ChemPubSoc Europe
DOI: 10.1002/chem.201400185
CHEMISTRY
A European Journal
Full Paper

Molecular Frameworks

New Polydentate Trimethylsilyl Chalcogenide Reagents for the Assembly of Polyferrocenyl Architectures

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Abstract: A series of polychalcogenotrimethylsilane complexes $Ar(CH_2ESiMe_3)_n$, (Ar = aryl; E = S, Se; $n = 2$, 3, and 4) can be prepared from the corresponding polyorganobromide and $M[ESiMe_3]$ (M = Na, Li). These represent the first examples of the incorporation of such a large number of reactive $-ESiMe_3$ moieties onto an organic molecular framework. They are shown to be convenient reagents for the preparation of the polyferrocenylseleno- and thioesters from ferrocenoyl chloride. The synthesis, structures, and spectroscopic properties of the new silyl chalcogen complexes 1,4-$(Me_3SiECH_2)_2(C_6Me_4)$ (E = S, **1**; E = Se, **2**), 1,3,5-$(Me_3SiECH_2)_3(C_6Me_3)$ (E = S, **3**; E = Se, **4**) and 1,2,4,5-$(Me_3SiECH_2)_4(C_6H_2)$ (E = S, **5**; E = Se, **6**) and the polyferrocenyl chalcogenoesters [1,4-$\{FcC(O)ECH_2\}_2(C_6Me_4)$] (E = S, **7**; E = Se, **8**), [1,3,5-$\{FcC(O)ECH_2\}_3(C_6Me_3)$] (E = S, **9**; E = Se, **10**) and [1,2,4,5-$\{FcC(O)ECH_2\}_4(C_6H_2)$] (E = S, **11** illustrated; E = Se, **12**) are reported. The new polysilylated reagents and polyferrocenyl chalcogenoesters have been characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{77}Se), electrospray ionization mass spectrometry and, for complexes **1**, **2**, **3**, **4**, **7**, **8**, and **11**, single-crystal X-ray diffraction. The cyclic voltammograms of complexes **7**–**11** are presented.

Introduction

The chemistry of ferrocene (Fc)-containing molecules and materials continues to develop due to the favorable electronic (redox) properties of ferrocene and its ease of functionalization.[1–3] Such systems have a wide range of applications in materials science including use as sensors,[4] catalysts,[4a, 5] electroactive materials[6] and aerospace materials,[7] in cancer therapeutics[8] and other medicinal applications,[9] and as a smokeless fuel additive.[10]

Much research focus has been placed on polyferrocene architectures in which the organometallic units are linked with different organic spacers such as alkenes,[11] alkynes,[12] arenes,[13] heterocycles,[14] annulenes,[15] and even larger molecules such as C_{60}.[16] These types of complexes are suitable for investigating intramolecular electronic interactions in the corresponding mixed-valent species between the ferrocenyl units through the organic backbone.[14a–e, 17] Efforts have also been devoted to the incorporation of multiple ferrocene units into polymers,[18] dendrimeric frameworks,[19] and inorganic nanoclusters.[20]

In a complementary vein for this work, the preparation of polyferrocenylthio- and selenoesters has been pursued.[21] The chemistry of chalcogenoesters has had a strong development, due to the importance of these types of compounds as intermediates in synthetic organic chemistry.[22–24] Chalcogenoesters have been employed as acylating reagents in synthesis of corresponding acids,[25] esters,[25] amides,[25a,b, 26] ketones,[27, 28] and aldehydes.[29, 30] Acyl chalcogenides are also employed as building blocks for the synthesis of asymmetric aldols[31] and heterocyclic compounds such as oxazoles[32] and β-lactone.[33] Chalcogenoesters also have been applied to the synthesis of natural compounds such as proteins[34] and alkaloids.[35]

Developed methodologies for the incorporation of these molecules into organic compounds generally involve the preparation of acyl radicals[36, 37] and anions[38] under mild conditions. New methods for the synthesis of thio- and selenoesters are still being developed; organo(trimethylsilyl) chalcogenides have been shown to be a convenient source of organochalcogenide (RE^-)[39] including for the synthesis of chalcogenoesters,[21a] and are of course well-developed for the preparation of metal chalcogen complexes.[40] The preparation of new frameworks with multiple $-ESiMe_3$ moieties would offer routes to the assembly of polythio- and selenoesters. Rimpler first reported that the sulfur silane reagent $Me_3SiOC(O)CH_2SSiMe_3$ reacts directly with acyl chloride under ambient conditions to yield the corresponding thioester $Me_3SiOC(O)CH_2SC(O)R$ via the formation of Me_3SiCl.[41] Aryl- and alkyl(trimethylsilyl)chalcogenides offer a convenient, easily handled source of "ArE^-" and "RE^-" (E = S, Se, Te), respectively. Ogura and co-workers demonstrated a similar methodology for the heavier congener tellurium reagent $PhTeSiMe_3$.[42] Twelve years later, reductive cleavage

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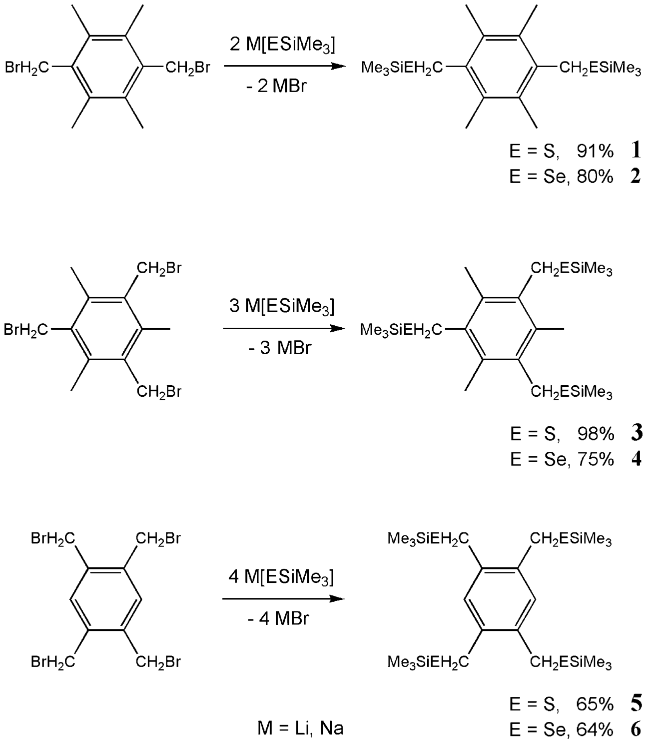
of the Se–Si bond in arylselenotrimethylsilane $PhSeSiMe_3$ was reported by Zhang and Zhang as a novel method for the synthesis of selenoesters.[43]

In contrast to sulfur and tellurium, the chemistry of selenium Ar-/R-$SeSiMe_3$ has not been as extensively developed for the preparation of chalcogenoesters. Recently the use of nucleophilic fluoride anion to increase the reactivity of $PhSeSiMe_3$ in the reaction with acid chloride has been demonstrated.[44] Concomitantly, we reported a new series of diselenoesters from the simple reaction of mono- or di(acid chlorides) with di- or monosubstituted organochalcogen–silane reagents in both solvent and under solvent-free conditions.[21a] The synthesis of an oligoselenoester complex in this work outlined the potential of this chemistry for the formation of polyselenoester complexes, including small oligomers. Herein, we describe the preparation of a new class of di-, tri-, and tetrasubstituted thio- and selenotrimethylsilanes and demonstrate their utility for the assembly of a series of polysubstituted ferrocenylthio- and selenoesters, via their reaction with ferrocenoyl chloride.

