Preparation and reaction of phosphorus peri-bridged naphthalenes and their adducts with Lewis acids

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Abstract

The reaction of dilithionaphthalene with R_2NPCl_2 ($R = {}^iPr$ and Et) gave diisopropylamino-naphtho[1,8-*bc*]phosphete **3a** and its diethyl analog **3b** (phosphorus versions of single-atom peri-bridged naphthalene). The nature of the strained four-membered ring thus formed was examined by treating **3a** with four types of electrophiles, BH_3, elemental sulfur, methyltriflate, and a metal fragment $W(CO)_5$, all of which gave the corresponding electrophile adducts with the strained ring retained. X-ray analysis was performed for **3b** and all of the above adducts, showing that the trigonal plane of the amino group was commonly oriented almost perpendicular to the naphthalene plane, which was rationally understood on the basis of the favorable overlap between the lone pair orbital of the sp^2 nitrogen center and the σ^* orbital(s) of the two P–C bonds. In addition, when the $W(CO)_5$ adduct, $W(\mathbf{3a})(CO)_5$, was treated with $Pt(PPh_3)_4$ and then with a CO gas, its four-membered ring was expanded to give a tungsten–platinum heterodinuclear complex having a five-membered platina–phospha heterocycle.
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1. Introduction

Single-atom peri-bridged naphthalenes (**1**) possess a fascinating four-membered ring potentially useful for the preparation of naphthalene derivatives because it readily undergoes a ring-opening reaction. The first example of **1** was reported for $E = SO_2$ in 1965 [1], and since then, some analogs bridged by group 13 (BR, BR_2^-) [2], group 14 (CR_2, SiR_2, and GeR_2) [3], and group 16 (S, SO, and SO_2) [4] moieties have been reported. However, to the best of our knowledge, no group 15 analogs have been prepared nor fully characterized so far [5]. On the other hand, the strained phosphorus heterocycles have attracted considerable interest owing not only to their peculiar structures and reactivities, but also to their utilities as a ligand toward a variety of transition metal fragments [6]. Recently, we have successfully prepared a phosphorus version of single-atom peri-bridged naphthalene (naphtho[1,8-*bc*]phosphete), as communicated briefly [7]. Here, details of the preparation, structural properties, and some reactivities are reported for R_2NP peri-bridged naphthalenes and their adducts with some Lewis acids.
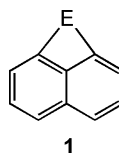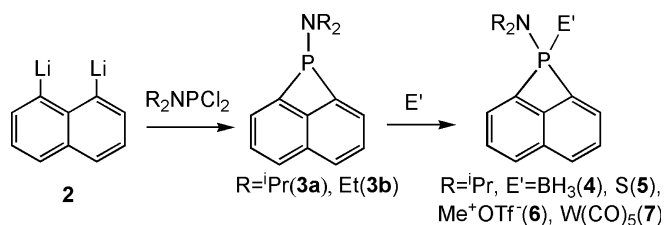
E: Group 13 (BR, BR_2^-)
Group 14 (CR_2, SiR_2, GeR_2)
Group 15 (PR, $P(E')R$ this work)
Group 16 (S, SO, SO_2)

1

2. Results and discussion

2.1. Preparation and reactivity

1,8-Dilithionaphthalene (**2**) is a useful starting material for the preparation of **1**, as demonstrated by a successful

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Scheme 1.

preparation of R_2Si-bridged analogs [3]. In addition, the dilithio compound **2** is readily obtained by a double lithiation of 1,8-dibromonaphthalene [8a] or by stepwise lithiations starting from commercially available 1-bromonaphthalene [8b]. Although the former method led to a better yield of **2**, the latter was suitable for the large-scale preparation. The reaction of **2** with $^iPr_2NPCl_2$ successfully gave the expected product **3a** (Scheme 1). The $^{31}P\{^1H\}$ NMR signal of **3a** was observed at 94.9 ppm, which is considerably shifted to lower field than 36.7 ppm of its acyclic counterpart $P(N^iPr_2)Ph_2$ [9]. Such a low-field shift has been characteristically observed for the phosphorus atoms in a four-membered ring [6,10]. A $^{13}C\{^1H\}$ NMR spectrum of **3a** exhibited six signals in an aromatic region, 122.5–147.2 ppm, which is consistent with a symmetrically substituted naphthalene ring. A similar reaction of **2** with Et_2NPCl_2 also gave the corresponding peri-bridged product **3b** in a much lower yield, the reason

for which is not clear. On the other hand, the reaction with $PhPCl_2$ gave not a desired single-atom-bridged species, but $(PhP)_2$-brigded naphthalene having a five-membered ring as reported previously [7,11].

To explore the nature of the strained four-membered ring in **3**, reactivity of **3a** toward electrophiles was examined using BH_3, elemental sulfur, methyltriflate (MeOTf), and a metal fragment $W(CO)_5$ (Scheme 1). In all cases, the reaction proceeded smoothly to give the corresponding electrophile adducts **4**, **5**, **6**, and **7** respectively, which had $^{31}P\{^1H\}$ NMR signals at 104.4, 78.0, 69.3, and 95.0 ppm, respectively. Six $^{13}C\{^1H\}$ NMR signals assigned to the aromatic carbons were observed as before for all the adducts **4–7** at positions almost comparable to those of the starting **3a**, indicating that the symmetry of the naphthalene moiety was retained. The molecular structures of **4–7** were finally determined by the X-ray analysis as described in the following section, which confirmed that the strained four-membered ring was retained upon the reaction with the above electrophiles.

2.2. Molecular structures

X-ray structures of **3a** [7], **3b**, and **4–6**, and **7** were illustrated in Figs. 1 and 2, respectively, with numbering schemes adopted. Their crystallographic data and selected bond distances and angles were summarized in Tables 1 and 2, respectively. In the crystal of **3b**, two molecules were
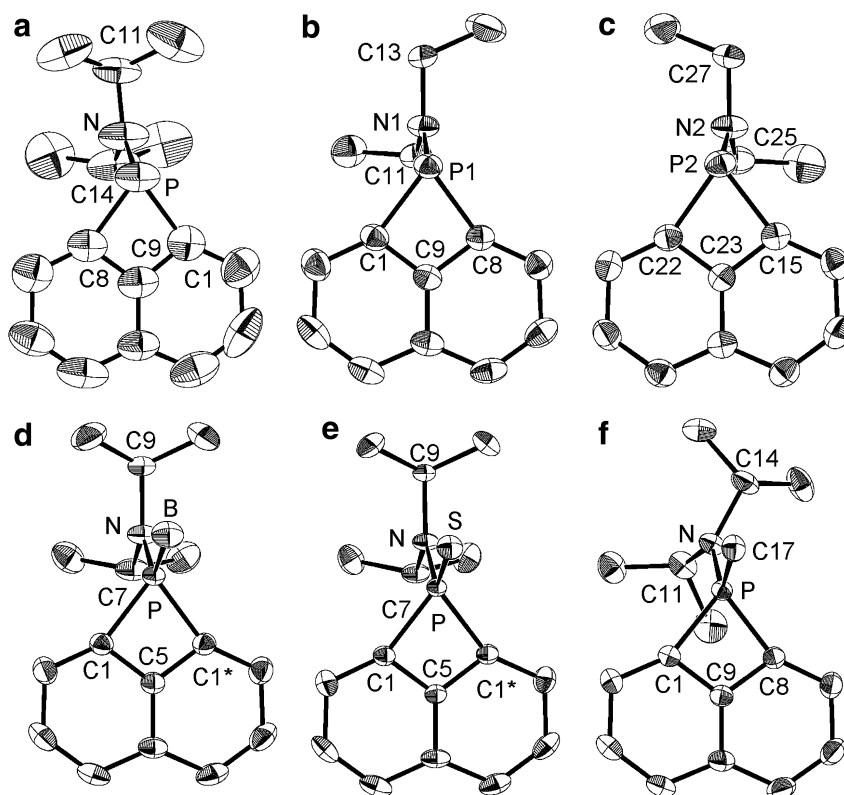

