Extremely Bulky Amido-Group 14 Element Chloride Complexes: Potential Synthons for Low Oxidation State Main Group Chemistry

Jiaye Li, Andreas Stasch, Christian Schenk and Cameron Jones*

School of Chemistry, PO Box 23, Monash University, VIC, 3800, Australia.

SUPPLEMENTARY MATERIAL

Table S1. Summary of crystallographic data for **1**, **3**, **4**, **7**, **9**, **10**, **12**, **13**, **15**, [Li(L){N(SiMe$_3$)(Ar*)}] (L = OEt$_2$ **1S** or THF **2S**); [Na(THF)$_3${N(SiMe$_3$)(Ar*)}] **3S** and [K(OEt$_2$){N(SiPh$_3$)(Ar*)}] **4S**.

	1	**3**	**4**	**7**	**9**·(OEt$_2$)$_{1.5}$	**10**·(toluene)$_2$	**12**
empirical formula	$C_{36}H_{37}NSi$	$C_{51}H_{43}NSi$	$C_{36}H_{36}ClGeNSi$	$C_{36}H_{36}ClNSiSn$	$C_{57}H_{57}ClNO_{1.5}SiSn$	$C_{86}H_{88}Cl_2N_2Pb_2Si_2$	$C_{36}H_{36}Cl_3NSi_2$
formula weight	511.76	697.95	618.79	664.89	962.27	1691.04	645.19
crystal system	orthorhombic	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*Pnma*	$P2_1/c$	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
T (K)	173(2)	123(2)	173(2)	173(2)	123(2)	173(2)	173(2)
a (Å)	16.6936(8)	20.5915(12)	9.839(2)	9.799(2)	13.4198(3)	9.8669(4)	10.0788(7)
b (Å)	22.4261(9)	10.8266(5)	18.298(4)	18.329(4)	14.0960(3)	13.0330(5)	13.1075(9)
c (Å)	7.6390(3)	17.5359(7)	19.291(4)	19.472(4)	14.4193(3)	15.5728(7)	13.1687(9)
α (deg.)	90	90	104.22(3)	103.50(3)	66.512(2)	79.153(2)	90.754(3)
β (deg)	90	95.691(5)	98.69(3)	98.96(3)	81.228(2)	84.525(2)	108.006(4)
γ (deg.)	90	90	104.60(3)	104.63(3)	86.827(2)	72.621(2)	96.141(4)
vol (Å^3)	2859.8(2)	3890.1(3)	3172.7(11)	3203.5(11)	2472.33(9)	1875.38(13)	1643.0(2)
Z	4	4	4	4	2	1	2
ρ (calcd) (g.cm^{-3})	1.189	1.192	1.295	1.379	1.293	1.497	1.304
μ (mm^{-1})	0.107	0.097	1.113	0.943	0.636	4.632	0.379
F(000)	1096	1480	1288	1360	998	844	676

reflections collected	37410	17699	21013	21201	16094	41818	46831
unique reflections	2569	7218	11121	11268	9670	7238	6423
R_{int}	0.0767	0.0219	0.0443	0.0527	0.0652	0.0687	0.0432
R1 indices [$I>2\sigma(I)$]	0.0491	0.0399	0.0457	0.0452	0.0444	0.0363	0.0476
*w*R2 indices (all data)	0.1185	0.0977	0.1129	0.1155	0.1281	0.0726	0.1021
Largest peak and hole ($e.A^{-3}$)	0.30, -0.33	0.40, -0.37	0.38, -0.46	1.08, -0.74	1.96 (near Sn1), -0.67	1.18, -0.75	0.32, -0.36

	13	**15**	**1S**	**2S**	**3S**	**4S**
empirical formula	$C_{46}H_{40}Cl_3NSi_2$	$C_{36}H_{37}Cl_2NSi_2$	$C_{40}H_{46}LiNOSi$	$C_{40}H_{44}LiNOSi$	$C_{48}H_{60}NNaO_3Si$	$C_{55}H_{52}KNOSi$
formula weight	769.32	610.75	591.81	589.79	750.05	810.17
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	*P*-1	$P2_1/c$	*P*-1	*P*-1	*P*-1	*P*1
T (K)	123(2)	173(2)	123(2)	123(2)	123(2)	123(2)
a (Å)	10.4843(7)	12.5080(7)	9.8835(6)	9.7625(4)	10.8967(7)	10.6752(4)
b (Å)	12.8042(8)	17.0460(10)	10.1932(11)	10.1602(4)	11.1647(7)	12.6029(4)
c (Å)	14.8588(9)	15.5962(9)	18.8112(14)	18.8405(7)	18.3301(12)	18.4402(7)
α (deg.)	82.135(5)	90	74.610(8)	105.507(3)	78.746(4)	91.644(3)
β (deg)	85.347(5)	97.400(2)	88.130(6)	90.534(3)	89.505(4)	97.180(3)
γ (deg.)	80.847(5)	90	68.295(8)	112.600(4)	75.339(4)	114.573(3)

