

## Preparation and Photophysical Properties of Phosphino- and Phosphine Oxide-Linked Siloles

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## Introduction

The last two decades have witnessed a dramatic increase in the research of silole-based  $\pi$ -conjugated systems due to their distinctive electronic and photophysical properties arising from a low LUMO energy level due to  $\sigma^* - \pi^*$  conjugation between the exocyclic bonds at silicon with the  $\pi^*$  orbital of the butadiene unit.<sup>1</sup> Siloles have shown promising

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applications in organic light emitting diodes (OLEDs),<sup>2–4</sup> organic field-effect transistors (OFETs),<sup>5</sup> and photovoltaic devices,<sup>6</sup> and as sensors,<sup>4,7</sup> due to high electron mobility<sup>8</sup> and affinity<sup>9</sup> and strong photoluminescence.<sup>10</sup>

Extensive studies on the preparation, characterization, and reactivity of siloles have been reported over the last two decades.<sup>11</sup> Two key synthetic routes are generally used for the preparation of siloles. The reductive cyclization of bis(phenylethynyl)silanes has been used to prepare a number of 2,5-disubstituted-3,4-diphenylsiloles.<sup>12,13</sup> Another method involves the regioselective coupling of internal and terminal alkynes through a titanacyclopentadiene intermediate followed by halogenolysis to produce the corresponding 1,4dihalobutadienes. Subsequent lithium-halogen exchange with *n*BuLi followed by reaction with Si(OMe)<sub>4</sub> or a dihalosilane produces the silole.<sup>14</sup> The electronic properties of siloles can be fine-tuned depending upon the nature of the exocyclic substituents at the silicon center<sup>15</sup> or more significantly from the groups at the 2,5-positions of the silole ring.<sup>16</sup> In order to further explore the optimization of the electronic properties of siloles, we have examined the effects of incorporating phosphino or phosphine oxide groups into the conjugated framework either by direct attachment to the silole ring or by linking the heteroatom unit to the terminal positions of the conjugated groups in the 2,5positions. In addition, the presence of the reactive phosphino groups enables these systems to be building blocks for the construction of a variety of conjugated materials including the incorporation of transition metal centers. Recently,

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bis(diarylphosphino)dithioenosilole derivatives and the corresponding phosphine oxide systems have been prepared, and the photoluminescence was found to be significantly affected by the oxidation state of the phosphorus center.<sup>1</sup> The coordination chemistry of related phosphioras content tuted oligothiophenes with gold<sup>18</sup> and  $\pi$ -conjugated phosp-holes<sup>19</sup> through coordination of the phosphorus to a variety of transition metal centers has resulted in the formation of a diverse array of supramolecular architectures. The reductive cyclization method has also been used to prepare 2,5-disubstituted siloles containing 7-azaindolylaryl or 2,2'-dipyridylamino groups and the latter complex coordinated to zinc centers at the open nitrogen sites.<sup>20</sup> We now report the preparation and characterization of several 1,1-dimethyl-2,5-disubstituted-3,4-diphenylsiloles containing diphenylphosphino or diphenylphosphine oxide groups directly bound to or linked to the terminal positions of a conjugated organic group bound to the 2,5-positions of the silole ring. We also report the coordination chemistry of 1.1-dimethyl-2,5-bis(4'-diphenylphosphinophenyl)-3,4-diphenylsilole with (chloro)gold(tetrahydrothiopene) to produce the novel digold complex 1,1-dimethyl-2,5-bis(4'-diphenylphosphino(chlorogold)phenyl)-3,4-diphenylsilole.

## **Results and Discussion**

Several substituted silacyclopentadienes have been prepared that contain a diphenylphosphino (1a-5a) or phosphine oxide (1b-5b) group bound directly to the 2,5positions of the silole ring or linked at the terminal positions to a conjugated organic group, as shown in Chart 1. The new siloles were isolated as yellow to greenish-yellow solids for 1-5 and were generally characterized by multinuclear NMR, UV-vis, and fluorescence spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography (2b and 4a).

The five-membered silole ring of compounds 1-5 was formed utilizing the reductive cyclization method reported by Tamao and co-workers from reaction of bis(phenylethynyl)dimethylsilane with lithium naphthalenide.<sup>12</sup> Subsequent reactions were performed on the resulting 2,5dilithio-substituted silole to produce the final products as shown in Chart 1 and described in the following paragraphs. The intermediate 2,5-dilithio-substituted silole (R = Li, Chart 1) was reacted with 2 equiv of PPh<sub>2</sub>Cl to afford air- and moisture-sensitive compound 1a in 66% yield (Scheme 1). Oxidation of 1a with 30% H<sub>2</sub>O<sub>2</sub> afforded the corresponding phosphine oxide compound 1b in 62% yield (Scheme 1). The mixed phosphine/phosphine oxide compound **1a**,**b** was produced in 48% yield by the slow oxidation of **1a** in air. The phosphine oxides prepared in this study were found to be hygroscopic.

Compound **2a** was prepared in 54% yield from the reaction of 1,1-dimethyl-2,5-bis(*p*-bromophenyl)-3,4-diphenylsilole<sup>21</sup> with a slight excess of *n*-BuLi followed by 2 equiv of PPh<sub>2</sub>Cl, as shown in eq 1. The related silole, 1,1-dimethyl-2,5-bis(*m*-diphenylphosphinophenyl)-3,4-diphenylsilole, **3a**, was prepared in 63% yield by a similar procedure starting from the corresponding 2,5-bis(*m*-bromophenyl)-substituted silole. Both phosphine oxides **2b** and **3b** were synthesized in 93% and 89% yields from **2a** and **3a**, respectively, by treatment with 30% H<sub>2</sub>O<sub>2</sub> solution.



Compound **4b** was prepared in 72% yield by the coupling reaction<sup>13</sup> of 1,1-dimethyl-2,5-bis(chlorozinc)-3,4-diphenylsilole<sup>22</sup> with (4'-bromobiphenyl-4-yl)diphenylphosphine oxide in the presence of the catalyst,  $(Ph_3P)_2PdCl_2$  (Scheme 2). The silole **4a** was then prepared in 41% yield from **4b** by treatment with excess HSiCl<sub>3</sub> and NEt<sub>3</sub> (Scheme 2).<sup>23</sup>

The phosphine oxide-linked silole **5b** was prepared in 17% yield from the reaction of 1,1-dimethyl-2,5-bis(4-bromophenyl)-3,4-diphenylsilole<sup>21</sup> with diphenyl(4-ethynyl phenyl)-phosphine oxide<sup>24</sup> in the presence of CuI, Pd(PPh<sub>3</sub>)<sub>4</sub>, and NEt<sub>3</sub> (eq 2). The corresponding diphenylphosphino-terminated silole **5a** was prepared in 15% yield by treatment of **5b** with an excess of HSiCl<sub>3</sub> and NEt<sub>3</sub>.

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Coordination of the phosphine centers to gold was accomplished by reaction of silole **2a** with 2 equiv of (chloro)-gold(tetrahydrothiophene), [(Cl)Au(tht)],<sup>26</sup> to form the digold complex **9** as a yellow solid in 89% yield (eq 3). The structure **9** was confirmed by X-ray crystallography.



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The <sup>13</sup>C{<sup>1</sup>H} NMR spectra for the siloles **1–5** and **9** all exhibit resonances generally above about 135 ppm for the silole ring carbons,<sup>27</sup> and the <sup>29</sup>Si{<sup>1</sup>H} resonances were generally observed near 8–9 ppm except for siloles **1a** and **1b**, which were shifted slightly downfield at 15 and 20 ppm, respectively. The phosphine-linked siloles **2a–4a** exhibited singlet resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra between – 5 and – 6 ppm, whereas the signal of **1a** was observed slightly upfield at –12 ppm. The <sup>31</sup>P{<sup>1</sup>H} NMR resonances of the phosphine oxide-linked siloles **2b–5b** were observed near 29 ppm; however, the signal of **1b** was observed slightly upfield at 22 ppm. Coordination of the phosphorus centers to gold in complex **9** resulted in a downfield shift of the resonance to 32 ppm.