Fig. 1. Molecular structures of phosphorus peri-bridged naphthalenes **3a** (a), **3b** (b and c), **4** (d), **5** (e), **6** (f). Hydrogen atoms and a triflate anion of **6** were eliminated for clarity.

found to be crystallographically independent, and in **4** and **5**, the crystallographic mirror plane present made a half of each molecule unique. The structures of the free phosphines **3a** and **3b** and the adducts **4–7** confirm the common existence of the strained four-membered ring containing a severely distorted tri- or tetra-coordinate phosphorus center. The C–P–C angle of 72.69(7)° observed for **3b** is the most acute among the corresponding angles of the single-atom peri-bridged naphthalenes (**1**; E = BR_n, CR_n, SiR_2) reported so far [2–4]. The C–P–C angles of other molecules in Figs. 1 and 2 are almost comparable but are somewhat enlarged with the P–C bond distances reduced, particularly in **6**, which is not surprising from a geometrical viewpoint, since three corners of the quadrangle are fixed in the rigid naphthalene framework. Thus, **3b** having the longer P–C bonds should have the more acute C–P–C angle.

To examine the strain of the four-membered ring in **3a** or **3b**, a less strained analog, diisopropylamino-dibenzo-phosphole **8**, was newly prepared and its molecular structure determined by X-ray analysis is shown in Fig. 3, where another sp^2-carbon center has been incorporated into the heterocycle to form a five-membered ring. The geometrical parameters given in Table 2 demonstrate that the internal bond angles of the five-membered ring in the two crystallographically independent **8** molecules are much greater than those of the four-membered ring in **3a** and **3b**, reflecting the reduced strain in **8**. In conformity with this reduction, the P–C bond distances of 1.8277(5)–1.8347(17) Å in **8** are significantly smaller than 1.885(7)–1.8968(18) Å in the free phosphines **3a** and **3b**. Thus, the greater angle distortion in **3a** and **3b** than in **8** is obviously responsible for the longer P–C bonds in the four-membered ring.

$^iPr_2N$

8
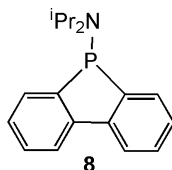
The P–C bonds of **3a** were shortened by 0.010–0.069 Å upon the formation of the adducts with Lewis acids, BH_3, sulfur, Me^+, and $W(CO)_5$. A reduction in electron density at the phosphorus center is probably responsible for the shortening; for example, the adduct with the strongest Lewis acid, Me^+, possesses the shortest P–C bonds among the four Lewis acid adducts.

A noteworthy structural property of **3–7** is a conformation adopted by their amino groups. The summations of the bond angles around each nitrogen center are all close to 360° as listed in Table 2, indicating that all amino groups of **3–7** have a trigonal-planar geometry. In addition, the nitrogen planes are oriented almost perpendicular to the naphthalene plane (Figs. 1 and 2), as can be confirmed by the dihedral angles between these two planes; they are
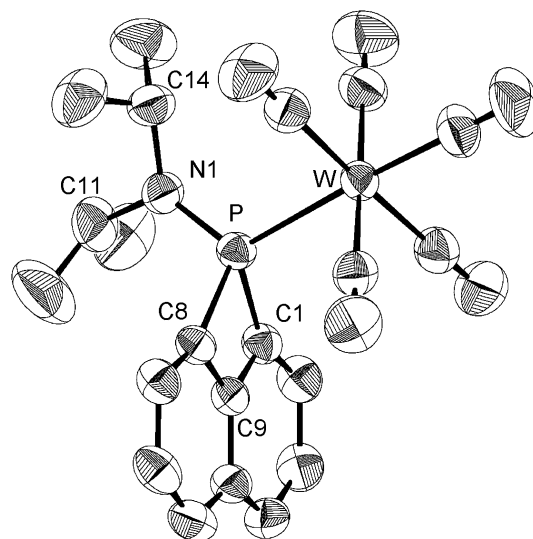

Fig. 2. A molecular structure of the $W(CO)_5$ adduct **7**. Hydrogen atoms were eliminated for clarity.

almost 90 ° for **3a**, **3b**, **4**, and **5**, though those for **6** and **7** are somewhat deviated from 90° by 15.28(4)° and 8.89(12)°, respectively. It is a general phenomenon in an amino-phosphorus moiety that a nitrogen atom of the amino group adopts the sp^2 hybridization so as to donate its π-electrons to σ* orbital(s) of other bonds around the phosphorus center [12]. In **3–7** as well as in **8**, the σ* orbitals of the two P–C bonds are symmetrically located at both sides of the phosphorus center as depicted in Fig. 4. Thus, the perpendicular orientation of the nitrogen plane is rationally understood, since the overlap between the lone pair orbital and the σ* orbital(s) becomes the greatest at the conformation observed. This π-bond interaction is responsible for the significantly shorter P–N bonds (1.6139–1.6793 Å) in Table 2 than the "ideal" P–N single bond (1.800(4) Å) reported for $H_3N^+–PO_3^{2-}$ [13].

To examine this π-donation phenomenon further, low-temperature NMR spectra of **3a** were measured with an expectation that a rotation of the N^iPr_2 group around the P–N bond would be frozen with the orientation close to that found in solid state. A ^1H NMR spectrum of **3a** at room temperature showed a single methyl signal at 1.18 ppm and a single methine signal at 3.29 ppm. Upon cooling down to −90 °C, each signal was separated into two signals as shown in Fig. 5, indicating that the two ^iPr groups on the nitrogen are exposed to nonequivalent environments due to their slow exchange. Although dispositions of the two ^iPr groups could not be established from the NMR data only, it is highly plausible that **3a** adopts the same orientation at −90 °C as found in crystal.

