



Account/Revue

π -conjugated phosphasilenes stabilized by fused-ring bulky “Rind” groups

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ABSTRACT

Recent progress in the chemistry of π -conjugated phosphasilenes stabilized by bulky protecting groups based on a fused-ring octa-R-substituted *s*-hydrindacene skeleton (Rind groups) is reviewed. The phosphasilenes with a variety of aryl substituents at the silicon atom are covered in detail. The X-ray crystallography analysis showed the highly coplanar π -framework reinforced by the perpendicularly-fixed Rind groups. Strong π - π^* absorptions have been observed, demonstrating the extension of π -conjugation over the skeleton. The DFT calculations indicated that the LUMO involves significant contribution by the $3p\pi^*(\text{Si-P})$ - $2p\pi^*(\text{carbon } \pi\text{-electron system})$ conjugation. The preparation of the gold(I) complexes of the π -conjugated phosphasilenes is also included.

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1. Introduction

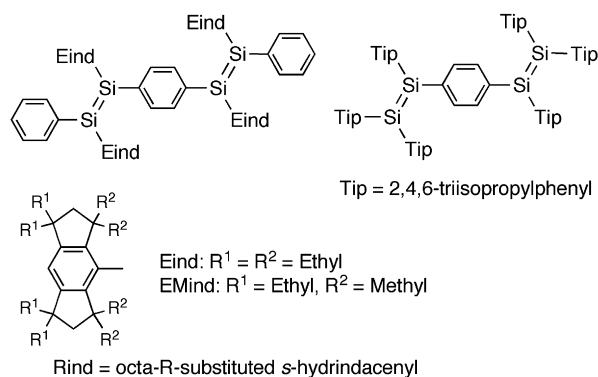
In 1981, a new concept of bulky protecting groups was introduced for the kinetic stabilization of highly reactive unsaturated bonds between the main group elements heavier than the second row elements [1]. Since then, many experimental efforts have been directed toward a variety of unsaturated compounds of the heavy elements [2], including the Si=P compounds, i.e., phosphasilenes [3]. In 1984, Bickelhaupt et al. reported the first stable compound containing a Si=P double bond [4a]. Since then, various phosphasilenes have been prepared by taking advantage of the steric protection with appropriate bulky substituents [4–7]. For example, the first X-ray structural analysis of phosphasilene was reported by Niecke et al. in 1993 [5a]. A series of phosphasilenes having bulky silyl groups at the phosphorus atom have been studied by Driess et al. [6a–d]. The “half”-parent phosphasilene with a

PH group and its metallated compounds were also reported [6e,f]. However, despite the unconventional polar heavy double bonds, the electronic properties of the phosphasilenes have been only slightly explored; weak absorptions probably due to the n - π^* transition have been reported only in rare cases [4c, 6c]. Very recently, a “push-pull” phosphasilene was synthesized by Sekiguchi and Escudié groups [7], the EPR studies of its anion radical species was reported.

Last year, we reported the first experimental evidence for the π -conjugation between the Si=P double bond and the carbon π -electron system linked to the silicon atom [8]. Organic π -conjugated architectures comprised of multiple bonds of the heavier main group elements have attracted much attention because of their potentially useful properties and unique functions [9]. For example, a variety of oligomers and polymers encapsulating P=E (E = C, P) [10] and Si=Si [11] bonds have been investigated, which would open the way to new elemento-organic hybrid materials. In 2007, Scheschkewitz’s group [12] and we [13] independently reported the synthesis and characterization of the disilene analogues of the oligo(*p*-phenylenevinylene)s (Si-OPVs) (Scheme 1). In our case, the

