Syntheses of Oligometalloles by Catalytic Dehydrocoupling

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The dehydrocoupling polycondensation of dihydro(tetraphenyl)metalloles (M = Si or Ge) with 0.2 mol % $H_2PtCl_6{\cdot}xH_2O$ and excess cyclohexene produces the respective oligometallole in high yield (>80%), where every silicon or germanium atom of the oligomer backbone is part of a silole or germole ring. Slightly less reactive catalyst systems of 1 mol % of Wilkinson's catalyst, ($RhCl(PPh_3)_3$), or $Pd(PPh_3)_4$ yield the respective oligometallole in good yield (∼60%). With these latter systems, and under less vigorous reflux conditions, the (tetraphenyl)silole dimer may be isolated in 40% yield. X-ray structural characterization of the dimer reveals a Si−Si bond length of 2.363(2) Å and an H−Si−Si−H torsion angle of 90(2)°. Using excess cyclohexene as a coreagent with $RhCl(PPh_3)_3$ increases the yield of oligomer and also eliminates dimer byproduct. The methyl-terminated dimer forms in the reaction between $H_2PtCl_6{\cdot}xH_2O$ and methylhydro(tetraphenyl)silole, but not in the similar reaction with the Rh and Pd catalysts. The methyl-terminated dimer has a Si−Si bond length of 2.375(1) Å and an H−Si−Si−H torsion angle of 92.3(1)°. Additionally, the oligosilole may be prepared by placing 1:2 dihydrosilole/cyclohexene and 1 mol % Wilkinson's catalyst in an Emrys Optimizer microwave synthesizer for 2 h. The molecular weight (M_w) of the oligometalloles ranges from 3000 to 7000. Even though the metallole possesses a secondary metalloid atom and contains bulky phenyl groups, polymerization may occur because the tetraphenylmetallole monomers have small angles at C−M−C (93.21° on C−Si−C and 90.14° on C−Ge−C), resulting in less steric hindrance at the metalloid center. Oligo(tetraphenyl)germole exhibits an absorption at 378 nm (ϵ = 5400 L/mol Ge·cm). The germole is photoluminescent in toluene solution, emitting blue-green light (498 nm, Φ = 0.01). The hydrogen-terminated silole dimer shows a similar UV−vis absorption at 372 nm (ϵ = 9600 L/mol·cm) and luminesces green at 506 nm (Φ = 0.007). The methyl-terminated dimer absorbs at 370 nm (ϵ = 11 800 L/mol·cm) and luminesces blue at 468 nm (Φ = 0.004).

Introduction

Siloles and germoles have attracted attention in recent years, because of their unusual electronic properties[1,2] and their applications as electron-transporting materials in electronic devices,[3] polymer light-emitting diodes (PLEDs),[4−6] and inorganic polymer sensors.[7] Polymetalloles (M = Si or Ge) are unique in having both a M−M backbone and an unsaturated five-membered ring system. Characteristic features of the metallole unit are a low reduction potential and a low-lying LUMO, due to $\sigma^*-\pi^*$ conjugation from the interaction between the σ^* orbital of the Si−Si or Ge−Ge chains and the π^* orbital of the butadiene moiety of the ring.[8,9] In addition, polymetalloles exhibit $\sigma-\sigma^*$ delocalization[10] of the conjugated electrons along the M−M backbone.

Potential applications for polymetalloles have stimulated the search for more efficient synthetic methods. Current preparative routes use hazardous reagents and are of low efficiency. For example, poly(tetraphenyl)silole has been synthesized by Wurtz-type polycondensation of dichloro(tetraphenyl)silole; however, the reaction yields are low (ca. ∼30%).[4] Catalytic dehydrocoupling of dihydrosilole is an attractive alternative, since Wurtz-type coupling is also problematic in large-scale synthe-

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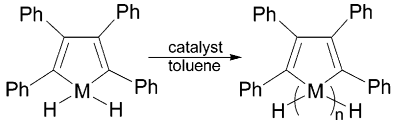

1 M = Si
2 M = Ge

3a(4a) M = Si(Ge), 0.2% H_2PtCl_6, C_6H_{12}, reflux
3b(4b) M = Si(Ge), 1% $Rh(PPh_3)_3Cl$; reflux
3c(4c) M = Si(Ge), 1% $Pd(PPh_3)_4$; reflux
3d(4d) M = Si(Ge), 1% $Rh(PPh_3)_3Cl$, C_6H_{12}, reflux
3e M = Si, $Rh(PPh_3)_3Cl$, C_6H_{12}, microwave

Figure 1. Catalytic dehydrocoupling of dihydrometalloles.

