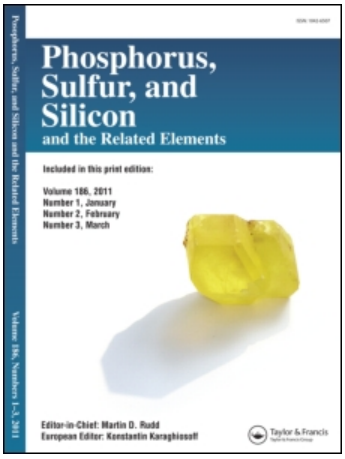

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STEPWISE ELIMINATION OF ETHANE TO SYNTHESISE NEW CYCLIC AND CAGE-LIKE GALLIUM-PHOSPHORUS COMPOUNDS

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STEPWISE ELIMINATION OF ETHANE TO SYNTHESISE NEW CYCLIC AND CAGE-LIKE GALLIUM-PHOSPHORUS COMPOUNDS

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*The reaction of $GaEt_3$ with H_2PSiMe_2R ($R = CMe_2iPr$) initially yields the cyclic compound $[(Et_2Ga)_2\{P(H)SiMe_2R\}_2]$ **1**. **1** appears as a mixture of* cis *and* trans *isomers and has been characterized by ^{31}P NMR spectroscopy, IR spectroscopy, and mass spectrometry. **1** decomposes at 180°C under elimination of ethane during 1 h to form the cage-like compound $[EtGaPSiMe_2R]_4$ (**2**). Central structural motif of **2** is a Ga_4P_4 heterocubane cage.*

Keywords: Cluster; crystal structure; gallium; phosphorus; silicon

Reactions of primary silylphosphines or silylarsins with alkyl compounds of the elements of group 13 have been applied for the synthesis of molecular 13/15 compounds several times over the last few years.[1–4] Here we report the reaction of $GaEt_3$ with the silylphosphane H_2PSiMe_2R ($R = CMe_2iPr$) which yield the new compounds $[Et_2GaP(H)SiMe_2R]_2$ (**1**) and $[EtGaPSiMe_2R]_4$ (**2**).

RESULTS AND DISCUSSION

$GaEt_3$ reacts with H_2PSiMe_2R ($R = CMe_2iPr$) in heptane at ambient temperature with elimination of ethane and the formation of a clear solution. After removal of the solvent under reduced pressure the cyclic compound $[Et_2GaP(H)SiMe_2R]_2$ (**1**) can be obtained as a colourless liquid (Scheme 1). **1** appears as a *cis*/*trans* isomeric mixture. Therefore the ^{31}P NMR spectrum shows two multipetts of the AA′XX′ spin systems (AA′ parts) at $\delta = -214.6$ and -218.0, whereas the $^{31}P\{^1H\}$-NMR spectrum reveals two singletts. Similar isomeric mixtures have also been observed for the aluminium-phosphorus and

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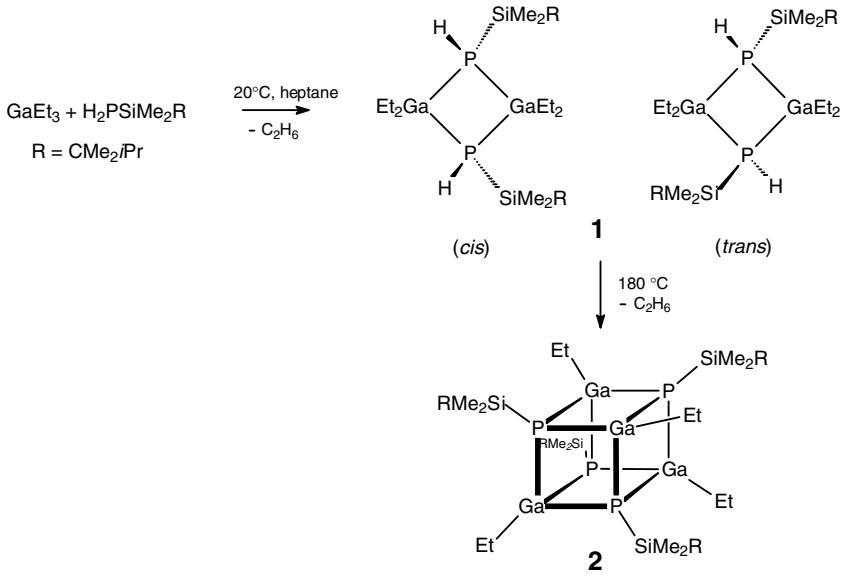