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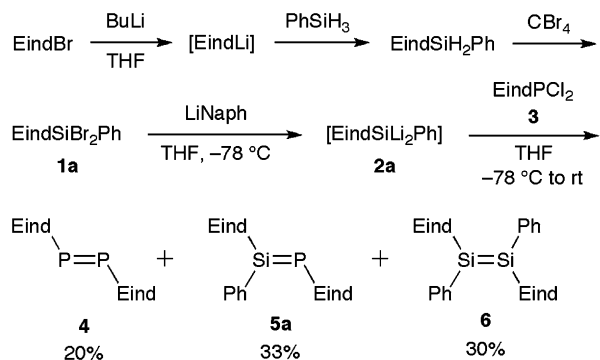
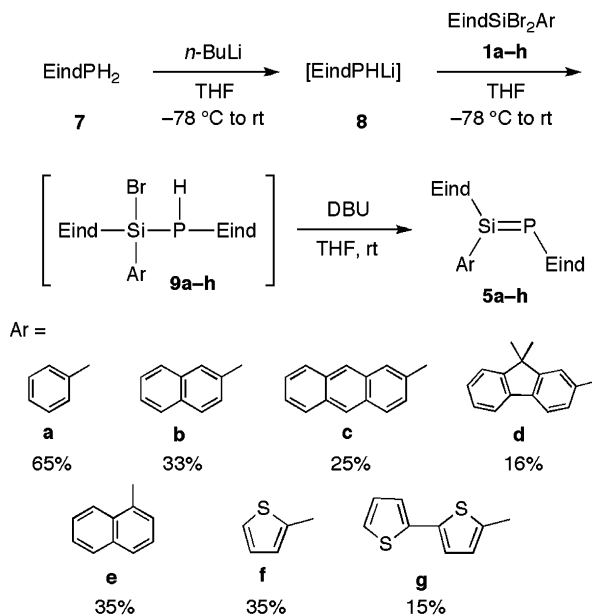
Scheme 1. Si-OPV dimers and Rind groups.

newly developed fused-ring bulky 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl groups, abbreviated as “Eind” groups (“E” for ethyl), effectively protect the reactive Si=Si fragments, thus providing the highly coplanar arrangement of the Si-OPV dimer framework. Notably, our 1,4-bis(disilenyl)benzene derivative showed a unique fluorescence at room temperature based on the efficient π -delocalization over the skeleton.

After the initial findings of the effectiveness of the Eind groups in the Si-OPVs, we concentrated on the development of π -conjugated systems containing heavy unsaturated bonds by taking advantage of the bulky “Rind” groups based on a fused-ring octa-R-substituted *s*-hydrindacene skeleton [14], where R denotes the initial of the substituents. For example, 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacene-4-yl group, abbreviated as an “EMind” group (“M” for methyl), is sometimes useful as the less bulky group. In this report, we review our recent results for a series of π -conjugated phosphasilenes and their gold(I) complexes.

2. Preparation of π -conjugated phosphasilenes

At the beginning of this study, as shown in Scheme 2, we examined the one-step coupling reaction between the Eind-dichlorophosphine **3** and Eind-dilithiosilane **2a**, which was formed by the reaction of the dibromosilane **1a** with lithium naphthalenide (LiNaph) in THF at low temperature [7,15]. This reaction, however, led to a

Scheme 2. Synthesis of **4**, **5a**, and **6**.Scheme 3. Synthesis of **5a–g**.

mixture of the Eind-stabilized diphosphene **4** [16], phosphasilene **5a**, and disilene **6** [13]. We have isolated **4** as orange crystals, **5a** as yellow crystals, and **6** as orange crystals in 20, 33, and 30% yields, respectively, using silica gel chromatography in a glove box filled with argon gas. However, this synthetic approach seemed to be not suitable for the large-scale synthesis of the phosphasilenes.

