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Neutral and Cationic Gold(I) Complexes with π-Conjugated Phosphasilene Ligands

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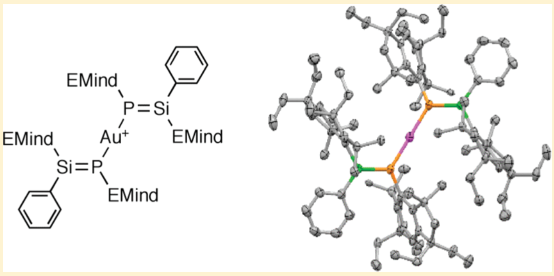
S *Supporting Information*

ABSTRACT: A series of neutral and cationic Au(I) complexes incorporating π-conjugated phosphasilene ligands stabilized by the bulky 1,1,3,3,5,5,7,7-octa-R-substituted *s*-hydrindacen-4-yl (Rind) groups have been synthesized. X-ray crystallographic studies show the η^1-coordination mode of the phosphasilene ligand, accommodating the linear *trans* two-coordinate geometry around the gold center. While the metal coordination slightly enhances the intensity of the strong $\pi-\pi^*$ absorption of the phosphasilene chromophores, the phosphashilene π-conjugation is not extended through the Au atom.



Since stable compounds comprising $\mathrm{P{=}C}$,[1] $\mathrm{P{=}P}$,[2] $\mathrm{Si{=}C}$,[3] and $\mathrm{Si{=}Si}$[4] fragments were synthesized by introducing the concept of kinetic stabilization with bulky substituents, many experimental and computational efforts have been directed toward the study of a variety of unsaturated compounds of the heavier main group elements in the last three decades.[5] Transition metal complexes of phosphaalkenes[6] and diphosphenes[7] have also been extensively investigated, thus demonstrating various coordination modes.

The first stable $\mathrm{Si{=}P}$ compound, phosphasilene, was reported by Bickelhaupt et al. in 1984, as a rare case of a heavy heteronuclear double bond species between group 14 and 15 elements.[8] After that, a number of phosphasilene derivatives have been successfully synthesized by taking advantage of the steric protection with appropriate bulky groups on the phosphorus and silicon atoms.[9−12] A half-parent phosphasilene with a PH group and its metalated compounds were also isolated and structurally characterized by Driess et al.[11] Very recently, a cyclic compound, 2,4-disila-1,3-diphosphacyclobutadiene, has been synthesized by two independent groups.[13] However, transition metal complexes having a neutral phosphasilene ligand remain unknown, which would provide new aspects of coordination modes and homogeneous catalysis.

In 2009, we reported the synthesis of two π-conjugated phosphasilenes, **1a** and **2a**, stabilized by the fused-ring bulky 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) groups (Chart 1).[14] The Eind groups encapsulate the reactive $\mathrm{Si{=}P}$ moieties and produce highly coplanar π-conjugated frameworks by their orthogonal arrays to exhibit a strong $\pi-\pi^*$ absorption on the basis of the efficient π-delocalization over the skeleton,[15] which is in sharp contrast to the previously reported phosphasilenes with a weak $n-\pi^*$ absorption. Herein, we report the rational design and synthesis of neutral and cationic Au(I) complexes of phosphasilenes **1** and **2** with the bulky Eind and the less bulky EMind[16] groups (Chart 1). Our research interests are directed toward photophysical properties of the phosphasilene complexes: whether the π-conjugation can be extended through the Au atom.

