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Notes

A Ferrocenyldiphosphene−Platinum Complex: Structural Features and Theoretical Calculations

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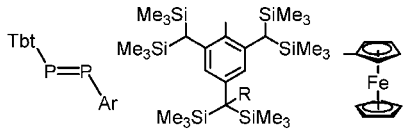
Summary: The ligand exchange reaction of (E)-TbtP=PFc (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Fc = ferrocenyl) and ethylenebis(triphenylphosphine)platinum(0) resulted in the formation of the corresponding η^2-diphosphene−platinum complex in 82% yield. The molecular structure of the platinum complex was confirmed by spectroscopic and X-ray crystallographic analyses.

Chart 1



1a (Ar = Tbt) Tbt (R = H) Fc
1b (Ar = Fc) Bbt (R = $SiMe_3$)

Since the first synthesis of a stable diphosphene (Mes*P=PMes*; Mes* = 2,4,6-tri-*tert*-butylphenyl) by taking advantage of kinetic stabilization,[1] an impressive advance has been made in the chemistry of double-bond compounds between heavier group 15 elements (dipnictenes).[2] We also succeeded in the synthesis of novel doubly bonded systems between heavier group 15 elements, diphosphene (RP=PR), distibene (RSb=SbR), dibismuthene (RBi=BiR), phosphabismuthene (RP=BiR), and stibabismuthene (RSb=BiR), by using the 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) (Chart 1).[3] Furthermore, we extended this chemistry to the construction of novel d−π systems containing a diphosphene unit and succeeded in the synthesis of the stable (*E*)-ferrocenyldiphosphene[3h] and 1,1′-bis[(*E*)-diphosphenyl]ferrocenes.[3k,n]

Whereas the isolable diphosphenes are prevented from dimerization by steric protection groups, these stabilized diphosphenes are known to show considerable reactivity:[2a,d] e.g., oxidation (diatomic oxygen), chalcogenation (elemental sulfur and selenium), halogenation (chlorine, bromine, and iodine), cycloaddition (dienes), and metalation (group 6, 8, 10, and 11 elements) reactions. It is particularly attractive for chemists to elucidate the properties of diphosphene−platinum complexes from the viewpoint of not only the reactivity of dipnictene species but also the development of promising candidates for new homogeneous catalysts. Although a few reports have been known so far for the formation of diphosphene−platinum complexes,[4−8] the detailed structural features and bonding properties of the diphosphene−platinum complexes, especially whether they exhibit three-membered-ring or π-complex character as shown in Figure 1, have not been revealed in the previous reports.

During the course of our research on the novel d−π electron systems ferrocenyldiphosphenes, the platinum complex of Tbt-substituted ferrocenyldiphosphene was obtained and structurally characterized. In this note, we report the reaction of ferrocenyldiphosphene **1b**, (*E*)-TbtP=PFc (Fc = ferrocenyl), with a

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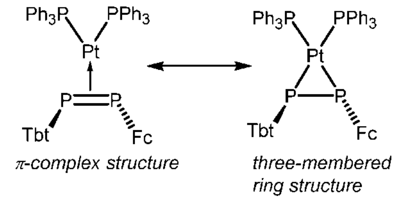


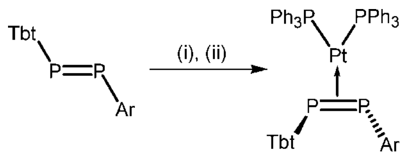
Figure 1. Resonance structures of **2b**.

platinum(0) complex leading to the formation of the corresponding platinum−diphosphene complex [Pt(η^2-TbtP=PFc)$(PPh_3)_2$] and its structural properties from the standpoints of the NMR spectra and X-ray crystallographic analysis together with theoretical calculations using a model complex.

