New reagents for the synthesis of a series of ferrocenoyl functionalized copper and silver chalcogenolate complexes[†]

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A series of silylated ferrocenoyl chalcogenide reagents, FcC(O)ESiMe₃ (E = S, Se, Te; Fc = ferrocene), can be prepared in very good yield from FcC(O)Cl and LiESiMe₃. These reagents are used in the preparation of triphenylphosphine-ligated copper and silver ferrocenoyl thiolate and selenolate complexes, $[M_4(E{O}CFc)_4(PPh_3)_4]$, (M = Cu, Ag; E = S, Se) and $[Cu_2(\mu-Se{O}CFc)_2(PPh_3)_3]$ from solubilized copper(I) and silver(I) acetate. The structures of these complexes have been determined *via* single-crystal X-ray diffraction. The driving force for these reactions is the thermodynamically favorable formation and elimination of AcOSiMe₃. The synthesis and characterization of both starting reagents and cluster complexes are discussed.

Introduction

The synthesis of cluster complexes containing multiple ferrocene units has been the focus of attention in many research groups recently.1 This interest stems, in part, from the unique electrochemical properties the complexes exhibit as well as the potential applications of these materials in molecular electronics and chemical sensors.² Recent efforts have also been devoted to the incorporation of multiple ferrocene units into polymers,³ aromatic,⁴ dendrimeric⁵ frameworks and inorganic cores.⁶ Silylated chalcogen reagents have been shown to offer a controlled route to the formation of structurally characterized metal-chalcogenolate clusters and nanoclusters which are monodisperse in nature.7 Similarly, metal-chalcogenolate supported multiferrocene assemblies are readily prepared in a reaction involving a silvlated ferrocenechalcogen reagent and a metal salt.8 These silvlated reagents react readily with metal salts, through the thermodynamically favorable formation of $XSiMe_3$ (X = Cl, OAc), to form metalchalcogenolate (RE⁻) bonds. In addition, the soluble XSiMe₃ does not impede the formation and crystallization of the nanometer sized cluster complexes. The tunability of the "R" substituent presents the opportunity to easily control the characteristics of the surface of the generated particles. These reagents can be tailored to introduce specific chemical functionalities onto the surface of the cluster.8 Herein we describe the synthesis and characterization of a series of ferrocenoyl chalcogenides, $FcC(O)ESiMe_3$ (E = S, Se, Te) 1a, 1b, and 1c and their application in the preparation of polyferrocene functionalized metal-chalcogenolate complexes 2-6.

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Results and discussion

The silvlated ferrocenoyl chalcogenides **1a**, **b**, and **c** are readily prepared in good yield from the reaction of ferrocenoylchloride9 with lithio(trimethylsilyl)-chalcogenolate¹⁰ (Scheme 1). When LiSSiMe₃ or LiSeSiMe₃ was added to a stirred solution of FcC(O)Cl in Et₂O at 0 °C, compound 1a or 1b were isolated as a red or blood red oil, respectively. The tellurolate 1c can be prepared at -40 °C and isolated as a brown oil. Compounds 1a, 1b and 1c all decompose readily in the presence of air and are susceptible to decomposition over time, even when stored cold and under inert atmosphere. In addition to decomposition in air, 1c also is sensitive to ambient light. The ¹H NMR spectrum of 1a shows three well resolved peaks at 4.16, 4.51 and 4.95 ppm and a singlet at 0.48 ppm, the latter corresponding to the protons of the trimethylsilyl moiety. For both the Se (1b) and Te (1c) analogs the ¹H NMR spectra display the same four characteristic peaks, although they are shifted downfield relative to those observed for 1a. Due to the instability of reagents 1a-1c elemental analysis could not be obtained, although high resolution mass spectrometry confirmed the chemical formula. These ferrocenoyl chalcogenides are excellent precursors for the synthesis of metal-chalcogenolate complexes. Unlike ferrocenecarboxylate ligands ($FcC(O)O^{-}$) which can bond to Cu or Ag through both oxygen atoms in a bidentate fashion,¹¹ reagents **1a**, **1b** bond exclusively through the sulfur or selenium atom (vide infra). When one equivalent of 1a is reacted with one equivalent of



