

Synthesis, structures and properties of biferrocenyl- and ruthenocenyl-substituted diphosphenes†‡

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Biferrocenyl and ruthenocenyl diphosphenes were synthesized in a stable crystalline form as new members of a family of d- π systems containing heavier main group elements. Their structures and redox behavior were revealed using X-ray crystallographic analysis and cyclic voltammetry.

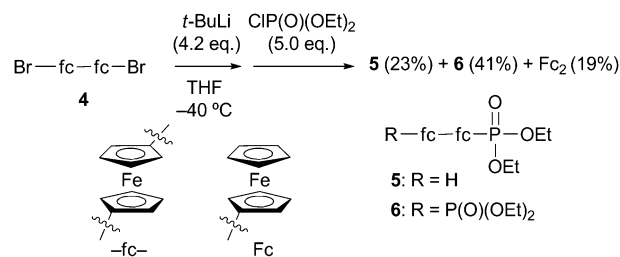
Multiply-bonded systems between heavier group 15 elements, such as diphosphenes (RP=PR), are interesting species as unique and novel π electron systems.¹ Although such multiple bond compounds between heavier main group elements are generally highly reactive and very difficult to isolate under ambient conditions, it has been demonstrated that such reactive π bond systems can be isolable when they are kinetically stabilized by taking advantage of bulky substituents. For example, a series of heavier congeners of azo compounds (RE=ER, E=P, As, Sb, Bi) bearing bulky substituents have been synthesized and isolated as stable compounds,² since the first isolation of a stable diphosphene, Mes*P=P Mes* (Mes* = 2,4,6-tri-*t*-butylphenyl).³ Recently, there has been much interest in the creation of functionalized π electron-conjugated systems containing such unique π electron systems of heavier main group elements.^{4–6} From this viewpoint, much attention has been focused on the synthesis of novel d- π electron systems containing heavier main group elements and transition metals,^{6,7} since initiative works with Mes*P=P Fc (Fc = ferrocenyl).^{6f} We have already reported the synthesis of stable ferrocenyl-substituted diphosphenes TbtP=P Fc⁸ (**3**) and (ArP=P)₂fc (Ar = Tbt or Bbt, Tbt = 2,4,6-[CH(SiMe₃)₂]₃-C₆H₂, Bbt = 2,6-[CH(SiMe₃)₂]₂-4-[C(SiMe₃)₃]-C₆H₂, fc = 1,1'-ferrocenyldiene),^{9,10} and stable metallocenyl-substituted disilenes (*E*)-Tip(Fc)Si=Si(Fc)Tip and (*E*)-Tip(Rc)Si=Si(Rc)Tip (Tip = 2,4,6-triisopropylphenyl, Rc = ruthenocenyl),¹¹ and revealed their unique electrochemical properties. These were isolated as stable crystalline compounds due to the steric protection afforded by the Tbt and Tip groups. In this Letter, we present the synthesis of biferrocenyldiphosphene **1** as a more extended d- π electron system than ferrocenyldiphosphene **3** and ruthenocenyldiphosphene **2** as a heavier analogue of **3**,

reflecting the difference in electronic properties between Fe and Ru in these unique d- π electron systems.

Dilithiation of dibromobiferrocene **4**¹² with *t*-BuLi followed by the addition of an excess amount of ClP(O)(OEt)₂ afforded a mixture of phosphinobiferrocenes **5** and **6**, which were separated using GPLC (CHCl₃) (Scheme 1). The treatment of **5** with Me₃SiCl/LiAlH₄, giving the corresponding primary phosphine **8**, followed by chlorination with PCl₅, afforded biferrocenyldichlorophosphine **10**. Ruthenocenyldichlorophosphine **11** was prepared in a similar way to **10**.¹³