Results and Discussion

At first, we attempted the synthesis of the platinum(0) complex of *trans*-TbtP=PTbt (**1a**), which can be easily prepared by the reductive coupling reaction of $TbtPCl_2$ with magnesium quantitatively,[3f] by the reaction of **1a** with $[Pt(C_2H_4)(PPh_3)_2]$ (5.0 equiv). As a result, **1a** was found to undergo no ligand exchange reaction, even under severe conditions (at 100 °C for 48 h in benzene-d_6 in a sealed tube), probably due to the steric reasons. In contrast to the case for **1a**, the treatment of diphosphene **1b** bearing a ferrocenyl group, which is less hindered than the Tbt group, with $[Pt(C_2H_4)(PPh_3)_2]$ (1.6 equiv) in benzene-d_6 at room temperature for 2 h afforded diphosphene−platinum(0) complex **2b** as orange crystals in 82% isolated yield (Scheme 1). Complex **2b** was found to be stable enough to be handled in air and even on silica gel. The ^{31}P NMR spectrum of **2b** in benzene-d_6 showed an ABMX spin system at 28.3, 27.9, 6.20, and −33.1 ppm, the first two signals of which were assignable to the phosphorus atoms of the two triphenylphosphine ligands of **2b** compared with those of platinum complexes **3**−**5** (Table 1).[4,5,8] The third signal (6.20 ppm) appeared slightly upfield as compared with those for platinum complexes **3** and **5**.[4,8] The last signal (−33.1 ppm) was found to be close to those of the ferrocenyl-substituted phosphorus atoms in diphosphene−platinum complexes **4** and **5**.[5,8] While the $^1J_{PP}$ value of **2b** (397 Hz) lies in the range of those for the reported diphosphene−platinum complexes (275−439 Hz),[4−8] it is considerably smaller than that of the corresponding diphosphene **1b** (546 Hz)[3h] and is somewhat larger than those for the reported diphosphanes (152−250 Hz),[9] showing that the phosphorus−phosphorus bond of **2b** features almost intermediate character between double and single bonds in solution. Interestingly, two of the $^1J_{PtP}$ values of **2b**, 266 (PTbt) and 143 Hz (PFc), are far different in magnitude from the other two $^1J_{PtP}$ values, 3420 and 3400 Hz (PPh_3), indicating that the P−Pt bonds in **2b** should have p orbital character higher than that of the coordination bonds of the PPh_3 ligands.

Scheme 1. Reactions of Diphosphenes 1a,b with a Platinum(0) Complex[a]

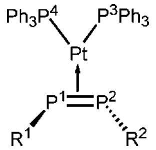


1a (Ar = Tbt)
1b (Ar = Fc)

2a (no reaction)
2b (82%)

[a] Reagents and conditions: (i) $[Pt(C_2H_4)(PPh_3)_2]$ (5.0 equiv)/C_6D_6, 100 °C, 48 h, in a sealed tube (for **1a**); (ii) $[Pt(C_2H_4)(PPh_3)_2]$ (1.6 equiv)/C_6D_6, room temperature, 2 h (for **1b**).

Table 1. ^{31}P NMR Data of [Pt(η^2-R^1P=PR^2)$(PPh_3)_2$]



		δ_P (ppm)	$\lvert {}^1J_{PP} \rvert$(Hz)	$^2J_{PP}$(Hz)	$^1J_{PtP}$ (Hz)	ref
R^1 = Tbt, R^2 = Fc (**2b**)[a]	P^1	6.20	397 (P^1−P^2)	60.0 (P^1−P^3)	266 (P^1)	this work
	P^2	−33.1		38.0 (P^2−P^4)	143 (P^2)	
	P^3	27.9		8.0 (P^3−P^4)	3420 (P^3)	
	P^4	28.3			3400 (P^4)	
R^1 = R^2 = Ph (**3**)[b]	P^1	18.1		60 (trans)	288 (P^1)	4
	P^3	28.3		4 (cis)	3353 (P^3)	
R^1 = R^2 = Fc (**4**)[a]	P^1	−8.2		31.8 (trans)	279.9 (P^1)	5
	P^3	27.6		2.6 (cis)	3339.8 (P^3)	
R^1 = Mes*, R^2 = Fc (**5**)[d]	P^1	25.5	424 (P^1−P^2)	52.5 (P^1−P^3)	*c*	8
	P^2	−16.1		36.0 (P^2−P^4)		
	P^3	24.8		4.0 (P^1−P^4)		
	P^4	26.4		3.0 (P^2−P^3) 8.0 (P^3−P^4)		