Scheme 1

[†] Electronic supplementary information (ESI) available: A plot of the molecular structure of **5**. CCDC reference numbers 681444–681448. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b804597f

Table 1 Selected bond lengths (Å) and angles (°) for 2

Cu(1)-S(1)	2.2432(9)
Cu(1) - P(1)	2.2614(8)
Cu(1) - P(2)	2.2510(8)
S(1) - Cu(1) - P(1)	115.05(3)
S(1)-Cu(1)-P(2)	120.82(3)
P(1)-Cu(1)-P(2)	124.08(3)



Scheme 2

triphenylphosphine solubilized copper acetate (Scheme 2), orange crystals of $[Cu(S{O}CFc)(PPh_3)_2]$ **2** are obtained upon layering with pentane at room temperature. The molecular structure of **2**, Fig. 1, shows a monomeric complex, which consists of a single trigonal planar copper bound to two triphenylphosphine ligands and a single ferrocenoylthiolate. Selected bond distances and angles are given in Table 1.



Fig. 1 The molecular structure of $[Cu(S{O}CFc)(PPh_3)_2]$ 2. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

The corresponding reaction in which one equivalent of the selenide reagent 1b is reacted with (Ph₃P)₂CuOAc gives rise to a very different structure from that observed for 2. Cooling solutions (Et₂O-THF) to -25 °C afforded orange crystals of dimeric $[Cu_2(\mu-Se{O}CFc)_2(PPh_3)_3]$ 3 (Fig. 2). The structure of 3 consists of one tetrahedral copper center and one trigonal planar copper, each bridged by two ferrocenoylselenolates and the remaining coordination sites are occupied by triphenylphosphine. The geometry about the Cu centers leads to shorter Cu-Se distances (2.3962(8) and 2.4140(8) Å) at the trigonal Cu(1) atom than the Cu-Se bond lengths (2.5640(8) and 2.5474(8) Å) at the tetrahedral Cu(2) atom. The distortion results in a Cu_2Se_2 rhombus with a Cu(1) \cdots Cu(2) distance of 2.6265(9) Å which is shorter than the sum of the van der Waals radii of copper (I) (2.8 Å).¹² Similar bonding arrangements are also reported for other $Cu_2(SeR)_2$ (R = 4-CH₃C₆H₄C(O), Ph).^{13,14} Selected bond lengths and angles are given in Table 2. The copper and

Cu(1)–Se(1)	2.3962(8)	P(1)-Cu(1)-Se(2)	116.31(4)
Cu(1)-Se(2)	2.4140(8)	Se(1)-Cu(1)-Se(2)	121.07(3)
Cu(2)-Se(1)	2.5640(8)	P(1)-Cu(1)-Se(1)	121.97(5)
Cu(2)-Se(2)	2.5474(8)	Se(2)-Cu(2)-Se(1)	110.04(3)
Cu(1) - P(1)	2.2366(14)	P(2)-Cu(2)-P(3)	124.23(5)
Cu(2) - P(2)	2.2571(13)	Se(1)-Cu(2)-P(2)	94.39(4)
Cu(2) - P(3)	2.2655(13)	Se(2)-Cu(2)-P(3)	93.18(4)
Cu(1)-Cu(2)	2.6265(9)		
C(11) - O(1)	1.209(6)		



