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Doubly bonded systems between heavier Group 15 elements†

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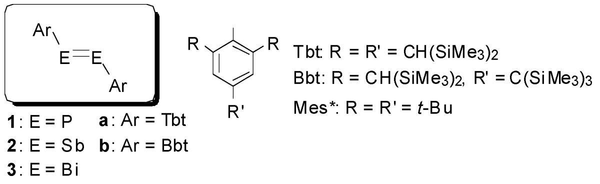
There has been much interest in the synthesis and properties of doubly bonded systems between heavier Group 15 elements, *i. e.* heavier analogues of *azo*-compounds (dipnictenes), from the viewpoints of fundamental and material chemistry. Although such double-bond compounds between heavier main group elements are known to be highly reactive, too much so to be isolated as stable compounds, a number of reports on the synthesis of kinetically stabilized diphosphenes (RP=PR), diarsenes (RAs=AsR), and phosphaarsenes (RP=AsR) bearing bulky substituent have been published since 1980. We have also succeeded in the synthesis of the first stable distibene (RSb=SbR) and dibismuthene (RBi=BiR) by taking advantage of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt), and revealed their structures and properties systematically. Thus, the doubly bonded compounds between heavier Group 15 elements are no longer imaginary species but are those with real existence which are stable, even in the case of the heaviest non-radioactive element bismuth, when they are appropriately protected by bulky substituents. This Perspective describes our research on the chemistry of kinetically stabilized double-bond compounds between heavier Group 15 elements.

1. Introduction

The syntheses of stable compounds containing multiple bonds between heavier main group elements have been among the frontiers of great interest in chemical research.[1] However, according to the so-called "classical double bond rule",[2] stable molecules featuring multiple bonding have been thought possible for a long time only with elements of the second-row in the periodic table. The statement that such multiple bonding in heavier elements would be impossible was rationalized by the long bond distances between the elements, which would not allow sufficient overlap of p-orbitals. This statement was supported by a number of unsuccessful attempts to synthesize compounds having a double bond between two heavier main group elements. The history of attempted syntheses of heavier congeners of *azo*-compounds dates back to 1877, when Köler and Michaelis reported that the condensation reaction of $PhPCl_2$ and $PhPH_2$ resulted in the formation of a compound formulated as "$C_6H_5P{=}PC_6H_5$", which they dubbed "phosphobenzene".[3] However, subsequent X-ray diffraction studies have revealed that this product has pentameric or hexameric structures in the solid state.[4] A similar mistake arose in the case of arsenic. Although the structure of the chemotherapeutic drug "Salvarsan" was first formulated as a monomeric diarsene structure by Ehrlich,[5] the X-ray crystallographic work on the compound of empirical composition C_6H_5As revealed its oligomeric character.[6] Based on these failures, it was realized that the introduction of sufficiently large substituents is necessary to avoid the oligomerization of these reactive double-bond species. The idea of kinetic stabilization of reactive multiple bonds by bulky ligands led to the first syntheses of disilene $Mes_2Si{=}SiMes_2$ (Mes = mesityl)[7] and diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl)[8] in 1981. These compounds are significant landmarks in the chemistry of doubly bonded systems between the heavier main group elements. Nowadays, as for the double-bond compounds between heavier Group 15 elements (dipnictenes), numerous examples of kinetically stabilized diphosphenes (RP=PR), diarsenes (RAs=AsR), and phosphaarsenes (RP=AsR) have been isolated and fully characterized.[1a,c,9]

Although theoretical calculations predicted that distibene (RSb=SbR) and dibismuthene (RBi=BiR) should be accessible by utilizing kinetic stabilization,[10] no stable doubly bonded compound between two antimony atoms or two bismuth atoms had been reported except for a few transition-metal complexes,[11] in which the multiple bond was supported by metal bridging, until our successful syntheses and isolation of the first stable distibene[12,13] and dibismuthene[13,14] utilizing very effective and bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt). In this Perspective, we present our systematic studies on the syntheses and properties of diphosphenes **1**, distibenes **2**, dibismuthenes **3**, and related compounds (Scheme 1), which are kinetically stabilized by Tbt or Bbt groups, together with the recent progress of our research on the chemistry of heavier dipnictenes.



Scheme 1

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† Dedicated to Prof. Renji Okazaki on the occasion of his 70th birthday.

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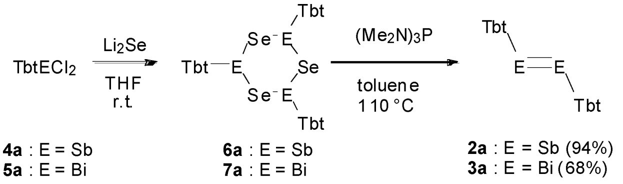
Norihiro Tokitoh, born in 1957, received his Ph.D. from The University of Tokyo in 1985. He became Research Associate (1986) and Assistant Professor (1987) at Tsukuba University, and then Assistant Professor (1989) and Associate Professor (1994) at The University of Tokyo. He was promoted to Professor of Chemistry at the Institute for Fundamental Research of Organic Chemistry, Kyushu University in 1998, and moved to Kyoto University as Professor of the Organoelement Chemistry Laboratory at the Institute for Chemical Research (ICR) in 2000. He was Visiting Professor of the Coordination Chemistry Laboratories at the Institute for Molecular Sciences during the period of 2001–2003, and is now serving as Vice-director of ICR (since 2005) and Director of the Pioneering Research Unit for Next Generation, Kyoto University (since 2006). Since 2004, he has served as Visiting Professor at Technische Universität Braunschweig, Germany. His main research fields are organoheteroatom and organometallic chemistry, and his current research interests are focused on the kinetic stabilization of highly reactive, low-coordinate compounds of heavier main group elements and the design and application of novel heteroatom ligands for coordination chemistry. He received the Progress Award in Synthetic Organic Chemistry of Japan in 1992, the Progress Award in Silicon Chemistry of Japan in 1996, the Japan IBM Science Award in 1998, the Bulletin of Chemical Society of Japan Awards in 2002, 2005, and 2007, the Chemical Society of Japan Award for Creative Work in 2003, and the Alexander von Humboldt Research Award in 2003.

2. Synthesis of distibenes and dibismuthenes

The natural and simple approach to the synthesis of a distibene may be that based on the methods used in the syntheses of diphosphenes, that is, the coupling reactions of dihalostibines. However, unsuccessful attempts to synthesize distibenes by taking advantage of some traditional bulky substituents used in the synthesis of stable diphosphenes and diarsenes[15] prompted us to choose much bulkier substituents as steric protection groups. We chose a Tbt group as a steric protection group, since we have already succeeded in the synthesis of a variety of compounds having a double bond between the heavier main group elements by taking advantage of kinetic stabilization using a Tbt group.

Dichlorostibine and dichlorobismuthine bearing a Tbt group $TbtECl_2$ (**4a**; E = Sb, **5a**; E = Bi) were readily prepared by the reaction of TbtLi with $SbCl_3$ and $BiCl_3$, respectively. The attempted coupling reactions of **4a** using various reducing reagents such as magnesium, lithium, lithium naphthalenide, and so on resulted in the recovery of a small amount of starting materials together with the formation of a mixture of insoluble inorganic salts and unidentified green powder. Although the inseparable green powder was unidentified at this stage, it was found to be distibene **2a** after the successful synthesis of **2a** by another method (*vide infra*).

Finally, we found an effective synthetic method for distibene **2a** and dibismuthene **3a**, that is, the deselenation reaction of the corresponding 1,3,5,2,4,6-triselenatripnictanes, $(TbtESe)_3$ (**6a**; E = Sb, **7a**; E = Bi), which were prepared by the reaction of **4a** and **5a** with Li_2Se in THF at room temperature, respectively (Scheme 2).[12,13] When **6a** and **7a** were heated in toluene together with an excess amount of $(Me_2N)_3P$ at 110 °C in a sealed tube, insoluble single crystals of distibene **2a** and dibismuthene **3a** were precipitated from the mixture on cooling. Compounds **2a** and **3a** were isolated by filtration in a glovebox filled with argon as deep green and purple single crystals in 94 and 68% yields, respectively. Fortunately, the extremely low solubility of **2a** and **3a** in toluene made their isolation quite simple.



Scheme 2

Thus, the first stable distibene and dibismuthene, *i.e.*, the long-sought after doubly bonded compounds consisting of antimony

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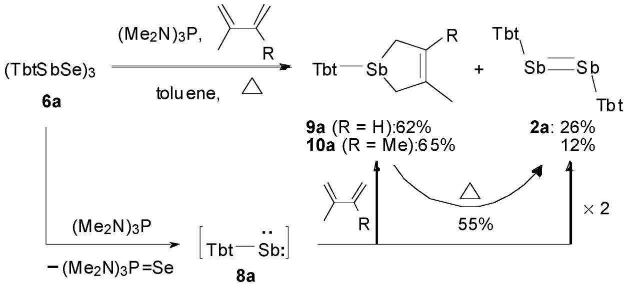
and bismuth, were synthesized and isolated as stable crystalline compounds, showing that a stable double-bond can be formed between the heavier Group 15 elements even in the case of the heaviest element, bismuth.

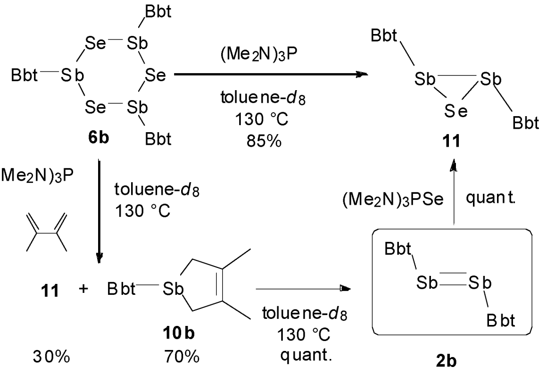
In the deselenation reaction of **6a** leading to the formation of distibene **2a**, the corresponding monovalent antimony species, stibinidene **8a**, can be thought as an intermediate.[13,16] Heating a toluene solution of **6a** and $(Me_2N)_3P$ in the presence of an excess amount of isoprene at 110 °C in a sealed tube for 22 h afforded stibolene **9a** as a main product (62%) together with a small amount of green crystals of **2a** (26%) (Scheme 3). Stibolene **10a** was also obtained (65%) in a similar deselenation reaction of **6a** using 2,3-dimethyl-1,3-butadiene instead of isoprene. Thus, it could be suggested that stibinidene **8a** is generated by the thermal reaction of **6a** with $(Me_2N)_3P$ as an initial intermediate along with $(Me_2N)_3PSe$, and then **8a**, which can be trapped by isoprene or 2,3-dimethyl-1,3-butadiene to afford **9a** or **10a**, respectively, readily undergoes dimerization to give distibene **2a**. In addition, thermolysis of **9a** in toluene-d_8 at 120 °C for 19 h afforded distibene **2a** in 55% yield, suggesting the dimerization of the stibinidene intermediate **8a** is generated *via* the thermal retro [1 + 4] cycloaddition reaction of **9a**. It was evidenced that thermolysis of a stibolene can be used as another synthetic method for a distibene.