The selective synthesis of phosphasilenes has been achieved by the stepwise construction of the Si=P double bonds, starting from the Eind-phosphine **7** as shown in Scheme 3. The coupling reaction between the lithium phosphide (**8**) and **1a** and subsequent removal of HBr from the resulting phosphasilane **9a** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded the Eind-stabilized phosphasilene **5a** in 65% yield. Similarly, we synthesized a series of Eind-stabilized phosphasilenes **5b–g** with various aryl substituents at the silicon atom: 2-naphthyl (**5b**), 2-anthryl (**5c**), 2-fluorenyl (**5d**) [17], 1-naphthyl (**5e**) [17], 2-thienyl (**5f**) [17], and 2,2'-bithienyl (**5g**) [17]. Each compound was isolated as yellow to yellow-orange crystals in 15–35% yields. We have also synthesized the 1,4-bis(phosphasilenyl)benzene **12**, in which two Si=P bonds are connected by a *para*-phenylene linker as shown in Scheme 4. Thus, the reaction of 1,4-bis(dibromosilyl)benzene **10** with 2 equiv. of **8** and subsequent treatment with DBU produced **12** as orange crystals in 29% yield.

The ²⁹Si and ³¹P NMR spectral data of **5a–g** are listed in Table 1. In the ²⁹Si NMR spectra of **5a–d**, **5f** and **5g**, one signal is observed at δ = 147.7–162.1 ppm as a doublet with a ¹J_{SiP} coupling constant of 171–178 Hz. The characteristic ³¹P NMR signal is found at δ = 77.2–89.7 ppm. Compound **5e** exhibits two signals in both the ²⁹Si and ³¹P NMR spectra, respectively, indicating the existence of two rotational isomers around the Si-C_{ipso}(aryl) bond, the *s*-cis and *s*-trans, in solution as shown in Fig. 1. However, all attempts to separate the isomers

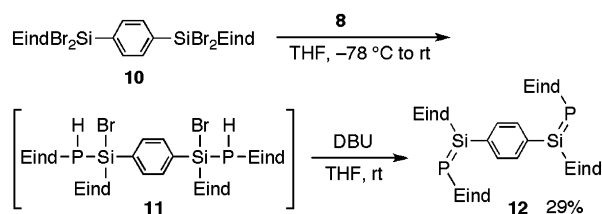
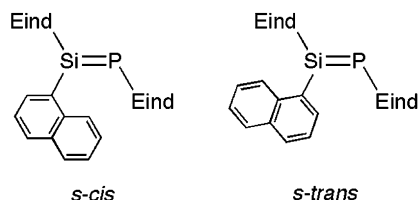
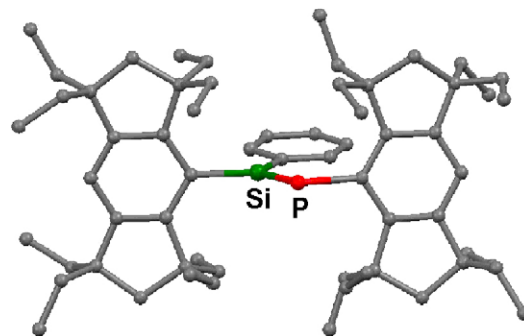
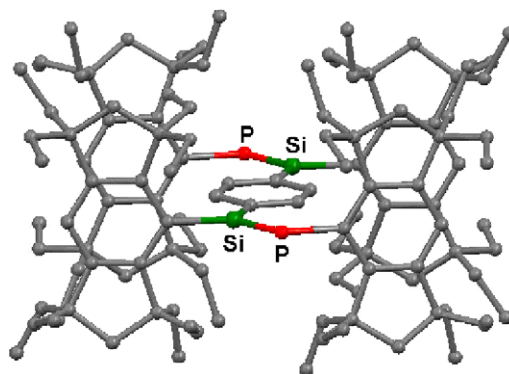
Scheme 4. Synthesis of **12**.Fig. 1. Rotational isomers of **5e**.

Table 1
Selected NMR spectral data for phosphasilenes.

