Syntheses, Structures, and Properties of the First Stable 1,1′-Bis(diphosphenyl)ferrocenes

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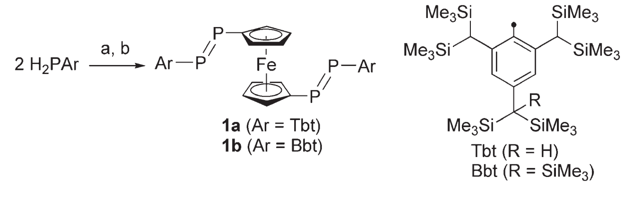
Kinetically stabilized 1,1′-bis(diphosphenyl)ferrocenes have been synthesized by taking advantage of extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl (Bbt) groups, and fully characterized by the spectroscopic and X-ray crystallographic analyses. The electrochemical behavior showed well-defined two reversible one-electron reduction couples.

Remarkable progress has been made in the chemistry of double-bond compounds containing heavier group 15 elements, especially in the field of diphosphenes[1] and their heavier congeners.[2] It is well-known that diphosphenes, which have relatively low lying π^* orbitals, undergo one-electron reduction to give their anion-radical species.[3] We have also reported the synthesis of novel doubly bonded systems between heavier group 15 elements by taking advantage of efficient steric protection groups, Tbt and Bbt.[4] Furthermore, the redox properties of BbtE=EBbt (E = P, Sb, and Bi) have been systematically elucidated based on the measurement of cyclic voltammetry and DFT calculations.[4i] Yoshifuji et al. synthesized the first bis(diphosphene) derivative, the voltammogram of which exhibited one reduction wave and indicating no electronic interaction between the intramolecular diphosphene units.[5] Recently, 1,4-bis(diphosphenyl)-benzene derivatives, in which the P=P π electron systems are extended to those of the conjugated aromatic rings, have been synthesized by Protasiewicz and co-workers, and they have disclosed the unique electrochemical behavior of the newly obtained π-conjugated diphosphenes.[6]

On the other hand, organometallic architectures incorporating metal atoms in organic π-frameworks have given rise to a great deal of interest from the viewpoint of the elaboration of molecular materials.[7] In 1996, Niecke et al. have reported the first synthesis of the ferrocenyldiphosphene consisted of two redox active sites.[8] Recently, we have also reported the structural characterization of a new ferrocenyldiphosphene bearing a Tbt group and revealed its unique electrochemical behavior.[4h] As an extension of the studies on novel d–π systems containing heavier group 15 elements, we report here the syntheses, structural characterization, and properties of the first 1,1′-bis(diphosphenyl)ferrocenes, **1a** and **1b**, kinetically stabilized by the Tbt and Bbt groups.



Scheme 1. (a) n-BuLi, Et$_2$O, −40 °C; (b) 1,1′-bis(dichlorophosphino)ferrocene, C$_6$H$_6$, rt; (c) DBU, rt.

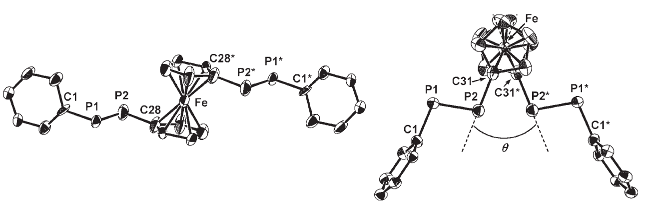


Figure 1. ORTEP drawings of **1a** (left) and **1b** (right) with thermal ellipsoid plots (50% probability). The CH(SiMe$_3$)$_2$ and C(SiMe$_3$)$_3$ groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **1a**/**1b**: P(1)–P(2) 2.015(3)/2.0398(18), P(1)–C(1) 1.860(4)/1.854(4), P(2)–C(28/31) 1.797(9)/1.807(6), C(1)–P(1)–P(2) 98.5(2)/103.25(15), C(28/31)–P(2)–P(1) 102.1(5)/101.9(3).

Treatment of 1,1′-bis(dichlorophosphino)ferrocene[9] with two molar amounts of LiP(H)Ar (Ar = Tbt or Bbt) followed by the double-dehydrochlorination reaction using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded 1,1′-bis(diphosphenyl)-ferrocenes **1a** and **1b** in 68 and 62% isolated yields, respectively (Scheme 1).[10]

The ^{31}P NMR spectra of **1a** and **1b** in C$_6$D$_6$ showed a diagnostic pair of doublets at 497.3 and 488.9 ppm (**1a**) and 496.9 and 491.1 ppm (**1b**), respectively, with $^1J_{\mathrm{PP}} = 550$ Hz (both **1a** and **1b**), which are characteristic of unsymmetric E-diphosphenes. The observed coupling constants of **1a** and **1b** were somewhat smaller than those of the reported diphosphenes having two different bulky aryl groups,[1a] indicating their characteristic polarized resonance structures similar to the case of the reported ferrocenyldiphosphenes.[4h,8]