Scheme 3

Although the first stable distibene **2a** and dibismuthene **3a** have been isolated as crystalline compounds, the extremely low solubility of **2a** and **3a** in common organic solvents (*e.g.*, hexane, benzene, toluene, $CHCl_3$, CH_2Cl_2, THF, Et_2O, *etc.*) prevented further studies on their chemical properties in solution. On the other hand, we have developed another bulky aromatic substituent, Bbt, which is expected to be a potentially useful steric protection group together with Tbt.[13,17] Taking account of the empirical fact that TbtH has a very low solubility while BbtH is comparatively more soluble than TbtH, the synthesis of the Bbt-substituted distibene **2b** was examined in the hope of obtaining a new distibene having higher solubility than **2a**.

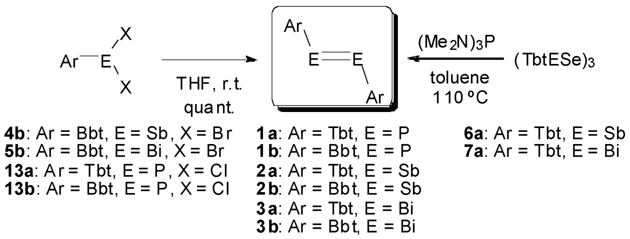
When 1,3,5,2,4,6-triselenatristibane $(BbtSbSe)_3$ (**6b**), which was prepared by the reaction of $BbtSbBr_2$ **4b** with Li_2Se in THF, was treated with $(Me_2N)_3P$ in toluene at 130 °C in a sealed tube in a manner similar to that used for the transformation of the Tbt analogue **6a** into **2a**, not distibene **2b** but the selenadistibirane derivative **11** was obtained as air-stable orange crystals in 85% yield.[13,18] Although the result seems to be strange, it was found based on further studies (*vide infra*) that **11** was formed by the reaction of the resulting distibene **2b**, which would have considerable solubility, with the resulting $(Me_2N)_3PSe$. On the other hand, the deselenation reaction of **6b** with $(Me_2N)_3P$ in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene afforded stibolene **10b** in 70% yield together with **11** (30%) (Scheme 4). As in the case of the generation of **2a** by the thermolysis of stibolene **9a**, thermolysis of stibolene **10b** gave distibene **2b** having a considerably high solubility in common organic solvents, *via* a retro [1 + 4] cycloaddition reaction. It was confirmed that the treatment of **2b**, which was isolated by the thermolysis of **10b**, with $(Me_2N)_3PSe$ afforded selenadistibirane **11** almost quantitatively. Anyway, Bbt-substituted distibene **2b** was found to be soluble in organic solvents in contrast to the case of Tbt-substituted distibene **2a**.[13]



Scheme 4

Thus, it was found that Bbt-substituted distibene **2b** cannot be isolated by the deselenation reaction of **6b** but can be prepared and isolated as a stable compound by a stepwise transformation *via* stibolene derivative **10b**. However, it is necessary to investigate other synthetic methods for the soluble dibismuthene **3b**, since 1,3,5,2,4,6-triselenatribismutane $(BbtBiSe)_3$ is not stable enough to be isolated.

Since Bbt-substituted distibene **2b** was found to be soluble in hexane, the direct reductive coupling reaction was examined for the synthesis of **2b**. Bbt-substituted dibromostibine **4b** was treated with Mg metal in THF at room temperature for 30 min and then the reaction mixture was extracted with hexane. Removal of inorganic salts and subsequent evaporation of hexane gave the expected distibene **2b** almost quantitatively (Scheme 5). This efficient synthetic method was found to be applicable to Bbt-substituted dibismuthene **3b**. The treatment of dibromobismuthine **5b** with Mg in THF at room temperature resulted in the almost quantitative formation of a purple powder (**3b**), which has a high solubility in common organic solvents as expected. Thus, Bbt group makes it easy to synthesize and isolate distibene and dibismuthene derivatives. In addition, Tbt- and Bbt-substituted diphosphenes



Scheme 5 Synthesis of diphosphenes, distibenes, and dibismuthenes.

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1a,**b** can also be synthesized by the reductive coupling reaction of the corresponding dichlorophosphines **13a**,**b**, respectively.[19] With **1a**,**b** in hand, we can make a systematic comparison of the properties between series of the heavier dipnictenes bearing the same steric protection groups, Tbt and Bbt.

3. Structures of diphosphenes, distibenes, and dibismuthenes bearing Tbt and Bbt groups

Systematic comparison of molecular structures among a series of heavier dipnictenes **1–3** is of great intrest and importance. Particularly, it is very important to know the structures and definitive structural parameters for the Bi=Bi double bond, since dibismuthenes **3a**,**b** are the first compounds containg a Bi=Bi double bond, which is the 'heaviest" double bond among those consisting of non-radioactive elements in the periodic table.

The structural parameters of **1–3** obtained by their X-ray crystallographic analyses (Fig. 1) are summarized in Table 1.[13,19] In all cases of distibenes **2a**,**b** and dibismuthenes **3a**,**b**, their molecular structures have a center of symmetry in the middle of the E=E double bond (E = Sb, Bi) and have *trans* configurations with the plane of the aryl rings of the Tbt or Bbt groups perpendicular to their C–E–E–C (E = Sb, Bi) planes. Although diphosphenes **1a** and **1b** also have *trans* configurations as well as the case of **2a**,**b** and **3a**,**b**, diphosphenes **1a**,**b** have no intramolecular center of symmetry, and the two Tbt and Bbt groups in **1a**,**b** are intertwined with each other in sharp contrast to **2a**,**b** and **3a**,**b** probably due to the severe steric repulsion between Tbt or Bbt groups caused by the shorter C–P and P=P bonds than C–E and E=E (E = Sb and Bi) bonds.[19]

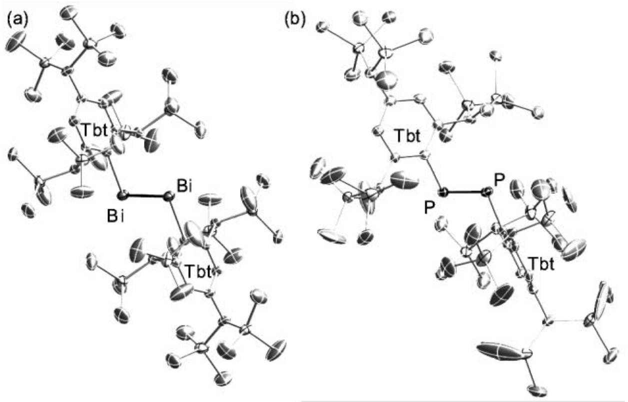

Fig. 1 ORTEP drawing (30% probability) of (a) dibismuthene **3a** and (b) diphosphene **1a**.

Table 1 Structural parameters of dipnictenes **1–3**

ArE=EAr	E–E/Å	E–E–C/°	E–E (in Ph_4E_2)/Å
TbtP=PTbt (**1a**)[a]	2.051(2)	106.4(2) 104.5(2)	2.217[c]
BbtP=PBbt (**1b**)[a]	2.043(1)	97.8(1) 114.9(1)	2.217[c]
TbtSb=SbTbt (**2a**)[b]	2.6422(7)	101.4(1)	2.837[d]
BbtSb=SbBbt (**2b**)[a]	2.7037(6)	105.4(1)	2.837[d]
TbtBi=BiTbt (**3a**)[b]	2.8206(8)	100.5(2)	2.990[e]
BbtBi=BiBbt (**1a**)[a]	2.8699(6)	104.2(1)	2.990[e]

[a] Measured at −170 °C. [b] Measured at 25 °C. [c] Ref. 20. [d] Ref. 21. [e] Ref. 22.

Table 2 Theoretically optimized structural parameters for RE=ER[a] systems calculated at B3LYP/6-31G(d) (TZ(2d)+diffuse for E)[b]

RE=ER	E = P	E = As	E = Sb	E = Bi
R = H				
E–E/Å	2.046	2.268	2.653	2.765
E–E–C/°	94.4	92.6	91.2	90.3
R =Me				
E–E/Å	2.043	2.265	2.654	2.767
E–E–C/°	101.4	99.3	97.4	96.6
R = Ph				
E–E/Å	2.059	2.280	2.664	2.775
E–E–C/°	101.9	99.5	97.1	95.6
R = Mes				
E–E/Å	2.050	2.272	2.659	2.771
E–E–C/°	101.0	99.0	97.0	95.6

[a] E = P, As, Sb, Bi. R = H, Me, Ph, Mes. [b] Ref. 25.

All of the lengths of the E=E bonds in **1–3** were found to be shorter by *ca.* 7% than those of the corresponding E–E single bonds in $Ph_2E–EPh_2$ (E = P, Sb, Bi),[20–22] indicating the considerable double-bond character of **1–3**. The observed E–E–C bond angles in **1–3** deviate greatly from the ideal sp^2 hybridized bond angle (120°). Although we have not extended our chemistry to that of arsenic analogues, such structural features of RE=ER systems were again evidenced by Power and co-workes, who successfully applied their original *m*-terphenyl ligands (2,6-$Ar_2C_6H_3$, Ar = Mes and Tip) to the synthesis of all the series of heavier dipnictenes RE=ER (E = P, As, Sb, Bi).[23] In addition, theoretical calculations (Table 2) for the RE=ER systems (R = H, Me, Ph, Mes; E = P, As, Sb, Bi) also show that the E–E–H angles get closer to 90° as the central element "E" goes from P to Bi, because the use of these three orthogonal 6p orbitals without significant hybridization leads to a bond angle of approximately 90° at bismuth. That is, the experimentally observed structural features are most likely interpreted in terms of the lower tendency of heavy atoms to form a hybridized orbital and prefer to maintain the $(ns)^2(np)^3$ valence electron configuration.[24] Although the experimentally observed Bi–Bi–C bond angles in **3a**,**b** were widened upto *ca.* 100° probably due to steric reasons and were found to be larger than the optimized structural parameters of the less hindered models, RBi=BiR (Table 2), the narrow bond angles of **3a**,**b** should be important as experimental evidence for the non-hybridization effect of bismuth.

