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An easy route to 1-germaindenes via a transmetallation zirconium–germanium reaction

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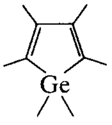
Abstract

Several 1-zirconaindenes (**4**) have been obtained easily by heating phenylmethylzirconocene with various symmetrical (R = R' = CH_3, C_2H_5, n-C_3H_7, $Si(CH_3)_3$ and unsymmetrical (R = CH_3, R' = $Si(CH_3)_3$) alkynes (R–C≡C–R'). Under similar experimental conditions, the ynamine, diethylaminotrimethylsilylethyne, led to a regioselective reaction. From the X-ray structure of the zirconaindene product, the trimethylsilyl group was found close to the zirconium atom. Compounds **4** with germanium tetrachloride afford new 1-germaindenes (**7**), characterized by ^1H and ^{13}C NMR and mass spectrometry, in good yield.

1. Introduction

The chemistry of Group 14 metalloles has been extensively studied [1,2] to develop a chemistry similar to that of the cyclopentadiene. Although this objective has failed partially, a fascinating reactivity of metalloles, particularly siloles, has been discovered. Recently, several complexes of zirconium used as synthons allowed significant progress in germole (**1**) chemistry [3–6].



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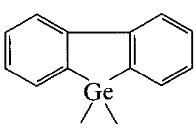

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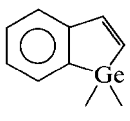

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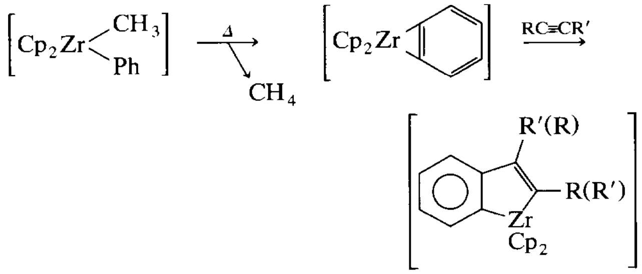
In spite of the interest in germafluorenes (**2**) and germaindenes (**3**) for example in the stabilization of anionic species, these two families have been described very little [7–15]. The present paper deals with general access to 1-germaindenes (**3**) by a transmetallation reaction from the easily synthesized 1-zirconaindenes, for which the structure of one representative has been established by X-ray diffraction.

2. Results and discussion

2.1. *1-Zirconaindenes*

The 1-zirconaindenes (**4**) were prepared by insertion of various alkynes into the Zr–C bond of benzynezirconocene formed *in situ* when methylphenylzirconocene is heated [16,17].



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R = R' = CH_3 (**a**); C_2H_5 (**b**); n-C_3H_7 (**c**); $Si(CH_3)_3$ (**d**)
R,R' = $Si(CH_3)_3$, CH_3 (**e**)

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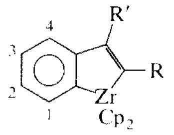
TABLE 1. Spectroscopic data for zirconacycles **4** (**c**, **d**, **e**) and **5**



(4)