Fig. 2 The molecular structure of $[Cu_2(\mu-Se\{O\}CFc)_2(PPh_3)_3]$ 3. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

selenium atoms all lie in the roughly the same plane (sum of angles $Cu_2Se_2 = 358.8^\circ$, with mean deviation of the plane 0.083 Å) with one ferrocenoyl unit extending above the plane and one below much like that reported for $[Cu_2(SeC{O}C_6H_4CH_3-4)_2(PPh_3)_3]^{14}$ Temperature control proved to be important when synthesizing the copper selenolate complexes. When the reaction mixture was warmed to room temperature and subsequently layered with diethylether, dark orange crystals of $[Cu_4(\mu-Se{O}CFc)_4(PPh_3)_4]$ 4 were obtained in high yield with no evidence for the formation of dimeric 3 even if additional PPh₃ (3 equivalents) was added. The X-ray structural determination of complex 4 indicated an arrangement of four [Cu(Se{O}CFc)(PPh₃)] units, as shown in Fig. 3. The M₄ fragments are arranged in a distorted tetrahedral fashion with Cu-Cu distances of 3.2956(6)-4.1454(9) Å, which are considerably longer than the sum of the van der Waals radii (2.8 Å) and those observed for 3. Each copper has a trigonal planar geometry (sum of bond angles around Cu are 359.9°) and is bridged by two ferrocenoylselenolate ligands and is bonded to a terminal triphenylphosphine. The Cu-Se bond distances are 2.3770(13) and 2.4060(13) for Cu(1)-Se(1) and Cu(1)-Se(1B), respectively (Table 3), which are in accord with the Cu-Se bond lengths (trigonal planar Cu atoms) in $[Cu_6(\mu\text{-}dppm)_4(\mu_3\text{-}SePh)_4](BF_4)_2.^{15\alpha}$ The molecule crystallizes in the tetragonal space group $I\overline{4}$ with each [Cu(Se{O}CFc)(PPh₃)] moiety crystallographically equivalent.

The addition of **1b** to PPh₃-solubilized AgOAc at -40 °C results in the gradual lightening of the reaction solution upon warming to room temperature. A reduction in the volume, followed by slow diffusion of Et₂O led to the formation of red



Fig. 3 The molecular structure of $[Cu_4(\mu-Se\{O\}CFc)_4(PPh_3)_4]$ 4. Hydrogen atoms have been omitted for clarity. The same molecular arrangement is also observed in 5.

crystals of $[Ag_4(\mu-Se{O}CFc)_4(PPh_3)_4]$ **5**. X-Ray analysis indicates that **5** (Fig. S1, electronic supplementary information, ESI[†]) is composed of four equivalent $[Ag(Se{O}CFc)(PPh_3)]$ units and is isomorphous to **4**. The Ag–Ag distances (3.3143(1)–4.1765(2) Å) are outside the range for reported Ag–Ag interactions,¹⁶ although the Ag(1)...Ag(1A) distance is within the sum of the van der Waals radii for silver (3.4 Å). Each silver atom is trigonal planar (sum of angles around Ag are 359.9°) with one Ag–Se bond distance shorter than the other (Ag(1)–Se(1) 2.5862(8) Å, Ag(1)– Se(1A) 2.6260(9) Å) (Table 4). This disparity is comparable to that observed in **4** and other trigonal planar silver chalcogenolates reported,^{156,17} and the Ag–Se distances are in a typical range observed for μ_2 -selenolate ligands between silver atoms.¹⁷

The addition of **1a** to PPh₃-solubilized AgOAc at -40 °C results in the gradual lightening of the reaction solution as it is warmed to RT. From this solution, orange-red crystals of $[Ag_4(\mu-S{O}CFc)_4(PPh_3)_4]$ **6** (Fig. 4) could be obtained upon slow diffusion of diethylether and single crystal X-ray analysis confirmed that the reaction of **1a** with AgOAc also resulted in the formation of a tetrameric complex. The molecule crystallizes in the space group $P\overline{1}$ with a molecule of chloroform and resides about a crystallographic inversion center, with the two halves of the molecule equivalent. Selected bond lengths and angles for **6** are summarized in Table 5. Unlike in **5**, **6** contains a central 8-membered Ag_4S_4 ring, similar to that observed for