4. Physical properties of the dipnictenes

4-1. Electronic spectra

The heavier congeners of *azo*-compounds are intensely colored. Their colors arise from the E=E double-bond chromophores, which appear as two absorption maxima in each case assignable as the symmetry allowed π–π* (intense) and symmetry forbidden n–π* (weak) electron transitions at wavelengths longer than 300 nm. The absorption maxima for **1–3** are summerized in Table 3.[13,19] In both series of Tbt- (**1a–3a**) and Bbt- (**1b–3b**) derivatives, it can be seen that their π–π* and n–π* transitions shift to longer wavelength regions as the element row is descended. These trends

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Table 3 Observed absorption maxima (nm) for **1–3** and calculated electron transitioins (nm) for RE=ER (R = H, Mes; E = P, As, Sb, Bi)

RE=ER	E = P	E = As	E = Sb	E = Bi
R = Tbt[a]				
π–π* (ε)	405 (13000)	—	466 (5200)	525 (4000)
n–π*(ε)	530 (2000)	—	599 (170)	660 (100)
R = Bbt[a]				
π–π*(ε)	418 (12000)	—	490 (6000)	537 (6000)
n–π*(ε)	532 (1000)	—	594 (200)	670 (20)
R = =Mes[b]				
π–π*	393	411	434	470
n–π*	507	546	601	596
$\Delta_{\text{HOMO–LUMO}}$[c]	3.37	3.15	2.88	2.68
R = H[b]				
π–π*	277	322	409	443
n–π*	389	414	485	488
$\Delta_{\text{HOMO–LUMO}}$[c]	4.18	3.78	2.98	2.77

[a] Observed in hexane solution. [b] Calculated at TD-B3LYP/6-31G(d) (TZ(2d)+diffuse for E) level. [c] Energy gaps between KS-HOMO and KS-LUMO in eV.

for the electron transitions indicate the weakening of the π-bond as the principal quantum number increases, and it is consistent with the results of TDDFT calculations and the frontier orbital energy gaps for RE=ER (E = P, As, Sb, and Bi).[25,26] In addition, similar trends are also observed for the absorption maxima of the 2,6-Mes_2-C_6H_3 and 2,6-Tip_2-C_6H_3 derivatives reported by Power *et al.*[23]

4-2. Raman spectra

In order to identify the double-bond character of the central E=E bonds in heavier dipnictenes **1–3**, the frequencies of the E=E stretching vibrations were measured by resonance Raman spectroscopy. The results are summarized in Table 4,[13,19] together with the calculated stretching vibrations for HE=EH and H_2E–EH_2. The observed strong Raman shifts for **1–3** (except for **3b**) assignable to the E=E stretching vibrations (E = P, Sb, Bi) are higher than those for the corresponding dipnictanes, Ph_2E–EPh_2, suggesting that dipnictenes **1–3** feature stronger E=E bonds as compared with the corresponding E–E single bonds (E = P, Sb, Bi).

4-3. Electrochemical properties

Table 5 Observed redox potentials for **1b**, **2b**, and **3b** along with calculated electron affinities and KS-LUMO levels for RE=ER (R = H, Me, Ph, Mes; E = P, As, Sb, Bi)

RE=ER	E = P	E = As	E = Sb	E = Bi
R = Bbt				
$E_{1/2}$[a]/V	−1.84	—	−1.65	−1.79
R = H				
KS-LUMO[b]	−3.12	−3.23	−3.30	−3.14
EA[b,c]/kcal mol^{-1}	25.73	30.17	35.46	32.89
R = Me				
KS-LUMO[b]	−2.37	−2.59	−2.80	−2.69
EA[b,c]/kcal mol^{-1}	14.29	19.87	26.94	25.27
R = Ph				
KS-LUMO[b]	−2.61	−2.76	−2.91	−2.83
EA[b,c]/kcal mol^{-1}	27.56	30.41	34.55	32.92
R = Mes				
KS-LUMO[b]	−2.41	−2.60	−2.74	−2.66
EA[b,c]/kcal mol^{-1}	23.34	27.61	32.00	30.51

[a] Observed in THF solution with $Bu_4N^+PF_6^-$ (0.1 M) at r.t. (*vs.* Ag/Ag^+). [b] Calculated at (U)B3LYP/6-31G(d) (TZ(2d)+diffuse for E) level. [c] EA is adiabatic electron affinity, which represents the difference between the total energies of the neutral and anionic species [EA = *E*(neutral) − *E*(anion radical)].

The redox behavior of dipnictenes **1b**, **2b**, and **3b**, which possess sufficient solubility in organic solvents, has been revealed by cyclic voltammetry.[25,30] In the oxidation region, irreversible oxidation waves were observed for **1b**, **2b**, and **3b** around E_{pa} = +1.01, +1.02, and +0.74 V *vs.* Ag/Ag^+, respectively, suggesting that the corresponding radical cations and/or dications of **1b**, **2b**, and **3b** are unstable under these conditions. On the other hand, **1b**, **2b**, and **3b** showed reversible one-electron redox couples in the reduction region, respectively (Table 5). It should be noted that distibene **2b** showed the lowest $E_{1/2}$ value as reduction potential among the three dipnictenes **1b–3b**. The experimental results observed here indicate that a distibene system may undergo facile one-electron reduction as compared with the other heavier dipnictenes. The experimental results were supported by theoretical calculations on the electron affinities and KS-LUMO levels (π*-orbital) for model compounds (RE=ER, R = H, Me, Ph, Mes; E = P, As, Sb, Bi), where the reduction of distibene systems, RSb=SbR, should be the most exothermic among those of the dipnictenes in all cases R = H, Me, Ph, and Mes (Table 5). The unique tendency of π-electron systems of heavier Group 15 elements observed here, which may be contradictory to the intuitive expectation that the π*-orbital level of an E=E double-bond will be lowered as the element row descends, can be most likely interpreted in terms of the "relativistic effect of the 6th row elements".[31]

5. Reactivities of the dipnictenes

5-1. Reduction reactions

The systematic studies on the redox behavior described in section 4-3 naturally prompted us to obtain the anion radical species of the dipnictenes. Although there are a number of reports on the ESR observation of anion radical species of kinetically stabi-

Table 4 Observed and calculated vibrational frequencies (cm^{-1}) of E–E and E=E stretchings (E = P, Sb, Bi)

E	TbtE=ETbt[a]	BbtE=EBbt[a]	Ph_2E–EPh_2	HE=EH[b]	H_2E–EH_2[b]
P	609	603	530[c]	613	426
Sb	207	196	141[d]	225	165
Bi	135	—[e]	103[f]	160	120

[a] Observed Raman shifts (solid; excitation, He-Ne laser 632.8 nm). [b] Calculated values without correction at B3LYP/6-31G(d) (TZ(2d)+diffuse for E) level. [c] Ref. 27. [d] Ref. 28. [e] Decomposed under the measurement conditions. [f] Ref. 29.

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lized dipnictenes (diphosphene, diarsenes, and phosphaarsenes) generated *in situ*,[32] such radical species cannot be handled as crystalline compounds most likely due to their extremely high reactivity and/or instability. Furthermore, there is no report on the attempted generation of the anion radical species of a distibene or a dibismuthene until our research.

After several examinations, the reduction of diphosphene **1b** and distibene **2b** with lithium metal in DME was found to afford the corresponding anion radical species as stable compounds, which were isolated as stable powders of [Li$^+$(dme)$_3$][**1b**$^{\bullet-}$] and [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$], respectively.[25] The anion-radical species of **1b** was characterized by the ESR spectrum, which displayed a hyperfine structure due to two equivalent phosphorus atoms [g = 2.009, $A(^{31}P)$ = 135 MHz] as well as the previously reported anion-radical species of kinetically stabilized diphosphenes [g = 2.007–2.018, $A(^{31}P)$ = 120–150 MHz].[32] On the other hand, the THF solution of [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$] showed a highly broadened signal with g = 2.097 (Fig. 2(b)), while a complicated spectrum was obtained from the powder-pattern ESR spectra. It should be noted that the complicated spectrum can be reasonably explained by coupling with two antimony atoms, which have two isotopes of ^{121}Sb (57.25%, I = 5/2) and ^{123}Sb (42.75%, I = 7/2) with parameters of g_{xx} = 1.961, g_{yy} = 2.030, g_{zz} = 2.368, A_{xx} = 644 MHz, A_{yy} = 350 MHz, and A_{zz} = 126 MHz (g_{iso} = 2.1197), indicating that the bulkiness of the Bbt groups of **2b**$^{\bullet-}$ might prevent the intermolecular interaction of the radical species.

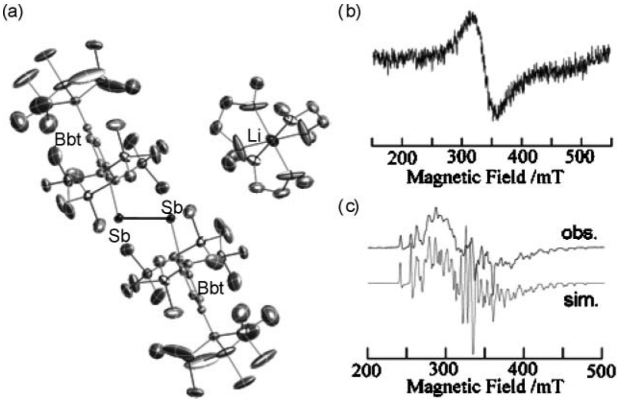

Fig. 2 (a) ORTEP drawing of [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$] (50% probability). (b) ESR spectrum of [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$] in THF solution. (c) Observed and simulated spectra of [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$] in the solid state.

The UV-vis spectra of [Li$^+$(dme)$_3$][**1b**$^{\bullet-}$] and [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$] in DME showed characteristic absorption maxima in the region of longer wavelengths at 539 and 812 nm, respectively, which can be assigned to the corresponding π–π* transitions based on TDDFT calculations on the model compounds, $[Mes_2P_2]^{\bullet-}$ and $[Mes_2Sb_2]^{\bullet-}$. Thus, their π–π* transitions are red-shifted as compared with those of the corresponding neutral species (**1b**: 418 nm, **2b**: 490 nm), indicating their weakened π-bonds. Furthermore, Raman spectra (in the solid state) of [Li$^+$(dme)$_3$][**1b**$^{\bullet-}$] and [Li$^+$(dme)$_3$][**2b**$^{\bullet-}$] provided important information on the bonding character of the anion radical species, showing strong Raman lines attributable to the corresponding E–E (E = P and Sb) stretching vibrations at 537 and 188 cm^{-1}, respectively. These observed values are higher than those of the corresponding single bonds, $Ph_2P–PPh_2$[27] and $Ph_2Sb–SbPh_2$,[28] and lower than those of the corresponding neutral double-bonds, **1b** and **2b** (see, Table 4), respectively. Those of $[Mes_2P_2]^{\bullet-}$ and $[Mes_2Sb_2]^{\bullet-}$ were estimated by theoretical calculations to be 571 and 189 cm^{-1}, respectively. These features of the anion radical species **1b**$^{\bullet-}$ and **2b**$^{\bullet-}$ were reasonably explained in terms of the introduction of one electron onto the antibonding π*-orbital of the neutral double-bond compounds, **1b** and **2b**, leading to the elongation of the E–E (E = P, Sb) bond lengths. Finally, the structural parameters of [Li$^+$(dme)$_3$][**2b**$^-$] were determined by X-ray crystallographic analysis (Fig. 2(a)). There should be no interaction between the [**2b**$^{\bullet-}$] and [Li$^+$(dme)$_3$] moieties in the crystalline state as judged by the long Sb–Li distance (*ca.* 6.7 Å). The geometry of [**2b**$^{\bullet-}$] is similar to that of **2b**, having a center of symmetry in the middle of its Sb–Sb bond with a *trans*-configuration. The small Sb–Sb–C(Bbt) angle of 102.29(8)° can be explained in terms of the tendency to maintain the $(5s)^2(5p)^3$ configuration of the Sb atoms in the case of **2b**. The Sb–Sb bond length of [**2b**$^{\bullet-}$] is 2.7511(4) Å, which is the medium value between the Sb–Sb single and double bonds (see, Table 1), indicating the introduction of one electron into the antibonding π*-orbital of **2b**.

