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<td>Citation</td>
<td>Polyhedron (2010), 29(1): 425-433</td>
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<td>Issue Date</td>
<td>2010-01-13</td>
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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.

Keywords: Schiff base; Phosphorus; Phosphaalkene; Rhodium; Steric protection; Trans-influence

1. Introduction

Schiff-base-type N,N’-chelating ligands such as β-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 β-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 π-electron conjugation in the cyclic skeleton of the resulting complexes.

<insert Scheme 1 here>

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 π*-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 π*-orbital level showing strong π-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 sp²-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 β-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-diketiminate 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*H (Scheme 3). Taking this report into consideration, the more strained β-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-2H-isoiindole 10 along with the elimination of Mes*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.
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* 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 (Figures 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* and Dip 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, phosphaalkenylamine 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*P=CHPh [1.660(6) Å] [13] and typical diarylamines.

In the \(^{31}\)P NMR spectrum, compound 9 showed \( \delta_p = -62.7 \) in the high field region similar to those of secondary phosphines. In the \(^1\)H NMR spectrum of 9, a characteristic doublet signal due to the P–H moiety was observed at 6.51 ppm with \( J_{PH} = 258.3 \) Hz, which
is relatively low-field shifted as compared with those of diarylphosphines (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 $^4J_{PH} = 1.6$ Hz. On the other hand, 12 showed a characteristically low-field shifted signal of $\delta_P = 241.2$ in the $^{31}P$ NMR spectrum, supporting the sp$^2$-hybridized phosphorus atom with the P=C double bond character. In the $^1H$ NMR spectrum of 12, the signal due to the P=CH moiety was observed at $\delta_H = 8.53$ as a doublet signal with $^2J_{PH} = 23.7$ Hz, which is similar to that of (E)-Mes*$^*$P=CHPh [the chemical shift of P=CH moiety is $\delta_H = 8.12$ with $^2J_{PH} = 25.3$ Hz] [15]. Interestingly, the N–H proton of 12 was observed at $\delta_H = 6.93$, 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 $^1J_{PH}$ 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 THF at room temperature. However, heating of C$_6$D$_6$ suspension of 9 in the presence of KH at 60 °C afforded 2-phospha-2H-isoiindole 10 along with Mes*$^*$H as described above (Scheme 5) [12]. When 9 was treated with 0.5 eq. of [RhCl(CO)$_2$]$_2$ in THF at room temperature, the reaction proceeded slowly to give an unidentified complex X, which showed a characteristic signal at $\delta_P = -14.1$ with $^1J_{PRh} = 164$ Hz and $^1J_{PH} = 378$ Hz in the $^{31}P$ NMR spectrum. Treatment of the reaction mixture with an excess amount of Et$_3$N at 60 °C for 6 h afforded the rhodium-carbonyl complex 11 as a stable purple crystalline compound (Scheme 6). Similarly, heating of the C$_6$D$_6$ solution of 12 with 0.5 eq. of [RhCl(CO)$_2$]$_2$ in the presence of an excess amount of Et$_3$N afforded the corresponding rhodium-carbonyl complex 13 as a stable purple 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*$^*$ and Dip.
The structural parameters of rhodium-carbonyl complexes 11 and 13 were revealed by the X-ray crystallographic analysis (Figures 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 π-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_{opt} [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 11_{opt} is 717°, Figure 7). However, the structural optimization of the less hindered model compound 11_{Me} bearing a methyl group instead of Mes* 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* group of 11 should play an important role to afford the steric effect on the phosphorus atom for keeping the relatively planar geometry with sp²-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_{opt} [17] is similar to those observed by the X-ray crystallographic analysis of 13. However, the methyl-substituted model 13_{Me} exhibits a (2,6-diisopropylphenyl) groups.
slightly twisted structure as in the case of $11_{Me}$ (the sum of the internal angles of the Rh–P–C–C–C–N six-membered ring skeleton is $712^\circ$), suggesting the steric effect of Dip and Mes*. 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 $13$].