ses. Bis(cyclopentadienyl) complexes of group 4 have been extensively studied and are shown to catalyze the dehydrocoupling of hydrosilanes to polysilanes by the formation of Si−Si bonds;[11−13] however, only primary organosilanes are polymerized. Secondary and tertiary silanes afford dimers or oligomers in low yields.[14,15] It has been reported that the reactivity decreases dramatically with increasing substitution at the silicon atom, since reactions catalyzed by metallocenes are typically very sensitive to steric effects.[15,16] Mechanisms for dehydrocoupling of silanes with metallocenes have also been extensively investigated, which involve σ-bond metathesis.[17,18] Studies using Wilkinson's catalyst for dehydrogenative coupling of primary silanes show that only short chain oligomers are formed.[19,20] A platinum-complex-catalyzed dehydrocoupling polymerization of a silafluorene has been reported[21] using 4 mol % catalyst, yielding a bimodal weight distribution, in equal proportions, as determined by GPC (M_w = 8100 and 3000, relative to polystyrene). Silafluorene has also been polymerized via dehydrocoupling with Cp_2ZrMe_2, Cp_2TiMe_2, Cp_2ZrCl_2/n-BuLi, and Wilkinson's catalyst. However, only the dimer and trimer were formed in significant yields, along with minor amounts of short chain oligomers.[22] Inorganic hydrides have also been used to effect the dehydrocoupling of dihydrosilole to form polysilole (M_w = 4000−6000).[23]

Results and Discussion

Herein is reported the dehydrocoupling polycondensation of dihydro(tetraphenyl)metalloles, where every silicon or germanium atom of the oligomer backbone is part of a silole or germole ring (Figure 1). Dehydrocoupling of dihydro(tetraphenyl)silole (**1**) or dihydro(tetraphenyl)germole (**2**) with 0.2 mol % $H_2PtCl_6 \cdot xH_2O$ and 2 equiv of cyclohexene produces the oligomer **3a** or **4a** in 88% and 81% isolated yields, respectively. An alternative catalyst system of 1 mol % of Wilkinson's catalyst, $RhCl(PPh_3)_3$, or $Pd(PPh_3)_4$ catalyst yields the respective oligosilole **3b**,**c** and oligogermole **4b**,**c** in good yield (~60%). Adding cyclohexene along with Wilkinson's catalyst improves the yield of oligosilole **3d** to 82%, although the yield of oligogermole **4d** does not change. The dihydrometallole was completely consumed in the reaction for each catalyst system, as observed by ^1H NMR spectroscopy, and Si-29 NMR spectra are consistent with those previously reported for poly(tetraphenyl)silole.[23] Catalytic dehydrocoupling significantly improves isolated oligomer yields over traditional Wurtz-type coupling.

If less vigorous reflux conditions are used with only the $RhCl(PPh_3)_3$ or $Pd(PPh_3)_4$ catalyst, or if the solvent is not sufficiently degassed, the silole dimer (**5**) ($n = 2$) is observed to form in ~40% yield. This product is slightly soluble in hot toluene and precipitates from the reaction mixture during reflux, and even more so upon cooling. Addition of 2 equiv of cyclohexene with the $RhCl(PPh_3)_3$ catalyst, however, prevents dimer formation and aids in the further polymerization of the shorter chain oligomers. Wilkinson's catalyst is known to be a hydrogenation catalyst,[24] and it is likely that addition of the alkene provides a means for more efficient hydrogen removal by the catalysts. When 1-hexene or 1-dodecene is used as the alkene coreagent, however, competing reactions of polymerization and hydrosilation are observed, with hydrosilation being dominant. This is not surprising since Wilkinson's reagent is also a hydrosilation catalyst.[25] The steric bulk of the internal alkene, cyclohexene, favors hydrogenation over hydrosilation and dehydrocoupling predominates, although a minor amount of hydrosilation is sometimes visible by ^1H NMR.

Similar results are observed with $H_2PtCl_6 \cdot xH_2O$. In the absence of an alkene coreagent, large amounts of dimer and lesser amounts of oligomer exist after 24 h reflux. The addition of cyclohexene produces oligomers of higher molecular weights than the syntheses with Wilkinson's catalyst, and no hydrosilation products are observed. Both hydrosilation and polymerization products are observed when 1-hexene is used with $H_2PtCl_6 \cdot xH_2O$, as observed with Wilkinson's catalyst.[25] One advantage of the Pt catalyst is that polymerization proceeds much more quickly (1 day versus 3 days for Wilkinson's catalyst). Additionally, removal of the heterogeneous catalyst formed from the H_2PtCl_6 is simpler. After reflux, black particles are seen in solution and are easily removed by filtration. Most likely the particles are Pt colloids, the proposed active catalytic species for H_2PtCl_6-catalyzed hydrosilation.[26,27]

The synthesis of oligosilole, under each catalytic system, was also carried out with the use of an Emrys Optimizer microwave synthesizer. Polymerization occurs in only 2 h at 170 °C with Wilkinson's catalyst

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Table 1. Results of Dehydrocoupling Syntheses of Oligo(tetraphenyl)metalloles