vol ($Å^3$)	1947.2(2)	3297.6(3)	1693.1(2)	1649.22(11)	2114.0(2)	2229.57(14)
Z	2	4	2	2	2	2
ρ (calcd) ($g.cm^{-3}$)	1.312	1.230	1.161	1.188	1.178	1.207
μ (mm^{-1})	0.332	0.295	0.836	0.103	0.107	0.186
$F(000)$	804	1288	636	632	808	860
reflections collected	12610	43632	20449	10292	40150	15243
unique reflections	6849	5597	6002	6437	9058	10800
R_{int}	0.0443	0.0536	0.0414	0.0292	0.0688	0.0312
R1 indices [$I>2\sigma(I)$][a]	0.0575	0.0810	0.0407	0.0459	0.0563	0.0485
wR2 indices (all data)[b]	0.1424	0.2215	0.1134	0.1022	0.1405	0.1288
Largest peak and hole ($e.A^{-3}$)	0.63, -0.40	1.40, -0.71	0.30, -0.29	0.31, -0.34	0.34, -0.29	0.47, -0.30

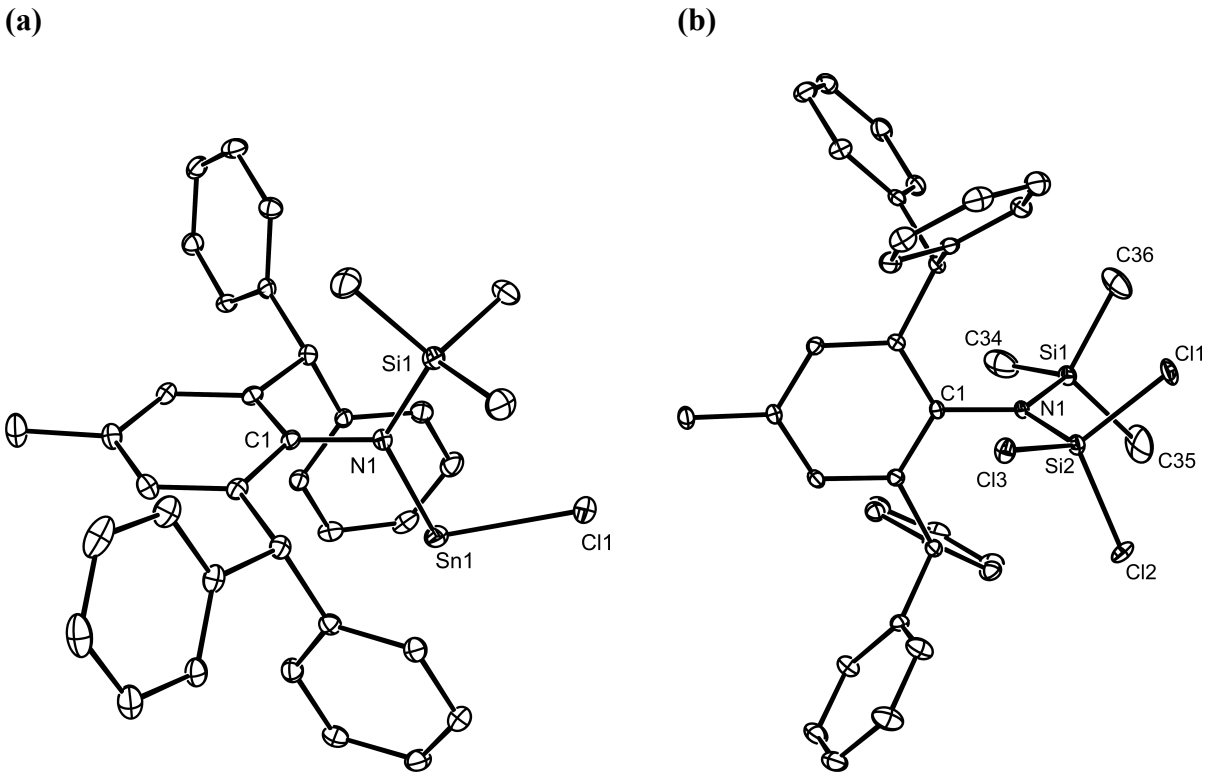

Figure S1. Molecular structure of (a) **7** and (b) **12** (25% displacement ellipsoids are shown; hydrogens omitted). See main text for geometrical parameters.