The molecular structures of **1a** and **1b** were determined by the X-ray crystallographic analyses (Figure 1).[11] The conformations of **1a** and **1b** in the solid states are curiously different to each other in spite of the similarity between Tbt and Bbt groups. That is, **1a** (triclinic, $P\bar{1}$) has a crystallographic centrosymmetry on the Fe atom, though **1b** (monoclinic, $C2/c$) shows a two-fold rotation axis through the Fe atom. The torsion angle between the centoroid(Cp)–P(2) moieties of **1b** (θ in the Figure 1) exhibits 48.0°, while that of **1a** is inherently 180°. Both **1a** and **1b** show the E-conformations with the C–P–P–C torsion angles of 179.3(4) and 176.0(2)°, respectively, and their C–P–P–C planes are almost coplanar with the adjacent Cp ring, suggesting a conjugative interaction between the π-electrons of the diphosphene units with those of the Cp rings of **1a** and **1b**. Their P=P bond lengths [2.015(3) Å for **1a** and 2.0398(18) Å for **1b**] are considerably shorter than the typical P–P single-bond lengths[12] and are within the range of those for the previously reported diaryldiphosphenes (1.985–2.049 Å),[1a,4f] revealing the concrete P=P double-bond character of **1a** and **1b** in the solid state. Interestingly, the characteristic P=P vibrational frequencies of **1a**/**1b** were found to be active for both Raman ($\nu = 612/611$ cm^{-1}) and IR ($\nu = 614/615$ cm^{-1}) spectra in the solid state due to the symmetric and asymmetric stretching modes, the assignment of which was supported by the theoretical calculations for the model compound, (DmpP=PC_5H_4)$_2$Fe (Dmp = 2,6-dimethylphenyl).[13]

The UV–vis spectra of **1a**/**1b** in C_6H_6 showed three absorption maxima at 384/389 (ε 7300/7400), 480/485 (sh, ε 1800/1300), and 539/553 nm (ε 2200/2200).[10] The first one ($\lambda_{\mathrm{max}} = 384/389$ nm), which should be assigned to the π–π^* electron transitions due to the large ε, was within the range of those for the reported diaryldiphosphenes (277–418 nm),[1a,4f] while it was found to show a hypsochromic shift as compared with those for the 1,4-bis(diphosphenyl)benzenes (398 and 422 nm).[6] The second one ($\lambda_{\mathrm{max}} = 480/485$ nm) was assignable to the n–π^* electron transitions for the diphosphene units in consideration of the λ_{max} values of those for the diaryldiphosphenes (437–532 nm)[1a,4f] and 1,4-bis(diphosphenyl)benzenes (476 and 481 nm).[6] The third one ($\lambda_{\mathrm{max}} = 539/553$ nm) should be attributed to the MLCT band due to the electron transitions from *d* orbitals of the iron atom to the π^* orbital of the P=P moiety, indicating a subtle bathochromic shift as compared with those for the ferrocenyldiphosphenes ArP=$PC_5H_4FeC_5H_5$ (Ar = Mes*; 515 nm,[8] Ar = Tbt; 542 nm[4h]). In addition, assignment of the observed absorption maxima for **1a**/**1b** are reasonably supported by theoretical calculations for the excited states of the model molecule.[13]

The redox behavior of **1a** and **1b** has been furnished by cyclic voltammetry.[10] In the THF solution, two reversible one-electron redox waves due to the intramolecular two redox centers was observed at −1.84 and −2.19 V (**1a**) and −1.78 and −2.13 V (**1b**) vs Ag/Ag$^+$, respectively. In both cases of **1a** and **1b**, 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 $K_c = 5.6 \times 10^5$ in THF–(n-Bu)$_4$NBF$_4$].[6]

In summary, we have succeeded in the syntheses of the first stable 1,1′-bis(diphosphenyl)ferrocenes **1a** and **1b** by taking advantage of the effective steric protection groups, Tbt and Bbt. The solid-state structures and the unique properties of **1a** and **1b** indicate that these novel d–π systems containing P=P units may be good candidates for molecular electronics and give helpful information to understand the electronic communications between diphosphene units. Further investigation on the properties and the reactivity of **1a** and **1b** are currently in progress.

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10 Experimental procedures, the analytical, spectral, and voltammetric data for **1a** and **1b** are in the Supporting Information.

11 Crystallographic data for **1a**; $C_{64}H_{126}FeP_4Si_{12}$, MW = 1412.46, triclinic, $P\bar{1}$ (# 2), $a = 10.834(3)$ Å, $b = 10.640(3)$ Å, $c = 19.972(6)$ Å, $\alpha = 75.001(10)°$, $\beta = 87.417(12)°$, $\gamma = 71.851(9)°$, $V = 2111.7(11)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.111$ g cm^{-3}, $2\theta_{\mathrm{max}} = 50.0°$, 13923/7272 measured/independent reflections, 668 refined parameters, R_1 ($_{\mathrm{w}}R_2$) = 0.079 (0.163) [$I > 2\sigma(I)$], R_1 ($_{\mathrm{w}}R_2$) = 0.131 (0.197) (for all data), $T = 103(2)$ K, GOF = 1.096. Crystallographic data for **1b**; $C_{70}H_{142}FeP_4Si_{14}$, MW = 1556.83, monoclinic, $C2/c$ (# 15), $a = 22.9804(5)$ Å, $b = 11.6477(3)$ Å, $c = 34.7151(8)$ Å, $\beta = 96.8190(9)°$, $V = 9226.4(4)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.121$ g cm^{-3}, $2\theta_{\mathrm{max}} = 50.0°$, 36323/8118 measured/independent reflections, 510 refined parameters, R_1 ($_{\mathrm{w}}R_2$) = 0.077 (0.210) [$I > 2\sigma(I)$], R_1 ($_{\mathrm{w}}R_2$) = 0.100 (0.228) (for all data), $T = 103(2)$ K, GOF = 1.049. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-287252 (**1a**) and -287251 (**1b**). Copies of the 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 deposit@ccdc.cam.ac.uk).

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13 Details of the theoretical calculations of the model molecule, (DmpP=PC_5H_4)$_2$Fe, are shown in the Supporting Information.

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