2.3. Ring-opening reaction

The strained four-membered ring of **3a** was retained upon the reaction with a range of electrophiles as described above. On the other hand, several research groups and we

Table 1
Crystallographic data

	3b	4	5	6
Formula	$C_{14}H_{16}NP$	$C_{16}H_{23}BNP$	$C_{16}H_{20}NPS$	$C_{18}H_{23}F_3NO_3PS$
Crystal color	Colorless	Colorless	Colorless	Colorless
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Pca2_1$ (# 29)	$Pnma$ (# 52)	$Pnma$ (# 52)	$P2_1/n$ (# 14)
a (Å)	14.8080(2)	7.7320(2)	7.4500(1)	8.4060(1)
b (Å)	7.8830(1)	12.6260(4)	12.4890(2)	17.3590(3)
c (Å)	21.5610(3)	16.5690(6)	16.6470(4)	13.9300(3)
α (°)	90	90	90	90
β (°)	90	90	90	93.993(1)
γ (°)	90	90	90	90
V (Å^3)	2516.85(6)	1617.54(9)	1548.89(5)	2027.73(6)
Z	8	4	4	4
Temperature (K)	200	200	200	200
μ (Mo Kα) (mm^{-1})	0.19	0.16	0.30	0.28
No. of reflections				
Measured	3078	1987	1865	4523
Observed ($I > 2\sigma(I)$, $2\theta < 55°$)	3073	1964	1836	4342
No. variables	294	147	140	337
R_1 [$I > 2\sigma(I)$]	0.036	0.046	0.033	0.033
wR_2[a]	0.099	0.113	0.083	0.089
Highest peak (e/Å^3)	0.38 (0.87 Å from P1)	0.37 (1.15 Å from H8)	0.76 (1.20 Å from C1)	0.32 (0.68 Å from C8)
Goodness of fit on F	1.214	1.149	1.061	1.073
a/b[a]	0.0501/0.57	0.0433/0.96	0.0389/0.93	0.0457/0.76

	7	8	9
Formula	$C_{21}H_{20}NO_5PW$	$C_{18}H_{22}NP$	$C_{40}H_{35}NO_6P_2WPt$
Crystal color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (# 14)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
a (Å)	25.369(8)	7.5300(2)	15.3970(1)
b (Å)	9.791(2)	13.8810(4)	16.1550(2)
c (Å)	9.084(4)	15.7610(3)	18.0190(2)
α (°)	90	94.398(2)	82.256(1)
β (°)	94.52(3)	94.866(2)	68.636(1)
γ (°)	90	90.776(10)	75.434(1)
V (Å^3)	2249.3(14)	1636.30(7)	4035.25(7)
Z	4	4	4
Temperature (K)	295	200	200
μ (Mo Kα) (mm^{-1})	5.24	0.16	6.44
No. of reflections			
Measured	6556	7199	15,855
Observed ($I > 2\sigma(I)$, $2\theta < 55°$)	4943	6586	14,275
No. variables	267	536	928
R_1 [$I > 2\sigma(I)$]	0.030	0.044	0.057
wR_2[a]	0.078	0.104	0.160
Highest peak (e/Å^3)	1.22 (0.57 Å from W)	0.30 (0.67 Å from C25)	3.90 (1.10 Å from Pt1)
Goodness of fit on F	1.018	1.117	1.058
a/b[a]	0.0450/0.03	0.0329/0.95	0.1175/7.56

[a] $wR_2 = \left\{ \sum \left[w(F_o^2 - F_c^2)^2 \right] \Big/ \sum [w(F_o^2)^2] \right\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

reported that a low valent transition metal such as a zero-valent platinum complex reacts with a strained phospha-heterocyle coordinating to a metal fragment to give a ring-expanded product with a platinum fragment inserted into a P–C bond [14,15]. Thus, **7** in which **3a** is coordinating to a W(CO)$_5$ fragment was allowed to react with Pt(PPh$_3$)$_4$ [7]. ^{31}P{^{1}H} NMR spectra of the reaction mixture indicated the formation of several species, the major one of which had signals at 21 ppm (d, $J_{PP} = 222$ Hz, $J_{PPt} = 1952$ Hz), 29 ppm (d, $J_{PP} = 51$ Hz, $J_{PW} = 280$ Hz),

and 88 ppm (dd, $J_{PP} = 51$ and 225 Hz, $J_{PPt} = 1676$ Hz). The two signals at 21 and 29 ppm could be assigned to PPh$_3$ ligands coordinating to the platinum and tungsten centers, respectively, whereas the signal at 88 ppm was assigned to the phosphorus moiety derived from **7**. This species gradually decomposed upon prolonged heating. On the other hand, when a CO gas was bubbled into the reaction mixture, the ^{31}P{^{1}H} NMR spectrum of the solution showed only two major signals due to a single product **9**, which were observed as doublets coupled to each other

Table 2
Selected bond distances and angles

Crystal	3a	3b (1)	3b (2)	4 (E = BH$_3$)
Distances (Å)				
P–N	1.654(5)	1.6642(10)	1.6655(10)	1.6420(14)
P–C1	1.885(7)	1.8890(11)	1.8867(11)	1.8599(10)
P–C8	1.885(7)	1.8925(11)	1.8973(11)	
P–E			1.9211(19)	
Angles (°)				
C1–P–C8	73.1(3)	72.60(5)	73.01(5)	74.50(6)
C1–P–N1	109.8(3)	108.92(5)	108.88(5)	112.31(5)
C8–P–N1	108.3(3)	108.78(5)	109.24(5)	
P1–C1–C9	89.7(4)	90.41(7)	90.40(7)	89.40(7)
P1–C8–C9	90.4(5)	90.32(7)	89.84(7)	
C1–C9–C8	106.1(6)	106.18(9)	106.23(9)	106.55(12)
Sum of angles[a]	359.6	359.9	360.0	360.0
Dihedral angle (°)[b]	87.60(16)	88.49(3)	88.44(3)	90

Crystal	5 (E = S)	6 (E = Me)	7 (E = W(CO)$_5$)	8 (1)	8 (2)
Distances (Å)					
P–N	1.6380(16)	1.6139(10)	1.658(3)	1.6753(12)	1.6793(13)
P–C1	1.8555(12)	1.8159(12)	1.865(4)	1.8285(15)	1.8277(15)
P–C8		1.8264(12)	1.874(3)	1.8285(17)	1.8347(17)
P–E	1.9407(6)	1.7824(12)	2.5227(10)		
Angles (°)					
C1–P–C8	74.77(7)	76.65(5)	73.11(15)	88.89(7)	88.79(7)
C1–P–N1	111.81(6)	119.05(5)	111.15(16)	106.96(6)	106.28(7)
C8–P–N1		122.25(6)	114.31(16)	106.28(7)	108.06(7)
P1–C1–C9	89.42(8)	88.35(8)	89.8(2)	112.18(11)	112.09(12)
P1–C8–C9		87.93(8)	90.1(2)	112.29(12)	112.04(12)
C1–C9–C8	106.30(14)	106.97(10)	106.5(3)		
Sum of angles[a]	360.0	358.3	358.8	360.0	359.5
Dihedral angle (°)[b]	90	74.72(4)	81.11(12)	88.50(4)	89.00(5)

[a] The summation of the bond angles around the nitrogen center.
[b] The dihedral angle between the naphthalene plane and the nitrogen plane having the trigonal-planar geometry.
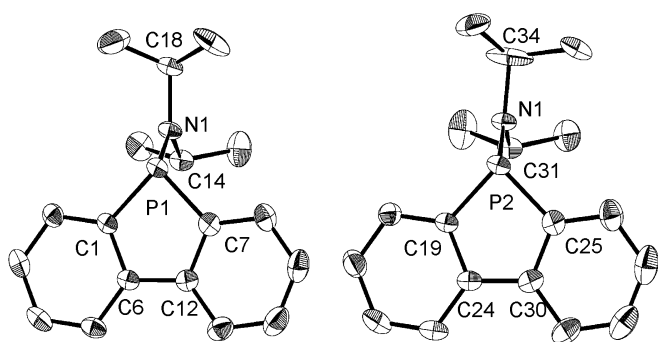

Fig. 3. Molecular structures of two independent dibenzophospholes 8. Hydrogen atoms were eliminated for clarity.

