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# Synthesis of rhodium–carbonyl complexes bearing a novel P,N-chelating ligand of Schiff-base type

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#### ABSTRACT

Schiff-base type N,P-chelating ligands, phosphorus analogues of imino–anilido ligands, were designed and synthesized as a new type of ligands toward transition metals, and the rhodium–carbonyl complexes bearing the novel imino–phosphido and phosphaalkenyl-anilido ligands were synthesized as stable crystalline compounds. Their structures were definitively revealed by X-ray crystallographic analysis, showing the unique electronic features of the ligands. In addition, the effective *trans*-influence of the phosphorus atom was suggested on the basis of the structural parameters and spectroscopic features of the isolated complexes.

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#### 1. Introduction

Schiff-base type N,N'-chelating ligands such as  $\beta$ -diketiminato and imino–anilido ligands (Scheme 1) have been utilized for the stabilization of unique species of transition metals and main group elements [1]. Thus, the coordination chemistry of the Schiff-base ligands has attracted much interest in the research field of not only fundamental chemistry but also industrial chemistry from the viewpoints of supporting ligands of the catalysts for olefin polymerization [2]. The features of the  $\beta$ -diketiminato and imino–anilido ligands can be mentioned as follows: (i) facile preparation, (ii) strong coordination ability to the central atom in a monovalent and bidentate fashion, (iii) steric effect afforded by the substituents on the nitrogen atoms, (iv) electronic effect due to the  $\pi$ -electron conjugation in the cyclic skeleton of the resulting complexes.

On the other hand, the coordination chemistry of low-coordinated organophosphorus compounds has drawn a great deal of recent attention due to their unique electronic features, i.e., the characteristic low-lying  $\pi^*$ -orbital level [3]. Generally, low-coordinated organophosphorus compounds are highly reactive toward oxygen and moisture and difficult to be handled under ambient conditions due to their extremely high reactivity toward self-oligomerization. However, several numbers of low-coordinated organophosphorus compounds such as phosphaalkenes (P=C) and diphosphenes (P=P) have been synthesized and isolated as stable compounds by taking advantage of kinetic stabilization using bulky substituents [4], since the isolation of stable phosphaalkenes [5,6]. Recently, such low-coordinated organophosphorus compounds should be one of the exciting research targets as new promising ligands toward transition metals in catalytic chemistry [3], since the low-coordinated phosphorus species exhibit low-lying  $\pi^*$ -orbital level showing strong  $\pi$ -electron accepting character with effective *trans*-effect.

Recently, we have designed a novel β-ketophosphenato ligand, which is a heavier congener of β-ketiminato ligand, as a monovalent and bidentate ligand bearing an extremely bulky steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) group, on the phosphorus atom (Scheme 2) [7]. It was demonstrated that the rhodium complex 2 coordinated with the β-ketophosphenato ligand was synthesized as a stable crystalline compound, showing strong trans-influence and trans-effect of the sp<sup>2</sup>-hybridized phosphorus atom. Now, much attention has been focused on the heavier element analogue of β-diketiminato and imino-anilido ligands due to their expected features reflecting the unique characters of both  $\beta$ -diketiminate-type skeleton and low-coordinated organophosphorus compounds (Scheme 1). While the complexation of an iminophospholido ligand with copper is known to give a unique cluster complex, the iminophospholido ligand did not work as a monovalent and bidentate ligand [8]. Although Mindiola et al. have postulated the existence of an intermediary titanium complex 3 bearing a P,N-chelating Schiff-base ligand (Scheme 3) [9], there has been no example for the isolation of a transition metal complex bearing such phosphorus analogue of a β-diketiminato ligand [10]. On the other hand, Ionkin et al. have reported the attempted synthesis of a phosphorus analogue of β-diketiminate 6 bearing 2,4,6-tri-tert-butylphenyl (denoted as Mes) group [11]. However, it was suggested that 6 undergoes ready intramolecular cyclization to afford 1H-[1,2]diphosphole derivative **5** along with the elimination of Mes<sup>H</sup> (Scheme 3). Taking this





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report into consideration, the more strained  $\beta$ -iminophosphido skeleton fused with a benzene ring may be helpful to avoid such intramolecular cyclization. Thus, we have designed benzo-fused P,N-chelating ligand **7** as a phosphorus analogue of a Schiff-base ligand (Scheme 4). In this case, however, the reaction of **9** with KH as a base afforded the corresponding 2-phospha-2*H*-isoindole **10** along with the elimination of Mes<sup>\*</sup> H (Scheme 5) [12].

In this paper, we report the synthesis of novel rhodium–carbonyl complexes **11** and **13**, which are isomeric complexes bearing different types of phosphorus analogues of Schiff-base ligands **7** and **8**, respectively, as stable crystalline compounds (Scheme 6). Their structures and properties were revealed on the basis of spectroscopic and X-ray crystallographic analyses, indicating the *trans*influence of the low-coordinated phosphorus atoms.



Schiff-base type N,P-chelating ligands

Scheme 4.



Scheme 5.





Scheme 6.

#### 2. Results and discussion

Two types of novel ligands 7 and 8 were designed as phosphorus analogues of Schiff-base type ligands, and we prepared **9** and 12 as their precursors. Since such secondary phosphine and phosphaalkene derivatives should have high liability to oxidation and self-oligomerization, bulky Mes group should be introduced on the phosphorus atom for the steric protection. Compound 9 was prepared according to the previously reported procedures [12]. Similarly, compound **12** was synthesized as shown in Scheme 7. The structures of **9** and **12** were reasonably supported by the spectroscopic and X-ray crystallographic analyses Figs. 1 and 2. Both 9 and 12 exhibit high planarity of the skeleton consisting of the central P, N, C atoms, the fused aromatic ring, and ipso-carbon atoms of Mes<sup>\*</sup> and Dip (2,6-diisopropylphenyl) groups. While the position of the hydrogen atom of the NH and PH moieties cannot be definitively determined due to the inherent principle of X-ray crystallographic analysis, the N=C moiety of 9 and the P=C moiety of 12 are oriented toward the PH and NH moieties, respectively, indicating the existence of weak N-H-P hydrogen bonding. The P-C1 and N=C3 bond lengths of **9** [1.8440(18) and 1.265(2) Å, respectively] are similar to those of typical P-C and N=C bond lengths and suggest little contribution of the resonance structure **9B** with effective  $\pi$ -conjugation shown in Scheme 8. Similarly, phosphaalkenvlamine 12 dominantly exhibit the canonical structure of 12A (Scheme 8) on the basis of its P=C3 and N-C1 bond lengths [1.687(2) and 1.372(3) Å, respectively], which are similar to those of (E)–Mes<sup>P</sup>=CHPh [1.660(6) Å] [13] and typical diarylamines.