The structural and electronic features of $11$ and $13$ in solution should be discussed on the basis of their NMR spectra. In $^{31}$P NMR spectrum, $11$ showed a surprisingly low-field shifted signal at $\delta_P = 91.9$ with $^{1}J_{PRh} = 122$ Hz, in contrast to those of rhodium-phosphine complexes (e.g., $\delta_P = 25.3$ with $^{1}J_{PRh} = 127.3$ Hz for [RhCl(PPH$_3$)(CO)$_2$]) [14]) [18], indicating the sp$^2$-character of the phosphorus atom of $11$. On the other hand, rhodium complex $13$ showed a characteristic signal at $\delta_P = 158.6$ with $^{1}J_{PRh} = 157$ 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$_3$)(CO)$_2$]) [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 $\pi$ bonds of a phospaalkene (RP=CR$_2$) 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 PPh₃ 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 PPh₃. Due to the less hindered situation of the phosphorus atom of a phosphaalkene as compared with PPh₃, the lone pair of a phosphaalkene exhibit higher s-character than that of PPh₃. Thus, the relatively large $^1J_{\text{PRh}}$ value of 13 should reflect the bonding properties of its P=C unit. On the other hand, the $^1J_{\text{PRh}}$ coupling constant of 11 ($^1J_{\text{PRh}} = 122$ Hz) is similar to or slightly smaller than that of 14 ($^1J_{\text{PRh}} = 127.3$), 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 sp²-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 π-conjugation on the imino-phosphido ligand of 11.

In $^{13}$C NMR spectra, 11 showed two signals assignable to the carbonyl groups at δ_C = 185.7 ($^1J_{\text{RhC}} = 62.6$ Hz, $^2J_{\text{CP}} = 97.3$ Hz) and δ_C = 191.9 ($^1J_{\text{RhC}} = 67.1$ Hz, $^2J_{\text{CP}} = 21.9$ 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 $^2J_{\text{CP}}$ values of [RhCl(PPh₃)(CO)₂] (14, δ_C = 183.0, $^2J_{\text{CP}} = 16.3$ for cis-CO for PPh₃, δ_C = 183.3, $^2J_{\text{CP}} = 123.4$ Hz for trans-CO for PPh₃) [18]. The smaller $^1J_{\text{RhC}}$ 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 groups of 13 were δ_C = 179.8 ($^1J_{\text{RhC}} = 65.4$ Hz, $^2J_{\text{CP}} = 131.5$ Hz, trans-CO for the phosphorus atom) and δ_C = 189.9 ($^1J_{\text{RhC}} = 58.1$ Hz, $^2J_{\text{CP}} = 20.4$ Hz, cis-CO for the phosphorus atom). The $^1J_{\text{RhC}}$ 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 $^1J_{\text{RhC}}$ value is not clear at present.

Preliminarily, we have performed the reaction of cyclohexanone 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\(^2\)-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\(^2\)-hybridized phosphorus atom. Further investigations on the synthesis of other transition metal complexes bearing such P,N-chelating ligands having an sp\(^2\)-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. \(^1\)H NMR (300 MHz) and \(^{13}\)C NMR (75 MHz) spectra were measured in CDCl\(_3\) or C\(_6\)D\(_6\) with a JEOL JNM AL-300 spectrometer. Signals
due to CHCl₃ (7.25 ppm) and C₆D₅H (7.15 ppm) were used as references in ¹H NMR, and those due to CDCl₃ (77 ppm) and C₆D₆ (128 ppm) were used in ¹³C NMR. Multiplicity of signals in ¹³C NMR spectra was determined by DEPT and CH-COSY techniques. ³¹P NMR (120 MHz) spectra were measured in CDCl₃ or C₆D₆ with JEOL AL-300 spectrometer using 86% H₃PO₄ in water (0 ppm) as an external standard. All the P–H coupling constants were determined on the basis of both ¹H and non-decoupled ³¹P NMR spectra. High resolution mass spectral data were obtained on a JEOL JMS-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.