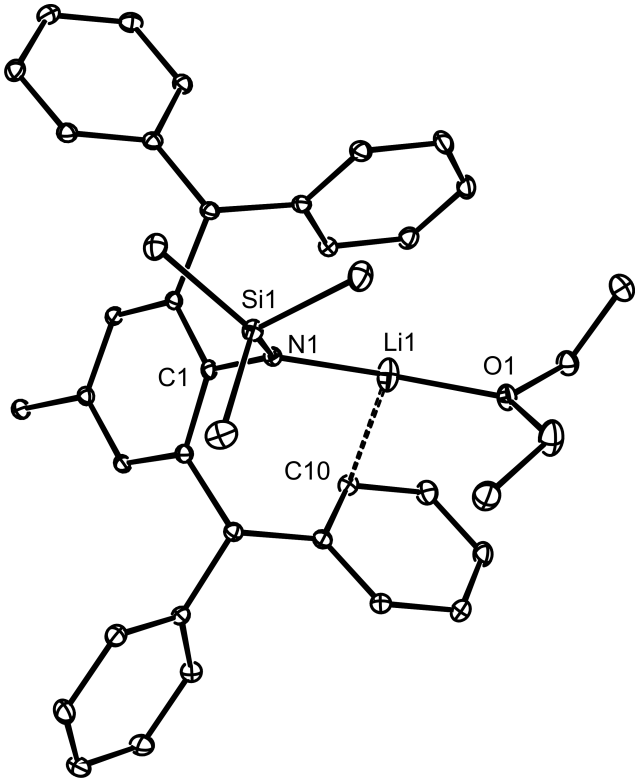

Figure S2. Molecular structure of [Li(OEt$_2$){N(SiMe$_3$)(Ar*)}] **1S** (25% displacement ellipsoids are shown; hydrogens omitted; Li···C contact at less than 2.80 Å shown as a dotted line). Selected bond lengths (Å) and angles (°): Si(1)-N(1) 1.6846(14), N(1)-C(1) 1.391(2), N(1)-Li(1) 1.883(4), Li(1)-C(10) 2.655(4), O(1)-Li(1) 1.880(4), C(1)-N(1)-Si(1) 125.53(11), C(1)-N(1)-Li(1) 114.39(14), Si(1)-N(1)-Li(1) 119.98(13).

