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1,2-Bis(ferrocenyl)dipnictenes: Bimetallic Systems with a Pn=Pn Heavy π-Spacer (Pn: P, Sb, and Bi)[#]

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1,2-Bis(ferrocenyl)dipnictenes bearing a Pn=Pn π-spacer (Pn: P (**1**), Sb (**2**), and Bi (**3**)) between two ferrocenyl units have been synthesized as stable compounds. Not only their molecular structures and fundamental properties but also their redox behavior have been systematically disclosed. Interestingly, in the reduction region, the dipnictenes showed two pseudo-reversible one-electron redox couples at low temperature, suggesting possible generation of the corresponding radical anion and dianion species. On the other hand, they showed three-step one-electron oxidation processes in the oxidation region. The first two oxidation steps would correspond to those of the two ferrocenyl moieties, while the third step would be that of the Pn=Pn π-spacer moiety, respectively. Thus, these 1,2-bis(ferrocenyl)dipnictenes with a Pn=Pn π-spacer should be stable multiredox systems reflecting unique properties of a double bond between heavier 15 group elements. As a result, all Pn=Pn units (Pn: P, Sb, and Bi) were found to work as a more effective π-spacer than those of 2nd row elements such as C=C and N=N.

Organometallic π-conjugated systems are attracting much interest from the viewpoint of showing interesting electronic, optical, and magnetic properties. In this research field, d–π conjugated systems of bimetallic complexes tethered with a π-electron spacer, [M(Ligand)]–(π-electron spacer)–[M(Ligand)] (M: transition metal), have been actively investigated.[1] These compounds are a unique class of appropriate models of mixed-valence states giving insight on the ability of the π-electron system as a π-spacer in the context of fundamental organic electronic materials such as molecular switches and molecular wires.[2] In this background, ferrocene is frequently used as an effective d-electron moiety in such d–π conjugated systems, because it should be a promisingly stable and effective redox system and amenable to modification with a variety of established substituents.[3] Thus, ferrocenyl-based bimetallic d–π electron systems should be a touchstone for investigating the ability of a π-electron system as a "π-spacer." Although several numbers of d–π conjugated systems with two ferrocenyl groups bridged by a π-electron spacer have been reported to be investigated, e.g., Ph(Fc)C=C(Fc)Ph,[4] FcC≡CFc,[5] Fc–N=N–Fc[6] (Fc: ferrocenyl), and bis(ferrocenyl)thiophene derivatives,[7] the π-electron systems in these compounds are limited to those consisting of 2nd row main group elements. The advantageous and required properties as a d–π electron system toward organometallic electronic materials should be (i) relatively low redox potential, (ii) stable multistep redox behavior, and (iii) controllable redox system. Regarding all of these points, π-bonds between heavier main group elements are thought to be superior to those of 2nd row elements as a π-spacer in d–π electron systems, because π-bond compounds between heavier main group elements are known to exhibit smaller π–π^* energy gaps than those of 2nd row elements due to the smaller overlapping of np orbitals.[8] In addition, π-bond compounds between heavier group 15 elements (P=P, As=As, Sb=Sb, and Bi=Bi, called dipnictenes) are known to afford stable anion radical species upon chemical reduction, showing their lower LUMO level and stable redox behavior.[9] From a standpoint of using a dipnictene moiety as a π-spacer, the points of (ii) and (iii) should be clarified and investigated by the construction of bimetallic systems bearing a dipnictene moiety as a π-spacer. Here again, it is expected that π-bonds between heavier group 15 elements should be promisingly more effective π-electron spacers than those of 2nd row elements. However, it has been difficult to develop such chemistry of heavier π-electron spacers so far due to the difficulty in synthesis of the compounds, arising from their extremely high reactivity toward self-oligomerization and addition reaction with aerobic oxygen or moisture. On the other hand, it has been demonstrated that the double-bond compounds between heavier group 15 elements can be stabilized enough to be treated under

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ambient conditions when sterically demanding substituents are introduced at the reactive π-bond moiety as steric protection groups.[10] Indeed, a series of heavier dipnictenes have been synthesized and isolated by taking advantage of very bulky substituents.[9–11] Furthermore, these compounds exhibit unique electrochemical properties due to their low-lying LUMO. We have reported that these heavier dipnictenes can be reduced by lithium metal to give the corresponding anion radical species.[9] Thus, it is suggested such π-bonds between heavier group 15 elements should work as an effective π-spacer for metal moieties. Combined with such striking developments in the field of extended π-electron systems containing heavier main group elements and d–π electron systems,[12] this research background prompted us to investigate the chemistry of a new type of d–π electron systems containing a π-electron system of heavier group 15 elements. Although the simplest model compound for 1,2-bis(ferrocenyl)diphosphenes is Fc–P=P–Fc (Fc: ferrocenyl), the phosphorus analogue of Fc–N=N–Fc, all of our synthetic attempts to isolate FcP=PFc and those by other groups have been unsuccessful so far.[3b,13] A book[3b] mentions the preparation of FcP=PFc from the reductive dehalogenation of $FcPCl_2$, but unfortunately, we were not able to obtain synthetic and/or characterization details for this reference ("private communication"), suggesting the instability of FcP=PFc under ambient conditions and the limited steric demand of the ferrocenyl groups should however offer only insufficient protection for the reactive P=P bond.[13] As a solution of this synthetic challenge, we reported the synthesis of a custom-tailored ferrocenyl unit with an increased ability for steric protection, and its subsequent implementation in the synthesis of 1,2-bis(ferrocenyl)diphosphene as a stable crystalline compound.[14] Thus, we have recently succeeded in the synthesis of novel 1,2-bis(ferrocenyl)dipnictene derivatives and developed two bulky ferrocenyl units, 2,5-Ar_2-1-ferrocenyl groups (Fc′: Ar = 3,5-dimethylphenyl, Fc*: Ar = Dtp (Dtp: 3,5-di-*tert*-butylphenyl), tethered with a Pn=Pn π-spacer (Pn: P, Sb, and Bi).[14,15] The systematic evaluation of the π-electron units of heavier main group elements as a π-spacer should be of great interest and importance. In this paper, we describe systematic studies of the properties of 1,2-bis(ferrocenyl)dipnictenes **1**–**3** including structural features and redox behavior (Figure 1).

Results and Discussion

Synthesis of 1,2-Bis(ferrocenyl)dipnictenes. We have reported the synthesis of the first stable 1,2-bis(ferrocenyl)diphosphene, Fc′P=PFc′ (**4**, Fc′: 2,5-bis(3,5-dimethylphenyl)-1-ferrocenyl).[14] Since attempted synthesis of 1,2-bis(ferrocenyl)distibene and dibismuthene bearing the same substituents, Fc′Sb=SbFc′ and Fc′Bi=BiFc′, have been unsuccessful, we have developed bulkier ferrocenyl group Fc* (2,5-bis(3,5-di-*tert*-butylphenyl)-1-ferrocenyl) and successfully applied it to the synthesis of Fc*Sb=SbFc* and Fc*Bi=BiFc*, which exhibit unique electrochemical properties.[15] Herein, we have prepared a series of 1,2-bis(ferrocenyl)dipnictenes bearing the same ferrocenyl moieties for the systematic comparison of their redox properties on the basis of the intrinsic nature of dipnictene π-bonds. That is, we decided to synthesize a series of Fc*Pn=PnFc* (Pn = P, Sb, and Bi) to evaluate the characteristics of a Pn=Pn bond as a π-spacer systematically.

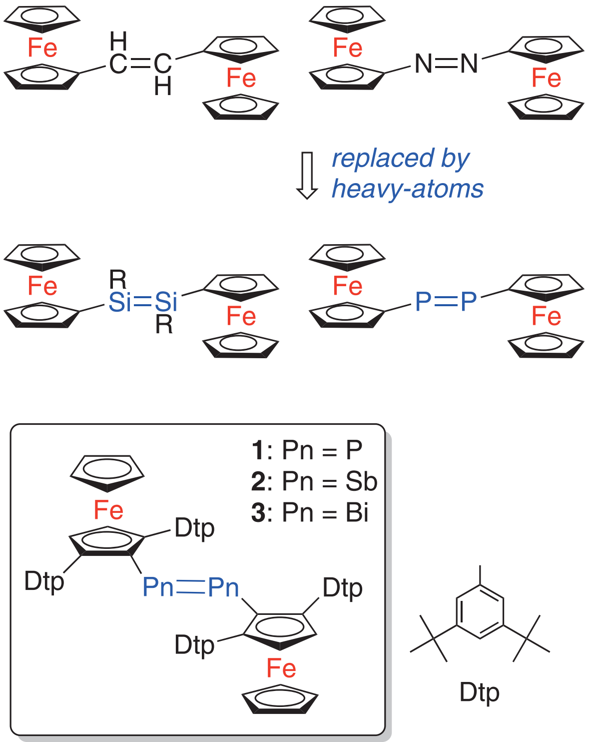
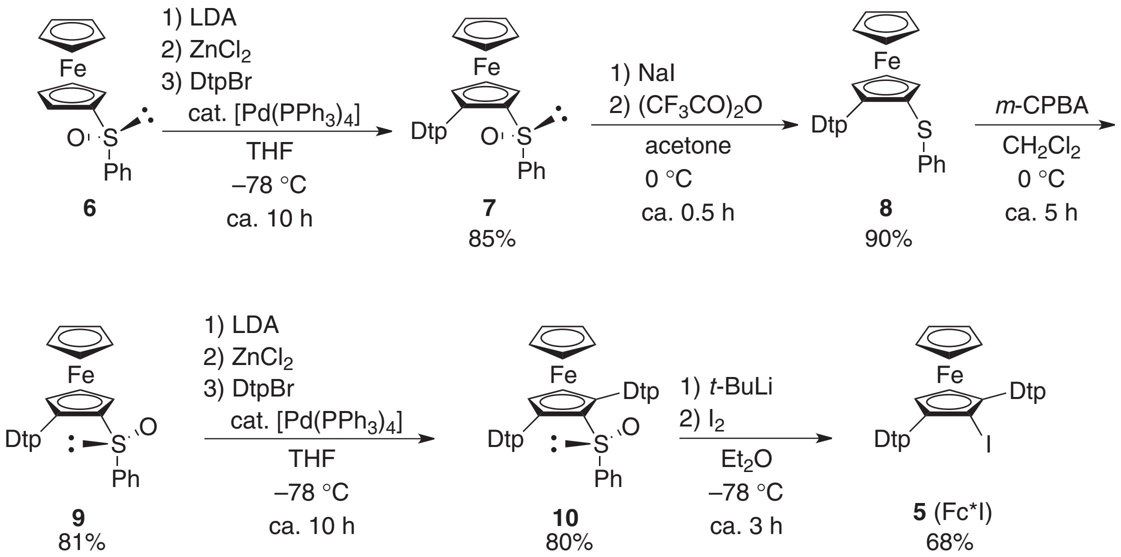