Results and Discussion

Various synthetic methods for chalcogenoesters have been reported and are usually based on the reactions of acyl chloride or acid anhydrides with a source of chalcogenide anion such as chalcogenols (by deprotonation),[45] dichalcogenides (by reduction),[46] or alkali metal chalcogenolates.[47,48] Additional methods, including metal-catalyzed reactions, have also been reported.[49–57] The demonstrated reactivity of disubstituted 1,1′-bis(trimethylsilylseleno)ferrocene and related reagents for the preparation of diselenoesters[21a,58] suggests that polychalcogenosilanes could behave efficiently in transferring chalcogeno moieties for the formation the polychalcogenoesters.[20a,b,59]

The polychalcogenosilanes of the general formula Ar($CH_2ESiMe_3)_n$ (Ar = aryl; E = S, Se; $n = 2$–4) **1**–**6** are readily prepared in good yield by the reaction of lithium (trimethylsilyl) chalcogenolate $Li[ESiMe_3]$ with the corresponding di-, tri-, and tetra-bromobenzyl arene (Scheme 1). $Li[ESiMe_3]$ is first prepared in situ through the addition of bis(trimethylsilyl)chalcogenide $E(SiMe_3)_2$ to a stirred solution of *n*BuLi in tetrahydrofuran at 0°.[60] The portion-wise addition of organobromine reagents to the solution of $Li[ESiMe_3]$ in Et_2O at room temperature, followed by stirring for 12 h, yielded **1**, **3**, and **5** (white powders) and **2**, **4**, and **6** (pale-yellow powders) upon extraction with a hydrocarbon solvent. Similar reactions to substitute the bromine centers by using $Na[ESiMe_3]$[61] are equally effective in the formation of **1**–**6**. The addition of the organobromine reagents to a suspension of $Na[ESiMe_3]$ in tetrahydrofuran at room temperature, and production of NaBr, makes the extraction of **1**–**6** somewhat easier, with comparable yields of products. All six compounds are highly air sensitive; however, they are stable for several days in solution at room temperature under an inert atmosphere.



Scheme 1. Synthesis of **1**–**6**.

The solution NMR chemical shifts of **1**–**6** are reported in Table 1. The chemical shift values of the di- and tri- substituted complexes **1**–**4** are similar, although they differ slightly compared to those of the corresponding tetrasubstituted aromatics **5**–**6**. The chemical shifts of the $Si(CH_3)_3$ moieties in the selenium complexes appear to lower field in both ^1H and $^{13}C\{^1H\}$ NMR spectra versus the corresponding sulfur complexes. The ^1H NMR spectra display the expected singlet for the equivalent methylene groups. All $–CH_2–$ groups in analogous compounds show similar chemical shift values in their ^1H NMR spectra (**1**, **2** = 3.72, 3.75 ppm; **3**, **4** = 3.72 ppm; and **5**, **6** = 3.83 ppm), but the corresponding resonances in the $^{13}C\{^1H\}$ NMR spectra of the selenides have lower chemical shift values (**1**, **3**, and **5** = 25.9–27.5 ppm; **2**, **4**, and **6** = 18.0–18.7 ppm). The $^{77}Se\{^1H\}$ chemical shift for tetrasubstituted **6** is significantly shifted (−19.0 ppm) compared to the corresponding values for the di- and trisubstituted complexes **2** and **4** (−70.2 and −70.7 ppm, respectively); this is likely to be due to interamolecular Se···Se nonbonding interactions in solution, as described for complementary systems.[62]

Table 1. NMR spectroscopic data for **1**–**6** in $CDCl_3$. Chemical shifts are reported in ppm.

		^1H				^{13}C				^{77}Se
		$Si(CH_3)_3$	CH_3	CH_2	CH	$Si(CH_3)_3$	CH_3	CH_2	–C–	
Sulfides	**1**	0.41	2.32	3.72		0.7	16.1	26.1	132.7, 135.1	
	3	0.40	2.46	3.72		0.7	15.6	25.9	134.2, 134.7	
	5	0.34		3.83	7.21	0.9		27.5	131.8, 137.4	
Selenides	**2**	0.49	2.32	3.75		1.6	16.1	18.4	132.6, 135.2	-70.7
	4	0.47	2.42	3.72		1.6	16.0	18.0	133.6, 134.9	-70.2
	6	0.44		3.83	7.09	1.8		18.7	132.1, 137.5	- 19.0

Table 2. Crystallographic data and parameters for compounds **1**–**4**, **6**–**8** and **11**.[a]

	1	**2**	**3**	**4**	**6**	**7**	**8**	**11**
formula	$C_{18}H_{34}S_2Si_2$	$C_{18}H_{34}Se_2Si_2$	$C_{21}H_{42}S_3Si_3$	$C_{21}H_{42}Se_3Si_3$	$C_{22}H_{46}Se_4Si_4$	$C_{34}H_{34}Fe_2O_2S_2$	$C_{34}H_{34}Fe_2O_2Se_2$	$C_{54}H_{46}Fe_4O_4S_4$
formula weight	370.75	464.55	475.00	615.70	738.79	650.43	744.23	1110.55
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	6.4020(5)	6.2310(3)	10.0634(1)	10.125(2)	11.5701(11)	8.0896(16)	5.748(2)	5.7476(5)
b [Å]	7.3238(4)	7.5548(4)	11.5851(2)	11.630(2)	6.5046(5)	10.354(2)	23.046(10)	13.3324(12)
c [Å]	11.9751(9)	12.1830(7)	13.0520(2)	13.257(3)	21.8713(18)	18.010(4)	21.718(8)	14.9342(13)
α [°]	103.313(4)	103.265(2)	86.4372(9)	87.81(3)	90	94.803(15)	90	91.675(4)
β [°]	97.665(3)	97.939(3)	68.2215(9)	67.71(3)	95.733(5)	100.219(10)	95.791(10)	100.183(4)
γ [°]	92.821(5)	93.901(3)	79.5821(9)	82.00(3)	90	98.517(14)	90	93.298(4)
V [Å^3]	539.64(7)	549.88(5)	1389.75(4)	1430.2(6)	1637.8(2)	1458.8(5)	2862.3(19)	1123.60(17)
Z	1	1	2	2	2	2	4	1
ρ_{cal} [g cm^{-3}]	1.141	1.403	1.135	1.430	1.498	1.481	1.727	1.641
M (Mo$_{K\alpha}$) [mm^{-1}]	0.354	3.468	0.402	3.990	4.636	1.168	3.588	1.501
F(000)	202	238	516	624	740	676	1496	570
temperature [K]	150	150	150	150	150	110	110	110
θ_{min}, θ_{max} [°]	3.0, 27.8	2.8, 27.7	1.7, 39.8	2.2, 27.6	1.8, 25.0	1.2, 28.0	2.8, 26.4	1.4, 27.5
total reflns	4614	4460	90834	11696	47682	20483	47265	21808
unique reflns	2492	2510	16840	6548	2880	20483	5860	5171
R(int)	0.025	0.024	0.071	0.034	0.252	0.000	0.094	0.061
$R1$	0.0405,	0.0397,	0.0543,	0.0496,	0.0438,	0.0525,	0.0415,	0.0639
w$R2$ [$I \geq 2\sigma(I)$]	0.0932	0.1021	0.1269	0.1198	0.0714	0.0952	0.0838	0.1683
$R1$ (all data)	0.0551	0.0470	0.1550	0.0816	0.1195	0.1081	0.0754	0.0904
w$R2$ (all data)	0.1007	0.1051	0.1736	0.1360	0.0856	0.1138	0.0955	0.1935
GOF	1.046	1.173	0.992	1.042	0.913	1.008	1.016	1.079
min peak	-0.298	-0.596	-0.626	-0.687	-0.601	-0.534	-0.562	-0.699
max peak	0.284	0.546	1.012	1.494	0.134	0.529	0.855	2.064

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^2)]^{1/2}$, GOF $= [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{observns} - N_{params})]^{1/2}$.