In the <sup>31</sup>P NMR spectrum, compound **9** showed  $\delta_P = -62.7$  in the high field region similar to those of secondary phosphines. In the <sup>1</sup>H NMR spectrum of **9**, a characteristic doublet signal due to the P–H moiety was observed at 6.51 ppm with <sup>1</sup>J<sub>PH</sub> = 258.3 Hz, which is relatively low-field shifted as compared with those of diaryl-phosphines (around 5 ppm) [14], indicating the weak P–H–N hydrogen bonding. The signal due to the N=CH moiety was observed at  $\delta_H$  = 8.53 as a doublet signal with <sup>4</sup>J<sub>PH</sub> = 1.6 Hz. On the other hand, **12** showed a characteristically low-field shifted signal of  $\delta_P$  = 241.2 in the <sup>31</sup>P NMR spectrum, supporting the sp<sup>2</sup>-hybrid-



**Fig. 1.** Molecular structure of **9**. Displacement ellipsoids were drawn at the 50% level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): P-C1, 1.8440(18); P-C(Mes<sup>\*</sup>), 1.8475(7); N-C3, 1.265(2), N-C(Dip), 1.428(2); C1-C2, 1.417(2); C2-C3, 1.465(2); (Mes<sup>\*</sup>)C-P-C1, 100.33(7); P-C1-C2, 121.37(12); C1-C2-C3, 123.37(15); C2-C3-N, 123.45(15); C3-N-C(Dip), 119.36(14).

ized phosphorus atom with the P=C double bond character. In the <sup>1</sup>H NMR spectrum of **12**, the signal due to the P=CH moiety was observed at  $\delta_{\rm H}$  = 8.53 as a doublet signal with <sup>2</sup>*J*<sub>PH</sub> = 23.7 Hz, which is similar to that of (E)-Mes<sup>\*</sup>P=CHPh [the chemical shift of P=CH moiety is  $\delta_{\rm H}$  = 8.12 with <sup>2</sup>*J*<sub>PH</sub> = 25.3 Hz] [15]. Interestingly, the N-H proton of **12** was observed at  $\delta_{\rm H}$  = 6.93, which is in lower field than that of diphenylamine (ca. 5.6 ppm) [16], as a doublet signal with the coupling constant of 20.7 Hz. The observed *J* coupling should be due to the through-space <sup>1</sup>*J*<sub>PH</sub> coupling of the N-H-P moiety, strongly indicating the N-H-P hydrogen bonding. Thus, the structural and spectroscopic features of **9** and **12** suggested the little contribution of their canonical structures of B type (Scheme 8) and the N-H-P hydrogen bonding with the formation of the N-H-P-C-C-C ring system.

Attempted deprotonation reactions of **9** and **12** using *n*-BuLi and LDA were unsuccessful to give a complicated mixture, while **9** was found to be inert toward KH in  $C_6H_6$  at room temperature. However, heating of  $C_6D_6$  suspension of **9** in the presence of KH at 60 °C afforded 2-phospha-2*H*-isoindole **10** along with Mes<sup>\*</sup>H



Scheme 7.



**Fig. 2.** Molecular structure of **12**. Displacement ellipsoids were drawn at the 50% level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): N–C1, 1.372(3); N–C(Dip), 1.432(3); P–C3, 1.687(2), P–C(Mes<sup>\*</sup>), 1.841(2); C1–C2, 1.425(3); C2–C3, 1.454(3); (Dip)C–N–C1, 124.49(17); N–C1–C2, 120.58(18); C1–C2–C3, 124.47(18); C2–C3–P, 129.24(16); C3–P–C(Mes<sup>\*</sup>), 102.62(9).



as described above (Scheme 5) [12]. When **9** was treated with 0.5 eq. of [RhCl(CO)<sub>2</sub>]<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> at room temperature, the reaction proceeded slowly to give an unidentified complex X, which showed a characteristic signal at  $\delta_P = -14.1$  with  ${}^{1}J_{PRh} = 164$  Hz and  ${}^{1}J_{PH} = 378$  Hz in the  ${}^{31}P$  NMR spectrum. Treatment of the reaction mixture with an excess amount of Et<sub>3</sub>N at 60 °C for 6 h afforded the rhodium–carbonyl complex **11** as a stable deep purple crystalline compound (Scheme 6). Similarly, heating of the C<sub>6</sub>H<sub>6</sub> solution of **12** with 0.5 eq. of [RhCl(CO)<sub>2</sub>]<sub>2</sub> in the presence of an excess amount of Et<sub>3</sub>N afforded the corresponding rhodium–carbonyl complex **13** as a stable purplish red crystalline compound. Rhodium complexes **11** and **13** can be handled in the air without any decomposition probably due to the steric effect afforded by Mes<sup>\*</sup> and Dip groups (Figs. 3 and 4).

The structural parameters of rhodium–carbonyl complexes **11** and **13** were revealed by the X-ray crystallographic analysis (Figs. 3–7). In the case of **11**, the P–C1 and C2–C3 bonds are shortened and the C1–C2 and C3–N bonds are elongated as compared with the corresponding bonds of **9**, suggesting the considerably delocalized  $\pi$ -electrons of the central six-membered ring skeleton of Rh–P–C–C–C–N. The sum of the internal angles of the Rh–P–C–C–C–N six-membered ring skeleton of **11** is 717°, showing its high planarity with the slightly pyramidalized phosphorus atom. The theoretically optimized structure of **11**<sub>opt</sub> [17] is similar to that of **11** with the slightly pyramidalized phosphorus atom (the sum of the internal angles of the Rh–P–C–C–C–N six–membered ring skeleton of



**Fig. 3.** Molecular structure of **11**. Displacement ellipsoids were drawn at the 50% level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): P–Rh, 2.2665(11); N–Rh, 2.080(3); Rh–C4, 1.852(4); Rh–C5, 1.943(4); C4–O1, 1.142(4); C5–O2, 1.106(4); P–C1, 1.768(3); P–C(Mes ), 1.840(3); N–C3, 1.308(4), N–C(Dip), 1.452(4); C1–C2, 1.424(4); C2–C3, 1.432(4); P–Rh–N, 89.93(7); Rh–P–C1, 116.64(10); Rh–N–C3, 132.5(2); (Mes )C–P–C1, 109.62(15); P–C1–C2, 121.6(2); C1–C2–C3, 126.2(3); C2–C3–N, 130.0(3); C3–N–C(Dip), 114.0(3).