Figure 1.

The iodoferrocene derivative **5** (Fc*I) as a source of a bulky ferrocenyl unit was synthesized in 6 steps from ferrocene. It has two 3,5-di-*tert*-butylphenyl (Dtp) groups at the 2- and 5-positions of one of the Cp (cyclopentadienyl) rings (Scheme 1). Sulfoxide **7** was obtained from a Negishi cross-coupling reaction of ferrocenyl phenyl sulfoxide (**6**)[16] with DtpBr. Reduction of **7** with NaI and $(CF_3CO)_2O$ afforded sulfide **8**,[17] which was oxidized with *m*CPBA to give sulfoxide **9**, a structural isomer of **7**. The inversion of the sulfinyl group at this stage is the key step for the introduction of another Dtp group to give sulfoxide **10**, which was achieved by the second Negishi cross-coupling reaction between **9** and DtpBr. Treatment of sulfoxide **10** with *t*-BuLi followed by quenching with I_2 resulted in the formation of **5**. While the molecular structure of **5** is shown in Figure 2, one can recognize the effective steric protection ability of the Fc* group. As precursors for the 1,2-bis(ferrocenyl)dipnictenes, the corresponding ferrocenyldihalopnictanes, Fc^*PCl_2 (**11**), Fc^*SbCl_2 (**12**),[15] and Fc^*BiBr_2 (**13**),[15] were prepared by the lithiation of iodoferrocene **5** with *t*-BuLi followed by addition of PCl_3, $SbCl_3$, and $BiBr_3$, respectively. The targeted 1,2-bis(ferrocenyl)dipnictenes **1**–**3** were isolated as stable compounds by the reductive coupling reactions of the corresponding dihalopnictanes, **11**–**13**, using magnesium metal in THF at r.t. (Scheme 2). These compounds are stable under ambient conditions with strong colors of pink (diphosphene **1**), green (distibene **2**), and violet (dibismuthene **3**), respectively. In all of **1**–**3**, their ^1H NMR spectra in C_6D_6 at r.t. suggested their symmetric structures in solution. That is, one singlet signal for the *t*-Bu protons of Dtp groups and that for unsubstituted Cp ring were observed, indicating free rotation around the C(Cp)–C(Dtp) and C(Cp)–E. The ^{31}P NMR spectrum of **1** showed one resonance for the P nuclei at 471 ppm, which is in a region



Scheme 1.

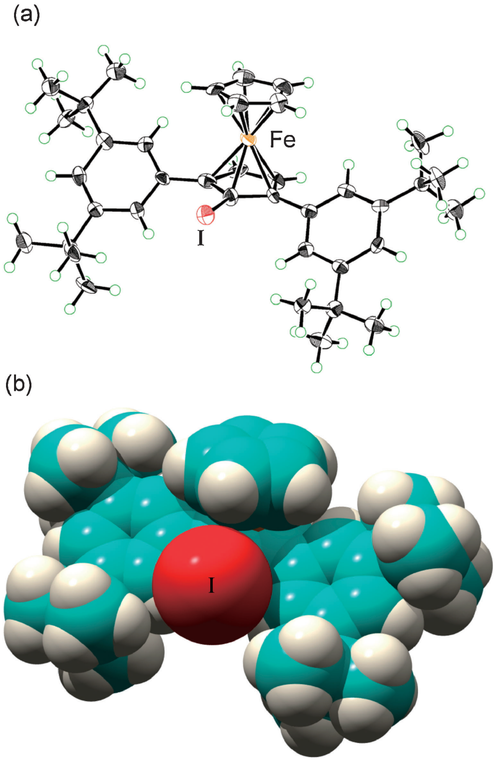
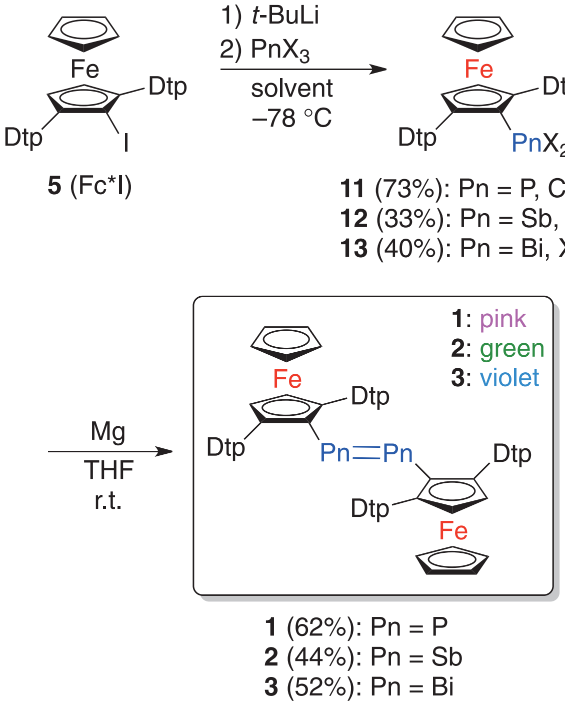


Figure 2. (a) Molecular structure of Fc*I (**5**) with thermal displacement ellipsoids at 50% probability. (b) Space-filling model of **5**.

similar to those of the previously reported ferrocenyldiphosphenes and diaryldiphosphenes.[11,12c–12h,14]

Molecular Structures. The structural parameters of 1,2-bis(ferrocenyl)dipnictenes **1**–**3** were definitively determined by X-ray diffraction analysis (Figure 3). While diphosphene **1** was found to exhibit C_1 geometry without any symmetric element in the independent moiety, both distibene **2** and dibismuthene **3** have the crystallographic center of symmetry at the middle of their Pn=Pn bonds with C_i symmetry.[15] The structural parameters and crystal data are summarized in Tables 1 and 2.



Scheme 2.

The Pn=Pn bond lengths of 2.0286(6) (**1**), 2.6700(7) (**2**), and 2.8307(3) Å (**3**) are shorter than the corresponding single-bond lengths [e.g., 2.215 Å for Ph_2P–PPh_2,[19] 2.837 Å for Ph_2Sb–$SbPh_2$,[20] and 2.990 Å for Ph_2Bi–$BiPh_2$[21]] and similar to those of the previously reported dipnictenes (e.g., 2.043(1) Å for BbtP=PBbt (**14**),[18] 2.7037(6) Å BbtSb=SbBbt (**15**),[11b] 2.8699(6) Å for BbtBi=BiBbt (**16**)[11b] (Bbt: 2,6-[CH-$(SiMe_3)_2]_2$-4-[C$(SiMe_3)_3$]-C_6H_2). Thus, all of the Pn=Pn bonds of **1**–**3** were found to exhibit considerable double-bond character on the basis of the bond lengths. Also, the vibrational

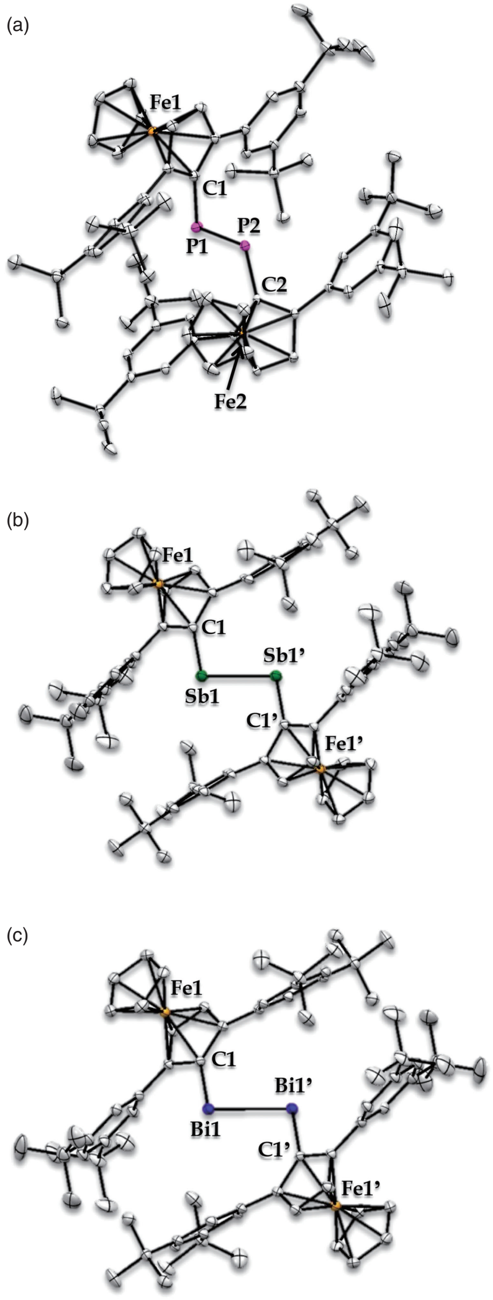


Figure 3. Molecular structures of (a) diphosphene **1**, (b) distibene **2**, and (c) dibismuthene **3** with thermal displacement ellipsoids at 50% probability. Ether molecule in (a) **[1·Et$_2$O]** and all hydrogen atoms in (a)–(c) have been omitted for clarity.