To date, only a few crystal structures with –CESiMe$_3$ groups have been reported,[59a,63] although the structural chemistry of Ar(CH$_2$ER)$_n$ in general is more mature.[64] The structures of **1**–**4** and **6** were confirmed by X-ray crystallographic analyses. Crystallographic data and data collection parameters are summarized in Table 2. Complexes **1**–**4** crystallized in the triclinic space group $P\bar{1}$. Complex **6** crystallized in the space group $P2_1/c$. The molecular structures of **1**–**4** and **6** and some of the selected intermolecular bond distances and angles are provided in Figure 1, Figure 2, Figure 3, and Figures S1 and S2 in the Supporting Information. The S–Si [2.1387(7)–553(7) Å], Se–Si [2.276(2)–87(2) Å], S–C [1.837(2)–52(2) Å] and Se–C [1.982(5)–97(6) Å] distances in these four compounds are typical for the sulfur-silicon, selenium–silicon, sulfur–carbon and selenium–carbon single bonds.[65]

Examination of the structures of **1** and **2** shows that they have a crystallographic center of symmetry. The two –ESiMe$_3$ groups are held in *trans* configuration in the crystalline state and the C–E–Si moieties are approximately perpendicular to the central C$_6$ plane (**1** 87.89°, **2** 88.85°). In the crystal structures of **3** and **4**, two –ESiMe$_3$ groups lie on one side of the aromatic ring with the third group on the opposite face. These patterns mirror the structural features of ArMe$_{6-x}$(CH$_2$ER)$_x$ (R = alkyl, aryl).[66] The structure of **6** also has a center of symmetry; in this case adjacent –SeSiMe$_3$ groups are on opposite sides of the C$_6$ ring;[64a] this conformation minimizes steric constraints.

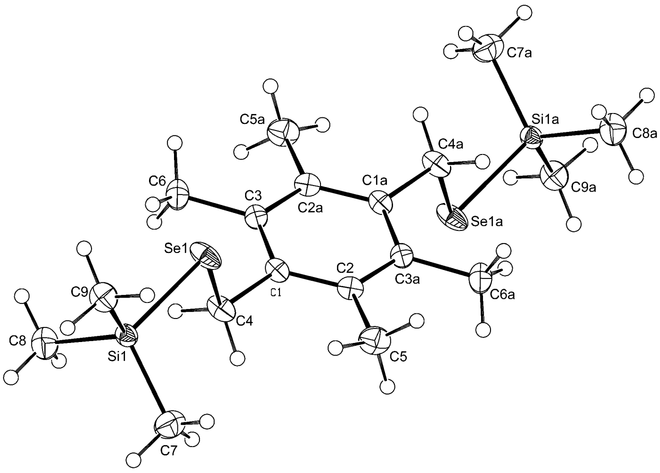


Figure 1. Thermal ellipsoid plot (40% probability level) of **2** with the atom numbering scheme. The chalcogenoesters reside about crystallographic inversions center relating the two halves of the molecules. Selected bond distances [Å] and angles [°]: C(4)–Se(1) 1.995(4), Se(1)–Si(1) 2.285(1), C(4)-Se(1)-Si(1) 97.5(1).

The demonstrated reactivity of –SeSiMe$_3$ moieties towards acid chlorides suggested a facile route for the formation of polyferrocenylchalcogenoesters using **1**–**6**. In the first attempt to synthesize polyferrocene based chalcogenoesters, 1,4-[(CH$_3$)$_3$SiSeCH$_2$]$_2$(C$_6$Me$_4$) **2** was reacted with ferrocynoyl chloride at room temperature in tetrahydrofuran. After stirring for six hours, workup and purification yielded 1,4-[{FcC(O)SeCH$_2$}$_2$-

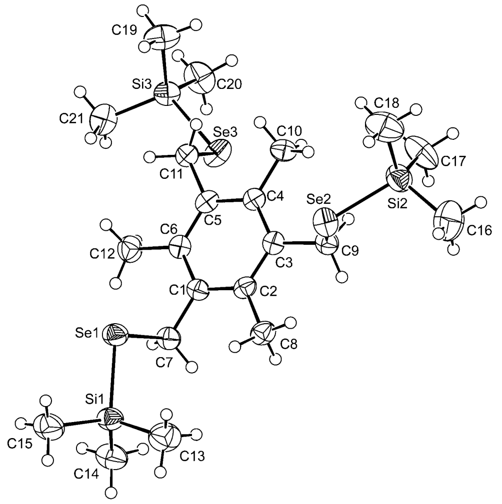


Figure 2. Thermal ellipsoid plot (40 % probability level) of **4** with the atom numbering scheme. Selected bond distances [Å] and angles [°]: C(7)–Se(1) 1.997(6), C(9)–Se(2) 1.982(5), C(11)–Se(3) 1.994(5), Se(1)–Si(1) 2.283(2), Se(2)–Si(2) 2.276(2), Se(3)–Si(3) 2.287(2), C(7)-Se(1)-Si(1) 98.7(1), C(9)-Se(2)-Si(2) 102.2(1), C(11)-Se(3)-Si(3) 100.4(1).

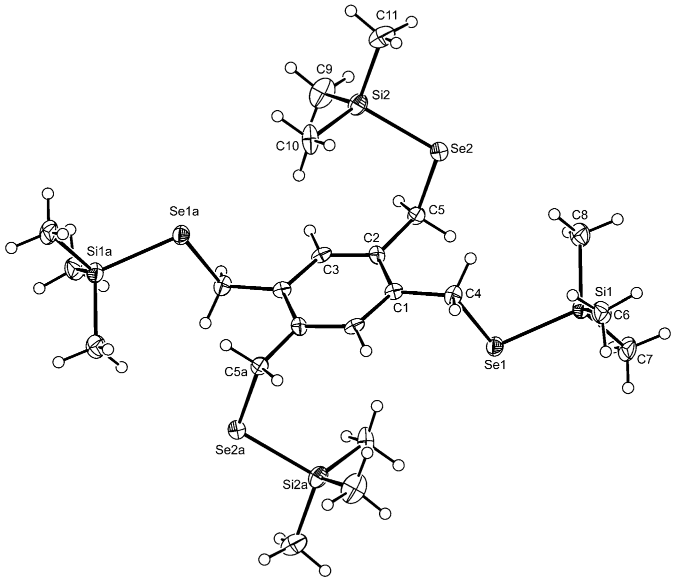
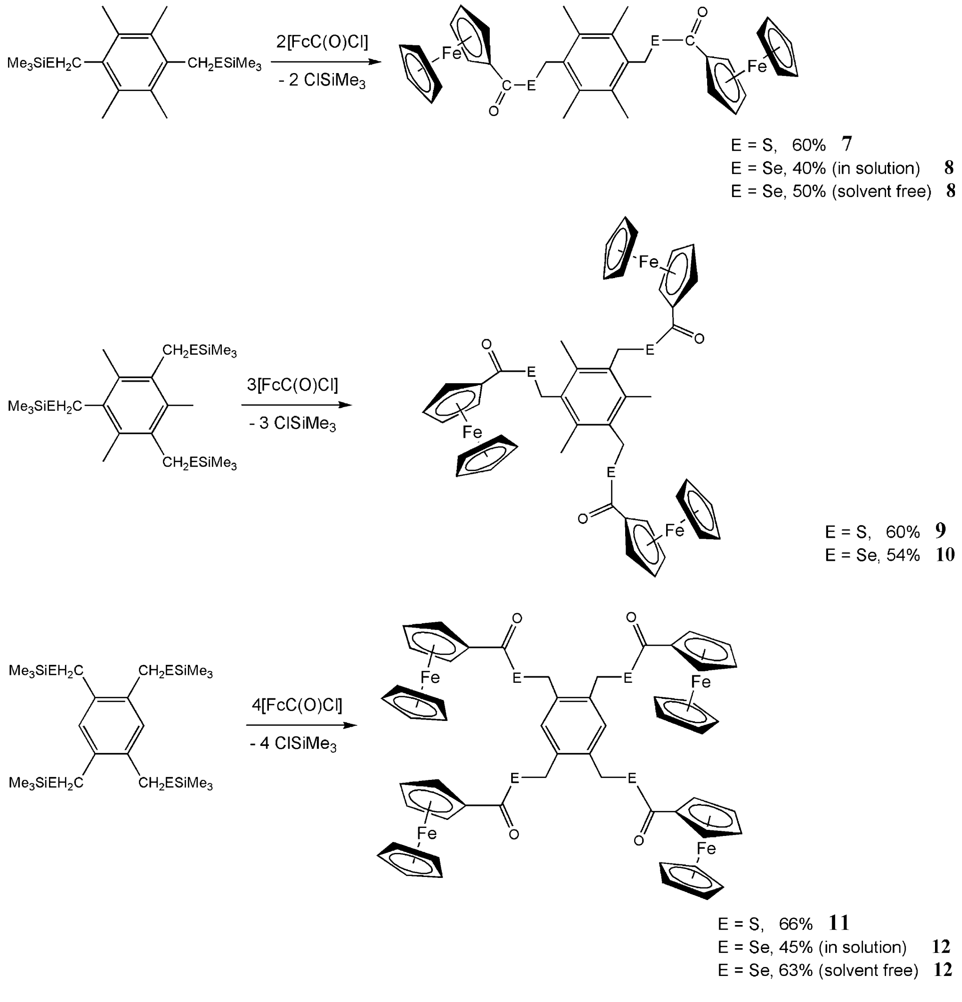


