A Kinetically Stabilized Ferrocenyl Diphosphene: Synthesis, Structure, Properties, and Redox Behavior

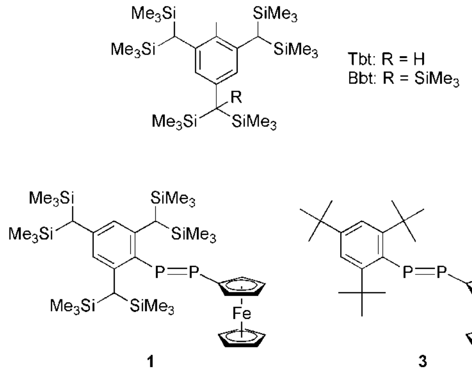
Noriyoshi Nagahora, Takahiro Sasamori, Nobuhiro Takeda, and Norihiro Tokitoh*[a]

Abstract: A new, stable ferrocenyl diphosphene [Tbt-P=P-Fc] (**1**) (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl, Fc = ferrocenyl) was synthesized by the dehydrochlorination reaction of the corresponding diphosphane, [Tbt-P(H)-P(Cl)-Fc] (**8**), with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in good yield. Diphosphene **1** is very stable in the solid state and also in solution. In the ^{31}P NMR spectrum (C$_6$D$_6$), diphosphene **1** showed a low-fielded AB quartet at δ 501.7 and 479.5 ppm with the coupling constant $^1J_{PP} = 546$ Hz, which is characteristic of an unsymmetrically substituted *trans*-diphosphene. The molecular structure of **1** was established by X-ray crystallographic analysis, which showed a *trans*-diphosphene with a C-P-P-C torsion angle of 177.86(17)°. The phosphorus–phosphorus bond length of **1** [2.0285(15) Å] which is considerably shorter than the typical P–P single-bond lengths (ca. 2.22–2.24 Å) and within the range of reported P=P double-bond lengths (1.985–2.051 Å) for diaryl diphosphenes, evidenced the P=P double-bond character of **1** in the solid state. In addition, the cyclic voltammograms of **1** showed reversible reduction and oxidation couples at −1.95 and +0.34 V versus SCE, respectively. The electrochemical results for **1** were reasonably supported by the DFT calculations, which suggested that the LUMO and HOMO orbitals should be mainly π* orbital of the diphosphene moiety and d orbitals of the iron(II) atom, respectively.

Keywords: cyclic voltammetry · metallocenes · phosphorus · UV/Vis spectroscopy · X-ray diffraction

Introduction

Multiple-bond compounds between heavier Group 15 elements have fascinated many chemists for several decades.[1] Since the first synthesis of diphosphene by Yoshifuji et al.,[2] the syntheses and properties of kinetically stabilized diphosphenes, diarsenes, and phosphaarsenes bearing sterically hindered substituents have been numerously reported.[1,3] We also succeeded in the synthesis of novel doubly bonded systems between Group 15 elements, that is, distibene (RSb=SbR), dibismuthene (RBi=BiR), phosphabismuthene (RP=BiR), and stibabismuthene (RSb=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) groups (Scheme 1).[4]



Scheme 1. Efficient steric protection groups (top); ferrocenyl diphosphenes **1** and **3** (bottom).

Meanwhile, organic and organometallic π-conjugated compounds have received substantial attention in the field of material science.[5] A number of reports on interesting properties of low-coordinated phosphorus compounds, such as photochemical properties, redox behavior, and magnetic properties, appeared recently.[6] Based on these reports, we thought that the unique properties of low-coordinated phosphorus compounds, especially diphosphenes, are most likely interpreted in terms of their low-lying π* orbital level.[7] In this context, several diphosphene derivatives having redox-active units, such as bis(diphosphene)s,[6c,d] diphosphenes having triarylamino units,[8] and ferrocenyl diphosphenes,[9]