<insert Scheme 10 here>

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*PCl₂ (347 mg, 1.0 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®. The filtrate was purified with WCC (hexane/ether = 20/1) to afford 18 (271 mg, 0.588 mmol, 74%). 18: pale yellow liquid; ¹H NMR (300 MHz, CDCl₃, 298 K) δ 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); ¹³C{¹H} NMR (75 MHz, CDCl₃, 298 K) δ 31.1 (CH₃), 33.8 (CH₃), 33.9 (CH₃), 34.8 (C), 39.9 (C), 84.8 (CH₂), 85.1 (CH₂), 100.0 (CH, d, ³JPC = 7.5 Hz), 124.0 (CH), 125.9 (CH), 128.7 (CH), 128.9 (CH), 131.9 (CH, d, ³JPC = 8.3 Hz), 138.7 (CH, d, ³JPC = 22.5 Hz), 139.0 (C), 139.8 (C), 152.8 (C), 161.1 (C, d, ³JPC = 20.3 Hz); ³¹P{¹H} NMR (120 MHz, CDCl₃, 298 K) δ 77.4. High-resolution MS (ESI): m/z
Calcd for C_{27}H_{39}O_2PCl 461.2376. Found 461.2334 ([M+H]^+).

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®. The purification of the filtrate with WCC (hexane/ether = 20/1) gave 19 (98 mg, 0.23 mmol, 85%). 19: pale yellow liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\), 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, \(J\text{\textsubscript{PH}} = 241.6\) 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); \(^{13}\)C\(^{\text{\textsubscript{1}H}}\) NMR (75 MHz, CDCl\(_3\), 298 K) \(\delta\) 31.5 (CH\(_3\)), 33.5 (CH\(_3\)), 35.3 (C), 38.6 (C), 65.4 (CH\(_2\)), 65.6 (CH\(_2\)), 102.4 (CH, \(J\text{\textsubscript{PC}} = 20.3\) 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, \(J\text{\textsubscript{PC}} = 16.5\) Hz), 139.8 (C, d, \(J\text{\textsubscript{PC}} = 23.5\) Hz), 150.8 (C); \(^{31}\)P\(^{\text{\textsubscript{1}H}}\) NMR (120 MHz, CDCl\(_3\), 298 K) \(\delta\) –73.9. High-resolution MS (FAB): m/z Calcd for C_{27}H_{39}O_2P 426.2688. Found. 426.2696 ([M]^+).

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; \(^1\)H NMR (300 MHz, CDCl\(_3\), 298 K) \(\delta\) 1.37 (s, 9H), 1.45 (s, 18H), 5.97 (dd, \(J = 3.7, 7.3\) Hz, 1H), 6.51 (d, \(J\text{\textsubscript{PH}} = 255.3\) 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, \(J\text{\textsubscript{PH}} = 2.3\) Hz, 1H); \(^{13}\)C\(^{\text{\textsubscript{1}H}}\) NMR (75 MHz, CDCl\(_3\), 298 K) \(\delta\) 31.3 (CH\(_3\)), 33.3 (CH\(_3\)), 35.2 (C), 38.4 (C), 119.4 (C), 122.6 (CH), 126.6 (CH), 128.5 (C, d, \(J\text{\textsubscript{PC}} = 29.0\) Hz.), 132.8 (CH), 132.9 (CH), 134.0 (CH), 136.2 (C, d, \(J\text{\textsubscript{PC}} = 9.3\) Hz), 146.1 (C, d, \(J\text{\textsubscript{PC}} = 34.6\) Hz).
Hz), 150.9 (C), 193.2 (CH, d, J\textsubscript{PC} = 4.3 Hz); \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (120 MHz, CDCl\textsubscript{3}, 298 K) δ –60.1.

High-resolution MS (FAB): m/z Calcd for C\textsubscript{25}H\textsubscript{35}OP 382.2426. Found. 382.2426 ([M]+).