The treatment of a benzene solution of biferrocenyldichlorophosphine **10** with an ether solution of TbtPHLi^{8a,9} at r.t. afforded an orange suspension, which may contain the possible intermediates of a diastereomer mixture of Fc-fc-P(Cl)-P(H)-Tbt (**12**) [as judged by the two sets of AX signals in the ³¹P NMR spectrum: δ = 109, -56.1 (*J* = 186 Hz) and δ = 93.2, -52.6 (*J* = 230 Hz)]. Biferrocenyldiphosphene **1** was obtained as a purple crystalline compound by the addition of DBU as a base to the reaction mixture (Scheme 2). Similarly, the reaction of ruthenocenyldichlorophosphine **11** with TbtPHLi, followed by a treatment with DBU, afforded ruthenocenyldiphosphene **2** as stable deep-red crystals. The intermediacy of the diastereomer mixture of chlorodiphosphanes, **13**, was confirmed by ³¹P NMR spectroscopy [as judged by the two sets of AX signals in the ³¹P NMR spectrum: δ = 98.0, -68.5 (*J* = 170 Hz) and δ = 87.8, -54.1 (*J* = 250 Hz)], as in the case of the synthesis of **1**.

The ³¹P NMR spectra of metallocenyldiphosphenes **1** and **2** in C₆D₆ showed AX signals at δ_P = 501.6, 477.1 (*J* = 552 Hz) for **1** and δ_P = 492.8, 473.5 (*J* = 553 Hz) for **2** in the low-field region characteristic of diphosphenes, respectively. The characteristic δ_P and ¹*J*_{PP} values of **1** and **2** were found to be similar to those of previously reported stable diaryldiphosphenes^{1a} (e.g., Mes*P=P Mes: δ_P = 540.4, 467.6, ¹*J*_{PP} = 573.7 Hz)¹⁴ and ferrocenyldiphosphenes (e.g. Mes*P=P Fc: δ_P = 471.2, 442.6, ¹*J*_{PP} = 532 Hz and TbtP=P Fc (**3**):^{8a} δ_P = 501.7, 479.5, ¹*J*_{PP} = 546 Hz), showing the P=P double bond character of **1**

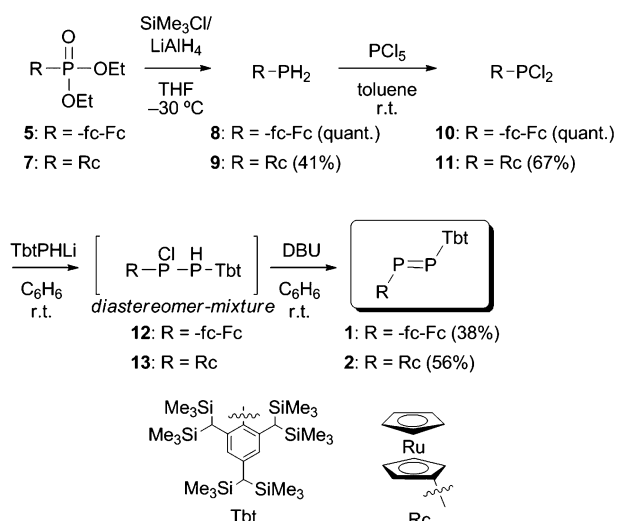


Scheme 1 The synthesis of phosphinated biferrocene.

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† Dedicated to the late Professor Pascal Le Floch. This article is part of a themed issue on Main Group chemistry.

‡ Electronic supplementary information (ESI) available: Synthetic procedures and spectral data of biferrocenyldichlorophosphine **10** and ruthenocenyldichlorophosphine **11**. CCDC reference numbers 762039 and 762040. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00062k



Scheme 2 The synthesis of biferrocenyldiphosphene **1** and ruthenocenyldiphosphene **2**.

and **2** in solution and the negligible electronic effect of the metallocenyl moieties towards the P=P moiety.