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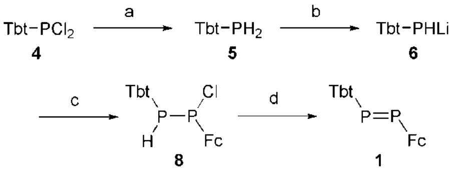
were synthesized in the hope of a discovery of novel electrochemical properties. Indeed, a bis(diphosphene) derivative reported by Protasiewicz and co-workers was well furnished by electrochemical technique and reduced to give the dianion species with paramagnetic properties.[6d] As for a ferrocenyl diphosphene a pioneering study on the synthesis and spectroscopic characterization of **3** was reported by Pietschnig and Niecke,[9] though the structural characterization and studies on electrochemical properties of **3** have not been fully accomplished due to its instability in solution (stable only below to −30 °C in the absence of light). Here, we report the synthesis, structure, properties, and multi-switchable electrochemical behavior of kinetically well-stabilized diphosphene **1** bearing ferrocenyl (Fc) and Tbt groups (Scheme 2).



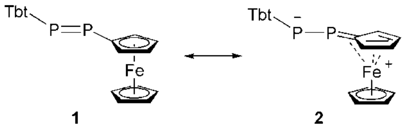
Scheme 2. a) $LiAlH_4$, THF, 0 °C; b) *n*BuLi, Et_2O, −78 °C; c) dichloroferrocenylphosphine (**7**), Et_2O, −78 °C; d) DBU, room temperature, 92 % from **5**.

Results and Discussion

Bulky phosphine **5** was readily prepared by the treatment of dichlorophosphine **4**[4f] with a lithium aluminium hydride. The reaction of dichloroferrocenylphosphine[10] **7** with lithium phosphide **6**, prepared by the deprotonation reaction of phosphine **5** with an equimolar amount of *n*-butyllithium, afforded a mixture of two diastereomers of diphosphane **8** as air-sensitive yellow crystals, which showed characteristic two AB quartets in the ^{31}P NMR spectrum in [D$_6$]benzene (δ −59.1 and 107.0 ppm; $^1J_{PP}=182$ Hz, δ −52.8 and 92.7; $^1J_{PP}=217$ Hz). When **8** was treated with 1.2 equimolar amount of DBU in diethyl ether, the reaction mixture immediately turned purple. After removal of inorganic salts, ferrocenyl diphosphene **1** was obtained as purple crystals in 92 % isolated yield.

In sharp contrast to **3**, diphosphene **1** is quite stable in the solid state (m.p. 182–184 °C) or in a [D$_6$]benzene solution (stable at 100 °C for a month in a sealed tube) on exposure to scattered light, and neither decomposition nor dimerization was observed at ambient temperature. The remarkable stability of **1** reflects the prominent protecting ability of a Tbt group.

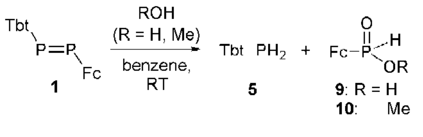
The ^{31}P NMR spectrum of **1** in [D$_6$]benzene solution showed a AB quartet at δ 479.5 and 501.7 ppm, which was characteristic of unsymmetric *trans*-diphosphenes.[1a,6c,6d,9,11] The coupling constant ($^1J_{PP}=546$ Hz) of **1** is very similar to that of **3**, though somewhat smaller than those of diphosphenes protected by two bulky aryl groups (J = 572–584 Hz).[1a] It was suggested that the P=P double-bond character was slightly reduced in solution due to electronic interaction (as shown in Scheme 3) between the ferrocenyl group



Scheme 3. Conceivable resonance structures for diphosphene **1**.

and the P=P π bond as well as the case of **3**.[9] In addition, in the ^1H NMR spectral features also supported the electronic interaction in both cases of **1** and **3**. As for the ^1H NMR spectrum of **3**, the signals due to two α-protons of the substituted cyclopentadienyl ring of the ferrocenyl group were detected unequivalently (δ 4.65 and 4.76 ppm) and their chemical shifts were different from the β-protons (δ 4.29 ppm) by ≈0.4 ppm. Pietschnig and Niecke also mentioned these spectral features as an explanation of such electronic interactions in **3**. Although the signals corresponding to α-protons of the substituted cyclopentadienyl ring of the ferrocenyl group for **1** were observed equivalently at room temperature, the difference between the chemical shifts ($\Delta\delta_H$) of the α and β-protons for **1** (0.58 ppm) was larger than those for **3**. Taking into account that these $\Delta\delta_H$ values of **1** and **3** are much larger than those for reported non-conjugated ferrocenylphosphines, for example, $\Delta\delta_H$ of **7** is ≈0.2 ppm,[10,12] and $\Delta\delta_H$ of Fc-PH$_2$ is 0 ppm.[12] These spectral features of **1** might imply the presence of an electronic interaction between the P=P π bond and the cyclopentadienyl ring of the ferrocenyl group, that is, the contribution of resonance structure **2** in the solution as well as **3**.