Compound	δ (Si, ppm)	J_{SiP} (Hz)	δ (P, ppm)
5a ^a	161.7	171	89.2
5b ^a	161.9	174	89.7
5c ^a	162.1	174	89.2
5d ^a	160.0	174	82.5
5e ^a	149.6 (major)	183	84.0 (major)
	147.9 (minor)	180	84.4 (minor)
5f ^a	147.7	178	77.2
5g ^a	148.6	175	81.5
12 ^b	160.9	182	109.1
			97.9 ^c

^a In benzene-*d*₆ at 25 °C.^b In the solid state.^c In THF-*d*₈ at 65 °C.Fig. 2. Molecular structure of **5a**. Hydrogen atoms are omitted for the clarity.Fig. 3. Molecular structure of **12**. Hydrogen atoms are omitted for the clarity.

have been unsuccessful. For compound **12**, the solid-state NMR experiments have been utilized due to its poor solubility in organic solvents. Both the ²⁹Si and ³¹P NMR spectral peaks appear as single signals, indicating a highly symmetrical structure for **12** in the solid-state, which is in agreement with the crystal structure (*vide infra*).

The resulting phosphasilenes are stable in air for months in the solid state and for a week as a dilute solution, demonstrating the efficient protection ability of the Eind groups. Each compound has a high thermal stability; **5a–g** melted at > 200 °C without decomposition under an argon atmosphere in a sealed tube. The dimer **12** has decomposition points of > 340 °C under an argon atmosphere in a sealed tube.

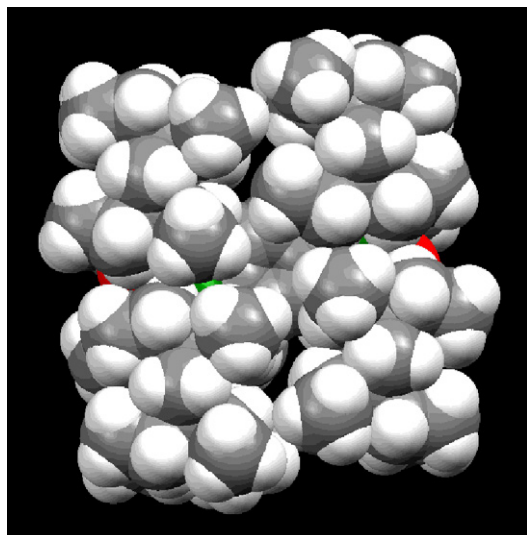
3. X-ray structural aspects

The molecular structures of **5a–c** and **12** have been determined by X-ray crystallography; their structural parameters are summarized in Table 2, and two of them, **5a** and **12**, are reproduced in Figs. 2 and 3. The aryl and the arylene groups are entirely coplanar with the Si=P double bond(s), having the P–Si–C–C torsion angles of 3.04(13) (**5a**), 1.1(4) (**5b**), 2.0(2) (**5c**), and 0.8(2)° (**12**), respectively,

which is well suited for the 2p_π–3p_π conjugation. This coplanarity is apparently attained by the rigid Eind groups, oriented *trans* and perpendicular with respect to the Si=P bond, as observed in the disilene case [13]. The space-filling model of **12** shows that the peripheral ethyl groups effectively protect the Si=P moieties (Fig. 4). The ethyl side chains on the rigid *s*-hydrindacene skeletons interlock with one another above and below the Si=P moiety to

Table 2
Selected X-ray crystal structural data for phosphasilenes.

Compound	Bond lengths (Å)				Torsion angle (°)
	Si=P	Si–C(Eind)	Si–C(aryl)	P–C	P–Si–C–C
5a	2.0917(5)	1.9006(12)	1.8633(13)	1.8706(12)	3.04(13)
5b	2.0958(16)	1.901(4)	1.855(4)	1.876(4)	1.1(4)
5c	2.0915(8)	1.899(2)	1.860(2)	1.872(2)	2.0(2)
12	2.0980(9)	1.902(3)	1.857(3)	1.871(3)	0.8(2)

Fig. 4. Space-filling model of **12**.

enforce the planar geometry. The resulting cavity surrounded by the ethyl groups can fix the framework aryl groups in a coplanar conformation with the P=Si plane, which is ideal for the extension of the π -conjugation.