The electronic absorption and fluorescence data of 1–5 and 9 are summarized in Table 1. The UV–vis spectra exhibit absorption bands between 308 and 385 nm that are attributed to the  $\pi$ – $\pi^*$  transition of the silole ring (Figures 1 and 2).<sup>3g,20,22,28</sup> Siloles **5a** and **5b** show an additional absorption at 307 and 304 nm, respectively, which is assigned to the  $\pi$ – $\pi^*$  transition for the alkyne units.<sup>29</sup> The absorption maximum for silole **2a** is red-shifted by 15 nm compared to 1,1-dimethyl-2,3,4,5-tetraphenylsilole<sup>22</sup> (**2c**,  $\lambda_{abs} = 359$  nm) due to the presence of the phosphino group in **2a**. However, placement of the phosphino group in the *meta*-position of the aryl group as in **3a** or at the *para*-position of the biphenyl unit in **4a** results in essentially no change in the absorption maximum compared to **2c** and 1,1-dimethyl-2,5-bis-(biphenyl)-3,4-diphenylsilole<sup>22</sup> (**4c**,  $\lambda_{abs} = 381$  nm), respectively. The presence of a phosphino group has resulted in

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Table 1. Photoluminescent Data for Compounds 1-5 and 9

compound	$absorption^a \lambda_{abs}/nm$	$\log(\varepsilon)$	$\substack{\text{emission}^b\\\lambda_{\text{em}}/\text{nm}}$	$\phi_{ ext{F}}{}^{c}$
1a	384	4.26		
1a/1b	381	4.36		
2a	374	4.18	503	$0.69 \times 10^{-2}$
3a	360	4.14	485	$0.65 \times 10^{-2}$
4a	382	4.24	511	$1.59 \times 10^{-2}$
5a	385	4.38	514	$2.38 \times 10^{-2}$
1b	308	4.44		
2b	367	4.48	487	$0.24 \times 10^{-2}$
3b	360	4.36	474	$0.52 \times 10^{-2}$
4b	375	4.53	505	$1.41 \times 10^{-2}$
5b	383	4.56	512	$1.61 \times 10^{-2d}$
9	364	4.29	416	$1.21 \times 10^{-2}$

<sup>*a*</sup>Concentration:  $[M] = 1 \times 10^{-5} \text{ M}$  in CH<sub>2</sub>Cl<sub>2</sub> at 298 K. <sup>*b*</sup>Concentration:  $[M] = 1 \times 10^{-4} \text{ M}$  in CH<sub>2</sub>Cl<sub>2</sub> at 298 K. <sup>*c*</sup> Determined with reference to anthracene. <sup>*d*</sup> Absorption minimal above 350 nm. Defined maximum not observed between 260 and 375 nm.



Figure 1. Electronic absorption spectra of compounds 1a-5a in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K.



Figure 2. Electronic absorption spectra of compounds 1b-5b in  $CH_2Cl_2$  solution at 298 K.

bathochromic shifts in the absorption maxima of phosphinesubstituted thiophenes relative to the unsubstituted systems by enhancing the conjugation.<sup>30</sup> As expected, the absorption wavelength for 1-5 increases as the conjugation chain length at the 2,5-positions of the silole ring increases,<sup>25</sup> and silole **5a** exhibits the lowest energy absorption band in the current study at 385 nm. Upon oxidation, the phosphorus centers in siloles **2b**, **3b**, and **4b** exhibit little or no shift of the absorption



Figure 3. Emission spectra of compounds 2a-5a in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K. Excitation wavelengths (nm): 2a (429), 3a (394), 4a (447), 5a (419).

maxima to higher energy compared to the corresponding siloles, 2a, 3a, and 4a, respectively. However, a remarkable hypsochromic shift is observed for silole 1b compared to 1a, where the phosphorus centers are bound directly to the silole ring. A smaller shift of the absorption maximum to higher energy is observed for complex 9 ( $\lambda_{abs} = 364$  nm) and the phosphine oxide **2b** ( $\lambda_{abs} = 367 \text{ nm}$ ) compared to the silole **2a**  $(\lambda_{abs} = 374 \text{ nm})$ . Hypsochromic shifts in the absorption maxima have been observed for bis(diarylphosphine oxide)dithienosiloles ( $\lambda_{abs} = 361 \text{ nm}$ ) and the corresponding phosphine derivatives ( $\lambda_{abs} = 380 \text{ nm}$ ).<sup>17</sup> A similar trend was also observed for the absorption maxima for 2,5-bis-(diphenylphosphino)thiophene (PTP,  $\lambda_{abs} = 300$  nm), the related phosphine oxide (OTPTO,  $\lambda_{abs} = 273$  nm), and coordination complex (ClAu(PTP)AuCl,  $\lambda_{abs} = 276$  nm), where the latter complex exhibited a smaller hypsochromic shift compared to the oxide. The larger hypsochromic shift for the oxide (OTPTO) was suggested to possibly be due to the higher electronegativity of O compared to Au.<sup>18</sup>

The fluorescence spectra of 2-5 and 9 exhibit emission bands between 416 and 514 nm (Figures 3 and 4). The emission spectra for 2-5 also exhibit a shift to lower energy as the chain length increases. The siloles 1a, 1b, and the mixed phosphine/phosphine oxide 1a,b with the phosphino or phosphine oxide unit bound directly to the 2,5-positions of the silole ring, respectively, do not show any emission maxima. The absence of any emission in these compounds may be due to negligible overlap between the phosphorus lone pair and the  $\pi^*$  LUMO orbital of the ring. The emission spectra for the related 2-diphenylphosphino- and 2,5-(diphenylphosphino)thiophenes (PT and PTP, respectively) exhibit weak emission and a large Stoke's shift, and the emission bands were assigned to the  $\pi^*$ -n transition. These results are consistent with DFT calculations, which supported a HOMO with significant P lone-pair character and a LUMO localized primarily on the thienyl group.<sup>3</sup>

The emission maximum for complex **9** is blue-shifted significantly compared to silole **2a**. Coordination of the phosphorus centers in some phosphino(oligothiophenes) to gold centers has also resulted in blue shifts in the emission maxima compared to the free ligand.<sup>18,30</sup> Complexation of zinc centers to a 2,2'-dipyridylamino-functionalized silole has also been reported to result in a blue shift of the absorption and emission maxima due to an alteration of the conjugation with the silole ring.<sup>20</sup> The photoluminescent

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Figure 4. Emission spectra of compounds 2b-5b in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K. Excitation wavelengths (nm): 2b (403), 3b (394), 4b (435), 5b (436).

quantum efficiencies were determined for siloles 1-5 and 9 in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature, and the moderate values observed are similar of those reported for other siloles.<sup>22,25</sup> Solid-state luminescent measurements could not be performed due to the limitations of our spectrometer. However, solid samples of compounds **2a**, **2b**, **3a**, **3b**, **4b**, **5a**, and **5b** were exposed to UV light from a hand-held black light, and all showed fluorescence, whereas compounds **1a**,**b** and **1b** did not.

