



Arenechromiumtricarbonyl complexes of silyl(germyl)(stannyl)- and silyl(germyl)(plumbyl)methanes including the unexpected formation of arenechromiumtricarbonyldimethylsilanol, $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{SiMe}_2\text{OH}$

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ABSTRACT

Treatment of $\text{PhMe}_2\text{SiCH}_2\text{GeMe}_3$ (**1**) with *t*-BuLi followed by addition of Me_3ECl , E = Sn, Pb, results in the formation of phenylsilyl(germyl)stannyl- and phenylsilyl(germyl)plumbyl-methanes, $\text{PhMe}_2\text{Si}(\text{Me}_3\text{Ge})(\text{E}\text{Me}_3)\text{CH}$, E = Sn (**2**), Pb (**3**). The thermal reaction of **1**, **2** and **3** with $\text{Cr}(\text{CO})_6$ yields the corresponding aryl- $\text{Cr}(\text{CO})_3$ analogs, $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}\text{Me}_2\text{Si}(\text{Me}_3\text{Ge})\text{CH}_2$ (**4**) and $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}\text{Me}_2\text{Si}(\text{Me}_3\text{Ge})(\text{E}\text{Me}_3)\text{CH}$, E = Sn (**5**), Pb (**6**). The thermal treatment of **2** with $\text{Cr}(\text{CO})_6$ in a wet THF/*di-n*-butyl ether mixture results in the formation of the arenechromiumtricarbonyl silanol $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}\text{Me}_2\text{SiOH}$ (**7**) which exhibits amphiphilic character, forming H-bonded chains in the solid state in a head-to-head arrangement of the arene $\text{Cr}(\text{CO})_3$ units.

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1. Introduction

Di- and trisubstituted Group 14 homoleptic methyl groups, R_2CH and R_3C , R = $\text{R}'_3\text{Si}$, $\text{R}'_3\text{Ge}$, $\text{R}'_3\text{Sn}$, are routinely used as stabilizing groups to isolate kinetically labile methylenes and dimethylenes of Group 14 elements [1,2]. They are also versatile reagents in synthetic chemistry [3,4] and for example, functionalized allylic silanes have been synthesized in high yield from the reaction of tris(trimethylsilyl)methyl borane $(\text{Me}_3\text{Si})_3\text{CBH}_2$ with alkenyl lithium reagent [4]. However, related heteroleptic systems with differing group 14 groups have received only scant attention [5–7]. We and Shimizu group reported the synthesis of mixed group 14 methanes, $(\text{Me}_3\text{Si})(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})\text{CH}$ [5,6]. In continuation of such studies, we report the synthesis and characterization of arenechromiumtricarbonyl complexes of the mixed group 14 methanes, $(\text{PhMe}_2\text{Si})(\text{Me}_3\text{Ge})(\text{Me}_3\text{E})\text{CH}$ (E = Sn, Pb). A crystal structure of the silanol, $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{SiMe}_2\text{OH}$, obtained from the thermal reaction of $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}\text{Me}_2\text{Si}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Sn})\text{CH}$ with $\text{Cr}(\text{CO})_6$ in wet THF/butyl ether mixture, is also reported.

2. Results and discussion

Treatment of phenyldimethylsilyl(trimethylgermyl)methane, $\text{PhMe}_2\text{SiCH}_2\text{GeMe}_3$, (**1**) with *t*-BuLi in a 4:1 THF/HMPA mixture at -78°C led to the formation of $[\text{PhMe}_2\text{SiCHGeMe}_3]^- \text{Li}^+$. Subse-