The Si=P bond lengths of **5a–c** and **12** (ca. 2.09–2.10 Å) are in the range of those for typical phosphasilenes [5–7]. The Si–C_{ipso}(Eind) bond lengths (ca. 1.90 Å) are somewhat longer than the Si–C_{ipso}(aryl) bond lengths (ca. 1.86 Å), presumably due to the small steric repulsion between the ethyl groups of the Eind groups. The P–C bond lengths (ca. 1.87–1.88 Å) are normal. Each silicon atom in **5a–c** and **12** adopts an essentially planar geometry; the sum of the bond angles around the Si atom are ca. 360°.

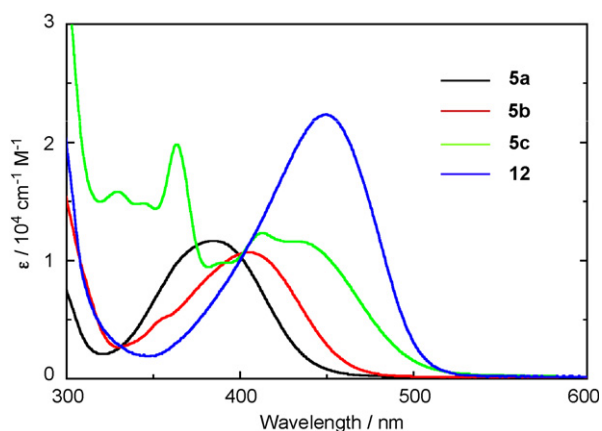
For **5b** and **5c**, the arrangement between the Si=P bond and the polycyclic aromatic substituents about the intervening Si–C_{ipso}(aryl) bond is described as an *s-cis* conformational geometry [18] in the crystals.

4. Photophysical and electrochemical properties

Phosphasilenes **5a–g** and **12** exhibit an intense absorption band in the electronic absorption spectrum. The data are summarized in Table 3. The UV-visible absorption spectra of **5a–c** and **12** are shown in Fig. 5 [8]. The phenyl-substituted phosphasilene **5a** shows an absorption peak (λ_{max}) at 385 nm ($\epsilon = 1.16 \times 10^4$), which

Table 3
Electronic absorption data for phosphasilenes in THF.

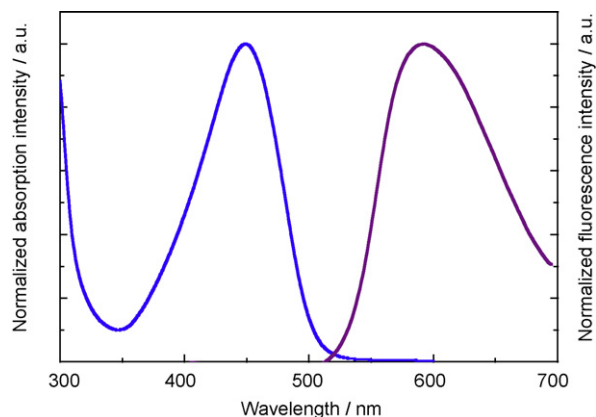
Compound	λ_{max} (nm)	ν_{max} (cm ^{−1})	ϵ (cm ^{−1} M ^{−1})
5a	385	26,000	11,600
5b	405	24,700	10,600
5c	430 (sh)	23,300	12,700
5d	403	24,800	15,500
5e	404	24,800	9,200
5f	394	25,400	9,500
5g	425	23,500	10,600
12	449	22,300	22,000

Fig. 5. UV-vis absorption spectra of **5a–c** and **12** in THF.

is about 50 nm bathochromically shifted and two-orders stronger relative to the λ_{max} and ϵ of the previously reported phosphasilenes [4c,6c]. The introduction of the 2-naphthyl (**5b**) and the 2-anthryl (**5c**) groups to the silicon atom causes further λ_{max} red-shifts to 405 nm ($\epsilon = 1.06 \times 10^4$) and 430 nm (sh, $\epsilon = 1.27 \times 10^4$), respectively. Moreover, the λ_{max} of **12** is observed at 449 nm ($\epsilon = 2.20 \times 10^4$), which is 64 nm red-shifted from **5a**, indicating the extension of the π -conjugation over the 1,4-bis(phosphasilenyl)benzene skeleton.