SCHEME 1 Synthesis of **1** and **2**.

indium-phosphorus compounds $[i\text{Bu}_2\text{AlP(H)SiPh}_3]_2$,[2] $[t\text{Bu}_2\text{InP(H)SiMe}_3)]_2$,[3] and $[\text{Et}_2\text{InP(H)Si}i\text{Pr}_3]_2$.[4] The mass spectrum of **1** shows the highest peak at m/z = 577 (correspond to $M^+ - \text{Et}$) as well as peaks of the fragments $\text{Et}_4\text{Ga}_2\text{P(H)SiMe}_2\text{CMe}_2i\text{Pr}$ and $\text{Et}_2\text{Ga}_2\text{P}_2\text{H}_2$. The IR spectrum reveals the P–H stretch vibration at 2321 cm^{-1}.

If a sample of **1** is thermolyzed at 180°C gas formation can be observed again. After 1 h a white solid has been formed. Recrystallization of this residue from heptane yields colorless crystals of the compound $[\text{EtGaPSiMe}_2\text{R}]_4$ (**2**) (Scheme 1). The ^{31}P NMR spectrum of **2** possesses merely a singlett at $\delta = -137.8$. **2** crystallizes in the monoclinic space group *P*2/*n*; central structural motif is a Ga_4P_4 cage with an almost ideal cube structure crystallographic data are provided in Tables I–IV. The molecular structure of **2** is shown in Figure 1.*

*__2__: $a = 1069.5(2)$, $b = 1284.1(3)$, $c = 2179.2(4)$ pm, $\beta = 103.81(3)$, $V = 2906.4(9) \times 10^6$ pm^3; monoclinic, *P*2/*n*, Z = 2, $\rho_{\text{calc}} = 1.246$ g/cm^3, $\mu(\text{Mo}_{K\alpha}) = 2.051$ mm^{-1}, $T = 200$ K, $2\Theta_{\max} = 45°$, 9447 reflections measured, 3287 independent reflections ($R_{\text{int}} = 0.0603$). The structure was solved by direct methods and refined by full-matrix least square techniques against F^2, 235 parameters (Ga, P, Si, C refined anisotropically, H atoms were calculated at ideal positions); $R1 = 0.0476$; $wR2 = 0.1422$ (all data); maximum peak 0.479 eÅ^{-3}. CCDC-217207 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

TABLE I Crystal Data and Structure Refinement for Ga4P4

Empirical formula	C40 H96 Ga4 P4 Si4
Formula weight	1092.29
Temperature	200 (2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2/n
Unit cell dimensions	a = 10.695 (2) A, alpha = 90 deg. b = 12.841 (3) A, beta = 103.81 (3) deg. c = 21.792 (4) A, gamma = 90 deg.
Volume	2906.4 (10) A^3
Z, Calculated density	2, 1.248 mg/m^3
Absorption coefficient	2.051 mm^{-1}
F (000)	1152
Theta range for data collection	1.59 to 22.50 deg.
Limiting indices	$-11 \leq h \leq 8$, $-13 \leq k \leq 13$, $-23 \leq 1 \leq 18$
Reflections collected/unique	9447/3287 [R (int) = 0.0603]
Completeness to theta = 22.50	96.5%
Refinement method	Full-metrix least-squares on F^2
Data/restraints/parameters	3287/0/235
Goodness-of-fit on F^2	1.065
Final R indices [I > 2 sigma(I)]	R1 = 0.0475, wR2 = 0.1404
R indices (all data)	R1 = 0.0525, wR2 = 0.1443
Largest diff. peak and hole	0.480 and -0.322 eA^{-3}