Figure 3. Thermal ellipsoid plot (40 % probability level) of **6** with the atom numbering scheme. Selected bond distances [Å] and angles [°]: C(4)–Se(1) 1.9839(1), C(5)–Se(2) 1.9849(2), Se(1)–Si(1) 2.2873(2), Se(2)–Si(2) 2.2857(2), C(4)-Se(1)-Si(1) 97.64(14), C(5)-Se(2)-Si(2) 102.85(16).

$(C_6Me_4)]$ **8** in 40 % yield (Scheme 2). The reaction of ferrocenoyl chloride with the other silyl–selenium complexes required more forcing conditions. Thus, compound **6**, with four $-SeSiMe_3$ groups about the aryl ring, reacted cleanly with four equivalents of [FcC(O)Cl] at 40–45 °C to form the corresponding 1,2,4,5-$[\{FcC(O)SeCH_2\}_4(C_6H_2)]$ **12** in 45 % yield. Similar reaction conditions with the sulfur complexes **1**, **3**, and **5** did not lead to the formation of thioesters; higher reaction temperature yielded only modest evidence of S–Si activation, as indicated by ^1H NMR spectroscopy.

However, when reactions were performed by heating the silyl chalcogen reagents at 60–65 °C in the presence of ferrocenoyl chloride (solvent free conditions), both seleno- and thioesters proved readily accessible. Using this methodology, the polyferrocenyl complexes [1,4-$\{FcC(O)ECH_2\}_2(C_6Me_4)]$ (E = S, **7**; E = Se, **8**), [1,3,5-$\{FcC(O)ECH_2\}_3$-$(C_6Me_3)]$ (E = S, **9**; E = Se, **10**) and [1,2,4,5-$\{FcC(O)ECH_2\}_4(C_6H_2)]$ (E = S, **11**; E = Se, **12**) were prepared (Scheme 2).



Scheme 2. Synthesis of **7**–**12**.

Table 3. NMR spectroscopic data for **7–12** in $CDCl_3$. Chemical shifts are reported in ppm.

		^1H Fc	CH_3	CH_2	CH	^{13}C Fc	CH_3	CH_2	–C–	C=O
Sulfides	**7**	4.24, 4.49, 4.87	2.34	4.37		68.7, 70.4,71.6, 79.0	16.5	29.2	132.0, 133.5	193.8
	9	4.24, 4.51, 4.83	2.43	4.37		68.9, 70.8, 72.0, 81.4	16.6	25.3	133.1, 135.2	195.0
	11	4.17, 4.45, 4.83		4.33	7.45	69.0, 70.6, 71.8, 79.0		29.8	132.9, 135.8	192.8
Selenides	**8**	4.24, 4.51, 4.84	2.31	4.38		68.9, 70.8, 72.0, 81.5	17.0	25.6	133.3, 133.4	195.2
	10	4.22, 4.48, 4.86	2.46	4.37		68.9, 70.6, 71.8, 79.1	16.5	29.2	131.8, 136.3	193.9
	12	4.20, 4.48, 4.81		4.31	7.36	69.0, 70.8, 72.0, 81.2		25.3	132.8, 136.8	194.0

The NMR chemical shifts for the chalcogeno esters **7–12** are listed in Table 3. The ^1H NMR spectra show one singlet (4.17–4.24 ppm) and two virtual triplets (4.48–4.87 ppm) assigned to the C_5H_5 and substituted Cp rings of ferrocene, respectively. The chemical shift values of the CH_2 groups are shifted downfield (4.31–4.38 ppm) compared with the corresponding silyl–chalcogen precursor (3.72–3.83 ppm). Unlike the downfield shift of arene CH resonance in **11** and **12** ($\delta\Delta \approx 0.2$ ppm), there is no considerable change in the chemical shifts of the arene CH_3 groups in **7**, **8**, **9**, and **10**. The chemical shift values in the ^{13}C NMR spectra of the methylene groups for the selenoesters generally appear downfield of their respective $-SeSiMe_3$ precursor, with smaller changes observed for the thioesters. The large downfield shifts in ^{77}Se NMR of the selenoesters compared to **2**, **4**, and **6** may be explained with the introduction of withdrawing C=O group bonded to the selenium atom versus Me_3Si. The carbonyl carbon chemical shifts are observed between 192–195 ppm in their respective ^{13}C NMR spectra.

The structure of $[1,4\text{-}\{FcC(O)SCH_2\}_2(C_6Me_4)]$ **7** was solved and refined in the triclinic space group $P\bar{1}$., while $[1,4\text{-}\{FcC(O)SeCH_2\}_2(C_6Me_4)]$ **8** crystallizes in monoclinic space group $P2_1/c$. The molecular structure in the crystal together with selected bond lengths and angles for complexes **7** and **8** are presented in Figures 4 and 5, respectively. The C=O [1.205(6)–1.216(5) Å] and E–C [E = S; 1.782(3)–1.821(4) Å, E = Se; 1.957(5)–1.975(5) Å] distances are in the range observed for thio- and selenoester complexes.[67,68] Like their corresponding silylated precursors, the chalcogenoester groups are oriented in a *trans* configuration; in both complexes, the cyclopentadienyl rings adopting a staggered conformation.

In complex **7** the two ferrocenoyl groups are nearly perpendicular, with an angle of 88.09° between C_5-Fe-C_5 vectors. The central arene C_6 is not parallel with either of the two substituted C_5H_4 rings (rotated 60.46° and 65.12°). With dihedral angles C13-C12-S1-C11 and C16-C23-S2-C24 of 173.56° and 132.45°, respectively, one of the thioester groups is perpendicular to the central C_6 whereas the other is rotated by about 40°. The analogous configuration for complex **8** is not observed in the solid state; here the two selenoester groups are held in a *trans* configuration but with the two ferrocenoyl