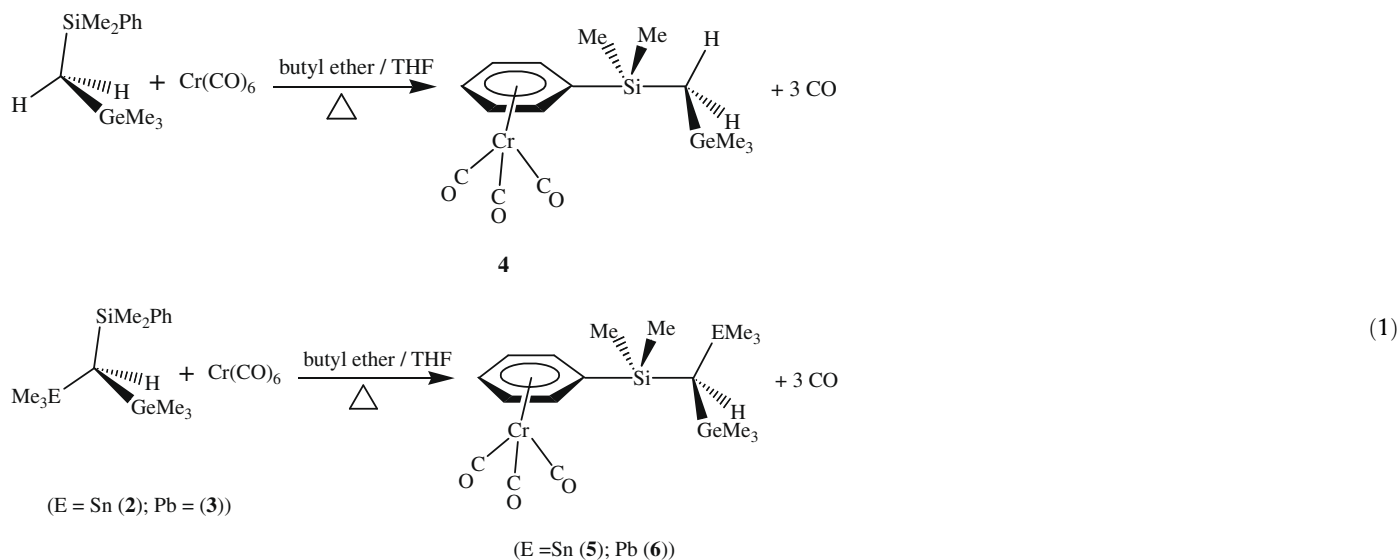
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quent quenching with Me_3ECl (E = Sn, Pb) resulted in mixed-tri-substituted methanes, $(\text{PhMe}_2\text{Si})(\text{Me}_3\text{Ge})(\text{Me}_3\text{E})\text{CH}$ (E = Sn, Pb) (E = Sn (**2**); Pb (**3**)) after hydrolytic workup in 72% and 40% yields respectively, as colorless oils. If the metallation reaction is performed with *n*-BuLi, only poor yields of **2** and **3** were obtained. The new compounds were characterized by NMR spectroscopy, Table 1. The ^1H and ^{13}C NMR of **2** and **3** exhibited two resonances for the diastereotopic methyl protons and carbons of the SiMe_2 groups. The related ^{119}Sn NMR and ^{207}Pb NMR were significantly shifted to low field compared to Me_4Sn and Me_4Pb , i.e. 14 ppm and 63 ppm, respectively.

The thermal reactions of **1**, **2** and **3** with $\text{Cr}(\text{CO})_6$ in a refluxing 7:1 *di-n*-butylether/THF solvent mixture resulted in the formation of yellow crystalline chromium tricarbonyl complexes, **4**, **5** and **6** in moderate yields, Eq. (1).

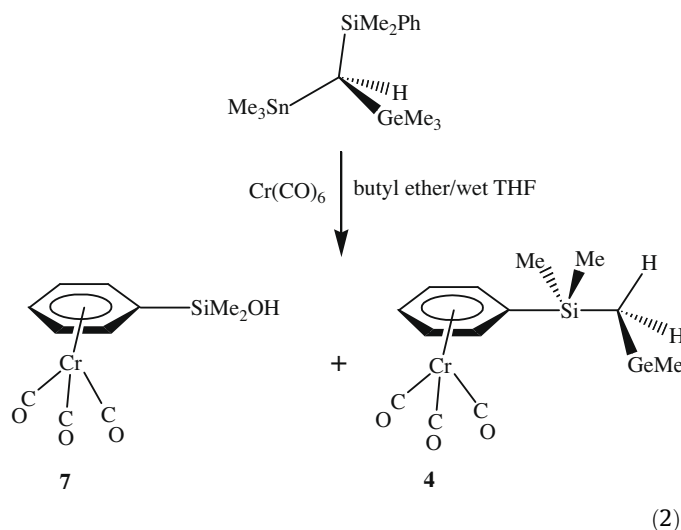
The yellow complexes slowly oxidize in the solid state, whereas in solution the decomposition is more rapid; their spectral and analytical data are reported in the experimental section. As expected the NMR spectra of the chromium complexes **4–6** exhibited an upfield displacement of chemical shifts of the aromatic protons and carbons of ~ 2 ppm and $\sim 30\text{--}40$ ppm, respectively [8,9]. No significant change in the chemical shifts for the ^{119}Sn and ^{207}Pb resonances of the arenechromiumtricarbonyl complexes **5** and **6** were observed compared to those of the precursors **2** and **3**.

Our attempts to deprotonate complex **5** with LDA (lithium diisopropamide) and subsequent quenching with Me_3PbBr which would have allowed access to arenechromiumtricarbonyl methane with four different group 14 elements, catorcane molecule [5], have not, thus far, been successful.



2.1. Hydrolysis reaction

Thermal treatment of **2** with $\text{Cr}(\text{CO})_6$, in a wet *n*-butyl ether/THF solvent mixture at 140 °C for three days produced the *unexpected* arenechromiumtricarbonyl silanol **7** as well as complex **4** in an approximately 1:2 ratio, Eq. (2).