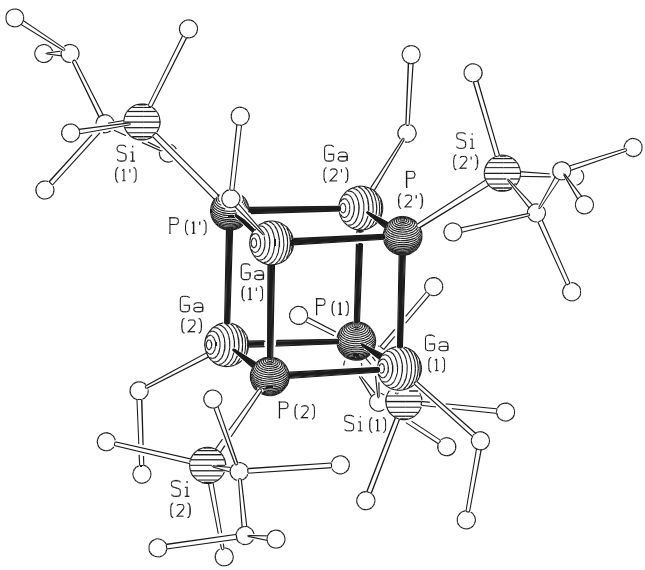

FIGURE 1 Molecular structure of **2**: selected bond lengths/pm and bond angles/°: Ga—P: 241.1(2)–242.1(2), P—Si: 223.8(3); Ga—P—Ga: 88.05(5)–89.78(5), P—Ga—P: 90.19(5)–91.92(5); Si—P—Ga: 121.4(1)–132.1(1).

TABLE II Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for Ga4P4 U (eq) is Defined as One Third of the Trace of the Orthogonalized Uij tensor

	x	y	z	U (eq)
C(1)	−269 (7)	10691 (5)	1421 (3)	80 (2)
C(2)	−447 (9)	10582 (6)	732 (4)	111 (3)
C(3)	4238 (10)	7035 (5)	1440 (4)	104 (2)
C(4)	3866 (14)	7189 (8)	747 (5)	156 (4)
C(5)	−185 (14)	7225 (8)	447 (5)	238 (4)
C(6)	−1987 (10)	7704 (7)	2230 (7)	159 (4)
C(7)	−432 (8)	5596 (5)	1464 (4)	95 (2)
C(8)	966 (10)	5280 (6)	1783 (6)	149 (4)
C(9)	−1140 (13)	5537 (8)	2021 (6)	158 (4)
C(10)	−1039 (11)	4878 (6)	955 (5)	120 (3)
C(11)	−953 (11)	3722 (5)	1113 (6)	141 (4)
C(12)	−2317 (13)	5162 (7)	589 (6)	157 (4)
C(13)	3529 (10)	10381 (6	465 (4)	109 (3)
C(14)	5974 (9)	10016 (7)	1435 (6)	136 (4)
C(15)	4498 (14)	12111 (6)	1442 (5)	138 (4)
C(16)	5393 (16)	12318 (8)	2100 (6)	196 (6)
C(17)	2922 (16)	12502 (9)	1522 (10)	225 (7)
C(18)	4330 (30)	12816 (10)	1005 (11)	253 (9)
C(19)	5650 (20)	12464 (11)	841 (9)	219 (7)
C(20)	4403 (18)	13998 (8)	1113 (8)	210 (7)
Si(1)	−468 (2)	7026 (1)	1258 (1)	84 (1)
Si(2)	4391 (2)	10663 (1)	1296 (1)	72 (1)
P(1)	1081 (2)	7920 (1)	1921 (1)	70 (1)
P(2)	3331 (2)	9830 (1)	1919 (1)	65 (1)
Ga(1)	1080 (1)	9800 (1)	1942 (1)	65 (1)
Ga(2)	3351 (1)	7951 (1)	1936 (1)	71 (1)

The P—Ga—P angels are in the range of 90.2 to 91.9°, the Ga—P—Ga angels amount to 88.1–89.8°. The Ga—P bond lengths are 241.7 pm on average, which is in the usual range for Ga—P single bonds (240–250 pm).[5] Each of the phosphorus atoms in **2** is bound to a exocyclic silyl substituent, the gallium atoms possess one ethyl group each.