Table 1. Selected Bond Lengths and Angles of Dipnictenes **1**–**3** and Related Compounds (Bbt: 2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl)

LPn=PnL	Pn=Pn/Å	Pn–C/Å	Pn–Pn–C/°
Fc*P=PFc* (**1**)	2.0286(6)	1.8080(17)	111.23(5)
		1.8454(17)	93.22(5)
BbtP=PBbt (**14**)[18]	2.043(1)	1.834(4)	114.9(1)
		1.845(4)	97.8(1)
Fc*Sb=SbFc* (**2**)[15]	2.6700(7)	2.158(5)	98.28(13)
BbtSb=SbBbt (**15**)[11b]	2.7037(6)	2.197(4)	105.38(10)
Fc*Bi=BiFc* (**3**)[15]	2.8307(3)	2.268(3)	96.17(9)
BbtBi=BiBbt (**16**)[11b]	2.8699(6)	2.291(5)	104.15(12)

frequencies of the central Pn=Pn bonds of **1**–**3** supported double-bond character. In Raman spectra, strong Raman shifts were observed at $\nu = 611$ (**1**), 223 (**2**), and 140 (**3**) cm^{-1} assignable to Pn=Pn (Pn: P, Sb, and Bi) stretching vibrational frequencies, respectively. These vibrational frequencies were reasonably reproduced by theoretical calculations (B3PW91, 624 (**1**), 231 (**2**), and 162 (**3**) cm^{-1}), and these $\nu_{\rm PnPn}$ vibrational frequencies are larger than those of the corresponding single-bond compounds (530 cm^{-1} for Ph$_2$P–PPh$_2$,[22] 141 cm^{-1} for Ph$_2$Sb–SbPh$_2$,[23] 103 cm^{-1} Ph$_2$Bi–BiPh$_2$[24]) and similar to those of previously reported dipnictenes (609 cm^{-1} for TbtP=PTbt (**17**),[11a,18] 207 cm^{-1} for TbtSb=SbTbt (**18**),[11a,11b] 135 cm^{-1} for TbtBi=BiTbt (**19**);[11a,11b] Tbt: 2,4,6-[CH(SiMe$_3$)$_2$]$_3$-C$_6$H$_2$), suggesting considerable degrees of double-bond character for the Pn=Pn bonds in **1**, **2**, and **3**. In attention to the Pn–C(Fc*) in **2** and **3** bond lengths, these are slightly shorter than the Pn–C(Ar) bond lengths of the corresponding previously reported diaryldipnictenes, i.e., 2.158(5) Å for Sb–C(Fc*) of **2** vs. 2.197(4) Å for Sb–C(Bbt) of **15**,[11b] 2.268(3) Å for Bi–C(Fc*) of **3** vs. 2.291(5) Å for Bi–C(Bbt) of **16**,[11b] indicating slight but apparent conjugative electronic communication between the ferrocenyl moieties and the Pn=Pn π-bond. In the case of **1**, the P2–P1–C1(Fc*) angle (111.23(5)°) is wider than the corresponding opposite P1–P2–C2(Fc*) angle (93.22(5)°) probably due to packing effects. In addition, one of the dihedral angles between the Cp ring vs. P1–P2–C2(Fc*) plane is almost perpendicular (ca. 88°) and that of the other side (the Cp ring vs. P2–P1–C1(Fc*)) is nearly parallel (ca. 23°) due to the steric repulsion between the two 3,5-di-*tert*-butylphenyl groups.[18] Here, the P1–C1(Fc*) bond (1.8080(17) Å), where the P2–P1–C1 plane is almost parallel to the Cp ring, is shorter than the another one (P2–C2(Fc*) = 1.8454(17) Å), also suggesting the existence of conjugative electronic communication between the ferrocenyl moieties and the P=P π-bond especially in the case of the P=P π-plane lying parallel with the Cp plane. The Pn–Pn–C(Cp) angles of **2** and **3** are 98.28(13) and 96.17(9)°, respectively, i.e., Pn–Pn–C(Cp) angles gets smaller and closer to 90° as Pn is gets heavier from P to Bi, indicating non-hybridized orbitals, one of the characteristics of heavier main group elements.[9,11a,25] The dihedral angles between the E–E–C(Cp) and the Cp planes of **2** and **3** are 38 (E = Sb) and 37° (E = Bi), respectively, indicating effective conjugation between the Pn=Pn π-electrons and ligand moieties of Fc* in **2** and **3** as compared with the case of ArPn=PnAr, where the aryl rings of the Ar ligands are almost perpendicular to the Pn=Pn–C plane.[11]

UV–vis Spectra. In the UV–vis spectra of these 1,2-bis(ferrocenyl)dipnictenes **1**–**3** shown in Figure 4, characteristic absorptions including that corresponding to d–π* electron transitions from the filled d-orbitals at the Fe center to the π* orbital of the Pn=Pn π-spacer were observed (Table 3). In the case of diphosphene **1**, three characteristic absorption bands around 350, 440, and 550 nm were observed in either THF or hexane solution. The first and second absorptions would

Table 2. Crystallographic Data of Dipnictenes **1**–**3**

	Compounds		
	Fc*P=PFc*•(Et_2O) (**[1•Et_2O]**)	Fc*Sb=SbFc* (**2**)[15]	Fc*Bi=BiFc* (**3**)[15]
Formula	$C_{76}H_{98}Fe_2P_2{\cdot}C_4H_{10}O$	$C_{76}H_{98}Fe_2Sb_2$	$C_{76}H_{98}Bi_2Fe_2$
Molecular weight	1259.30	1366.74	1541.20
Temperature/K	100	100	100
λ/Å	0.71069	0.83077	0.71069
Crystal size/mm^3	0.02 × 0.02 × 0.01	0.04 × 0.03 × 0.02	0.10 × 0.08 × 0.02
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a/Å	13.8620(1)	9.8957(8)	9.8783(1)
b/Å	34.1010(4)	12.2498(10)	12.2940(2)
c/Å	15.5269(3)	16.4043(14)	16.4895(2)
α/°	90	69.437(3)	69.511(1)
β/°	104.6656(6)	74.142(3)	74.0991(8)
γ/°	90	69.623(3)	69.9873(8)
V/Å^3	7100.56(17)	1719.3(2)	1735.34(4)
Z	4	1	1
μ	0.497	1.855	5.504
D_{calcd}/g cm^{-3}	1.178	1.320	1.475
θ_{max}	25.5	29.87	26.0
Refl./restr./param.	13188/0/841	6158/36/389	6694/0/398
Completeness	99.8%	99.1%	98.1%
GOF	1.029	1.001	1.114
R_1 ($I > 2\sigma(I)$)	0.0334	0.0556	0.0259
wR_2 ($I > 2\sigma(I)$)	0.0824	0.1291	0.0669
R_1 (all data)	0.0394	0.0644	0.0275
wR_2 (all data)	0.0869	0.1337	0.0677
Largest diif. peak and hole/e Å^{-3}	0.555, −0.401	1.713, −1.006	1.685, −0.896
CCDC number	941816	912009	912010

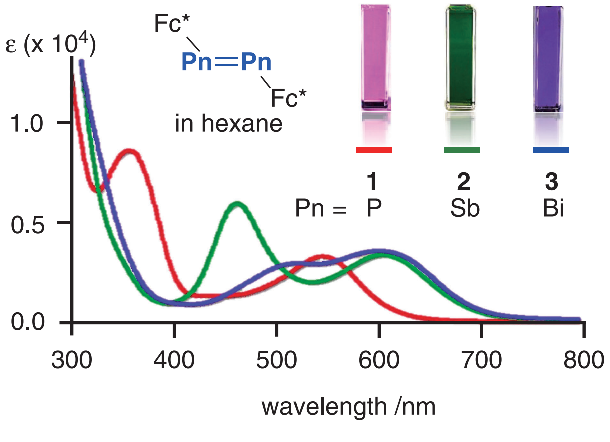


Figure 4. UV–vis spectra of dipnictenes **1**–**3** in hexane.