4.1.4. Compound 9

To a toluene solution (5 mL) of 20 (50 mg, 0.13 mmol) was added DipNH\textsubscript{2} (250 μL, 1.3 mmol) and trifluoroborane diethyl etherate (14 μL, 0.11 mmol). After the reflux for 10 h, the solvent 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\textsubscript{6}H\textsubscript{6} solution (0.70 mL) of 9 (54 mg, 0.10 mmol) and [RhCl(CO)\textsubscript{2}]\textsubscript{2} (19 mg, 0.049 mmol) was added triethylamine (140 μL, 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\textsuperscript{®} filtration (hexane) gave 11 (69 mg, 0.12 mmol, 98%). 11: deep purple crystals; m.p. 118 °C (decomp.); \textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) δ 0.98 (d, \textsuperscript{3}J\textsubscript{HH} = 7.2 Hz, 6H), 1.32 (d, \textsuperscript{3}J\textsubscript{HH} = 7.2 Hz, 6H), 1.33 (s, 9H), 1.77 (s, 18H), 3.36 (sept, \textsuperscript{3}J\textsubscript{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); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (75 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) δ 23.0 (CH\textsubscript{3}), 25.1 (CH\textsubscript{3}), 28.4 (CH), 31.4 (CH\textsubscript{3}), 34.2 (CH\textsubscript{3}), 35.3 (C), 40.2 (C), 120.1 (CH), 123.8 (CH), 124.3 (CH, d, J\textsubscript{PC} = 8.0 Hz), 125.1 (C, d, J\textsubscript{PC} = 16.1 Hz), 127.4 (C), 128.5 (CH), 129.0 (CH, d, J\textsubscript{PC} = 9.3 Hz), 138.2 (CH, d, J\textsubscript{PC} = 4.4 Hz), 139.7 (C), 150.7 (C, d, J\textsubscript{PC} = 7.4 Hz), 151.8 (C, d, J\textsubscript{PC} = 2.5 Hz), 157.1 (C, d, J\textsubscript{PC} = 6.2 Hz), 161.1 (C), 161.6 (CH, d, J\textsubscript{PC} = 16.1 Hz), 185.7 (C, dd, J = 62.6, 97.3 Hz), 191.9 (C, dd, J = 21.9, 67.1 Hz); \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (120 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K) δ 91.9 (d, \textsuperscript{1}J\textsubscript{PRh} = 122 Hz); IR(KBr) \nu\textsuperscript{CO} = 1988.7, 2045.78 cm\textsuperscript{-1}; High-resolution MS (FAB): m/z Calcd for C\textsubscript{39}H\textsubscript{51}O\textsubscript{2}NPRh 699.2712. Found 699.2724 ([M]+); Anal. Calcd for C\textsubscript{39}H\textsubscript{51}O\textsubscript{2}NPRh: 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$_2$ (500 µL, 2.65 mmol) in toluene (6 mL) was added Pd(OAc)$_2$ (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® filtration (hexane) and HPLC (CHCl$_3$) afforded 15 (648 mg, 1.99 mmol, 75%). 15: pale yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$, 298 K) δ 1.16 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H), 1.21 (d, $^3$J$_{HH}$ = 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$_{HH}$ = 8.4 Hz, 1H), 6.38 (s, 1H), 6.75 (t, $^3$J$_{HH}$ = 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); $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, 298 K) δ 22.7 (CH$_3$), 24.5 (CH$_3$), 28.1 (CH), 64.7 (CH$_2$), 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 Calcd for C$_{21}$H$_{27}$O$_2$N 325.2042. Found. 325.2046 ([M]+).

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$_2$O and extracted with toluene. The organic layer was dried with MgSO$_4$. The solvent was removed under the reduced pressure to afford 16 (165 mg, 0.586 mmol, 91%). 16: yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$, 298 K) δ 1.11 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H), 1.16 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H), 3.07 (sept, $^3$J$_{HH}$ = 6.9 Hz, 2H), 6.23 (d, $^3$J$_{HH}$ = 8.7 Hz, 1H), 6.72 (t, $^3$J$_{HH}$ = 7.2 Hz, 1H), 7.20-7.36 (m, 3H), 7.56 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H), 9.57 (s, 1H), 9.97 (s, 1H); $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, 298 K) δ 22.7 (CH$_3$), 24.5 (CH$_3$), 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 Calcd for C$_{19}$H$_{23}$ON 281.1780. Found. 281.1779 ([M]+).