at 75 and 22 ppm [7]. The former signal accompanied by the satellite signals due to [183]W and [195]Pt could be assigned to the phosphorus atom bridging tungsten and platinum centers. The latter having the [195]Pt satellite signals only was assigned to PPh$_3$ coordinating to a Pt(II) center. The molecular structure of the product 9 was finally determined by X-ray analysis as shown in Fig. 6. All spectroscopic data as well as microanalytical data are consistent with the structure in Fig. 6, in which a platinum fragment has been inserted into the P–C bond of the strained four-membered ring of 7 to form a five-membered platina–phospha heterocycle. The two remaining coordination sites are occupied with CO and original PPh$_3$. It is generally accepted that a CO ligand coordinating to a Pt(II) center is readily replaced with other ligands [16]. However, the CO group in 9 was not replaced in the reaction with an excess amount of PEt$_3$; PPh$_3$ on the platinum center was instead replaced with PEt$_3$ as shown in Scheme 2. The significant steric demands of W(CO)$_5$ and N^{i}Pr$_2$ moieties are the most probable reason for the unusual selectivity observed in above substitution reaction. On the other hand, a bidentale ligand such as dppe could replace not only PPh$_3$ but also CO, when heated in toluene at 55 °C for 4 h, indicating that steric demands exerted by the monodentate phosphines, PEt$_3$ and/or PPh$_3$, is crucial for the substitution of the CO group at the sterically hindered position.

3. Experimental

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents
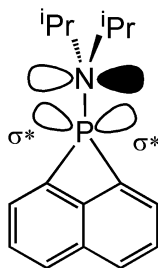
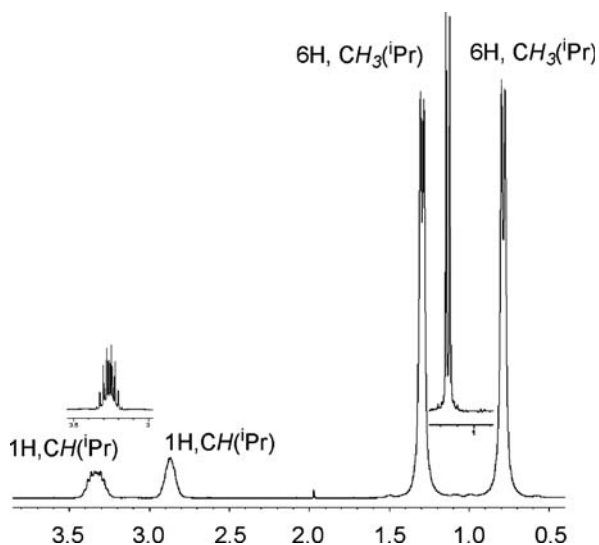Fig. 4. Schematic drawing of a π-orbital on the nitrogen atom and two σ* orbitals on the phosphorus atom.

Fig. 5. ^{1}H NMR (300.4 MHz, CD$_2$Cl$_2$) spectra of the two ^{i}Pr groups in **3a** at −90 °C. The spectra superimposed are those recorded at room temperature.

were dried and distilled from sodium (hexane), sodium/benzophenone (toluene, ether, and THF), or P$_2$O$_5$ (CH$_2$Cl$_2$). These purified solvents were stored under an N$_2$ atmosphere. 2,2′-Dibromobiphenyl [17] and **9** [7] were prepared according to previously described methods. Other reagents were used as received.

NMR spectra were recorded on a JEOL LA-300 and -500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts were reported relative to Me$_4$Si and were determined by reference to the residual solvent peaks. ^{31}P NMR chemical shifts were reported relative to H$_3$PO$_4$ (85%) used as an external reference. Elemental analyses were performed with a Perkin–Elmer 2400CHN elemental analyzer.

Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The emission-lines used and their relative intensities (in parenthesis) were as follows: 577.0 (69), 546.1 (82), 435.8 (69), 404.7 (42), 365.0 (100), 334.1 (7), 312.6 (38), and 302.2 (9). Preparative-scale GPC was performed with a recycling HPLC system (Japan Analytical
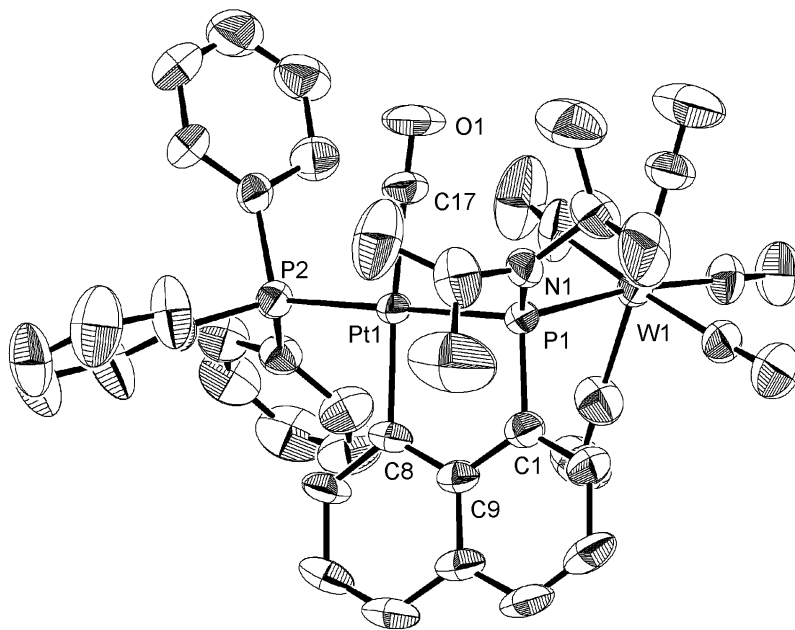

Fig. 6. Molecular structure of one of the two independent W–Pt complexes **9**. The other one has a structure almost similar to the above one. Hydrogen atoms were eliminated for clarity. Selected bond distances (Å) and angles (°): Pt1–C17 1.934(7), Pt1–C8 2.073(6), Pt1–P1 2.3371(15), Pt1–P2 2.3706(16), W1–P1 2.5908(17), P1–N1 1.703(6), P1–C1 1.827(7), C8–Pt1–P1 84.6(2), C1–P1–Pt1 100.0(2), C9–C1–P1 115.5(5), C9–C8–Pt1 118.5(5), C1–C9–C8 121.2(6).
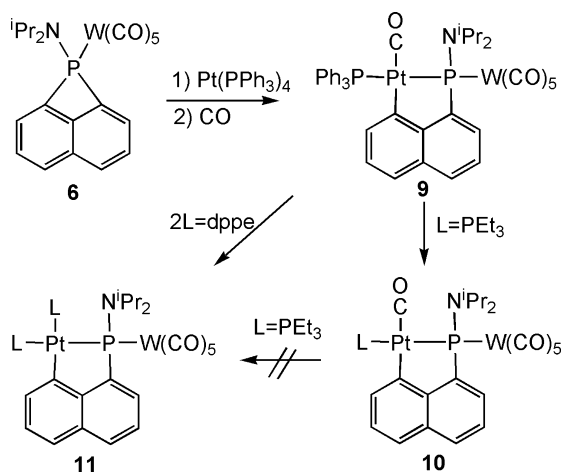
Scheme 2.

Industry Model LC-908) with JAIGEL-1H (20 mm i.d. × 600 mm; exclusion limit 1.0×10^3) and JAIGEL-2H (20 mm i.d. × 600 mm; exclusion limit 5.0×10^3) columns using CHCl$_3$ as an eluent.