correspond to symmetry-allowed π–π^* and symmetry-forbidden n–π^* electron transitions, since these absorptions are similar to those of the previously reported diaryldiphosphenes.[11] The third absorption is assignable to d–π^* electron transitions on the basis of theoretical calculations (TD-B3PW91), where the electron transitions from HOMO(Fe, d) to LUMO(P=P, π^*) and those from HOMO−3(Fe, d) to LUMO(P=P, π^*) would be estimated as 560 and 551 nm, respectively (Figure 5). In contrast to the d–π^* electron transitions of the previously reported 1,2-bis(ferrocenyl)diphosphene, Fc′P=PFc′, showing a little solvent dependency (546 nm in hexane, 556 nm in THF, $\Delta\lambda_{max} = 9$ nm),[14] those of diphosphene **1** showed no apparent solvent dependency in hexane and THF solution. In the UV–vis spectra of distibene **2** and dibismuthene **3**, two characteristic absorption bands were observed around 500 and 600 nm in either THF or hexane solution. Similar to the case of diphosphene **1**, the former absorption can be assigned as symmetry-allowed π–π^* transitions of Sb=Sb and Bi=Bi chromophores on the basis of those for the previously reported diaryldistibenes and dibismuthenes (e.g., TbtSb=SbTbt (**18**), $\lambda_{max} = 466$ nm (ε 5200, π–π^*) in hexane; TbtBi=BiTbt (**19**), $\lambda_{max} = 525$ nm (ε 4000, π–π^*) in hexane).[11a,11b] The latter absorptions at longer wavelengths are most likely interpreted in terms of the overlap of several d–π^* electron transitions from filled d-orbitals of the Fe center to the π^* orbitals of the Pn=Pn π-spacers as in the case of diphosphene **1**. Similarly, theoretical calculations support the assignment of these absorptions (For **2**, 497 nm ($f = 0.0787$), HOMO(Sb=Sb, π)–LUMO(Sb=Sb, π^*), 573 nm ($f = 0.0242$), HOMO−4(Fe, d)–LUMO(Sb=Sb, π^*). For **3**, 526 nm ($f = 0.0353$), HOMO(Bi=Bi, π)–LUMO(Bi=Bi, π^*), 566 nm ($f = 0.0327$), HOMO−3(Fe, d)–LUMO(Bi=Bi, π^*). Although the absorption due to d–π^* electron transitions in dibismuthene **3** showed no apparent solvent dependency as well as that of diphosphene **1**, that of **2** showed only small solvent dependency in hexane (606 nm) and THF (612 nm)

Table 3. Absorption Maxima of 1,2-Bis(ferrocenyl)dipnictenes **1**–**3** and Related Compounds in UV–vis Spectra

Compound	Solvent	λ^1/nm (ε) π–π^*	λ^2/nm (ε) n–π^*	λ^3/nm (ε) d–π^*
Fc*P=PFc* (**1**)	hexane	354 (9800)	436 (1400)	547 (3700)
	THF	351 (9900)	440 (1700)	547 (3500)
Fc*Sb=SbFc* (**2**)[15]	hexane	462 (6700)	*Overlapped*	606 (3800)
	THF	463 (7700)	*Overlapped*	612 (4100)
Fc*Bi=BiFc* (**3**)[15]	hexane	522 (3300)	*Overlapped*	603 (4000)
	THF	520 (3700)	*Overlapped*	602 (4200)
Fc′P=PFc′ (**4**)[14]	hexane	349 (6100)	446 (990)	546 (2000)
	THF	351 (9000)	448 (1400)	556 (3000)
BbtP=PBbt (**14**)[11a,18]	hexane	418 (12000)	532 (1000)	—
BbtSb=SbBbt (**15**)[11a,11b]	hexane	490 (6000)	594 (200)	—
BbtBi=BiBbt (**16**)[11a,11b]	hexane	537 (6000)	670 (20)	—
TbtP=PTbt (**17**)[11a,18]	hexane	405 (13000)	530 (2000)	—
TbtSb=SbTbt (**18**)[11a,11b]	hexane	466 (5200)	599 (170)	—
TbtBi=BiTbt (**19**)[11a,11b]	hexane	525 (4000)	660 (100)	—
FcN=NFc[1a,6]	CH_2Cl_2	315	375	510

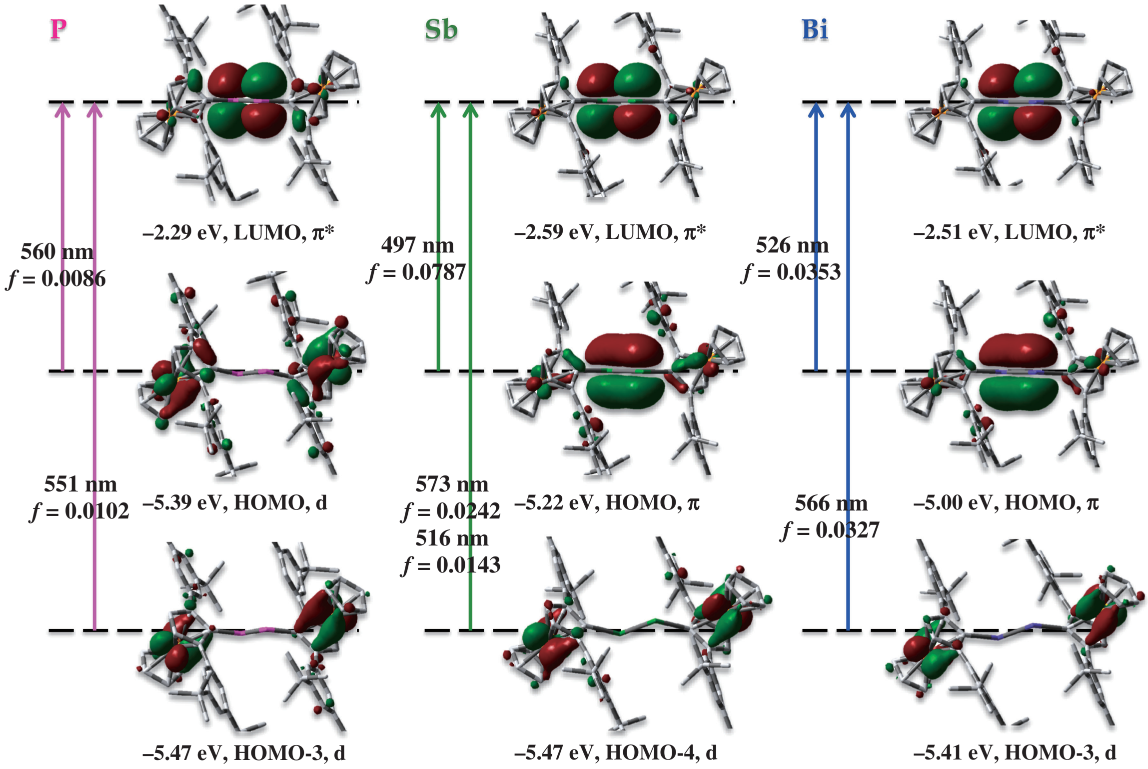
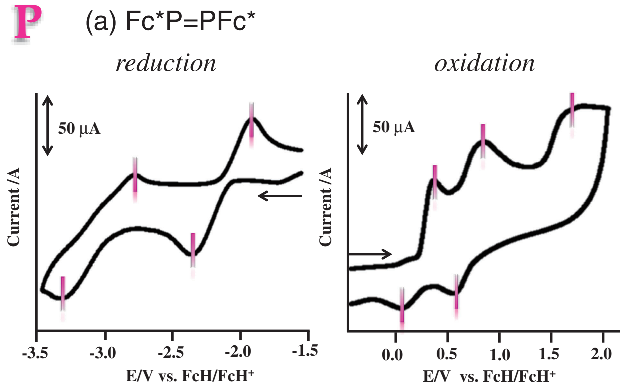
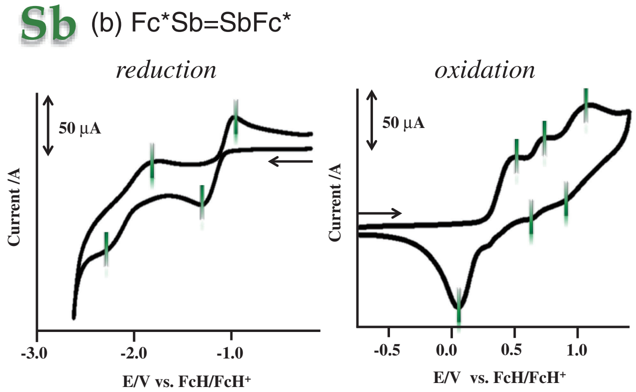


Figure 5. TDDFT-calculations of dipnictenes **1**–**3** with C_i symmetries.