[a] In benzene-d_6. Values of $^2J_{P^1}P^4$ and $^2J_{P^2}P^3$ were estimated to be under 5.0 Hz. [b] In benzene. [c] The value was not reported. [d] In toluene.

Although there have been three reports on the crystal structures of [Pt(η^2-R^1P=PR^2)$(PPh_3)_2$] (R^1, R^2: C_6F_5, C_6F_5 (**6**);[10] $EtMe_4CpFe(CO)_2$, Mes* (**7**);[7] *t*-Bu_2P, *t*-Bu_2P (**8**)[11]) revealed by X-ray crystallographic analysis, the structural features of platinum complexes have not been fully investigated until now. The molecular structure of **2b** was determined by X-ray crystallographic analysis (Figure 2), and the selected structural parameters are summarized in Table 2. It was found that the Tbt and ferrocenyl groups of **2b** are oriented in a trans conformation with a torsion angle of 156.6(2)°. The Pt−P(PPh_3) bond lengths for **2b** (2.2841(12) and 2.3025(12) Å) lie in the range of those for platinum complexes **6**−**8** (2.276−2.349 Å).[7,10,11] The Pt−P(P=P) bond lengths for **2b** were 2.3838(12) Å (Tbt group) and 2.3916(12) Å (Fc group), which are similar to those for complexes **6**−**8** (2.319−2.400 Å).[7,10,11] Accordingly, the Pt−P(PPh_3) bond lengths were shorter than Pt−P(P=P), as in the case of the reported Pt complexes **7** and **8**,[7,11] suggesting that the p character of the Pt−P(P=P) bond of **2b** is higher than those of the Pt−P(PPh_3) bonds. The P−P bond length of **2b** (2.1549(17) Å), being within the range of those for the reported complexes **6**−**8** (2.140−2.156 Å),[7,10,11] is shorter than typical P−P single-bond lengths (ca. 2.19−2.24 Å)[9] and longer than the typical P=P double-bond lengths of the reported (*E*)-diaryldiphosphenes (1.985−2.051 Å).[2a,d] This structural feature can be explained by the π back-donation from d orbitals of the Pt atom into the π* orbital of the P=P unit in **2b**.

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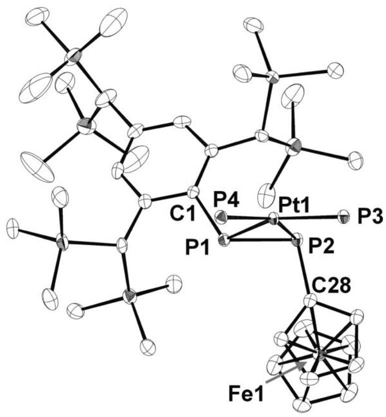

Figure 2. Molecular structure of the major disordered moiety of [Pt(η^2-TbtP=PFc)(PPh$_3$)$_2$]·0.5C$_6$H$_{14}$. Displacement ellipsoids were drawn at the 50% probability level. The phenyl groups of triphenylphosphines, *n*-hexane, and hydrogen atoms were omitted for clarity.