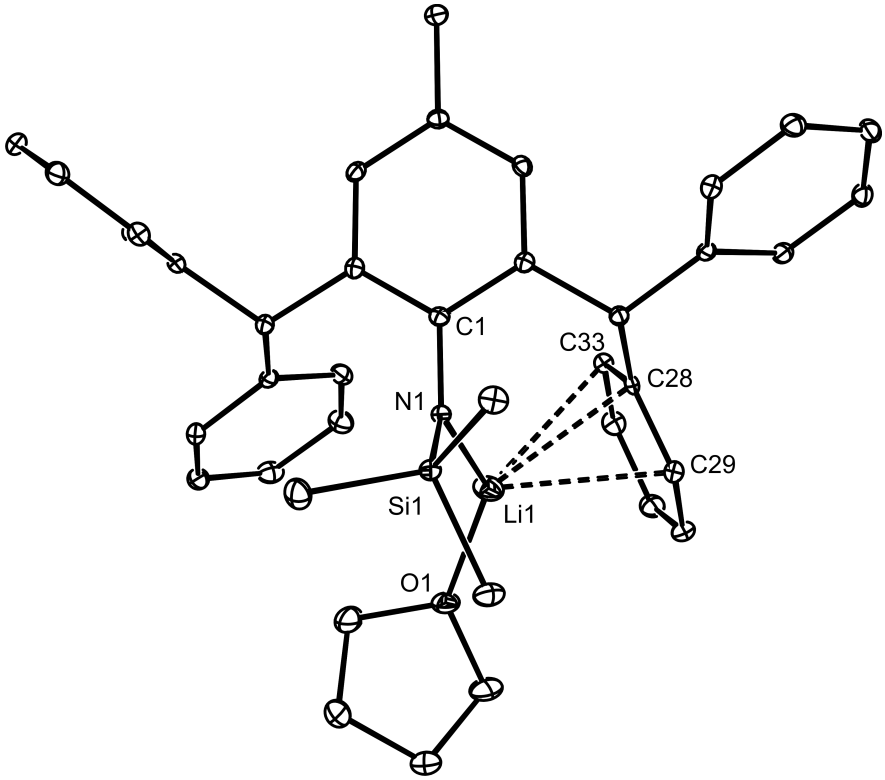

Figure S3. Molecular structure of [Li(THF){N(SiMe$_3$)(Ar*)}] **2S** (25% displacement ellipsoids are shown; hydrogens omitted; Li···C contacts at less than 2.80 Å shown as dotted lines). Selected bond lengths (Å) and angles (°): Si(1)-N(1) 1.6871(13), O(1)-Li(1) 1.895(3), N(1)-C(1) 1.3925(19), N(1)-Li(1) 1.912(3), C(28)-Li(1) 2.564(3), C(29)-Li(1) 2.703(4), C(33)-Li(1) 2.707(4), C(1)-N(1)-Si(1) 123.85(11), C(1)-N(1)-Li(1) 117.82(14), Si(1)-N(1)-Li(1) 116.37(11),

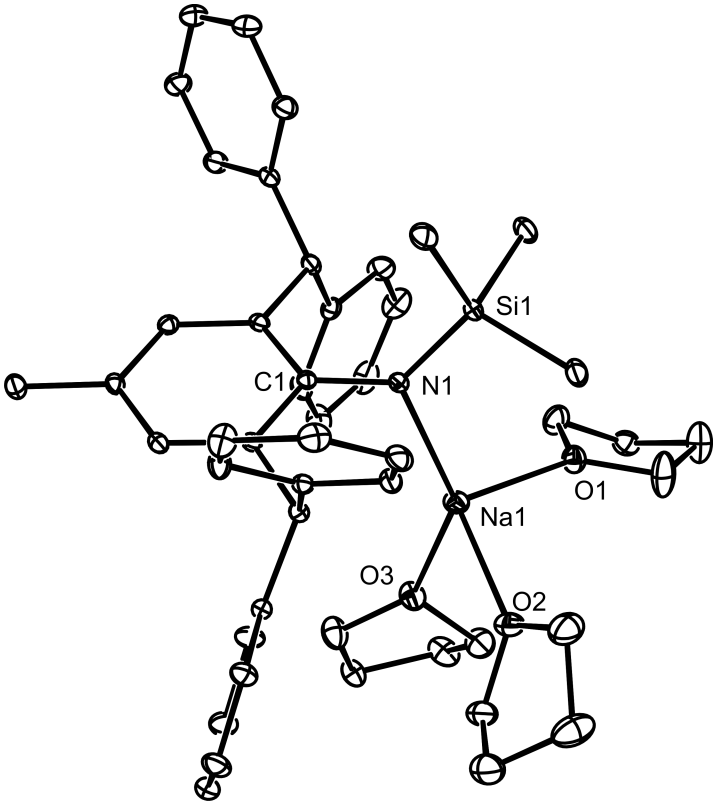

Figure S4. Molecular structure of [Na(THF)$_3${N(SiMe$_3$)(Ar*)}] **3S** (25% displacement ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Si(1)-N(1) 1.6733(18), Na(1)-O(1) 2.3162(17), Na(1)-N(1) 2.3411(18), Na(1)-O(2) 2.3491(18), Na(1)-O(3) 2.3632(18), N(1)-C(1) 1.377(2), C(1)-N(1)-Si(1) 130.11(14), C(1)-N(1)-Na(1) 112.91(12), Si(1)-N(1)-Na(1) 116.93(9).