Table 3Selected bond lengths (Å) and angles (°) for 4

Cu(1)–Se(1) Cu(1)–Se(1B)	2.3770(13) 2.4060(13)	Se(1)-Cu(1)-Se(1B) Se(1)-Cu(1)-P(1)	110.82(5) 129.05(8)
Cu(1)–P(1) C(11)–O(1)	2.226(3) 1.249(10)	Se(1)'-Cu(1)-P(1)	120.07(8)

Table 4Selected bond lengths (Å) and angles (°) for 5

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Table 5	Selected b	ond lengths	(Å) and	angles	(°)	for	6
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Ag(1) - P(1)	2.4162(11)	P(1)-Ag(1)-S(1)	126.55(4)
Ag(1)-S(1)	2.5171(10)	P(1) - Ag(1) - S(2)	124.03(4)
Ag(1)-S(2)	2.5364(11)	S(1) - Ag(1) - S(2)	109.40(3)
Ag(2)-P(2)	2.4181(11)	P(2) - Ag(2) - S(1)	123.45(4)
Ag(2) - S(2)	2.5310(11)	P(2)-Ag(2)-S(1)'	129.10(4)
Ag(2)-S(1)'	2.5245(10)	S(1)' - Ag(1) - S(2)	104.50(3)
Ag(1)-Ag(2)	3.2760(5)		



Fig. 4 The molecular structure of $[Ag_4(\mu-S{O}CFc)_4(PPh_3)_4]$ 6. Phenyl rings and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

the recently reported cluster {Ag[N(Ph₂PTe)₂]}₂.¹⁸ There are no significant Ag–Ag interactions (3.2760(5)–4.3113(13) Å observed in **6**), and each silver center exhibits a trigonal planar geometry (sum of bond angles around Ag 359.9°) bound to two bridging ferrocenoylthiolates and one triphenylphosphine ligand. The Ag–S bond distances range from 2.5171(10)–2.5364(11) Å, which is in accord with other μ_2 -thiolate ligands between silver atoms.¹⁹ As seen in Fig. 4, the ferrocenoylthiolate ligands are arranged together with the PPh₃ ligands about a Ag₄S₄ ring. The Ag₄S₄ chair conformation observed in **6** contrasts with the twist boat M₄Se₄ frameworks observed in **4** and **5**.²⁰ Due to the sensitivity of the FcC(O)TeSiMe₃ reagent **1c**, analogous tellurolate complexes have yet to be successfully isolated using these methods.

Cyclic voltammetric measurements on dilute solutions of 2-6 were performed in CH_2Cl_2 with $[NBu_4][BF_4]$ (0.1 M) as the supporting electrolyte. A typical voltammogram of 4 is illustrated in Fig. 5. Complex 4 undergoes a single irreversible oxidation at 669 mV followed by two quasi-reversible oxidations at $E_{1/2}$ of 903 and 1041 mV, respectively (Table 6). Complexes 2-6 all display similar voltammograms to those observed for 4 with slightly differing E° and $E_{1/2}$ values. The potentials for these compounds are given in Table 6. After several cycles, a black solid was observed precipitating out of solution. Work up and isolation of the products following bulk electrolysis of a solution of 3 (698 mV) gave FcC(O)Se(O)CFc. The product was confirmed by comparison with reported ¹H NMR spectra.²¹ We have previously described a similar observation with ferrocenyl chalcogenolate clusters in which an initial irreversible oxidation results in cluster decomposition.8



Fig. 5 Cyclic voltammogram of a 0.5 mM solution of **4** in CH_2Cl_2 with 0.1 M [NBu₄][BF₄] at a scan rate of 100 mV s⁻¹. The peak potentials are referenced to SCE. Arrows indicate direction of scan.