X-ray Crystallography. The molecular structures of 2b, 4a, and 9 were determined by X-ray crystallography and are shown in Figures 5, 6, and 7 respectively. Two unique molecules of 2b were found in the asymmetric unit, and only one of these molecules is shown in Figure 5. The phosphorus center P2 and an associated phenyl group are disordered in 4a. The central silole ring in 2b, 4a, and 9 is planar with a tetrahedral environment at the silicon centers. The four aryl substituents bound to the silole ring carbons adopt a noncoplanar propeller-like arrangement. The dihedral angles between the aryl groups in the 2,5-positions of 2b and 4a and the silole ring were 54.9-55.7° and 41.9-49.6° respectively. The molecular structures of 2b and 4a are similar to 1,1-dimethyl-2,3,4,5-tetraphenylsilole<sup>31</sup> and a series of structurally characterized 1,1-dimethyl-2,5-bis(p-monosubstituted phenyl)-3,4-diphenylsiloles.<sup>22</sup> The P-O distances in **2b** (1.41-1.43 Å) are slightly shorter than those observed for OPPh<sub>3</sub> (1.48 Å).<sup>32</sup>

The two gold centers in **9** (Figure 7) are coordinated to one phosphorus center at each end of ligand **2a** in an almost linear coordination with Cl–Au–P angles of 177.64(7)° and 178.73(8)°. The Au–Cl and Au–P bond lengths of ca. 2.28–2.29 and 2.25–2.26 Å, respectively, are similar to those observed for the related chloro(triphenylphosphine)gold, which exhibited an Au–Cl distance of 2.279(3) Å, an Au–P distance of 2.235(3) Å, and a P–Au–Cl angle of 179.68(8)°.<sup>33</sup> The dihedral angles between the aryl groups in the 2,5-positions of **9** and the silole ring were 49.2–59.0° and



Figure 5. Molecular structure of 2b (with thermal ellipsoids shown at the 50% probability level) showing one of the two unique molecules in the unit cell. Selected bond distances (Å) and angles (deg): Si1-C1 = 1.865(5), Si1-C4 = 1.873(5), Si1-C5 = 1.839(5), Si1-C6 = 1.858(5), C1-C2 = 1.360(7), C2-C3 = 1.513(7), C3-C4 = 1.364(7), P1-O1 = 1.435(5), P1-C22 = 1.803(5), P1-C25 = 1.780(6), P1-C31 = 1.794(6),P2-O2 = 1.415(5), P2-C40 = 1.805(5), P2-C43 = 1.794(6),P2-C49 = 1.792(6); C5-Si1-C6 = 111.5(2), C1-Si1-C4 = 92.1(2), C2 -C1-Si1 = 108.3(4), C3-C4-Si1 = 108.3(4), C1-C2-C3 = 115.8(4), C4-C3-C2 = 115.2(4), C25-P1-C22 = 106.9(3), C25-P1-C31 = 106.5(3), C31 -P1-C22 =106.3(3), O1-P1-C22 = 111.6(3), O1-P1-C25 = 115.2(3),O1-P1-C31 = 109.9(3), C49-P2-C40 = 105.6(2), C49-P2-C43 = 106.7(3), C43-P2-C40 = 105.4(2), O2-P2-C40 =113.2(3), O2-P2-C49 = 111.9(3), O2-P2-C43 = 113.4(3).



Figure 6. Molecular structure of 4a (with thermal ellipsoids shown at the 30% probability level). Selected bond distances (Å) and angles (deg): Si1-C1 = 1.875(7), Si1-C4 = 1.883(7), Si1-C5 = 1.864(7), Si1-C6 = 1.868(7), C1-C2 = 1.341(9), C2-C3 = 1.535(9), C3-C4 = 1.355(9), P1-C28 = 1.829(8), P1-C31 = 1.843(9), P1-C37 = 1.830(9), P2-C52 = 1.875(11), P2-C55 = 1.831(12), P2-C61 = 1.778(10), P2'-C52 = 1.825(16), P2'-C55 = 1.900(19); C5-Si1-C6 = 108.3(3), C1-Si1-C4 = 91.8(3), C2-C1-Si1 = 109.2(5), C3-C4-Si1 = 107.8(5), C1-C2-C3 = 115.0(6), C4-C3-C2 = 116.1(6), C28-P1-C37 = 102.2(4), C28-P1-C31 = 102.2(4), C37-P1-C31 = 100.7(4), C61-P2-C55 = 105.9(7), C61-P2-C52 = 111.0(7), C55-P2-C52 = 96.5(6), C52-P2'-C55 = 95.9(8).

are only slightly larger than those observed for 2b. The solidstate structure of 9 shows no short intermolecular Au $\cdots$ Au interactions.

In conclusion, we prepared 1,1-dimethyl-2,5-disubstituted-3,4-diphenylsiloles terminated at the 2,5-positions with a phosphino or phosphine oxide group that show blue-green luminescence in solution with the notable absence of emission from the siloles **1a** and **1b**, where the phosphine units are directly bound to the ring. The phosphino-linked siloles can

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Figure 7. Molecular structure of 9 (with thermal ellipsoids shown at the 50% probability level). Selected bond distances (Å) and angles (deg): Au1-P1 = 2.2267(18), Au1-C11 =2.2941(17), Au2-P2 = 2.225(2), Au2-C12 = 2.282(2),  $Au1\cdots$ Au2 = 16.8, Si1-C1 = 1.875(7), Si1-C4 = 1.875(8), Si1-C5 = 1.860(8), Si1-C6 = 1.858(9), C1-C2 = 1.350(10), C2-C3 =1.508(10), C3-C4 = 1.366(10), P1-C10 = 1.809(7), P1-C31 = 1.813(7), P1-C37 = 1.825(7), P2-C28 = 1.781(7), P2-C49 = 1.821(7), P2-C43 = 1.834(9); P1-Au1-Cl1 = 177.64(7),P2-Au2-Cl2 = 178.73(8), C10-P1-C37 = 107.3(3), C10-P1-C31=104.4(3), C10-P1-Au1=112.1(2), C37-P1-C31= 105.3(3), C37-P1-Au1 = 114.1(2), C31-P1-Au1 = 113.0(2),C28-P2-C49 = 107.3(3), C28-P2-C43 = 105.9(4), C49-P2-C43 = 105.5(4), C28-P2-Au2 = 112.6(3), C49-P2-Au2 =114.2(3), C43-P2-Au2 = 110.8(3), C5-Si1-C6 = 109.9(4),C1-Si1-C4 = 91.3(3), C2 -C1-Si1 = 108.7(5), C3-C4-Si1 = 108.8(5), C1-C2-C3 = 116.2(6), C4-C3-C2 = 114.9(7),C28-P1-C37 = 102.2(4), C28-P1-C31 = 102.2(4), C37-P1-C31=100.7(4), C61-P2-C55 = 105.9(7), C61-P2-C52 = 111.0(7), C55-P2-C52 = 96.5(6), C52-P2'-C55 = 95.9(8).

be used as precursors to the corresponding phosphine oxides (and vice versa) as well as building blocks for the formation of luminescent organometallic complexes through coordination of the phosphorus centers to transition metals, as demonstrated by the formation of the digold complex 9. The nature of the environment at the phosphorus center has a notable impact on the electronic properties of the siloles studied. The absorption and emission maxima for the phosphino-terminated siloles were found to be at lower energy than the corresponding phosphine oxides especially when the conjugated chain linking the silole to the phosphino group was small or zero. The coordination of the phosphino groups in 2a to gold to give complex 9 resulted in a relatively small blue shift in the absorption maximum of 9 but a significant shift to higher energy in the emission spectrum probably due to reduced conjugation and an increase in the HOMO-LUMO energy gap. Thus, the coordination chemistry of the phosphino-linked siloles with metal centers will enable us to tune the emission color by altering the nature of the silole and metal center used. Further studies involving the coordination of the phosphino groups to other transition metals and their effects on the absorption and emission of these silolebased systems are in progress.