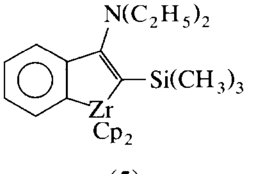
R	R′	NMR spectroscopy								Mass spectrometry Main fragment (%)
		^1H (C_6D_6) δ (ppm/TMS), *J* (Hz))							^{13}C ($CDCl_3$) (ppm/TMS)	
		Cp	H^1	H^2	H^3	H^4	R	R′		
n-C_3H_7	n-C_3H_7	5.94 (s/10)	6.57 (dd/1, *J* = 7.5 and 1.4)	7.04 (td/1, *J* = 7.5 and 1.4)	7.19 (d/1 *J* = 7.5 and 1.4)	7.35 (d/1, *J* = 7.5)	0.95 (t/3, CH_3) 1.10 (m/2, CH_2) 2.11 (t/2, CH_2)	1.05 (t/3, CH_3) 1.65 (m/2, CH_2) 2.48 (t/2, CH_2)	14.5 (CH_3); 15.3 (CH_3); 22.2 (CH_2); 23.8 (CH_2); 30.2 (CH_2); 38.2 (CH_2); 111.7 (Cp); 121.15 (Ph); 122.3 (Ph); 125.0 (Ph); 135.6 (Ph)	406 ($M^{+\cdot}$, 26); 363 ($M^+ - C_3H_7$, 4); 220 (Cp_2Zr, 100)
$Si(CH_3)_3$	$Si(CH_3)_3$	5.75 (s/10)	7.0–7.5 (m/4)				0.13 (s/9, CH_3)	0.44 (s/9, CH_3)	4.1 ($Si(CH_3)_3$); 4.3 ($Si(CH_3)_3$); 112.3 (Cp) 124.4 (Ph); 126.4 (Ph) 126.5 (Ph); 135.5 (Ph)	466 ($M^{+\cdot}$, 25) 393 ($M - SiCH_3)_3$, 70)
$Si(CH_3)_3$	CH_3	5.95 (s/10)	6.52 (dd/1, *J* = 7.5 and 1.4)	7.07 (td/1, *J* = 7.5 and 1.4)	7.28 (dd/1, *J* = 7.5 and 1.4)	7.14 (td/1, *J* = 7.5 and 1.4)	0.09 (s/9, CH_3)	2.13 (s/3, CH_3)	1.8 ($Si(CH_3)_3$); 23.3 (CH_3) 112.0 (Cp); 122.0 (Ph) 124.0 (Ph); 124.8 (Ph) 135.8 (Ph)	408 ($M^{+\cdot}$, 30) 393 ($M - CH_3$, 14) 335 ($M - Si(CH_3)_3$, 12) 220 (Cp_2Zr, 30) 43 ($SiCH_3$, 100)
$Si(CH_3)_3$	$N(C_2H_5)_2$	5.98 (s/10)	6.52 (d/1, *J* = 6.3)	7.00 (t/1, *J* = 6.3)	7.07 (t/1, *J* = 6.3)	7.22 (d/1, *J* = 6.3)	0.11 (s/9, CH_3)	1.15 (q/6, CH_3) 3.12 (q/4, CH_2)	2.4 ($Si(CH_3)_3$); 13.8 (CH_3) 47.5 (CH_2); 112.0 (Cp) 123.2 (Ph); 123.5 (Ph) 124.5 (Ph); 135.6 (Ph)	465 ($M^{+\cdot}$, 20) 393 ($M - N(C_2H_5)_2$ 32) 295 ($Cp_2ZrC_6H_4$, 8) 220 (Cp_2Zr, 62) 43 ($SiCH_3$, 10)

TABLE 2. Crystal data for **5**

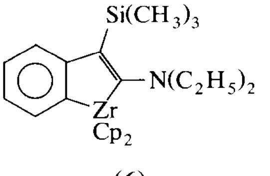
Formula	$C_{25}H_{34}NSiZr$
FW	467.9
System	Orthorhombic
Space group	*Pbca*
a (Å)	10.324(2)
b (Å)	15.378(2)
c (Å)	29.492(4)
V (Å^3)	4683(1)
Z	8
μ(Mo Kα) (cm^{-1})	5.21
$D_{\text{calc.}}$ (g cm^{-3})	1.32
2θ range (°)	$3 < 2\theta < 50$
Scan type	$\omega/2\theta$
Scan width (°)	$0.8 + 0.345\text{tg}\theta$
Scan speed (° min^{-1})	1.65–16.5
Diffractometer	CAD4F
No. of reflections collected	4632
No. of reflections with $I > 3\sigma(I)$	1693
Absorption corrected by	DIFABS
R	0.0516
R_w	0.0597
Weighting scheme [a]	$w = w'[1-(\Delta F/6\sigma(F)^2]^2$
Coefficient A_r for the Chebyshev series	6.08, −6.62, 4.86, −1.92
No. of variables (NV)	291
GOF	1.26

[a] $w' = 1/\Sigma_1^n A_r T_r(X)$ where n ($n = 4$) is the number of coefficients, $A_{r'}$ for a Chebyshev polynomial series for which X is F_c/F_c(max) [29].