Table 6Oxidation potentials of clusters 2-6 in CH_2Cl_2

Complex	E°/mV	$E_{1/2} 1/{ m mV}$	$E_{1/2} 2/{\rm mV}$
2	614	838	_
3	698	732	872
4	669	903	1041
5	718	477	773
6	519	572	667

The UV-Vis absorption spectra of solutions of complexes 2– 6 all show very similar absorption profiles with two characteristic maxima in the range 455–464 and 339–349 nm (Table 7). Each shows a slight red shift relative to the absorptions of free ferrocene.²² There is an additional band observed for all complexes at ~270 nm which may be attributed to metal–ligand charge transfer (MLCT) transitions.²³ The molar absorptivities for ferrocene based transitions in **2–6** complexes are considerably greater than those observed for free ferrocene²² but are similar to other reported ferrocenoyl complexes.²⁴

Experimental

All syntheses were performed under an inert atmosphere using standard Schlenk-line techniques or a nitrogen-filled glovebox unless otherwise stated. Solvents tetrahydrofuran, diethyl ether, hexanes, and pentane purchased from Caledon (HPLC Grade) were dried by passing through packed columns of activated alumina using commercially available MBraun MB-SP Series solvent purification system. Dichloromethane and chloroform, purchased from Caledon, were distilled over P₂O₅. Starting reagents $E(SiMe_3)_2$,¹⁰ FcC(O)OH,²⁵ FcC(O)Cl,⁹ LiESiMe₃,¹⁰ (E = S, Se, Te) CuOAc,²⁶ were prepared and purified according to literature preparations. AgOAc and PPh₃ were purchased from Strem Chemicals and Aldrich Chemicals, respectively.

 1 H, 13 C{ 1 H}, 31 P{ 1 H}, 77 Se{ 1 H} NMR spectra were obtained on a Varian INOVA 400 MHz spectrometer at operating frequencies of 399.763, 100.522, 161.96, 161.83 MHz, respectively, and are reported in ppm. 1 H, 13 C{ 1 H}, NMR spectra were referenced internally to residual H and C atoms, respectively, of the deuterated solvent relative to TMS at 0 ppm. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, Canada).

Table 7 Molar absorption coefficients, ε , at the corresponding wavelength, λ , of complexes **2–6**

Complex	$\lambda/nm (\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1})$
$[Cu(S{O}CFc)(PPh_3)_2] 2$	351 (4300); 462 (1200)
$[Cu_2(\mu-Se{O}CFc)_2(PPh_3)_3]$ 3	344 (3300); 464 (860)
$[Cu_4(\mu-Se{O}CFc)_4(PPh_3)_4]$ 4	349 (24000); 464 (8200)
$[Ag_4(\mu-Se{O}CFc)_4(PPh_3)_4]$ 5	339 (24000); 455 (7200)
$[Ag_4(\mu-S{O}CFc)(PPh_3)_4]$ 6	351 (6900); 454 (2600)

Single crystal X-ray diffraction measurements were performed on an Enraf-Nonius KappaCCD X-ray diffractometer in a cold nitrogen stream at 150 K (data for 5 were collected at room temperature) using graphite-monochromated Mo-Ka radiation $(\lambda = 0.71073 \text{ Å})$ with φ and ω scans. Data reduction was performed using Nonius HKL DENZO and SCALEPACK software.27 Molecular structures were determined via direct methods and Patterson (SHELXS-97) and refined by a full matrix least squares method based on F² using SHELXTL 5.0 software.²⁸ Except as mentioned below, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated geometrically and were riding on their respective atoms. In complex 4 there was two site disorder of two of the phenyl rings bonded to P(1) and in complex 5 a similar two site disorder was observed for one of the phenyl rings bound to P(1). The molecules were best refined isotropically with 50:50 occupancy with mild restraints. Crystals of complex 5 were weakly diffracting. Crystallographic data and parameters are summarized in Table 8.

A BAS 100 electrochemical workstation using a 3-electrode system, with gold working electrode, platinum flag counter electrode, and a silver wire reference electrode with 0.1 M NBu₄BF₄ in CH₂Cl₂ as the supporting electrolyte was used for electrochemical measurements. The potentials are reported *versus* SCE and were referenced internally to ferrocene (0.528 V), added at the end of the experiments. UV-Vis absorption measurements were performed on a Varian Cary Bio 50 spectrometer in CH₂Cl₂.