This interpretation was actually supported by the reactivity of **1** (Scheme 4). Diphosphene **1** underwent ready hydrolysis by the addition of water toward the P=P moiety leading to the formation of Tbt-PH$_2$ (**5**) and Fc-PH(O)OH (**9**). Compound **9** is known to be an isolable, isomeric form of Fc-P(OH)$_2$.[10,13] Similarly, treatment of **1** with methanol afforded Tbt-PH$_2$ (**5**) and Fc-PH(O)OMe (**10**), which may be formed by the decomposition of Fc-P(OMe)$_2$ during separation.[13] Thus, **1** retains inherently high reactivity toward hydrolysis and methanolysis similar to **3**, though **1** is kinetically well-stabilized by the extremely bulky Tbt substituent. The regioselectivity observed for the addition of hydroxy or methoxy group to the P=P double bond of **1** is in good agreement with the polarized resonance structure **2**.



Scheme 4. Reactions of diphosphene **1**.

The molecular structure of **1** was determined by X-ray crystallographic analysis (Figure 1). It was found that the structure of **1** showed a *trans*-configuration with a C-P-P-C torsion angle of 177.86(17)°; the C-P-P-C plane was almost coplanar with the cyclopentadienyl ring of the ferrocenyl group, which suggests conjugative interaction between the π-electrons of the diphosphene unit with those of the cyclopentadienyl ring. Furthermore, the C-P-P-C plane is oriented perpendicular to the benzene ring of the Tbt group. The phosphorus-phosphorus bond length of **1** is 2.0285(15) Å, comparable to those of previously reported diaryl diphosphenes (1.985–2.051 Å).[1a,4f] Thus, the P=P bond length was found not to be affected by the conjugation between P=P π bond and cyclopentadienyl group in the solid state.

In the Raman spectrum (measured in the solid state) of **1**, strong line attributable to the P=P stretching was observed at $\tilde{\nu}$ 609 cm^{-1}. The value is higher than the frequencies observed for diphosphanes (e.g. Ph_2P-PPh_2, 530 cm^{-1})[14] and very similar to those observed for Mes*P=PMes* (610 cm^{-1})[15] and TbtP=PTbt (609 cm^{-1}).[4f] Consequently, the phosphorus–phosphorus double-bond character in **1** in the solid state is supported by not only its P=P bond length but also vibrational information on its P=P bond.

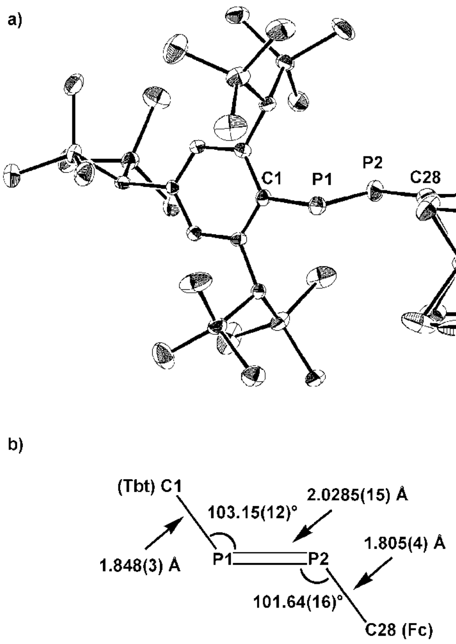


Figure 1. a) ORTEP drawing of diphosphene **1** with thermal ellipsoid plots (50 % probability). Hydrogen atoms are omitted for clarity. b) Schematic drawing of **1** with some selected bond lengths and angles.