oligomer	catalyst (1 mol %)	alkene (2 equiv)	method	yield %	M_n (IR)	M_n (NMR)	M_w (M_w/M_n) (GPC)
3a	H_2PtCl_6[a]	C_6H_{12}	reflux 24 h	88	6500	6500	5600 (1.1), 2400 (1.1), 1300 (1.0)
3b	$RhCl(PPh_3)_3$	none	reflux 72 h	62	3500	4100	4800 (1.2), 1800 (1.0), 1200 (1.0)
3c	$Pd(PPh_3)_4$	none	reflux 72 h	58	3500	4800	4800 (1.2), 1700 (1.0), 1200 (1.0)
3d	$RhCl(PPh_3)_3$	C_6H_{12}	reflux 72 h	82	4000	5200	5100 (1.1), 2100 (1.0), 1300 (1.0)
3e	$RhCl(PPh_3)_3$	C_6H_{12}	microwave 2 h	78	2700	2800	3300 (1.3), 1200 (1.0)
4a	H_2PtCl_6[a]	C_6H_{12}	reflux 24 h	81	3600	4000	3400 (1.1), 1300 (1.0)
4b	$RhCl(PPh_3)_3$	none	reflux 72 h	50	3400	3800	4000 (3.3), 1200 (1.0)
4c	$Pd(PPh_3)_4$	none	reflux 72 h	67	5500	6900	4800 (1.9), 1200 (1.0)
4d	$RhCl(PPh_3)_3$	C_6H_{12}	reflux 72 h	49	5600	5700	3600 (1.3), 1200 (1.0)

[a] Catalytic concentration of 0.2 mol % used.

when cyclohexene is present (**3e**). When no alkene is present, only limited polymerization takes place, and mostly monomer and dimer are observed by NMR after 2 h reaction time. Microwave synthesis offers the advantage of more rapid polymerizations, although lower M_w's are obtained. Microwave syntheses with $Pd(PPh_3)_4$ and H_2PtCl_6 catalysts were not successful. A summary of reaction conditions and results is shown in Table 1.

The molecular weight (M_w) of the oligosilole is in the range 3000−7000, even though the silole possesses a secondary silicon atom and contains bulky phenyl groups (Table 1). The oligomers obtained are slightly lower in M_w than those obtained from Wurtz-coupling polycondensation. A similar result is also obtained from the catalytic dehydrocoupling of dihydro(tetraphenyl)germole. The molecular weights of the oligometalloles were estimated in three ways. First, the M_n were calculated using infrared spectroscopy by integrating the phenyl C−H stretch region relative to the Si−H or Ge−H stretch, compared to the ratio in the dihydro monomers. Similarly, NMR was used to calculate M_n, by integrating the phenyl protons relative to the Si−H or Ge−H end-groups. Finally the M_w was determined by gel permeation chromatography (GPC). For the siloles, higher molecular weights are obtained using the H_2PtCl_6 catalyst, followed by Wilkinson's catalyst with the alkene coreagent, $Pd(PPh_3)_4$, and then Wilkinson's catalyst alone. For the germoles, highest molecular weights are obtained using $Pd(PPh_3)_4$, followed by Wilkinson's catalyst with the alkene coreagent, H_2PtCl_6, and then Wilkinson's catalyst alone. Molecular weights determined by IR were slightly higher than those determined by GPC, and the NMR measurements yielded the highest molecular weights.

NMR is the most reliable method for determining actual molecular weights because it does not, as GPC does, calculate M_w based on the size exclusion of individual polymer strands relative to an external standard. The Si−H end-group of the dimer appears at $\delta = 5.3$ ppm, and end-groups of the oligomers appear to shift increasingly downfield as chain length increases, arising near $\delta = 5.5$ ppm for **3b**,**e**, near 5.6 for **3c**,**d**, and 5.7 for **3a**. For the oligogermoles, the end-group Ge−H resonance appears at $\delta = 5.37$ ppm for **3a** and 5.45 for **3b**,**c**,**d**, shifting downfield with increasing molecular weight. GPC, however, reveals the size distribution of the polymer. Polysiloles **3a**−**d** are trimodal in weight distribution, and **3e** and polygermoles **4a**−**d** are bimodal, each in roughly equal proportion, plus or minus 5%.

Polymerization may take place for the disubstituted silicon or germanium since the tetraphenylmetalloles have small angles at C−M−C in the metallacyclopentadiene ring, which results in less steric hindrance at the metalloid center. The angles of C−M−C of dihydro(tetraphenyl)silole (**1**) (Figure 2) and dihydro(tetraphenyl)germole (**2**) (Figure 3) are 93.21° and 90.14°, respectively. In addition, no polymer is observed using an H atom abstracting reagent, such as AIBN, which suggests that the monomers are not simply undergoing free radical polymerization. The bulky phenyl groups of the silole might reduce the formation of a cyclic hexamer, which is often problematic in polysilane syntheses.[28] Nevertheless, the GPC profiles of the

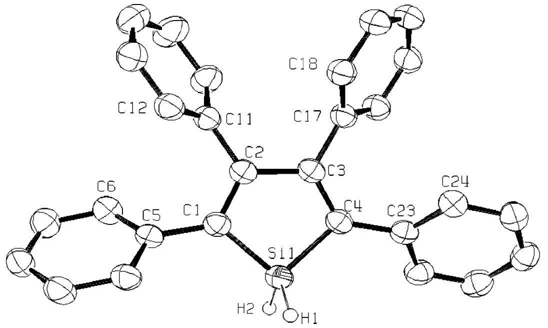


Figure 2. Thermal ellipsoid plot of **1** at the 50% probability level. Selected bond lengths (Å): Si1−C1 1.856(2), Si1−C4 1.866(1), C1−C2 1.358(2), C2−C3 1.506(2), C3−C4 1.359(2), Si1−H1 1.40(2), Si1−H2 1.37(2). Delected bond angles (deg): C1−Si1−C4 93.21(6), Si1−C1−C2 107.4(1), Si1−C4−C3 107.0(1), C1−C2−C3 116.1(1), C2−C3−C4 116.3(1), H1−Si1−H2 109(1).