EXPERIMENTAL SECTION

All manipulations were performed under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded on a Bruker DPX Avance 300 instrument. H_2PSiMe_2R and $GaEt_3$ were prepared according to the literature.[6]

TABLE III Bond Lengths [A] and Angles [deg] for Ga4P4

C(1)—C(2)	1.475 (10)
C(1)—Ga(1)	1.974 (6)
C(3)—C(4)	1.480 (14)
C(3)—Ga(2)	1.986 (7)
C(5)—Si(1)	1.877 (11)
C(6)—Si(1)	1.832 (10)
C(7)—C(10)	1.470 (12)
C(7)—C(8)	1.544 (13)
C(7)—C(9)	1.579 (12)
C(7)—Si(1)	1.889 (7)
C(10)—C(12)	1.455 (15)
C(10)—C(11)	1.521 (10)
C(13)—Si(2)	1.860 (8)
C(14)—Si(2)	1.845 (9)
C(15)—C(18)	1.295 (19)
C(15)—C(16)	1.546 (15)
C(15)—C(17)	1.807 (19)
C(15)—Si(2)	1.885 (9)
C(18)—C(20)	1.535 (15)
C(18)—C(19)	1.61 (3)
Si(1)—P(1)	2.238 (3)
Si(2)—P(2)	2.238 (2)
P(1)—Ga(1)	2.4138 (16)
P(1)—Ga(2) #1	2.4186 (19)
P(1)—Ga(2)	2.421 (2)
P(2)—Ga(1) #1	2.4112 (18)
P(2)—Ga(2)	2.4123 (15)
P(2)—Ga(1)	2.4206 (18)
Ga(1)—P(2) #1	2.4112 (18)
Ga(2)—P(1) #1	2.4186 (19)
C(2)—C—Ga(1)	115.4 (5)
C(4)—C(3)—Ga(2)	115.4 (7)
C(10)—C(7)—C(8)	112.3 (8)
C(10)—C(7)—C(9)	110.1 (7)
C(8)—C(7)—C(9)	103.5 (9)
C(10)—C(7)—Si(1)	116.7 (7)
C(8)—C(7)—Si(1)	109.0 (5)
C(9)—C(7)—Si(1)	104.1 (6)
C(12)—C(10)—C(7)	116.4 (8)
C(12)—C(10)—C(11)	111.5 (8)
C(7)—C(10)—C(11)	116.7 (9)
C(18)—C(15)—C(16)	120.6 (12)
C(18)—C(15)—C(17)	84.6 (15)
C(16)—C(15)—C(17)	104.3 (11)
C(18)—C(15)—Si(2)	125.0 (12)
C(16)—C(15)—Si(2)	109.0 (7)
C(17)—C(15)—Si(2)	105.7 (7)
C(15)—C(18)—C(20)	125.8 (18)

(Continued on next page)

TABLE III Bond Lengths [A] and Angles [deg] for Ga4P4 *(Continued)*

C(15)—C(18)—C(19)	89.4 (14)
C(20)—C(18)—C(19)	107.1 (17)
C(6)—Si(1)—C(5)	104.4 (7)
C(6)—Si(1)—C(7)	115.9 (4)
C(5)—Si(1)—C(7)	110.5 (4)
C(6)—Si(1)—P(1)	106.9 (4)
C(5)—Si(1)—P(1)	106.3 (3)
C(7)—Si(1)—P(1)	112.0 (3)
C(14)—Si(2)—C(13)	107.1 (5)
C(14)—Si(2)—C(15)	113.6 (5)
C(13)—Si(2)—C(15)	110.6 (4)
C(14)—Si(2)—P(2)	105.2 (3)
C(13)—Si(2)—P(2)	107.0 (3)
C(15)—Si(2)—P(2)	112.9 (4)
Si(1)—P(1)—Ga(1)	121.42 (9)
Si(1)—P(1)—Ga(2) #1	129.73 (9)
Ga(1)—P(1)—Ga(2) #1	88.05 (5)
Si(1)—P(1)—Ga(2)	127.01 (9)
Ga(1)—P(1)—Ga(2)	89.33 (5)
Ga(2) #1—P(1)—Ga(2)	88.92 (7)
Si(2)—P(2)—Ga(1) #1	125.91 (9)
Si(2)—P(2)—Ga(2)	118.91 (8)
Ga(1) #1—P(2)—Ga(2)	88.26 (5)
Si(2)—P(2)—Ga(1)	132.06 (9)
Ga(1) #1—P(2)—Ga(1)	89.77 (6)
Ga(2)—P(2)—Ga(1)	89.37 (5)
C(1)—Ga(1)—P(2) #1	123.9 (2)
C(1)—Ga(1)—P(1)	124.9 (2)
P(2) #1—Ga(1)—P(1)	91.91 (5)
C(1)—Ga(1)—P(2)	125.0 (2)
P(2) #1—Ga(1)—P(2)	90.20 (6)
P(1)—Ga(1)—P(2)	90.60 (5)
C(3)—Ga(2)—P(2)	126.0 (2)
C(3)—Ga(2)—P(1) #1	121.0 (3)
P(2)—Ga(2)—P(1) #1	91.77 (5)
C(3)—Ga(2)—P(1)	126.2 (3)
P(2)—Ga(2)—P(1)	90.63 (5)
P(1) #1—Ga(2)—P(1)	91.05 (7)

Symmetry transformations used to generate equivalent atoms: #1, $-x + 1/2$, y, $-z + 1/2$.