The UV/Vis spectrum of **1** in hexane shows two absorption maxima at 371 (ε 2500) and 542 nm (ε 900) (Figure 2). The former can be assigned to the π–π* electron transition for the P=P chromophore, since the λ_{max} value is similar to those for reported diaryl diphosphenes (277–418 nm).[1a,4f] The latter should be assigned to the metal-to-ligand charge transfer (MLCT) band due to the electron transition from d orbitals of the iron(II) to the π* orbital of the P=P moiety. These absorption maxima were observed in longer wavelength region compared with those for azoferrocenes,[16] which were known to show two absorption maxima at 321–328 (π–π* band) and 522–539 nm (MLCT band). The bathochromic shift of **1** may indicate the lower π* orbital energy level of **1** than those of azoferrocenes. In addition, assignment of the observed absorption maxima for **1** are reasonably supported by theoretical calculations for the excited state of the model compound, ferrocenyl-mesityl diphosphene (**11**) [359 (π–π*) and 567 nm (MLCT) for **11**, computed at the TD-B3LYP/TZV for Fe, 6-311+G(2d) for P, and 6-31G(d) for C,H level], and calculated λ_{max} and relative intensity are shown in Figure 2.

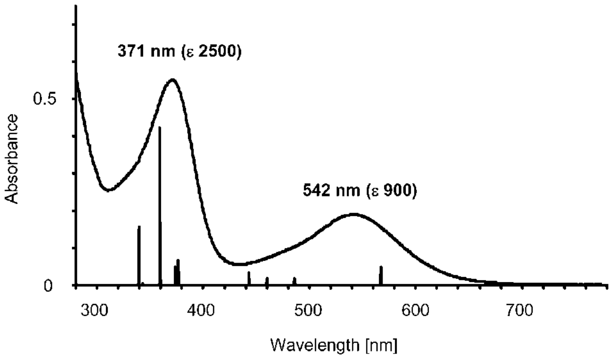


Figure 2. Experimental UV/Vis spectrum of **1** in *n*-hexane (2.2×10^{-4} M) and calculated electron transitions (bars) of **11**.

The electrochemical properties of **1** were furnished by cyclic voltammetry, measurements of which were carried out in CH_2Cl_2 (oxidation) and THF (reduction) with nBu_4NBF_4 as an electrolyte at room temperature. The voltammograms were shown in Figure 3 and summarized in Table 1. As a

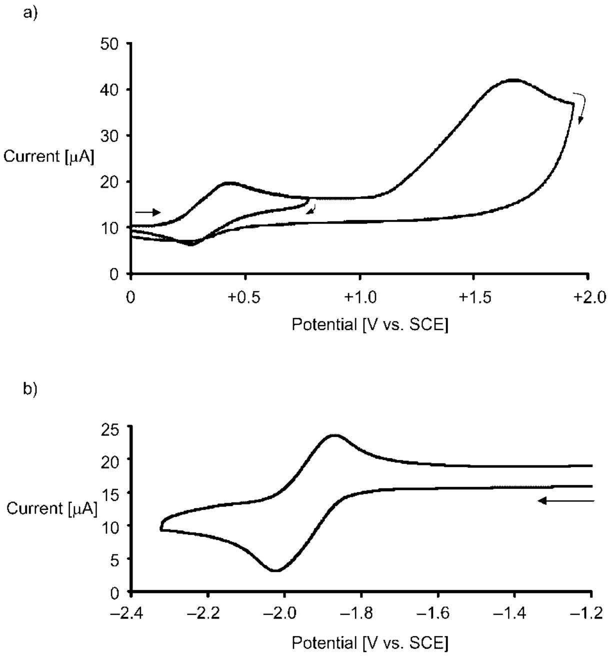


Figure 3. Cyclic voltammograms of **1** (2.0×10^{-3} M) with a scan rate of 100 mV s^{-1} at room temperature. a) In 0.1 M nBu_4NBF_4/CH_2Cl_2, b) in 0.1 M nBu_4NBF_4/THF.

Table 1. Redox potentials [V vs. SCE] of **1**.