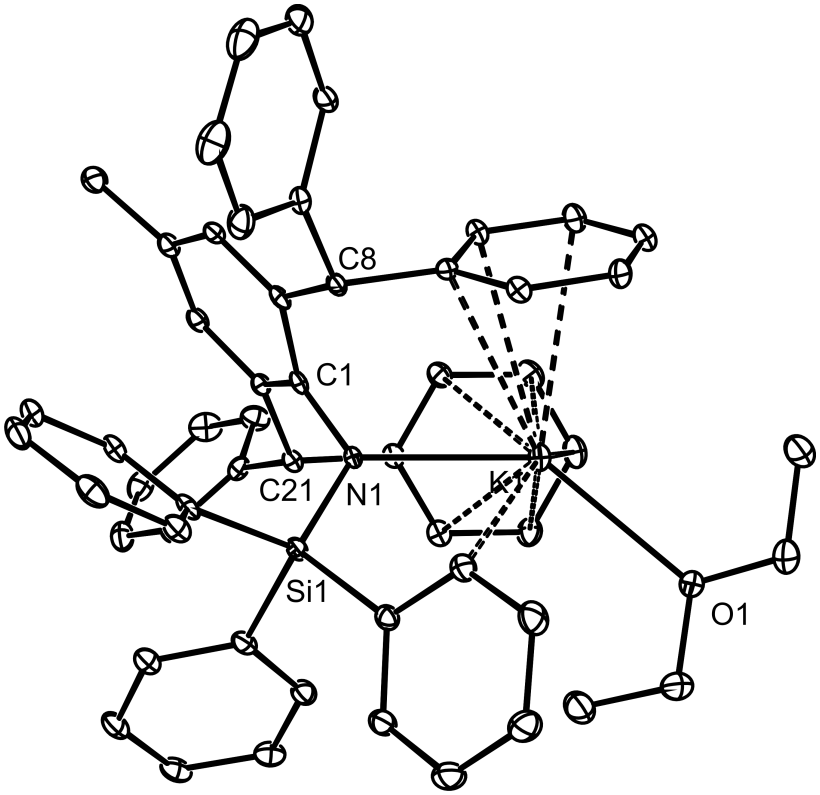

Figure S5. Molecular structure of [K(OEt$_2$){N(SiPh$_3$)(Ar*)}] **4S** (25% displacement ellipsoids are shown; hydrogens omitted; K···C contacts at less than 3.50 Å shown as dotted lines). Selected bond lengths (Å) and angles (°): K(1)-N(1) 2.649(3), K(1)-O(1) 2.778(3), Si(1)-N(1) 1.675(3), N(1)-C(1) 1.390(5), C(1)-N(1)-Si(1) 118.8(2), C(1)-N(1)-K(1) 119.9(2), Si(1)-N(1)-K(1) 121.27(14).

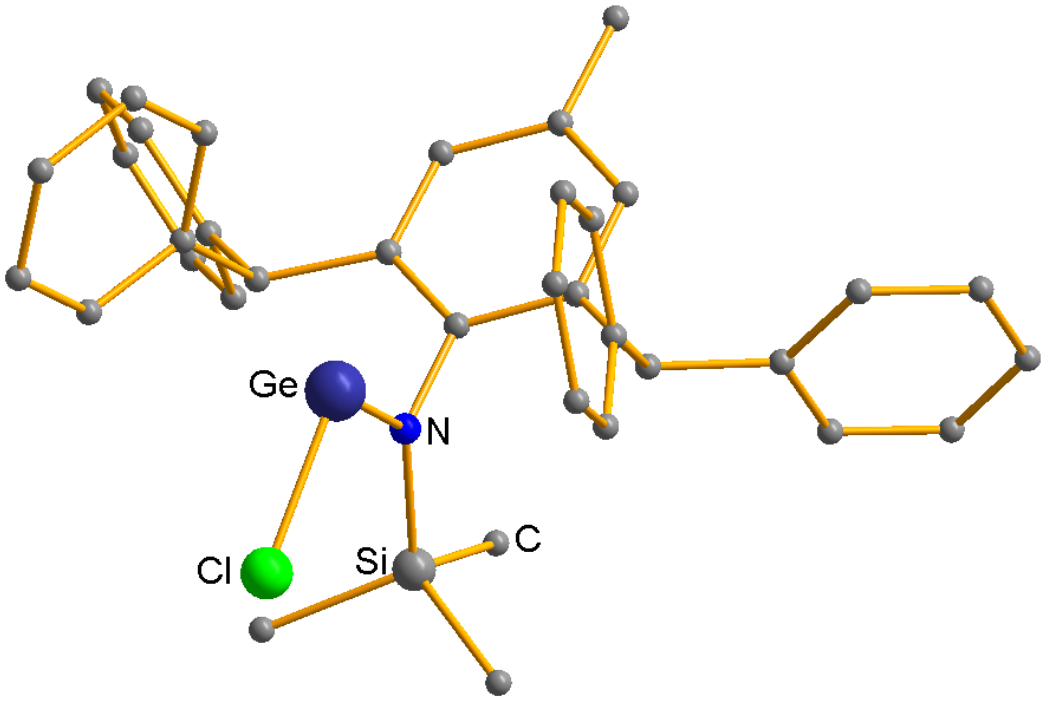

Figure S6. Calculated structure of **4** (BP86/RI-DFT/SVP, hydrogen atoms are omitted for clarity).