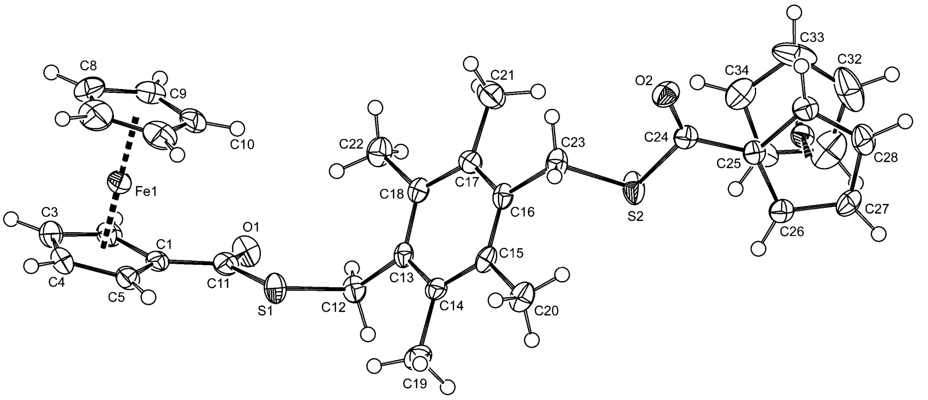


Figure 4. Thermal ellipsoid plot (40 % probability level) of **7** with the atom numbering scheme. Selected bond distances [Å] and angles [°]: C(12)–S (1) 1.821(4), C(11)–S(1) 1.780(4), C(1)–C(11) 1.469(5), C(23)–S(2) 1.821(4), C(24)–S(2) 1.782(3), C(24)–C(25) 1.470(5), C(11)-S(1)-C(12) 101.7(2), C(1)-C(11)-S(1) 113.2(3), C(23)-S(2)-C(24) 101.7(2), C(25)-C(24)-S(2) 114.0(3), C(1)-C(11)-S(1)-C(12) 178.1(3), C(25)-C(24)-S(2)-C(23) 169.8(3), C(13)-C(12)-S(1)-C(11) 132.4(3), C(16)-C(23)-S(2)-C(24) 173.6(3).

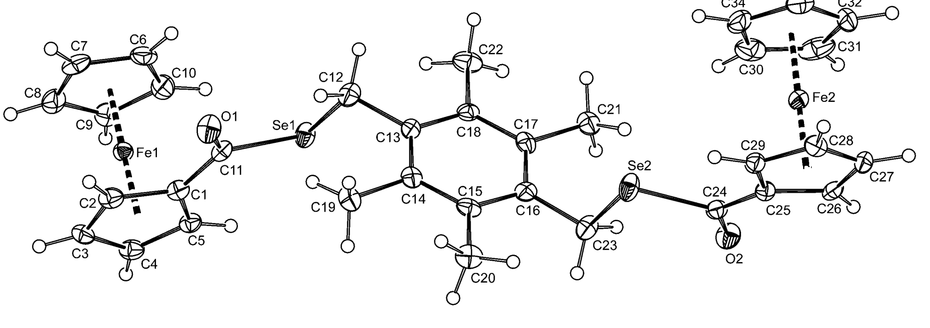


Figure 5. Thermal ellipsoid plot (40 % probability level) of **8** with the atom numbering scheme. Selected bond distances [Å] and angles [°]: C(12)–Se(1) 1.975(5), C(11)–Se(1) 1.961(4), C(11)–C(1) 1.458(6), C(23)–Se(2) 1.957(5), C(24)–Se(2) 1.947(4), C(24)–C(25) 1.461(6), C(11)-Se(1)-C(12) 98.0(2), C(1)-C(11)-Se(1) 113.9(3), C(23)-Se(2)-C(24) 96.2(2), C(25)-C(24)-Se(2) 113.8(3), C(1)-C(11)-Se(1)-C(12) 171.1(3), C(25)-C(24)-Se(2)-C(23) 175.9(3), C(13)-C(12)-Se(1)-C(11) 124.5(3), C(16)-C(23)-Se(2)-C(24) 150.0(3).

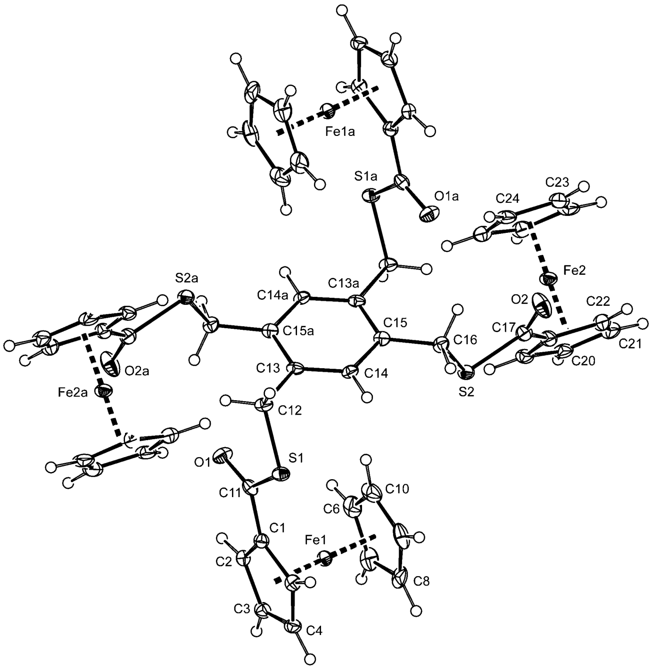


Figure 6. Thermal ellipsoid plot (40% probability level) of **11** with the atom numbering scheme. Selected bond distances [Å] and angles [°]: C(11)–S(1) 1.7634(2), C(12)–S(1) 1.8067(1), C(12)–C(13) 1.5225(1), C(17)–S(2) 1.7765(1), C(16)–S(2) 1.8293(1), C(15)–C(16) 1.5013(1), C(11)-S(1)-C(12) 98.66(2), C(1)-C(11)-S(1) 114.6(3), C(16)-S(2)-C(17) 99.8(2), C(18)-C(17)-S(2) 113.6(3), C(1)-C(11)-S(1)-C(12) 172.9(3), C(13)-C(12)-S(1)-C(11) 74.0(4), C(18)-C(17)-S(2)-C(16) 168.9(3), C(15)-C(16)-S(2)-C(17) 138.9(3).

groups nearly parallel, with an angle of only 11.74° between planes defined by the C_5 rings.

$[1,2,4,5\text{-}\{FcC(O)SCH_2\}_4(C_6H_2)]$ **11** crystallized in the triclinic space group $P\bar{1}$. with a center of inversion relating two halves of the molecule. The molecular structure and some of the selected intermolecular bond distances and angles are provided in Figure 6. As expected the large, adjacent ferrocenylthioester groups reside on opposite sides of the C_6 ring. Two of the equivalent C_5H_4 rings (bonded to Fe1/Fe1A) are rotated 61.67° out of the plane defined by the central C_6, while the other two are nearly perpendicular, twisted by 88.31°.

Electrochemistry studies

Given the incorporation of the ferrocene units onto complexes **7**–**12**, it was incumbent to measure their electrochemical behavior by using cyclic voltammetry. To this end, 1 mM solutions of each polyferrocenyl complex **7**–**12** in dichloromethane containing 0.1 M tetrabuthylammonium hexafluorophosphate ($TBAPF_6$) were prepared. The cyclic voltammograms were measured under inert atmosphere using a glassy carbon working electrode and the potentials were calibrated using ferrocene as an internal standard (0.34 V vs. SCE).[69] Figure 7 shows cyclic voltammograms (CVs) of ferrocene and complexes **7**–**11**.

The CVs of **7**–**10** (Figure 7 B, C), show what appears to be single chemically reversible oxidation processes with anodic to cathodic peak current ratios (I_{pa}/I_{pc}) for all four complexes **7**–**10** near unity. These are due to the reversible oxidation of the ferrocene moieties incorporated on these complexes. The current increases with the increasing ferrocene content of each of the complexes, with the integrated current area proportional to the number of ferrocene units in each of the complexes, relative to ferrocene. The apparent single, chemically reversible oxidation for each complex indicates that the ferrocenyl moieties on them oxidize at the same (or very similar potential) with little or no interaction between them.[70] The oxidation potentials of **7**–**12** are shifted to more positive potentials than that observed for ferrocene ($E_o = 0.34$ V vs SCE) under the same conditions with peak potential (E_p) values of about 0.68 V (E = S) and 0.72 V (E = Se), due to the presence of the electron-withdrawing chalcogenoester groups on the C_5H_4 rings.[68b] The CVs for complexes **11** and **12** also show a single oxidation for the oxidation of the ferrocene moiety, but the reverse scan shows evidence for adsorption of these compounds onto the electrode (Figure 7 D), likely due to their limited solubility in this solvent, particularly upon oxidation.