	Oxidation[a]		Reduction[b]	
E_{pa}	+0.43	+1.68	E_{pc}	−2.03
E_{pc}	+0.25	–	E_{pa}	−1.87
$E_{1/2}$	+0.34	–	$E_{1/2}$	−1.95

[a] 0.1 M nBu_4NBF_4 in CH_2Cl_2, $E_{1/2}$(FcH/FcH$^+$) = +0.26 V vs. SCE. [b] 0.1 M nBu_4NBF_4 in THF.

result, reversible one-electron oxidation and reduction waves were observed at $E_{1/2}(\mathrm{ox}) = +0.34$ and $E_{1/2}(\mathrm{red}) = -1.95$ V versus SCE, respectively. The former couple can be attributed to iron(II)/iron(III) redox of the ferrocenyl group, since the $E_{1/2}(\mathrm{ox})$ value for **1** is almost the same that for a parent ferrocene. The latter couple features the reduction wave of the diphosphene unit of **1**, as in the case of the reduction for previously reported diphosphenes.[7] These well-defined reversible redox waves indicate that the corresponding ferrocenium cation and diphosphene anion radical are easily generated and have substantial chemical stability under such conditions. Furthermore, an irreversible oxidation process was also observed at considerably positive potential (ca. +1.7 V vs SCE). The observed irreversible oxidation wave, comparable to those of previously reported diphosphenes,[7c–e] might correspond to the oxidation of the diphosphene moiety of $\mathbf{1}^{+}$, and indicates that the dication $\mathbf{1}^{2+}$ is unstable under these conditions.

In order to study the electronic structure of **1** in more detail, DFT calculations were carried out on the model molecule **11**. All the optimized structural parameters of **11** are in satisfactory agreement with the crystal structure of **1**. The HOMO and LUMO of the ground-state structure of **11** are depicted in Figure 4. It should be noted that the HOMO orbitals are localized on d orbitals of the iron(II) atom, while the LUMO orbitals are mainly π* ones composed by the orbitals of a diphosphene fragment.

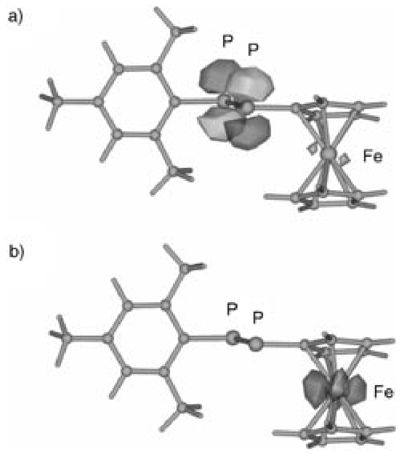


Figure 4. Contour plots of the a) LUMO and b) HOMO orbitals of **11**.

Conclusion

We have succeeded in the synthesis of a new, stable ferrocenyl diphosphene **1** by taking advantage of kinetic stabilization by using an extremely bulky Tbt group. Thus, the combination of a Tbt group with a redox active substituent, a ferrocenyl group, enabled us to synthesize such a unique class of diphosphene derivative. In solution, the contribution of the polarized resonance structure **2** was supported by their NMR spectral features and reactivity of **1**. In spite of the kinetic stability of **1**, hydrolysis and methanolysis of **1** allowed us to elucidate its reactivity in solution, which will be described elsewhere in the near future. The X-ray crystallographic analysis of **1** revealed that **1** has a nearly planar C-P-P-C plane and a phosphorus–phosphorus bond with a sufficient double-bond character in the solid state. Moreover, the Raman shift for the stretching of the P=P bond (609 cm^{-1}) for **1** is very similar to the values of previously reported diphosphene derivatives. In addition, the absorption maxima due to the MLCT transition of **1** appeared at 542 nm, being red-shifted compared with the corresponding azo analogues (Ar-N=N-Fc).

The cyclic voltammograms of **1** showed the reversible reduction and oxidation couples at −1.95 and +0.34 V versus SCE, respectively. The electrochemical results for **1** were reasonably interpreted in terms of the DFT calculations on the model molecule **11**, which indicate that the LUMO orbital is mainly π* orbital of the diphosphene moiety and the HOMO orbital is largely d orbitals of the iron(II) atom. These results may be helpful to develop a new chemistry of diphosphene derivatives. Further investigation of the chemical properties of **1** is currently in progress.