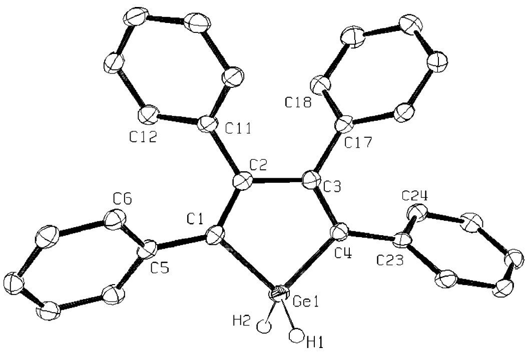
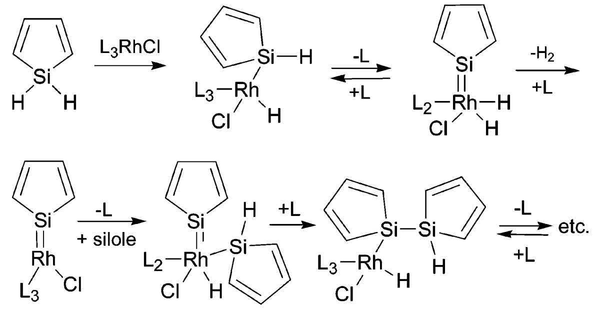
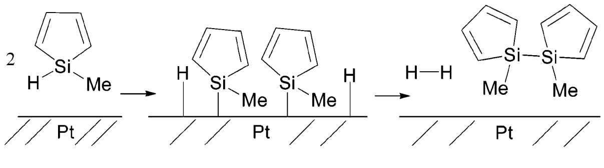


Figure 3. Thermal ellipsoid plot for **2** at the 30% probability level. Selected bond lengths (Å): Ge1−C1 1.949(2), Ge1−C4 1.935(2), C1−C2 1.361(3), C2−C3 1.506(3), C3−C4 1.358(3), Ge1−H1 1.40(3), Ge1−H2 1.43(3). Selected bond angles (deg): C1−Ge1−C4 90.14(9), Ge1−C1−C2 107.4(2), Ge1−C4−C3 108.0(2), C1−C2−C3 117.2(2), C2−C3−C4 117.2(2), H1−Ge1−H2 106(2).

Scheme 1. Proposed Dehydrocoupling Mechanism for Rh- and Pd-Catalyzed Oligosilole Synthesis



Scheme 2. Proposed Dehydrocoupling Mechanism of Methylhydrosilole on Pt Colloids Formed from H_2PtCl_6



oligomers prepared by each method show a peak centered around $M_w = 1200$ with a low polydispersity of 1.0. This may indicate the formation of a cyclic species or a low molecular weight oligomer. In addition to the Si-29 resonances of polysilole at $\delta = -34.2$ (terminal Si) and -40.1 (internal Si), a small resonance at $\delta = -32.0$ is sometimes visible, which may indicate a cyclic species or low M_w oligomer. The NMR spectra contain a broad phenyl region with very small Si−H resonances, suggesting that the low molecular weight fraction is probably cyclic.

The reaction of 1-methyl-1-hydro(tetraphenyl)silole with 1 mol % of Wilkinson's catalyst, RhCl(PPh$_3$)$_3$, or Pd(PPh$_3$)$_4$ catalyst yielded no dimer, $C_4Ph_4Si(CH_3)-(CH_3)SiC_4Ph_4$, with or without added cyclohexene. However, the same reaction with $H_2PtCl_6{\cdot}xH_2O$ catalyst does yield the methyl-terminated dimer (**6**) in 40% isolated yield. This demonstrates the higher reactivity of the Pt catalyst, as do the higher M_w silole oligomers obtained. Scheme 1 shows a proposed reaction mechanism for the homogeneous catalysts (Rh and Pd catalysts) with a putative silylene intermediate formed after oxidative addition of the Si−H bond to the metal center. Electronic stabilization of the silylene intermediate by π-conjugation with the silole ring may contribute to the unexpected observation of catalytic dehydrocoupling for a secondary silane. This scheme is consistent with the fact that no dimer is observed with the methylhydrosilole because an Si−Me bond would not oxidatively add to the metal center to form the silylene intermediate. However, dimerization of the methylhydrosilole is observed using the Pt catalyst. This suggests that the surface-catalyzed reaction on the Pt colloid proceeds by oxidative addition of the Si−H of the silole, followed by reductive elimination of H_2 and dimer (Scheme 2).