4.1.8. Compound 12 [22]

To a THF solution (10 mL) of Mes*PH$_2$ (200 mg, 0.72 mmol) was added n-butyllithium (1.51
M hexane solution, 480 μL, 0.72 mmol) at –78 °C. After stirring at –78 °C for 15 min, the reaction temperature 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®. The filtrate was purified with WCC (hexane) to afford 12 (85 mg, 0.16 mmol, 22%). 12: yellow crystals, mp 192 °C (decomp.); 1H NMR (300 MHz, CDCl3, 298 K) δ 1.23 (d, 3JHH = 6.9 Hz, 6H), 1.30 (s, 9H), 1.45 (s, 9H), 1.63 (s, 18H), 3.23 (sept, 3JHH = 6.9 Hz, 2H), 6.36 (d, 3JHH = 8.0 Hz, 1H), 6.73 (t, 3JHH = 7.4 Hz, 1H), 6.93 (d, JPH = 20.7 Hz, 1H), 7.03 (t, 3JHH = 7.4 Hz, 1H), 7.17 (d, 3JHH = 8.0 Hz, 1H), 7.33-7.42 (m, 3H), 7.57 (s, 2H), 8.51 (d, 3JPH = 23.7 Hz, 1H); 13C{1H} NMR (75 MHz, CDCl3, 298 K) δ 22.8 (CH3), 25.1 (CH3), 28.4 (CH), 31.4 (CH3), 33.8 (CH3), 33.9 (CH3), 35.0 (C), 38.3 (C), 112.5 (CH), 116.8 (CH), 121.9 (CH), 123.9 (CH), 124.3 (C, d, JPC = 3.1 Hz), 127.5 (CH), 128.6 (C, d, JPC = 8.0 Hz), 132.0 (C, d, JPC = 17.9 Hz), 135.0 (C), 139.9 (C, d, JPC = 53.7 Hz), 146.5 (C), 147.4 (C), 149.9 (C), 154.1 (C), 176.6 (CH, d, JPC = 38.9 Hz); 31P{1H} NMR (120 MHz, CDCl3, 298 K) δ 241.2; High-resolution MS (EI): m/z Calcd for C37H52NP 541.3837. Found. 541.3833 ([M]+); Anal. Calcd for C37H52NP: 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 C6H6 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® filtration (hexane) gave 13 (29 mg, 0.036 mmol, 97%). 13: purplish red crystals, mp 120 °C (decomp.); 1H NMR (300 MHz, C6D6, 298 K) δ 1.03 (d, 3JHH = 7.2 Hz, 6H), 1.28 (s, 9H), 1.46 (d, 3JHH = 7.2 Hz, 6H), 1.73 (s, 18H), 3.29 (sept, 3JHH = 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, $^3J_{HH} = 3.3$ Hz, 2H), 8.42 (d, $^2J_{PH} = 17.7$ Hz, 1H); $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$, 298 K) δ 24.5 (CH$_3$), 24.8 (CH$_3$), 27.9 (CH), 30.9 (CH$_3$), 34.9 (CH$_3$), 35.4 (C), 39.4 (C), 115.1 (CH), 117.5 (CH), 1213.3 (CH, d, $J_{PC} = 9.2$ Hz), 124.0 (CH), 124.7 (CH), 126.3 (CH), 129.3 (C, d, $J_{PC} = 27.8$ Hz), 129.9 (CH), 134.1 (CH, d, $J_{PC} = 24.1$ Hz), 141.7 (C), 149.4 (C), 153.3 (C), 155.4 (CH, d, $J_{PC} = 40.1$ Hz), 156.7 (C), 163.0 (C); $^{31}$P{$^1$H} NMR (120 MHz, C$_6$D$_6$, 298 K) δ 158.6 (d, $^1J_{PRh} = 157$ Hz).

4.1.10. Hydrosilylation reaction

To a benzene solution (2 mL) of rhodium complex 11 (3.5 mg, 5.0 μmol) was added 2-cyclohexen-1-one (96 μL, 1.0 mmol) and Et$_3$SiH (480 μL, 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 [13-C$_6$H$_6$].** The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation (λ = 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 [13-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 F2 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, $β = 108.2538(12)^o$, $V = 3316.67(15)$ Å$^3$, $Z = 4$, $D_{calc} = 1.085$ gcm$^{-3}$, $μ = 0.107$ mm$^{-1}$, $2θ_{max} = 51.0$, 29226 measured reflections, 6173 independent reflections ($R_{int} = 0.0520$), 420 refined parameters, GOF = 1.049, $R_1 = 0.0447$ and $wR_2 = 0.1150$ [$I>2σ(I)$], $R_1 = 0.0710$ and $wR_2 =
0.1247 [for all data], largest diff. peak and hole 0.375 and -0.559 e.Å⁻³. **11**: C₃₉H₅₁NO₂PRh, \( \text{M} = 699.69 \), \( T = 103(2) \) K, triclinic, \( P-\text{I} \) (no.2), \( a = 9.149(3) \) Å, \( b = 10.890(4) \) Å, \( c = 20.211(7) \) Å, \( \alpha = 97.934(4)° \), \( \beta = 101.609(3)° \), \( \gamma = 106.9868(16)° \), \( V = 1844.4(10) \) Å³, \( Z = 2 \), \( D_{\text{calc}} = 1.260 \text{ gcm}^{-3} \), \( \mu = 0.538 \text{ mm}^{-1} \), \( 2\theta_{\text{max}} = 51.0 \), 16107 measured reflections, 6795 independent reflections (\( R_{\text{int}} = 0.0378 \)), 410 refined parameters, \( \text{GOF} = 0.969 \), \( R_1 = 0.0387 \) and \( wR_2 = 0.1190 \) [\( I > 2\sigma(I) \)], \( R_1 = 0.0483 \) and \( wR_2 = 0.1337 \) [for all data], largest diff. peak and hole 0.602 and -0.771 e.Å⁻³.