**Fig. 4.** Molecular structure of **13**. Displacement ellipsoids were drawn at the 50% level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): P–Rh, 2.2261(12); N–Rh, 2.066(4); Rh–C4, 1.933(5); Rh–C5, 1.844(5); C4–O1, 1.131(5); C5–O2, 1.143(6); N–C1, 1.374(6); N–C(Dip), 1.450(6); P–C3, 1.666(5), P–C(Mes), 1.818(5); C1–C2, 1.435(7); C2–C3, 1.428(7); N–Rh–P, 88.29(11); Rh–N–C1, 136.6(3); Rh–P–C3, 118.91(17); (Dip)C–N–C1, 115.3(4); N–C1–C2, 124.0(4); C1–C2–C3, 125.5(4); C2–C3–P, 126.6(4); C3–P–C(Mes), 110.5(2).

11<sub>opt</sub> is 717°, Fig. 7). However, the structural optimization of the less hindered model compound  $11_{Me}$  bearing a methyl group instead of Mes<sup>®</sup> group in **11** was found to have a highly distorted structure with a phosphorus atom showing a pyramidal geometry (the sum of the internal angles of the Rh-P-C-C-C-N six-membered ring skeleton is 686°). That is, the Mes<sup>\*</sup> group of **11** should play an important role to afford the steric effect on the phosphorus atom for keeping the relatively planar geometry with sp<sup>2</sup>-hybridization and preventing the phosphorus atom from pyramidalization. On the other hand, the structural parameters of the ligand moiety of 13 are similar to those of 12, indicating the less electronic effect toward the ligand moiety by the complexation with a rhodium atom. That is, the N-C [1.374(6)Å] and P=C [1.666(5)Å] bond lengths of 13 are similar to those of 12 [N-C: 1.372(3) Å and P=C: 1.687(2) Å] in contrast to the case of **9** and 11 as described above. As in the case of 11, the central six-membered ring skeleton of Rh-P-C-C-C-N of 13 exhibits an almost planar skeleton (the sum of the internal angles of the Rh-P-C-C-C-N six-membered ring skeleton is 720°), while the theoretically optimized structure of 13<sub>opt</sub> [17] is similar to those observed by the X-ray crystallographic analysis of 13. However, the methyl-substituted model  $\mathbf{13}_{Me}$  exhibits a slightly twisted structure as in the case of 11<sub>Me</sub> (the sum of the internal angles of the Rh-P-C-C-C-N six-membered ring skeleton is 712°), suggesting the steric effect





Fig. 5. (a) Observed structure of 11. (b) Optimized structure of  $11_{opt}$  [17]. (c) Optimized structure of  $11_{Me}$  [17].

of Dip and Mes<sup>\*</sup>. In both cases of **11** and **13**, the lengths of the Rh–CO bonds located at the *trans*-position of the phosphorus atom [1.943(4) Å for **11**, 1.933(5) for **13**] are longer than those located at the *trans*-position of the nitrogen atom [1.852(4) Å for **11** and 1.844(5) Å for **13**], suggesting the effective *trans*-influence of the coordinated phosphorus atom. Thus, it should be of great note that the two carbonyl groups on the rhodium center should be in non-equivalent situation in both cases of **11** and **13**, indicating the expectation of the novel reactivity of the rhodium–carbonyl complexes. In addition, the *trans*-influence of the phosphorus atom of **11** should be slightly stronger than that of **13** on the basis of their *trans*-C=O bond lengths [1.106(4) Å for **11**, 1.131(5) Å for **13**] (Figs. 5–7).

The structural and electronic features of **11** and **13** in solution should be discussed on the basis of their NMR spectra. In <sup>31</sup>P NMR spectrum, **11** showed a surprisingly low-field shifted signal at  $\delta_P = 91.9$  with <sup>1</sup> $J_{PRh} = 122$  Hz, in contrast to those of rhodiumphosphine complexes (e.g.,  $\delta_P = 25.3$  with <sup>1</sup> $J_{PRh} = 127.3$  Hz for [RhCl(PPh<sub>3</sub>)(CO)<sub>2</sub>] (**14**)) [18], indicating the sp<sup>2</sup>-character of the phosphorus atom of **11**. On the other hand, rhodium complex **13** showed a characteristic signal at  $\delta_P = 158.6$  with <sup>1</sup> $J_{PRh} = 157$  Hz, which is in the considerably low-field region as compared with that of **14** reflecting the P=C double bond character but in a region higher than that of precursor **12**.

The larger  ${}^{1}J_{PRh}$  coupling constant of **13** ( ${}^{1}J_{PRh}$  = 157 Hz) than that of [RhCl(PPh<sub>3</sub>)(CO)<sub>2</sub>] (**14**,  ${}^{1}J_{PRh}$  = 127.3 Hz) [18] should be due to the high s-character of the P–Rh bond of **13**, which may consist of the lone-pair of the phosphorus atom. Generally, the  $\sigma$  and  $\pi$ 

Fig. 6. (a) Observed structure of 13. (b) Optimized structure of  $13_{opt}$  [17]. (c) Optimized structure of  $13_{Me}$  [17].

bonds of a phosphaalkene (RP=CR<sub>2</sub>) exhibit high p-character and its lone pair dominantly consists of 3s orbital of the phosphorus atom, since a phosphorus atom has a tendency of keeping its intrinsic configuration of valence electrons,  $(3s)^2(3p)^3$  [19]. Although the lone pair of PPh<sub>3</sub> should dominantly consist of 3s orbital of the phosphorus atom, the widened C-P-C angles than 90° due to the steric repulsion between the phenyl groups should enhance the p-character of the lone pair of PPh<sub>3</sub>. Due to the less hindered situation of the phosphorus atom of a phosphaalkene as compared with PPh<sub>3</sub>, the lone pair of a phosphaalkene exhibit higher s-character than that of PPh<sub>3</sub>. Thus, the relatively large  ${}^{1}J_{PRh}$ value of 13 should reflect the bonding properties of its P=C unit. On the other hand, the  ${}^{1}J_{PRh}$  coupling constant of **11** ( ${}^{1}J_{PRh}$  = 122 Hz) is similar to or slightly smaller than that of **14** ( ${}^{1}J_{PRh}$  = 127.3 Hz), suggesting the higher p-character of the P-Rh bond of 11 than that of **14**. That is, the P-Rh bond should consist of sp<sup>2</sup>-orbital of the phosphorus atom, suggesting that the lone pair of the phosphorus atom should exhibit high p-character and it should take part in the  $\pi$ -conjugation on the imino-phosphido ligand of **11**.

