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Synthesis of a Stable 1,2-Bis(ferrocenyl)diphosphene

Takahiro Sasamori,*^a Michiyasu Sakagami,^a Masatoshi Niwa,^a Heisuke Sakai,^b Yukio Furukawa,^b and Norihiro Tokitoh*^a

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The synthesis and characterization of a stable 1,2bis(ferrocenyl)diphosphene, wherein a P=P π -bond connects two ferrocenyl units will be reported. This represents an unprecedented example for a d- π electron system containing 10 a heavier pnictogen π -spacer group. Stabilization of the highly reactive P=P π -bond was achieved by steric protection using two bulky ferrocenyl moieties.

The sustained interest in d- π electron systems of bimetallic complexes with π -bond spacers, *i.e.*, M–(π -conjugated ¹⁵ spacer)–M (M = transition metal), is due to their unusual electronic, optical, and magnetic properties.¹ Moreover, they can serve as models for compounds with mixed-valence states and for molecular wires, since the high energy level of the occupied orbitals and the small HOMO-LUMO gap facilitates ²⁰ electron delocalization over the d and π orbitals. In such d- π electron moiety because (i) ferrocene exhibits a stable redox behavior, (ii) the Cp ligands of ferrocene effectively correlate the d-orbitals (Fe) with the external π -electron system and (iii)

- ²⁵ organic π -electron systems can be easily attached onto the Cp rings by a variety of established synthetic tools such as metallations or cross-coupling reactions.² Some d- π electron systems with two ferrocenyl groups bridged by a π -bond moiety, e.g., Ph(Fc)C=C(Fc)Ph³ or Fc-N=N-Fc⁴ (Fc = ³⁰ ferrocenyl) have been reported and they show the unique properties of multi-step redox systems. A still prevailing
- limitation for the π -electron systems in these compounds is the restriction to the 2nd row of the p-block elements, even though the chemistry of π -electron systems containing heavier ³⁵ main group elements such as disilenes (R₂Si=SiR₂) and
- diphosphenes (RP=PR) has recently been the subject of substantial progress. Although they are known to be highly reactive, the isolation of compounds containing π -bonds of heavier main group elements is possible at ambient 40 temperature, when the π -bond is sufficiently stabilized by
- sterically demanding substituents.⁵ Still, systematic investigations into the synthesis and properties of $d-\pi$ electron systems containing heavier main group element π -spacers remain scarce to date. Recent reports on phosphorus-based π -
- ⁴⁵ electron systems proposed an immense potential for these compounds, not only with respect to applications in functional materials but also from a fundamental perspective.⁶ Combined with the recent developments in the field of extended π -

electron systems containing phosphorus, this prompted us to ⁵⁰ investigate the chemistry of the corresponding phosphoruscontaining d- π electron systems.⁷ The simplest conceivable model compound for 1,2-bis(ferrocenyl)diphosphenes is Fc-P=P-Fc, the phosphorus analogue of Fc-N=N-Fc,^{1b,4} The limited steric demand of the ferrocenyl groups should ⁵⁵ however offer only insufficient protection for the reactive P=P bond.⁸ As a solution of this synthetic challenge,⁹ we would like to report the synthesis of a custom-tailored ferrocenyl unit with an increased ability for steric protection, and its subsequent implementation in the synthesis of 1,2-⁶⁰ bis(ferrocenyl)diphosphene **1** as a stable crystalline compound.



Scheme 1 Synthesis of bulky ferrocenylphosphines 7 and 8.

As a suitable ferrocenyl precursor, we identified 2,5-Dmp₂-1-iodoferrocene (**6**, Fc*I, Dmp = 3,5-dimethylphenyl) bearing ⁶⁵ two Dmp groups in 2 and 5-positions of iodoferrocene (Scheme 1).¹⁰ Sulfoxide **2** was obtained from a Negishi-crosscoupling reaction of ferrocenylphenylsulfoxide¹¹ with DmpI.¹² Reduction of **2** with NaI and (CF₃CO)₂O afforded sulfide **3**,¹³ which was oxidized with *m*CPBA to give sulfoxide **4**, a ⁷⁰ structural isomer of **2**. The inversion of the sulfoxide at this point is the key step for the introduction of another Dmp group to give sulfoxide **5**, which was achived by a second Negishi-cross-coupling reaction between **4** and DmpI.