5-2. Oxidation and chalcogenation reactions

In contrast to the systematic studies on the oxidation and chalcogenation reactions of dimetallenes (or metallylenes) of heavier Group 14 elements,[1,33] the reactivities of dipnictenes have been concealed except for the case of the kinetically stabilized diphosphenes and diarsenes due to the lack of stable examples of a distibene and dibismuthene until our research. We have revealed the unique reactivity of a series of stable dipnictenes **1–3** toward oxidation and chalcogenation reactions with aerobic oxygen and elemental chalcogens (Table 6).[34]

Although dipnictenes **1–3** are quite stable compounds under ambient conditions in inert atmosphere, Tbt-substituted distibene **2a** and dibismuthene **3a**, which are almost insoluble in organic solvents, were found to undergo gradual oxidation reactions with aerobic oxygen leading to the formation of 1,3,2,4-dioxadipnictanes **14a** and **15a** in the crystalline state, respectively. Interestingly, these oxidation reactions are "single crystals to single crystals" reactions, that is, they proceed maintianing crystallinity through the oxidation process. Although similar oxidation reactions of crystals of **2b** also gave **14b** under the same conditions, those of a C_6D_6 solution of **2b** afforded only BbtH. Whereas Mes*-substituted diphosphene (Mes*P=PMes*, **16**) is quite stable in air, **1b** underwent a unique oxidation reaction with aerobic oxygen in the crystalline state leading to the formation of novel oxadiphosphirane **17**, which was identified based on its NMR (^{1}H and ^{31}P) and FAB-mass spectra and elemental analysis together with preliminary X-ray crystallographic analysis results.[35] Since Bbt and Tbt effectively prevent the E=E moiety from dimerization but do not obstruct the reaction with small molecules such as oxygen, unique reactivity of a diphosphene with aerobic oxygen was revealed in the case of **1b**.

The sulfurization reaction of **1b** proceeded under relatively severe conditions, that is, heating of **1b** with elemental sulfur (S_8, 10 eq. as S) in the presence of Et_3N (10 eq.) at 120 °C in C_6D_6 for 40 h afforded thiadiphosphirane **18** (88%)[19] as in the case of sulfurization of Mes*P=PMes* with elemental sulfur.[36] In contrast to the case of **1b**, the sulfurization reaction of **2b** and

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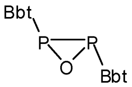
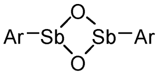
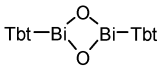
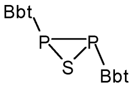
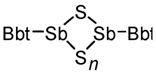
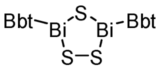
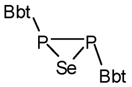
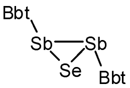
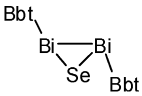
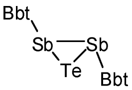
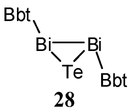
Table 6 Oxidation and chalcogenation reactions of the dipnictenes **1–3**

	BbtP=PBbt	ArSb=SbBbt	ArBi=BiAr
Oxidation (aerobic oxygen)	 **17**	 **14a** (Ar = Tbt) **14b** (Ar = Bbt)	 **15a**
Sulfurization (S_8)	 **18**	 **20** (n = 2) **21** (n = 3) **22** (n = 1)	 **19**
Selenization (Se)	 **25**	 **23**	 **24**
Tellurization (Bu_3PTe)	No reaction	 **27**	 **28**

3b with an excess amount of elemental sulfur (S_8) in benzene readily proceeds at room temperature to give the corresponding heterocycles containing sulfur and pnictogen (Sb, Bi) atoms, respectively.[34,37] Although the sulfurization of **3b** afforded exclusively 1,2,4,3,5-trithiadibismolane derivative **19**, that of **2b** under the same conditions gave three types of antimony-containing cyclic polysulfides, *i.e.*, 1,2,4,3,5-trithiadistibolane **20** (69%), 1,2,3,5,4,6-tetrathiadistibinane **21** (17%), and 1,3,2,4-dithiadistibetane **22** (14%), without any other identifiable compound.

On the other hand, the selenization reactions of **2b** and **3b** using elemental selenium in the presence of Et_3N in C_6D_6 at high temperature (60 °C and 80 °C, respectively) afforded the corresponding three-membered ring compounds, selenadipnictiranes **23** and **24** in high yield,[19] while that of **1b** gave selenadiphosphirane **25** together with diselenoxophosphorane $BbtPSe_2$ (**26**), which could not be isolated due to its high sensitivity toward light, as in the case of Mes*P=PMes*.[38] In contrast to the sulfurization and selenization reactions of **1b**, the tellurization reaction of **1b** using elemental tellurium or $(n\text{-Bu})_3P{=}Te$, which has been known as a good tellurization reagent, ended up with no reaction even on heating at 120–150 °C in C_6D_6 in a sealed tube. On the other hand, heating of **2b** with elemental tellurium (10 eq.) in C_6D_6 in a sealed tube at 120 °C for 2 d afforded the corresponding telluradistibirane **27** as a stable compound in 15% yield. At last, we found that a phosphine telluride could work as a good tellurization reagent toward **2b** and **3b** under mild conditions. As a result, novel telluradipnictiranes **27** (50%) and **28** (43%) were successfully isolated by the treatment of **2b** and **3b** with $(n\text{-Bu})_3P{=}Te$ in C_6H_6 at room temperature for 2 h.[34,39] Telluradibismirane **28** is the "heaviest" example among stable three-membered heterocyclic compounds isolated so far. Thus, it was found that the doubly bonded systems between heavier Group 15 elements are good precursors for unique and novel heterocycles containing pnictogen atoms. The molecular structures of the obtained heterocyclic compounds were established by spectroscopic and X-ray crystallographic analyses (Fig. 3).

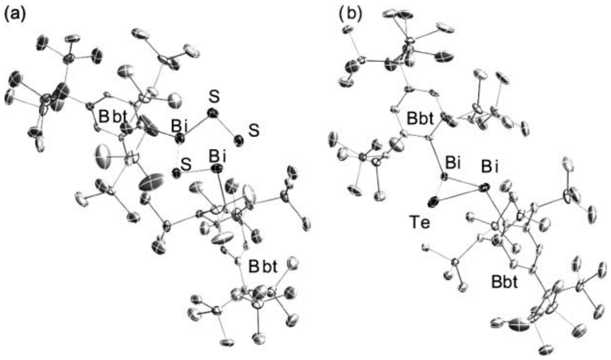


Fig. 3 ORTEP drawings (50% probability) of (a) 1,2,4,3,5-trithiadibismolane **19** and (b) telluradibismirane **28**.

5-3. Cycloaddition reactions

As descrived in section 5-2, it was demonstrated that the doubly bonded systems between heavier Group 15 elements are good precursors for unique and novel heterocycles containing pnictogen atoms. In addition, many examples have been reported for the [2 + 4]-cycloaddition reactions of kinetically stabilized diphosphenes with dienes giving the corresponding six-membered ring compounds containing a P–P bond. Whereas **1–3** did not react with 2,3-dimethyl-1,3-butadiene even on heating, it was found that distibene **2b** reacted with MesCNO as a 1,3-dipole to afford the corresponding cycloadduct, 1,5,2,3-oxazadistibacyclopent-4-ene **29** (Scheme 6).[40] It is unclear at present why only **2b** can readily undergo the [2 + 3]-cycloaddition with MesCNO in contrast to the

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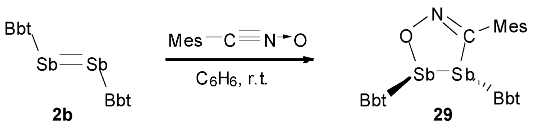


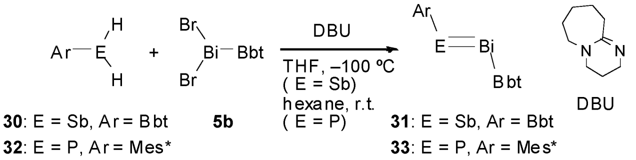
Scheme 6 Reaction of **2b** with MesCNO.

case of diphosphene **1b** and dibismuthene **3b**, which were found to be completely inert with MesCNO even on heating.

6. Synthesis of heteronuclear double-bond compounds containing the bismuth atom

Since it was demonstrated that homonuclear doubly bonded systems between heavier Group 15 elements are no longer imaginary species even in the heaviest case of bismuth, the next target molecules should be the heteronuclear doubly bonded systems, which may be key compounds of great importance in the systematic elucidation of the intrinsic nature of low-coordinated compounds of heavier main group elements. Although some examples of phosphaarsenes and phosphastibenes have already been reported,[1,9,41] no heteronuclear double bonds between bismuth and another Group 15 element have been discovered until our research, probably due to the weakness of the π-bond between Bi and another atom caused by the difference in the size of the p-orbitals.

The condensation reaction of dihydrostibine $RSbH_2$ with dibromobismuthine **5b** was thought to be a good synthetic route in view of the previous reports on the synthesis of unsymmetrically substituted diphosphenes such as Mes*P=PMes.[42] Although a dihydrostibine generally shows thermal instability and decomposes in minutes or hours at ambient temperature, Bbt-substituted dihydrostibine **30** was successfully synthesized as a stable crystalline compound by the reaction of dibromostibine **4b** with $LiAlH_4$. Preliminarily, it was demonstarated as a novel synthetic method for **2b** that the condensation reaction of **30** with **4b** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in THF afforded distibene **2b** as expected.[35] Furthermore, condensation reaction of **30** with dibromobismuthine **5b** in THF at −95 °C afforded stibabismuthene **31** as red-purple crystals quantitatively (Scheme 7).[43] Unfortunately, the definite structural parameters for **31** have not been obtained yet due to the inevitable disorder of the antimony and bismuth atoms, which cannot be solved by data collection with a number of different single crystals of **31** even at −180 °C (Fig. 4). However, the structure of **31** was distinctly characterized by spectroscopic analyses. In the Raman spectrum (in the solid state) of **31**, a strong line attributable to Sb–Bi stretching was observed at 169 cm^{-1}. This vibrational frequency lies between the values of the Sb=Sb stretching vibration in distibenes **2** and that of the Bi=Bi stretching vibration in dibismuthene **3a** (see, Table 4), and is higher than the Sb–Sb and Bi–Bi stretching frequencies for $Ph_2E–EPh_2$.[28,29]



Scheme 7 Synthesis of stibabismuthene **31** and phosphabismuthene **33**.