In <sup>13</sup>C NMR spectra, **11** showed two signals assignable to the carbonyl groups at  $\delta_{\rm C} = 185.7$  ( ${}^{1}J_{\rm RhC} = 62.6$  Hz,  ${}^{2}J_{\rm CP} = 97.3$  Hz) and  $\delta_{\rm C} = 191.9$  ( ${}^{1}J_{\rm RhC} = 67.1$  Hz,  ${}^{2}J_{\rm CP} = 21.9$  Hz). The former signal should be assignable to the CO group located at the *trans*-position of the phosphorus atom on the basis of the reported  ${}^{2}J_{\rm CP}$  values of [RhCl(PPh<sub>3</sub>)(CO)<sub>2</sub>] (**14**,  $\delta_{\rm C} = 183.0$ ,  ${}^{2}J_{\rm CP} = 16.3$  Hz for *cis*-CO for PPh<sub>3</sub>,  $\delta_{\rm C} = 183.3$ ,  ${}^{2}J_{\rm CP} = 123.4$  Hz for *trans*-CO for PPh<sub>3</sub>) [18]. The smaller  ${}^{1}J_{\rm RhC}$  value of the *trans*-CO for the phosphorus atom than that for the nitrogen atom should indicates the *trans*-influence of the phosphorus atom. Similarly, the  ${}^{13}$ C NMR data for the CO



	11	11 <sub>opt</sub>	11 <sub>Me</sub>	13	13 <sub>opt</sub>	13 <sub>Me</sub>
Rh–E1/Å	2.2665(11)	2.300	2.349	2.066(4)	2.111	2.088
Rh–E2/Å	2.080(3)	2.122	2.163	2.2261(12)	2.269	2.271
E1-C1/Å	1.768(3)	1.767	1.818	1.374(6)	1.367	1.359
C1–C2/Å	1.424(4)	1.431	1.424	1.435(7)	1.448	1.451
C2–C3/Å	1.432(4)	1.432	1.450	1.428(7)	1.421	1.416
C3-E2/Å	1.308(4)	1.308	1.289	1.666(5)	1.675	1.685
Rh–C4/Å	1.852(4)	1.861	1.848	1.933(5)	1.943	1.926
Rh–C5/Å	1.943(4)	1.931	1.932	1.844(5)	1.860	1.871
C4–O1/Å	1.142(4)	1.152	1.153	1.131(5)	1.146	1.149
C5–O2/Å	1.106(4)	1.150	1.151	1.143(6)	1.153	1.153
$\Sigma^*$	717°	717°	686°	720°	720°	712°

Fig. 7. Summary of observed and optimized structural parameters of **11**, **11**<sub>opt</sub>, **13**, **13**<sub>opt</sub> and **13**<sub>Me</sub> [17]. \*The sum of internal angles of the Rh–P–C–C–C–N six-membered ring skeleton.

groups of **13** were  $\delta_{\rm C}$  = 179.8 ( ${}^{1}J_{\rm RhC}$  = 65.4 Hz,  ${}^{2}J_{\rm CP}$  = 131.5 Hz, *trans*-CO for the phosphorus atom) and  $\delta_{\rm C}$  = 189.9 ( ${}^{1}J_{\rm RhC}$  = 58.1 Hz,  ${}^{2}J_{\rm CP}$  = 20.4 Hz, *cis*-CO for the phosphorus atom). The  ${}^{1}J_{\rm RhC}$  value of the *trans*-CO for the phosphorus atom is unexpectedly larger than that for the nitrogen atom, though the results of X-ray crystallographic analysis of **13** indicate the *trans*-influence of the phosphorus atom in the crystalline state. The reason for the relatively large  ${}^{1}J_{\rm RhC}$  value is not clear at present.

Preliminarily, we have performed the reaction of cyclohexenone with triethylsilane in the presence of a catalytic amount of **11** in the expectation that **11** can promote 1,4-hydrosilylation reaction even though **11** has CO groups on the rhodium atom. As a result, the treatment of cyclohexanone with 3 eq. of triethylsilane in the presence of 0.5 mol% of **11** in benzene under reflux conditions for 4 h afforded the corresponding silylenolate **17** in an almost quantitative yield (Scheme 9) [20]. Thus, it was demonstrated that **11** 



can work as a catalyst for hydrosilylation probably due to the *trans*-effect of the phosphorus atom promoting the initial elimination of the *trans*-CO group for the phosphorus atom.

#### 3. Conclusion

We have designed novel P,N-chelating monovalent and bidentate ligands with an sp<sup>2</sup>-hybridized phosphorus atom and succeeded in the synthesis of their rhodium-carbonyl complexes. The structural parameters of 11 and 13 suggested the effective trans-influence of their phosphorus atom. Interestingly, rhodium complexes 11 and 13, which are isomers to each other and bear imino-phosphido and phosphaalkenyl-anilido ligands 7 and 8, respectively, exhibited noticeable difference between their electronic properties on the basis of X-ray crystallographic and spectroscopic analyses. The preliminary demonstration using 11 toward catalytic hydrosilylation suggested that the imino-phosphido ligand 7 should be a possibly unique and attractive ligand for transition metals with strong *trans*-influence due to the sp<sup>2</sup>hybridized phosphorus atom. Further investigations on the synthesis of other transition metal complexes bearing such P,N-chelating ligands having an sp<sup>2</sup>-phosphorus atom and the catalytic reactions using **11** and **13** are currently in progress.