Compounds **4a**, **4b** and **4c** have already been reported by Buchwald [16,18] and they react with sulphur dichloride to prepare benzothiophenes [19] by a one-pot process. In our case, the isolation and purification of the intermediate zirconaindenes were essential because germaindenes containing Ge–Cl bonds have been obtained as oily air-sensitive products. Thus we repeated the synthesis of pure compounds **4a** and **4b** and extended the reaction to **4c** and **4d**. The insertion of the ynamine, diethylaminotrimethylsilylethyne $(CH_3)_3SiC{\equiv}CN(C_2H_5)_2$, into the benzynezirconocene have also been investigated. The latter reaction, which could theoretically afford two regioisomers **5** and **6** is regiospecific for the non-substituted cyclopentadienyls.

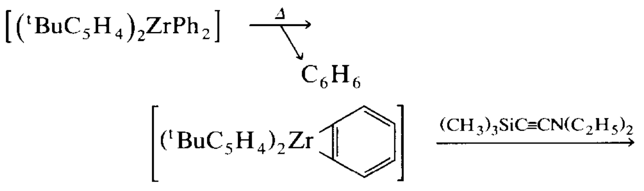


(**5**)



(**6**)

The structure **5** was reasonably assigned to the unique product formed, by comparison with the product from **4e**. The synthesis of the regioisomer **6** was expected from the more sterically congested tert-butylcyclopentadienyl series, but in this case, the reaction was only regioselective. A mixture of the two isomers was obtained from which **6** was never isolated pure.



5 + **6** (90:10)

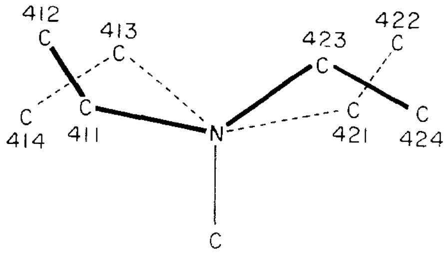
The spectroscopic data related to 1-zirconaindenes synthesized (Table 1) are in accordance with the proposed structure. Molecular peaks and typical fragmentations are observed by mass spectrometry. The ^1H NMR spectra exhibit a singlet near 6 ppm assigned to the cyclopentadienyl protons, and the aromatic protons appear as four groups of signals consistent with an ABCD system of spins. In ^{13}C NMR spectra, the carbon atoms of the cyclopentadienyl ligands normally fall in the range of 120–140 ppm but the signals attached to the quaternary carbon atoms were not detected.

The structure of the unique zirconaindene formed in the cyclopentadienyl series has been determined by X-ray diffraction analysis. To the best of our knowledge this is the first zirconaindene structure. The ORTEP view in Fig. 1 corresponds to the regioisomer **5**. The atomic distances, angle values and crystal data are reported in Tables 2, 3 and 4.

The molecular structure of the compound **5** is typical of a bent metallocene. The pseudotetrahedral environment of the zirconium atom consists of two cyclopentadienyl π-ligands and two σ-bonded carbon atoms from the metallaindene moiety. The silicon atom is located near the zirconium atom. The length of the Zr–C_6 (phenyl) bond (2.275(9) Å) is slightly shorter than those measured for other molecules containing zirconium-aromatic carbon bonds: $Cp_2Zr[CH(SiMe_3)_2]Ph$, 2.324(7) Å [20]; $(^tBuCp)_2Zr(C_5H_4)_2Fe$, 2.284(2) Å [21]; $C_5Me_2Zr(Ph)Me_4C_5CH_2$, 2.285(5) Å [22].

The Zr–C_2 (2.246 Å) distance lies in the range normally observed for a zirconium–carbon (sp^2) bond, for example $[\{Cp_2ZrOC\{=W(CO)_5\}C_6H_4\}_n]$, Zr–C = 2.284(9) Å [23]; $[Cp_2Zr\eta^2\text{-N,C-picolyl})(PMe_3)]$, Zr–C = 2.29(2) Å [24]; $[(Cp^*)_2Zr\{OC(CHPh)C_2(C_4H_4)\}]$, Zr–C = 2.276(2) Å [25].