**12**: C₃₇H₅₂NP, \( M = 541.77 \), \( T = 103(2) \) K, triclinic, \( P-\text{I} \) (no.2), \( a = 9.484(3) \) Å, \( b = 13.720(4) \) Å, \( c = 13.737(4) \) Å, \( \alpha = 93.542(2)° \), \( \beta = 99.935(3)° \), \( \gamma = 109.895(4)° \), \( V = 1641.6(9) \) Å³, \( Z = 2 \), \( D_{\text{calc}} = 1.096 \text{ gcm}^{-3} \), \( \mu = 0.108 \text{ mm}^{-1} \), \( 2\theta_{\text{max}} = 51.0 \), 11551 measured reflections, 5989 independent reflections (\( R_{\text{int}} = 0.0329 \)), 390 refined parameters, \( \text{GOF} = 1.069 \), \( R_1 = 0.0515 \) and \( wR_2 = 0.1094 \) [\( I > 2\sigma(I) \)], \( R_1 = 0.0746 \) and \( wR_2 = 0.1235 \) [for all data], largest diff. peak and hole 0.248 and -0.259 e.Å⁻³. **[13•C₆H₆]**: C₄₅H₅₇NO₂PRh, \( M = 777.80 \), \( T = 113(2) \) K, orthorhombic, \( P2_12_12_1 \) (no.19), \( a = 9.5822(5) \) Å, \( b = 16.9794(11) \) Å, \( c = 24.7695(16) \) Å, \( V = 4030.0(4) \) Å³, \( Z = 4 \), \( D_{\text{calc}} = 1.282 \text{ gcm}^{-3} \), \( \mu = 0.500 \text{ mm}^{-1} \), \( 2\theta_{\text{max}} = 51.0 \), 35424 measured reflections, 7492 independent reflections (\( R_{\text{int}} = 0.0802 \)), 452 refined parameters, \( \text{GOF} = 1.192 \), \( R_1 = 0.0498 \) and \( wR_2 = 0.0893 \) [\( I > 2\sigma(I) \)], \( R_1 = 0.0629 \) and \( wR_2 = 0.0963 \) [for all data], largest diff. peak and hole 0.742 and -0.559 e.Å⁻³.

**Appendix A. Supplementary data**: CCDC 729128-729131 contains the supplementary crystallographic data for 9, 11, 12, and **[13•C₆H₆]**, respectively. 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.

**5. Acknowledgment**

This work was supported by Grant-in-Aid for Creative Scientific Research (No. 17GS0207), Science Research on Priority Areas (No. 20036024, "Synergy of Elements"), and the Global COE Program ("Integrated Materials Science", Kyoto University) from Ministry of Education, Culture, Sports, Science and Technology, Japan.
References


[17] All calculations were conducted using the Gaussian 03 series of electronic structure programs. The geometries were optimized with density functional theory at the B3PW91 level using 6-31G(d) basis sets (for C, H, N, and O), 6-311G(3d) (for P), and Lanl2DZ (for Rh). It was confirmed by frequency calculations that the optimized structures have minimum energies. Computation time was provided by the Super Computer Laboratory, Institute for Chemical Research, Kyoto University.