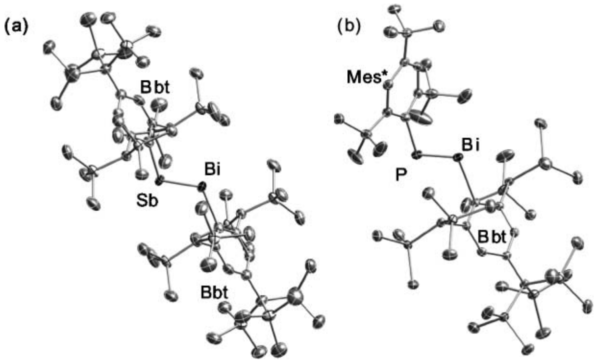


Fig. 4 ORTEP drawings (50% probability) of (a) stibabismuthene **31** (Sb and Bi atoms are highly disordered) and (b) phosphabismuthene **33**.

The UV/vis spectrum of **31** in hexane shows two absorption maxima at 709 nm (ε 200 dm^3 mol^{-1} cm^{-1}) and 516 nm (ε 7500 dm^3 mol^{-1} cm^{-1}), which are most likely assignable to the forbidden n–π* and the allowed π–π* transitions of the Sb=Bi chromophore, respectively. The λ_{max} value for the π–π* transition of **31** is between those of **2b** and **3b**.

Similarly, the condensation reaction of $BbtBiBr_2$ (**5b**) with Mes*PH_2 (**32**) in the presence of DBU in hexane at room temperature afforded a deep orange powder, the ^{31}P NMR spectrum of which showed a characteristic broad singlet at 612 ppm. The broadening of the signal is most likely due to the 9/2 nuclear spin of the adjacent Bi atom. Since the low-field chemical shift of 612 ppm is characteristic of a low-coordinated phosphorus atom, this result strongly suggests the formation of phosphabismuthene **33** in this reaction.[44] It is noteworthy that **33** is not only a new member of a novel class of heteronuclear doubly bonded systems between heavier Group 15 elements but also the first example of a stable species with a double bond between the third and sixth row main group elements. The molecular structure of **33** was determined by X-ray crystallographic analysis (Fig. 4), showing its *trans*-configuration with a C–Bi–P–C torsion angle of 179.79(9)°. The length of the P–Bi bond of **33** is 2.4541(6) Å, which is just intermediate between the E=E bond lengths of the corresponding diphosphene **16**[8] [Mes*P=PMes*, 2.034(2) Å] and dibismuthene **3b**, and is *ca.* 8% shorter than the sum of the covalent radii of the phosphorus and bismuth atoms (2.66 Å). Unfortunately, the Raman spectral data could not be obtained due to sample decomposition under the measurement conditions. The UV/vis spectrum of **33** in hexane shows characteristically red-shifted absorption maxima at 455 (ε 10000 dm^3 mol^{-1} cm^{-1}), 540 (sh, ε 1000 dm^3 mol^{-1} cm^{-1}), and 670 (ε 300 dm^3 mol^{-1} cm^{-1}) nm, whereas the previously-known heavier congeners of *azo*-compounds show only two absorption maxima corresponding to the symmetry allowed (π–π*) and the symmetry forbidden (n–π*) electron transitions. The λ_{max} value of 455 nm attributable to the π–π* transition of the P=Bi chromophore is between those of Mes*P=PMes* (**16**)[8] [340 nm (ε 7690 dm^3 mol^{-1} cm^{-1})] and BbtBi=BiBbt (**3b**). Although the latter two λ_{max} values observed for **33** (540 and 670 nm) are most likely assignable to the n–π* transitions and one of them at 540 nm is reasonably found between the λ_{max} value of **16** [460 nm (ε 1360 dm^3 mol^{-1} cm^{-1})] and that of **3b**, another one at 670 nm lies at a strangely longer wavelength. Although we have no clear explanation for the additional n–π*

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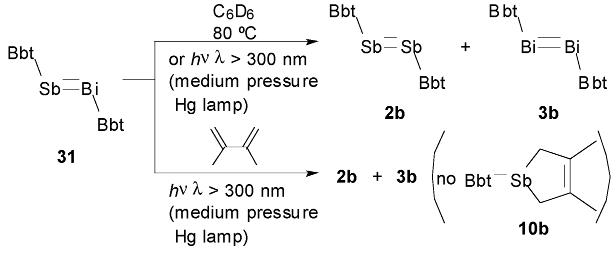
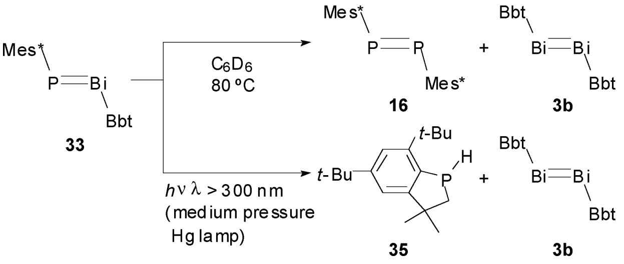
transition for **33** observed in the longer wavelength region, it may be consistent to assume that heteronuclear doubly bonded systems between heavier Group 15 elements should have two weak n–π* transitions due to the two chemically distinct lone pairs on the phosphorus and bismuth atoms. The outcomes for **33** discussed above are also of great importance in the understanding of the spectroscopic properties of stibabismuthene **31**, that is, it can be thought that only one n–π* transition at a longer wavelength (709 nm) is observed for **31** but the other one might be hidden by the intense π–π* transitions at 516 nm.

Now, as for the heavier Group 15 elements, not only the homonuclear doubly bonded compounds but also the heteronuclear systems containing a bismuth atom are in hand as stable compounds, even in the case between extremely different row elements.

Interestingly, the themolysis of **31** and **33** in C_6D_6 (sealed tube) at 80 °C gave the corresponding homonuclear double-bond compounds, respectively, that is, **2b** and **3b** were obtained from **31** (Scheme 8), and **16** and **3b** were generated from **33** (Scheme 9).[35,43] In addition, the photoirradiation of **31** also afforded **2b** and **3b**. Although the formation of **2b** and **3b** may be intuitively interpreted in terms of the dissociation of the Sb=Bi bond of **31** followed by the dimerization of the resulting stibinidene BbtSb: (**8b**) and bismuthinidene BbtBi: (**34**), the attempted trapping reaction of the stibinidene intermediate **8b** was unsuccessful. Thus, no stibolene **10b**, the expected [1 + 4]-cycloaddition product of **8b** (see, Scheme 3), was obtained by the photolysis of **31** in the presence of 2,3-dimethyl-1,3-butadiene under the same conditions, suggesting the formation of **2b** and **3b** is most likely interpreted in terms of the photochemical head-to-head [2 + 2]-dimerization of **31** followed by the retro [2 + 2]-reaction. On the other hand, the photoirradiation of **33** gave **3b** and phosphaindane **35** in a ratio of 1 : 2. Phosphaindane **35** is known to be formed *via* the intramolecular cyclization of the phosphinidene (Mes*P:) generated by the photchemical dissociation of **16**.[35,45] Although the generation of **35** may be explained by the dissociative cleavage of the P=Bi bond of **33** under irradiation, **35** may also be generated from **16**, which can be initially generated by the photolysis of **33** along with **3b** as in the case of the photolysis of **31**. Although it is important and interesting to elucidate the reaction mechanism, it is still unclear at present.



Scheme 8 Thermolysis and photolysis of **31**.



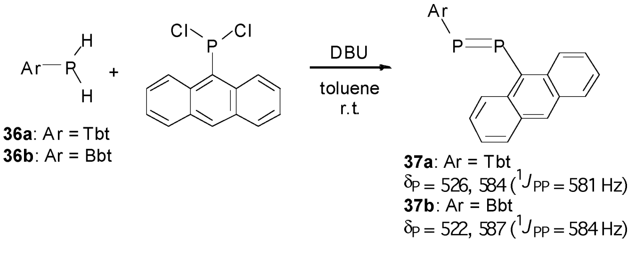
Scheme 9 Thermolysis and photolysis of **33**.

7. Recent topics: functionalized diphosphenes

Recently, much attention has been focused on the unique electrochemical properties of phosphaalkenes and diphosphenes from the viewpoints of material science, since they are known to be more easily reduced than olefins or *azo*-compounds.[32,46] To date, a number of π-conjugated systems containing low-coordinated phosphorus atoms have been reported.[47] Particularly, Gates *et al.* and Protasiewicz *et al.* reported their initial work on the photochemical properties of the "phospha-PPVs", poly(*p*-phenylenephosphaalkene)s,[48] which exhibit unique fluorescence due to the π-conjugated P=C units. Since a P=P double bond should possess an apparently smaller HOMO − LUMO energy gap compared with those of a P=C double bond, fundamental studies on the properties of a π-electron extended system of a diphosphene should also be interesting and important for beginning new chemistry of material science. Recently, we have reported the first stable 9-anthryldiphosphene,[49] ferrocenyldiphosphene,[50] and 1,1′-bis(diphosphenyl)ferrocenes[51,52] as new candidates for a family of π-conjugated diphosphenes. Furthermore, a novel β-ketophosphenato ligand,[53] which should feature unique properties reflected by the low-coordinated phosphorus atom, was designed, synthesized, and applied to transition metal complexation.

7-1. 9-Anthryldiphosphenes

Condensation reactions of $ArPH_2$ (**36a**: Ar = Tbt, **36b**: Ar = Bbt), which were prepared by the reaction of $ArPCl_2$ (**13a**,**b**) with $LiAlH_4$, $AnthPCl_2$ (Anth = 9-anthryl) in the presence of DBU in toluene at room temperature afforded the first stable 9-anthryldiphosphenes **37a**,**b** as stable red crystals (Scheme 10).[49] It should be noted that both **37a** and **37b** are quite stable under an inert atmosphere even in solution (C_6D_6, 80 °C for 26 h) reflecting the superior steric protecting ability of Tbt and Bbt for preventing oligomerization. X-Ray crystallographic analysis of **37a** (Fig. 5) revealed its *trans*-configured geometry along with the intermolecular π–π interaction (*ca.* 3.55 Å) between the anthryl moieties of **37a** in the packing structure. The P=P bond length and P–P–C angles were found to be 2.0352(16) Å and *ca.* 101°, respectively, which are within the range of the previously reported structural parameters of diaryldiphosphenes. The anthryl group is nearly perpendicular (81.7°) to the P=P axis probably due to steric reasons, indicating the less effective π-electron conjugation between the P=P and anthryl moieties in the solid state.



Scheme 10 Synthesis of 9-anthryldiphosphenes **37**.