## **Experimental Section**

**General Procedures.** All reactions were carried out under an inert atmosphere of argon or nitrogen using standard Schlenk techniques or a drybox using solvents dried by standard procedures. Dichlorodimethylsilane and trichlorosilane were purchased from Aldrich Chemical Co. and distilled over  $K_2CO_3$  prior to use. Other commercially available reagents were used as received. Chloroform- $d_1$  was purchased from Cambridge

Isotopes, Inc., and dried over activated molecular sieves before use. The following compounds were prepared by literature methods, 1,1-dimethyl-2,5-bis(4'-bromophenyl)-3,4-diphenylsilole,<sup>21</sup> 1,1-dimethyl-2,5-dibromo-3,4-diphenylsilole,<sup>34</sup> dimethylbis(phenylethynyl)silane,<sup>35</sup>4-(bromophenyl)diphenylphosphine,<sup>36</sup> (4-bromophenyl)diphenylphosphine oxide,<sup>37</sup> ZnCl<sub>2</sub>(TMEDA),<sup>38</sup>  $(Ph_3P)_2PdCl_2$ ,<sup>39</sup> and [AuCl(tht)] (tht = tetrahydrothiophene).<sup>26</sup> The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>29</sup>Si{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker ARX-500 MHz in CDCl3 at room temperature. Proton and carbon NMR chemical shifts ( $\delta$ ) were referenced to the residual peaks of the solvents used. Silicon NMR chemical shifts were referenced to external SiMe<sub>4</sub>. Phosphorus NMR chemical shifts are referenced relative to external H<sub>3</sub>PO<sub>4</sub>. Mass spectral data were obtained in either EI or FAB mode with nitrobenyl alcohol (NBA) on a JEOL M Station-JMS700. UV-vis and fluorescence spectra were recorded on Cary 50 Bio UV-visible and Cary Eclipse Fluorescence spectrophotometers, respectively. Emission spectra were measured using the  $\lambda_{max}$  value for each compound obtained from the absorption spectra and also by the computer-optimized excitation energy, resulting in spectra of identical shape and position but with differing intensity. Elemental analysis determinations were obtained from Atlantic Microlabs, Inc., Norcross, GA. X-ray crystallographic determinations were performed on a Bruker Apex II diffractometer equipped with a CCD area detector.

Preparation of 1,1-Dimethyl-2,5-bis(diphenylphosphine)-3,4diphenylsilole (1a). A mixture of lithium wire that was cut into small pieces (84 mg, 12 mmol) and naphthalene (1.54 g, 12.1 mmol) in 40 mL of dry THF was stirred at room temperature for 5 h to produce a deep green solution containing lithium naphthalenide. A solution of dimethylbis(phenylethynyl)silane (0.79 g, 3.0 mmol) in 5 mL of THF was added to the LiNaph solution dropwise over 5 min at room temperature. After stirring for 10 min the mixture was cooled to -78 °C. A solution of Ph2PCl (1.6 g, 7.0 mmol) in 10 mL of THF was added dropwise and the mixture stirred for 2 h at low temperature. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed by under reduced pressure, and the crude reaction mixture was subjected to silica gel column chromatography under argon (neat hexane then hexane/CH<sub>2</sub>Cl<sub>2</sub>, 4:1). Compound 1a was obtained as an airsensitive yellow solid in 66% yield (1.25 g). Mp: 159–161 °C. <sup>1</sup>H NMR (500 MHz): δ 7.39-7.34 (m, 8H, ArH), 7.29-7.25 (m, H, ArH, overlapping with CHCl<sub>3</sub> solvent), 7.00-6.95 (m, 6H, ArH), 6.89–6.86 (m, 4H, ArH), -0.59 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  166.6 (dd,  $J_{PC} = 27, 5.5$  Hz), 140.8 (d,  $J_{\rm PC} = 21$  Hz), 139.6 (d,  $J_{\rm PC} = 7$  Hz), 138.7 (d,  $J_{\rm PC} = 11$  Hz), 134.0 (d,  $J_{PC} = 20$  Hz), 129.2 (d,  $J_{PC} = 3$  Hz), 128.5, 128.3 (d,  $J_{PC} = 7$  Hz), 127.2, 126.9, -2.7.  $^{29}Si\{^{1}H\}$  NMR (99 MHz, DEPT):  $\delta$  15.1 (t,  $J_{PSi} = 5$  Hz).  $^{31}P\{^{1}H\}$  NMR (202 MHz):  $\delta$  -12.2. HRMS (EI): m/z calcd for C<sub>42</sub>H<sub>36</sub>P<sub>2</sub>Si, 630.20615; found, 630.2067. Anal. Calcd for C42H36P2Si: C, 79.97; H, 5.75. Found: C, 79.88; H, 5.76.

**1,1-Dimethyl-2,5-bis(diphenylphosphineoxide)-3,4-diphenylsilole (1b).** Compound **1b** was prepared according to the procedure described for the preparation of diphenyl-[(4-trimethylsilylethynyl)phenyl]phosphine oxide.<sup>24</sup> To a solution of **1a** (1.9 g, 3.0 mmol) in 50 mL each of dichloromethane and methanol was slowly added hydrogen peroxide (30% solution, 1.8 mL).

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After stirring for 2 h the resulting mixture was quenched with aqueous Na<sub>2</sub>SO<sub>3</sub> solution and then extracted with dichloromethane. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude reaction mixture was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/acetone, 5:1) to afford compound 1b as a white solid (1.23 g, 62% yield). Mp: 266-267 °C. An analytically pure sample of 1b was dried under vacuum over P2O5 overnight and was found to contain 0.7 molecule of water per molecule of 1b based on integration of the H<sub>2</sub>O and SiMe resonances in the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (500 MHz):  $\delta$  7.52–7.46 (m, 8H, ArH), 7.36-7.31 (m, 4H, ArH), 7.28-7.22 (m, overlapping with CHCl<sub>3</sub>, 8H, ArH), 6.74-6.69 (m, 2H, ArH), 6.66-6.58 (m, 8H, ArH), 0.09 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz): δ 169.2 (d,  $J_{\rm PC} = 20$  Hz), 140.9 (dd,  $J_{\rm PC} = 86, 2$  Hz), 137.0 (d,  $J_{\rm PC} = 8$  Hz), 134.0 (d,  $J_{PC} = 105$  Hz), 131.5 (d,  $J_{PC} = 10$  Hz), 131.3, 129.2, 128.2 (d,  $J_{PC} = 105$  Hz), 127.1, 126.7, -3.3. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  20.5 (t, <sup>2</sup> $J_{Psi} = 19$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  22.5. Anal. Calcd for C<sub>42</sub>H<sub>36</sub>O<sub>2</sub>P<sub>2</sub>Si · 0.7H<sub>2</sub>O: C, 74.69; H, 5.58. Found: C, 74.73; H, 5.40.

1,1-Dimethyl-2-(diphenylphosphine)-5-(diphenylphosphineoxide)-3,4-diphenylsilole (1a,b). Compound 1a (1.0 g, 1.6 mmol) was dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the resulting solution was exposed to air for one week. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to afford **1a**,**b** as a slightly air sensitive yellow solid (0.49 g, 48%). Mp: 211–212 °C. <sup>1</sup>H NMR (500 MHz): δ 7.54-7.46 (m, 6H, ArH), 7.36-7.30 (m, 8H, ArH), 7.28-7.19 (m, overlapping with CHCl<sub>3</sub>, 14H, ArH), 6.90-6.84 (m, 4H, ArH), 6.77-6.64 (m, 8H, ArH),-0.22 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  169.4 (d,  $J_{PC} = 5$  Hz), 166.0 (dd,  $J_{PC} = 25$ , 19 Hz), 146.0  $(dd, J_{PC} = 24, 2 Hz), 138.7 (d, J_{PC} = 6 Hz), 137.9 (d, J_{PC} = 8 Hz),$ 137.5 (d,  $J_{PC}$  = 11 Hz), 137.0, 136.3, 135.0, 134.1 (d,  $J_{PC}$  = 19 Hz),  $131.5 (d, J_{PC} = 9 Hz), 131.0 (d, J_{PC} = 3 Hz), 129.2, 129.1 (d, J_{PC} = 2 Hz), 129.2 Hz$ 3 Hz), 128.7, 128.3 (d,  $J_{PC} = 7$  Hz), 128.1 (d,  $J_{PC} = 11$  Hz), 127.2, 127.0, 126.9, 126.8, -3.1.<sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  17.7 (dd,  $J_{SiP} = 18$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  23.1, -10.9. HRMS (FAB): m/z calcd for C42H36OP2SiH, 647.2088; found,  $647.2100 (M + H)^+$ 