Presumably, product **7** derives from the hydrolytic cleavage of the Si–CH bond at high temperature, a reaction that would also produce $\text{Me}_3\text{SnCH}_2\text{GeMe}_3$. Indeed the NMR spectral analysis of the liquid obtained after removing the butyl ether did exhibit the expected ^{119}Sn resonance at 13.3 ppm assigned to $\text{Me}_3\text{SnCH}_2\text{GeMe}_3$ [7e]. Complex **7** was characterized by NMR spectroscopy and recrystallization from toluene afforded yellow crystals suitable for X-ray crystallography, *vide infra*.

In addition to the cleavage of the Si–CH bond, there is significant cleavage of the Sn–CH bond to produce the chromium complex **4**, i.e. we obtained two unexpected arenechromiumtricarbonyl products at the same time, without formation of the expected product **5**. It is not, however, clear at this time whether the cleavage reactions occur prior to, or subsequent to, chromiumtricarbonyl complexation. The cleavage of the Sn–CH₂ bond in

$\text{Me}_3\text{SnCH}_2\text{EMe}_3$ (E = Si, Ge) by electrophiles and acids under mild conditions has been described previously [10]. The Me_3E group appears to activate the Sn–CH₂ toward such reactions, thus in our system the presence of water can be expected to result in such Sn–CH bond cleavage. The cleavage of the Si–CH₂ bond in the $\text{Me}_3\text{SnCH}_2\text{SiMe}_3$ was not observed [10] and suggests that the equivalent bond in our system, Si–CH, is activated by the presence of the $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ group. The fact that there appears to be no Ge–CH cleavage supports this suggestion and is currently being tested. It is well documented that the benzylic carbon is activated by the chromiumtricarbonyl species to produce stable benzylic cations [11]. The electrochemical studies of the (organosilyl)arenechromium tricarbonyl complexes also suggests the stability of the oxidized (organosilyl)arenechromiumtricarbonyl compounds which is solvent and substituent depended [12].

2.2. X-ray structure of $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}\text{Me}_2\text{SiOH}$ (**7**)

The structure of compound **7**, Fig. 1, exhibits the classical η^6 -arene-ML₃ form of a piano stool with a planar benzene ring seat lying symmetrically above the π -bonded chromium atom with the three carbonyl groups oriented in a tripod fashion in opposite direction to the benzene ring [8,9]. The structural parameters and selected bond angles and distances are provided in Tables 2 and 3. The torsion angles $C_{\text{ipso}}\text{-ring centroid-Cr-C}_n(\text{O})$ ($n = 7, 8$ and 9 in Fig. 1) are -168.40 , $+72.60$ and -50.95 degrees respectively, the tripod arrangement is about 12° from the ideally eclipsed conformation (torsion angles -60 , $+60$ and $+180$ degrees) relative to the *para* and two *ortho* carbon atoms in the ring.

Table 1
Selected ^{29}Si , ^{119}Sn and ^{207}Pb NMR shifts (δ ppm) for **1–6**.

Compd	^{29}Si	^{119}Sn	^{207}Pb
1	–2.98		
2	–1.72	14.1	
3	–0.56		63.2
4	1.13		
5	2.29	12.5	
6	3.45		59.3

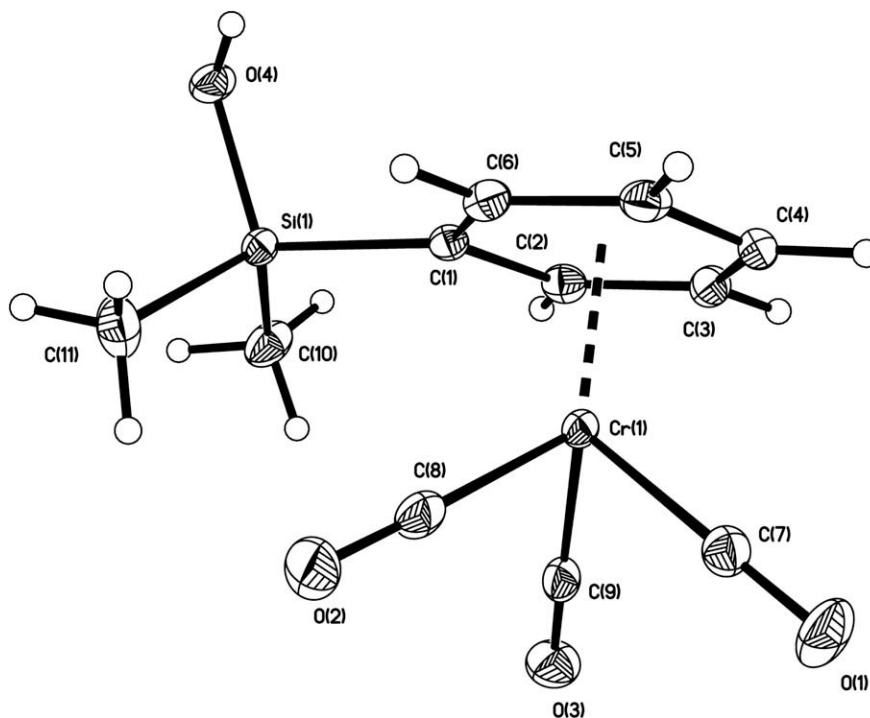


Fig. 1. Molecular structure of **7**. Thermal ellipsoids set at 50% of probability, only one position for the disordered hydroxyl hydrogen is shown.