Scheme 1 shows the synthesis of mononuclear neutral complexes **3** and cationic complex **4** bearing phenylphosphasilene ligands **1a** and **1b**. The treatment of **1** with AuCl(tht) (tht = tetrahydrothiophene) in benzene afforded AuCl complexes **3** as a yellow powder. The formation of **3** has been clearly confirmed by ^{29}Si and ^{31}P NMR spectra. The ^{29}Si NMR signal of **3a** (144.4 ppm) is shifted upfield relative to **1a** (161.7 ppm) with a decreasing $^1J_{\mathrm{SiP}}$ coupling constant (39 Hz for **3a** and 171 Hz for **1a**). The ^{31}P NMR signal of **3a** (43.2 ppm) is also shifted to a higher field with respect to **1a** (89.2 ppm), which is similar to phosphaalkene Au(I) complexes.[17] The Eind-based **3a** is stable in air for months in the solid state and for weeks as a dilute solution, whereas the less bulky EMind-based **3b** decomposes in air within a few weeks in the solid state and a few hours in solution.

The molecular structure of **3a** was determined by X-ray crystallography (Figure 1a).[18] The phosphasilene ligand links to the gold atom through the phosphorus atom in an η^1-fashion with a virtually linear two-coordinate geometry at the gold atom with a P−Au−Cl angle of 178.828(6)°. The $\mathrm{Si{=}P}$ bond length in **3a** [2.0924(2) Å] is comparable to that in **1a** [2.0917(5) Å]. Compounds **3** are discrete metal chloride complexes and can be regarded as good precursors for the cationic Au(I) complexes.

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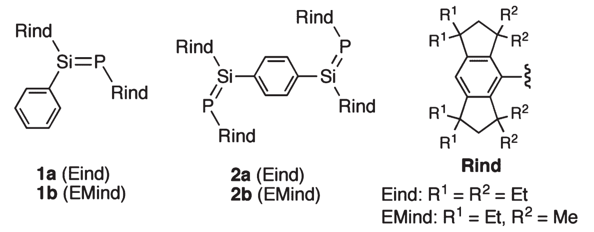
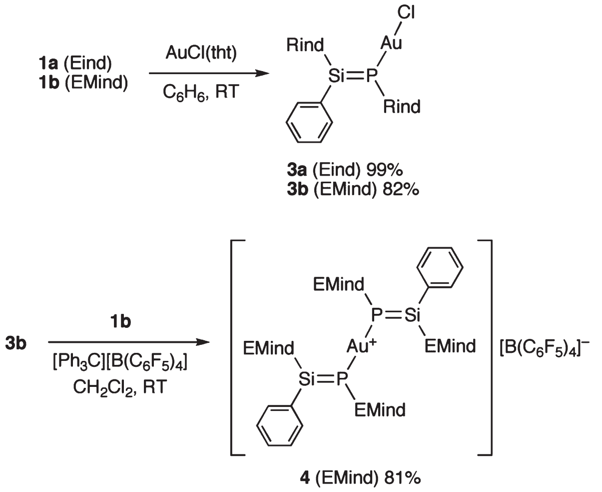
In fact, as shown in Scheme 1, the chlorine atom in **3b** can be removed, in the presence of another molecule of phosphasilene **1b**, by the action of $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 to produce the cationic complex **4** with two EMind-based phosphasilene ligands as yellow crystals in 81% yield. The ^{31}P NMR spectrum of **4** shows only one signal appearing at 48.1 ppm, which indicates a highly symmetric structure in solution. A similar reaction of the bulkier Eind-based **3a** with **1a** was also examined, but no formation of such a cationic complex was observed due to the steric repulsion between the bulky Eind groups. A cross-combination between **3b** and **1a** afforded a mixture of complex **4** and a cationic complex bearing both **1a** and **1b** ligands due to the ligand exchange, as observed by the NMR studies; however, none of them were isolated.

Chart 1. Phosphasilenes and Rind Groups



Scheme 1. Synthesis of Complexes 3 and 4



The X-ray molecular structure of the cation in **4** has C_2-symmetry in the crystal with the 2-fold axis passing through the Au atom (Figure 1b). A linear two-coordination is found at the gold center with a P—Au—P angle of 178.13(6)°. The P—Au distance in **4** [2.2807(13) Å] is slightly longer than that in **3a** [2.2295(3) Å], which indicates the sterically overcrowded metal center. While the phenyl groups on the Si atoms are nearly coplanar with the Si═P bonds with a P—Si—C—C torsion angle of 6.7(4)°, the dihedral angle between the two terminal benzene rings is 39.3°, thus producing a twisted arrangement between the two phenylphosphasilene skeletons in the crystal.