Conclusion

In summary, we have demonstrated a straightforward synthesis of a novel series of di-, tri-, and tetra-polychalcogenotrimethylsilanes $Ar(CH_2ESiMe_3)_n$ ($n = 2$–4). These have been used as "protected chalcogenides" for the facile preparation of polyferrocenylseleno- and thioester assemblies by reaction with ferrocene acid chloride. The synthetic methodology is likely to be useful in the synthesis of other chalcogenoesters, and $Ar(CH_2ESiMe_3)_n$

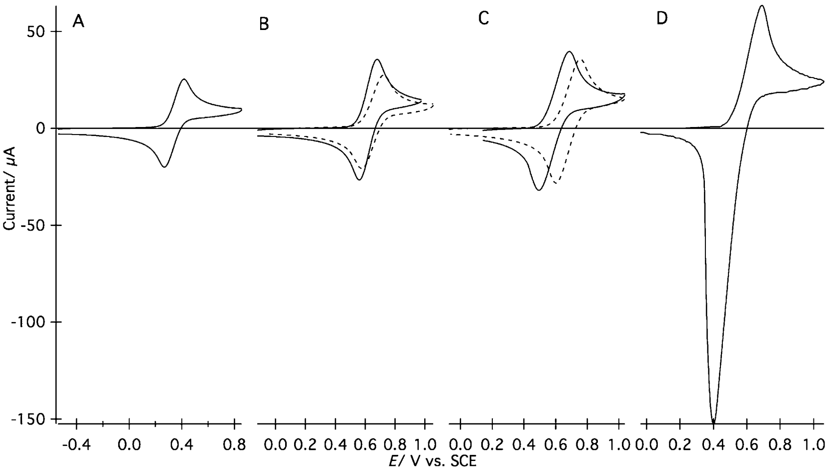


Figure 7. Cyclic voltammograms (CVs) of 1 mM solutions of A) ferrocene, B) compounds **7** (solid) and **8** (dashed), C) compounds **9** (solid) and **10** (dashed), and D) compound **11** in dichloromethane with 0.1 M $TBAPF_6$ as supporting electrolyte. All the CVs shown are recorded at 100 mV s^{-1} and are referenced to ferrocene at 0.34 V vs SCE.

themselves hold enormous potential for the assembly of polynuclear metal–chalcogen (cluster) architectures. We are currently developing this reaction chemistry.

Experimental Section

All syntheses were carried out under an atmosphere of high-purity dried nitrogen using standard double-manifold Schlenk line techniques and nitrogen-filled glove boxes unless otherwise stated. Solvents were dried and collected using an MBraun MB-SP Series solvent purification system with tandem activated alumina (tetrahydrofuran) and an activated alumina/copper redox catalyst (pentane).

Chlorinated solvents (dichloromethane, chloroform and [D]chloroform) were dried and distilled over P_2O_5. Chemicals were used as received from Alfa Aesar and/or Aldrich. [FcC(O)Cl],[71] 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene,[72] 1,2,4,5-tetrakis(bromomethyl)benzene,[73] Li[$ESiMe_3$][60] and Na[$ESiMe_3$][61] (E = S, Se) were synthesized according to literature procedures. 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene was prepared according to similar procedure for 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene.[72] ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 4.61$ (s, 4 H, CH_2), 2.34 ppm (s, 12 H, Ar–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 134.6$, 134.0 (C6), 31.0 (CH_2), 15.9 ppm (Ar–CH_3).

A BAS 100B\W Electrochemical Analyzer was used for cyclic voltammetry (CV) experiments. A homemade glassy carbon (GC, Tokai GC-20) working electrode 3 mm in diameter was prepared by polishing over silicon carbide papers (500, 1200, 2400, and 4000) followed by diamond paste (Struers, 1 and 0.25 mm). The GC electrodes were stored in ethanol and polished before each set of experiments with the 0.25 mm diamond paste (Struers), rinsed with dry ethanol (Commercial Alcohols) and sonicated in dry ethanol for 5 min. Platinum wires served as the reference and counter electrodes. Electrochemical experiments were carried out in dry CH_2Cl_2 (Caledon) containing 0.1 м tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. Potentials are referenced internally to ferrocene (0.342 V vs. SCE) added at the end of the experiments.

Mass spectra and exact mass determinations were performed on a Bruker micrOTOF II instrument or Finningan MAT 8400. Elemental analysis was performed by Laboratoire d'Analyze Élementaire de l'Université de Montréal, Montréal, Canada, and Chemisar Laboratories, Guelph, Canada.

Single-crystal X-ray diffraction measurements were completed on Enraf–Nonius KappaCCD (**1**, **2**, and **4**) and Bruker APEX-II CCD (**3**, **4**, **7**, **8** and **11**) diffractometers equipped with graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. Single crystals of the complexes were carefully selected, immersed in paraffin oil and mounted on MiteGen micromounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL.[74] All non-hydrogen atoms, with the exception of disordered carbon centers, were refined with anisotropic thermal parameters. Hydrogen atoms were included as riding on their respective carbon atoms. For **7**, the TWIN command in SHELXTL was used to refine the structure. CCDC-978321 (**1**), CCDC-978322 (**2**), CCDC-978323 (**3**), CCDC-978324 (**4**), CCDC-978325 (**6**), CCDC-978326 (**7**), CCDC-978327 (**8**), and CCDC-978328 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Synthesis of 1

Method 1: 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (0.500 g, 1.56 mmol) and freshly prepared Li[$SSiMe_3$] (3.13 mmol) were each dissolved in anhydrous diethyl ether (30 mL and 15 mL, respectively) and cooled to 0 °C. The solutions were mixed and stirred for 1 h at this temperature and overnight at room temperature resulting in an opaque suspension. The solvent was removed in vacuum and chloroform (30 mL) and pentane (15 mL) were added to solubilize the product **1**. The solid LiBr was removed by twice passing the mixture through a sintered glass frit packed with Celite. The solvent was removed in vacuo yielding an off-white solid.

Method 2: 0.322 g (2.51 mmol) of Na[$SSiMe_3$] was added portionwise to a solution of (0.400 g, 1.25 mmol) 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene in tetrahydrofuran (40 mL) at room temperature followed by stirring overnight. The product was extracted as described above. Platelike, colorless single crystals suitable for X-ray crystallography were obtained from slow evaporation of **1** in heptane (91 % yield). M.p. 122–126 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 3.72$ (s, 4 H, CH_2), 2.32 (s, 12 H, Ar–CH_3), 0.41 ppm (s, 18 H, Si–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 135.1$, 132.7 (C6), 26.1 (CH_2), 16.1 (Ar–CH_3), 0.7 ppm (Si–CH_3); HRMS (EI): *m/z* calcd for $C_{18}H_{34}S_2Si_2$: 370.1640 [M^+]; found: 370.1645; elemental analysis calcd (%) for $C_{18}H_{34}S_2Si_2$ (370.76): C 58.31, H 9.24, S 17.30; found: C 58.12, H 9.30, S 17.05.