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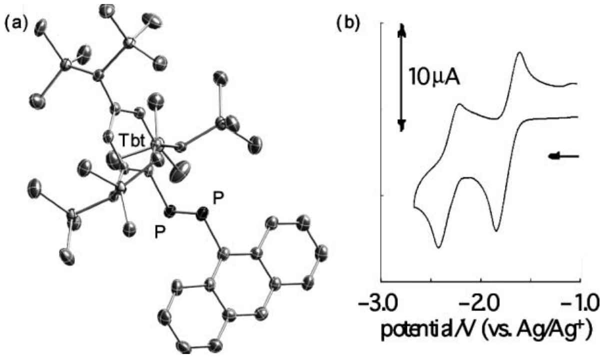


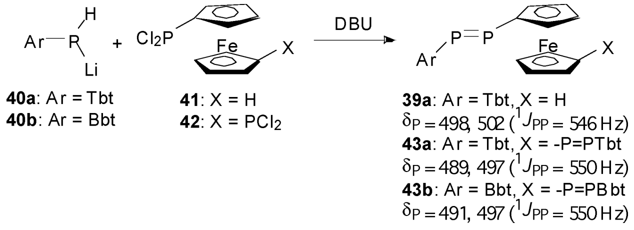
Fig. 5 (a) ORTEP drawing (50% probability) and (b) cyclic voltammogram (0.1 M Bu_4NBF_4 in THF) of **37a**.

The electrochemical data for **37a** were determined by cyclic voltammetry, showing two reversible one-electron redox couples at $E_{1/2} = -1.73$ and -2.32 V (*vs.* Ag/Ag$^+$). It should be noted that the first reduction potential in a less negative region than that of TbtP=PTbt (**1a**, $E_{1/2} = -1.93$ V *vs.* Ag/Ag$^+$) and anthracene ($E_{1/2} = -2.42$ V *vs.* Ag/Ag$^+$) evidenced the stability of the anion radical species of **37a** due to the delocalization of the unpaired electron on the P=P and the anthryl moieties in solution. In the UV/vis spectrum of **37a** in hexane, a complicated pattern due to the π–π* electron transitions of the anthryl and P=P moieties was observed in the longer wavelength region than that of anthracene, indicating the extended π-electron conjugation in solution. Interestingly, 9-anthryldiphosphene **37a** shows weak but apparent fluorescence emissions in the range of *ca.* 400–500 nm ($\Phi = 1.2 \times 10^{-3}$), though a π-conjugated polymer containing P=P units reported by Protasiewicz *et al.* and other kinetically stabilized diphosphenes previously reported exhibit no appreciable luminescence.[48d] The observed lifetime of the photoluminescence of **37a** is *ca.* 8–10 ns suggesting that the luminescence of **37a** should be not phosphorescence but fluorescence.

7-2. Ferrocenyldiphosphenes

Ferrocenyldiphosphenes are expected to be a unique class of intramolecular donor–acceptor system, where a diphosphene and a ferrocene unit should work as an acceptor and a donor, respectively, since the P=P double bond should be easily reduced to give the corresponding anion radical when it is kinetically well stabilized as shown in section 4-3. Pietschnig and Niecke began the chemistry of ferrocenyldiphosphene and have reported their initial study on the synthesis and spectroscopic characterization of Mes*P=PFc (**38**, Fc = ferrocenyl),[54] though the structural characterization and further investigation from the viewpoint of its electrochemical properties have not been accomplished due to its instability (stable only below −30 °C in the absence of daylight).

Tbt-substituted ferrocenyldiphosphene, TbtP=PFc (**39a**), was sucessfully synthesized and isolated as a stable crystalline compound (mp 182–184 °C, stable up 100 °C in C_6H_6, inert to light) by reaction of TbtPHLi (**40a**) with $FcPCl_2$ (**41**) followed by treatment with DBU *in situ* (Scheme 11).[50] The remarkable stability of **39a** compared with **38** reflects the superior protecting ability of Tbt. In the crystal structure, **39a** shows a *trans*-configuration with a C–P–P–C dihedral angle of *ca.* 180°, and the C–P–P–C plane is almost coplanar with the Cp ring of the ferrocenyl moiety, suggesting a conjugative interaction between the π-electrons of the P=P unit and those of the Cp unit. However, the P=P bond length of **39a** [2.0285(15) Å] seems to be little affected by the conjugation, since it is in the range of the previously reported non-conjugated diaryldiphosphenes (*ca.* 2.00–2.05 Å).[1] The UV/vis spectrum of **39a** in hexane shows two characteristic absorption maxima at 371 (ε 2500 dm^3 mol^{-1} cm^{-1}) and 542 (ε 900 dm^3 mol^{-1} cm^{-1}) nm, which are assignable to the π–π* electron transition of the P=P unit and the metal-to-ligand charge transfer (MLCT) band from the d-orbital of the Fe atom to the π*-orbital of the P=P unit, respectively. The red-shifted absorption of **39a** as compared with that of azoferrocenes (321–328 nm for π–π* transitions, 522–539 nm for MLCT)[55] can be explained by the lower level of the π*-orbital of the P=P unit than that of the N=N unit. In addition, the cyclic voltammograms of **39a** showed $E_{1/2}$ values of +0.36 (ox.) and −1.93 (red.) V (*vs.* Ag/Ag$^+$), which are in the region similar to those of ferrocene and diphosphene **1a**.



Scheme 11 Synthesis of ferrocenyldiphosphenes **39a**, **43a**, and **43b**.

We have also extend the chemistry of ferrocenyldiphosphenes to that of 1,1′-bis(diphosphenyl)ferrocenes. The treatment of ArPHLi (**40a**,**b**) with 1,1′-bis(dichlorophosphino)ferrocene afforded the first stable 1,1′-bis(diphosphenyl)ferrocenes **43a** and **43b**.[51,52] At almost the same time, Pietschnig and co-workers independently reported the synthesis of another type of stable 1,1′-bis(dichlorophosphino)ferrocene bearing *m*-terphenyl ligands, 2,6-Mes$_2$-C$_6$H$_3$.[56] The structural and spectroscopic features of **43a**,**b** are similar to those of **39a**. Interestingly, the P=P vibrational frequencies for the two P=P units of **43a**,**b** are both Raman and IR active due to the symmetric and asymmetric vibrations of the two P=P units, though the P=P vibration of ferrocenyldiphosphene **39a** is active for only Raman spectra. The redox behavior of **43a** and **43b** has been furnished by cyclic voltammetry, showing two reversible one-electron redox waves due to the intramolecular two redox centers observed at −1.84 and −2.19 V (**43a**) and −1.78 and −2.13 V (**43b**) *vs.* Ag/Ag$^+$, respectively (see Table 7). In both cases, the difference between the half-potentials ($\Delta E_{1/2} = 0.35$ V) means a comproportionation constant of $K_c = 8.2 \times 10^5$ for the mixed-valence state, indicating an effective electronic interaction through the central ferrocene unit to some extent similar to the case of the previously reported 1,4-bis(diphosphenyl)benzene [$\Delta E_{1/2} = 0.34$ V and $K_c = 5.6 \times 10^5$].

As the next stage, we applied 1,1′-bis(diphosphenyl)ferrocene **43b** as a novel bidentate ligand bearing two P=P units linked by the ferrocenyl unit toward transition metal complexes in the expectation of obtaining a unique d–π conjugated bimetallic systems containing P=P units. Heating of **43b** in the presence of an excess amount of [M(CO)$_5$(CH$_3$CN)] (M = Cr, Mo, W) at 50 °C in C$_6$D$_6$ for 2–3 h afforded novel dinuclear metal complexes **44–46** (Scheme 12),[52] the structures of which were supported by their spectroscopic analyses and the X-ray crystallographic analysis

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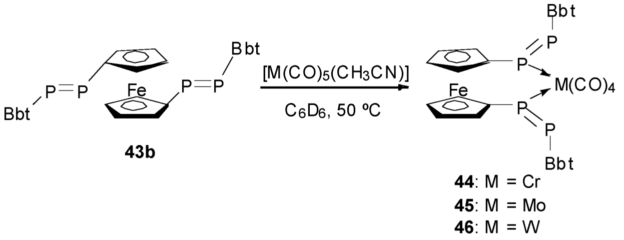
Table 7 Redox potentials (E/V *vs.* Ag/Ag^+) of ferrocenyldiphosphenes

Compounds	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V	$\Delta E_{1/2}$/V
39a (ox.)[a]	+0.45	+0.28	+0.36	
39a (red.)[b]	−1.85	−2.10	−1.93	
43a (ox.)[a]	+0.17	+0.10	+0.14	
43a (red.)[b]	−1.66	−2.02	−1.84	0.35
	−2.02	−2.35	−2.19	
43b (ox.)[a]	+0.18	+0.12	+0.15	
43b (red.)[b]	−1.67	−1.89	−1.78	0.35
	−2.02	−2.24	−2.13	

[a] 0.1 M $(n\text{-Bu})_4NBF_4$ in CH_2Cl_2, $E_{1/2}$ $(FcH/FcH^+) = +0.24$ V *vs.* Ag/Ag^+.
[b] 0.1 M $(n\text{-Bu})_4NBF_4$ in THF.

for **46** (Fig. 6). In all cases of **44–46**, the two P=P units were found to coordinate to the Group 6 metals in a *cis*-configuration with η^1-fashion. Interestingly, all the P=P units of **44–46** are (*Z*,*Z*)-isomers, though the starting material, ligand **43b**, is an (*E*,*E*)-isomer. That is, the diphosphene units of **43b** underwent *E*-to-*Z* isomerization during complexation with Group 6 metals, whereas kinetically stabilized diaryldiphosphenes are known to undergo *E*-to-*Z* isomerization not thermally but photochemically. Thus, it was demonstrated that 1,1′-bis(diphosphenyl)ferrocene **43b** can work as a bidentate ligand toward Group 6 metals. Further investigations on the physical properties, reactivities, electrochemical properties, and catalytic ability of **44–46** are currently in progress.



Scheme 12 Synthesis of dinuclear metal complexes **44–46**.

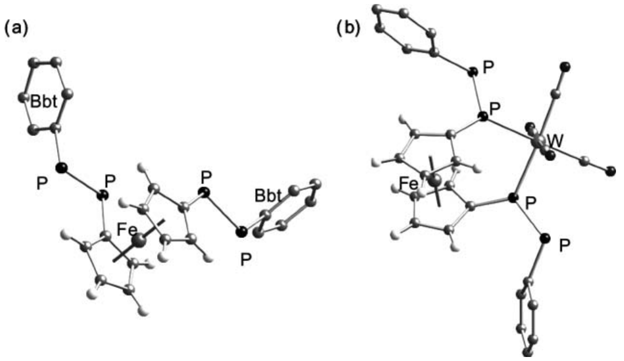
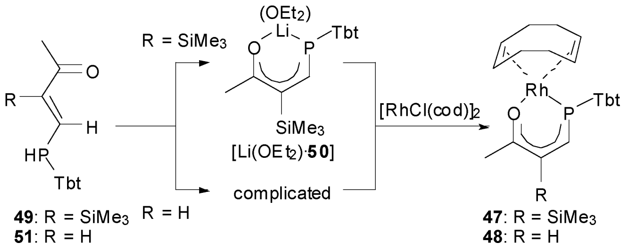


Fig. 6 Molecular structures of (a) **43b** and (b) **46**. Substituents on the Bbt groups were omitted for clarity.