Crystal structures for both the hydrogen-terminated and methyl-terminated dimers were obtained. The H-terminated dimer (**5**) has a H1−Si1−Si2−H2 torsion angle of 90(2)° (Figure 4), and the Me-terminated dimer (**6**) has a similar torsion angle of 92.3(1)° (Figure 5). This torsion angle is larger than that of the 51.2° observed for the chlorosilole dimer.[29] This deviation is obviously not due to sterics, as Me and Cl ligands are of similar size, but perhaps arises from electronic effects of the interaction of the π system with the halide. The torsion angles suggest that the structure of the oligomers is helical, as previously proposed,[7b] and as established for several disubstituted polysilanes.[30]

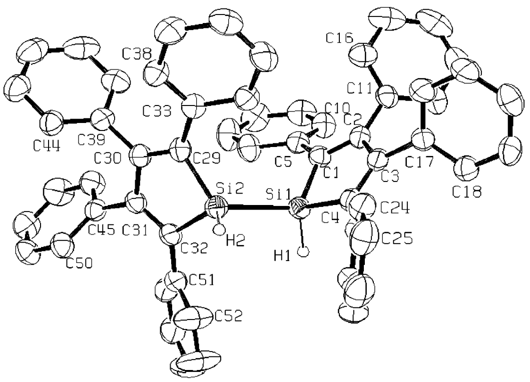


Figure 4. Thermal ellipsoid plot for **5** at the 50% probability level. Selected bond lengths (Å): Si1−Si2 2.363(2), Si1−H1 1.47(4), Si2−H2 1.48(4), Si1−C1 1.870(5), C1−C2 1.363(7), C2−C3 1.503(7). Selected bond angles (deg): H1−Si1−Si2 106(2), Si1−Si2−H2 107(2), C1−Si1−C4 92.8(2). Selected torsion angles (deg): H1−Si1−Si2−H2 90(2), C1−Si1−Si2−C32 94.6(2).

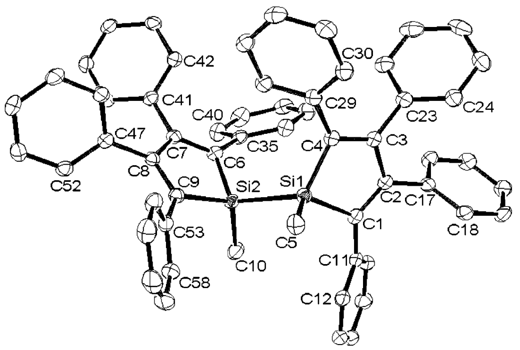


Figure 5. Thermal ellipsoid plot for **6** at the 50% probability level. Selected bond lengths (Å): Si1−Si2 2.375(1), Si1−C5 1.867(2), Si2−C10 1.873(2), Si1−C1 1.881(2), C1−C2 1.355(2), C2−C3 1.502(2). Selected bond angles (deg): C5−Si1−Si2 109.32(6), Si1−Si2−C10 108.80(6), C1−Si1−C4 91.99(7). Selected torsion angles (deg): C5−Si1−Si2−C10−92.3(1), C1−Si1−Si2−C9 164.88(8), C4−Si2−Si1−C6 10.09(8).

The hydrogen-terminated dimer has a UV−vis absorption at 372 nm, similar to that of the dihydro monomer at 368 nm, which is assigned to the $\pi-\pi^*$ transition of the silole ring. The dimeric compound is strongly luminescent, much more so than the monomer, emitting green light at 506 nm when excited at 360 nm (Figure 6). Similarly the Me-terminated dimer is much more luminescent than both methylhydrosilole and dimethylsilole, emitting at 468 nm. Fluorescence spectra of 20 mg/L metallole samples in toluene are shown in Figure 6. The broad emission spectra could possibly be

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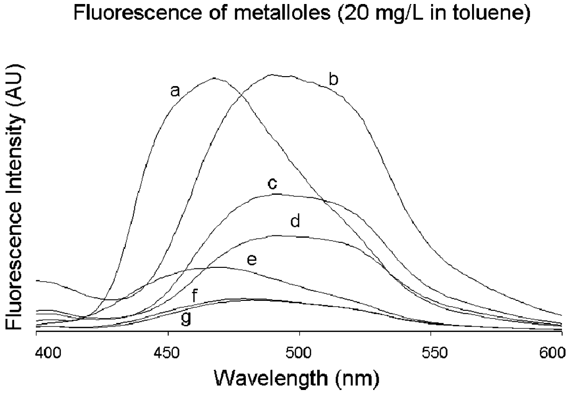

Figure 6. Fluorescence spectra of 20 mg/L toluene solutions of (a) methyl dimer, (b) oligogermole, (c) hydrogen dimer, (d) oligosilole, (e) dihydrogermole (THF), (f) methylhydrosilole, and (g) dihydrosilole on excitation at 360 nm.

due to the overlapping of emission from the $\pi-\pi^*$ and $\sigma-\pi^*$ transitions. Absorbance and fluorescence data are summarized in Table 2.