Table 2
Structure determination summary of **7**.

Empirical formula	C ₁₁ H ₁₂ CrO ₄ Si
Crystal color	Yellow
Crystal habit	Plate
Crystal size (mm ³)	0.18 × 0.10 × 0.02
<i>a</i> (Å)	29.902(3)
<i>b</i> (Å)	10.9871(9)
<i>c</i> (Å)	7.6276(6)
α (°)	90
β (°)	94.146(2)
γ (°)	90
<i>V</i> (Å ³)	2499.4(4)
Crystal system	Monoclinic
Space group	C2/c
<i>Z</i>	8
<i>D</i> _{calc} (g cm ⁻³)	1.532
μ (mm ⁻¹)	1.01
Absorption correction	Bruker SADABS program
<i>T</i> (K)	100
λ (Å)	0.71073
Monochromator	Graphite
Diffractometer	Bruker SMART with Apex CCD
Reflections collected	6967
Independent reflections (<i>R</i> _{int})	2463 (0.0212)
Structure solution technique	Direct methods
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Refinement technique	Full-matrix least-squares on <i>F</i> ²
Refinement program	SHELXS-97 (Sheldrick, 1997)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Goodness-of-fit (GOF) on <i>F</i> ²	1.072
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0312, 0.0791
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0332, 0.0806

Table 3
Selected bond lengths (Å) and angles (°) for **7**.

Cr–C1	2.2204(19)	Cr–C4	2.2074(19)
Cr–C9	1.857(2)	Si–O4	1.6518(14)
Si–C10	1.848(2)	Si–C11	1.853(2)
Si–C1	1.878(2)	O3–C9	1.149(3)
C1–C6	1.429(3)	C1–C2	1.421(3)
C2–C3	1.404(3)	C3–C4	1.402(3)
C4–C5	1.412(3)	C5–C6	1.402(3)
O4–Si–C10	108.79(9)	O4–Si–C11	108.28(10)
C10–Si–C11	111.35(12)	O4–Si–C1	108.22(8)
C10–Si–C1	108.68(10)	C11–Si–C1	111.44(10)

hydrogen atom of the OH group of **7** is disordered over two positions with half occupancy at each site. The structure of **8** exhibits the *gauche* orientation of arenechromiumtricarbonyl with respect to the OH group, where as in **7** the orientation is *anti*. These two features accounts for the H-bonding (HB) patterns noted in **7**, *vide infra*, which are largely absent in **8** presumably due to the steric reasons.

X-ray structures of a number of organometallic silanols, RR₂SiOH (R = organometallic group), have been reported and the majority of them exhibit some type of hydrogen-bonding dictated by the steric demand of the organometallic group [13], Fig. 2. Thus, discrete linear dimers [14,15], four-membered cyclic dimers, [15,16] and tetrameric species are known [16,17] and we have reported that the related ferrocenyl dimethylsilanol, FcSiMe₂OH, **10** forms a cyclic H-bonded hexameric arrangement of SiOH groups [18] reminiscent of hexameric forms of water [19]. The organometallic silanols also form infinite chains depending upon the steric demands of the substituents on silicon [17b].

In silanol **7**, the hydrogen atom of the silanol group is disordered over two positions, with O4...O4B = 2.691 Å, O–H41...O4B = 159.6°, O...O4A = 2.708 Å and O–H42...O4A = 154.3°. The disorder is due to the centrosymmetric structure. This disorder is also observed for {(η⁵-C₅Me₅)(CO)₂}FeCH₂SiMe₂OH (**9**) which

The Si–C bond distances, in the range of 1.847–1.878 Å, and a Si–O bond distance of 1.652(1) Å are typical of organosilanols [11,13–18]. The O–Si–C bond angles between 108.22–108.87° signify tetrahedral geometry and compare well with the reported values for its diphenyl analog, {(η⁶-C₆H₅)Cr(CO)₃}Ph₂SiOH, **8** [11]. The

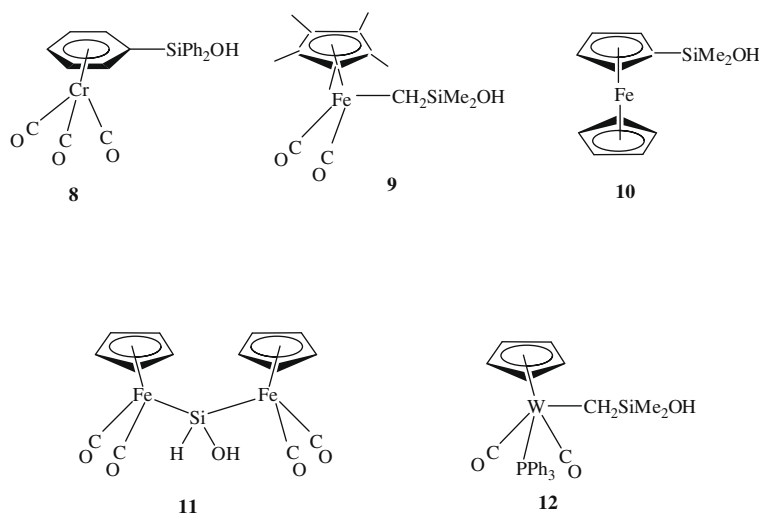


Fig. 2. Selected examples for organometallic Silanols 8–12.