7-3. β-Ketophosphenato ligands

The coordination chemistry of β-diketiminato and β-ketoiminato ligands has attracted much interest especially in the field of olefin polymerization based on late transition metals.[57] Particularly, a β-ketoiminato ligand features unique properties due to its moderate coordination ability towards a transition metal center lying between β-diketiminato (stronger) and Schiff-base (weaker) ligands to the same metal center and its unsymmetrical *trans*-effect based on the difference of the coordinating atoms (N and O).[58] On the other hand, the coordination chemistry of phosphaalkenes has also drawn a great deal of recent attention due to the unique electronic properties of the C=P double bond, whose characteristic low-lying π*-orbital make it possible to function as a good π-accepter towards a transition metal center.[59] During the course of our investigations on the low-coordinated species of the heavier Group 15 elements, we designed hitherto unknown β-ketophosphenato ligands,[60] which have both features of β-ketoiminato and low-coordinated phosphorus ligands, and succeeded in the synthesis of stable rhodium–cod β-ketophosphenates **47** and **48** as touchstones for the elucidation of the properties of β-ketophosphenato ligands.



Scheme 13 Synthesis of rhodium β-ketophosphenates **47** and **48**.

Deprotonation reactions of precursor **49** with LDA in THF afforded lithium β-ketophosphenate [Li(OEt$_2$)·**50**], the structure of which was identified by spectroscopic and X-ray crystallographic analyses. The reaction of [Li(OEt$_2$)·**50**] with $[RhCl(cod)]_2$ resulted in the formation of rhodium β-ketophosphenate **47** in 98% yield (Scheme 13).[53] Similarly, rhodium β-ketophosphenate **48** was also isolated as a stable compound using precursor **51**, where the intermediate lithium β-ketophosphenate could not be isolated.

Structures of the rhodium complex **48** and rhodium β-ketoiminate **52**, which was prepared as a comparative compound, were revealed by X-ray crystallographic analysis (Fig. 7). It was found that both **48** and **52** possessed an almost planar structure for the central six-membered ring moiety, [–Rh–O–C–C–C–E–] (E = N and P), where every bond length of the central hexagonal ring was between those of the corresponding single and double bonds, suggesting a delocalized cyclic π-electron system. It should be noted that the two kinds of Rh–C(cod) distance of **48** were apparently different from each other, though those of **52** were

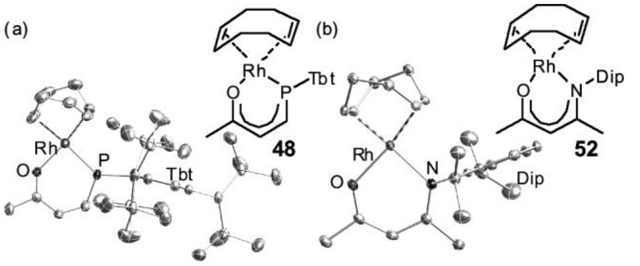


Fig. 7 ORTEP drawings (50% probability) of (a) rhodium β-ketophosphenate **48** and (b) rhodium β-ketoiminate **52**.

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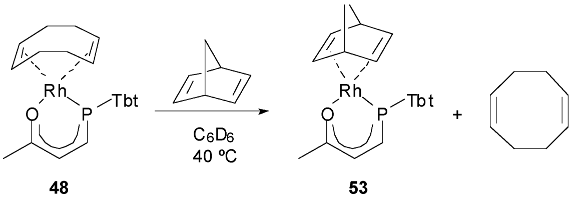
similar to each other, suggesting a stronger *trans*-influence of the phosphorus moiety of the β-ketophosphenato ligand of **48** as compared with its oxygen moiety in contrast to the similar degree of *trans*-influence of N and O atoms in the β-ketoiminto ligand. Such a unique unsymmetrical electronic feature of the β-ketophosphenato ligand is most likely interpreted in terms of a high σ-donating ability due to the electropositive phosphorus atom and the effective π-electron accepting ability due to the low-lying π*-orbital of the sp^2-hybridized phosphorus atom. Furthermore, heating of rhodium β-ketophosphenate **48** in the presence of norbornadiene (10 eq.) in C_6D_6 at 40 °C for 5 h afforded the corresponding diene-exchange product **53** almost quantitatively (Scheme 14), though no diene-exchange reaction was observed in the case of rhodium β-ketoiminate **52** under the same conditions. The lower barrier of the diene-exchange reaction of **48** than that of **51** might be due to the strong *trans*-effect of the P atoms of the β-ketophosphenato ligand. Thus, it was demonstrated for the first time that the β-ketophosphenato ligands should be unique and useful ligands.



Scheme 14 Diene exchange reaction of **48**.

8. Conclusion and outlook

The isolation and characterization of kinetically stabilized heavier dipnictenes have been almost accomplished, though some unprecedented double bonds still remain as interesting synthetic targets, *e.g.*, Sb=As and Bi=As. Now, it has been evidenced that the doubly bonded compounds between heavier Group 15 elements can be isolated in hand as "bottlable" compounds even in the heaviest non-radioactive element bismuth, when they are appropriately protected by bulky substituents such as Tbt and Bbt. While the concept of kinetic stabilization should certainly be of great use for the construction of these unprecedented chemical bonds, in the case of not only heavier Group 15 elements but also other main group elements, a number of homo- and heteronuclear double bonds between heavier main group elements have been constructed and their unique properties have been revealed. Thus, this is a turning point in the chemistry of main group elements, where the synthetic work for the doubly bonded systems and/or low-coordinated species of heavier main group elements have been almost established. Now, there will be much interest in the expansion of the chemistry of low-coordinated heavier main group elements to functional chemistry and material science from the standpoints of element chemistry. As we demonstrated the application of the low-coordinated phosphorus species toward the synthesis of π-conjugated systems, such as anthryl- and ferrocenyl-substituted diphosphenes, and also toward the development of novel heteroatom ligands for transition metals, the chemistry is just starting as a basis at the frontier of element chemistry. We believe that element chemistry can play an important role in several fields of material science in the near future.

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Notes and references

1 (*a*) P. P. Power, *Chem. Rev.*, 1999, **99**, 3463; (*b*) G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419; (*c*) N. Tokitoh, *J. Organomet. Chem.*, 2000, **611**, 217; (*d*) N. Tokitoh and R. Okazaki, *Coord. Chem. Rev.*, 2000, **210**, 251; (*e*) N. Tokitoh and R. Okazaki, *Adv. Organomet. Chem.*, 2001, **47**, 121; (*f*) N. Tokitoh, *Acc. Chem. Res.*, 2004, **37**, 86; (*g*) P. P. Power, *J. Organomet. Chem.*, 2004, **689**, 3904.

2 K. Pitzer, *J. Am. Chem. Soc.*, 1948, **70**, 2140.

3 H. Köler and A. Michaelis, *Ber. Dtsch. Chem. Ges.*, 1877, **10**, 807.

4 (*a*) W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2296; (*b*) J. J. Daly and L. Maier, *Nature*, 1964, **203**, 1167; (*c*) J. J. Daly and L. Maier, *Nature*, 1965, **208**, 383; (*d*) J. J. Daly, *J. Chem. Soc.*, 1964, 6147; (*e*) J. J. Daly, *J. Chem. Soc.*, 1965, 4789; (*f*) J. J. Daly, *J. Chem. Soc. A*, 1966, 428.

5 (*a*) P. Ehrlich, *Lancet*, 1907, **173**, 351; (*b*) P. Ehrlich and A. Bertheim, *Ber. Dtsch. Chem. Ges.*, 1911, **44**, 1265; (*c*) P. Ehrlich and A. Bertheim, *Ber. Dtsch. Chem. Ges.*, 1912, **45**, 761.

6 (*a*) K. Hedberg, E. W. Hughes and J. Waser, *Acta Crystallogr.*, 1961, **14**, 369; (*b*) A. C. Rheingold and P. J. Sullivan, *Organometallics*, 1983, **2**, 327; (*c*) N. C. Lloyd, H. W. Morgan, B. K. Nicholson and R. S. Ronimus, *Angew. Chem., Int. Ed.*, 2005, **44**, 941.

7 R. West and M. J. Fink, *Science*, 1981, **214**, 1343.

8 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587.

9 For the first stable diarsenes and phosphaarsenes, see: (*a*) A. H. Cowley, J. G. Lasch, N. C. Norman and M. Pakulski, *J. Am. Chem. Soc.*, 1983, **105**, 5506; A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski and B. R. Whittlesey, *J. Chem. Soc., Chem. Commun.*, 1983, 881; J. Escudié, C. Couret, H. Ranaivonjatovo and J. G. Wolf, *Tetrahedron Lett.*, 1983, **24**, 3625; C. Couret, J. Escudié, Y. Madaule, H. Ranaivonjatovo and J. G. Wolf, *Tetrahedron Lett.*, 1983, **24**, 2769; (*b*) L. Weber, *Chem. Rev.*, 1992, **92**, 1839 and references cited therein.

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10 S. Nagase, S. Suzuki and T. Kurakake, *J. Chem. Soc., Chem. Commun.*, 1990, 1724.

11 (*a*) C. Jones, *Coord. Chem. Rev.*, 2001, **215**, 151; (*b*) S. J. Black, D. E. Hibbs, M. B. Hursthouse, C. Jones and J. W. Steed, *Chem. Commun.*, 1998, 2199; (*c*) K. Plossl, G. Huttner and L. Zsolnai, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 446; (*d*) U. Weber, G. Huttner, O. Scheidsteger and L. Zsolnai, *J. Organomet. Chem.*, 1985, **289**, 357; (*e*) A. H. Cowley, N. C. Norman and M. Pakulski, *J. Am. Chem. Soc.*, 1984, **106**, 6844; (*f*) A. H. Cowley, N. C. Norman, M. Pakulski, D. L. Bricker and D. H. Russell, *J. Am. Chem. Soc.*, 1985, **107**, 8211; (*g*) G. Huttner, U. Weber, B. Sigwarth and O. Scheidsteger, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 215.

12 N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa and Y. Ohashi, *J. Am. Chem. Soc.*, 1998, **120**, 433.

13 T. Sasamori, Y. Arai, N. Takeda, R. Okazaki, Y. Furukawa, M. Kimura, S. Nagase and N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 661.

14 N. Tokitoh, Y. Arai, R. Okazaki and S. Nagase, *Science*, 1997, **277**, 78.

15 (*a*) M. Ates, H. J. Breunig, S. Gulec, W. Offermann, K. Häberle and M Dräger, *Chem. Ber.*, 1989, **122**, 473; (*b*) M. Ates, H. J. Breunig, K. Ebert, S. Gülec, R. Kaller and M. Dräger, *Organometallics*, 1992, **11**, 145.