1: 0.85 g $GaEt_3$ (5.4 mmol) are added under agitation to a solution of 0.95 g H_2PSiMe_2R ($R = CMe_2iPr$) (5.4 mmol) in 20 ml of heptane. After 20 h steering the solvent was removed in vacuum. The product appears in quantitative yield as a colorless liquid. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -213.9$ (s), -217.2 (s). MS (EI 70 eV, 80°C) m/z: 577 ($[M-Et]^+$, 45.3%),

TABLE IV Anisotropic Displacement Parameters ($A^2 \times 10^3$) for Ga4P4

	U11	U22	U33	U23	U13	U12
C(1)	80 (4)	75 (4)	80 (4)	7 (3)	10 (4)	6 (3)
C(2)	128 (7)	100 (5)	86 (5)	8 (4)	−10 (5)	−4 (4)
C(3)	132 (7)	90 (5)	94 (6)	−18 (4)	38 (5)	3 (4)
C(4)	194 (11)	158 (8)	131 (9)	−36 (6)	64 (9)	−5 (7)
C(5)	215 (11)	150 (7)	89 (6)	4 (5)	0 (7)	−83 (7)
C(6)	105 (7)	114 (6)	237 (13)	−37 (7)	3 (8)	−4 (5)
C(7)	114 (6)	72 (4)	95 (5)	−8 (3)	19 (5)	−20 (4)
C(8)	135 (8)	67 (4)	215 (12)	0 (5)	−19 (8)	2 (4)
C(9)	210 (11)	126 (7)	151 (9)	−3 (6)	67 (9)	−60 (7)
C(10)	144 (8)	75 (4)	130 (8)	−14 (4)	13 (7)	−19 (4)
C(11)	177 (9)	73 (5)	168 (10)	−22 (5)	31 (8)	−21 (5)
C(12)	167 (10)	110 (6)	160 (10)	−3 (6)	−29 (8)	−34 (6)
C(13)	143 (7)	115 (5)	72 (5)	−5 (4)	33 (5)	−30 (5)
C(14)	92 (6)	139 (7)	181 (11)	29 (6)	41 (7)	−4 (5)
C(15)	218 (11)	87 (5)	99 (6)	27 (4)	15 (7)	−45 (6)
C(16)	292 (15)	126 (7)	128 (9)	−2 (6)	−31 (10)	−85 (9)
C(17)	211 (13)	116 (7)	381 (18)	2 (10)	137 (13)	21 (8)
C(18)	331 (19)	118 (9)	252 (17)	2 (10)	−47 (15)	8 (11)
C(19)	282 (17)	148 (10)	245 (15)	5 (9)	100 (14)	−50 (11)
C(20)	279 (16)	104 (7)	223 (14)	20 (7)	10 (12)	2 (8)
Si(1)	90 (1)	62 (1)	90 (1)	−6 (1)	2 (1)	−12 (1)
Si(2)	75 (1)	69 (1)	72 (1)	5 (1)	20 (1)	−9 (1)
P(1)	83 (1)	58 (1)	65 (1)	−6 (1)	14 (1)	−12 (1)
P(2)	76 (1)	58 (1)	60 (1)	2 (1)	16 (1)	−5 (1)
Ga(1)	72 (1)	59 (1)	60 (1)	1 (1)	10 (1)	−3 (1)
Ga(2)	88 (1)	59 (1)	68 (1)	−5 (1)	24 (1)	0 (1)

The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}\ U11 + \cdots + 2\ h\ k\ a^*\ b^*\ U12]$.

431 ($[Et_4Ga_2P(H)SiMe_2CM_2iPr]^+$, 22.6%), 262 ($[Et_2Ga_2P_2H_2]^+$, 55.1%), 127 ($Thex^+ - CH_4$, 100%); IR [$cm^{-1}$]: 2321 (P—H stretch vibration).