Synthesis of FcC(O)SSiMe₃ (1a)

LiSSiMe₃ (1.90 mmol) in 5 mL of Et₂O was added dropwise to a solution of FcC(O)Cl (1.29 mmol) in 10 mL of Et₂O at 0 °C and the reaction was stirred overnight. The resulting cloudy red solution was filtered over dried Celite and the solvent was removed *in vacuo* to yield **1a** as a red oil (0.32 g, 80%). NMR data (400 MHz, CDCl₃, 23 °C) $\delta_{\rm H}$ 4.95 (2H, m, CH), 4.51 (2H, m, CH), 4.16 (5H, s, Cp), 0.48 (9H, s, SiMe₃). $\delta_{\rm C}$ 217.5 (1C, s, C(O)), 83.9 (1C, s, C), 72.5 (2C, s, CH), 70.9 (5C, s, Cp), 70.9 (2C, s, CH), 0.5 (3C, s, SiMe₃). *m/z* 321 (M⁺, 1.9%), 320 (10.9), 319 (23.6), 318 (100), 317 (1.3), 316 (6.3). Anal. Calc. for C₁₄H₁₈FeOSSi: [M⁺] 318.019709; Found: [M⁺] 318.019493.

Synthesis of FcC(O)SeSiMe₃ (1b)

LiSeSiMe₃ (2.89 mmol) in 9 mL of Et₂O was added dropwise to a solution of FcC(O)Cl (2.50 mmol) in 15 mL of Et₂O at 0 °C and the reaction stirred overnight. The resulting cloudy red solution was filtered through dried Celite and the solvent subsequently removed *in vacuo* to yield a dark red oil, **1b** (0.64 g, 75%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 4.97 (2H, m, CH), 4.57 (2H, m, CH), 4.16 (5H, s, Cp), 0.53 (9H, s, SiMe₃). $\delta_{\rm C}$ 225.2 (1C, s, C(O)), 88.9 (1C, s,

Table 8	Selected crystal data,	data collection,	and refinement	a parameters for complexes 2-6	,
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	2	3	4	5	6
Formula	C ₄₇ H ₃₉ CuFeO- P ₂ S	$C_{76}H_{63}Cu_2Fe_2O_2-P_3Se_2\cdot 3(C_4H_{10}O)$	$C_{116}H_{96}Cu_4Fe_4O_4-P_4Se_4$	$C_{116}H_{96}Ag_4Fe_4O_4-P_4Se_4$	$C_{116}H_{96}Ag_4Fe_4O_4$ $P_4S_4 \cdot 2(CH_2Cl_2)$
Formula weight	833.17	1720.23	2471.21	2648.53	2630.78
Crystal system	Triclinic	Triclinic	Tetragonal	Tetragonal	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$	IĪ	IĀ	$P\overline{1}$
a/Å	9.7676(3)	14.7283(6)	18.1709(11)	18.5033(8)	13.8164(3)
b/Å	11.2468(3)	16.8262(5)			14.4554(3)
c/Å	19.1313(5)	17.1464(6)	15.2964(10)	15.5266(8)	15.5570(3)
$a/^{\circ}$	75.811(1)	105.192(2)			94.993(3)
$\beta/^{\circ}$	88.090(1)	103.360(2)			114.451(3)
y/°	71.848(1)	91.768(2)			106.023(3)
$V/Å^3$	1934.02(9)	3970.8(3)	5050.6(5)	5315.9(4)	2645.6(9)
Ζ	2	2	2	2	1
$D_{\rm calc}/{ m g~cm^{-1}}$	1.431	1.439	1.625	1.655	1.651
μ/mm^{-1}	1.098	1.915	2.942	2.732	1.551
F(000)	860	1768	2480	2624	1324
Reflections collected	39708	39245	25354	27163	47730
Independent reflections (R_{int})	12318(0.0595)	18212(0.1695)	5817(0.1306)	5560(0.1057)	13690(0.0733)
$R1 (\hat{I} > 2\sigma(I))$	0.0578	0.0653	0.0657	0.0397	0.0548
$wR2(I > 2\sigma(I))$	0.1549	0.1621	0.1141	0.0707	0.1299
Collection temperature/K	150	150	150	296	150