Dinuclear neutral AuCl complexes **5a** and **5b** were also synthesized employing 1,4-bis(phosphasilenyl)benzenes **2a** and **2b** as ligands (Scheme 2). The Eind-based complex **5a** and the less bulky EMind-based **5b** exhibit air stability similar to that of the corresponding mononuclear complexes **3a** and **3b**. The X-ray structural analysis of **5a** demonstrates the maintenance of the high coplanarity of the 1,4-bis(phosphasilenyl)benzene skeleton containing two AuCl fragments, as shown in Figure 1c.

The synthesis of the dinuclear dicationic complexes was not easy. After several attempts with possible combinations of two different phosphasilene ligands **1** and **2**, we have finally succeeded in the synthesis of a mixed dinuclear dicationic complex **6**, consisting of the Eind-based **2a** and the less bulky EMind-based **1b**. It should be noted that the use of bulky Eind-based **2a** was essential as the central ligand for **6**: a combination of less bulky **2b** instead of **2a** as the central ligand with **1b** resulted in a complex mixture containing oligonuclear compounds. In the successful case, **5a** and **1b** in a 1:2 ratio were allowed to react with two equivalents of $[Ph_3C][B(C_6F_5)_4]$ to afford **6**, together with a small amount of **4**. After washing of the precipitates with CH_2Cl_2/hexane, **6** was isolated as orange solids in 81% yield. Complex **6** is highly air-sensitive but thermally stable. No ligand redistribution occurs in solution at room temperature, as confirmed by NMR studies. Thus, in the ^{31}P NMR spectrum of **6** in $CDCl_3$, a pair of doublets appear at 52.6 and 65.9 ppm with a large $^2J_{PP}$ coupling constant of 388 Hz; such a large $^2J_{PP}$ is characteristic of the linear two-coordinate geometry around the metal center.[19] Also in the ESI-HRMS spectrum, the observed ion peak at m/z 1843.2043 is in good agreement with the counterion-free molecular ion, $[M - 2B(C_6F_5)_4]^{2+}$ (calcd for $[C_{226}H_{342}Au_2Si_4P_4]^{2+}$: m/z 1843.2060).