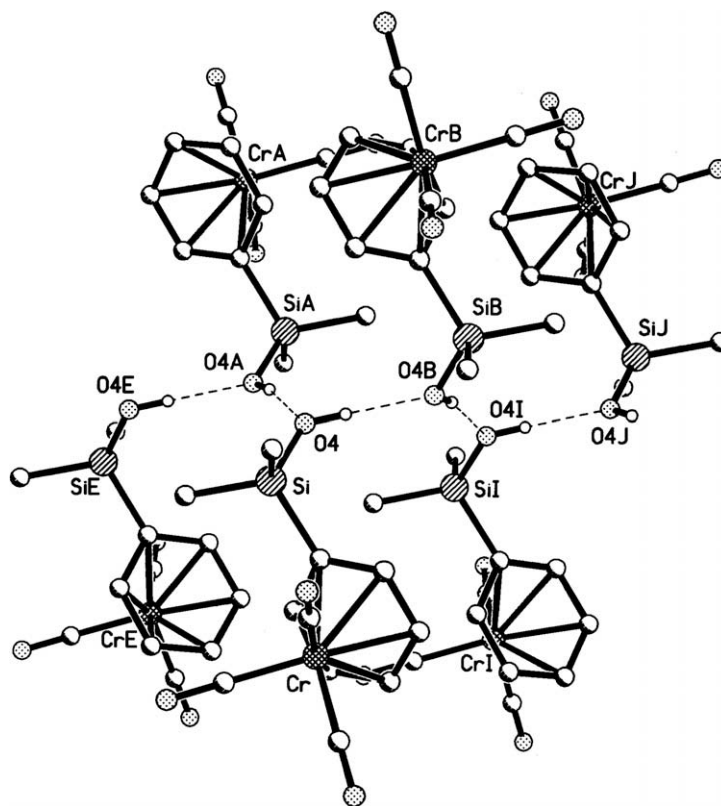


Fig. 3. Crystal packing of **7** exhibits H-bonding showing chain along the *c* axis illustrating head-to-head arrangement of the areneCr(CO)₃ units.

crystallizes in the same spatial group C2/c generating the identical HB motif (Fig. 3) [17b]. Both, compound **7** and **9**, are amphiphiles which are packed in head-to-head fashion with a HB chain running parallel to the *c* axis of the crystal structure; where the hydrophobic Cr(CO)₃ units are protecting the hydrophilic Si–OH groups (Fig. 4). The chain formed is not linear; it represents a spiro[2.2]pentane molecule as shown in (Fig. 5). The occurrence of the chain instead of a 2-D bilayer is due to the generation of another type of HB by the Cr(CO)₃ units through the carbonyl groups (C3–H3...O1, 2.54 Å; C5–H5...O2, 2.56 Å; C5–H5...O3, 2.54 Å), essentially identical interactions present in the crystal structure of **9** [17b,20].

3. Experimental

3.1. General procedures

All syntheses were performed under an argon atmosphere using standard Schlenk techniques. Tetrahydrofuran and hexanes were distilled over sodium and benzophenone ketal. Hexamethylphosphoramide (HMPA) was distilled over calcium oxide. *t*-Butyllithium (1.7 M in pentane), Me₃SnCl and Cr(CO)₆ were purchased from Aldrich Chemicals; Me₃SiCH₂Cl and Me₃GeCl were purchased from Gelest; Me₃PbBr was obtained from the bromination of Me₄Pb [21], PhMe₂SiCH₂GeMe₃, **1** [7d], PhMe₂Si(Me₃Ge)(Me₃Sn)CH, **2**

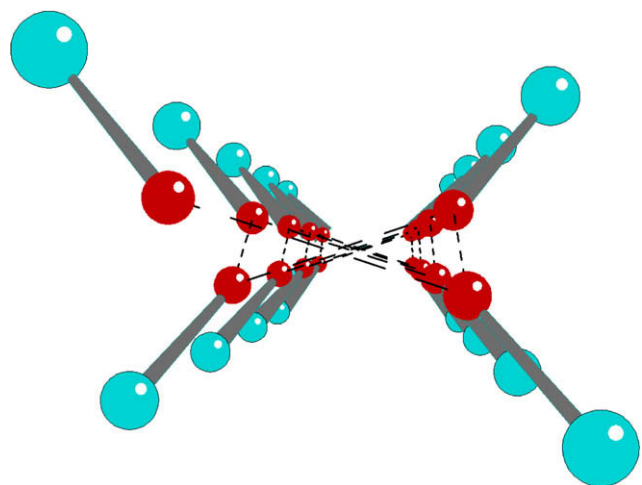


Fig. 4. View along the Si(OH) hydrogen-bonding chains illustrating the ribbon character of the extended system, Si blue, O red.