The zirconaindene ring is not perfectly planar and the dihedral angle between the benzene ring and the metallacycle is 3.36°. Both the C_2H_5 substituents are disordered and a reasonable model has a statistical distribution of each of the carbon atoms on two sites as shown below.



These disordered ethyl groups are severely constrained to chemically reasonable dimensions (N–C = 1.47(1) Å; C–C = 1.53(1) Å; C–N–C angle = 111(1)°; N–C–C angle = 109(1)°).

2.2. 1-Germaindenes

The germanium tetrachloride reacts with 1-zirconaindenes affording in good yield (80–95%) a new family of substituted 1-germaindenes with two germanium–chlorine bonds.

TABLE 3. Bond distances (Å) and angles (°); e.s.d.s in parentheses refers to the last significant digit

Zr(1)–CEN(2) [a]	2.219(1)	Zr(1)–CEN(1)	2.226(1)
Zr(1)–C(2)	2.246(9)	Si(1)–C(13)	1.88(1)
Zr(1)–C(6)	2.275(9)	Si(1)–C(14)	1.85(2)
Zr(1)–C(15)	2.512(9)	C(15)–C(16)	1.39(1)
Zr(1)–C(16)	2.534(9)	C(15)–C(19)	1.42(1)
Zr(1)–C(17)	2.524(9)	C(16)–C(17)	1.38(1)
Zr(1)–C(18)	2.525(9)	C(17)–C(18)	1.38(1)
Zr(1)–C(19)	2.51(1)	C(18)–C(19)	1.39(2)
Zr(1)–C(20)	2.51(1)	C(19)–C(20)	1.35(2)
Zr(1)–C(21)	2.52(1)	C(20)–C(21)	1.40(2)
Zr(1)–C(22)	2.52(1)	C(21)–C(22)	1.36(2)
Zr(1)–C(23)	2.50(1)	C(22)–C(23)	1.38(2)
Zr(1)–C(24)	2.50(1)	C(23)–C(24)	1.40(2)
C(2)–Si(1)	1.870(9)	C(3)–N(4)	1.47(1)
C(2)–C(3)	1.35(1)	N(4)–C(411)	1.50(1)
C(5)–C(6)	1.40(1)	N(4)–C(413)	1.473(9)
C(5)–C(10)	1.39(1)	N(4)–C(421)	1.49(1)
C(5)–C(3)	1.50(1)	N(4)–C(423)	1.48(1)
C(6)–C(7)	1.40(1)	C(411)–C(412)	1.523(9)
C(7)–C(8)	1.37(1)	C(413)–C(414)	1.516(9)
C(8)–C(9)	1.37(1)	C(421)–C(422)	1.516(9)
C(9)–C(10)	1.39(1)	C(423)–C(424)	1.522(9)
Si(1)–C(12)	1.84(1)		
CEN(2)–Zr(1)–C(2)	109.9(2)	C(19)–C(15)–C(16)	106.5(9)
CEN(2)–Zr(1)–C(6)	103.2(2)	C(17)–C(16)–C(15)	109.0(9)
CEN(2)–Zr(1)–CEN(1)	136.74(4)	C(18)–C(17)–C(16)	108.8(9)
C(6)–Zr(1)–C(2)	79.0(3)	C(19)–C(18)–C(17)	107.7(9)
C(14)–Si(1)–C(13)	103.7(8)	C(18)–C(19)–C(15)	108.0(9)
Si(1)–C(2)–Zr(1)	124.5(5)	C(24)–C(20)–C(21)	109.0(11)
C(3)–C(2)–Zr(1)	111.4(6)	C(22)–C(21)–C(20)	109.5(12)
C(3)–C(2)–Si(1)	124.1(7)	C(23)–C(22)–C(21)	107.7(13)
C(10)–C(5)–Si(1)	118.5(8)	C(24)–C(23)–C(22)	108.3(11)
C(3)–C(5)–C(6)	119.5(7)	C(23)–C(24)–C(20)	105.5(12)
C(3)–C(5)–C(10)	112.0(8)	C(5)–C(3)–C(2)	120.5(8)
C(5)–C(6)–Zr(1)	109.6(6)	N(4)–C(3)–C(2)	120.6(8)
C(7)–C(6)–Zr(1)	131.5(7)	N(4)–C(3)–C(5)	118.8(7)
C(7)–C(6)–C(5)	118.8(8)	C(411)–N(4)–C(3)	108.3(7)
C(8)–C(7)–C(6)	122.2(9)	C(413)–N(4)–C(3)	116.6(7)
C(9)–C(8)–C(7)	118.8(9)	C(421)–N(4)–C(3)	106.4(7)
C(10)–C(9)–C(8)	120.4(9)	C(421)–N(4)–C(3)	119.2(13)
C(9)–C(10)–C(5)	121.2(9)	C(423)–N(4)–C(3)	115.1(8)
C(12)–Si(1)–C(2)	115.4(6)	C(423)–N(4)–C(411)	116.8(12)
C(13)–Si(1)–C(2)	109.7(5)	C(412)–C(411)–N(4)	111.3(9)
C(14)–Si(1)–C(2)	113.5(6)	C(412)–C(411)–N(4)	109.0(8)
C(14)–Si(1)–C(12)	110.1(9)	C(422)–C(421)–N(4)	111.0(9)
		C(424)–C(423)–N(4)	108.4(9)