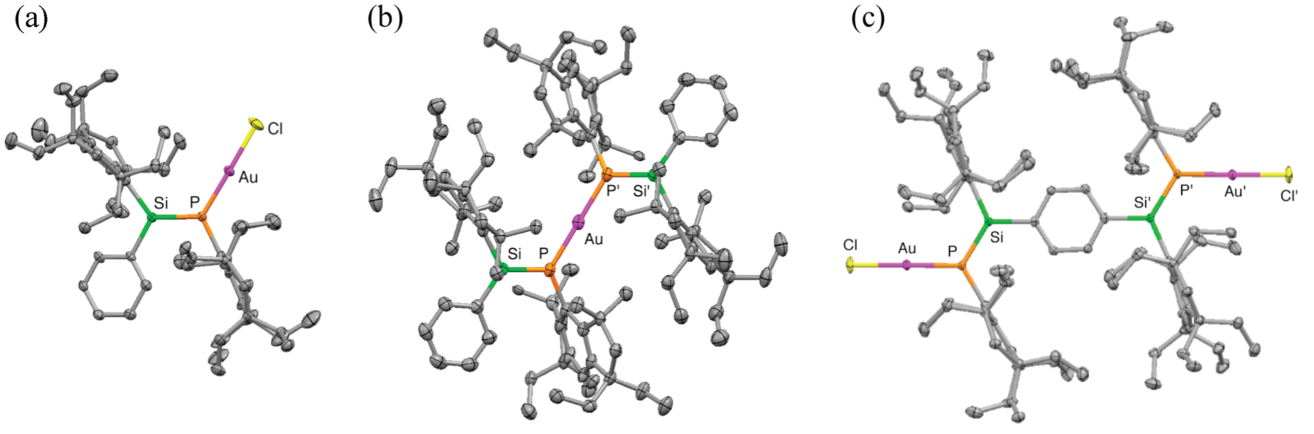


Figure 1. Molecular structures of (a) **3a**, (b) **4**, and (c) **5a**. Hydrogen atoms and counteranion of **4** are omitted for clarity.

Scheme 2. Synthesis of Complexes 5 and 6

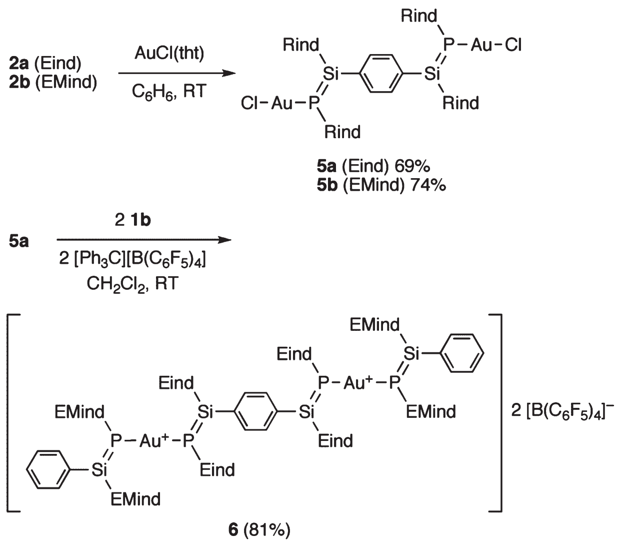


Table 1. UV−Vis Absorption Data[a] of Phosphasilenes 1 and 2 and Their Gold Complexes 3−6 Measured at Room Temperature

cmpd	λ_{max}/nm	ε/cm^{-1} M^{-1}
phosphasilenes		
1a[b]	385[c]	1.2×10^4
1b	378	1.0×10^4
2a[b]	449[c]	2.2×10^4
2b	436	2.0×10^4
Au(I) complexes		
3a	395[c]	1.8×10^4
3b	386	1.7×10^4
4	408	4.0×10^4
5a	460	3.3×10^4
5b	445	3.0×10^4
6	383	2.6×10^4
	465	5.3×10^4

[a] Measured in CH_2Cl_2. [b] See ref 14. [c] Measured in THF.

Table 1 summarizes the UV−vis absorption data for the phosphasilenes and their gold complexes. The mononuclear AuCl complexes **3a** and **3b** in CH_2Cl_2 show the π−π* absorption peak at 395 and 386 nm, which are 10 and 8 nm red-shifted from **1a** and **1b**, respectively, together with the slightly enhanced absorption intensity. The strong π−π* absorption for the cationic bis-phosphasilene complex **4** at 408 nm is red-shifted by 22 nm relative to that of neutral **3b**. The latter data suggest a certain π-conjugation between the two phenylphosphasilene ligands through the Au atom. However, the UV−vis spectrum of **6**, which has two different phosphasilene chromophores, shows two distinct absorption peaks at 383 and 465 nm; each of them is essentially the same as that of the corresponding free ligands [378 (**1b**) and 460 (**5a**) nm]. This fact indicates a simple electronic accumulation of the two different phosphasilene chromophores in **6**; thus, the π-conjugation is not extended through the Au atoms.[20]

DFT computations were performed for **3a** and **4′** (a counterion-free form of **4**) and their parent phosphasilene complexes,