Synthesis of 2

1,4-Bis(bromomethyl)-2,3,5,6-tetramethylbenzene (0.500 g, 1.56 mmol) in tetrahydrofuran (30 mL) was reacted with Na[$SeSiMe_3$] (0.547 g, 3.12 mmol), which was added portion-wise. The suspension was stirred for 12 h at room temperature resulting in a white cloudy suspension. The solvent was removed in vacuum and pentane (50 mL) was added to solubilize **2**. NaBr was removed by passing the mixture through a sintered glass frit packed with Celite. The solvent was removed in vacuo yielding an off-white solid (80 % yield). Colorless plate like single crystals suitable for X-ray diffraction were obtained by slow evaporation of **2** in hexanes. M.p. 151–152 °C; ^1H NMR (399.8 MHz, $CDCl_3$, 23 °C): $\delta = 3.75$ (s, 4 H, CH_2), 2.32 (s, 12 H, Ar–CH_3), 0.49 ppm (s, 18 H, Si–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 135.2$, 132.6 (C6), 18.4 (CH_2), 16.1 (Ar–CH_3), 1.6 ppm (Si–CH_3); $^{77}Se\{^1H\}$ NMR (76.2 MHz, $CDCl_3$, 23 °C): $\delta = -70.7$ ppm; HRMS (EI): *m/z* calcd for $C_{18}H_{34}[^{76}Se][^{80}Se]Si_2$: 464.0556 [$M^+$]; found: 464.0555.

Synthesis of 3

1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (0.500 g, 1.25 mmol) in tetrahydrofuran (30 mL) was reacted with Na[$SSiMe_3$] (0.482 g, 3.76 mmol) as described for the preparation of **2** (98 % yield). Colorless cubic prism single crystals suitable for X-ray diffraction were obtained by slow evaporation of **3** in hexanes. M.p. 134–137 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 3.72$ (s, 6 H, CH_2), 2.46 (s, 9 H,Ar–CH_3), 0.40 ppm (s, 27 H, Si–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 134.7$, 134.2 (C6), 25.9 (CH_2), 15.6 (Ar–CH_3), 0.7 ppm (Si–CH_3); HRMS (EI): *m/z* calcd for $C_{21}H_{42}S_3Si_3$: 474.1756 [M^+]; found: 474.1766; elemental analysis calcd (%) for $C_{21}H_{42}S_3Si_3$ (475.01): C, 53.10; H, 8.91; S, 20.25; found: C, 52.94; H, 8.67; S, 20.01.

Synthesis of 4

1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (0.500 g, 1.25 mmol) was reacted with Na[$SeSiMe_3$] (0.658 g, 3.76 mmol, in 80 mL tetrahydrofuran) as described for the preparation of **2** (75 % yield). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of **4** in hexanes. M.p. 129–132 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 3.72$ (s, 6 H, CH_2), 2.42 (s, 9 H, Ar–CH_3), 0.47 ppm (s, 27 H, Si–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 134.9$, 133.6 (C6), 18.0 (CH_2), 16.0 (Ar–CH_3), 1.6 ppm (Si–CH_3); $^{77}Se\{^1H\}$ NMR (76.2 MHz, $CDCl_3$, 23 °C): $\delta = -70.2$ ppm; HRMS (EI): *m/z* calcd for $C_{21}H_{42}[^{78}Se][^{80}Se]_2Si_3$: 616.0098 [$M^+$]; found: 616.0084.

Synthesis of 5

1,2,4,5-Tetrakis(bromomethyl)benzene (0.700 g, 1.56 mmol) in diethyl ether (20 mL) was reacted with freshly prepared Li[$SSiMe_3$] (6.22 mmol in 50 mL diethyl ether) as described for **1** (65 % yield). M.p. 104–107 °C; ^1H NMR 400.1 MHz, $CDCl_3$, 23 °C): $\delta = 7.21$ (s, 2 H, H–Ar), 3.83 (s, 8 H, CH_2), 0.34 ppm (s, 36 H, Si–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 137.4$, 131.8 (C6), 27.5 (CH_2), 0.9 ppm (Si–CH_3); HRMS (ESI): *m/z* calcd for $C_{22}H_{46}S_4Si_4$: 550.1559 [M^+]; found: 550.1552.

Synthesis of 6

1,2,4,5-Tetrakis(bromomethyl)benzene (0.600 g, 1.33 mmol) was reacted with freshly prepared Li[$SSiMe_3$] (5.34 mmol in 70 mL diethyl ether) as described for **1** (64 % yield). Colorless needlelike single crystals suitable for X-ray diffraction were obtained by slow evaporation of **6** in heptane. M.p. 104–107 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 7.09$ (s, 2 H, H–Ar), 3.83 (s, 8 H, CH_2), 0.44 ppm (s, 36 H, Si–CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 137.5$, 132.1 (C6), 18.7 (CH_2), 1.8 ppm (Si–CH_3); $^{77}Se\{^1H\}$ NMR ($<$76.2 MHz, $CDCl_3$, 23 °C): $\delta = -19.0$ ppm.

Synthesis of 7

1,4-(Me_3SiSCH_2)$_2$(C_6Me_4) (0.186 g, 0.502 mmol) was mixed with 2 equiv of [FcC(O)Cl] (0.249 g, 1.00 mmol) as solids in an evacuated Schlenk tube. The sample was placed in a preheated (65 °C) oven, whereupon the reagents formed a dark-red solid. After 10 h the mixture was cooled to room temperature. $ClSiMe_3$ was removed in vacuo, and the residue was washed with *n*-pentane. The crude compound was then purified by column chromatography and eluted using 25:75 acetonitrile/dichloromethane (60 % yield). Small orange platelike single crystals of **7** were obtained by slow evaporation of 1:20 acetonitrile:dichloromethane solution. M.p. 206–209 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 4.87$ (vt, 4 H) (vt = virtual triplet), 4.49 (vt, 4 H), 4.37 (s, 4 H, CH_2), 4.24 (s, 10 H, Cp), 2.37 ppm (s, 12 H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta =$ 193.8 (C=O),133.5, 132.0 (C6), 79.0, 71.6, 70.4, 68.7 (Fc), 29.2 (CH_2), 16.5 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{34}H_{34}Fe_2O_2S_2$: 650.0699 [M^+]; found: 650.0700; elemental analysis calcd (%) for $C_{34}H_{34}Fe_2O_2S_2$ (650.45): C 62.78, H 5.27, S 9.86; found: C 62.89, H 5.44, S 9.86.

Synthesis of 8

Method 1: To 1,4-($Me_3SiSeCH_2$)$_2$(C_6Me_4) (0.093 g, 0.200 mmol) in tetrahydrofuran (10 mL), a solution of [FcC(O)Cl] (0.100 mg, 0.401 mmol, 2 equiv) in tetrahydrofuran (10 mL) was mixed at 25 °C. After 2 h of stirring at room temperature, the solvent and volatile $ClSiMe_3$ were removed under vacuum. After washing the residue with *n*-pentane, the remaining dark-red solid was purified by column chromatography and eluted using 25:75 acetonitrile:dichloromethane (40 % yield). M.p. 187–190 °C.

Method 2: 1,4-($Me_3SiSeCH_2$)$_2$(C_6Me_4) (0.220 g, 0.473 mmol) was mixed with 2 equiv of [FcC(O)Cl] (0.235 g, 0.947 mmol) as solids in a Schlenk tube under vacuum. The sample was placed in a preheated (65 °C) oven, whereupon the reagents formed a dark-red solid. After 12 h the mixture was cooled to room temperature. $ClSiMe_3$ was removed in vacuo, and the residue was washed with *n*-pentane. The residue was purified by column chromatography and eluted using 25:75 acetonitrile:dichloromethane (50 % yield). Orange platelike single crystals of **8** were obtained by diffusing *n*-pentane onto dichloromethane solution. ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 4.84$ (vt, 4 H), 4.51 (vt, 4 H), 4.38 (s, 4 H, CH_2), 4.24 (s, 10 H, Cp), 2.31 ppm (s, 12 H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 195.2$ (C=O), 133.4, 133.3 (C6), 81.5, 72.0, 70.8, 68.9 (Fc), 25.6 (CH_2), 17.0 ppm (CH_3); $^{77}Se\{^1H\}$ NMR (76.2 MHz, $CDCl_3$, 23 °C): $\delta = 528.4$ ppm; HRMS (ESI): *m/z* calcd for $C_{34}H_{34}Fe_2O_2[^{78}Se][^{80}Se]$: 743.9596 [$M^+$]; found: 743.9604; elemental analysis calcd (%) for $C_{34}H_{34}Fe_2O_2Se_2$ (744.24): C 54.87, H 4.60; found: C 54.59, H 4.70.