[a] CEN(1) and CEN(2) are the centroids of the Cp rings.

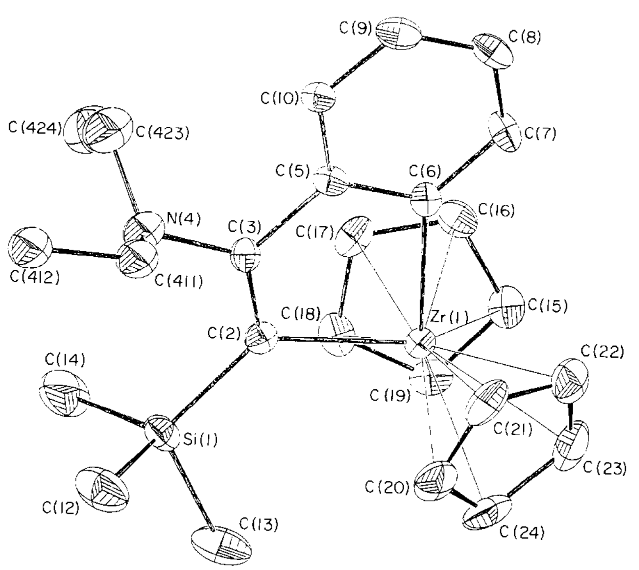
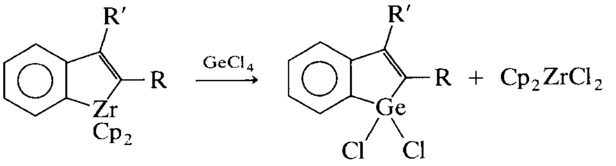


Fig. 1.

TABLE 4. Fractional atomic coordinates with e.s.d.s in parentheses, and equivalent isotropic thermal parameter U_{eq} ($Å^2$)

