ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Unsymmetrical PNP-Pincer Type Phosphaalkene Ligands Protected by a Fused-Ring Bulky Eind Group: Synthesis and Applications to Rh(I) and Ir(I) Complexes

Hiro-omi Taguchi,[†] Daichi Sasaki,[†] Katsuhiko Takeuchi,[†] Shota Tsujimoto,[‡] Tsukasa Matsuo,[‡] Hiromasa Tanaka,[§] Kazunari Yoshizawa,[§] and Fumiyuki Ozawa*[,†]

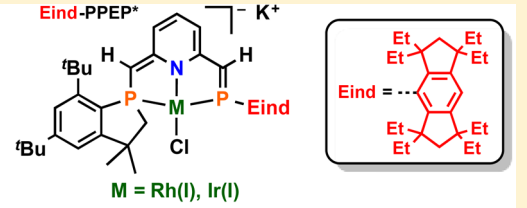
[†]International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

[‡]Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Osaka 577-8502, Japan

[§]Institute for Materials Chemistry and Engineering, International Research Center for Molecular Systems, Kyushu University, Nishi-ku, Fukuoka 819-0395, Japan

Supporting Information

ABSTRACT: We recently reported that 2-(phospholanylmethyl)-6-(2-phosphaethenyl)pyridine (PPEP) with a 2,4,6-tri-*tert*-butylphenyl group (Mes*) as steric protection of the P═C bond serves as a noninnocent ligand on Ir(I), leading to extremely high reactivity toward metal−ligand cooperative activation of ammonia and acetonitrile. The high reactivity is largely due to the strong π-accepting properties of the P═C bond. However, PPEP had a stability problem that provokes the loss of the P═C bond on other transition metals, including Rh(I), and restricts its utilization. This paper describes the synthesis of Eind-PPEP protected by an octaethyl-*s*-hydrindacen-4-yl group (Eind) instead of Mes*. The fused-ring bulky Eind group successfully prevents the loss of the P═C bond and enables us to compare the reactivity of Rh(I) and Ir(I) complexes toward ammonia. The complex K[RhCl(Eind-PPEP*)], bearing a dearomatized Eind-PPEP* ligand, undergoes simple ligand displacement to give [Rh(NH_3)(Eind-PPEP*)], whereas the iridium analogue K[IrCl(Eind-PPEP*)] causes N−H bond cleavage to form [Ir(NH_2)(Eind-PPEP)]. DFT calculations indicate a thermodynamic cause of the metal-dependent product change.



Non-innocent PNP-Pincer Type Phosphaalkene Ligand Protected by a Fused-Ring Bulky Eind group

INTRODUCTION

Phosphaalkenes with a P═C double bond are an interesting class of phosphorus compounds, which possess an extremely low lying π^* orbital and thus serve as strong π acceptors toward transition metals.[1] We are currently interested in the application of this particular ligand property in organometallic chemistry.[2−4] This paper describes the synthesis of a novel pyridine-based PNP-pincer type phosphaalkene ligand that exhibits noninnocent behavior on group 9 metals.

Metal−ligand cooperative activation of chemical bonds aided by noninnocent behavior of pyridine-based pincer ligands has found wide application in catalytic transformations.[5] PNP- and PNN-pincer complexes with a phosphanylmethyl group on the pyridine core undergo deprotonation at the benzylic position to cause dearomatization of the pyridine ring. The dearomatized complex cleaves chemical bonds in a heterolytic manner, along with regeneration of the aromatic pyridine ring, where the metal center and the dearomatized ligand serve as a Lewis acid and a Brønsted base, respectively.

We recently found that the reactivity of dearomatized PNP-pincer complexes of Ir(I) toward metal−ligand cooperation could be remarkably enhanced by incorporating a phosphaalkene unit into the PNP-pincer scaffold.[3d−g] For example, complex K[**3b**] in Scheme 1 bearing a dearomatized PNP-pincer type phosphaalkene ligand (PPEP*) causes instant cleavage of the N−H bond of ammonia (1 atm) at room temperature.[3d] DFT calculations have revealed that the reactivity is effectively enhanced by strong π back-donation from the metal to the phosphaalkene unit.