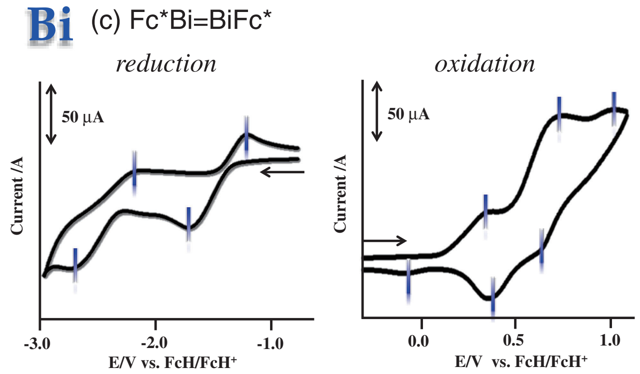
by $\Delta\lambda_{\max} = 6$ nm. Such negligible solvent effect of the d–π^* electron transitions in UV–vis spectra of 1,2-bis(ferrocenyl)-dipnictenes **1**–**3** would be explained by the symmetric structures of their excited states symmetric with little polarity due to the extended d–π conjugation. At this stage, it is difficult to draw a clear conclusion on the details of the electron transitions, since we have some unclear results in the electronic spectra. Although the HOMO of distibene **2** and dibismuthene **3** are dominantly composed of their Pn=Pn π-orbitals and their d-orbital levels lie on the lower levels (Figure 5) on the basis of theoretical calculations, the d–π^* transitions are computed as the longest wavelengths. Thus, the structures of the dipnictenes at their excited states would be different from those at their ground states. Further theoretical calculations on the excited states would be necessary in order to understand the electron transitions in detail. In summary, the π–π^* absorptions due to Pn=Pn chromophores move toward longer wavelengths as the central elements descend from P to Bi. On the other hand, the absorption due to the d–π^* transitions of **1** is at shorter wavelength than those of **2** and **3**, and those of **2** and **3** are similar to each other, indicating (i) lower levels of the occupied d- and π-orbitals and the higher LUMO (π^*) level of **1** than those of **2** and **3** and (ii) slightly higher level of LUMO (π^*) of **2** than that of **3**, but the slightly higher occupied d- and π-orbitals of **2**,



P (a) Fc*P=PFc*



Sb (b) Fc*Sb=SbFc*



Bi (c) Fc*Bi=BiFc*

Figure 6. Cyclic voltammograms of (a) diphosphene **1**, (b) distibene **2**, and (c) dibismuthene **3**. Conditions: 4.0 mM, 0.1 M n-Bu$_4$NBF$_4$, −78 °C, in THF (reduction), in CH$_2$Cl$_2$ (oxidation).

Table 4. Redox Potentials and the Comproportionation Constants of 1,2-Bis(ferrocenyl)dipnictenes **1–3**[a)]

	Compound		
	Fc*P=PFc* (**1**)	Fc*Sb=SbFc* (**2**)	Fc*Bi=BiFc* (**3**)
<Reduction>			
$E_{pc}{}^1$/V	−2.27	−1.33	−1.77
$E_{pa}{}^1$/V	−1.82	−0.92	−1.35
$E_{1/2}{}^1$/V	**−2.05**	**−1.13**	**−1.56**
$E_{pc}{}^2$/V	−3.33	−2.43	−2.63
$E_{pa}{}^2$/V	−2.71	−1.83	−2.11
$E_{1/2}{}^2$/V	**−3.02**	**−2.14**	**−2.37**
$\Delta(E^1\text{–}E^2)$/V	0.97	1.01	0.81
K_{com} $(E^1\text{–}E^2)$	1.12×10^{25}	1.21×10^{25}	8.28×10^{20}
<Oxidation>			
$E_{pa}{}^1$/V	+0.40	+0.51	+0.31
$E_{pc}{}^1$/V	+0.06	+0.05	−0.13
$E_{1/2}{}^1$/V	**+0.23**	**+0.28**	**+0.09**
$E_{pa}{}^2$/V	+0.94	+0.72	+0.75
$E_{pc}{}^2$/V	+0.61	+0.63	+0.38
$E_{1/2}{}^2$/V	**+0.78**	**+0.70**	**+0.57**
$E_{pa}{}^3$/V	+1.74	+1.12	+1.02
$E_{pc}{}^3$/V	—	+0.82	+0.62
$E_{1/2}{}^3$/V	—	**+1.00**	**+0.82**
$\Delta(E^2\text{–}E^1)$/V	**0.55**	**0.42**	**0.48**
K_{com} $(E^2\text{–}E^1)$	1.60×10^{14}	7.02×10^{10}	2.49×10^{12}
$\Delta(E^3\text{–}E^2)$/V		0.30	0.25
K_{com} $(E^3\text{–}E^2)$		5.59×10^7	2.86×10^6

a) Conditions: 4.0 mM, 0.1 M n-Bu$_4$NBF$_4$, −78 °C, in THF (reduction), in CH$_2$Cl$_2$ (oxidation).

which would be affected by the orbital level of Sb=Sb moiety, relative to those of **3**, resulting in similar λ_{max} values assignable to the d–π^* electron transitions in **2** and **3**.

Electrochemical Measurements for 1,2-Bis(ferrocenyl)-dipnictenes 1–3. The electrochemical properties of 1,2-bis(ferrocenyl)dipnictenes **1–3** have been investigated by cyclic and differential potential voltammetries (Figure 6). All of these dipnictenes showed two-step pseudo-reversible one-electron redox couples in the reduction region at −78 °C, i.e., $E_{1/2} = -2.05$ and −3.02 V for **1**; $E_{1/2} = -1.13$ and −2.14 V for **2**; $E_{1/2} = -1.56$ and −2.37 V for **3** (all potentials referenced vs. FcH/FcH$^+$). As one can see in Table 4, these compounds showed significantly lower reduction potential than that of FcN=NFc (−2.32 V),[1a] and those of the corresponding diaryl derivatives ($E_{1/2} = -1.84$ V for BbtP=PBbt (**14**), −1.65 V for BbtSb=SbBbt (**15**), −1.79 V for BbtBi=BiBbt (**16**)).[9] Such smaller reduction potentials of **1–3** than those of diaryldipnictenes **14–16** would be due to d–π conjugation between Fc* moieties and π^* orbitals of Pn=Pn moiety. Thus, it should be noted that the bulky ferrocenyl ligand should stabilize the anionic species, and even the corresponding dianion of the 1,2-bis(ferrocenyl)dipnictenes would be promisingly generated under these conditions. In the systematic comparison, distibene **2** showed the lowest reduction potential among those of 1,2-bis(ferrocenyl)dipnictenes, as in the case of reduction potentials of diaryldipnictenes **14–16** shown in the previously reported systematic investigation.[9] Thus, 1,2-bis(ferrocenyl)distibene **2** should work as an effective electron acceptor of a d–π electron system, reflecting the intrinsic nature of the Sb=Sb bond.

In the oxidation region, these dipnictenes showed three one-electron oxidation steps at −78 °C (Table 4). The first two oxidation potentials should be assignable to the oxidation processes of two ferrocenyl moieties, whereas the third ones should be assigned to those of the corresponding Pn=Pn π-spacer moiety. Diphosphene **1** showed pseudo-reversible redox couples for the 1st and 2nd steps at $E_{1/2} = +0.23$ and +0.78 V, but the 3rd step was an irreversible oxidation wave at $E_{pa} = +1.74$ V, which was similar to the 3rd step of the previously reported ferrocenyldiphosphene (TbtP=PFc, $E_{pa} = 1.75$ V).[12h]

Both distibene **2** and dibismuthene **3** showed pseudo-reversible redox couples for all steps at $E_{1/2} = +0.28$, $+0.70$, and $+1.00$ V for **2**, $E_{1/2} = +0.09$, $+0.57$, and 0.82 V for **3**, respectively. While all 1,2-bis(ferrocenyl)dipnictenes **1**–**3** exhibit higher oxidation potentials than those of FcN=NFc, which are +0.08 and +0.29 V (r.t. in PhCN),[1a] the first oxidation potential of dibismuthene **3** is the lowest oxidation potential among those of 1,2-bis(ferrocenyl)dipnictenes and close to that of FcN=NFc, suggesting that the Bi=Bi moiety should work as an effective electron donor, reflecting the intrinsic nature of the Bi=Bi bond. Although both FcN=NFc and Fc*Bi=BiFc* exhibit such low oxidation potentials similarly, the reason would be different for each. That is, the N=N moiety of FcN=NFc would raise the energy level of the d-electrons in its HOMO orbitals via mesomeric effect with π-electron donation, making the oxidation potentials of the ferrocenyl moieties lower. On the other hand, the Bi=Bi moiety itself should work as an electron donor, because the Bi=Bi π-orbital is the HOMO of **3**, exhibiting higher π-orbital level than the d-orbital levels of the ferrocenyl moieties. After the oxidation, the electron distributions of the cationic species of **3** would be relaxed through the d–π electron conjugation through the $[\mathrm{Fc^*–Bi=Bi–Fc^*}]^+$ unit, because it would have enough time to be relaxed during adiabatic excitation in the electrochemical measurements. Thus, the Pn=Pn π-orbital levels should play important roles in the case of such d–π electron systems of the heavier elements of pnictogens.

Difference between the oxidation potentials is commonly considered a touchstone of the extent of electronic communication between two electron-transfer sites.[26] It should be noted that the oxidation processes of both ferrocenyl moieties were observed as two separate steps with $\Delta(E^1–E^2) = 0.55$ (**1**), 0.42 (**2**), and 0.48 V (**3**), respectively, which are considerably larger than the separation observed in FcN=NFc ($\Delta E = 0.21$ V) and (*E*)-Fc(Ph)C=C(Ph)Fc ($\Delta E = 0.18$ V). The separations of the oxidation potentials $[\Delta(E^1–E^2)]$ should be converted to comproportionation constants K_{com} (equilibrium constant between $[\mathrm{Fc^*Pn{=}PnFc^*}]^{2+}$ + [Fc*Pn=PnFc*] and 2 × $[\mathrm{Fc^*Pn{=}PnFc^*}]^{+}$) = 1.60×10^{14} (**1**), 7.02×10^{10} (**2**), and 2.49×10^{12} (**3**) at −78 °C, which suggest much stronger electronic communication between the two ferrocenyl moieties through the Pn=Pn π-spacers than those in FcN=NFc ($K_{\mathrm{com}} = 3.5 \times 10^3$)[1a,6] and (*E*)-Fc(Ph)C=C(Ph)Fc ($K_{\mathrm{com}} = 1.1 \times 10^3$).[4] Notably, $\Delta(E^1–E^2)$ of diphosphene **1** was found to be the largest among those of the 1,2-bis(ferrocenyl)dipnictenes. Such unique electrochemical properties of these 1,2-bis(ferrocenyl)dipnictenes as d–π electron systems should reflect the intrinsic nature of Pn=Pn double bonds of π-spacers. In summary, the P=P moiety works as an effective π-spacer, suggesting stabilization of the corresponding mixed-valence state, the Sb=Sb system should enhanced its electron-accepting ability, and the Bi=Bi dibismuthene system exhibits the lowest oxidation potential reflecting the high energy level of the Bi=Bi π-orbital.