#### 4. Experimental

#### 4.1. General procedure

All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods and then dried by using an Ultimate Solvent System (Glass Contour Company) [21]. All solvents used in the reactions and spectroscopy were dried by using a potassium mirror. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were measured in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> with a JEOL JNM AL-300 spectrometer. Signals due to  $CHCl_3$  (7.25 ppm) and  $C_6D_5H$  (7.15 ppm) were used as references in <sup>1</sup>H NMR, and those due to CDCl<sub>3</sub> (77 ppm) and C<sub>6</sub>D<sub>6</sub> (128 ppm) were used in <sup>13</sup>C NMR. Multiplicity of signals in <sup>13</sup>C NMR spectra was determined by DEPT and CH-COSY techniques. <sup>31</sup>P NMR (120 MHz) spectra were measured in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> with JEOL AL-300 spectrometer using 86% H<sub>3</sub>PO<sub>4</sub> in water (0 ppm) as an external standard. All the P-H coupling constants were determined on the basis of both <sup>1</sup>H and non-decoupled <sup>31</sup>P NMR spectra. High resolution mass spectral data were obtained on a IEOL IMS-700 spectrometer (FAB) or a Bruker microTOF (ESI, APPI-TOF). Wet column chromatography (WCC) was performed with Wakogel C-200. All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

#### 4.1.1. Chlorophosphine **18** (Scheme 10)

To a THF solution (8 mL) of 14 (152 µL, 1.0 mmol) was added *n*-butyllithium (1.51 M hexane solution, 0.66 mL, 1.0 mmol) at -78 °C. After stirring at -78 °C for 30 min, a THF solution (8 mL) of Mes<sup>PCl<sub>2</sub></sup> (347 mg, 1.00 mmol) was added. The reaction mixture was gradually warmed up to room temperature and stirred for 3 h. After the removal of the solvent under the reduced pressure, the crude product was dissolved in hexane and then filtered through Celite<sup>®</sup>. The filtrate was purified with WCC (hexane/ether = 20/1) to afford **18** (271 mg, 0.588 mmol, 74%). **18**: pale yellow liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  1.33 (s, 9H), 1.35 (s, 18H), 3.58-3.66 (m, 2H), 3.87-3.93 (m, 2H), 4.05 (s, 1H), 7.29-7.35 (m, 2H), 7.39 (s, 2H), 7.47-7.52 (m, 1H), 7.83–7.87 (m, 1H); <sup>13</sup>C{1H} NMR (75 MHz, CDCl<sub>3</sub>, 298 K) δ 31.1 (CH<sub>3</sub>), 33.8 (CH<sub>3</sub>), 33.9 (CH<sub>3</sub>), 34.8 (C), 39.9 (C), 84.8 (CH<sub>2</sub>), 85.1 (CH<sub>2</sub>), 100.0 (CH, d,  ${}^{3}J_{PC}$  = 7.5 Hz), 124.0 (CH), 125.9 (CH), 128.7 (CH), 128.9 (CH), 131.9 (CH, d, J<sub>PC</sub> = 8.3 Hz), 138.7 (CH, d,  $J_{PC}$  = 22.5 Hz), 139.0 (C), 139.8 (C), 152.8 (C), 161.1 (C, d,  $J_{PC} = 20.3 \text{ Hz}$ ; <sup>31</sup>P{1H} NMR (120 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  77.4. High-resolution MS (ESI): m/z Calc. for C<sub>27</sub>H<sub>39</sub>O<sub>2</sub>PCI: 461.2376. Found: 461.2334 ([M+H]<sup>+</sup>).

#### 4.1.2. Diarylphosphine 19

To a diethyl ether solution (10 mL) of **18** (123 mg, 0.267 mmol) was added lithium aluminum hydride (10 mg, 0.27 mmol) at 0 °C. The reaction mixture was gradually warmed up to room temperature and stirred for 30 min. Ethyl acetate was added to the reaction mixture for quench. After removal of the solvent under the reduced pressure, the crude product was dissolved in hexane and then filtered through Celite<sup>®</sup>. The purification of the filtrate with WCC (hexane/ether = 20/1) gave **19** (98 mg, 0.23 mmol, 85%). **19**: pale vellow liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  1.38 (s, 9H), 1.42 (s, 9H), 1.51 (s, 9H), 4.09–4.24 (m, 4H), 5.86 (dd, J=4.0, 7.7 Hz, 1H), 6.12 (d, J<sub>PH</sub> = 241.6 Hz, 1H), 6.28 (d, J = 4.2 Hz, 1H), 6.97 (dpt, J = 1.1, 7.7 Hz, 1H), 7.15 (pt, J = 7.5 Hz, 1H), 7.51–7.55 (m, 3H); <sup>13</sup>C{1H} NMR (75 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  31.5 (CH<sub>3</sub>), 33.5 (CH<sub>3</sub>), 35.3 (C), 38.6 (C), 65.4 (CH<sub>2</sub>), 65.6 (CH<sub>2</sub>), 102.4 (CH, J<sub>PC</sub> = 20.3 Hz), 122.6 (CH), 125.4 (CH), 127.0 (CH), 127.6 (C), 128.0 (C), 128.8 (CH), 132.4 (CH), 138.2 (C, d, J<sub>PC</sub> = 16.5 Hz), 139.8 (C, d,  $J_{PC}$  = 23.5 Hz), 150.8 (C); <sup>31</sup>P{1H} NMR (120 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ -73.9. High-resolution MS (FAB): m/z Calc. for  $C_{27}H_{39}O_2P$ : 426.2688. Found: 426.2696 ([M]<sup>+</sup>).

#### 4.1.3. Ketophosphine 20

An acetone solution (50 mL) of 19 (780 mg, 1.83 mmol) and p-toluenesulfonic acid monohydrate (32 mg, 0.18 mmol) was refluxed for 10 h. After the removal of the solvent under the reduced pressure, the purification of the crude product with WCC (hexane) gave 20 (523 mg, 1.37 mmol, 75%). 20: yellow liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  1.37 (s, 9H), 1.45 (s, 18H), 5.97 (dd, J = 3.7, 7.3 Hz, 1H), 6.51 (d,  ${}^{1}J_{PH} = 255.3$  Hz, 1H), 7.18 (pt, J = 7.3 Hz, 1H), 7.29 (pt, J = 7.5 Hz, 1H), 7.53 (s, 1H), 7.54 (s, 1H), 7.78 (ddd, J = 1.4, 3.1, 7.5 Hz, 1H), 10.25 (d,  ${}^{4}J_{PH} = 2.3$  Hz, 1H); <sup>13</sup>C{1H} NMR (75 MHz, CDCl<sub>3</sub>, 298 K) δ 31.3 (CH<sub>3</sub>), 33.3 (CH<sub>3</sub>), 35.2 (C), 38.4 (C), 119.4 (C), 122.6 (CH), 126.6 (CH), 128.5 (C, d, J<sub>PC</sub> = 29.0 Hz,), 132.8 (CH), 132.9 (CH), 134.0 (CH), 136.2 (C, d,  $J_{PC}$  = 9.3 Hz), 146.1 (C, d,  $J_{PC}$  = 34.6 Hz), 150.9 (C), 193.2 (CH, d,  $J_{PC}$  = 4.3 Hz); <sup>31</sup>P{1H} NMR (120 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  -60.1. High-resolution MS (FAB): m/z Calc. for C<sub>25</sub>H<sub>35</sub>OP: 382.2426. Found: 382.2426 ([M]<sup>+</sup>).