1,1-Dimethyl-2,5-bis(4'-diphenylphosphinophenyl)-3,4-diphenylsilole (2a). To a solution of 1,1-dimethyl-2,5-bis(4'-bromophenyl)-3,4-diphenylsilole (1.5 g, 2.62 mmol) in diethyl ether (100 mL) was added TMEDA (1.2 mL, 7.8 mmol). The mixture was cooled to -78 °C, and a solution of *n*-butyllithium in hexane (2.5 M, 3.2 mL, 7.8 mmol) was added dropwise. The mixture was stirred for 1.5 h, then warmed to 0 °C, stirred for 1 h, and recooled to -78 °C. A solution of chlorodiphenylphosphine (3.0 g, 7.8 mmol) in 5 mL of THF was added dropwise and the solution stirred at -78 °C for 1 h. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and the crude reaction mixture subjected to alumina column chromatography (hexane/CH2Cl2, 5:1) to afford compound 2a as a yellow powder (1.1 g, 54% yield). Mp: 103-105 °C. <sup>1</sup>H NMR (500 MHz): δ 7.38-7.33 (m, 10H, ArH), 7.32-7.26 (m, 8H, ArH), 7.11-7.00 (m, 12H, ArH), 6.95-6.91 (m, 4H, ArH), 6.85-6.80 (m, 4H, ArH), 0.51 (s, 6H, SiMe).  $^{13}C(^{1}H)$  NMR (125 MHz):  $\delta$  154.8, 141.8, 140.7, 138.8, 137.6 (d,  $J_{\rm PC} = 11$  Hz), 133.9 (d,  $J_{\rm PC} = 9$  Hz), 133.9 (d,  $J_{\rm PC} = 19$  Hz), 133.5 (d,  $J_{PC} = 19$  Hz), 130.1, 129.1 (d,  $J_{PC} = 7$  Hz), 128.8, 128.6 (d,  $J_{PC} = 7$  Hz), 127.6, 126.6, -3.6. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta 8.0$ . <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta -5.7$  (s). Anal. Calcd for C<sub>54</sub>H<sub>44</sub>P<sub>2</sub>Si: C, 82.84; H, 5.66. Found: C, 82.65; H, 5.94.

**1,1-Dimethyl-2,5-bis**(4'-diphenylphosphinophenyloxide)-3,4-diphenylsilole (2b). Compound 2b was prepared by a similar procedure as that used for the preparation of 1b but using 2a (2.3 g, 3.0 mmol) and  $H_2O_2$  (30% solution, 1.7 mL). The crude product was subjected to alumina column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub>, 4:1) to afford compound 2b as a yellow powder (2.27 g, 93% yield). Mp: 282 °C (dec). X-ray quality crystals of 2b were obtained by slow diffusion of hexanes into a

CH<sub>2</sub>Cl<sub>2</sub> solution of **2b** at room temperature. <sup>1</sup>H NMR (500 MHz):  $\delta$  7.66–7.60 (m, 8H, ArH), 7.55–7.52 (m, 4H, ArH), 7.47–7.36 (m, 12H, ArH), 7.04–6.96 (m, 10H, ArH), 6.78–6.74 (m, 4H, ArH), 0.47 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  155.7, 144.0 (d,  $J_{PC} = 3$  Hz), 141.9, 138.0, 133.2, 132.4, 132.2 (d,  $J_{PC} = 10$  Hz), 132.0 (d,  $J_{PC} = 7$  Hz), 131.9, 129.9, 128.8 (d,  $J_{PC} = 12$  Hz), 128.6 (d,  $J_{PC} = 12$  Hz), 127.7, 126.9, –3.8. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  8.8. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  29.2. HRMS(NaI): m/z calcd for C<sub>54</sub>H<sub>44</sub>O<sub>2</sub>P<sub>2</sub>SiNa, 837.2483; found, 837.2480 (M + Na)<sup>+</sup>. Anal. Calcd for C<sub>54</sub>H<sub>44</sub>OP<sub>2</sub>Si: C, 79.58; H, 5.44. Found: C, 78.49; H, 5.50.

Compound **2b** was also synthesized by an alternative route as described for the preparation of **4b** using lithium naphthalenide (8 mmol), bis(phenylethynyl)dimethylsilane (0.52 g, 2.0 mmol), ZnCl<sub>2</sub>(TMEDA) (2.2 g, 8.8 mmol), 4'-bromophenyl)diphenyl-phosphine oxide (1.6 g, 4.4 mmol), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (80 mg, 0.11 mmol). The crude residue was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/acetone, 5:1) to afford compound **2b** as a yellow powder (1.27 g, 78% yield).

1,1-Dimethyl-2,5-bis(3'-diphenylphosphinophenyl)-3,4-diphenylsilole (3a). Compound 3a was prepared by a similar procedure as that used for the preparation of 2a but using 1,1-dimethyl-2,5bis(3'-bromophenyl)-3,4-diphenylsilole (7) (1.5 g, 2.6 mmol), TMEDA (1.2 mL, 7.8 mmol), n-butyllithium (2.5 M in hexane, 3.2 mL, 7.8 mmol), and chlorodiphenylphosphine (3.0 g, 7.8 mmol). The crude product was subjected to alumina column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1). Compound 3a was isolated as a yellow powder (1.29 g, 63% yield). Mp: 84-86 °C. <sup>1</sup>H NMR (500 MHz): δ 7.36-7.29 (m, 12H, ArH), 7.23-7.17 (m, 8H, ArH), 7.12-7.06 (m, 4H, ArH), 7.00-6.94 (m, 6H, ArH), 6.89-6.83 (m, 4H, ArH), 6.76-6.70 (m, 4H, ArH), 0.18 (s, 6H, SiMe). <sup>13</sup>C $\{^{1}H\}$  NMR (125 MHz):  $\delta$  154.3, 141.9, 140.3 (d,  $J_{PC} = 5$  Hz), 138.6, 137.4 (d,  $J_{PC} = 11$  Hz), 136.8 (d,  $J_{PC} = 10$ Hz), 134.1, 133.9 (d,  $J_{PC} = 20$  Hz), 131.3 (d,  $J_{PC} = 25$  Hz), 130.0, 129.0, 128.7, 128.6 (d,  $J_{PC} = 7$  Hz), 128.2 (d,  $J_{PC} = 9$  Hz), 127.6, 126.4, -4.1. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  8.1. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  – 5.3. Anal. Calcd for C<sub>54</sub>H<sub>44</sub>P<sub>2</sub>Si: C, 82.84; H, 5.66. Found: C, 82.09; H, 5.66.

1,1-Dimethyl-2,5-bis(3'-diphenylphosphinophenyloxide)-3,4-diphenylsilole (3b). Compound 3b was prepared by a similar procedure to that used for the preparation of 1b but using 3a (2.3 g, 3.0 mmol) and H<sub>2</sub>O<sub>2</sub> (30% solution, 1.7 mL). The crude product was subjected to alumina column chromatography (hexane/ CH<sub>2</sub>Cl<sub>2</sub>, 4:1). Compound **3b** was recrystallized from acetone/ hexane and was isolated as a yellow powder (2.1 g, 89% yield). Mp: 94-95 °C. An analytically pure sample of 3b was dried under vacuum over P2O5 overnight and was found to contain 0.63 molecule of water and 0.14 molecule of acetone per molecule of 3b based on integration of these signals and the SiMe resonances in the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (500 MHz): δ 7.53-7.44 (m, 14H, ArH), 7.38-7.43 (m, 8H, ArH), 7.27-7.23 (m, overlapping with CHCl<sub>3</sub>, 2H, ArH), 7.10-7.07 (m, 2H, ArH), 7.10-7.06 (m, 2H, ArH), 7.02-6.92 (m, 6H, ArH), 6.68–6.64 (m, 4H, ArH), 0.21 (s, 6H, SiMe).  ${}^{13}C{}^{1}H{}$ NMR (125 MHz):  $\delta$  154.5, 141.0, 139.6 (d,  $J_{PC} = 12$  Hz), 137.6, 132.6, 132.5, 131.9 (d,  $J_{PC} = 11$  Hz), 131.7, 131.6 (d,  $J_{PC} = 10$ Hz), 131.5 (d,  $J_{PC}$  = 3 Hz), 129.5, 129.0 (d,  $J_{PC}$  = 9 Hz), 128.2 (d,  $J_{PC}$  = 12 Hz), 128.1 (d,  $J_{PC}$  = 12 Hz), 127.3, 126.2, -4.5. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  8.5. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  29.2. HRMS (FAB): m/z calcd for C<sub>54</sub>H<sub>44</sub>O<sub>2</sub>P<sub>2</sub>SiH, 815.2664; found, 815.2635 (M + H)<sup>+</sup>. Anal. Calcd for  $\tilde{C}_{54}H_{44}$ -O<sub>2</sub>P<sub>2</sub>Si · 0.63H<sub>2</sub>O+0.14(CH<sub>3</sub>)<sub>2</sub>CO: C, 78.33; H, 5.57. Found: C, 77.98; H, 5.49.