Conclusion

We have synthesized a series of 1,2-bis(ferrocenyl)dipnictenes with a Pn=Pn (Pn = P, Sb, and Bi) π-spacer by utilizing the originally developed bulky ferrocenyl group. The systematic comparison of their structural parameters and physical properties allowed us to recognize they should be unique d–π electron systems with their considerable Pn=Pn double-bond characters. On the basis of the electrochemical analysis, it can be concluded that the P=P moiety in 1,2-bis(ferrocenyl)-diphosphene **1** works as an effective π-spacer, stabilizing the corresponding mixed-valence state, the Sb=Sb moiety in 1,2-bis(ferrocenyl)distibene **2** should be an electron accepter reflecting the intrinsic nature of a Sb=Sb bond, and the Bi=Bi moiety in 1,2-bis(ferrocenyl)dibismuthene **3** exhibits low oxidation potential reflecting the high energy level of the Bi=Bi π-orbital. Thus, these systematic studies on the 1,2-bis(ferrocenyl)dipnictenes with a π-bond of heavier elements are expected to open new chemistry in d–π electron systems.

Experimental

General Procedure. Unless otherwise noted, all experiments were performed under dry argon. Prior to use, all solvents were purified and dried by standard methods and/or The Ultimate Solvent System (Glass Contour Co.).[27] Preparative column chromatography was performed on Wakogel C-200. The ^{1}H (300 MHz), ^{13}C (75 Hz), and ^{31}P (120 MHz) NMR spectra were measured in C_6D_6 using a JEOL AL-300 spectrometer. Chemical shifts were referenced to residual C_6HD_5 ($\delta = 7.15$ ppm for ^{1}H NMR) and C_6D_6 ($\delta = 128.0$ ppm for ^{13}C NMR) as internal standards or 85% H_3PO_4 in water ($\delta = 0$ ppm for ^{31}P NMR) as an external standard. High-resolution mass spectrometry data were obtained from a JEOL JMS-700 spectrometer (FAB) or a Bruker microTOF (APPI-TOF). Electronic spectra were recorded on a SHIMADZU-1700 UV–vis spectrophotometer. Raman spectra were measured on a Raman spectrometer consisting of a Spex 1877 Triplemate and an EG&G PARC 1421 intensified photodiode array detector. An NEC GLG 108 He/Ne laser (633 nm) was used for Raman excitation. All melting points were determined on a BÜCHI Melting Point M-565. All elemental analyses were performed in the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Ferrocenyl phenyl sulfoxide was prepared according to the reported procedure.[16] 1-Bromo-3,5-di-*tert*-butylbenzene was received by from MANAC Incorporated, the cooperation of which is appreciated.

Preparation of 1-(3,5-Di-*t*-butylphenyl)-2-(phenylsulfinyl)ferrocene (7). A solution of diisopropylamine (8.33 mL, 59.5 mmol) in THF (20 mL) was treated with *n*-BuLi (36.1 mL, 1.65 M in hexane, 59.5 mmol), and the resulting solution of lithium diisopropylamide (LDA) was added to a solution of ferrocenyl phenyl sulfoxide (**6**) (12.3 g, 39.7 mmol) in THF (100 mL) at −78 °C. After stirring at −78 °C for 30 min, the resulting solution was transferred to a suspension of $ZnCl_2$ (16.2 g, 119 mmol) in THF (100 mL) at −78 °C. After stirring at −78 °C for 1 h, the reaction mixture was warmed to room temperature, where stirring was maintained for 1 h. The resulting solution was added to a solution of 1-bromo-3,5-di-*t*-butylbenzene (10.7 g, 39.7 mmol) and $[\mathrm{Pd(PPh_3)_4}]$ (2.30 g, 1.99 mmol) in THF (50 mL). The reaction mixture was heated at 60 °C for 10 h, and then the reaction was quenched with a saturated aqueous sodium hydrogen carbonate solution. The reaction mixture was extracted with Et_2O, and the combined organic phases were washed with water and dried over $MgSO_4$. After filtration, the filtrate was evaporated to remove the solvent under reduced pressure. The obtained residue was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1) to give **7** (16.8 g, 33.7 mmol, 85%). **7**: yellow crystals; mp 139–140 °C; ^{1}H NMR (300 MHz, C_6D_6): δ 1.40 (s, 18H), 3.97 (pt, $^{3}J_{HH} = 2.6$ Hz, 1H), 4.08 (s, 5H), 4.11 (dd, $^{3}J_{HH} = 2.6$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H), 4.45 (dd, $^{3}J_{HH} = 2.6$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H), 6.88–6.91 (m, 3H), 7.43 (t, $^{3}J_{HH} = 1.8$ Hz, 1H), 7.60–7.63 (m, 2H), 7.92 (d, $^{3}J_{HH} = 1.8$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.8 (q), 35.1 (s), 68.8 (d), 71.0 (d), 71.5 (d), 72.5 (d), 91.6 (s), 94.2 (s), 121.2 (d), 125.5 (d), 125.6 (d), 128.3 (d), 130.0 (d), 135.6 (s), 145.4 (s), 150.4 (s); HRMS (FAB), *m/z* 498.1676 ([M$^+$]), Calcd for $C_{30}H_{34}{}^{56}FeO^{32}S$: 498.1680; Anal. Calcd for $C_{30}H_{34}FeOS$: C, 72.28; H, 6.87%. Found: C, 72.47; H, 6.97%.

Preparation of 1-(3,5-Di-*t*-butylphenyl)-2-(phenylsulfanyl)ferrocene (8). To a solution of compound **7** (16.8 g, 33.7 mmol) and NaI (11.1 g, 74.1 mmol) in acetone (100 mL) at 0 °C was added to a solution of trifluoroacetic anhydride (10.3 mL, 74.1 mmol) in acetone (50 mL). After stirring for 30 min at 0 °C, the reaction mixture was extracted with Et_2O. The combined organic phases were washed with 10% sodium thiosulfate solution and dried over $MgSO_4$. After filtration, the filtrate was evaporated under reduced pressure. The obtained residue was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1) to give **8** (14.6 g, 30.3 mmol, 90%). **8**: yellow crystals; mp 151–152 °C; ^{1}H NMR (300 MHz, C_6D_6): δ 1.28 (s, 18H), 4.06 (s, 5H), 4.12 (pt, $^{3}J_{HH} = 2.6$ Hz, 1H), 4.45 (dd, $^{3}J_{HH} = 2.6$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H), 4.58 (dd, $^{3}J_{HH} = 2.6$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H), 6.78–6.83 (m, 1H), 6.92–6.97 (m, 2H), 7.18–7.21 (m, 2H), 7.42 (t, $^{3}J_{HH} = 1.8$ Hz, 1H), 7.71 (d, $^{3}J_{HH} = 1.8$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.7 (q), 34.9 (s), 69.4 (d), 71.5 (d), 72.2 (d), 73.6 (d), 77.2 (s), 82.6 (s), 120.7 (d), 124.1 (d), 124.7 (d), 125.6 (d), 129.1 (d), 136.7 (s), 142.2 (s), 150.3 (s); HRMS (FAB), *m/z* 482.1729 ([M$^+$]), Calcd for $C_{30}H_{34}{}^{56}Fe^{32}S$: 482.1731; Anal. Calcd for $C_{30}H_{34}FeS$: C, 74.68; H, 7.10%. Found: C, 74.86; H, 7.22%.

Preparation of 1-(3,5-Di-*t*-butylphenyl)-2-(phenylsulfinyl)ferrocene (9). A solution of compound **8** (14.6 g, 30.3 mmol) in CH_2Cl_2 (100 mL) was cooled to 0 °C, and a solution of *m*-CPBA (6.27 g, 36.4 mmol) in CH_2Cl_2 (150 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 5 h before being extracted with CH_2Cl_2. The combined organic phases were consecutively washed with NaOH(aq) and water. After drying over $MgSO_4$, filtration and evaporation of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1) to give **9** (12.2 g, 24.5 mmol, 81%). **9**: yellow crystals; mp 49–50 °C; ^{1}H NMR (300 MHz, C_6D_6): δ 1.33 (s, 18H), 4.06 (pt, $^{3}J_{HH} = 2.6$ Hz, 1H), 4.31 (s, 5H), 4.43 (dd, $^{3}J_{HH} = 2.6$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H), 4.75 (dd, $^{3}J_{HH} = 2.6$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H), 6.62–6.90 (m, 3H), 7.47–7.52 (m, 3H), 7.74 (d, $^{3}J_{HH} = 1.8$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.7 (q), 35.0 (s), 65.9 (d), 68.9 (d), 70.4 (d), 71.8 (d), 90.5 (s), 96.0 (s), 121.3 (d), 124.5 (d), 124.7 (d), 128.9 (d), 130.1 (d), 136.3 (s), 148.5 (s), 151.1 (s); HRMS (FAB), *m/z* 498.1677 ([M$^+$]), Calcd for $C_{30}H_{34}{}^{56}FeO^{32}S$: 498.1680; Anal. Calcd for $C_{30}H_{34}FeOS$: C, 72.28; H, 6.87%. Found: C, 72.26; H, 6.93%.