Some control experiments have been examined as follows: (i) Reaction of 2-cyclohexen-1-one (96 μL, 1.0 mmol) with Et₃SiH (480 μL, 3.0 mmol) in benzene (2 mL) in the absence of any catalysis under the reflux conditions for 4 h. (ii) Reaction of 2-cyclohexen-1-one (96 μL, 1.0 mmol) with Et₃SiH (480 μL, 3.0 mmol) in benzene (2 mL) in the presence of ligand 9 (2.7 mg, 5.0 μmol) under the reflux conditions for 4 h. (iii) Reaction of 2-cyclohexen-1-one (96 μL, 1.0 mmol) with Et₃SiH (480 μL, 3.0 mmol) in benzene (2 mL) in the presence of [RhCl(CO)₂]₂ (1.0 mg, 2.5 μmol) under the reflux conditions for 4 h. All of these control reactions were unsuccessful with the quantitative recover of 2-cyclohexen-1-one.
< Figures and Schemes >

**Scheme 1**

β-diketiminate   imino-anilide

N,N-Chelating ligands

↓ phosphorus analogues

imino-phosphide   phosphaalkenyl-anilide

N,P-Chelating ligands
Scheme 2

1) LDA
2) [RhCl(cod)]₂

THF

R = H, SiMe₃

Tbt = 2,4,6-tris[trimethylsilyl)methyl]phenyl

cod = cyclooctadiene
Scheme 3

3

proposed as a possible intermediate

Mes*: R = R' = t-Bu
Dip: R = i-Pr, R' = H

4

5

6

Mes*\leftarrow P\rightarrow Mes*
Scheme 4

7   8

imino-phosphide phospaalkenyil-anilide

Schiff-base type N,P-chelating ligands
Scheme 5

\[ \text{Mes}^*\text{PH}_2\text{N}^*\text{Dip} + \text{KH} \xrightarrow{\text{C}_6\text{D}_6, 60 \degree \text{C}} \text{Mes}^*\text{H} + \text{10} \]

10
Scheme 6

\[ \text{Mes}^*\text{PH} \overset{N}{\underset{\text{Dip}}{\longrightarrow}} \text{Mes}^*\text{N} \overset{\text{Dip}}{\longrightarrow} \]

\[ 9 \xrightarrow{[\text{RhCl(CO)}_2]_2, \text{Et}_3\text{N}} \xrightarrow{\text{THF}} \xrightarrow{60 \, ^\circ\text{C}} 11 \]

\[ \text{Dip} \overset{\text{N}}{\underset{\text{P-Mes}^*}{\longrightarrow}} \]

\[ 12 \xrightarrow{[\text{RhCl(CO)}_2]_2, \text{Et}_3\text{N}} \xrightarrow{\text{C}_6\text{D}_6} \xrightarrow{60 \, ^\circ\text{C}} 13 \]
Scheme 7

$$\text{Br} \quad \text{O} \quad \text{O} \quad + \quad \text{DipNH}_2 \quad \xrightarrow{\text{NaO(t-Bu) (1.4 eq.)}} \quad \text{Dip} \quad \text{NH} \quad \text{O} \quad \text{O} \quad \xrightarrow{\text{Pd(OAc)}_2 (2.4 \text{ mol\%}) \quad \text{DPEphos (3.6 \text{ mol\%})}} \quad \text{toluene} \quad \text{95-120 } \circ\text{C} \quad \text{14} \quad \xrightarrow{75\%} \text{15}$$

$$\text{p-TsOH} \quad \text{toluene} \quad \text{r.t.}$$

$$\text{Dip} \quad \text{NH} \quad \text{O} \quad \xrightarrow{\text{Mes}^*\text{P(SiMe}_3\text{)Li}} \quad \text{Dip} \quad \text{NH} \quad \text{P} \quad \text{Mes}^* \quad \xrightarrow{\text{THF} \quad -78 \circ\text{C}} \quad \text{16} \quad \xrightarrow{91\%} \text{12} \quad \xrightarrow{22\%}$$

DPEphos = \[
\begin{array}{c}
\text{O} \\
\text{Ph}^2 \\
\text{Ph}^2
\end{array}
\]
Scheme 8

9A ⇌ 9B

12A ⇌ 12B
Scheme 9.

\[ \text{ketone} + \text{Et}_3\text{SiH} \rightarrow \text{OSiEt}_3 \]