C), 73.1 (2C, s, CH), 71.4 (5C, s, Cp), 71.3 (2C, s, CH), 0.7 (3C, s, SiMe₃). m/z 371 (M⁺, 0.2%), 370 (1.1), 369 (4.7), 368 (22.9), 367 (22.5), 366 (100), 365 (12.8), 364 (56.6), 363 (19.5), 362 (21.3), 361 (1.6), 360 (2.9). Anal. Calc. for C₁₄H₁₈FeOSeSi: [M⁺] 365.96412. Found: [M⁺] 365.96587.

Synthesis of FcC(O)TeSiMe₃ (1c)

LiTeSiMe₃ (0.896 mmol) in 3mL of Et₂O was added dropwise to a solution of FcC(O)Cl (0.725 mmol) in 5 mL of Et₂O at -40 °C and the reaction stirred overnight protected from light. The resulting cloudy brown-orange solution was filtered through dried Celite and the solvent subsequently removed *in vacuo* to yield a brown oil (0.19 g, 65%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 4.96 (2H, m, CH), 4.68 (2H, m, CH), 4.19 (5H, s, Cp), 0.62 (9H, s, SiMe₃). $\delta_{\rm C}$ 221.2 (1C, s, C(O)), 98.2 (1C, s, C), 73.9 (2C, s, CH), 72.1 (5C, s, Cp), 70.9 (2C, s, CH), 1.3 (3C, s, SiMe₃).

Synthesis of $[Cu(S\{O\}CFc)(PPh_3)_2]$ (2)

CuOAc (0.529 mmol) was dissolved in 5 mL of THF with PPh₃ (1.159 mmol) and cooled to 0 °C. FcC(O)SSiMe₃ (0.579 mmol) in 5 mL of THF at 0 °C was then added dropwise with stirring. The orange solution was warmed slowly to RT and stirred overnight. The volume was reduced and the solution was layered with pentane to yield red-orange crystals of **2** (0.35 g, 85%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 7.41 (12H, m, CH), 7.30 (12H, m, CH), 7.22 (6H, m, CH), 4.79 (2H, br singlet, CH), 4.24 (2H, br singlet, CH), 4.05 (5H, s, Cp). $\lambda_{\rm max}/\rm{nm}$ 351 (ε = 4300) and 462 (ε = 1200). Anal. Calc. (%) for C₄₇H₃₉CuFeOPS: C 67.75, H 4.72. Found: found C 67.38, H 5.02.

Synthesis of $[Cu_2(Se\{O\}CFc)_2(PPh_3)_3]$ (3)

CuOAc (0.754 mmol) was dissolved in 5 mL of THF with PPh₃ (1.508 mmol) and cooled to 0 °C. FcC(O)SeSiMe₃ (0.754 mmol) in 5 mL THF was then added dropwise with stirring. The orange

solution was stirred for 1.5 h at 0 °C then stored at 3 °C overnight. Et₂O was then slowly diffused at RT and the layered reaction was stored at -25 °C. After several days, orange crystals of **3** were obtained (0.38 g, 86%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 7.42 (18H, m, CH), 7.29 (18H, m, CH), 7.20 (9H, m, CH), 4.69 (4H, br singlet, CH), 4.22 (4H, br singlet, CH), 4.01 (10H, s, Cp). $\lambda_{\rm max}/{\rm nm}$ 344 (ϵ = 3300) and 464(ϵ = 860). Anal. Calc. (%) for C₇₆H₆₃Cu₂Fe₂O₂P₃Se₂: C 60.94 H 4.24. Found: C 62.11, H 4.15.