Fluorescence quantum yields (Φ) of the metalloles were measured relative to a diphenylanthracene (DPA) standard and are listed in Table 2.[31] The Φ_{rel} of the oligogermole is roughly 10 times greater than dihydrogermole, and the quantum yields of the siloles follow the order oligosilole > H-dimer > dihydrosilole. One possible explanation of this series order is the fact that coupling of the excited state to high frequency (Si−H or Ge−H) vibrations of the ground state increases the efficiency of nonradiative decay processes.[32] To test this hypothesis, the dideuterometallole monomers were prepared, along with dimethylsilole and methylhydrosilole, in order to vary the vibrational frequencies directly coupled to the metallole chromophore. Infrared spectra of dideuterosilole (**7**) and dideuterogermole (**8**) show the decrease in vibrational frequencies of the metal−deuterium stretches ($\nu = 1543$ cm^{-1} for Si−D and 1476 cm^{-1} for Ge−D) relative to the metal−hydrogen analogues ($\nu = 2140$ cm^{-1} for Si−H and 2053 cm^{-1} for Ge−H), which is consistent with the increase in the reduced mass. Dideuterogermole has a slightly higher Φ_{rel} than the dihydrogermole, but dihydrosilole has a very slightly higher Φ_{rel} than dideutersilole. The dimethyl- and methylhydrosiloles have quantum yields comparable to the other silole monomers. Because emission intensity and quantum yield are not significantly affected by the varying vibrational frequencies coupled to the chromophore, vibrational relaxation does not appear to be the dominant pathway in determining the variation in metallole fluorescence quantum yields. Interestingly, the hydrogen-terminated dimer is more than 8 times more luminescent than monomer, while the oligomer is about 13 times more luminescent. The enhanced quantum yields of the dimer and oligomer may possibly be attributed to restricted conformations about the Si−Si bond. It may also result from shielding of the metallole excited state from solvent. Polysilole and siloles are dramatically more luminescent in the solid state than in fluid solution.[7cd,33]

The UV−vis absorption spectrum of oligo(tetraphenyl)germole has an absorption at 378 nm, which is slightly red shifted to that of the corresponding oligosilole (370 nm), and is assigned to both the $\sigma-\sigma^*$ transition of the germanium−germanium backbone chain and the $\pi-\pi^*$ transition of the germole ring. Like oligosilole, the oligogermole is highly photoluminescent, emitting blue-green light at 498 nm when excited at 360 nm, which is 12 nm blue shifted to that of the analogous oligosilole (510 nm). Germole species are much more intensely photoluminescent than the corresponding siloles. The wavelengths of fluorescence red shift with increasing chain length, which is consistent with the lowering of the LUMO energy due to $\sigma-\sigma^*$ conjugation along the metalloid backbone.

Experimental Section

General Procedures. All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard Schlenk techniques. Solvents were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl. NMR data were collected with Varian Unity 300 or 500 MHz spectrometers (300.1 MHz for ^{1}H, 77.5 MHz for ^{13}C, and 99.4 MHz for ^{29}Si NMR). Infrared spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. GPC data were obtained with the use of a Viscotek GPCmax VE 2001 GPC and a Viscotek VE 3580 refractive index detector. A calibration curve was obtained using **1**, **5**, and three polysilole samples calibrated by Viscotek using RI, viscosity, and light-scattering detectors (this triple detection method yields absolute molecular weights). Fluorescence emission and excitation spectra were recorded with the use of a Perkin-Elmer LS 50B luminescence spectrometer. UV−vis spectra were obtained with the use of a Hewlett-Packard 8452A diode array spectrometer.

X-ray Crystal Structure Determinations. Diffraction intensity data were collected with a Bruker P4/CCD diffractometer at 213 K (**1**, **6**) and 218 K (**5**) and a Bruker P4/CCD Smart Apex CCD diffractometer at 100 K (**2**). Crystal, data collection, and refinement parameters are given in Table 3. The space groups were chosen on the basis of the systematic absences (**1**, **2**, **6**) and intensity statistics (**5**). The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. SADABS absorption corrections were applied to all data. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All H atoms in **1**, **2**, and **6** and the H atoms bonded to the Si atoms in **5** were found on the difference maps and refined with isotropic thermal parameters. Other H atoms in **5** were treated as idealized contributions. The structures of **7** and **8** were also determined and are isomorphous with their protio analogues. Data for **7** and **8** are included in the Supporting Information only. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

1,1-Dihydro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (Dihydrosilole) (1). Diphenylacetylene (18 g, 0.10 mol) and Li (0.25 mol) in dry ether (130 mL) were stirred for 2.5 h and then frozen with liquid nitrogen. Dichlorosilane (25% in xylenes, 20 mL, 0.20 mol) was added, and the solution was thawed and stirred for 4 h at room temperature. The solvent was evaporated, and the solid was extracted with toluene,

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Table 2. Summary of Absorbance (THF) and Fluorescence (toluene) Data of Various Metalloles

metallole	λ_{abs} (nm)	$\epsilon_{max}{}^{a}$ (L/mol·cm)	$\lambda_{flu}{}^{e}$ (nm)	fluor. quantum yield $(\Phi)^{f}$	relative Φ
dihydrosilole	368	9500	495	0.83×10^{-3}	1.0
dideuterosilole	370	10 500	484	0.79×10^{-3}	0.95
methylhydrosilole[a]	368	10 250	495	0.75×10^{-3}	0.90
dimethylsilole[a]	362	9500	473	1.0×10^{-3}	1.2
hydrogen dimer[b]	372	4800	506	6.9×10^{-3}	8.3
methyl dimer[b,c]	370	5900	468	3.6×10^{-3}	4.3
oligosilole	370	2230	510	11×10^{-3}	13
dihydrogermole[d]	360	11 200	469	1.4×10^{-3}	1.7
dideuterogermole[a]	362	9200	470	2.1×10^{-3}	2.5
oligogermole[a]	378	5400	498	13×10^{-3}	16

[a] UV−vis taken in toluene. [b] Absorptivities are reported per mole of metalloid; actual molar absorptivities of dimers are twice the reported value. [c] UV−vis data taken in $CHCl_3$. [d] Fluorescence taken in THF. [e] $\lambda_{ex} = 360$ nm. [f] ±30%, relative to 9,10-diphenylanthracene[31], $\lambda_{ex} = 360$ nm.