2: 0.5 g **1** (0.83 mmol) were heated to 180°C for 1 h. The white residue obtained was resolved in 5 ml of heptane and subsequently cooled to 6°C. Compound **2** formed as large colorless crystals within 3 days.

Yield: 0.34 g (75%); $C_{40}H_{96}Ga_4P_4Si_4$ (1092.3): calc.: C 43.98, H 8.86; found.: C 44.26, H 8.86. ^{1}H NMR(C_6D_6): $\delta = 0.56$ (m, $SiCH_3$ 24H), 1.07 (d, $CH(CH_3)_2$, 24H, $^3J_{HH}$: 6.8 Hz), 1.12 (s, $SiC(CH_3)_2iPr$, 24H), 1.36 (q, $GaCH_2CH_3$, 8H, $^3J_{HH} = 8.0$ Hz), 1.64 (t, $GaCH_2CH_3$, 12H, $^3J_{HH} = 8.0$ Hz), 1.91 (sept, $CH(CH_3)_2$, $^3J_{HH}$: 6.8 Hz); $^{13}C\{^1H\}$: $\delta = 2.2$ (t, $SiCH_3$, $^2J_{PC} =$ xx Hz), 11.3 (s, $GaCH_2CH_3$), 12.7 (t, $SiC(CH_3)_2iPr$, $^2J_{PC} =$ xx Hz), 19.5 (s, $SiC(CH_3)_2iPr$), 21.8 (s, $CH(CH_3)_2$), 26.1 (s, $CH(CH_3)_2$), 35.2 (s, $GaCH_2CH_3$); $^{29}Si\{^1H\}$: $\delta = 16.5$ (m); $^{31}P\{^1H\}$: $\delta = -137.8$ (s).

TABLE V Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($A^2 \times 10^3$) for Ga4P4

	x	y	z	U (eq)
H(1B)	−1097	10532	1529	−96
H(1A)	−58	11427	1536	96
H(2C)	−1134	11050	514	133
H(2B)	−682	9861	608	133
H(2A)	357	10761	615	133
H(3B)	5177	7148	1587	124
H(3A)	4063	6301	1532	124
H(4C)	4356	6708	544	188
H(4B)	4053	7908	647	188
H(4A)	2943	7052	591	188
H(5C)	605	6852	419	189
H(5B)	−98	7960	369	189
H(5A)	−915	6931	131	189
H(6C)	−2200	7648	1642	190
H(6B)	−2675	7388	905	190
H(6A)	−1899	8440	1129	190
H(8C)	1486	5288	1469	179
H(8B)	972	4578	1960	179
H(8A)	1326	5773	2122	179
H(9C)	−2048	5727	1863	190
H(9B)	−732	6020	2357	190
H(9A)	−1082	4826	2190	190
H(10A)	−492	4950	644	144
H(11C)	−1393	3322	741	169
H(11B)	−1365	3588	1461	169
H(11A)	−47	3513	1238	169
H(12C)	−2617	4642	257	188
H(12B)	−2281	5847	395	188
H(12A)	−2912	5188	868	188
H(13C)	2690	10730	370	130
H(13B)	3404	9628	410	130
H(13A)	4039	10638	178	130
H(14C)	6456	10144	1871	163
H(14B)	6457	10295	1142	163
H(14A)	5851	9265	1367	163
H(16C)	6273	12107	2099	235
H(16B)	5093	11916	2419	235
H(16A)	5381	13062	2199	235
H(17C)	2295	12413	1116	270
H(17B)	2946	13235	1649	270
H(17A)	2671	12071	1843	270
H(18A)	3576	12635	650	304
H(19C)	5814	12899	498	263
H(19B)	5593	11733	708	263
H(19A)	6364	12547	1216	263
H(20C)	4518	14346	730	252
H(20B)	5135	14159	1466	252
H(20A)	3606	14242	1212	252

MS (EI 70 eV, 190°C) m/z: 1092 (M^+, 17.7%), 1063 (M^+ –Et, 38.0%), 1007 (M^+ —CMe_2iPr, 4.5%), 979 (M^+ —CMe_2iPr, —C_2H_4, 3.7%), 949 (M^+—$SiMe_2CMe_2iPr$, 3.3%).

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