While **5a** does not show any fluorescence, the π -extended **12** shows a weak, but distinct emission in the solid state, as shown in Fig. 6 [8]. The emission maximum of **12** is observed at 592 nm. The large Stokes (5380 cm^{−1}) shift may be attributed to the structural change from the coplanar structure in the ground state to the twisted structure in the excited state.

Although there have been a number of reports regarding the electrochemical properties of the diphosphenes [19], those of phosphasilenes have rarely been explored [7]. We performed the electrochemical studies of **5a** and **12** by cyclic voltammetry [8]. The irreversible oxidation waves at +0.94 V (**5a**) and +0.97 V (**12**) as well as

Fig. 6. Solid-state luminescence spectrum of **12** excited at 360 nm (purple). UV-vis absorption spectrum of **12** in THF (blue).

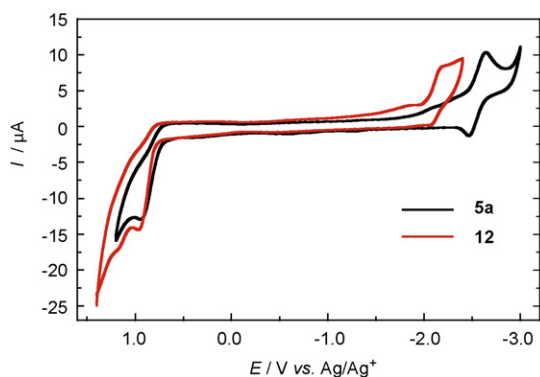


Fig. 7. Cyclic voltammograms of **5a** (black) and **12** (red).

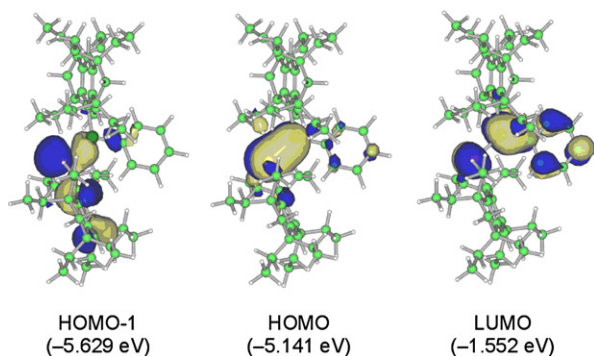


Fig. 8. Selected molecular orbitals of **5a** (top view).

the quasi-reversible and the irreversible reduction waves at -2.55 V (**5a**) and -2.12 V (**12**) were observed for the cyclic voltammograms, respectively (Fig. 7). These experimental results exhibit good qualitative agreement with the DFT calculations (*vide infra*).

5. Theoretical studies of π -conjugated phosphasilenes

To delineate the nature of the chemical bonding in the phosphasilenes, DFT computations at the B3LYP/6-31G** level were carried out for **5a** and **12**. The optimized structures well reproduced the X-ray crystal structures.

The three pertinent molecular orbitals (MOs) of **5a** are depicted in Fig. 8 [8]. While the HOMO of **5a** is primarily represented by the $3p_{\pi}(\text{Si-P})$ orbital, the LUMO involves the substantial contribution of the $3p_{\pi}^*(\text{Si-P})$ – $2p_{\pi}^*(\text{phenyl})$ conjugation. The lower-lying HOMO-1 involves the $3n$ – $2p_{\pi}$ conjugation due to the lone pair at the phosphorus atom and the π -orbital on the Eind benzene ring; the maximum orbital interaction of these two orbitals is attained by the perpendicularly-fixed Eind group.