Table 3. Summary of X-ray Crystallographic Data

	1	2	5	6
formula	$C_{28}H_{22}Si$	$C_{28}H_{22}Ge$	$C_{56}H_{42}Si_2$	$C_{58}H_{46}Si_2$
fw	386.55	431.05	771.08	799.13
space group	$I4_1/a$	$I4_1/a$	$P\bar{1}$	$P2_1/c$
a, Å	26.5859(7)	26.457(2)	10.023(2)	12.4024(9)
b, Å	26.5859(7)	26.457(2)	12.806(2)	19.9497(14)
c, Å	11.9092(7)	11.846(2)	17.695(3)	18.2523(13)
α, deg			89.440(3)	
β, deg			88.558(3)	104.951(1)
γ, deg			71.737(3)	
V, Å^3	8417.5(6)	8292(2)	2156.1(6)	4363.2(5)
Z, Z'	16, 1	16, 1	2, 1	4, 1
cryst color, habit	yellow, block	colorless, plate	green, block	light yellow, block
ρ(calc), g cm^{-3}	1.220	1.381	1.188	1.217
μ(Mo Kα), mm^{-1}	0.123	1.489	0.120	0.121
temp, K	213(2)	100(2)	218(2)	213(2)
no. of reflns measd	29 964	26 461	10 251	26 441
no. of reflns indep	5040 [$R_{int} = 0.0338$]	5045 [$R_{int} = 0.0495$]	6627 [$R_{int} = 0.0291$]	9645 [$R_{int} = 0.0303$]
$R(F)$ $(I > 2\sigma(I))^{a}$	0.0423	0.0390	0.0860	0.0493
$R(wF^2)$ $(I > 2\sigma(I))^{b}$	0.1111	0.0855	0.2774	0.1195

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R(wF^2) = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, $P = [2F_c{}^2 + \max(F_o,0)]/3$.

washed with water, and recrystallized from toluene to afford bright yellow crystals (10.3 g, 53%). Mp: 205−206 °C (lit. 209−210 °C[34]). ^{1}H NMR (300.133 MHz, $CDCl_3$): δ 6.80−6.85 and 7.00−7.24 (br m, 20H, Ph), 4.90 (s, 2H, SiH_2). ^{13}C{H} NMR (75.403 MHz, $CDCl_3$): δ 157.50, 138.74, 135.20, 131.63, 129.62, 129.36, 128.09, 127.72, 126.63, 126.23. ^{29}Si NMR (99.36 MHz, INEPT, $CDCl_3$, TMS (δ 0.0)): δ −35.03; IR (KBr): ν_{Si-H} 2140 cm^{-1}.

1,1-Dihydro-2,3,4,5-tetraphenyl-1-germaclopenta-2,4-diene (Dihydrogermole) (2). The dichlorogermole starting material was prepared according to the literature.[7b] To a dry THF (100 mL) solution of dichlorogermole (1.0 g, 2 mmol) was added $LiAlH_4$ (1 M in THF, 2 mL, 2 mmol). The solution was quenched with methanol and evaporated to dryness, and the product was extracted and recrystallized from hexanes to afford pale yellow crystals (0.44 g, 51%). Mp: 190−192 °C (lit. 192−193 °C[35]). ^{1}H NMR (300.133 MHz, $CDCl_3$): δ 6.80−6.84 and 6.95−7.07 (br m, 20H, Ph), 5.36 (s, 2H, GeH_2). ^{13}C{H} NMR (75.403 MHz, $CDCl_3$): δ 153.54, 139.33, 138.99, 138.01, 129.72, 129.43, 127.85, 127.55, 126.28, 126.01. IR (KBr): ν_{Ge-H} 2053 cm^{-1} (lit. 2060[35]).

Oligo(tetraphenyl)silole 3a. 1 (1.0 g, 2.59 mmol), 0.2 mol % $H_2PtCl_6 \cdot xH_2O$, and 2 molar equiv of cyclohexene in toluene (10 mL) were vigorously refluxed for 24 h. The solution was passed through a sintered glass frit and evaporated to dryness under an Ar atmosphere. Dissolution with THF (1 mL) and precipitation with methanol (10 mL) yielded the oligosilole in 88%.