**1,1-Dimethyl-2,5-bis**(4'-diphenylphosphine-4-biphenyl)-3,4-diphenylsilole (4a). To a mixture of 4b (1.0 g, 1.0 mmol) and Et<sub>3</sub>N (5.4 mL, 35 mmol in dry toluene (45 mL) was added HSiCl<sub>3</sub> (2 mL, 17.8 mmol) at 0 °C. The reaction mixture was refluxed for 18 h, then cooled to room temperature. The mixture was diluted with Et<sub>2</sub>O (50 mL) and quenched with aqueous NaHCO<sub>3</sub>. The resulting mixture was filtered through Celite, and the organic

layer was dried over MgSO<sub>4</sub>, then concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1) to afford compound **4a** as a yellow solid (0.39 g, 41% yield). Mp: 217 °C (dec). X-ray quality crystals of **4a** were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of **4a** at room temperature. <sup>1</sup>H NMR (500 MHz):  $\delta$  7.47–7.44 (m, 4H, ArH), 7.32–7.29 (m, 4H, ArH), 7.27–7.22 (m, overlapping with CHCl<sub>3</sub>, 24H, ArH), 6.97–6.91 (m, 10H, ArH), 6.79–6.76 (m, 4H, ArH), 0.47 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  154.5, 141.4, 141.2, 139.3, 139.0, 137.4 (d,  $J_{PC} = 3$  Hz), 137.3, 135.9 (d,  $J_{PC} = 10$  Hz), 134.3 (d,  $J_{PC} = 7$  Hz), 127.7, 126.9 (d,  $J_{PC} = 7$  Hz), 126.6, 126.5, -3.3. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  8.0. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  –6.0. Anal. Calcd for C<sub>66</sub>H<sub>52</sub>P<sub>2</sub>Si·1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 81.70; H, 5.46. Found: C, 82.12; H, 5.54.

1,1-Dimethyl-2,5-bis(4'-diphenylphosphineoxide-4-biphenyl)-3,4-diphenylsilole (4b). A mixture of lithium wire cut into small pieces (56 mg, 8 mmol) and naphthalene (1.038 g, 8 mmol) in 12 mL of THF was stirred at room temperature for 5 h to form a deep green solution of lithium naphthalenide (LiNaph). A solution of dimethylbis(phenylethynyl)silane (0.52 g, 2.0 mmol) in 5 mL of THF was added to the LiNaph solution dropwise over 5 min at room temperature. After stirring for 10 min, the mixture was cooled to 0 °C and ZnCl<sub>2</sub>(TMEDA) (2.2 g, 8.8 mmol) was added as a solid to the mixture, followed by dilution with THF (15 mL) to give a dark green suspension. After stirring for an additional hour at room temperature, (4'-bromobiphenyl-4-yl)diphenylphosphine oxide (1.9 g, 4.4 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (80 mg, 0.11 mmol) were added to the resulting suspension. The mixture was heated to reflux and stirred for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation, and the crude residue subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 5:1) to afford compound 4b as a yellow powder (1.39 g, 72% yield). Mp: 261 °C (dec). An analytically pure sample of 4b was dried under vacuum over P<sub>2</sub>O<sub>5</sub> overnight and was found to contain 1 molecule of water per molecule of 4b based on integration of the H<sub>2</sub>O and SiMe resonances in the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (500 MHz): δ 7.73-7.62 (m, 18H, ArH), 7.57-7.53 (m, 4H, ArH), 7.50-7.44 (m, 8H, ArH), 7.42-7.38 (m, 4H, ArH), 7.05-7.01 (m, 10H, ArH), 6.87-6.83 (m, 4H, ArH), 0.55 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  154.8, 144.4 (d, <sup>3</sup>J<sub>PC</sub> = 3 Hz), 141.4, 140.0, 138.9, 136.8, 133.2, 132.7 (d,  $J_{PC} = 11$  Hz), 132.3 (d,  $J_{PC} = 10$  Hz), 132.1 (d,  $J_{PC} = 3$  Hz), 131.3, 130.4, 130.1, 129.6, 128.7 (d,  $J_{PC} = 21$  Hz), 127.7, 126.93, 126.91 (d,  $J_{PC} = 12$  Hz), 126.6, -3.4. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$ 8.2. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  29.2. HRMS (NaI): m/z calcd for  $C_{66}H_{52}O_2P_2SiNa$ , 989.3109; found, 989.3110 (M + Na)<sup>+</sup>. Anal. Calcd for C<sub>66</sub>H<sub>52</sub>O<sub>2</sub>P<sub>2</sub>Si·H<sub>2</sub>O: C, 80.46; H, 5.52. Found: C,79.85; H, 5.26.

1,1-Dimethyl-2,5-bis{[(4-diphenylphosphine)phenylethynyl]phenyl}-3,4-diphenylsilole (5a). Compound 5a was prepared by a similar procedure to that used for the preparation of 4a. To a solution of compound 5b (1.0 g, 1.0 mmol) and Et<sub>3</sub>N (5.4 mL, 35 mmol) in dry toluene (45 mL) was added HSiCl<sub>3</sub> (2 mL, 17.8 mmol) at 0 °C. The reaction mixture was refluxed for 18 h, then cooled to room temperature. The mixture was diluted with Et<sub>2</sub>O (50 mL) and quenched with aqueous NaHCO<sub>3</sub>. The organic layer was separated and dried over MgSO<sub>4</sub>, then concentrated under reduced pressure. The crude mixture was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1) to afford compound **5a** as a yellow solid (0.15 g, 15% yield). Compound 5a could not be obtained in analytically pure form, but the major impurities were assigned to common reagents/ solvents (as determined by NMR spectroscopy, see Supporting Information) that should not affect the photophysical properties. Mp: 131–132 °C. <sup>1</sup>H NMR (500 MHz): δ 7.46–7.42 (m, 4H, ArH), 7.38-7.23 (m, overlapping with CHCl<sub>3</sub>, 26H, ArH), 7.06-7.00 (m, 8H, ArH), 6.93-6.89 (m, 4H, ArH), 6.83-6.79

(m, 4H, ArH), 0.50 (s, 6H, SiMe).  ${}^{13}C{}^{1}H{}$  NMR (125 MHz):  $\delta$  154.9, 141.8, 140.4, 138.6, 137.9 (d,  $J_{PC} = 12$  Hz), 136.9 (d,  $J_{PC} = 11$  Hz), 134.0 (d,  $J_{PC} = 19$  Hz), 133.6 (d,  $J_{PC} = 19.3$  Hz), 131.6, 131.5, 130.1, 129.1 (d,  $J_{PC} = 7$  Hz), 128.8 (d,  $J_{PC} = 7$  Hz), 127.8, 126.7, 123.9, 120.3, 91.0, 89.5, -3.6.  ${}^{29}Si{}^{1}H{}$  NMR (99 MHz, DEPT):  $\delta$ 8.2.  ${}^{31}P{}^{1}H{}$  NMR (202 MHz):  $\delta$  -4.9. HRMS (FAB, NaI): m/z calcd for  $C_{70}H_{52}P_2SiH$ , 983.3392; found, 983.3412 (M + H)<sup>+</sup>.