#### 4.1.4. Compound **9**

To a toluene solution (5 mL) of **20** (50 mg, 0.13 mmol) was added DipNH<sub>2</sub> (250  $\mu$ L, 1.3 mmol) and trifluoroborane diethyl etherate (14  $\mu$ L, 0.11 mmol). After the reflux for 10 h, the solvent



Scheme 10.

was removed under the reduced pressure. The purification of the crude product with WCC (hexane) gave **9** (69 mg, 0.12 mmol, 98%) [12].

#### 4.1.5. Rhodium complex 11

To a  $C_6H_6$  solution (0.70 mL) of **9** (54 mg, 0.10 mmol) and [RhCl(CO)<sub>2</sub>]<sub>2</sub> (19 mg, 0.049 mmol) was added triethylamine (140  $\mu\text{L},$  1.0 mmol). The reaction mixture was heated at 60 °C for 6.0 h. The solvent was removed in vacuo. The purification of the crude product with Celite<sup>®</sup> filtration (hexane) gave **11** (69 mg, 0.12 mmol, 98%). 11: deep purple crystals; m.p. 118 °C (decomp.); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  0.98 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 6H), 1.32 (d,  ${}^{3}J_{HH} = 7.2 \text{ Hz}$ , 6H), 1.33 (s, 9H), 1.77 (s, 18H), 3.36 (sept,  ${}^{3}J_{\rm HH}$  = 6.9 Hz, 6H), 6.61–6.67 (m, 1H), 6.72–6.79 (m, 1H), 7.07– 7.28 (m, 5H), 7.85 (s, 1H), 7.86 (s, 1H), 8.10 (dd, J = 3.3, 5.1 Hz, 1H); <sup>13</sup>C{1H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  23.0 (CH<sub>3</sub>), 25.1 (CH<sub>3</sub>), 28.4 (CH), 31.4 (CH<sub>3</sub>), 34.2 (CH<sub>3</sub>), 35.3 (C), 40.2 (C), 120.1 (CH), 123.8 (CH), 124.3 (CH, d,  $J_{PC}$  = 8.0 Hz), 125.1 (C, d,  $J_{PC}$  = 16.1 Hz), 127.4 (C), 128.5 (CH), 129.0 (CH, d,  $J_{PC}$  = 9.3 Hz), 138.2 (CH, d,  $J_{PC}$  = 4.4 Hz), 139.7 (C), 150.7 (C, d,  $J_{PC}$  = 7.4 Hz), 151.8 (C, d, J<sub>PC</sub> = 2.5 Hz), 157.1 (C, d, J<sub>PC</sub> = 6.2 Hz), 161.1 (C), 161.6 (CH, d, J<sub>PC</sub> = 16.1 Hz), 185.7 (C, dd, J = 62.6, 97.3 Hz), 191.9 (C, dd, I = 21.9, 67.1 Hz; <sup>31</sup>P{1H} NMR (120 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  91.9 (d,  $I_{PRh} = 122 \text{ Hz}$ ; IR(KBr)  $v_{CO} = 1988.7$ , 2045.78 cm<sup>-1</sup>; High-resolution MS (FAB): m/z Calc. for C<sub>39</sub>H<sub>51</sub>O<sub>2</sub>NPRh: 699.2712. Found: 699.2724 ([M]<sup>+</sup>); Anal. Calc. for  $C_{39}H_{51}O_2NPRh$ : C, 66.94; H, 7.35; N, 2.00. Found: C, 66.85; H, 7.46; N, 2.05%.

#### 4.1.6. Diarylamine 15

To DipNH<sub>2</sub> (500 µL, 2.65 mmol) in toluene (6 mL) was added Pd(OAc)<sub>2</sub> (18 mg, 0.080 mmol), NaO(*t*-Bu) (443 mg, 4.62 mmol), DPEphos (64 mg, 0.12 mmol) and 1 (500 µL, 3.3 mmol). The reaction mixture was stirred at 120 °C for 8.0 h. The solvent was removed in vacuo. The purification of the crude product with Celite<sup>®</sup> filtration (hexane) and HPLC (CHCl<sub>3</sub>) afforded **15** (648 mg, 1.99 mmol, 75%). **15**: pale yellow liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  1.16 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H), 1.21 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H), 3.19 (sept,  ${}^{3}J_{HH}$  = 6.9 Hz, 2H), 4.10–4.21 (m,4H), 6.04 (s, 1H), 6.23 (d,  $J_{\rm HH}$  = 8.4 Hz, 1H), 6.38 (s, 1H), 6.75 (t,  ${}^{3}J_{\rm HH}$  = 7.5 Hz, 1H), 7.10 (t,  ${}^{3}J_{HH}$  = 6.6 Hz, 1H), 7.24–7.32 (m, 3H), 7.43 (d,  ${}^{3}J_{HH}$  = 7.8 Hz, 1H); <sup>13</sup>C{1H} NMR (75 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  22.7 (CH<sub>3</sub>), 24.5 (CH<sub>3</sub>), 28.1 (CH), 64.7 (CH<sub>2</sub>), 103.4 (CH), 112.4 (CH), 116.9 (CH), 120.6 (C), 123.6 (CH), 126.7 (CH), 127.0 (CH), 129.7 (C), 135.5 (C), 146.4 (C), 146.7 (C); High-resolution MS (EI): *m*/*z* Calc. for C<sub>21</sub>H<sub>27</sub>O<sub>2</sub>N: 325.2042. Found: 325.2046 ([M]<sup>+</sup>).