Experimental Section

General methods: All reactions were carried out under an argon atmosphere, unless otherwise noted. All solvents were purified and dried by standard methods. Preparative thin-layer chromatography (PTLC) and column chromatography were performed with Merck Kieselgel 60 PF254. The ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 Hz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-400 or 300 spectrometer using $CHCl_3$ ($\delta = 7.25$ ppm) or C_6HD_5 ($\delta = 7.15$ ppm) for ^{1}H NMR, and $CDCl_3$ ($\delta = 77.0$ ppm) or C_6D_6 ($\delta = 128.0$ ppm) for ^{13}C NMR as internal standards, respectively. ^{31}P NMR (120 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-300 spectrometer using 85 % H_3PO_4 in water ($\delta = 0$ ppm) as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-270 mass spectrometer. The electronic spectra were recorded on a JASCO V-570 UV/Vis spectrometer. 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 (632.8 nm) was used for Raman excitation. All melting points were determined on a Yanaco micro-melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. The electrochemical experiments were carried out with an ALS 600A potentiostat/galvanostat using a glassy carbon disk working electrode, a Pt wire counter electrode, and Ag/0.01 M $AgNO_3$ reference electrode. The measurements were carried out in CH_2Cl_2 and THF solution containing 0.1 M $n\mathrm{Bu_4NBF_4}$ as a supporting electrolyte with scan rates of 10–500 mV s^{-1} in a glovebox filled with argon at ambient temperature. Tbt-PCl_2 (**4**) was prepared according to the reported procedure.[4f]

2,4,6-Tris[bis(trimethylsilyl)methyl]phenylphosphine (5): Lithium aluminium hydride (252 mg, 6.65 mmol) was added at 0 °C to a THF (50 mL) solution of **4** (4.35 g, 6.65 mmol). After stirring at the same temperature for 30 min, the reaction mixture was warmed at room temperature. The solvent was removed under reduced pressure, *n*-hexane was added to the residue. After the solution was filtered through Celite, the filtrate was purified by column chromatography (eluting with *n*-hexane) to afford phosphine **5** (3.76 g, 97 %) as colorless crystals. M.p. 151.2–152.0 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.02$ (brs, 36 H), 0.03 (s, 18 H), 1.30 (s, 1 H), 2.37 (s, 1 H), 2.48 (s, 1 H), 3.62 (d, $^{1}J_{PH} = 203$ Hz, 2 H), 6.32 (s, 1 H), 6.45 (s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 0.63$ (CH_3), 0.90 (CH_3, 2C), 29.93 (CH), 30.03 (CH), 30.36 (CH), 119.68 (d, $^{1}J_{PC} = 4$ Hz), 121.58 (CH), 126.37 (CH), 142.62, 148.67 (d, $^{2}J_{PC} = 14$ Hz), 148.94 (d, $^{2}J_{PC} = 12$ Hz); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C): $\delta = -145.2$; HRMS (FAB): m/z: calcd for $C_{27}H_{61}PSi_6$: 584.3127; found: 584.3106 $[M]^+$; elemental analysis calcd (%) for $C_{27}H_{61}PSi_6$: C 55.41, H 10.51; found: C 55.63, H 10.34.