Table 2. Selected Structural Parameters of [Pt(η^2-TbtP=PFc)(PPh$_3$)$_2$]·0.5C$_6$H$_{14}$

Bond Lengths (Å)			
Pt(1)−P(1)	2.3838(12)	P(1)−P(2)	2.1549(17)
Pt(1)−P(2)	2.3916(12)	P(1)−C(1)	1.867(5)
Pt(1)−P(3)	2.2841(12)	P(2)−C(28)	1.839(5)
Pt(1)−P(4)	2.3025(12)		

Bond Angles (deg)			
P(1)−Pt(1)−P(2)	53.65(4)	P(1)−Pt(1)−P(4)	99.62(4)
Pt(1)−P(1)−P(2)	63.36(5)	P(2)−Pt(1)−P(3)	100.47(4)
Pt(1)−P(2)−P(1)	62.99(5)	C(1)−P(1)−P(2)	112.13(15)
P(3)−Pt(1)−P(4)	104.01(4)	C(28)−P(2)−P(1)	99.68(16)

Torsion Angle (deg)	
C(1)−P(1)−P(2)−C(28)	156.6(2)

The P(2)−P(1)−C(1) bond angle of 112.13(15)° for **2b**, which is larger than that of diphosphene **1b** (103.15(12)°), is similar to those (121.4(3) and 111.3(6)°) of the reported complexes **6** and **7**, bearing C$_6$F$_5$ and Mes* groups, respectively. The sum of the bond angles around the platinum atom of **2b** was found to be 370.26°, indicating that the platinum atom of **2b** slightly deviates from a square-planar geometry as compared with those of the reported complexes **6** (363.2°)[10] and **7** (360.0°),[11] probably due to the severe steric congestion between the Tbt and the triphenylphosphine ligands (Figures S1 and S2 in the Supporting Information). Complex **2b** exhibits a C(28)−P(2)−P(1) angle of 99.68(16)°, which is slightly narrowed as compared with that of diphosphene **1b** (101.64(16)°). The bond angle of **2b** is the smallest in those of complexes **6**−**8** (102.0(6)−121.4(3)°),[7,10,11] indicating that the P(2) atom should preserve its original valence-electron configuration, (3n)^2(3p)^3, as well as that of diphosphene **1b**. Consequently, these results indicate that the P=P moiety of **2b** should be formed by high p-character orbitals, and it should be noted that **2b** has a π-complex structure in the solid state as well as in solution (Figure 1).

In order to elucidate the bonding character between the P=P unit and the Pt atom as the resonance structures shown in Figure 1, we carried out theoretical calculations for [Pt(η^2-DmpP=PFc)(PH$_3$)$_2$] (Dmp = 2,6-dimethylphenyl) as a model molecule. In the structural optimization of the model molecule using the B3LYP method, one local minimum (**2c**) was found with geometries similar to the crystalline structure of **2b** (Table S5 in the Supporting Information). NBO calculations for **2c** showed that the P−P bond in **2c** consisted of the two σ_{PP} and π_{PP} bonds with high p character (ca. 86% and 96% p character, respectively), as in the case of (*E*)-DmpP=PFc (**1c**) (σ_{PP} and π_{PP} should have ca. 84% and 99% p character, respectively), whereas no covalent Pt−P bond for **2c** was found in the calculations (Table S6). Although the occupancy of the π^*_{PP} orbital for **1c** was ca. 0.10, that for **2c** was computed as 0.63. Moreover, an NBO analysis of **2c** based on second-order perturbation theory exhibited two effective donor−acceptor interactions: that is, those from the π_{PP} bond into the unoccupied 6s orbital of the Pt atom and from the occupied 5d orbital of the Pt atom into the empty π^*_{PP} bond (Table S7). Thus, it can be concluded that the bonding property of the Pt−P−P three-membered ring system in **2c** should be predominantly a "π complex", as shown in Figure 1.[12]