#### 4.1.7. Diarylamine 16

A toluene solution (10 mL) of **15** (197 mg, 0.605 mmol) and *p*toluenesulfonic acid monohydrate (60 mg, 0.31 mmol) was stirred for 1.0 h. To the reaction mixture was added H<sub>2</sub>O and extracted with toluene. The organic layer was dried with MgSO<sub>4</sub>. The solvent was removed under the reduced pressure to afford **16** (165 mg, 0.586 mmol, 91%). **16**: yellow liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  1.11 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 6H), 1.16 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 6H), 3.07 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 2H), 6.23 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 1H), 6.72 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 1H), 7.20–7.36 (m, 3H), 7.56 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, 1H), 9.57 (s, 1H), 9.97 (s, 1H); <sup>13</sup>C{1H} NMR (75 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ 23.0 (CH<sub>3</sub>), 24.5 (CH<sub>3</sub>), 28.4 (CH), 112.6 (CH), 115.7 (CH), 118.0 (C), 123.9 (CH), 128.0 (CH), 133.4 (C), 135.6 (CH), 136.2 (CH), 147.4 (C), 151.0 (C), 194.3 (C); High-resolution MS (EI): *m/z* Calc. for C<sub>19</sub>H<sub>23</sub>ON: 281.1780. Found: 281.1779 ([M]<sup>+</sup>).

#### 4.1.8. Compound 12 [22]

To a THF solution (10 mL) of Mes<sup>•</sup>PH<sub>2</sub> (200 mg, 0.72 mmol) was added *n*-butyllithium (1.51 M hexane solution, 480  $\mu$ L, 0.72 mmol) at -78 °C. After stirring at -78 °C for 15 min, the reaction temper-

ature was raised up to room temperature and then the reaction mixture was stirred for 30 min. To the reaction mixture was added trimethylsilyl chloride (91 µL, 0.72 mmol) and keep stirring for 30 min. To the reaction mixture was added *n*-butyllithium (1.51 M hexane solution, 480 µL, 0.72 mmol). To the reaction mixture was added **16** at -78 °C and stirred for 3.0 h. After the removal of the solvent under the reduced pressure, the crude product was dissolved in hexane and then filtered through Celite<sup>®</sup>. The filtrate was purified with WCC (hexane) to afford 12 (85 mg, 0.16 mmol, 22%). 12: yellow crystals, mp 192 °C (decomp.); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  1.23 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H), 1.30 (d,  ${}^{3}J_{\rm HH}$  = 6.9 Hz, 6H), 1.45 (s, 9H), 1.63 (s, 18H), 3.23 (sept,  ${}^{3}J_{HH}$  = 6.9 Hz, 2H), 6.36 (d,  ${}^{3}J_{HH}$  = 8.0 Hz, 1H), 6.73 (t,  ${}^{3}J_{HH}$  = 7.4 Hz, 1H), 6.93 (d,  $J_{PH}$  = 20.7 Hz, 1H), 7.03 (t,  ${}^{3}J_{HH}$  = 7.4 Hz, 1H), 7.17 (d,  ${}^{3}J_{HH}$  = 8.0 Hz, 1H), 7.33–7.42 (m, 3H), 7.57 (s, 2H), 8.51 (d,  $^{2}J_{\text{PH}} = 23.7 \text{ Hz}, 1\text{H}; \, ^{13}\text{C}\{1\text{H}\} \text{ NMR} (75 \text{ MHz}, \text{CDCl}_{3}, 298 \text{ K}) \delta 22.8$ (CH<sub>3</sub>), 25.1 (CH<sub>3</sub>), 28.4 (CH), 31.4 (CH<sub>3</sub>), 33.8 (CH<sub>3</sub>), 33.9 (CH<sub>3</sub>), 35.0 (C), 38.3 (C), 112.5 (CH), 116.8 (CH), 121.9 (CH), 123.9 (CH), 124.3 (C, d,  $J_{PC}$  = 3.1 Hz), 127.5 (CH), 128.6 (C, d,  $J_{PC}$  = 8.0 Hz), 132.0 (C, d,  $J_{PC}$  = 17.9 Hz), 135.0 (C), 139.9 (C, d,  $J_{PC}$  = 53.7 Hz), 146.5 (C), 147.4 (C), 149.9 (C), 154.1 (C), 176.6 (CH, d,  $J_{PC}$  = 38.9 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (120 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  241.2; High-resolution MS (EI): *m*/*z* Calc. for C<sub>37</sub>H<sub>52</sub>NP: 541.3837. Found: 541.3833 ([M]<sup>+</sup>); Anal. Calc. for C<sub>37</sub>H<sub>52</sub>NP: C, 82.02; H, 9.67; N, 2.59. Found: C, 82.00; H, 9.74; N, 2.54%.

#### 4.1.9. Rhodium complex 13

To a  $C_6H_6$  solution (0.70 mL) of **12** (20 mg, 0.037 mmol) and  $[RhCl(CO)_2]_2$  (7.3 mg, 0.019 mmol) was added triethylamine (50 µL, 0.37 mmol) at room temperature. The reaction mixture was heated at 60 °C for 4.0 h. The solvent was removed in vacuo. The purification of the crude product with Celite<sup>®</sup> filtration (hexane) gave 13 (29 mg, 0.036 mmol, 97%). 13: purplish red crystals, mp 120 °C (decomp.); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  1.03 (d,  ${}^{3}J_{HH}$  = 7.2 Hz, 6H), 1.28 (s, 9H), 1.46 (d,  ${}^{3}J_{HH}$  = 7.2 Hz, 6H), 1.73 (s, 18H), 3.29 (sept,  ${}^{3}J_{HH}$  = 7.2 Hz, 6H), 6.47–6.51 (m, 1H), 6.77–6.80 (m, 1H), 6.85-6.91 (m, 1H), 7.02-7.05 (s, 1H), 7.22 (s, 3H), 7.74 (d,  ${}^{3}J_{HH}$  = 3.3 Hz, 2H), 8.42 (d,  ${}^{2}J_{PH}$  = 17.7 Hz, 1H);  ${}^{13}C{1H}$  NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) & 24.5 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 27.9 (CH), 30.9 (CH<sub>3</sub>), 34.9 (CH<sub>3</sub>), 35.4 (C), 39.4 (C), 115.1 (CH), 117.5 (CH), 1213.3 (CH, d, J<sub>PC</sub> = 9.2 Hz), 124.0 (CH), 124.7 (CH), 126.3 (CH), 129.3 (C, d, J<sub>PC</sub> = 27.8 Hz), 129.9 (CH), 134.1 (CH, d, J<sub>PC</sub> = 24.1 Hz), 141.7 (C), 149.4 (C), 153.3 (C), 155.4 (CH, d, J<sub>PC</sub> = 40.1 Hz), 156.7 (C), 163.0 (C), 179.8 (C, dd, J = 65.4, 131.5 Hz), 189.9 (C, dd, J = 20.4, 58.1 Hz; <sup>31</sup>P{1H} NMR (120 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  158.6 (d,  ${}^{1}J_{PRh}$  = 157 Hz). High-resolution MS (ESI): m/z Calc. for C<sub>38</sub>H<sub>52</sub>ONPRh: 672.2836 ([M+H]<sup>+</sup>). Found: 682.2841 ([M-CO+H]<sup>+</sup>).

