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

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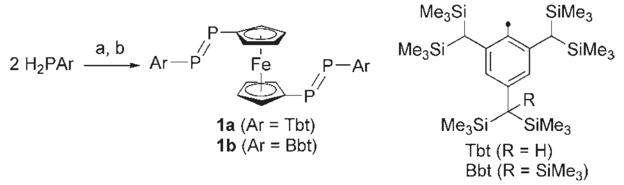
Kinetically stabilized 1,1′-bis(diphosphenyl)ferrocenes have been synthesized by taking advantage of extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl (Bbt) groups, and fully characterized by the 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_2O, $-40\,^\circ C$; (b) 1,1′-bis(dichlorophosphino)ferrocene, C_6H_6, rt; (c) DBU, rt.

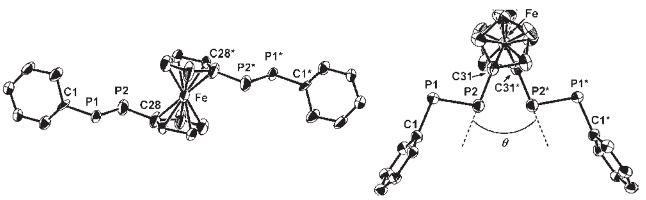


Figure 1. ORTEP drawings of **1a** (left) and **1b** (right) with thermal ellipsoid plots (50% probability). The $CH(SiMe_3)_2$ and $C(SiMe_3)_3$ groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **1a**/**1b**: P(1)–P(2) 2.015(3)/2.0398(18), P(1)–C(1) 1.860(4)/1.854(4), 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_6D_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 $^1J_{PP} = 550$ 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, $(DmpP{=}PC_5H_4)_2Fe$ (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 ($\lambda_{max} = 384/389$ 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 ($\lambda_{max} = 480/485$ 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 ($\lambda_{max} = 539/553$ 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–$(n\text{-}Bu)_4NBF_4$].[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.

This work was partially supported by Grant-in-Aid for Scientific Research (Nos. 12CE2005, 14078213, 15655011, 16750033, and 17GS0207) and the 21st Century COE on Kyoto University Alliance for Chemistry from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We are grateful to Prof. Yukio Furukawa, Waseda University, for the measurement of FT-Raman spectra.

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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, $\alpha = 75.001(10)^\circ$, $\beta = 87.417(12)^\circ$, $\gamma = 71.851(9)^\circ$, $V = 2111.7(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.111$ g cm^{-3}, $2\theta_{max} = 50.0^\circ$, 13923/7272 measured/independent reflections, 668 refined parameters, R_1 ($_wR_2$) = 0.079 (0.163) [$I > 2\sigma(I)$], R_1 ($_wR_2$) = 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, $\beta = 96.8190(9)^\circ$, $V = 9226.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.121$ g cm^{-3}, $2\theta_{max} = 50.0^\circ$, 36323/8118 measured/independent reflections, 510 refined parameters, R_1 ($_wR_2$) = 0.077 (0.210) [$I > 2\sigma(I)$], R_1 ($_wR_2$) = 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, $(DmpP{=}PC_5H_4)_2Fe$, are shown in the Supporting Information.

Published on the web (Advance View) January 21, 2006; DOI 10.1246/cl.2006.220