The molecular structures of **1** and **2** were revealed by X-ray crystallographic analysis (Fig. 1 and Table 1). Both diphosphenes **1** and **2** exhibit an *E*-configuration with C–P=P–C torsion angles of *ca.* 180°. It should be noted that the P–C(Cp) bond lengths of both **1** and **2** are slightly shorter than the P–C(Tbt) bond lengths, respectively, suggesting an effective interaction between the P=P and Cp units, as compared to those between the P=P and aryl (Tbt) moieties.¹⁶ The angle between the P=P–C(Cp) plane and the Cp ring of the metallocenyl moiety (defined as θ_1) in **1** is small (8.8°), indicating the conjugative interaction of the π electrons between the P=P and metallocenyl moieties.¹⁷ In addition, the angle between the two Cp rings of the two ferrocenyl units (defined as θ_2) of **1** is only 5.0°, showing the high coplanarity of the biferrocene units. On the other hand, θ_1 of ruthenocenyldiphosphene **2** is 22.3°, which is somewhat larger than those of **1** and ferrocenyldiphosphene **3** (5.7°).^{8a} The P=P bond lengths of **1** and **2** are 2.0384(9) (**1**) and 2.0361(8) (**2**) Å, which are slightly longer than those of TbtP=Pfc [2.021(2) Å]^{7a} and TbtP=Pfc–P=PTbt [2.015(3) Å],⁸ indicating a slightly more effective interaction between the π electrons of the P=P unit and the Cp ring of the biferrocenyl or ruthenocenyldiphosphenes in **1** and **2**.^{17,18}

Metallocenyldiphosphenes **1** and **2** are strongly colored purple and deep-red in solution, respectively, similar to the

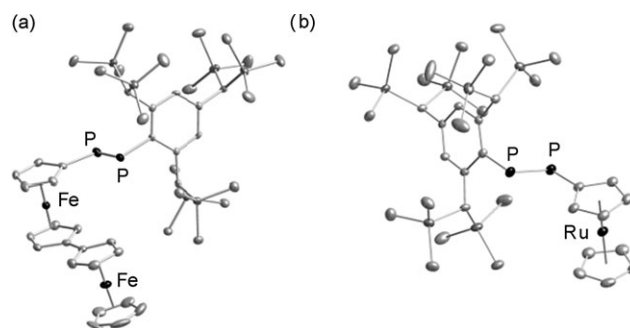


Fig. 1 The structures of (a) **1** and (b) **2**. Displacement ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity.

case of **3**. In the UV-vis spectra of **1** and **2** in hexane, characteristic absorptions were observed at $\lambda_{\text{max}}(\epsilon) = 375$ (9.4×10^4), 467 (2.1×10^3) and 557 (3.4×10^3) nm for **1**, and $\lambda_{\text{max}}(\epsilon) = 356$ (5.6×10^3), 420 (6.0×10^3) and 473 (2.9×10^3) nm for **2**. The absorption at the longest λ_{max} is assignable to the MLCT transitions, as in the case of Mes*P=Pfc [$\lambda_{\text{max}} = 515$ nm at -78°C]^{6f} and **3** [$\lambda_{\text{max}}(\epsilon) = 542$ nm (9.0×10^2)].^{8a,9b} Although the λ_{max} value of **1** is similar to that of **3**, the corresponding absorption coefficients (ϵ) for **1** are much larger than those for **3**, suggesting the effectively extended delocalization of π electrons. On the other hand, ruthenocenyldiphosphene **2**, colored deep-red, showed characteristic MLCT absorptions at shorter wavelengths than those of **1** and **3**. Although preliminary TDDFT calculations¹⁹ suggested that several types of MLCT transition would be included in the observed absorption, the assignment of the transitions is likely to be difficult due to the complication of electron transitions. Since ruthenocene is colorless, in contrast to ferrocene (colored orange), the difference in the electronic spectra between ruthenocenyldiphosphene **2** and ferrocenyldiphosphene **3** should reflect the electronic features of the metallocenes.