Conditions: benzene, reflux, 4.0 h
Scheme 10.

\[
\begin{align*}
\text{Br} & \quad \text{O} & \quad \text{O} \\
\text{THF} & \quad -78^\circ C \\
\text{n-ButLi} & \rightarrow \text{Mes}^*\text{PCl}_2 & \text{THF} \\
14 & \rightarrow & 18 \quad 74\% \\
\text{LiAlH}_4 & \rightarrow & \text{Mes}^*\text{PH} & \text{Et}_2\text{O} \\
& & 19 \quad 85\% \\
\text{TsoH/H}_2\text{O} & \rightarrow & \text{Mes}^*\text{PH} & \text{acetone} \\
& & \text{H} & \text{reflux} \\
20 & \quad 75\% \\
\text{DipNH}_2 & \rightarrow & \text{Mes}^*\text{PH} & \text{BF}_3 \cdot \text{Et}_2\text{O} \\
& & \text{Dip} \quad \text{N} & \text{toluene} \\
& & 9 \quad \text{quant.}
\end{align*}
\]
Figure 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 (deg): P–C1, 1.8440(18); P–C(Mes*), 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*)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).
**Figure 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 (deg): N–C1, 1.372(3); N–C(Dip), 1.432(3); P–C3, 1.687(2), P–C(Mes*), 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*), 102.62(9).
**Figure 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 (deg): 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).
Figure 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 (deg): 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).
Figure 5. (a) Observed structure of $11$. (b) Optimized structure of $11_{\text{opt}}$ [17]. (c) Optimized structure of $11_{\text{Me}}$ [17].
Figure 6. (a) Observed structure of 13. (b) Optimized structure of $13_{\text{opt}}$ [17]. (c) Optimized structure of $13_{\text{Me}}$ [17].
**Figure 7.** Summary of observed and optimized structural parameters of $11$, $11_{\text{opt}}$, $11_{\text{Me}}$, $13$, $13_{\text{opt}}$, and $13_{\text{Me}}$ [17]. *The sum of internal angles of the Rh–P–C–C–C–N six-membered ring skeleton.

![Diagram](image)

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<td>Rh–E1/Å</td>
<td>2.2665(11)</td>
<td>2.300</td>
<td>2.349</td>
<td>2.066(4)</td>
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<td>Rh–E2/Å</td>
<td>2.080(3)</td>
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<td>2.163</td>
<td>2.2261(12)</td>
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<td>2.271</td>
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<td>E1–C1/Å</td>
<td>1.768(3)</td>
<td>1.767</td>
<td>1.818</td>
<td>1.374(6)</td>
<td>1.367</td>
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<tr>
<td>C1–C2/Å</td>
<td>1.424(4)</td>
<td>1.431</td>
<td>1.424</td>
<td>1.435(7)</td>
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<tr>
<td>C2–C3/Å</td>
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<td>1.432</td>
<td>1.450</td>
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<td>1.421</td>
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<td>C3–E2/Å</td>
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<td>1.289</td>
<td>1.666(5)</td>
<td>1.675</td>
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<td>Rh–C4/Å</td>
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<td>1.848</td>
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<td>C4–O1/Å</td>
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<td>1.153</td>
<td>1.131(5)</td>
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<td>C5–O2/Å</td>
<td>1.106(4)</td>
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<td>1.151</td>
<td>1.143(6)</td>
<td>1.153</td>
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<tr>
<td>$\Sigma^*$</td>
<td>717°</td>
<td>717°</td>
<td>686°</td>
<td>720°</td>
<td>720°</td>
<td>712°</td>
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Graphical abstract

Schiff-base type N,P-chelating ligands, i.e., phosphorus analogues of imino-anilido ligands, were designed and synthesized as a new type of ligands toward a transition metal. Complexation reactions of the novel imino-phosphido and phosphaalkenyl-anilido ligands with $[\text{RhCl(CO)}_2]_2$ resulted in the formation of the corresponding rhodium-carbonyl complexes as stable crystalline compounds, the unique structural and electronic features of which were revealed based on their spectroscopic and X-ray crystallographic analyses.

Dip = 2,6-diisopropylphenyl
Mes* = 2,4,6-tri-$t$-butylphenyl