Synthesis of $[Cu_4(Se{O}CFc)_4(PPh_3)_4]$ (4)

CuOAc (0.685 mmol) was dissolved in 5 mL of THF with PPh₃ (1.370 mmol) and cooled to 0 °C. FcC(O)SeSiMe₃ (0.685 mmol) in 5 mL of THF at 0 °C was then added dropwise. The dark orange solution was warmed slowly to room temperature and stirred overnight. The volume was reduced under vacuum to ~ 3– 5 mL. Slow diffusion of Et₂O gave orange crystals of **4** (0.35 g, 81%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 7.46 (24H, m, CH), 7.28 (24H, m, CH), 7.20 (12H, m, CH), 4.70 (8H, br singlet, CH), 4.23 (8H, br singlet, CH), 4.03 (20H, s, Cp). $\lambda_{\rm max}/{\rm nm}$ 354 (ε = 24000) and 448 (ε = 8200). Anal. Calc. (%) for C₁₁₆H₉₆Cu₄Fe₄O₄P₄Se₄: C 56.38, H 3.92. Found: C 56.36, H 4.16.

Synthesis of $[Ag_4(Se{O}CFc)_4(PPh_3)_4]$ (5)

AgOAc (0.605 mmol) and 2 equiv of PPh₃ (1.21 mmol) in 5 mL of THF were cooled to ~ -40 °C and FcC(O)SeSiMe₃ (0.605 mmol) in 5 mL of THF at -40 °C was added dropwise. The dark orange solution was stirred for ~ 1.5 hrs at -40 °C then warmed slowly to 0 °C. The reaction was stored at -4 °C for 15 hrs. The volume was reduced to $\sim 3-5$ mL and layered with Et₂O to afford red crystals of **6** (0.34 g, 87%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 7.38 (24H, m, CH), 7.29 (24H, m, CH), 7.20 (12H, m, CH), 4.71 (8H, s, CH), 4.24 (8H, s, CH), 4.11 (20H, s, Cp). $\lambda_{\rm max}/{\rm nm}$ 339 (ε = 24000) and 455 (ε = 7200). Anal. Calc. (%) for C₁₁₆H₉₆Ag₄Fe₄O₄P₄Se₄: C 52.60, H 3.65. Found: C 52.35, H 3.39.

Synthesis of $[Ag_4(S{O}CFc)_4(PPh_3)_4]$ (6)

AgOAc (0.551 mmol) was dissolved in 5 mL of THF with PPh₃ (1.10 mmol) and the colorless solution was cooled to -40 °C. FcC(O)SSiMe₃ (0.551 mmol) in 5 mL of THF at -40 °C was added dropwise. The reaction was warmed to RT and stirred over night. The THF was removed and the solid was dissolved in 10 mL of CH₂Cl₂. Slow diffusion of Et₂O gave orange crystals of **5** (0.28 g, 85%). NMR data (CDCl₃, 23 °C) $\delta_{\rm H}$ 7.46 (24H, m, CH), 7.34 (24H, m, CH), 7.30 (12H, m, CH), 4.81 (8H, m, CH), 4.25 (8H, m, CH), 4.14 (20H, s, Cp). $\lambda_{\rm max}/{\rm nm}$ 351 (ε = 6900) and 454 (ε = 2600). Anal. Calc. (%) for C₁₁₆H₉₆Ag₄Fe₄O₄P₄S₄: C 56.61, H 3.93. Found: C 56.30, H 3.62.

Conclusions

In summary, multiple ferrocenoyl ligated copper(I) and silver(I) chalcogenolate cluster complexes can be conveniently prepared using the new ferrocenoyl chalcogenide reagents $FcC(O)ESiMe_3$. Although, incorporating a carbonyl moiety between the ferrocene and chalcogen has been shown to spatially remove two ferrocene units from one another,²¹ it does not prevent cluster decomposition upon oxidation of clusters **2–6**.

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