Fig. 9 shows the selected MOs of the π -extended **12**. Calculations for **12** have demonstrated that the LUMO level is lowered [-1.552 (**5a**) and -2.108 (**12**) eV], thus keeping the HOMO levels nearly constant [-5.141 (**5a**) and -5.137 (**12**) eV], in agreement with the orbital shapes for **5a** and the previously mentioned electrochemical experimental

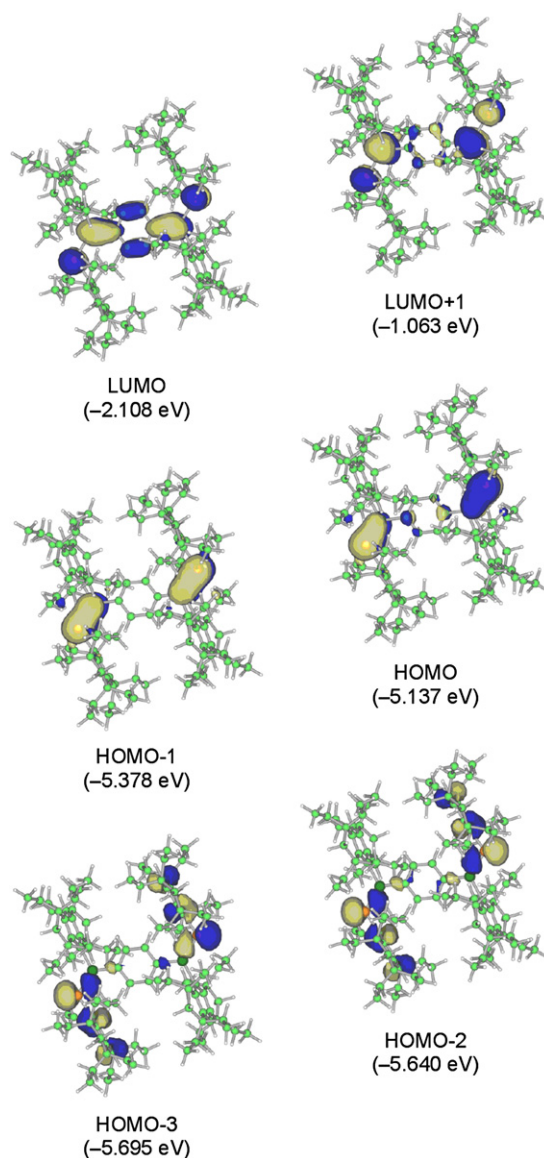


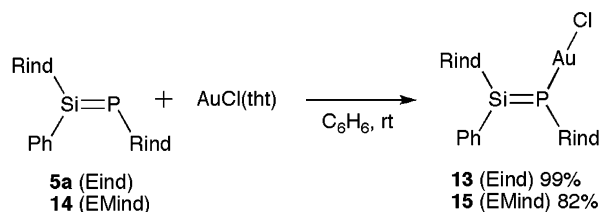
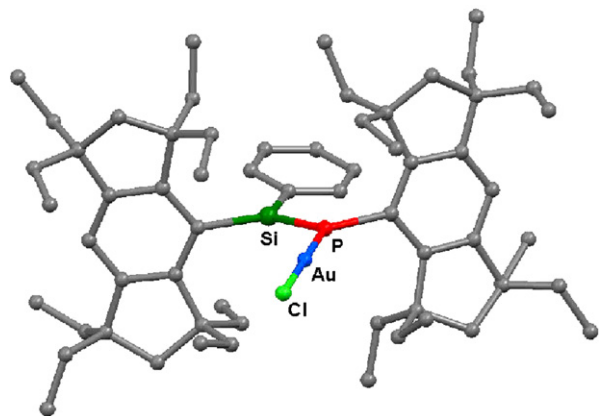
Fig. 9. Selected molecular orbitals of **12** (top view).

results. The significant $3n$ – $2p_{\pi}$ conjugation are also found in the HOMO-2 and HOMO-3 of **12**.