1,1-Dimethyl-2,5-bis{[(4-diphenylphosphineoxide)phenylethynyl]phenyl}-3,4-diphenylsilole (5b). To a solution of 1,1-dimethyl-2,5-bis(4'-bromophenyl)-3,4-diphenylsilole (0.50 g, 0.87 mmol) and diphenyl-(4-ethynylphenyl)phosphine oxide (0.55 g, 1.8 mmol) in a mixture of toluene (75 mL) and triethylamine (20 mL) were added CuI (9.5 mg, 0.05 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 g, 0.05 mmol). The resulting mixture was stirred for 24 h at 50 °C, then allowed to cool to room temperature and concentrated under vacuum. The residue was subjected to silica gel column chromatography  $(CH_2Cl_2/(CH_3)_2CO, 10:1)$  to afford compound 5b as a yellow solid (0.15 g, 17% yield). Mp: 149 °C (dec). An analytically pure sample of 5b was dried under vacuum over P2O5 overnight and was found to contain 1.7 molecules of water per molecule of 5b based on integration of the H<sub>2</sub>O and SiMe resonances in the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (500 MHz): δ 7.72-7.61 (m, 12H, ArH), 7.59-7.54 (m, 8H, ArH), 7.52-7.45 (m, 8H, ArH), 7.33-7.25 (m, overalapping with CHCl<sub>3</sub>, 4H, ArH), 7.07-6.99 (m, 6H, ArH), 6.95-6.90 (m, 4H, ArH), 6.83–6.78 (m, 4H, ArH), 0.50 (s, 6H, SiMe).  $^{13}C{^{1}H}$  NMR (125 MHz):  $\delta$  155.0, 141.8, 140.8, 138.5, 132.3 (d,  $J_{PC} = 8$  Hz), 132.2, 131.9, 131.6 (d,  $J_{PC} = 7$  Hz), 130.9 (d,  $J_{PC} = 9$  Hz), 130.2, 129.2, 129.1 (d,  $J_{PC} = 11$  Hz), 128.9 (d,  $J_{PC} = 12$  Hz), 128.5 (d,  $J_{PC} = 12$  Hz), 128.0, 127.7, 126.9, 119.9, 92.9, 89.0, -3.6.<sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz):  $\delta 8.2$ .<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta 28.8$  HRMS (FAB, NaI): m/z calcd for C<sub>70</sub>H<sub>52</sub>O<sub>2</sub>P<sub>2</sub>SiNa, 1037.3109; found,  $1037.3127 (M + Na)^+$ . Anal. Calcd for  $C_{70}H_{52}O_2P_2Si \cdot 1.7H_2O:C$ , 80.39; H, 5.34. Found: C, 80.73; H, 5.25.

Compound **5b** was was also prepared by a similar procedure to that used for the preparation of **4b**, starting from lithium naphthalenide (8 mmol), bis(phenylethynyl)dimethylsilane (0.52 g, 2.0 mmol), ZnCl<sub>2</sub>(TMEDA) (2.2 g, 8.8 mmol), (4'-bromophenylethynylphenyl)diphenylphosphine oxide (**8**, 2.01 g, 4.4 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (80 mg, 0.11 mmol). The crude residue was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/acetone, 5:2) to afford compound **5b** as a yellow powder (1.36 g, 67% yield).

1,1-Dimethyl-2,5-bis(3-bromophenyl)-3,4-diphenylsilole (6). A mixture of lithium wire that was cut into small pieces (56 mg, 8.0 mmol) and naphthalene (1.04 g, 8.0 mmol) in 12 mL of THF was stirred at room temperature for 5 h to produce a deep green solution containing lithium naphthalenide. A solution of dimethylbis(phenylethynyl)silane (0.52 g, 2.0 mmol) in 5 mL of THF was added to the LiNaph solution dropwise over 5 min at room temperature. After stirring for 10 min, the mixture was cooled to 0 °C and ZnCl2(TMEDA) (2.2 g, 8.8 mmol) was added as a solid to the reaction mixture, followed by the addition of THF (15 mL) to give a dark green suspension. After stirring for an additional hour at room temperature, 3-bromoiodobenzene (1.24 g, 4.4 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (80 mg, 0.11 mmol) were added to the resulting suspension. The mixture was heated to reflux and stirred for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation, and the crude reaction mixture subjected to silica gel column chromatography with hexane as the eluent to afford compound 6 as a yellow powder (0.59 g, 52% yield). Mp: 45-46 °C. <sup>1</sup>H NMR (500 MHz): δ 7.28–7.24 (m, 2H, ArH), 7.20 (br s, 2H, ArH), 7.12-7.07 (m, 6H, ArH), 7.06-7.01 (m, 2H, ArH), 6.95-6.92 (m, 2H ArH), 6.92-6.87 (m, 4H, ArH), 0.55 (s, 6H, SiMe).  ${}^{13}C{}^{1}H{}$  NMR (125 MHz):  $\delta$  155.0, 142.0, 140.9, 137.9, 131.6, 129.8, 129.6, 128.7, 127.7, 127.4, 126.7, 122.2, -3.9. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, DEPT):  $\delta$  8.5. HRMS (EI): m/z calcd for C<sub>30</sub>H<sub>24</sub><sup>79</sup>Br<sub>2</sub>Si, 570.00140; found, 570.0002 (M<sup>+</sup>).

	2b	<b>4</b> a	9
formula	$\mathrm{C}_{54}\mathrm{H}_{44}\mathrm{O}_{2}\mathrm{P}_{2}\mathrm{Si}$	$C_{66} H_{52} P_2 Si$	$C_{56}H_{44}Au_2Cl_2P_2Si$
fw	814.92	0.5CH <sub>2</sub> Cl <sub>2</sub> 977.57	2CH <sub>2</sub> Cl <sub>2</sub> 1417.61
cryst size/mm	$0.17 \times 0.13 \times 0.11$	$0.46 \times 0.12 \times 0.03$	0.52  imes 0.29  imes 0.22
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	C2/c	$P\overline{1}$
a/Å	11.5999(13)	46.444(8)	10.2869(11)
b/Å	16.7822(19)	9.5894(18)	13.7618(15)
c/Å	44.176(5)	24.803(5)	19.957(2)
a/deg	90	90	73.571(3)
$\beta/\text{deg}$	97.087(7)	106.484(15)	83.772(3)
$\gamma/\text{deg}$	90	90	88.086(3)
$V/Å^3$	8534.2(16)	10 593(3)	2693.9(5)
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.269	1.226	1.748
Z	8	4	2
abs coeff/mm <sup>-1</sup>	0.173	0.197	5.856
$\theta$ range/deg	1.86 to 25.00	2.17 to 25.00	2.97 to 26.22
reflns collected/ indep reflns	166 532/14 998	60845/9294	35 516/10 433
, <b>1</b>	[R(int) = 0.201]	[R(int) = 0.187]	[R(int) = 0.0391]
abs correct	numerical	semiempirical from equivalents	numerical
max. and min. transm	0.8703 and 0.8119	0.9935 and 0.9142	0.3538 and 0.1500
final R indices $[I > 2\sigma(I)]$	0.0840	0.0993	0.0422
R indices (all data)	0.1835	0.2647	0.0631
largest diff peak and hole/e $Å^{-3}$	0.419 and -0.599	0.806  and  -0.404	2.071 and -1.556