Preparation of 1,3-Bis(3,5-di-*t*-butylphenyl)-2-(phenylsulfinyl)ferrocene (10). Compound **9** (12.2 g, 24.5 mmol) was dissolved in THF (100 mL) and cooled to −78 °C. To this solution was added at −78 °C a freshly prepared solution of LDA from diisopropylamine (5.15 mL, 36.7 mmol) and *n*-BuLi (22.2 mL, 1.65 M, 36.7 mmol) in THF (50 mL). After stirring at −78 °C for 30 min, the resulting solution was added to a suspension of $ZnCl_2$ (12.1 g, 89.1 mmol) in THF (100 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and warmed to room temperature, where stirring was continued for 1 h. The resulting solution was added to a solution of 1-bromo-3,5-di-*t*-butylbenzene (6.60 g, 24.5 mmol) and [Pd(PPh_3)$_4$] (1.42 g, 1.22 mmol) in THF (50 mL). The resulting solution was heated at 60 °C for 10 h, before the reaction was quenched by addition of saturated aqueous sodium hydrogen carbonate. The reaction mixture was extracted with Et_2O and the combined organic phases were washed with water and dried over $MgSO_4$. After filtration and evaporation of all volatiles under reduced pressure, the obtained residue was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1) to give **10** (13.5 g, 19.7 mmol, 80%). **10**; orange crystals; mp 84–85 °C; ^{1}H NMR (300 MHz, C_6D_6): δ 1.37 (s, 18H), 1.39 (s, 18H), 4.42 (s, 5H), 4.52 (d, $^{3}J_{HH} = 2.5$ Hz, 1H), 4.65 (d, $^{3}J_{HH} = 2.5$ Hz, 1H), 6.61–6.62 (m, 3H), 7.20–7.22 (m, 2H), 7.27 (s, 1H), 7.54 (s, 1H), 7.70 (d, $^{4}J_{HH} = 1.5$ Hz, 2H), 7.92 (d, $^{4}J_{HH} = 1.5$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.7 (q), 31.8 (q), 34.9 (s), 35.1 (s), 69.5 (d), 70.5 (d), 73.3 (d), 92.3 (s), 94.9 (s), 95.1 (s), 121.1 (d), 121.6 (d), 124.9 (d), 125.7 (d), 126.5 (d), 127.6 (d), 128.6 (d), 135.7 (s), 136.0 (s), 145.8 (s), 149.3 (s), 150.7 (s); HRMS (FAB), *m/z* 686.3268 ([M$^+$]), Calcd for $C_{44}H_{54}{}^{56}FeO^{32}S$: 686.3246; Anal. Calcd for $C_{44}H_{54}FeOS$: C, 76.95; H, 7.92%. Found: C, 77.12; H, 8.05%.

Preparation of 1,3-Bis(3,5-di-*t*-butylphenyl)-2-iodoferrocene (5). A solution of compound **10** (13.5 g, 19.7 mmol) in Et_2O (100 mL) was treated with *t*-BuLi in pentane (27.0 mL, 1.61 M, 43.3 mmol) at −78 °C. After stirring for 5 min, iodine (12.4 g, 98.5 mmol) was added to the reaction mixture, and the reaction mixture was allowed to warm to room temperature. After stirring for 3 h, the reaction mixture was extracted with Et_2O. The combined organic phases were washed with 10% sodium thiosulfate solution and dried over $MgSO_4$. After filtration and evaporation of all volatiles under reduced pressure, the obtained residue was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1). The obtained solid was precipitated from Et_2O to afford iodide **5** (9.31 g, 13.5 mmol, 68%). **5**: yellow crystals; mp 218–219 °C; ^{1}H NMR (300 MHz, C_6D_6): δ 1.41 (s, 36H), 4.05 (s, 5H), 4.63 (s, 2H), 7.54 (s, 2H), 7.89 (s, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.5 (q), 34.9 (s), 49.4 (s), 69.0 (d), 74.0 (d), 92.1 (s), 120.9 (d), 125.3 (d), 137.0 (s), 149.9 (s); HRMS (FAB), *m/z* 688.2240 ([M$^+$]), Calcd for $C_{38}H_{49}{}^{56}FeI$: 688.2229; Anal. Calcd for $C_{38}H_{49}FeI$: C, 66.29; H, 7.17%. Found: C, 66.19; H, 7.17%.

Preparation of [1,3-Bis(3,5-di-*t*-butylphenyl)ferrocen-2-yl]dichlorophosphine (11). Iodoferrocene **5** (211 mg, 0.306 mmol) was dissolved in Et_2O (10.0 mL) and cooled to −78 °C, and then *t*-BuLi (0.42 mL, 1.61 M in pentane, 0.67 mmol) was added dropwise to the solution. After stirring for 1 h, the reaction mixture was warmed to room temperature for 30 min and then cooled down to −78 °C again. The resulting solution was added to a solution of PCl_3 (54 µL, 0.620 mmol) in Et_2O (2.0 mL) at −78 °C. After stirring for 1 h, the reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed under reduced pressure and the residue was extracted with hexane (50 mL). All insoluble inorganic salts were removed by filtration through a pad of Celite. After removal of the solvent from the filtrate, the residue was recrystallized from Et_2O/hexane to afford dichloro(ferrocenyl)phosphine **11** (148 mg, 0.223 µmol, 73%). **11**: orange crystals; mp 193 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): δ 1.42 (s, 36H), 4.16 (s, 5H), 4.63 (s, 2H), 7.53 (s, 2H), 7.83 (s, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.8 (q), 35.2 (s), 75.4 (d), 74.2 (d), 75.5 (s), 97.6 (s), 122 (d), 125 (d), 136 (s), 151 (s); ^{31}P NMR (120 MHz, C_6D_6): δ 156 (s); HRMS (FAB), *m*/*z* Found: 662.2286 ([M$^+$]), Calcd for $C_{38}H_{49}{}^{35}Cl^{37}Cl^{54}FeP$: 662.2300; Anal. Calcd for $C_{38}H_{49}Cl_2FeP$: C, 68.79; H, 7.44%. Found: C, 68.75; H, 7.58%.

Preparation of [1,3-Bis(3,5-di-*t*-butylphenyl)ferrocen-2-yl]dichlorostibine (12). Iodoferrocene **5** (164 mg, 0.238 mmol) was dissolved in Et_2O (5.0 mL) and cooled to −78 °C, and then *t*-BuLi (0.33 mL, 1.61 M in pentane, 0.52 mmol) was added dropwise to the solution. After stirring for 1 h, the reaction mixture was warmed to room temperature for 30 min and then cooled to −78 °C again. The resulting solution was added to a solution of $SbCl_3$ (138 mg, 0.606 mmol) in Et_2O (2.0 mL) at −78 °C. After 1 h, the reaction mixture was warmed up to room temperature and stirred for 12 h. The solvent was removed under reduced pressure and the residue was extracted with hexane (50 mL), while all insoluble inorganic salts were removed by filtration through a pad of Celite. After removal of the solvent from the filtrate, the residue was recrystallized from Et_2O/hexane to afford dichloroferrocenylstibine **12** (59.3 mg, 78.6 µmol, 33%). **12**: orange crystals; mp 170 (decomp) °C; ^{1}H NMR (300 MHz, C_6D_6): δ 1.41 (s, 36H), 4.14 (s, 5H), 4.70 (s, 2H), 7.51 (t, $^4J_{HH} = 3.0$ Hz, 2H), 7.70 (d, $^4J_{HH} = 3.0$ Hz, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.8 (q), 35.2 (s), 71.2 (s), 72.4 (d), 75.5 (d), 98.9 (s), 122.9 (d), 124.7 (d), 136.3 (s), 151.3 (s); HRMS (FAB), *m*/*z* 754.1604 ([M$^+$]), Calcd for $C_{38}H_{49}{}^{37}Cl_2{}^{54}Fe^{121}Sb$: 754.1593; Anal. Calcd for $C_{38}H_{49}Cl_2FeSb$: C, 60.51; H, 6.55%. Found: C, 60.36; H, 6.55%.

Preparation of Dibromo[1,3-bis(3,5-di-*t*-butylphenyl)ferrocen-2-yl]bismuthine (13). Iodoferrocene **5** (171 mg, 0.248 mmol) was dissolved in THF (5.0 mL) and cooled to −78 °C, and then *t*-BuLi (0.34 mL, 1.61 M, 0.55 mmol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 30 min and then cooled to −78 °C. The resulting solution was added to a solution of $BiBr_3$ (278 mg, 0.620 mmol) in THF (2.0 mL) at −78 °C. After stirring for 1 h, the reaction mixture was warmed up to room temperature and stirred for 12 h. The solvent was removed under reduced pressure and extracted with hexane (50 mL). All insoluble inorganic salts were removed by filtration through a pad of Celite. After removal of the solvent from the filtrate, the residue was recrystallized from Et_2O/hexane to afford dibromoferrocenylbismuthine **13** (92.3 mg, 99.2 µmol, 40%). **13**: purple crystals; mp 180 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): δ 1.44 (s, 36H), 4.20 (s, 5H), 4.76 (s, 2H), 7.54 (t, $^4J_{HH} = 3.0$ Hz, 2H), 7.71 (d, $^4J_{HH} = 3.0$ Hz, 4H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.9 (q), 35.3 (s), 65.9 (s), 68.6 (d), 72.1 (d), 77.7 (s), 122.1 (d), 124.4 (d), 136.5 (s), 151.5 (s); HRMS (FAB), *m*/*z* 930.1342 ([M$^+$]), Calcd for $C_{38}H_{49}Bi^{81}Br_2{}^{56}Fe$: 930.1339; Anal. Calcd for $C_{38}H_{49}BiBr_2Fe$: C, 49.05; H, 5.31%. Found: C, 48.81; H, 5.29%.