[5] were synthesized by the reported methods. NMR spectra were recorded on a Bruker 300 MHz spectrometer using CDCl_3 for **2** and **3** and using C_6D_6 for **4–7**. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories.

3.2. Synthesis of $\text{PhMe}_2\text{Si}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Pb})\text{CH}$, **3**

A 250 mL Schlenk flask was charged with 20 mL of a THF solution containing 4.0 g (15 mmol) of $\text{PhMe}_2\text{SiCH}_2\text{GeMe}_3$, **1**, and 5 mL of HMPA. The mixture was maintained at -78°C and *t*-butyllithium (15.0 mmol) was added dropwise *via* syringe. The solution became yellow immediately and finally became orange and was stirred for 90 min between -78 to -70°C . At this time a THF slurry of 4.98 g (15.0 mmol) of Me_3PbBr was added slowly at the same temperature. The color of the solution became bright yellow and finally greenish-black. The solution was permitted to warm to

room temperature and stirred overnight. The reaction was hydrolyzed with 25 mL of a 5% solution of NH_4Cl at 0°C . The organic layer was extracted with 25 mL of hexanes and dried over MgSO_4 . After filtration and removal of hexane on a rotary evaporator, the liquid was distilled through a column at $110\text{--}114^\circ\text{C}$ at 0.05 mm Hg to yield 3.1 g (40% yield) of **3**.

3.2.1. Analytical and spectroscopic data for $(\text{PhMe}_2\text{Si})(\text{GeMe}_3)(\text{PbMe}_3)\text{CH}$, **3**

Anal. Calc. Found: C, 34.76 (35.05); H, 7.03 (6.93%)
 ^1H : 0.076 (s, 9H, GeMe_3); 0.25 (s, 3H, SiMe), 0.26 (s, 3H, SiMe); 0.25 (s, 1H, $^2J_{207\text{Pb-H}} = 90.6$ Hz, CH); 0.63 (s, 9H, $^2J_{207\text{Pb-H}} = 57.0$ Hz, PbMe_3); 7.25, 7.43(m, 5H, Ph).

^{13}C : 1.01 ($^1J_{\text{Pb-C}} = 214.2$ Hz, PbMe_3); 1.16 (SiMe), 1.84 ($^3J_{\text{Pb-C}} = 32.6$ Hz, SiMe); 2.93 ($^3J_{\text{Pb-C}} = 25.4$ Hz, GeMe_3); 5.02 (CH), 127.66, 128.52, 133.40, 142.50 (ipso).

^{207}Pb : 63.21.

^{29}Si : -0.56 ($^2J_{29\text{Si-}^{207}\text{Pb}} = 37.5$ Hz).

3.3. Synthesis of $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{Me}_2\text{Si}\}(\text{Me}_3\text{Ge})(\text{Me}_3\text{Pb})\text{CH}$, **6**

This synthesis is typical for all the new arenechromiumtricarbonyl complexes.

A 100 mL round-bottom flask was charged with 0.7 g (1.35 mmol) of **3** and 0.3 g (1.36 mmol) of $\text{Cr}(\text{CO})_6$ in 20 mL of *n*-butyl ether and 3 mL of THF. The mixture was heated in oil bath under nitrogen atmosphere at 90°C for 24 h. The color of the solution turned gray due to the deposition of lead. After 24 h, the temperature of the oil bath was raised to 140°C and mixture was heated at this temperature for four days. The reaction mixture was cooled to room temperature and filtered over Celite. Butyl ether was removed by flash distillation under vacuum and the yellow residue was extracted with 10 mL of a 2:1 mixture of hexane and toluene. Filtration and removal of the solvents produced yellow oil which solidified in the refrigerator to yield, 0.37 g (42%) of **6**, which was further recrystallized from a mixture of hexane and toluene.