3.2. ^{i}Pr$_2$NP-bridged naphthalene (3a)

^{n}BuLi (10.9 mL, 17.33 mmol, 1.59 M hexane solution) and ether (11 mL) in a Pyrex Schlenk tube were cooled to −78 °C, and then 1-bromonaphthalene (2.0 ml, 14.4 mmol) was added. After the solution was stirred for 10 min, the solution was gradually warmed to room temperature over an hour. A precipitate of 1-lithionaphthalene formed was washed three times with hexane (50 mL), and then ^{n}BuLi (11.8 mL, 18.8 mmol) and tmeda (3.0 mL, 19.9 mmol) were added to the precipitate. The mixture was refluxed for 3 h, and cooled down to room temperature. A precipitate of 1,8-dilithionaphthalene was washed with hexane (50 mL, four times). After hexane (25 mL) was added to the residue, the mixture had been cooled to −78 °C, and then PCl$_2$N^{i}Pr$_2$ (2.7 mL, 14.3 mmol) was added. The mixture was gradually warmed to room temperature with stirring overnight. A dark red solution thus obtained was filtered with celite, and the residue on the celite was washed with hexane (50 mL, four times). The washings were added to the filtrate, and all volatiles were removed under a reduced pressure. The residue dissolved in hexane was passed through an Al$_2$O$_3$ column to give 2.57 g of a crude product after workup. Further purification with a preparative-scale GPC equipment gave **3a** (2.05 g, 55%) as a white powder. ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 1.18$ (d, $^3J_{HH} = 6.6$ Hz, 12H, CHMe_2), 3.29 (m, 2H, CHMe$_2$), 7.42 (d, $^3J_{HH} = 6.6$ Hz, 2H, Naph), 7.52 (m, 2H, Naph), 7.70 (d, $^3J_{HH} = 8.2$ Hz, 2H, Naph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 23.8$ (d, $J_{CP} = 8$ Hz, CHMe_2), 47.6 (d, $J_{CP} = 7$ Hz, CHMe$_2$), 122.5 (d, $J_{CP} = 4$ Hz, Naph), 123.8 (s, Naph), 127.5 (d, $J_{CP} = 2$ Hz, Naph), 129.4 (d, $J_{CP} = 2$ Hz, Naph), 147.16 (d, $J_{CP} = 17$ Hz, Naph), 147.17 (d, $J_{CP} = 16$ Hz, Naph). ^{31}P{^{1}H} NMR (121.45 MHz,

CDCl$_3$): $\delta = 94.9$. Anal. Calc. for C$_{16}$H$_{20}$NP: C, 74.68; H, 7.83; N, 5.44. Found: C, 74.50; H, 7.86; N, 5.39%.

3.3. Et$_2$NP-bridged naphthalene (3b)

To 1,8-dilithionaphthalene prepared from ^{n}BuLi (5.5 mL, 8.7 mmol, 1.59 M hexane solution) and 1-bromo-naphthalene (1.0 mL, 7.2 mmol) was added hexane (30 mL). After the mixture had been cooled to −78 °C, PCl$_2$NEt$_2$ (1.0 mL, 6.9 mmol) was added. The mixture was gradually warmed to room temperature with stirring overnight. A dark red solution thus obtained was filtered with celite, and the residue on the celite was washed with hexane (20 mL, three times). The washings were combined with the filtrate, and all volatiles were removed under a reduced pressure. The residual dark orange oil dissolved in hexane was passed through an Al$_2$O$_3$ column to give an air-sensitive white powder **3b** (0.394 g, 25%). ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 1.06$ (t, $^3J_{HH} = 7.0$ Hz, 6H, CH$_2$CH_3), 3.05 (dq, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 9.3$ Hz, 4H, CH_2CH$_3$), 7.46 (d, $^3J_{HH} = 6.4$ Hz, 2H, Naph), 7.53 (dq, $^3J_{HH} = 6.4$ Hz, $^3J_{HH} = 8.1$ Hz, $J_{HH} = 2.9$ Hz, 2H, Naph), 7.73 (d, $^3J_{HH} = 8.1$ Hz, 2H, Naph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 15.1$ (d, $J_{CP} = 4$ Hz, CH$_2$CH_3), 44.5 (d, $J_{CP} = 14$ Hz, CH$_2$CH$_3$), 122.8 (d, $J_{CP} = 5$ Hz, Naph), 124.1 (s, Naph), 127.8 (d, $J_{CP} = 2$ Hz, Naph), 129.3 (d, $J_{CP} = 3$ Hz, Naph), 146.7 (d, $J_{CP} = 16$ Hz, Naph), 147.0 (d, $J_{CP} = 16$ Hz, Naph). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 113.4$. Anal. Calc. for C$_{14}$H$_{16}$NP: C, 73.35; H, 7.03; N, 6.11. Found: C, 72.94; H, 7.06; N, 6.09%.

3.4. BH$_3$ adduct of ^{i}Pr$_2$NP-bridged naphthalene (4)

Compound **3a** (0.093 g, 0.36 mmol) was dissolved in THF (5 mL), and then BH$_3$ (0.48 mL, 0.54 mmol, 1.13 M THF solution) was added. After stirring for 2 h, all volatiles were removed under a reduced pressure to give the product **4** (0.095 g, 97%). ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 0.50$–1.70 (br, BH$_3$), 1.20 (d, $^3J_{HH} = 6.9$ Hz, 12H, CHMe_2), 3.78 (dsep, $^3J_{HP} = 14.4$ Hz, $^3J_{HH} = 6.9$ Hz, 2H, CHMe$_2$), 7.55–7.66 (m, 4H, Naph), 7.84 (ddd, $J = 1.3$ Hz, $J = 3.1$ Hz, $J = 7.7$ Hz, 2H, Naph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 23.0$ (d, $J_{CP} = 3$ Hz, CHMe_2), 49.7 (d, $J_{CP} = 5$ Hz, CHMe$_2$), 122.8 (d, $J_{CP} = 1$ Hz, Naph), 125.9 (d, $J_{CP} = 3$ Hz, Naph), 128.2 (d, $J_{CP} = 12$ Hz, Naph), 130.1 (d, $J_{CP} = 10$ Hz, Naph), 145.5 (d, $J_{CP} = 59$ Hz, Naph), 145.7 (d, $J_{CP} = 7$ Hz, Naph). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 104.4$.

3.5. Sulfur adduct of ^{i}Pr$_2$NP-bridged naphthalene (5)

Compound **3a** (0.127 g, 0.49 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL), and then S$_8$ (0.040 g, 0.16 mmol) was added. After stirring for 3 h, the solution was passed through a silica gel column, and the solvent was removed under a reduced pressure. The crude product (0.082 g,

57%) thus obtained was further purified with a preparative-scale GPC equipment. ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 1.29$ (d, $^3J_{HH} = 6.9$ Hz, 12H, CHMe_2), 3.80 (dsep, $^3J_{HP} = 18.2$ Hz, $^3J_{HH} = 6.9$ Hz, 2H, CHMe$_2$), 7.50–7.68 (m, 4H, Naph), 7.83 (ddd, $J = 0.8$ Hz, $J = 4.7$ Hz, $J = 7.9$ Hz, 2H, Naph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 22.9$ (d, $J_{CP} = 3$ Hz, CHMe_2), 48.7 (d, $J_{CP} = 5$ Hz, CHMe$_2$), 120.4 (s, Naph), 125.9 (d, $J_{CP} = 4$ Hz, Naph), 129.0 (d, $J_{CP} = 20$ Hz, Naph), 130.2 (d, $J_{CP} = 14$ Hz, Naph), 145.6 (d, $J_{CP} = 11$ Hz, Naph), 150.9 (d, $J_{CP} = 95$ Hz, Naph). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 78.0$.