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Treatment of sulfoxide **5** with *n*-BuLi and I₂ resulted in the formation of **6**, ^{12b} which was subjected to sequential treatment with *n*-BuLi and PCl₃ to form Fc*PCl₂ (7), which in turn was reduced with LiAlH₄ to give primary phosphine Fc*PH₂ (**8**).¹⁴ The targeted 1,2-bis(ferrocenyl)diphosphene **1** was obtained as a stable number of a stable number of the stable primary for the stable primary

as a stable, purple, crystalline solid in 40% yield from the reaction of 7 with Fc*PHLi (9), prepared from the deprotonation of 8 with n-BuLi, followed by dehydrochlorination using DBU (Scheme 2).



Scheme 2 Synthesis of 1,2-bis(ferrocenyl)diphosphene 1.



Fig. 1 Molecular structure of diphosphene 1 with thermal displacement ellipsoids at 50% probability. Two crystallographically independent
¹⁵ molecules (A and B) are contained per unit cell. All hydrogen atoms as well as one molecule of hexane have been omitted for clarity.

The X-ray diffraction (XRD) analysis of single crystals of **1** revealed two crystallographically independent molecules with similar structural parameters per unit cell (Fig. 1).^{10,15} Both ²⁰ P=P moieties exhibit *E*-configuration with C–P=P–C angles of *ca.* 180°. The P=P bond lengths of 2.0312(8) and 2.0379(8) Å are shorter than typical P–P single bonds (*ca.* 2.2 Å)¹⁶ and similar to those of previously reported diphosphenes.^{5,17} The dihedral angles between the P–P–C(Cp) and the Cp planes are ²⁵ *ca.* 42-45°. Stable metallocenyldiphosphenes such as

- TbtP=PMc (Mc = ferrocenyl or ruthenocenyl, Tbt = 2,4,6-[CH(SiMe_3)_2]_3-C_6H_2) show in contrast to that an almost coplanar alignment of the Cp–P=P moieties.^{7b,9f,9g} The relatively moderate dihedral angles of *ca*. 45° (*i.e.* not ³⁰ perpendicular) in **1** do not impose significant restrictions on
- the π -conjugative interaction. The solid state Raman spectrum of **1** shows one strong Raman shift at 621 cm⁻¹ for the v_{PP} vibration. This vibrational frequency is consistent with those for previously reported diphosphenes (*ca.* 610-650 cm⁻¹)¹⁷ and
- ³⁵ supported by theoretical calculations (647 cm⁻¹).¹⁸ Combined XRD analysis and Raman spectroscopy therefore suggests a degree of P=P double bond character for **1** in the solid state that is comparable to that in previously reported diphosphenes. The ¹H and ³¹P NMR spectra suggested a C_{2h} symmetric
- ⁴⁰ structure of **1** in C_6D_6 solution at room temperature.¹⁰ One singlet signal was observed for the methyl protons of the Dmp groups, indicative of facile rotation around the C(Cp)– C(Dmp) bonds. The ³¹P NMR spectra of **1** (C_6D_6) showed one resonance for the P nuclei at 482 ppm. This is consistent with