16 T. Sasamori, Y. Arai, N. Takeda, R. Okazaki and N. Tokitoh, *Chem. Lett.*, 2001, **30**, 42.

17 N. Kano, N. Tokitoh and R. Okazaki, *Organometallics*, 1998, **17**, 1241.

18 N. Tokitoh, T. Sasamori and R. Okazaki, *Chem. Lett.*, 1998, **27**, 725.

19 T. Sasamori, N. Takeda and N. Tokitoh, *J. Phys. Org. Chem.*, 2003, **16**, 450.

20 A. Dashti-Mommertz and B. Neumüller, *Z. Anorg. Allg. Chem.*, 1999, **625**, 954.

21 (*a*) K. von Deuten and D. Rehder, *Cryst. Struct. Commun.*, 1980, **9**, 167; (*b*) G. Becker, H. Freudenblum and C. Witthauer, *Z. Anorg. Allg. Chem.*, 1982, **492**, 37.

22 F. Calderazzo, R. Poli and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1984, **11**, 2365.

23 B. Twamley, C. D. Sofield, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1999, **121**, 3357.

24 S. Nagase, in *The Chemistry of Organic Arsenic, Antimony and Bismuth compounds*, ed. S. Patai, Wiley, New York, 1994, ch. 1, p. 1.

25 T. Sasamori, E. Mieda, N. Nagahora, K. Sato, D. Shiomi, T. Takui, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase and N. Tokitoh, *J. Am. Chem. Soc.*, 2006, **128**, 12582.

26 T. Sasamori and N. Tokitoh, unpublished results.

27 K. Hassler and F. Hofler, *Z. Anorg. Allg. Chem.*, 1978, **443**, 125.

28 A. R. Eujen, G. Becker, O. Mundt, M. Westerhausen and C. Witthauer, *J. Mol. Struct.*, 1983, **98**, 265.

29 A. J. Ashe, E. G. Ludwig and J. Oleksyszyn, *Organometallics*, 1983, **2**, 1859.

30 T. Sasamori, E. Mieda, N. Nagahora, N. Takeda, N. Takagi, S. Nagase and N. Tokitoh, *Chem. Lett.*, 2005, **34**, 166.

31 P. Pyykkö, *Chem. Rev.*, 1988, **88**, 563.

32 (*a*) B. Çetinkaya, A. Hudson, M. F. Lappert and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 609; (*b*) B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 691; (*c*) M. Culcasi, G. Gronchi, J. Escudie, C. Couret, L. Pujol and P. Tordo, *J. Am. Chem. Soc.*, 1986, **108**, 3130; (*d*) S. Shah, S. C. Burdette, S. Swavey, F. L. Urbach and J. D. Protasiewicz, *Organometallics*, 1997, **16**, 3395; (*e*) T. L. Allen, A. C. Scheiner and H. F. Schaefer, *J. Phys. Chem.*, 1990, **94**, 7780; (*f*) H. Binder, B. Riegel, G. Heckmann, M. Moscherosch, W. Kaim, H. G. vonSchnering, W. Honle, H. J. Flad and A. Savin, *Inorg. Chem.*, 1996, **35**, 2119; (*g*) J. Geier, J. Harmer and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2004, **43**, 4093; (*h*) A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski and G. A. Heath, *J. Chem. Soc., Dalton Trans.*, 1987, 249; (*i*) M. Geoffroy, A. Jouaiti, G. Terron, M. Cattanilorente and Y. Ellinger, *J. Phys. Chem.*, 1992, **96**, 8241; (*j*) K. Tsuji, Y. Fujii, S. Sasaki and M. Yoshifuji, *Chem. Lett.*, 1997, **26**, 855.

33 (*a*) T. Tsumuraya, Y. Kabe and W. Ando, *J. Chem. Soc., Chem. Commun.*, 1990, 1159; (*b*) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, 1988, **7**, 2015; (*c*) N. Tokitoh, K. Kishikawa, R. Okazaki, T. Sasamori, N. Nakata and N. Takeda, *Polyhedron*, 2002, **21**, 563; (*d*) M. Driess, S. Rell and H. Pritzkow, *J. Chem. Soc., Chem. Commun.*, 1995, 253; (*e*) K. L. Mckillop, G. R. Gillette, D. R. Powell and R. West, *J. Am. Chem. Soc.*, 1992, **114**, 5203; (*f*) M. J. Fink, K. J. Haller, R. West and J. Michl, *J. Am. Chem. Soc.*, 1984, **106**, 822; (*g*) A. J. Millevolte, D. R. Powell, S. G. Johnson and R. West, *Organometallics*, 1992, **11**, 1091; (*h*) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl and H. Marsmann, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 962; (*i*) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl and H. Marsmann, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 834; (*j*) H. Suzuki, N. Tokitoh and R. Okazaki, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2471; (*k*) S. Masamune, S. A. Batcheller, J. Park, W. M. Davis, O. Yamashita, Y. Ohta and Y. Kabe, *J. Am. Chem. Soc.*, 1989, **111**, 1888; (*l*) H. B. Yokelson, A. J. Millevolte, G. R. Gillette and R. West, *J. Am. Chem. Soc.*, 1987, **109**, 6865; (*m*) R. West, D. J. Deyoung and K. J. Haller, *J. Am. Chem. Soc.*, 1985, **107**, 4942; (*n*) R. P.-K. Tan, G. R. Gillette, D. R. Powell and R. West, *Organometallics*, 1991, **10**, 546.

34 T. Sasamori, E. Mieda, N. Tokitoh, *Bull. Chem. Soc. Jpn.*, in press.

35 T. Sasamori, Doctor Thesis, Kyushu University, Japan, 2002.

36 In the sulfurization reaction of Mes*P=PMes*, the corresponding diphosphene-1-sulfide, Mes*P(S)=PMes*, was obtained as an isolable intermediate. (*a*) M. Yoshifuji, K. Shibayama, I. Shima and N. Inamoto, *Phosphorus Sulfur Relat. Elem.*, 1983, **18**, 11; (*b*) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 1983, 862.

37 T. Sasamori, E. Mieda, N. Takeda and N. Tokitoh, *Chem. Lett.*, 2004, **33**, 104.

38 M. Yoshifuji, K. Shibayama and N. Inamoto, *Chem. Lett.*, 1984, **1984**, 603.

39 T. Sasamori, E. Mieda, N. Takeda and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2005, **44**, 3717.

40 T. Sasamori, E. Mieda, N. Nagahora and N. Tokitoh, *Chem. Heterocycl. Compd. (N. Y.)*, 2006, **42**, 1603.

41 (*a*) B. Twamley and P. P. Power, *Chem. Commun.*, 1998, 1979; (*b*) A. H. Cowley, J. G. Lasch, N. C. Norman and M. Pakulski, *J. Am. Chem. Soc.*, 1983, **105**, 5506; (*c*) A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski and B. R. Whittlesey, *J. Chem. Soc., Chem. Commun.*, 1983, 881.

42 M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita and K. Nishimoto, *J. Am. Chem. Soc.*, 1983, **105**, 2495.

43 T. Sasamori, N. Takeda and N. Tokitoh, *Chem. Commun.*, 2000, 1353.

44 T. Sasamori, N. Takeda, M. Fujio, M. Kimura, S. Nagase and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2002, **41**, 139.

45 M. Yoshifuji, T. Sato and N. Inamoto, *Chem. Lett.*, 1988, 1735.

46 K. Ito and S. Nagase, *Chem. Phys. Lett.*, 1986, **126**, 531.

47 For a review, see: T. Baumgartner and R. Reau, *Chem. Rev.*, 2006, **106**, 4681.

48 (*a*) V. A. Wright and D. P. Gates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2389; (*b*) V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **128**, 8836; (*c*) R. C. Smith, X. F. Chen and J. D. Protasiewicz, *Inorg. Chem.*, 2003, **42**, 5468; (*d*) R. C. Smith and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 2004, **126**, 2268; (*e*) R. C. Smith and J. D. Protasiewicz, *Eur. J. Inorg. Chem.*, 2004, 998; (*f*) S. Shah, T. Concolino, A. L. Rheingold and J. D. Protasiewicz, *Inorg. Chem.*, 2000, **39**, 3860; (*g*) C. Dutan, S. Shah, R. C. Smith, S. Choua, T. Berclaz, M. Geoffroy and J. D. Protasiewicz, *Inorg. Chem.*, 2003, **42**, 6241; (*h*) V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **128**, 8836.

49 T. Sasamori, A. Tsurusaki, N. Nagahora, K. Matsuda, Y. Kanemitsu, Y. Watanabe, Y. Furukawa and N. Tokitoh, *Chem. Lett.*, 2006, **35**, 1382.

50 (*a*) N. Nagahora, T. Sasamori, N. Takeda and N. Tokitoh, *Chem.–Eur. J.*, 2004, **10**, 6146; (*b*) N. Nagahora, T. Sasamori, N. Takeda and N. Tokitoh, *Organometallics*, 2005, **24**, 3074.

51 N. Nagahora, T. Sasamori and N. Tokitoh, *Chem. Lett.*, 2006, **35**, 220.

52 N. Nagahora, T. Sasamori, Y. Watanabe, Y. Furukawa and N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1884.

53 T. Sasamori, T. Matsumoto, N. Takeda and N. Tokitoh, *Organometallics*, 2007, **26**, 3621.

54 R. Pietschnig and E. Niecke, *Organometallics*, 1996, **15**, 891.

55 (*a*) T. Tsutsumi, M. Okubo, N. Yasuoka and Y. Katsube, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 237; (*b*) M. Kurihara, T. Matsuda, A.

Published on 14 November 2007. Downloaded by University of Western Ontario on 28/10/2014 17:13:23.

Hirooka, T. Yutaka and H. Nishihara, *J. Am. Chem. Soc.*, 2000, **122**, 12373.

56 C. Moser, M. Nieger and R. Pietschnig, *Organometallics*, 2006, **25**, 2667.

57 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.

58 (*a*) B. Y. Liu, C. Y. Tian, L. Zhang, W. D. Yan and W. J. Zhang, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6243; (*b*) D. Zhang, G. X. Jin, L. H. Weng and F. S. Wang, *Organometallics*, 2004, **23**, 3270; (*c*) X. F. Li, K. Dai, W. P. Ye, L. Pan and Y. S. Li, *Organometallics*, 2004, **23**, 1223.

59 (*a*) P. L. Floch, *Cood. Chem. Rev.*, 2006, **250**, 627; (*b*) F. Ozawa, S. Kawagishi, T. Ishiyama and M. Yoshifuji, *Organometallics*, 2004, **23**, 1325.

60 Although there have been a few reports on the theoretical calculations for a phosphorus analogue of a Shiff-base ligand from the viewpoint of catalytic activities, no example of such a unique ligand has been synthesized so far. (*a*) M. S. W. Chan, L. Q. Deng and T. Ziegler, *Organometallics*, 2000, **19**, 2741; (*b*) T. Z. Zhang, D. W. Guo, S. Y. Jie, W. H. Sun, T. Li and X. Z. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4765.

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