Atom	x	y	z	U_{eq} [a]
Zr(1)	0.11174(8)	0.04935(5)	0.16173(3)	0.0423
C(2)	−0.0289(9)	0.1040(6)	0.1111(3)	0.0443
C(5)	−0.1733(8)	0.0026(6)	0.1526(3)	0.0414
C(6)	−0.0719(9)	−0.0241(6)	0.1806(3)	0.0462
C(7)	−0.094(1)	−0.0906(7)	0.2120(3)	0.0567
C(8)	−0.213(1)	−0.1301(7)	0.2164(3)	0.0604
C(9)	−0.313(1)	−0.1020(7)	0.1897(4)	0.0595
C(10)	−0.2937(8)	−0.0369(6)	0.1578(3)	0.0507
Si(1)	0.0137(3)	0.1860(2)	0.06672(9)	0.0551
C(12)	−0.024(2)	0.154(1)	0.0082(4)	0.0967
C(13)	0.194(1)	0.203(1)	0.0657(4)	0.0877
C(14)	−0.052(2)	0.296(1)	0.0784(7)	0.1224
C(15)	0.211(1)	0.1007(7)	0.2348(3)	0.0548
C(16)	0.078(1)	0.1051(7)	0.2417(3)	0.0578
C(17)	0.026(1)	0.1671(7)	0.2133(3)	0.0514
C(18)	0.126(1)	0.2048(6)	0.1889(3)	0.0554
C(19)	0.241(1)	0.1646(7)	0.2019(3)	0.0582
C(20)	0.204(1)	−0.0260(9)	0.0936(4)	0.0735
C(21)	0.142(1)	−0.0885(8)	0.1169(5)	0.0702
C(22)	0.203(1)	−0.1024(8)	0.1571(5)	0.0793
C(23)	0.307(1)	−0.046(1)	0.1592(4)	0.0773
C(24)	0.310(1)	0.0031(9)	0.1193(5)	0.0756
C(3)	−0.1489(8)	0.0705(5)	0.1169(3)	0.0425
N(4)	−0.2590(9)	0.1039(6)	0.0908(3)	0.0798
C(411)	−0.287(2)	0.041(1)	0.0531(6)	0.0846
C(412)	−0.386(2)	0.078(2)	0.0201(7)	0.0996
C(413)	−0.330(1)	0.041(1)	0.0628(6)	0.0778
C(414)	−0.233(2)	−0.018(1)	0.0389(7)	0.0784
C(421)	−0.333(2)	0.162(2)	0.1220(5)	0.0981
C(422)	−0.402(3)	0.233(2)	0.0958(9)	0.1071
C(423)	−0.371(1)	0.133(2)	0.1182(7)	0.1079
C(424)	−0.331(3)	0.215(2)	0.144(1)	0.1163

[a] $U_{eq} = \frac{1}{3}[U(11) \times U(22) \times U(33)]$.



(4) (7)

$R = R' = CH_3$ (**a**); C_2H_5 (**b**); $n\text{-}C_3H_7$ (**c**); $Si(CH_3)_3$ (**d**)
$R = Si(CH_3)_3$; $R' = CH_3$ (**e**)
$R = Si(CH_3)_3$; $R' = N(C_2H_5)_2$ (**f**)

The reactions took some hours at room temperature in tetrahydrofuran solution. The germaindenes were extracted easily from the reaction mixture with pentane, leading to oily products in a good purity (95% by NMR) after evaporation of the solvent. The spectroscopic data are reported in Table 5.

There are differences in the NMR spectra compared to those of the zirconaindene precursors. The aromatic proton signals (H^1 to H^4) are much less well resolved and first-order analysis of the spectra appears difficult; the ^{13}C NMR spectra exhibit signals assignable to C^1–C^4 in a narrow range, 122–133 ppm.

3. Conclusion

We have prepared a new family of germaindenes. The reactivity of their germanium–chlorine bonds is currently being tested, and the synthesis of anionic species and complexes with transition metals is in progress.

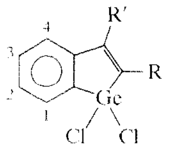
4. Experimental part

All reactions were routinely carried out in Schlenk type glassware under argon. Solvents were distilled from a sodium benzophenone ketyl complex prior to use. Microanalyses were performed by the Service Central d'Analyses du CNRS. NMR spectra were recorded on a Bruker WM 400 or a Bruker AC 200 spectrometers. The external reference was TMS. Mass spectra were obtained from a Kratos apparatus Concept S (electronic ionization = 70 eV). The alkynes were commercial reagents (Merck, Lancaster) used as received. Melting points were measured on a Kofler beam without any correction. Diethylaminotrimethylsilylethyne was prepared according to the literature [26].