In summary, we found the high reactivity of ferrocenyldiphosphene **1b** stabilized by a Tbt group toward the platinum(0) complex, which is in sharp contrast to that of the overcrowded diphosphene **1a** bearing two Tbt groups. The molecular structure of the resulting Pt(0) complex **2b** was characterized by its NMR spectra, and the crystalline structure of **2b** was established by X-ray crystallographic analysis. Taking into consideration these experimental results together with the theoretical calculations of the model complex, it can be concluded that **2b** exhibits a π complex character with the Pt atom coordinated by the P=P moiety in an η^2 fashion. These results are the first example of a detailed elucidation for the structural properties of the diphosphene−platinum(0) complex both in solution and in the solid state.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere or in a degassed and sealed tube, unless otherwise noted. All solvents were purified by standard methods and then dried by using an Ultimate Solvent System (Glass Contour Co.).[13] Benzene-*d*$_6$ for the NMR spectroscopy was dried by using a potassium mirror prior to use. Preparative thin-layer chromatography (PTLC) and column chromatography were performed with Merck Kieselgel 60 PF254. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-918 equipped with JAIgel 1H and 2H columns (Japan Analytical Industry Co., Ltd.) with toluene as an eluent. ^{1}H NMR (300 MHz) spectra were measured in C$_6$D$_6$ with a JEOL AL-300 spectrometer using C$_6$HD$_5$ (δ 7.15 ppm) as an internal standard. ^{31}P NMR (120 MHz) and ^{195}Pt NMR (85 MHz) spectra were measured in C$_6$D$_6$ with JEOL AL-300 and AL-400 spectrometers using 85% H$_3$PO$_4$ in water (δ 0 ppm) and Na$_2$PtCl$_6$ in water (δ 0 ppm) as external standards, respectively. High-resolution mass spectral data were obtained on a JEOL SX-270 mass spectrometer. 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. Ethylenebis(triphenylphosphine)platinum(0) was purchased from Aldrich Co., Ltd., and purified by recrystallization from *n*-hexane before use. *trans*-TbtP=PTbt (**1a**)[3f] and (*E*)-TbtP=PFc (**1b**)[3h] were prepared according to the procedures reported in the literature.

Reaction of (*E*)-TbtP=PFc (1b) with Ethylenebis(triphenylphosphine)platinum(0). A benzene-*d*$_6$ solution (0.7 mL) of **1b** (36.9 mg, 46.2 μmol) and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$]

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(12) In theoretical calculations for a diaryldiphosphene−platinum complex such as [Pt(η^2-DmpP=PDmp)(PH$_3$)$_2$], it has also been confirmed that bonding properties of the Pt−P−P three-membered-ring framework should be those of a π-complex character. The results of the theoretical calculations are in the Supporting Information.

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(55.0 mg, 73.6 μmol) was degassed and sealed in an NMR tube. When the mixture was allowed to stand at room temperature for 2 h, the ^{31}P NMR signals for **1b** completely disappeared. Separation of the mixture by GPLC and PTLC (with *n*-hexane as eluent) afforded platinum complex **2b** (57.5 mg, 37.8 μmol, 82%) as orange crystals. **2b**: mp 189 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 45 °C): δ -0.12 (s, 9H, $Si(CH_3)_3$), 0.33 (s, 18H, $Si(CH_3)_3$), 0.41 (s, 18H, $Si(CH_3)_3$), 0.62 (s, 9H, $Si(CH_3)_3$), 1.38 (s, 1H, CH), 1.60 (s, 1H, CH), 2.98 (brs, 1H, α-C_5H_4), 3.54 (br s, 1H, CH), 4.05 (br s, 1H, β-C_5H_4), 4.30 (s, 5H, C_5H_5), 4.35 (br s, 1H, β-C_5H_4), 4.98 (br s, 1H, α-C_5H_4), 6.82−7.01 (m, 22H, Ar H), 7.28 (m, 10H, Ar H). ^{31}P NMR (120 MHz, C_6D_6, 25 °C): δ 28.3 (br dd, $^2J_{PP} = 38.0$, 8.0 Hz with satellite signals of $^1J_{PtP} = 3400$ Hz), 27.9 (br dd, $^2J_{PP} = 60.0$, 8.0 Hz with satellite signals of $^1J_{PtP} = 3420$ Hz), 6.2 (dd, $^1J_{PP} = -397$ Hz, $^2J_{PP} = 60.0$ Hz with satellite signals of $^1J_{PtP} = 266$ Hz), -33.1 (dd, $^1J_{PP} = -397$ Hz, $^2J_{PP} = 38.0$ Hz with satellite signals of $^1J_{PtP} = 143$ Hz). ^{195}Pt NMR (85 MHz, C_6D_6, 25 °C): δ -5245 (m). HRMS (FAB): *m/z* found 1518.4301 ($[M + H]^+$), calcd for $C_{73}H_{98}FeP_4PtSi_6$ 1518.4310. Anal. Calcd for $C_{73}H_{98}FeP_4PtSi_6$: C, 57.73; H, 6.50. Found: C, 57.98; H, 6.75. Satisfactory ^{13}C NMR data for **2b** could not be obtained, due to its low solubility in common organic solvents.