The redox behavior of **1** and **2** was observed by cyclic and differential pulse voltammetry (Table 2). In the oxidation region, **1** exhibited reversible redox couples at $E_{1/2} = -0.07$ V (vs. FcH/FcH⁺), suggesting that **1** would undergo ready oxidation compared to ferrocene and ferrocenyldiphosphene **3**^{7a} ($E_{1/2} = +0.08$ V (vs. FcH/FcH⁺), probably due to the much extended d- π conjugation in **1**⁺. On the other hand, **2** showed an irreversible oxidation wave at $E_{\text{pa}} = +0.65$ V (vs. FcH/FcH⁺), reflecting the electrochemical properties of ruthenocene, which has been reported to show an irreversible or quasi-reversible oxidation wave under various conditions.²⁰ Thus, the oxidative features of metallocenyldiphosphenes **1**

Table 1 Observed and calculated^a structural parameters of **1**, **2**, and **3**

	P=P/Å	P–C(Cp)/Å	P–C(Tbt)/Å	P–P–C(Cp) (°)	P–P–C(Tbt) (°)
1 _{obs}	2.0384(9)	1.801(2)	1.849(2)	102.55(9)	98.94(8)
1 _{calc} ^a	2.044	1.808	1.853	103.34	102.14
2 _{obs}	2.0361(8)	1.805(2)	1.843(2)	100.97(8)	99.55(7)
2 _{calc} ^a	2.045	1.809	1.852	102.29	102.29
3 _{obs}	2.0285(15)	1.805(4)	1.848(3)	101.64(16)	103.15(12)
3 _{calc} ^a	2.043	1.807	1.850	102.85	103.37

^a B3LYP/6-311+G(3d) for P; 6-31G(d) for Si, C, H; DZVP for Fe, Ru.¹⁵

Table 2 Redox potentials (V vs. FcH/FcH⁺) of **1**, **2** and **3**

	1 ^a		2 ^a	3	
	1st	2nd	1st	1st	2nd
Oxidation					
<i>E</i> _{pa}	+0.06	+0.68	+0.65	+0.17 ^b	+0.42 ^b
<i>E</i> _{pc}	−0.21	—	—	−0.11 ^b	—
<i>E</i> _{1/2}	−0.07	—	—	+0.08 ^b	—
Reduction					
<i>E</i> _{pc}	−2.35	—	−2.37	−2.29 ^a	—
<i>E</i> _{pa}	−2.09	—	−2.01	−2.13 ^a	—
<i>E</i> _{1/2}	−2.22	—	−2.19	−2.21 ^a	—

^a 0.1 M (*n*-Bu)₄NBF₄ in THF. ^b 0.1 M (*n*-Bu)₄NBF₄ in CH₂Cl₂.

and **2** seem to be affected by the electrochemical properties of the metallocene unit. In the reductive region, both **1** and **2** showed reversible redox couples at *E*_{1/2} = −2.22 (**1**) and −2.19 (**2**) (vs. FcH/FcH⁺), respectively, which are redox potentials similar to those of ferrocenyldiphosphene **3** (*E*_{1/2} = −2.21 V)^{7a} and TbtP=PTbt (*E*_{1/2} = −2.21 V),²¹ suggesting that the reduction potentials of **1** and **2** are strongly affected by the P=P double bond character. It can be concluded that the biferrocenyl- and ruthenocenyl-diphosphenes can work as multi-redox systems, while the metallocenyl moieties take part with difficulty in the conjugative interaction for anionic species of **1** and **2**.

In summary, biferrocenyldiphosphene **1** and ruthenocenyl-diphosphene **2** were synthesized and characterized as novel *d*- π electron systems containing a P=P bond. It was demonstrated that **1** exhibits a unique multi-step redox behavior, indicating a possible application of π electron systems between heavier main group elements toward electrochemical materials. Further investigations on the properties of metallocenyl-diphosphenes are currently in progress.

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Experimental

Synthesis of biferrocenyldiphosphene **1**

To a solution of biferrocenyldichlorophosphine (**10**; 190 mg, 0.40 mmol) in benzene (5 mL) was added an Et₂O solution of TbtPHLi, which was freshly prepared by the treatment of TbtPH₂ (187 mg, 0.32 mmol) with *n*-BuLi (1.5 M in hexane, 0.23 mL, 0.35 mmol) in Et₂O (18 mL) at −78 °C. The reaction mixture was stirred for 0.5 h to give an orange suspension. After removal of the solvent under reduced pressure, the resulting reaction mixture was dissolved in benzene and then filtered through Celite®. The solvent of the filtrate was removed under reduced pressure to afford a light-orange solid of a diastereomer mixture of chlorodiphosphane **12** (411 mg, 0.40 mmol, quant.). Chlorodiphosphane **12** (295 mg, 0.29 mmol) was dissolved in benzene (10 mL), and then DBU (69 mg,