3.6. Methyltriflate adduct of ^{i}Pr$_2$NP-bridged naphthalene (6)

Compound **3a** (0.354 g, 1.38 mmol) was dissolved in toluene (5 mL), and then methyltriflate (0.20 mL, 1.77 mmol) was added. After stirring for 1 h, all volatiles were removed under a reduced pressure to give the product (0.588 g, quant.). ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 1.30$ (d, $^3J_{HH} = 6.8$ Hz, 12H, CHMe_2), 2.70 (d, $^3J_{HP} = 13.5$ Hz, 3H, PMe), 3.97 (dsep, $^3J_{HP} = 17.5$ Hz, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 7.83 (dt, $J = 6.9$ Hz, $J = 8.4$ Hz, 2H, Naph), 8.08 (dd, $J = 5.0$ Hz, $J = 6.8$ Hz, 2H, Naph), 8.11 (d, $J = 6.2$ Hz, 2H, Naph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 14.5$ (d, $J_{CP} = 55$ Hz, PMe), 22.6 (d, $J_{CP} = 3$ Hz, CHMe_2), 50.6 (d, $J_{CP} = 3$ Hz, CHMe$_2$), 126.6 (s, Naph), 128.0 (d, $J_{CP} = 19$ Hz, Naph), 129.1 (d, $J_{CP} = 4$ Hz, Naph), 131.7 (d, $J_{CP} = 14$ Hz, Naph), 137.8 (d, $J_{CP} = 96$ Hz, Naph), 146.8 (d, $J_{CP} = 10$ Hz, Naph). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 69.3$.

3.7. W(CO)$_5$ adduct of ^{i}Pr$_2$NP-bridged naphthalene (7)

W(CO)$_6$ (0.517 g, 1.47 mmol) and THF (100 mL) in a Pyrex Schlenk tube were irradiated with a 400 W mercury arc lamp at 0 °C for 3 h, and then **3a** (0.338 g, 1.31 mmol) was added. After stirring for 2 h, THF was removed under a reduced pressure, and then the residue dissolved in hexane was passed through an Al$_2$O$_3$ column. The effluent was dried under a reduced pressure to give **7** as a white powder (0.711 g, 93%). ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 1.19$ (d, $^3J_{HH} = 6.8$ Hz, 12H, CHMe_2), 4.13 (sep, $^3J_{HH} = 6.8$ Hz, 2H, CHMe$_2$), 7.52–7.64 (m, 4H, Naph), 7.80 (m, 2H, Naph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 23.3$ (d, $J_{CP} = 4$ Hz, CHMe_2), 52.2 (d, $J_{CP} = 7$ Hz, CHMe$_2$), 121.3 (d, $J_{CP} = 2$ Hz, Naph), 125.6 (d, $J_{CP} = 3$ Hz, Naph), 128.9 (d, $J_{CP} = 10$ Hz, Naph), 129.5 (d, $J_{CP} = 9$ Hz, Naph), 142.2 (d, $J_{CP} = 9$ Hz, Naph), 150.7 (d, $J_{CP} = 42$ Hz, Naph), 196.7 (d, $J_{CP} = 6$ Hz, $J_{CW} = 126$ Hz, *cis*-CO), 200.1 (d, $J_{CP} = 26$ Hz, $J_{CW} = 144$ Hz, *trans*-CO). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 95.9$ ($J_{PW} = 254$ Hz). IR (THF) νCO 1941 cm^{-1}. Anal. Calc. for C$_{21}$H$_{20}$NO$_5$PW: C, 43.40; H, 3.47; N, 2.41. Found: C, 43.26; H, 3.24; N, 2.22%.

3.8. ^{i}Pr$_2$N-dibenzophosphole (8)

A powder of 2,2′-dibromobiphenyl (0.346 g, 1.11 mmol) was put in a Pyrex Schlenk tube, to which ether (3 mL) and ^{n}BuLi (1.6 mL, 2.53 mmol, 1.59 M hexane solution) were added. After the solution was stirred for 45 min, it was transferred to an ether (3 mL) solution of PCl$_2$N^{i}Pr$_2$ (0.20 mL, 1.09 mmol) in another Schlenk tube at −10 °C. After the solution was gradually warmed to room temperature with stirring overnight, it was filtered, and the residue on the filter was washed twice with ether (25 mL). The washings were combined with the filtrate, and the volume was reduced under a reduced pressure to give a precipitate, which was washed with ether (5 mL). After workup, crude **8** (0.290 g, 94%) was obtained as a white powder, which was recrystallized from CH$_2$Cl$_2$/hexane at −10 °C. ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 0.83$ (br, 6H, CHMe_2), 1.42 (br, 62H, CHMe_2), 2.55 (br, 1H, CHMe$_2$), 3.32 (br, 1H, CHMe$_2$), 7.30 (ddt, $J = 1.1$ Hz, $J = 2.8$ Hz, $J = 7.4$ Hz, 2H, biph), 7.40 (tt, $J = 1.0$ Hz, $J = 7.3$ Hz, 2H, biph), 7.69 (dddd, $J = 0.7$ Hz, $J = 1.2$ Hz, $J = 4.4$ Hz, $J = 7.2$ Hz, 2H, biph), 7.84 (qd, $J = 1.0$ Hz, $J = 7.7$ Hz, 2H, biph). ^{13}C{^{1}H} NMR (75.45 MHz, CDCl$_3$): $\delta = 22.5$ (br, CHMe_2), 26.4 (br, CHMe_2), 43.2 (br, CHMe$_2$), 51.7 (br, CHMe$_2$), 120.9 (s, biph), 127.0 (ds, $J_{CP} = 6$ Hz, biph), 128.6 (s, biph), 130.0 (d, $J_{CP} = 7$ Hz, biph), 142.1 (d, $J_{CP} = 7$ Hz, biph), 143.5 (d, $J_{CP} = 3$ Hz, biph). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 32.2$. Anal. Calc. for C$_{18}$H$_{22}$NP: C, 74.30; H, 7.83; N, 4.94. Found: C, 76.03; H, 8.10; N, 4.96%.

3.9. (OC)$_5$W(μ-^{i}Pr$_2$NPnaph)Pt(CO)(PPh$_3$) (9)