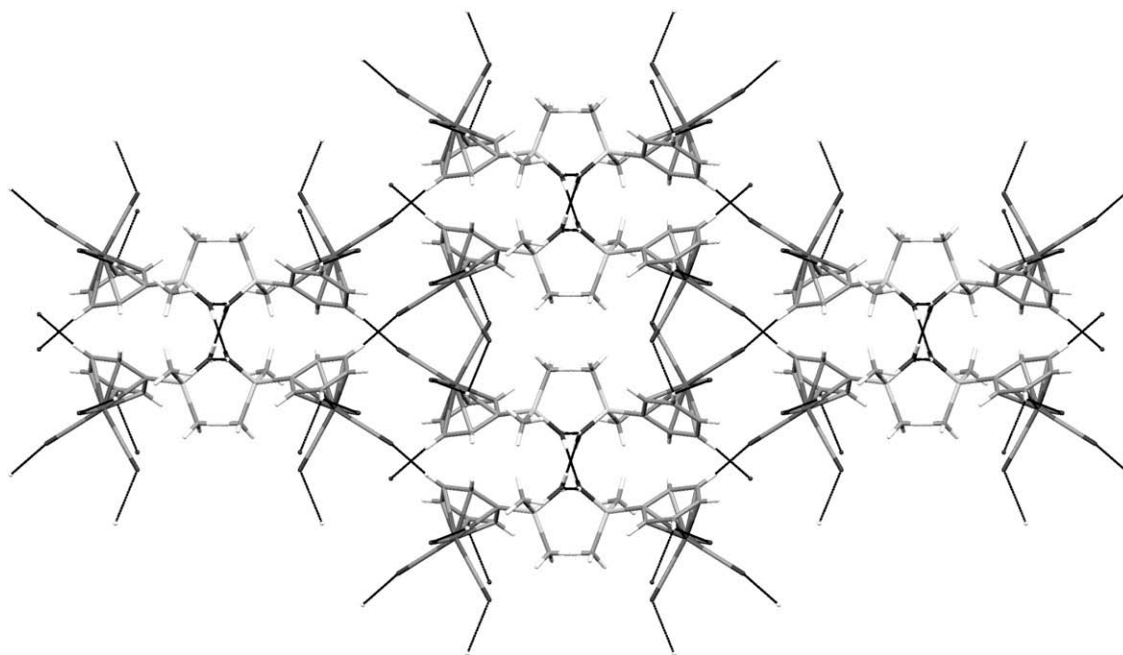


Fig. 5. View of the crystal packing through the *c* axis. Four chain motifs and the CO...H hydrogen bonds are shown.

3.3.1. Analytical and spectroscopic data for $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{Me}_2\text{Si}(\text{GeMe}_3)(\text{PbMe}_3)\text{CH}, \mathbf{6}$

Anal. Calc. Found: C, 33.04 (33.09); H, 4.62 (4.53)% m.p. 70–72 °C.

^1H : 0.043 (s, 1H, CH); 0.081 (s, 9 H, GeMe₃); 0.29 (s, 3H SiMe), 0.31 (s, 3H, SiMe); 0.70 (s, 9H, $^2J_{207\text{Pb-H}} = 56.6$ Hz, PbMe₃); 4.36 (t, $J = 6$ Hz, 2H, Ph), 4.72 (t, $J = 6$ Hz, 1H, Ph), 4.92 (d, $J = 7.5$ Hz, 2H, Ph).

^{13}C : 0.88 (SiMe), 0.97 (SiMe); 1.50 ($^1J_{\text{Pb-C}} = 218.0$ Hz, PbMe₃); 3.10 (GeMe₃), 5.40 (CH); 90.00, 95.50, 99.80 (Ph), 102.6 (ipso); 233.67 (CO).

^{207}Pb : 59.36.

^{29}Si : 3.45 ($^2J_{29\text{Si}-207\text{Pb}} = 44.5$ Hz).

IR (νCO) Hexane, cm⁻¹: 1977.1, 1911.4.

3.4. Synthesis of $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{SiMe}_2\text{OH}, \mathbf{7}$

A 100 mL round-bottom flask was charged with 1.74 g (4.04 mmol) of **2** and 0.891 g (4.04 mmol) of Cr(CO)₆ in 25 mL of *n*-butyl ether and 5 mL of wet THF. The mixture was treated as above for the synthesis of **6**. After removal of butyl ether by flash distillation under vacuum; a solid yellow residue (mixture of **4** and **7**) was obtained. The mixture was treated with 15 mL 2:1 mixture of hexanes and toluene, filtered and left in the refrigerator. The silanol **7** was crystallized from the solution. Recrystallization from toluene resulted in 0.29 g (25%) of **7**. Evaporation of the solvents from the filtrate produced crude **4** which was recrystallized from hexane to yield 0.80 g (49%) of **4**.

3.4.1. Analytical and spectroscopic data for $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{SiMe}_2\text{OH}, \mathbf{7}$

Anal. Calc. Found: C, 45.82 (45.59); H, 4.19 (4.22)%.

^1H : 0.14 (s, 6H, SiMe₂); 1.46 (1H, s, OH); 4.28 (t, $J = 6$ Hz, 2H, Ph), 4.62 (t, $J = 6$ Hz, 1H, Ph), 4.85 (d, $J = 6$ Hz, 2H, Ph).

^{13}C : -0.40 (SiMe₂); 90.34, 95.26, 97.97 (ipso) 98.85 (Ph); 233.46 (CO).

^{29}Si : 7.12.

IR (νCO) Hexane, cm⁻¹: 1978.0, 1911.7.