0.45 mmol) was added to the solution. The reaction mixture immediately turned into a deep-purple suspension. After stirring for 5 min, the solvent of the reaction mixture was removed under reduced pressure. The reaction mixture was dissolved in *n*-hexane and then filtered through Celite®. The filtrate was concentrated and precipitated from *n*-hexane to give biferrocenyldiphosphene **1** (112 mg, 0.11 mmol, 38%) as purple crystals.

1. Purple crystals, m.p. 142 °C (decomp.). δ_{H} (300 MHz, C₆D₆, Me₄Si): 6.82 (br s, 1H), 6.71 (br s, 1H), 4.77 (pseudo-t, ³*J*_{HH} = 1.82 Hz, 2H), 4.35 (pseudo-t, ³*J*_{HH} = 1.82 Hz, 2H), 4.30 (pseudo-t, ³*J*_{HH} = 1.82 Hz, 2H), 4.27 (pseudo-t, ³*J*_{HH} = 1.82 Hz, 2H), 4.22 (pseudo-t, ³*J*_{HH} = 1.82 Hz, 2H), 4.04 (pseudo-t, ³*J*_{HH} = 1.82 Hz, 2H), 3.94 (s, 5H), 2.73 (br s, 1H), 2.66 (br s, 1H), 1.55 (s, 1H), 0.28 (s, 36H), 0.23 (s, 18H). δ_{C} {¹H} (75 MHz, C₆D₆, Me₄Si): 146.7 (C), 144.2 (C), 133.6 (C, d, ¹*J*_{PC} = 85 Hz), 128.5 (C), 127.3 (CH), 122.7 (CH), 86.6 (C), 85.3 (C, dd, ¹*J*_{PC} = 58 Hz, ²*J*_{PC} = 16 Hz), 82.8 (C), 75.6 (CH), 73.4 (CH), 70.1 (CH), 69.7 (CH), 68.5 (CH), 68.1 (CH), 66.8 (CH), 31.3 (CH), 30.7 (CH), 1.42 (CH₃), 1.00 (CH₃). δ_{P} (120 MHz, C₆D₆, H₃PO₄): 501.6, 477.1 (AX system, ¹*J*_{PP} = 552 Hz). HRMS (FAB) *m/z* calc. for C₄₇H₇₇Fe₂P₂Si₆ 983.2819, found 983.2798 ([M + H]⁺).

Synthesis of ruthenocenyl-diphosphene **2**

To a solution of ruthenocenyl-dichlorophosphine (**11**; 400 mg, 1.20 mmol) in benzene (120 mL) was added an Et₂O solution of TbtPHLi, which was prepared by the treatment of TbtPH₂ (700 mg, 1.20 mmol) with *n*-BuLi (1.5 M in hexane, 0.80 mL, 1.20 mmol) in Et₂O (15 mL) at −78 °C. The reaction mixture was stirred for 1 h to give a dark-orange suspension. After removal of the solvent under reduced pressure, the resulting reaction mixture was dissolved in benzene and then filtrated through Celite®. The solvent of the filtrate was removed under reduced pressure to afford a dark-orange solid of a diastereomer mixture of chlorodiphosphanes **13**. The obtained crude mixture, including **13**, was dissolved in benzene (40 mL), and then DBU (180 μ L, 1.20 mmol) was added to the solution. The reaction mixture immediately turned into a deep-red suspension. After stirring for 20 min, the solvent of the reaction mixture was removed under reduced pressure. The reaction mixture was dissolved in *n*-hexane and then filtered through Celite®. The filtrate was concentrated and precipitated from *n*-hexane to give ruthenocenyl-diphosphene **2** (500 mg, 0.57 mmol, 56%) as deep-red crystals.