3b,c,d. 1 (1.0 g, 2.59 mmol) and 1 mol % of $RhCl(PPh_3)_3$ (**3b**) or $Pd(PPh_3)_4$ (**3c**) in toluene (10 mL) were placed under an Ar atmosphere and degassed through freeze−pump−thaw cycles. The reaction mixture was then vigorously refluxed for 72 h and then evaporated to dryness. THF (1 mL) was added to the reaction mixture, and the resulting solution was then poured into 10 mL of methanol. Polysilole was obtained as a pale yellow powder after filtration and freeze-drying. Addition of 2 equiv of cyclohexene with $RhCl(PPh_3)_3$ (**3d**) eliminates dimer precipitation and increases yield. **3b**: 62%, **3c**: 58%, **3d**: 82%. **3**: ^{1}H NMR (300.133 MHz, $CDCl_3$): δ 6.60−7.40 (br, m, Ph). ^{13}C{H} NMR (75.403 MHz, $CDCl_3$ (δ 77.00)): δ 125−132 (br m, Ph), 137−147 (silole carbons). ^{29}Si NMR (99.37 MHz, INEPT, $CDCl_3$, TMS (δ 0.0)): δ −31.8 (end-groups), −40.0 (backbone). IR (KBr): ν_{Si-H} 2146 cm^{-1}. CHN Anal. Calc: C: 87.4, H: 5.24. Found: C: 86.9, H: 5.19.

3e. 1 (0.5 g, 1.3 mmol), 1 mol % $RhCl(PPh_3)_3$, cyclohexene (2.6 mmol), and 5 mL of toluene were placed in an Emrys Optimizer microwave synthesizer for 2 h at 170 °C and 120 W. The solution was then evaporated to dryness. Dissolution with THF (1 mL) and precipitation with methanol (10 mL) yielded the oligsilole (78%).

Oligo(tetraphenyl)germoles 4a,b,c,d. Reaction conditions for preparing the oligogermole are the same as those for oligosilole. **4a**: 81%, **4b**: 50%, **4c**: 67%, **4d**: 49%. **4**: ^{1}H NMR (300.133 MHz, $CDCl_3$): δ 6.30−7.90 (br, m, Ph). ^{13}C{H} NMR (75.403 MHz, $CDCl_3$ (δ 77.00)): δ 124−130 (br m, Ph), 131−139 (germole carbons). IR (KBr): ν_{Ge-H} 2063 cm^{-1}. CHN Anal. Calc: C: 78.4, H: 4.70. Found: C: 78.2, H: 4.60.

Dihydrosilole Dimer (5). 1 (1.0 g, 2.59 mmol) and 1 mol % of $RhCl(PPh_3)_3$ in toluene (10 mL) were placed under an Ar atmosphere and degassed through freeze−pump−thaw cycles. The reaction mixture was vigorously refluxed for 72 h. The solid that precipitates during cooling was filtered and recrys-

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tallized from xylenes to afford bright yellow crystals (0.38 g, 38%). Mp ≥ 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$ (δ 7.26)): δ 6.4−7.4 (m, 40H, Ph), 5.30 (s, 2H). ^{13}C NMR (99.40 MHz, CD_2Cl_2 (δ 54.00)): δ 157.13, 139.27, 139.22, 137.99, 130.23, 129.95, 128.41, 127.76, 126.81, 126.52. ^{29}Si NMR (100 MHz, $CDCl_3$, TMS (δ 0.0)): δ −33.81 (dd, $J_{\mathrm{Si1-H1}} = 200$ Hz, $J_{\mathrm{Si1-H2}} = 8.4$ Hz). CHN Anal. Calc: C: 87.22, H: 5.49. Found: C: 86.67, H: 6.18. IR (KBr): $\nu_{\mathrm{Si-H}}$ 2112 cm^{-1}.

Methylsilole Dimer (6). Methylhydrosilole[36] (1.0 g, 2.5 mmol), 0.2 mol % $H_2PtCl_6 \cdot xH_2O$, and 2 molar equiv of cyclohexene in toluene (10 mL) were vigorously refluxed for 24 h. The solid that precipitates during cooling was filtered and recrystallized from toluene to afford bright yellow crystals (0.41 g, 40%). Mp ≥ 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$ (δ 7.26)): δ 6.7−6.8 and 6.9−7.2 (m, 40H, Ph), 0.19 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_3 (δ 77.00)): δ 154.6, 143.4, 139.9, 138.8, 130.3, 129.4, 127.9, 127.4, 126.3, 125.6, −6.0. ^{29}Si NMR (99.37 MHz, INEPT, $CDCl_3$, TMS (δ 0.0)): δ −9.34. CHN Anal. Calc: C: 87.16, H: 5.80. Found: C: 86.84, H: 5.87.

1,1-Dideuterometalloles (7, 8). Methods for synthesizing **7** and **8** are identical to the procedure described for preparing **2**, beginning with either dichlorosilole or dichlorogermole and reducing with $LiAlD_4$, and recrystallizing from toluene (**7**) or hexanes (**8**). **7**: 58%. CHN Anal. Calc: C: 86.55, H: 6.22. Found: C: 86.35, H: 6.37. Mp = 204−206 °C. IR (KBr): $\nu_{\mathrm{Si-D}}$ 1543 cm^{-1}. **8**: 52%. CHN Anal. Calc: C: 77.65, H: 5.58. Found: C: 77.62, H: 5.74. Mp = 191−193 °C. IR (KBr): $\nu_{\mathrm{Ge-D}}$ 1476 cm^{-1}.

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Supporting Information Available: Crystallographic information files (CIF) for compound **1**, **2**, **5**, **6**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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