- 45 chemical shifts previously reported for stable diaryl- and ferrocenyl-diphosphenes,^{7,9,17} corroborating the preservation of the P=P double bond in 1 in solution. The UV/vis spectra of 1 in THF or hexane showed three characteristic absorption nline bands at $\lambda_{max} = 351$ (ϵ 9,000), 448 (1,400), 556 (3,000) nm ₅₀ (THF) or $\lambda_{max} = 349$ (6,100), 446 (990), 546 (2,000) nm (hexane). Previous reports on stable diaryldiphosphenes, e.g., $Mes*P=PMes* (Mes* = 2,4,6-tri-t-butylphenyl)^{20}$ assigned the two absorptions at shorter wavelengths with $\lambda_{max} = ca.350$ and ca. 450 nm to symmetry-allowed π - π * and symmetry-55 forbidden n- π^* transitions of the P=P chromophore. The absorption of 1 at longer wavelengths (ca. 550 nm) should accordingly be attributed to $d-\pi^*$ electron transitions from filled d-orbitals at the Fe center to the π^* orbital of the P=P π spacer. This is supported by the solvochromacy of this 60 electron transition ($\Delta \lambda_{max} = 10 \text{ nm}$) as well as by the accurate reproducibility of the λ_{max} values from theoretical calculations, which suggest HOMO(Fe,d)-LUMO(P=P, π^*) and HOMO-3(Fe,d)-LUMO(P=P, π^*) electron transitions at 553 and 542
- nm, respectively.²¹ The cyclic voltammograms of 1 (Fig.2) showed one reversible redox couple in the reduction region at $E_{1/2} = -2.03$ V (all potentials referenced vs. FcH/FcH⁺), which is significantly lower than that of FcN=NFc (-2.32 V).^{1b} The lower reduction potential should be a direct consequence of ⁷⁰ the lower LUMO level of the P=P π -bond relative to that of the corresponding N=N π -bond.²² The reduction potential of **1** is also considerably lower than that of the previously reported diaryldiphosphenes, e.g., Mes*P=PMes* (ca. -2.4 V),²³⁻²⁵ which can probably be attributed to the effective π -75 conjugation in 1. The oxidation region showed three oxidation waves at $E_{pa} = +0.69$, +1.03, and +1.75 V. Upon reversing the sweep at E<1 V, the first wave was found to be reversibe (E_{pc} = +0.41 V), showing a first oxidation potential at $E_{1/2}$ = +0.55 V. The two subsequent oxidation steps at $E_{pa} = +1.03$ and ₈₀ +1.75 V were found to be irreversible, suggesting facile decomposition of the transient dicationic and/or tricationic species. By comparison with previously reported ferrocenyldiphosphenes such as Tbt-P=P-Fc,7b the first two oxidation potentials of 1 ($E_{pa} = +0.69, +1.03$ V) should be 85 assigned to the oxidation processes of the ferrocenyl moieties, whereas the third ($E_{pa} = +1.75$ V) should be assigned to that of the P=P moiety. We would like to point out that the oxidation processes of both ferrocenyl moieties were observed in two separate steps with $\Delta E = 0.34$ V, which is considerably larger ₉₀ than the separation in Ph(Fc)C=C(Fc)Ph^{3c} ($\Delta E = 0.18$ V) or Tip(Fc)Si=Si(Fc)Tip^{9a} ($\Delta E = 0.19$ V). The increased separation suggests an increase in electronic communication through the P=P π -electron moiety and thus leads to the conclusion that the P=P double bond is highly effective π -95 electron spacer for bimetallic $d-\pi$ electron systems.

In summary, we have shown here the synthesis of the first stable 1,2-bis(ferrocenyl)diphosphene by taking advantage of a bulky ferrocenyl group. The assessment of its structural parameters and physical properties allowed the conclusion ¹⁰⁰ that the P=P π -bond is stable both in the solid state and solution and can act as an efficient π -electron spacer to couple the d-electrons of two ferrocenyl groups.

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Fig. 2 Cyclic voltammograms of 1 (2.0 mM, 0.1 M n-Bu₄NBF₄): (a) Oxidation region, -78 °C, in CH₂Cl₂ (b) Reduction region, r. t., in THF.

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^a Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan. Fax: +81-774-38-3200; Tel: +81-774-38-3209; E-

- ¹⁵ mail: sasamori@boc.kuicr.kyoto-u.ac.jp, tokitoh@boc.kuicr.kyoto-u.ac.jp ^b Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.
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