The absorption wavelengths were calculated for the ground-state geometries using the TD-B3LYP/6-31G** method. The calculated wavelengths of 364 (**5a**) and 456 (**12**) nm are comparable to the observed values. The absorption at 364 nm of **5a** is assignable to the mixed version of the HOMO→LUMO (π – π^*) and HOMO-1→LUMO ($(n + \pi \text{ of Eind benzene})$ – π^*) transitions with almost equal weighting. In contrast, the absorption at 456 nm of **12** is mainly assigned to the HOMO→LUMO (π – π^*) transition.

6. Gold(I) complexes of π -conjugated phosphasilenes

Although the *P*-zincophosphasilene [6e] and *P*-plumbeniophosphasilene [6f] have been reported to be

Scheme 5. Synthesis of **13** and **15**.Fig. 10. Molecular structure of **13**. Hydrogen atoms are omitted for the clarity.

obtained by the metallation of the corresponding hydrogen-substituted phosphasilene, the transition metal complexes bearing neutral phosphasilene ligands had been unexplored until we succeeded quite recently in preparing some gold(I) complexes [20]. Thus, as a part of the studies aimed at developing new conjugated hybrid materials consisting of both the main group elements and transition metals, we have focused on the synthesis of the gold(I) complexes of π -conjugated phosphasilenes stabilized by the bulky Rind groups.

As shown in Scheme 5, the reaction of **5a** with AuCl(tht) (tht = tetrahydrothiophene) led to the quantitative formation of the phosphasilene gold(I) chloride complex **13** as a yellow powder. We have also designed a new phosphasilene **14** with the less bulky 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-s-hydrindacene-4-yl (EMind) groups. The corresponding AuCl complex **15** was prepared in 82% yield.

The molecular structure of **13** has been determined by X-ray crystallography (Fig. 10). The Au atom has a linear two-coordinate geometry with the P–Au–Cl angle of $178.83(5)^\circ$. The Au–P and Au–Cl distances are 2.2295(9) and 2.2739(10) Å, respectively. The Si=P bond length of **13** is 2.0924(12) Å, which is similar to that of **5a** [2.0917(5) Å]. The phenyl group is slightly twisted to the Si=P bond; the P–Si–C torsion angle is $13.83(15)^\circ$.

The ^{29}Si NMR signal of **13** ($\delta = 144.4$ ppm) is shifted upfield relative to **5a** ($\delta = 161.7$ ppm) with the decreasing $^1J_{\text{SiP}}$ coupling constant (39 Hz for **13**; 171 Hz for **5a**). The ^{31}P NMR signal of **13** ($\delta = 43.2$ ppm) is also shifted to a higher field relative to **5a** ($\delta = 89.2$ ppm). The complex **13** has an absorption maximum at 395 nm, which is 10 nm

red-shifted from **5a**, with a higher molar extinction coefficient ($\epsilon = 1.75 \times 10^4$). These data suggest that the degree of the π -conjugation has been increased by the Au(I) ion complexation.

7. Conclusions

We have described our recent results concerning the π -conjugated stable phosphasilenes based on the Rind groups in this report. The phosphasilenes with a variety of aryl groups have been clearly characterized by NMR spectroscopy and X-ray structural analyses. All of the phosphasilenes demonstrate the strong π – π^* absorptions resulting from the π -conjugation between the Si=P bond and the carbon π -electron system. The fused-ring bulky Rind groups successfully protect the reactive polar Si=P bonds, making the highly coplanar arrangement of the π -framework. The unique electronic properties of the π -conjugated phosphasilenes have been elucidated by UV-visible absorption spectroscopy as well as DFT calculations.

The gold(I) complexes of the π -conjugated phosphasilenes have also been isolated to demonstrate the extension of π -conjugation through the gold atom. Elucidation of the chemistry of the phosphasilene metal complexes has just begun and further investigations are needed in order to understand their properties and reactivities.

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