4.1. Synthesis of 1-zirconaindenes

The general method is described for the preparation of compounds **5**. To a solution of $[Cp_2Zr(Me)Ph]$ (0.61 g, 1.95 mmol) in 35 ml of benzene was added 0.33 g (1.95 mmol) of diethylaminotrimethylsilylethyne. The stirred mixture was heated under reflux for 20 h and

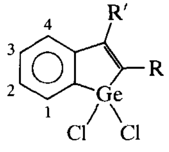
Table 5. Spectroscopic data for 1-germaindenes **7**



(7)

R	R′	NMR spectroscopy							Mass spectrometry Main fragments (%)
		^1H (C_6D_6) δ ((ppm/TMS), J (Hz))						^{13}C ($CDCl_3$) δ (ppm/TMS)	
		H1	H2	H3	H4	R	R′		
CH_3	CH_3	6.85 (dd/1. J = 7.2 and 1.4)	6.93 (td/1. J = 7.2 and 1.4)	7.03 (td/1. J = 7.2 and 1.4)	7.29 (dd/1. J = 7.2 and 1.4)	1.51 (s/3)	1.76 (s/3)	12.8 (CH_3); 13.1 (CH_3) 122.5 (Ph); 129.2 (Ph) 130.6 (Ph); 132.4 (Ph)	274 (M^+, 100) 259 (M−CH_3, 18) 238 (M−HCl, 41)
C_2H_5	C_2H_5	6.88 (dd/1. J = 7.3 and 1.2)	6.91 (td/1. J = 7.3 and 1.2)	7.01 (td/1. J = 7.3 and 1.2)	7.32 (dd/1. J = 7.3 and 1.2)	0.75 (t/3, CH_3) 2.07 (q/2, CH_2)	1.19 (t/3, CH_3) 2.25 (q/2, CH_2)	13.1 (CH_3); 14.4 (CH_3) 20.2 (CH_2); 21.9 (CH_2) 122.5 (Ph); 128.8 (Ph) 130.7 (Ph); 132.3 (Ph)	302 (M^+; 30) 273 (M−C_2H_5, 20) 238 (M−CH_3−$GeCl_2$, 100)
n-C_3H_7	n-C_3H_7	6.97 (m/3)			7.34 (d/1. J = 6.8)	0.73 (t/3, CH_3) 1.23 (sex/2, CH_2) 2.19 (t/2, CH_2)	0.85 (t/3, CH_3) 1.73 (sex/2, CH_2) 2.34 (t/2, CH_2)	14.2 (2CH_3); 21.8 (CH_2) 23.0 (CH_2); 29.1 (CH_2) 30.1 (CH_2); 122.6 (Ph) 128.8 (Ph); 130.7 (Ph) 132.3 (Ph)	330 (M^+; 50) 273 (M−C_3H_7, 10) 260 (M−CH_3−$GeCl_2$, 100)
Si$(CH_3)_3$	Si$(CH_3)_3$	7.15 (m/4)				0.19 (s/9, CH_3)	0.44 (s/9, CH_3)	2.5 (Si$(CH_3)_3$; Si $(CH_3)_3$ 127.2 (Ph); 129.5 (Ph) 132.3 (Ph); 133.0 (Ph)	390 (M^+; 23) 375 (M−CH_3, 13) 231 (M−CH_3−$GeCl_2$, 100)
Si$(CH_3)_3$	CH_3	7.05 (m/4)				0.21 (s/9, CH_3)	1.98 (s/3, CH_3)	0.9 (Si$(CH_3)_3$; 23.2 (CH_3) 127.1 (Ph); 127.7 (Ph) 132.3 (Ph); 133.1 (Ph)	332 (M^+, 20) 317 (M−CH_3, 100)
Si$(CH_3)_3$	N$(C_2H_5)_2$	7.00 (m/2)		7.26 (m/1. J = 7.3)	7.34 (m/1. J = 7.3)	0.24 (s/9, CH_3)	0.74 (t/6, CH_3) 2.90 (q/4, CH_2)	2.0 (Si$(CH_3)_3$; 13.6 (CH_3) 46.0 (CH_2); 124.8 (Ph) 129.8 (Ph); 130.1 (Ph) 131.4 (Ph)	389 (M^+, 30)