The complex **9** was prepared according to our previous report [7]. ^{1}H NMR (300.4 MHz, CDCl$_3$): $\delta = 1.20$ (d, $^3J_{HH} = 6.6$ Hz, 6H, CHMe_2), 1.35 (d, $^3J_{HH} = 6.8$ Hz, 6H, CHMe_2), 4.25 (m, 2H, CHMe$_2$), 6.77 (m, 1H, Naph), 7.30–7.60 (m, 13H, Naph and Ph), 7.73 (m, 6H, Naph and Ph), 7.87 (m, 1H, Naph). ^{13}C{^{1}H} NMR (125.4 MHz, CDCl$_3$): $\delta = 24.3$ (br, CHMe_2), 24.8 (br, CHMe_2), 53.5 (br, CHMe$_2$), 125.4 (d, $J_{CP} = 9$ Hz, Naph), 125.5 (d, $J_{CP} = 4$ Hz, Naph), 126.6 (s, Naph), 128.5 (s, Naph), 128.8 (d, $J_{CP} = 10$ Hz, Ph), 128.9 (m, Naph), 131.3 (d, $J_{CP} = 2$ Hz, Ph), 131.6 (d, $J_{CP} = 45$ Hz, Ph), 133.0 (d, $J_{CP} = 11$ Hz, Naph), 133.1 (d, $J_{CP} = 6$ Hz, Naph), 134.7 (d, $J_{CP} = 12$ Hz, Ph), 142.2 (d, $J_{CP} = 16$ Hz, Naph), 154.6 (d, $J_{CP} = 8$ Hz, Naph), 157.2 (d, $J_{CP} = 28$ Hz, Naph), 181.2 (t, $J_{CP} = 7$ Hz, Pt–CO), 198.3 (d, $J_{CP} = 7$ Hz, $J_{CW} = 127$ Hz, *cis*-W–CO), 201.8 (d, $J_{CP} = 19$ Hz, *trans*-W–CO). ^{31}P{^{1}H} NMR (121.45 MHz, CDCl$_3$): $\delta = 22.3$ (d, $^2J_{PP} = 225$ Hz, $^1J_{PPt} = 1736$ Hz, PPh$_3$), 75.2 (d, $^2J_{PP} = 225$ Hz, $^1J_{PPt} = 1660$ Hz, $^1J_{PW} = 225$ Hz). IR (CH$_2$Cl$_2$) ν CO 1926, 1972, 2060, 2074 cm^{-1}. Anal. Calc. for C$_{40}$H$_{35}$NO$_6$P$_2$PtW · Et$_2$O: C, 46.33; H, 3.98; N, 1.23. Found: C, 46.12; H, 3.77; N, 1.22%.

3.10. $(OC)_5W(\mu\text{-}^iPr_2NPnaph)Pt(CO)(PEt_3)$ (10)

Compound **9** (480 mg, 0.45 mmol) was dissolved in CH_2Cl_2 (5 mL). An excess amount of PEt_3 (0.78 mL, 5.2 mmol) was added to the solution. After stirring for 0.5 h, all volatiles were removed under reduced pressure, and then the residue was loaded to an Al_2O_3 column followed by elution with CH_2Cl_2/hexane (1/2). The complex thus separated from PPh_3 was recrystallized from CH_2Cl_2/hexane to give a pale yellow powder (380 mg, 92%). ^1H NMR (300.4 MHz, $CDCl_3$): $\delta = 1.09$ (d, $^3J_{HH} = 6.7$ Hz, 6H, $CHMe_2$), 1.18 (d, $^3J_{HH} = 7.6$ Hz, $^3J_{HP} = 16.9$ Hz, 9H, CH_2Me), 1.31 (d, $^3J_{HH} = 6.7$ Hz, 6H, $CHMe_2$), 2.18 (m, 6H, CH_2Me), 4.19 (m, 2H, $CHMe_2$), 7.29 (m, 1H, Naph), 7.48 (dt, $J = 2.3$ Hz, $J = 7.6$ Hz, 1H, Naph), 7.59 (d, $J = 8.0$ Hz, 1H, Naph), 7.66 (d, $J = 8.1$ Hz, 1H, Naph), 7.75 (d, $J = 7.0$ Hz, 1H, Naph), 7.80 (d, $J = 6.9$ Hz, $J = 10.2$ Hz, 1H, Naph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta = 8.7$ (s, $J_{CPt} = 17$ Hz, CH_2Me), 17.6 (d, $J_{CP} = 26$ Hz, $J_{CPt} = 17$ Hz, CH_2Me), 24.2 (s, $CHMe_2$), 24.9 (d, $J_{CP} = 3$ Hz, $CHMe_2$), 53.4 (br, $CHMe_2$), 125.6 (d, $J_{CP} = 3$ Hz, $J_{CPt} = 62$ Hz, Naph), 125.7 (d, $J_{CP} = 9$ Hz, Naph), 127.0 (s, Naph), 128.3 (s, $J_{CPt} = 11$ Hz, Naph), 129.0 (dd, $J_{CP} = 9$ Hz, $J_{CP} = 4$ Hz, Naph), 133.2 (d, $J_{CP} = 11$ Hz, Naph), 133.7 (d, $J_{CP} = 19$ Hz, Naph), 137.5 (d, $J_{CP} = 14$ Hz, $J_{CPt} = 38$ Hz, Naph), 156.1 (d, $J_{CP} = 8$ Hz, Naph), 157.7 (d, $J_{CP} = 25$ Hz, Naph), 182.0 (dd, $J_{CP} = 7$ Hz, $J_{CP} = 9$ Hz, Pt–CO), 198.4 (d, $J_{CP} = 5$ Hz, $J_{CPt} = 16$ Hz, $J_{CW} = 127$ Hz, cis-W–CO), 202.0 (d, $J_{CP} = 18$ Hz, trans-W–CO). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$): $\delta = 13.5$ (d, $^2J_{PP} = 227$ Hz, $^1J_{PPt} = 1708$ Hz, PEt_3), 72.0 (d, $^2J_{PP} = 227$ Hz, $^1J_{PPt} = 1627$ Hz, $^1J_{PW} = 221$ Hz). IR (THF) νCO 1920, 1932, 2055, 2064 cm^{-1}. Anal. Calc. for $C_{28}H_{35}NO_6P_2PtW$: C, 36.46; H, 3.82; N, 1.52. Found: C, 36.49; H, 3.67; N, 1.50%.

3.11. $(OC)_5W(\mu\text{-}^iPr_2NPnaph)Pt(dppe)$ (11)

Compound **9** (80 mg, 0.075 mmol), dppe (35 mg, 0.087 mmol) and toluene (10 mL) were put in a Schlenk tube, and then the solution was heated at 55 °C for 4 h. After the solvent was removed under a reduced pressure, the residue was recrystallized from CH_2Cl_2/hexane. The precipitate was washed with hexane (30 mL) three times and dried to give a white powder (70 mg, 80%). ^1H NMR (300.4 MHz, $CDCl_3$): $\delta = 0.85$ (d, $^3J_{HH} = 7.1$ Hz, 6H, $CHMe_2$), 1.17 (br, 6H, $CHMe_2$), 1.27 (m, 1H, CH_2), 2.30–2.90 (m, 3H, CH_2), 4.42 (m, 2H, $CHMe_2$), 6.76 (m, 1H, Naph), 7.10–8.10 (m, 20H, Naph and Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): $\delta = 25.3$ (d, $J_{CP} = 3$ Hz, $CHMe_2$), 25.7 (d, $J_{CP} = 2$ Hz, $CHMe_2$), 26.6 (dd, $J_{CP} = 21$ Hz, $J_{CP} = 32$ Hz, CH_2), 31.0 (dd, $J_{CP} = 20$ Hz, $J_{CP} = 32$ Hz, CH_2), 57.7 (br, $CHMe_2$), 124.9 (d, $J_{CP} = 8$ Hz), 125.2 (s), 125.9 (m), 127.3 (s), 128.1 (m), 128.4 (s), 128.6 (s), 128.8 (d, $J_{CP} = 3$ Hz), 128.9 (s), 129.0 (d, $J_{CP} = 6$ Hz), 130.4 (s), 130.6 (s), 131.5 (s), 132.8 (d, $J_{CP} = 10$ Hz), 133.3 (d, $J_{CP} = 10$ Hz), 135.5 (d,