3.4.2. Analytical and spectroscopic data for $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{Me}_2\text{Si}(\text{GeMe}_3)\text{CH}_2, \mathbf{4}$

Anal. Calc. Found: C, 44.70 (45.35); H, 5.50 (4.63)%, m.p. 79 °C

^1H : -0.18 (s, 2H, CH₂); 0.095 (s, 9H, GeMe₃); 0.16 (s, 6H, SiMe₂); 4.35 (t, $J = 6$ Hz, 2H, Ph), 4.80 (t, $J = 6$ Hz, 1H, Ph), 4.82 (d, $J = 6$ Hz, 2H, Ph).

^{13}C : -0.63 (SiMe₂); 0.72(GeMe₃); 2.09 (CH₂); 90.57, 95.02, 99.09 (Ph), 100.93 (ipso); 233.69 (CO).

^{29}Si : 1.13.

IR (νCO) Hexane, cm⁻¹: 1977.6, 1911.4.

3.4.3. Analytical and spectroscopic data for $(\text{PhMe}_2\text{Si})(\text{GeMe}_3)(\text{SnMe}_3)\text{CH}, \mathbf{2}$

Anal. Calc. Found: C, 41.90 (42.2); H, 7.04 (6.93)%.

^1H : -0.22 (s, 1H, $^2J_{119\text{Sn-H}} = 77.2$ Hz, $^2J_{117\text{Sn-H}} = 74.0$ Hz, CH); 0.05 (s, 9H, $^2J_{119\text{Sn-H}} = 51.0$ Hz, $^2J_{117\text{Sn-H}} = 49.8$ Hz, SnMe₃); 0.16 (s, 9H, GeMe₃); 0.33 (s, 3H, SiMe), 0.34 (s, 3H, SiMe); 7.32, 7.46 (m, 5H, Ph).

^{13}C : -5.89 ($^1J_{119\text{Sn-C}} = 328.0$ Hz, $^1J_{117\text{Sn-C}} = 313.0$ Hz, SnMe₃); -2.82 ($^1J_{119\text{Sn-C}} = 221.7$ Hz, CH); 1.20 (SiMe), 1.53 (SiMe); 2.74 (GeMe₃); 127.6, 128.5, 133.40, 142.0 (ipso).

^{119}Sn : 14.1.

^{29}Si : -1.72 ($^2J_{29\text{Si}-119\text{Sn}} = 25.8$ Hz).

3.4.4. Analytical and spectroscopic data for $\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\text{Me}_2\text{Si}(\text{GeMe}_3)(\text{SnMe}_3)\text{CH}, \mathbf{5}$

Anal. Calc. Found: C, 38.21 (38.56); H, 5.34 (5.60), m.p. 64 °C.

^1H : -0.65 (s, 1H, $^2J_{119\text{Sn-H}} = 78$ Hz, CH); 0.038 (s, 9H, $^2J_{119\text{Sn-H}} = 51.6$ Hz, $^2J_{117\text{Sn-H}} = 50.4$ Hz, SnMe₃); 0.087 (s, 9 H, GeMe₃); 0.29 (s,

3H SiMe), 0.31 (s, 3H, SiMe); 4.33 (t, $J = 6$ Hz, 2H, Ph), 4.70 (t, $J = 6$ Hz, 1H, Ph), 4.89 (d, $J = 6$ Hz, 2H, Ph).

^{13}C : -5.48 (SnMe₃); -1.74(CH); 0.88 (SiMe), 0.99 (SiMe); 3.02(GeMe₃); 89.92, 95.61, 99.95 (Ph), 102.1 (ipso); 233.68 (CO).

^{119}Sn : 12.51

^{29}Si : 2.29 ($^2J_{29\text{Si}-119\text{Sn}} = 24.3$ Hz).

IR (νCO) Hexane, cm⁻¹: 1977.5, 1911.7.

3.5. X-ray Crystal Structure for **7**

A yellow plate of silanol **7** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 100(2)K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å). The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package. A summary of the relevant crystallographic parameters for **7** is presented in Table 2, and selected bond lengths and angles are given in Table 3.

4. Conclusions

A convenient methodology for the synthesis of phenylsilyl(germyl)stannyl- and phenylsilyl(germyl)plumbyl-methanes, PhMe₂Si(Me₃Ge)(EMe₃)CH, (E = Sn, Pb) and their arenchromium-tricarbonyl-analogs is reported. The Sn-CH bond is labile in the presence of water, and the Si-CH₂ bond appears to be activated by the areneCr(CO)₃ substituent. The crystal structure of an arenchromium-tricarbonyl silanol exhibits intermolecular H-bonding forming chains along the *c* axis with the head-to-head arrangement of areneCr(CO)₃ units which provide hydrophobic exterior to hydrophilic silanol groups.

5. Supplementary material

CCDC 761242 contains the supplementary crystallographic data for compound **7**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <www.ccdc.cam.ac.uk/data_request/cif>.

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