Diphosphene 1: *n*-Butyllithium in *n*-hexane (1.50 M, 235 mL, 0.352 mmol) was added at −78 °C to a solution of Tbt-PH_2 (**5**) (206.0 mg, 0.352 mmol) in Et_2O (5 mL). The solution of lithium phosphide **6** obtained was warmed to room temperature for 0.5 h, and then cooled to −78 °C. The reaction mixture was added to a solution of dichloroferrocenylphosphine (**7**, 121.2 mg, 0.422 mmol) in Et_2O (5 mL) at −78 °C. After stirring at the same temperature for 1 h, the solution was allowed to be warmed to room temperature for 1 h. DBU (63.0 µL, 0.422 mmol) was added to the solution at room temperature, and the solution was stirred for 0.5 h. After removal of the solvent, *n*-hexane was added to the residue and the mixture was filtered through Celite. Evaporation of the filtrate under reduced pressure afforded diphosphene **1** (259.8 mg, 0.325 mmol, 92 %) as purple crystals. M.p. 182–184 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta =$ 0.22 (s, 18 H), 0.26 (s, 36 H), 1.54 (s, 1 H), 2.63 (s, 1 H), 2.71 (s, 1 H), 4.10 (s, 5 H), 4.28 (m, 2 H), 4.86 (m, 2 H), 6.70 (s, 1 H), 6.81 (s, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): $\delta = 0.94$ (CH_3), 1.21 (CH_3), 1.37 (CH_3), 30.61 (CH), 31.15 (CH), 31.46 (CH), 70.01 (C_5H_5), 72.21 (br d, α-C_5H_4), 73.30 (β-C_5H_4), 85.11 (dd, $^1J_{PC} = 55$, $^2J_{PC} = 17$ Hz, *ipso*-C_5H_4), 122.60 (*o*-C_6H_2), 127.14 (*o*-C_6H_2), 133.44 (d, $^3J_{PC} = 34$ Hz, *m*-C_6H_2), 143.14 (d, $^3J_{PC} =$ 30 Hz, *m*-C_6H_2), 144.91 (br d, $^1J_{PC} = 72$ Hz, *ipso*-C_6H_2), 146.63 (*p*-C_6H_2); ^{31}P NMR (120 MHz, C_6D_6, 25 °C): $\delta = 479.5$, 501.7 (ABq, $^1J_{PP} = 546$ Hz); UV/Vis (*n*-hexane): $\lambda_{max}(\varepsilon) = 542$ (900), 371 nm (2500); HRMS (EI): m/z: calcd for $C_{37}H_{68}FeP_2Si_6$: 798.2763; found: 798.2750 $[M]^+$; elemental analysis calcd (%) for $C_{37}H_{68}FeP_2Si_6$: C 55.60, H 8.58; found: C 55.51, H 8.84.

Reaction of diphosphene 1 with water: Degassed water (70 µL, 3.9 mmol) was added in an NMR tube under an argon atmosphere to a [D$_6$]benzene solution (0.7 mL) of **1** (28.4 mg, 35.6 µmol). When the suspension had allowed to stand for 24 h at room temperature, the ^{31}P NMR signals for **1** completely disappeared. The suspension was dried over sodium sulfate, filtrated, and concentrated in vacuo. Separation of the mixture by PTLC (eluting with *n*-hexane) afforded Tbt-PH_2 (**5**) (20.2 mg, 34.5 µmol, 97 %) and Fc-PH(O)OH (**9**) (8.0 mg, 32 µmol, 90 %).

Reaction of diphosphene 1 with methanol: Reaction of **1** (35.2 mg, 44.0 µmol) in benzene (5 mL) with methanol immediately proceeded at ambient temperature, separation of the reaction mixture by PTLC (eluting with *n*-hexane) afforded Tbt-PH_2 (**5**) (23.4 mg, 40.0 µmol, 92 %) and Fc-PH(O)OMe (**10**) (10.3 mg, 39.0 µmol, 89 %).

X-Ray crystallographic analysis of diphosphene 1: Single crystals of **1** were obtained by slow crystallization from hexane solution at room temperature in a glovebox filled with argon. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). The structure was solved by direct method (SHELXS-97)[17] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[18] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. Crystallographic data for **1**; $C_{37}H_{68}FeP_2Si_6$, $M =$ 799.24, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.855(6)$, $b =$ 10.966(3), $c = 25.472(8)$ Å, $\beta = 99.955(5)°$, $V = 4637(3)$ Å^3, $Z = 4$, $\rho_{calcd} =$ 1.145 g cm^{-3}, $\mu = 0.573$ mm^{-1}, $2\theta_{max} = 50.0°$, 29264 measured reflections, 8126 independent reflections, 433 refined parameters, R_1 (wR_2) = 0.063 (0.148) [$I > 2\sigma(I)$], R_1 (wR_2) = 0.078 (0.157) (for all data), $T = 103(2)$ K, GOF = 1.135, largest difference peak and hole 0.384 and −0.521 e Å^{-3}.

CCDC-236751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033; or email: deposit@ccdc.cam.ac.uk.

Theoretical calculations: All theoretical calculations were carried out using the Gaussian98[19] package program with density function theory at the B3LYP level. In calculations for diphosphene **11**, the TZV (for Fe), 6-311+G(2d) (for P), and 6-31G(d) (for C and H) were used as basis sets. TZV basis sets for Fe were obtained from the Extensible Computational Chemistry Environment Basis Set Database (http://www.emsl.pnl.gov/forms/basisform.html), as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, PO Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

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