Preparation of (4'-Bromobiphenyl-4-yl)diphenylphosphine Oxide (7). Compound 7 was prepared by similar procedures used for the synthesis of the related compounds 4-(bromophenyl)diphenylphosphine and (4-bromophenyl)diphenylphosphine oxide. A solution of 4,4'-dibromobiphenyl (4.05 g, 13.0 mmol) in 150 mL of THF was cooled to -95 °C with an acetone/ liquid nitrogen bath. A solution of n-BuLi (2.5 M in hexane, 5.2 mL, 13.0 mmol) was added dropwise, and the resulting solution was stirred at  $-95 \,^{\circ}$ C for 1 h; then chlorodiphenylphosphine (2.88 g, 13.0 mmol) was added dropwise. The solution was allowed to warm to room temperature over 3 h and concentrated under vacuum. The residue was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:5) to give a white solid. The white solid was dissolved in a mixture of dichloromethane (60 mL) and methanol (60 mL); then hydrogen peroxide (30% solution, 3.5 mL) was slowly added to the solution. The resulting mixture was stirred at room temperature for 2 h, then quenched with aqueous Na<sub>2</sub>SO<sub>3</sub> solution and extracted with dichloromethane. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under vacuum to give (4'-bromobiphenyl-4yl)diphenylphosphine oxide (7) as a white solid (3.48 g, 62%yield). Mp: 131–132 °C. <sup>1</sup>H NMR (500 MHz): δ 7.87–7.76 (m, 6H, ArH), 7.71–7.67 (m, 2H, ArH), 7.60–7.55 (m, 4H, ArH), 7.53–7.47 (m, 6H, ArH).  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR (125 MHz):  $\delta$  142.9  $(d, J_{PC} = 2 Hz)$ , 138.2, 132.5, 132.2  $(d, J_{PC} = 10 Hz)$ , 131.71  $(d, J_{PC} = 10 Hz)$  $J_{PC} = 8$  Hz), 131.60 (d,  $J_{PC} = 3$  Hz), 131.5, 130.9, 128.4, 128.1 (d,  $J_{PC} = 12 \text{ Hz}$ ), 126.5 (d,  $J_{PC} = 12 \text{ Hz}$ ), 122.1. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  28.3. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>BrOP: C, 66.53; H, 4.19. Found: C, 66.02; H, 4.24.

**Preparation of (4'-Bromophenylethynylphenyl)diphenylphosphine Oxide (8).** A solution of diphenyl-(4-ethynylphenyl)phosphine oxide (1.5 g, 3.5 mmol) in 25 mL of THF was slowly injected into a solution containing 1-bromo-4-iodobenzene (1.0 g, 3.5 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.1 g, 0.14 mmol), CuI (0.027 g, 0.14 mmol), NEt<sub>3</sub> (25 mL), and THF (25 mL). The reaction mixture was stirred at room temperature for 24 h. The volatiles were removed under vacuum, and the residue was subjected to silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:4) to give **8** as a white solid (0.95 g, 59%). Mp: 146–147 °C. <sup>1</sup>H NMR (500 MHz): δ 7.68–7.52 (m, 10H, ArH), 7.47–7.44 (m, 6H, ArH), 7.38–7.28 (m, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz): δ 133.5, 132.8, 132.5, 132.4 (d, *J*<sub>PC</sub> = 10 Hz), 132.1, 132.0, 131.8 (d, *J*<sub>PC</sub> = 12 Hz), 128.9 (d, *J*<sub>PC</sub> = 12 Hz), 128.8, 127.1, 123.5, 121.9,

91.3, 89.9. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz):  $\delta$  29.0. HRMS (FAB): m/z calcd for C<sub>26</sub>H<sub>18</sub><sup>79</sup>BrOPH, 457.0357; found, 457.0339 (M + H)<sup>+</sup>.

1,1-Dimethyl-2,5-bis(4'-diphenylphosphino(chlorogold)phenyl)-3,4-diphenylsilole (9). A solution of 2a (0.15 g, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to a solution of [AuCl(tht)] (0.13 g, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at room temperature. After 12 h, the volatiles were removed by vacuum. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), and Et<sub>2</sub>O (20 mL) was added. The resulting precipitate was washed with Et<sub>2</sub>O (3  $\times$  5 mL) to provide 9 as an air-stable yellow solid (0.22 g, 89% yield). <sup>1</sup>H NMR (500 MHz): δ 7.56-7.44 (m, 20H, ArH), 7.31-7.25 (m, 4H, ArH), 7.10-6.99 (m, 10H, ArH), 6.80-6.76 (m, 4H, ArH), 0.51 (s, 6H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz):  $\delta$  156.1, 144.1 (d,  $J_{PC} = 3$  Hz), 141.6, 137.9, 134.3 (d,  $J_{PC} = 14$  Hz), 133.9 (d,  $J_{PC} = 14$  Hz), 132.1 (d,  $J_{PC} = 2$  Hz), 129.9, 129.5 (d,  $J_{PC} =$ 12 Hz), 129.364, 129.367 (d,  $J_{PC} = 11$  Hz), 128.8, 127.8, 127.1, 125.5, 125.0, -3.7. <sup>29</sup>Si<sup>{1</sup>H} NMR (99 MHz):  $\delta$  9.0. <sup>31</sup>P<sup>{1</sup>H} NMR (202 MHz):  $\delta$  32.7. HRMS (FAB, NaI): m/z calcd for C<sub>54</sub>H<sub>44</sub>Au<sub>2</sub><sup>35</sup>ClP<sub>2</sub>Si, 1211.1707; found, 1211.1676 (M - Cl)<sup>+</sup>. Anal. Calcd for C<sub>56</sub>H<sub>44</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub>Si · 2CH<sub>2</sub>Cl<sub>2</sub>: C, 47.44; H, 3.41. Found: C, 47.45; H, 4.14.

X-ray Structure Determination of 2b, 4a, and 9. Crystals of X-ray diffraction quality of 2b, 4a, and 9 were obtained by slow evaporation from either a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane or from neat CH<sub>2</sub>Cl<sub>2</sub> at room temperature, respectively. Crystals of appropriate dimensions were mounted on Mitgen loops in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex II charge coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite-monochromated Mo Ka radiation ( $\lambda = 0.71073$  A) from a fine-focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of  $\omega$  and  $\phi$  scan frames with a typical scan width of 0.5° and counting time of 15-30 s/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages<sup>40</sup> were used for data

<sup>(40)</sup> APEX II and SAINT; Bruker Analytical X-Ray: Madison, WI, 2008.

collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Collected data were corrected for systematic errors using SADABS<sup>41</sup> based on the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out using the SHELXTL- PLUS software package.<sup>42</sup> The structures were solved by direct methods and refined successfully in the space groups  $P_{1/n}(Z = 8)$ , C2/c(Z = 4), and  $P\overline{1}(Z = 2)$ . Full matrix least-squares refinement was carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$ . All non-hydrogen atoms were refined anisotropically to convergence. Some of the atoms in compound **4a** had to be refined with restraints (EADP, SADI, ISOR, SIMU). Compound **4a** contains a half a molecule of CH<sub>2</sub>Cl<sub>2</sub> per molecule of **4a** in the crystal lattice that is disordered as well as disorder in the phosphorus center P2 and an associated phenyl group. The disorder was modeled with two orientations in the ratio of 60:40. Two molecules of CH<sub>2</sub>Cl<sub>2</sub> were located in the lattice with

complex 9, and one was found to be disordered. The disordered solvent was refined with partial occupancies of 80:20. All hydrogen atoms were treated using the appropriate riding model (AFIX m3). The final residual values, structure refinement parameters, and crystal data and intensity data collection parameters are listed in Table 2. A table of calculated and observed structure factors are available in electronic format from the authors.

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Supporting Information Available: CIF files and complete listings of geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms for complexes 2b, 4a, and 9, absorption spectra for 1a, 1b, 1ab, and 9, excitation and emission spectra for 2–5 and 9, and multinuclear NMR spectroscopic data for 1–9 are available free of charge via the Internet at http://pubs.acs.org.

<sup>(41)</sup> Blessing, R. H. Acta Crystallogr. 1995, A51, 33-38.

<sup>(42)</sup> Sheldrick, G. M. Bruker-SHELXTL. Acta Crystallogr. 2008, A64, 112–122.