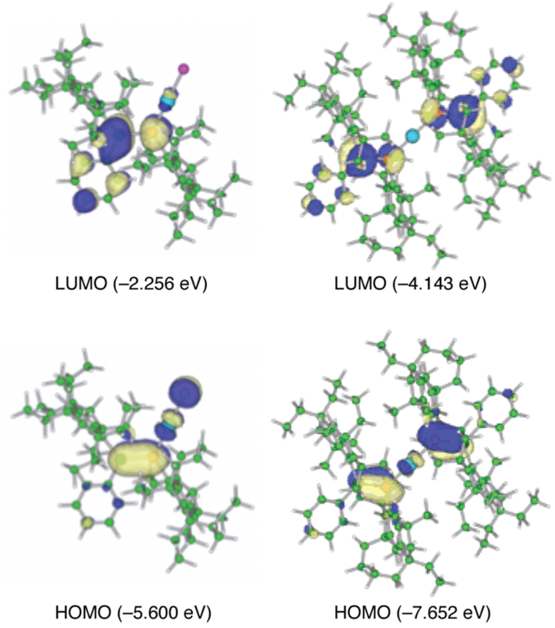


Figure 2. Frontier molecular orbitals of **3a** (left) and **4′** (right).

[PhSiH=PH]AuCl and $[PhSiH{=}PH]_2Au^+$, at the B3LYP/6-31G(d,p) level (B3LYP/cc-pVDZ-pp level for the Au atom) using the Gaussian 03 suite of programs.[21] The optimized structures of **3a** and **4′** reproduced well the X-ray molecular structures, while the parent counterparts were found to have an η^2-coordination of the phosphasilene ligand(s) in the equilibrium geometries. Thus, the experimentally observed η^1-coordination mode should be ascribed to the steric hindrance by the bulky Rind groups, covering the Si=P double bond.

In addition to the σ-donor through the phosphorus atom, the phosphasilene ligands would act as a π-acceptor for transition metals on the basis of their low-lying LUMO.[14] However, as shown in Figure 2, the LUMOs of **3a** and **4′** consist mainly of the Si−P π*-orbitals with essentially no contribution of the Au atomic orbital, although the LUMO energy levels are lowered by the complexation [−1.552 (**1a**) vs −2.256 (**3a**) and −4.143 (**4′**) eV]. The HOMOs of **3a** and **4′** are primarily represented by the Si−P π-orbital(s). Thus, the Au atom may interrupt the extended π-conjugation in **4′** as a defect, which is consistent with the experimental results. This is most probably due to the mismatching of the energy levels between the 3p-based frontier MOs of the phosphasilene ligands and the filled 5d-orbitals of the Au(I) ion. The TD-DFT calculations indicate that the absorptions observed in both **3a** and **4′** are mainly assigned to the HOMO → LUMO (π−π*) transition. The n−π* transition of **1** is hampered by the Au coordination through the nonbonding pairs of electrons on the phosphorus atom.[22]

We have demonstrated a rational approach for producing phosphasilene gold(I) complexes. The steric bulkiness of the Rind groups greatly affects the coordination mode from π-coordination to σ-coordination, air stability, and reactivity of the resulting complexes. An extension of the phosphasilene π-conjugation through the Au atom has not been found in the bis-phophasilene cationic complexes; these observations are theoretically supported by DFT calculations. Investigations on the use of the new complexes as a catalyst in organic synthesis are now in progress.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, CIF for **3a**, **4**, and **5a**, details for calculations of **3a** and **4′**, and full listing for ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) In the X-ray molecular structure of **3a**, the Cl−Au−P−Si−Ph moiety was disordered over two sites. Because of very low occupancy of the minor part (ca. 3%), their atomic distances and angles and temperature factors were strongly constrained to be the same as those of the major part in the refinements.

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(20) Complexes **5a** and **6** exhibit weak emission both in solution and in the solid state. Emission maxima are observed at 580 nm for **5a** and 585 nm for **6** in CH_2Cl_2, comparable to those found in the solid state (577 nm for **5a** and 586 nm for **6**).

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