Preparation of 1,2-Bis[1,3-bis(3,5-di-*t*-butylphenyl)ferrocen-2-yl]diphosphene (1). To a THF solution (2.0 mL) of dichloro(ferrocenyl)phosphine **11** (82.7 mg, 0.125 µmol) was added magnesium metal (15.1 mg, 0.617 mmol) at room temperature. After the reaction mixture was stirred for 30 min, the color of the solution changed to red. The solvent was evaporated under reduced pressure and 20 mL of hexane was added to the residue. Insoluble inorganic salts and the residual magnesium metal were removed by filtration through Celite. After removal of the solvent from the filtrate, the residue was recrystallized from Et_2O/hexane to afford diphosphene **1** (46.1 mg, 38.8 µmol, 62%). **1**: red crystals; mp 178 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): δ 1.35 (s, 72H), 4.04 (s, 10H), 4.72 (s, 4H), 7.40 (s, 4H), 7.75 (s, 8H); ^{13}C NMR (75 MHz, C_6D_6): δ 31.9 (q), 35.0 (s), 65.9 (s), 73.0 (d), 73.4 (d), 95.7 (s), 121 (d), 127 (d), 138 (s), 150 (s); ^{31}P NMR (120 MHz, C_6D_6): δ 471 (s); HRMS (FAB), *m*/*z* Found: 1184.5853 ([M$^+$]), Calcd for $C_{76}H_{98}{}^{56}Fe_2P_2$: 1184.5848; Anal. Calcd for $C_{76}H_{98}Fe_2P_2$: C, 77.02; H, 8.33%. Found: C, 76.87; H, 8.53%.

Preparation of 1,2-Bis[1,3-bis(3,5-di-*t*-butylphenyl)ferrocen-2-yl]distibene (2). To a THF solution (2.0 mL) of dichlorostibine **12** (35.4 mg, 46.9 µmol) was added magnesium metal (5.70 mg, 0.235 mmol) at room temperature. After the reaction mixture was stirred for 30 min, the color of the solution changed to deep green. The solvent was evaporated under reduced pressure and 20 mL of hexane was added to the residue. Insoluble inorganic salts and the residual magnesium metal were removed by filtration through Celite. After the removal of the solvent from the filtrate, the residue was recrystallized from Et_2O/hexane to give green crystals of distibene **2** (14.1 mg, 10.3 µmol, 44%). **2**: green crystals, mp 231–232 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 1.33 (s, 72H), 4.17 (s, 10H), 4.76 (s, 4H), 7.41 (s, 4H), 7.69 (s, 8H). ^{13}C NMR (125 MHz, C_6D_6): δ 32.0 (q), 35.1 (s), 71.9 (s), 72.4 (d), 73.9 (d), 99.1 (s), 121.3 (d), 126.8 (d), 139.0 (s), 150.1 (s). HRMS (FAB), *m*/*z* 1366.4440 ([M]$^+$), Calcd for $C_{76}H_{98}{}^{56}Fe_2{}^{121}Sb_2$: 1366.4465; Anal. Calcd for $C_{76}H_{98}Fe_2Sb_2$: C, 66.78; H, 7.23%. Found: C, 67.20; H, 7.35%.

Preparation of 1,2-Bis[1,3-bis(3,5-di-*t*-butylphenyl)ferrocen-2-yl]dibismuthene (3). To a THF solution (2.0 mL) of dibromobismuthine **13** (52.3 mg, 56.2 µmol) was added magnesium metal (6.83 mg, 0.281 mmol) at room temperature. After the reaction mixture was stirred for 15 min, the color of the solution changed to deep purple. The solvent was evaporated under reduced pressure and 20 mL of hexane was added to the residue. Insoluble inorganic salts and the residual magnesium metal were removed by filtration through Celite. After removal of the solvent from the filtrate, the residue was recrystallized from Et_2O/hexane to afford dibismuthene **3** (22.5 mg, 14.6 µmol, 52%), **3**: violet crystals; mp 121 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6): δ 1.37 (s, 72H), 4.13 (s, 10H), 4.81 (s, 4H), 7.44 (t, $^4J_{HH} = 3.0$ Hz, 4H), 7.76 (d, $^4J_{HH} = 3.0$ Hz, 8H); ^{13}C NMR (75 MHz, C_6D_6): δ 32.3 (q), 35.0 (s), 65.9 (s), 72.8 (d), 74.1 (d), 103.7 (s), 121.2 (d), 127.0 (d), 140.5 (s), 150.2 (s); HRMS (FAB), *m*/*z* 1540.5957 ([M$^+$]), Calcd for $C_{76}H_{98}Bi_2{}^{56}Fe_2$: 1540.5980; Anal. Calcd for $C_{76}H_{98}Bi_2Fe_2$: C, 59.23; H, 6.41%. Found: C, 59.35; H, 6.64%.

Theoretical Calculations. All calculations were conducted with the Gaussian 09 series[28] of electronic structure programs. Geometries were optimized using density functional theory at the B3PW91 level, with the basis sets of 6-31G(d) (C, H), TZ(2d) (P, Sb, Bi) and Lanl2DZ (Fe), and the TDDFT calculations were performed at the same level of theory and basis sets. Frequency (Raman) calculations confirmed the optimized structures to have minimum energies at the same level. Computational time was generously provided by the Supercomputer Laboratory at the Institute for Chemical Research of Kyoto University.

X-ray Crystallographic Analysis of 1, 2, and 3. The intensity data for compound **2** were collected at BL40XU in Spring-8 (JASRI, 2011B1545) on a Rigaku Saturn 724 CCD system with synchrotron radiation ($\lambda = 0.83077$ Å), and those for compound **1**, **3**, and **5** were collected on a RIGAKU Saturn70 CCD(system) with VariMax Mo Optic using Mo Kα radiation ($\lambda = 0.71070$ Å). Single crystals suitable for X-ray analysis were obtained by slow recrystallization from Et_2O or hexane at −40 °C. A single crystal was mounted on a glass fiber. The structures were solved by direct methods (SHELXS-97)[29] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[29] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Crystal data for **1**–**3** were summarized in Table 2. Crystal data for **5**: Formula $C_{38}H_{49}FeI$, $M_w = 688.52$; $T = -170$ °C; monoclinic; space group $C2$ (#5); $a = 32.689(2)$ Å, $b = 9.6693(9)$ Å, $c = 10.7948(10)$ Å; $Z = 4$; $V = 3409.1(5)$ Å^3; $\mu = 1.371$ mm^{-1}; $D_{\text{calcd}} = 1.341$ g cm^{-3}; $\theta_{\max} = 25.5°$; 13199 measured reflections, 5932 independent reflections [$R_{\text{int}} = 0.0911$], 373 refined parameters; GOF = 1.028; R_1 ($I > 2\sigma(I)$) = 0.0782; wR_2 (all data) = 0.1965; largest diff. peak and hole 3.400 (around I atom) and −0.783 e Å^{-3}. Cif files containing all crystallographic data for **1**, **2**, **3**, and **5** have been deposited at the Cambridge Crystallographic Data Centre (CCDC-941816 for **1**, CCDC-912009 for **2**, CCDC-912010 for **3**, and CCDC-942572 for **5**). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cyclic Voltammograms and Differential Potential Voltammetries of 1, 2, and 3. The custom-tailored glassware shown in Figure 7 for the electrochemical measurements for dipnictenes **1**–**3** were prepared. The solution (THF or CH_2Cl_2) of the targeted compound **1**, **2**, or **3** was degassed and closed in the flange-capped bottle of the apparatus equipped with three Pt electrodes, which are working, reference and counter electrodes. Electrochemical experiments were carried out on an ALS 1140A potentiostat/galvanostat. Electrochemical samples were recorded with scan rates of 10–500 mV s^{-1} at −78 °C or room temperature, respectively. Ferrocene was used as internal reference to determine the potentials. Sample solutions (CH_2Cl_2 or THF) were 1.5 mM in analyte and 0.1 M in n-Bu_4NBF_4 as the supporting electrolyte.

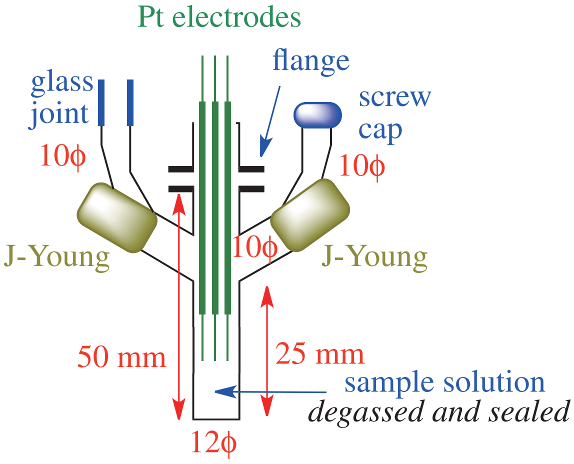


Figure 7. Custom-tailored glassware for electrochemical measurements for reactive species.

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\# Dedicate to Emeritus Professor Renji Okazaki on the occasion of his 77th birthday.

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