Synthesis of 9

A portion of 1,3,5-(Me_3SiSCH_2)$_3$(C_6Me_3) (0.116 g, 0.244 mmol) was reacted with (0.182 mg, 0.732 mmol) of [FcC(O)Cl] in solvent-free conditions, as described for the preparation of **8** (see above). After appropriate workup, **9** was isolated as a dark-red solid (60 % yield). M.p. 208–210 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 4.83$ (vt, 6 H), 4.51 (vt, 6 H), 4.37 (s, 6 H, CH_2), 4.24 (s, 15 H, Cp), 2.43 ppm (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 195.0$ (C=O), 135.2, 133.1 (C6), 81.4, 72.0, 70.8, 68.9 (Fc), 25.3 (CH_2), 16.6 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{45}H_{42}Fe_3O_3S_3$: 894.0344 [M^+]; found: 894.0356; elemental analysis calcd (%) for $C_{45}H_{42}Fe_3O_3S_3$ (894.54): C 60.42, H 4.73, S 10.75; found: C 59.75, H 4.80, S 10.86.

Synthesis of 10

A portion of 1,3,5-($Me_3SiSeCH_2$)$_3$(C_6Me_3) (0.294 g, 0.478 mmol) was reacted with (0.356 g, 1.43 mmol) of [FcC(O)Cl] as described for the preparation of **8** (see above). After appropriate workup, **10** was isolated as dark-red solid (45 % yield). M.p. 209–211 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 4.86$ (vt, 6 H), 4.48 (vt, 6 H), 4.37 (s, 6 H, CH_2), 4.22 (s, 15 H, Cp), 2.46 ppm (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 193.9$ (C=O), 136.3, 131.8 (C6), 79.1, 71.8, 70.6, 68.9 (Fc), 29.2 (CH_2), 16.5 ppm (CH_3); $^{77}Se\{^1H\}$ NMR (76.2 MHz, $CDCl_3$, 23 °C): $\delta = 528.2$ ppm; elemental analysis calcd (%) for $C_{45}H_{42}Fe_3O_3Se_3$ (1037.2): C 52.21, H 4.09; found: C 52.41, H 4.23.

Synthesis of 11

1,2,4,5-(Me_3SiSCH_2)$_4$(C_6H_2) (0.101 g, 0.183 mmol) was mixed with [FcC(O)Cl] (0.182 g, 0.731 mmol) at 25 °C in a Schlenk tube under vacuum. The sample was placed in a preheated (60–65 °C) oven. After 14 h, the mixture became solid. $ClSiMe_3$ was removed in vacuo, and the residue was washed with *n*-pentane. After appropriate workup, **11** was isolated as a dark-red solid (66 % yield). The residue was purified in two steps by silica and alumina column chromatography and eluted using 25:75 acetonitrile:dichloromethane and 12.5:87.5 heptane/dichloromethane, respectively. Small orange needlelike single crystals of **11** were obtained by slow evaporation of 1:5 heptane/dichloromethane solution (50 % yield). M.p. 185–189 °C; ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 7.45$ (s, 2 H, Ar–H), 4.83 (vt, 8 H), 4.45 (vt, 8 H), 4.33 (s, 8 H, CH_2), 4.17 ppm (s, 20 H, Cp); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 192.8$ (C=O), 135.8, 132.9 (C6), 79.0, 71.8, 70.6, 69.0 (Fc), 29.8 ppm (CH_2); HRMS (ESI): *m/z* calcd for $C_{54}H_{46}Fe_4O_4S_4$: 1109.9676 [M^+]; found: 1109.9655; elemental analysis calcd (%) for $C_{54}H_{46}Fe_4O_4S_4$ (1110.6): C 58.40, H 4.17, S 11.55; found: C 57.29, H 3.96, S 11.83.

Synthesis of 12

Method 1: To 1,2,4,5-$(Me_3SiSeCH_2)_4(C_6H_2)$ (0.111 g, 0.150 mmol) in tetrahydrofuran (15 mL), a solution of [FcC(O)Cl] (0.150 g, 0.601 mmol, 4 equiv) in tetrahydrofuran (10 mL) was mixed at 25 °C. After 4 h of stirring at room temperature, the solvent and $ClSiMe_3$ were removed under vacuum. The red solid was washed with *n*-pentane and the product was purified by column chromatography, eluted using 25:75 acetonitrile:dichloromethane (45% yield). M.p. 198–201 °C.

Method 2: 1,2,4,5-$(Me_3SiSeCH_2)_4(C_6H_2)$ (0.174 g, 0.236 mmol) was mixed with [FcC(O)Cl] (0.234 g, 0.943 mmol, 4 equiv) as solids in an evacuated Schlenk tube. The sample was placed in a preheated (60–65 °C) oven, whereupon the reagents formed a dark-red solid. After 14 h, the mixture was cooled to room temperature. $ClSiMe_3$ was removed in vacuo and after appropriate workup, **12** was isolated as a dark-red solid (63% yield). ^1H NMR (400.1 MHz, $CDCl_3$, 23 °C): $\delta = 7.36$ (s, 2H, Ar–H), 4.81 (vt, 8H), 4.48 (vt, 8H), 4.31 (s, 8H, CH_2), 4.20 ppm (s, 20H, Cp); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 23 °C): $\delta = 194.0$ (C=O), 136.8, 132.8 (C6), 81.2, 72.0, 70.8, 69.0 (Fc), 25.3 ppm (CH_2); $^{77}Se\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): $\delta = 528.4$ ppm; HRMS (ESI): *m/z* calcd for $C_{54}H_{46}Fe_4O_4[^{78}Se][^{80}Se]_3$: 1299.7462 [$M^+$]; found: 1299.7465; elemental analysis calcd (%) for $C_{54}H_{46}Fe_4O_4Se_4$ (1298.2): C 49.96, H 3.57; found: C 49.11, H 3.80.

Acknowledgements

We are grateful for financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) for this research. NSERC, the Government of Ontario, The University of Western Ontario and the Canada Foundation for Innovation are thanked for equipment funding.

Keywords: chalcogen · cyclic voltammetry · ferrocene · polydentate · selenoester · thioester

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Received: January 16, 2014

FULL PAPER

Molecular Frameworks

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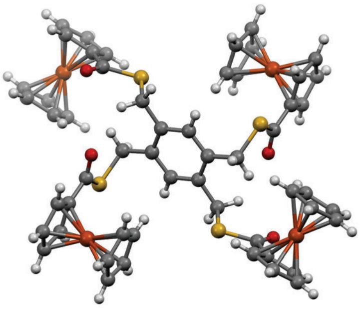
■■–■■

New Polydentate Trimethylsilyl Chalcogenide Reagents for the Assembly of Polyferrocenyl Architectures



Bond after bond: A series of polychalcogenotrimethylsilane complexes Ar(CH_2ESiMe_3)$_n$, (Ar = aryl; E = S, Se; n = 2, 3, and 4) have been prepared that incorporate a large number of reactive $-ESiMe_3$ moieties onto an organic molecular framework (see figure). They are shown to be convenient reagents for the preparation of the polyferrocenylseleno- and thioesters from ferrocenoyl chloride.

Polyferrocenyl architectures……are prepared from a series of new poly(trimethylsilylchalcogen) reagents and ferrocenoyl chloride. As described in the Full Paper by J. F. Corrigan et al. on p. ■■■■ ff., The assemblies are formed via thioester or selenoester linkages, tethering the ferrocenyl fragments to a central ring.