2. Deep-red crystals, m.p. 99 °C (decomp.). δ_{H} (300 MHz, C₆D₆, Me₄Si): 6.78 (br s, 1H), 6.68 (br s, 1H), 5.23 (m, 2H), 4.62 (m, 2H), 4.52 (s, 5H), 2.63 (br s, 1H), 2.56 (br s, 1H), 1.52 (s, 1H), 0.24 (s, 36H), 0.21 (s, 18H). δ_{P} (120 MHz, C₆D₆, H₃PO₄): 492.8, 473.5 (AX system, ¹*J*_{PP} = 553 Hz). HRMS (APPI-TOF) *m/z* calc. for C₃₇H₆₉P₂RuSi₆ 845.2537, found 845.2574 ([M + H]⁺). Elemental analysis calc. for C₃₇H₆₈P₂RuSi₆: C 52.62, H 8.12; found C 52.64, H 8.38%.

X-Ray crystallographic data for **1** and **2**†

1 (C₄₇H₇₆Fe₂P₂Si₆): *M* = 983.26, *T* = 103(2) K, triclinic, *P*-1 (no. 2), *a* = 12.3334(3), *b* = 12.9518(4), *c* = 17.4667(5) Å, α = 107.7383(10), β = 97.2601(10), γ = 93.3283(16)°, *V* = 2622.37(13) Å³, *Z* = 2, *D*_c = 1.245 g cm⁻³, μ = 0.782 mm⁻¹, λ = 0.71069 Å, $2\theta_{\text{max}}$ = 51.0, 23 442 measured reflections, 9703 independent reflections (*R*_{int} = 0.0462), 532 refined parameters, GOF = 1.014, *R*₁ = 0.0365 and *wR*₂ = 0.0612 [*I* > 2σ(*I*)], *R*₁ = 0.0688 and *wR*₂ = 0.0669 [for all data], largest differential peak and hole 0.462 and -0.377 e Å⁻³.

2 (C₃₇H₆₈P₂RuSi₆): *M* = 844.46, *T* = 103(2) K, triclinic, *P*-1 (no. 2), *a* = 9.6151(1), *b* = 10.6365(2), *c* = 24.8520(4) Å, α = 97.9195(7), β = 96.8663(6), γ = 110.1667(8)°, *V* = 2324.61(6) Å³, *Z* = 2, *D*_c = 1.206 g cm⁻³, μ = 0.584 mm⁻¹, λ = 0.71069 Å, $2\theta_{\text{max}}$ = 51.0, 20 542 measured reflections, 8550 independent reflections (*R*_{int} = 0.0244), 433 refined parameters, GOF = 1.052, *R*₁ = 0.0297 and *wR*₂ = 0.0760 [*I* > 2σ(*I*)], *R*₁ = 0.0332 and *wR*₂ = 0.0784 [for all data], largest differential peak and hole 0.838 and -0.741 e Å⁻³.

The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on *F*² for all reflections (SHELXL-97).

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- In the case of metallocenyldiphosphenes, the MLCT observed through UV-vis spectra would be one piece of experimental evidence for the electronic correlation between the d electrons of the metal and the π electrons of the P=P moiety. Thus, d-π electron systems containing heavier main group elements mean compounds containing a π-bond between heavier main group elements connected with a transition metal moiety, such as a metallocene unit, through an organic π-conjugated system, where there is an electronic correlation between the d electrons and the π electrons, should conceivably exist.
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- Simple calculations for the model compound Me–P=P–Fc suggest that the rotational barrier around the P–Cp axis is less than 15 kcal mol⁻¹ (see the ESI†). Thus, the metallocenyl moiety would rapidly rotate along the P–Cp axis. The observed θ values would be affected by packing forces in the crystal, and it should be discussed only in the crystalline state.
- The θ_1 and θ_2 values of the optimized structure of **1** are 17.9 and 11.34°, respectively, which are slightly larger than those actually observed for **1**. Similarly, the θ_1 value of the optimized structure of **2** is 29.0°, which is also slightly larger than actually observed for **2**. Although the structural parameters calculated for **1** and **2** are to some extent in good agreement with those observed, packing forces in the crystalline

state would not be negligible in these cases. Further investigation to elucidate the reason for the slight difference between the observed and calculated structural parameters is in progress.

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