$J_{CP} = 13$ Hz), 135.6 (d, $J_{CP} = 13$ Hz), 140.8 (d, $J_{CP} = 20$ Hz), 156.3 (d, $J_{CP} = 6$ Hz), 157.7 (d, $J_{CP} = 7$ Hz), 198.8 (d, $J_{CP} = 5$ Hz, $J_{CPt} = 15$ Hz, $J_{CW} = 127$ Hz, cis-W–CO), 201.9 (d, $J_{CP} = 16$ Hz, trans-W–CO). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$): $\delta = 30.8$ (dd, $^2J_{PP} = 4$ Hz, $^2J_{PP} = 9$ Hz, $^1J_{PPt} = 1940$ Hz, dppe), 35.8 (dd, $^2J_{PP} = 3$ Hz, $^2J_{PP} = 289$ Hz, $^1J_{PPt} = 1932$ Hz, dppe), 111.9 (dd, $^2J_{PP} = 9$ Hz, $^2J_{PP} = 283$ Hz, $^1J_{PPt} = 2161$ Hz, $^1J_{PW} = 218$ Hz). IR (toluene) νCO 1910, 1930, 2057 cm^{-1}. Anal. Calc. for $C_{47}H_{44}NO_5P_3PtW$: C, 48.06; H, 3.78; N, 1.19. Found: C, 47.92; H, 3.74; N, 1.09%.

3.12. Crystallographic study

Suitable crystals of **3b**, **4–9** were mounted separately on a glass fiber. All measurements for **3b**, **4–6**, **8**, and **9** were made on a Mac Science DIP2030 imaging plate area detector, while those for **7** was made on Mac Science MXC3κ. The data were collected to a maximum 2θ value of 55°. Cell parameters and intensities for the reflection were estimated using the program packages of HKL for **3b**, **4–6**, **8**, and **9**, and crystan for **7** [18]. The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions for **3b**, **7**, and **9**, while those for the other crystals were located on the basis of difference Fourier maps and refined isotropically. All calculations were performed using a SHELXL-97 crystallographic software package [19]. Details of data collection and refinement were listed in Table 1, and bond distances and angles, atomic coordinates, and anisotropic thermal parameters were given as Supplementary information.

Appendix A. Supplementary material

Crystallographic Information has been deposited with Cambridge Crystallographic Data Center, CCDC Nos. 299676–299682 for **3b**, and **4–9**, respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.057.

References

[1] R.W. Hoffmann, W. Sieber, Angew. Chem. 77 (1965) 810–811;
R.W. Hoffmann, W. Sieber, Angew. Chem., Int. Ed. Engl. 4 (1965) 786.

[2] (a) A. Hergel, H. Pritzkow, W. Siebert, Angew. Chem. 106 (1994) 1342–1343;
(aa) A. Hergel, H. Pritzkow, W. Siebert, Angew. Chem., Int. Ed. Engl. 33 (1994) 1247–1248;
(b) J.D. Hoefelmeyer, F.P. Gabbaï, Organometallics 21 (2002) 982–985.

[3] (a) A. Kumar, F.E. Friedli, L. Hsu, P.J. Card, N. Mathur, H. Shechter, J. Org. Chem. 56 (1991) 1663–1666, and references therein;
(b) L.S. Yang, H. Shechter, J. Chem. Soc., Chem. Comm. (1976) 775;
(c) J. Ohshita, K. Matsushige, A. Kunai, A. Adachi, K. Sakamaki, K. Okita, Organometallics 19 (2000) 5582–5588;
(d) M.A.G.M. Tinga, G.J.H. Buisman, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, A.L. Spek, J. Organomet. Chem. 484 (1994) 137–145.

[4] (a) J. Meinwald, S. Knapp, J. Am. Chem. Soc. 96 (1974) 6532–6534;
(b) J. Meinwald, S. Knapp, S.K. Obendorf, R.E. Hughes, J. Am. Chem. Soc. 98 (1976) 6643–6649.

[5] A triphosphazene-bridged naphthalene characterized insufficiently was reported M.B. Sayed, Thermochim. Acta 232 (1994) 249–260.

[6] For a recent review, see A. Marinetti, D. Carmichael, Chem. Rev. 102 (2002) 201–230.

[7] T. Mizuta, T. Nakazono, K. Miyoshi, Angew. Chem., Int. Ed. 41 (2002) 3897–3898.

[8] (a) R.L. Letsinger, J.A. Gilpin, W.J. Vullo, J. Org. Chem. 27 (1962) 672–674;
(b) L. Brandsma, H.D. VerkruijssePreparative Polar Organometallic Chemistry, vol. 1, Springer-Verlag, Berlin, 1987, pp. 195–197.

[9] P.W. Dyer, J. Fawcett, M.J. Hanton, R.D.W. Kemmitt, R. Padda, N. Singh, Dalton Trans. (2003) 104–113.

[10] D.B. Chesnutt, L.D. Quin, S.B. Wild, Heteroat. Chem. 8 (1997) 451.

[11] T. Mizuta, S. Kunikata, K. Miyoshi, J. Organomet. Chem. 689 (2004) 2624–2632.

[12] (a) P.E. Baskakova, A.V. Belyakov, A. Haaland, H.V. Volden, J. Mol. Struct. 567–568 (2001) 197–202;
(b) A.V. Belyakov, A. Haaland, D.J. Shorokhov, V.I. Sokolov, O. Swang, J. Mol. Struct. 445 (1998) 303–309;
(c) N.W. Mitzel, B.A. Smart, K.-H. Dreihäupl, D.W.H. Rankin, H. Schmidbaur, J. Am. Chem. Soc. 118 (1996) 12673–12682;
(d) D.G. Gilheany, Chem. Rev. 94 (1994) 1339–1374.

[13] (a) T.S. Cameron, C. Chan, W.J. Chute, Acta Crystallogr., Sect. B B36 (1980) 2391–2393;
(b) J. Emsley, D. Hall, The Chemistry of Phosphorus, Harper & Row, London, UK, 1976, pp. 34–38.

[14] T. Mizuta, M. Onishi, T. Nakazono, H. Nakazawa, K. Miyoshi, Organometallics 21 (2002) 717–726.

[15] (a) D. Carmichael, P.B. Hitchcock, J.F. Nixon, F. Mathey, A. Pidcock, J. Chem. Soc., Chem. Commun. (1986) 762;
(b) D. Carmichael, P.B. Hitchcock, J.F. Nixon, F. Mathey, L. Ricard, J. Chem. Soc., Chem. Commun. (1989) 1389;
(c) F. Mathey, Chem. Rev. 90 (1990) 997;
(d) S.S.A. Juaid, D. Carmichael, P.B. Hitchcock, A. Marinetti, F. Mathey, J.F. Nixon, J. Chem. Soc., Dalton Trans. (1991) 905;
(e) D. Carmichael, P.B. Hitchcock, J.F. Nixon, F. Mathey, L. Ricard, J. Chem. Soc., Dalton Trans. (1993) 1811.

[16] R.J. Cross, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Pergamon Press, Oxford, UK, 1995, pp. 405–409.

[17] G.P.M. van Klink, H.J.R. de Boer, G. Schat, O.S. Akkerman, F. Bickelhaupt, A.L. Spek, Organometallics 21 (2002) 2119–2135.

[18] Z. Otwinowski, W. Minor, in: C.W. CarterJr., R.M. Sweet (Eds.), Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, 1997, pp. 307–326.

[19] G.M. Scheldrick, SHELX-97: Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1997.