	molecular structure	**calculated structure**	**difference**
Cl-Ge	2.257	2.287	0.030
Ge-N	1.855	1.904	0.049
N-Si	1.769	1.817	0.048
N-C	1.460	1.441	-0.019
Cl-Ge-N	98.85	99.61	0.76
Ge-N-Si	130.54	129.81	0.73
Ge-N-C	110.95	110.92	0.03

Table S2. Comparison of the metrical parameters of the molecular structure of **4** with those of its calculated gas phase structure (bond lengths: Å and angles: °).

Table S3. Cartesian coordinates for the calculated structure of **4**.

76

N	-0.00100	1.00200	0.49100
Ge	-0.00500	0.00500	2.11300
Si	0.00400	2.80000	0.23100
C	0.00100	0.12500	-0.65200
C	-1.54300	3.61500	0.97000
C	0.00800	3.10200	-1.64500
C	1.55000	3.61100	0.97700
C	-1.22700	-0.33100	-1.21800
C	1.23100	-0.32700	-1.22000
H	-2.47900	3.27000	0.47500
H	-1.48300	4.72000	0.83400
H	-1.62100	3.40600	2.05800
H	0.90500	2.66800	-2.13800
H	0.00500	4.19800	-1.84200
H	-0.88500	2.66300	-2.14300
H	1.62800	3.39400	2.06400
H	1.48800	4.71600	0.84900
H	2.48700	3.27000	0.48100
C	-1.20200	-1.16700	-2.35100
C	-2.55600	0.05400	-0.55300
C	1.20800	-1.16200	-2.35100
C	2.55900	0.05800	-0.55100
H	-2.15900	-1.49200	-2.79200
C	0.00300	-1.58800	-2.94300
H	-2.43200	1.09600	-0.19300
C	-2.82100	-0.78700	0.70100
C	-3.74400	0.07500	-1.52500
H	2.16700	-1.48500	-2.79100
H	2.43800	1.10300	-0.19600
C	2.81600	-0.77800	0.70800
C	3.75100	0.07000	-1.51800
C	0.01000	-2.44900	-4.18700
C	-2.53400	-2.16900	0.75000
C	-3.38800	-0.18100	1.84500
C	-4.69600	-0.96200	-1.59700
C	-3.89400	1.17700	-2.39600
C	2.52900	-2.16000	0.75900
C	3.37400	-0.16700	1.85400
C	4.69800	-0.97200	-1.58100
C	3.91000	1.16800	-2.39300
H	0.19800	-1.83600	-5.09900
H	-0.96200	-2.96600	-4.33300
H	0.81000	-3.22100	-4.14800
H	-2.07200	-2.65700	-0.12400
C	-2.81200	-2.92300	1.90300
C	-3.65800	-0.93100	3.00300
H	-3.61900	0.89800	1.82800
H	-4.61600	-1.82600	-0.91700
C	-5.75900	-0.90500	-2.51700
C	-4.95200	1.23800	-3.31500
H	-3.16400	2.00300	-2.35200
H	2.07300	-2.65100	-0.11600
C	2.80100	-2.90900	1.91700
C	3.63700	-0.91300	3.01600
H	3.60400	0.91100	1.83500
H	4.61100	-1.83200	-0.89800
C	5.76500	-0.92300	-2.49800

C	4.97200	1.22100	-3.30800
H	3.18300	1.99800	-2.35500
H	-2.57800	-4.00000	1.92000
C	-3.37100	-2.30600	3.03500
H	-4.08900	-0.43300	3.88800
H	-6.49300	-1.72700	-2.55200
C	-5.89100	0.19400	-3.38100
H	-5.04700	2.11200	-3.98200
H	2.56800	-3.98700	1.93500
C	3.35300	-2.28900	3.05000
H	4.06200	-0.41200	3.90200
H	6.49500	-1.74900	-2.52600
C	5.90600	0.17200	-3.36500
H	5.07400	2.09100	-3.97800
H	-3.57800	-2.89500	3.94400
H	-6.72600	0.24100	-4.09900
H	3.55400	-2.87500	3.96200
H	6.74500	0.21100	-4.08000
Cl	-0.00700	1.72600	3.61900