#### 4.1.10. Hydrosilylation reaction

To a benzene solution (2 mL) of rhodium complex **11** (3.5 mg, 5.0  $\mu$ mol) was added 2-cyclohexen-1-one (96  $\mu$ L, 1.0 mmol) and Et<sub>3</sub>SiH (480  $\mu$ L, 3.0 mmol). The reaction mixture was heated at reflux temperature for 4 h. The solvent was removed in vacuo. The residue was purified with WCC (hexane) to afford silylenolate **17** (210 mg, 0.99 mmol, 99%) [23].

#### 4.2. X-ray crystallographic analysis

X-ray crystallographic analysis of **9**, **11**, **12** and  $[\mathbf{13} \cdot C_6 H_6]$ . The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å). Single crystals suitable for X-ray analysis were obtained by slow recrystallization from hexane/THF (for **9** and **12**), benzene (for **11** and  $[\mathbf{13} \cdot C_6 H_6]$ ). The single crystals were mounted on a glass fiber. The structures were solved by a direct method (siR-97 [24]) and refined by full-matrix least-squares procedures on  $F^2$ 

for all reflections (SHELXL-97 [25]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Crystal data: **9**:  $C_{37}H_{52}NP$ , M = 541.77, T = 103(2) K, monoclinic,  $P2_1/n$  (no. 14), a = 9.8299(3) Å, b = 26.7647(6) Å, c = 13.2744(3) Å,  $\beta = 108.2538(12)^\circ$ , V = 3316.67(15) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.085$  g cm<sup>-3</sup>,  $\mu = 0.107$  mm<sup>-1</sup>,  $2\theta_{max} = 51.0$ , 29226 measured reflections, 6173 independent reflections ( $R_{int} = 0.0520$ ), 420 refined parameters, GOF = 1.049,  $R_1$  = 0.0447 and  $wR_2$  = 0.1150 [ $I > 2\sigma(I)$ ],  $R_1 = 0.0710$  and  $wR_2 = 0.1247$  [for all data], largest difference in peak and hole 0.375 and  $-0.559 \text{ e} \text{ }^{\text{A}^{-3}}$ . **11**:  $C_{39}H_{51}NO_2PRh$ , M = 699.69, T = 103(2) K, triclinic,  $P\bar{1}$  (no. 2), a = 9.149(3) Å, b = 10.890(4) Å, c = 20.211(7) Å,  $\alpha = 97.934(4)^{\circ}$ ,  $\beta = 101.609(3)^\circ$ ,  $\gamma = 106.9868(16)^\circ$ , V = 1844.4(10) Å<sup>3</sup>, Z = 2,  $D_{calc} = 100.0000$ 1.260 g cm<sup>-3</sup>,  $\mu$  = 0.538 mm<sup>-1</sup>,  $2\theta_{max}$  = 51.0, 16107 measured reflections, 6795 independent reflections ( $R_{int} = 0.0378$ ), 410 refined parameters, GOF = 0.969,  $R_1 = 0.0387$  and  $wR_2 = 0.1190$  $[I > 2\sigma(I)]$ ,  $R_1 = 0.0483$  and  $wR_2 = 0.1337$  [for all data], largest difference in peak and hole 0.602 and  $-0.771 \text{ e} \text{ Å}^{-3}$ . **12**: C<sub>37</sub>H<sub>52</sub>NP, M = 541.77, T = 103(2) K, triclinic,  $P\bar{1}$  (no. 2), a = 9.484(3) Å, b = 10013.720(4) Å, c = 13.737(4) Å,  $\alpha = 93.542(2)^{\circ}$ ,  $\beta = 99.935(3)^{\circ}$ ,  $\gamma = 109.895(4)^{\circ}$ , V = 1641.6(9) Å<sup>3</sup>, Z = 2,  $D_{calc} = 1.096$  g cm<sup>-3</sup>,  $\mu =$  $0.108 \text{ mm}^{-1}$ ,  $2\theta_{\text{max.}}$  = 51.0, 11551 measured reflections, 5989 independent reflections ( $R_{int} = 0.0329$ ), 390 refined parameters, GOF = 1.069,  $R_1$  = 0.0515 and  $wR_2$  = 0.1094 [ $I > 2\sigma(I)$ ],  $R_1$  = 0.0746 and  $wR_2 = 0.1235$  [for all data], largest difference in peak and hole 0.248 and -0.259 e Å<sup>-3</sup>. [**13**·C<sub>6</sub>H<sub>6</sub>]: C<sub>45</sub>H<sub>57</sub>NO<sub>2</sub>PRh, *M* = 777.80, T = 113(2) K, orthorhombic,  $P2_12_12_1$  (no. 19), a = 9.5822(5) Å,  $b = 16.9794(11) \text{ Å}, \quad c = 24.7695(16) \text{ Å}, \quad V = 4030.0(4) \text{ Å}^3, \quad Z = 4, \\ D_{\text{calc}} = 1.282 \text{ g cm}^{-3}, \quad \mu = 0.500 \text{ mm}^{-1}, \quad 2\theta_{\text{max}} = 51.0, \quad 35424 \text{ mea-}$ sured reflections, 7492 independent reflections ( $R_{int} = 0.0802$ ), 452 refined parameters, GOF = 1.192,  $R_1$  = 0.0498 and  $wR_2$  = 0.0893 [ $I > 2\sigma(I)$ ],  $R_1 = 0.0629$  and  $wR_2 = 0.0963$  [for all data], largest difference in peak and hole 0.742 and  $-0.559 \text{ e} \text{ Å}^{-3}$ .

#### Supplementary data

CCDC 729128, 729129, 729130, 729131 contains the supplementary crystallographic data for **9**, **11**, **12** and  $[\mathbf{13} \cdot C_6H_6]$ . These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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