Table 6. Experimental conditions and microanalysis of 1-germaindenes 7



(7)

Zirconaindene	Temperature [a] (°C)	Time (h)	Product obtained	Yield (%)	Molecular formula	Analysis results C(%) Calc.	Analysis results C(%) Found	Analysis results H(%) Calc.	Analysis results H(%) Found
4a	R.T.	24	**7a**	90	$C_{10}H_{10}GeCl_2$	43.88	43.5	3.68	3.9
4b	R.T.	24	**7b**	95	$C_{12}H_{14}GeCl_2$	47.76	48.0	4.68	4.6
4c	R.T.	24	**7c**	96	$C_{14}H_{18}GeCl_2$	50.99	50.8	5.50	5.3
4d	R.T.	24	**7d**	94	$C_{14}H_{22}Si_2GeCl_2$	43.12	42.9	5.68	5.8
4c [b]	50	48	**7e**	85	$C_{12}H_{16}SiGeCl_2$	43.43	43.7	4.86	4.9
5	R.T.	24	**7f**	92	$C_{15}H_{23}NSiGeCl_2$	46.32	46.3	5.96	6.1

[a] R.T.: room temperature. [b] reagent: 40% excess.

the solvent evaporated under reduced pressure. The solid residue was recrystallized from a toluene/pentane mixture (1:2) affording 0.550 g (61% yield) of orange crystals; m.p. 188°C. Anal. Found: C, 64.13; H, 6.98. $C_{25}H_{29}NSiZr$, calc.: C, 64.31; H, 7.12%.

Other compounds **4** were prepared similarly: **4c**, m.p. 114°C; **4d**, m.p. (dec) 200°C.

The NMR spectra and mass fragmentation patterns are reported in Table 1.

4.2. Synthesis of 1-germaindenes

The synthesis of the compounds **7f** from **5** is reported as an example of the general process.

At room temperature, $GeCl_4$ (0.07 ml, 0.61 mmol) was slowly added to a stirred THF solution (5 ml) of **5** (0.19 g, 0.41 mmol). Stirring was maintained for 24 h and the solvent then pumped away. The solid residue was washed with pentane (25 ml). The $[Cp_2ZrCl_2]$ is insoluble and extracts afforded a light yellow oil (0.15 g, 93% yield) after the solvent was evaporated.

Other compounds **7** were obtained under similar conditions. Details and characterizations are reported in Tables 5 and 6.

4.3. Crystal data

Data were collected on the Enraf-Nonius CAD4F diffractometer at room temperature. Unit cell parameters and basic information about data collection and structure refinement are given in Table 2. Accurate lattice parameters and orientation matrix were obtained from least-squares refinement of the setting angles of 25 well centred reflections. The intensities of two standard reflections were monitored every hour; they showed no change during data collection. Corrections for Lorentz and polarization were applied.

The structure was solved by the heavy-atom technique. Zr was found from an unsharpened Patterson function. The subsequent F_0 syntheses indicated the Si, N and C atoms.

The structure was refined by least-squares techniques with approximation (in two blocks) to the normal matrix using CRYSTALS [27] adapted on a MicroVax II. All heavy atoms were refined anisotropically. H atoms with the exception of those of disordered ethyl groups were placed in calculated positions (H–C–H = 109°; H–C–C = 120°; C–H = 0.96 Å) and were not further refined but recalculated after each cycle. They were assigned isotropic thermal parameters 20% higher than those of C atoms to which they were attached. No attempt was made to introduce H atoms of the disordered ethyl group. Anomalous dispersion terms were applied. Empirical absorption correction using DIFABS [28] was used.

Lists of structure factors, least-squares planes, and fractional atomic coordinates are available from the authors.

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