X-ray Crystallographic Analysis of [Pt(η^2-TbtP=PFc)(PPh$_3$)$_2$]·0.5C$_6$H$_{14}$. Single crystals of **2b** were obtained by slow recrystallization from its chloroform/*n*-hexane solution at room temperature. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,70$ Å). The structure was solved by direct methods (SHELXS-97)[14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[15] All non-hydrogen atoms were refined anisotropically, except for the minor part of the *n*-hexane, which these atoms were refined isotropically. All hydrogen atoms were placed using AFIX instructions. The $CH(SiMe_3)_2$ group at the para position of the Tbt group of **2b** was disordered, and the occupancies were refined to be in the ratio 0.74:0.26. The disordered $CH(SiMe_3)_2$ groups of **2b** were restrained using SADI instructions. The methyl and methylene groups of the *n*-hexane molecule were disordered, and the occupancies were refined to be in the ratio 0.74:0.26. The disordered methyl and methylene groups were restrained by using DFIX and SADI instructions. Selected structural parameters and crystal data of **2b**·0.5C$_6$H$_{14}$ are given in Tables 2 and S2 (Supporting Information), respectively. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 651582.

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian 03W[16] and Jaguar 7.0[17] packages with density functional theory at the B3LYP[18] level. Geometries of (*E*)-DmpP=PFc (**1c**) and [Pt(η^2-DmpP=PFc)(PH$_3$)$_2$] (**2c**) were optimized using the 6-31G(d) basis set for C and H, 6-311+G(2d,p) for P, and lanl2dz[19] for Fe and Pt in the Gaussian 03W. It was confirmed by frequency calculations that the optimized structures of **1c** and **2c** have minimum energies. Theoretically optimized coordinates of **1c** and **2c** are shown in Tables S3 and S4 (Supporting Information), respectively. NBO analysis[20] of **1c** and **2c** was performed with the LACV3P* basis set (EPC for Fe and Pt and 6-311G* for all other atoms) by using the NBO 5.0 program[21] in Jaguar 7.0; the results are summarized in Tables S6 and S7.

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Supporting Information Available: Tables and figures giving NMR data of the reported η^2-diphosphene−platinum complexes (Table S1), crystallographic data of **2b**·0.5C$_6$H$_{14}$ (Table S2), theoretically optimized coordinates of **1c** and **2c** (Tables S3 and S4, respectively), selected structural parameters of **2b**·0.5C$_6$H$_{14}$, **2c**, and **1b** (Table S5), summarized results of NBO calculations of **1c** and **2c** (Table S6), NBO occupancies and donor−acceptor stabilization energies for **2c** (Table S7), and molecular structures of **2b**·0.5C$_6$H$_{14}$ (Figures S1 and S2) and a CIF file giving X-ray crystallographic data for **2b**·0.5C$_6$H$_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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