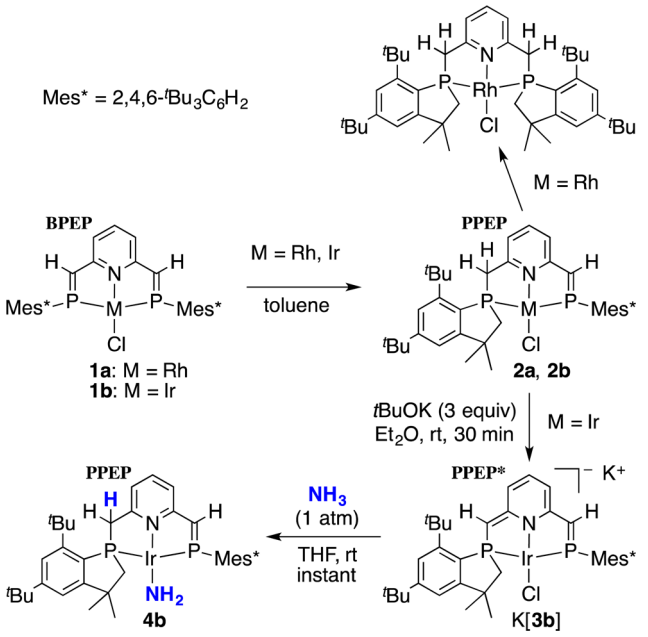
Complex K[**3b**] is prepared from **1b** bearing a 2,6-bis(phosphaethenyl)pyridine ligand (BPEP), as illustrated in Scheme 1.[3d] While the Mes* substituent is commonly used for steric protection of P═C bonds, the Mes*-P═CH group has been known to undergo C−H addition/cyclization on transition metals to form a phospholanylmethyl group in some instances.[6] The conversion of BPEP into the unsymmetrical PNP-pincer ligand PPEP in Scheme 1 (**1b** → **2b**) proceeds via this process. A crucial requirement is that BPEP undergoes C−H addition/cyclization exclusively at one of the Mes*-P═CH groups. The reaction of Ir(I) complex **1b** proceeded in perfect selectivity, and the resulting **2b** was

Special Issue: Organometallics in Asia

Received: February 10, 2016

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

Scheme 1



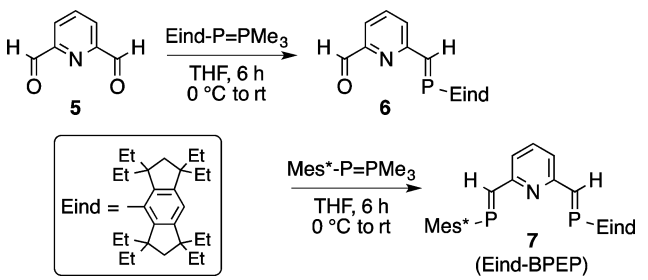
totally stable to further C−H addition/cyclization. On the other hand, attempts at other transition-metal complexes, including Rh(I) complex **1a**, were unsuccessful due to the occurrence of successive C−H addition/cyclization at both Mes*-P═CH groups, giving rise to complete loss of P═C bonds.[3f]

We therefore attempted to synthesize a novel BPEP ligand that can be selectively converted to PPEP on various metals. In this case, the most reliable way is the introduction of a steric protecting group that is stable to C−H addition/cyclization into one of the phosphaalkene units. We found that the 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl group (Eind),[7] having a fused-ring bulky structure, effectively prevents undesirable loss of the P═C bond. Using the newly synthesized phosphaalkene ligand Eind-PPEP, we could observe a distinct change in the reaction products of K[M(Cl)(Eind-PPEP*)] (M = Rh, Ir) and ammonia depending on the metals.

RESULTS AND DISCUSSION

Synthesis of Eind-BPEP (7). Compound **7**, having Mes*-P═CH and Eind-P═CH groups at the 2,6-positions of pyridine, was synthesized by a two-step procedure starting from 2,6-pyridinedicarboxaldehyde (**5**) (Scheme 2). While phosphaalkene units may be constructed either by a phospha-Peterson reaction[8] or by a phospha-Wittig reaction,[9] we chose the phospha-Wittig reaction due to the difficulty in preparing

Scheme 2

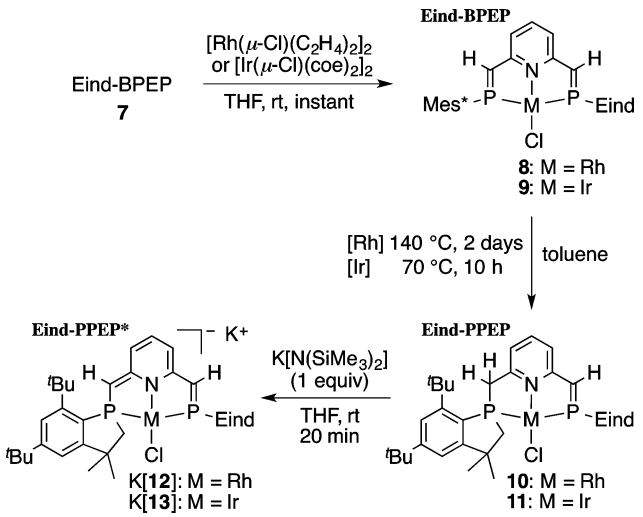


the phospha-Peterson reagent Eind-P(SiMe$_3$)Li. The first step is the treatment of **5** with Eind-P═PMe$_3$, generated in situ from Eind-PCl$_2$,[10] PMe$_3$, and zinc dust in THF. The phospha-Wittig reaction took place selectively at one of the formyl groups, and the desired compound **6** was isolated as a pale yellow powder in 74% yield by column chromatography.

Compound **6** was then treated with Mes*-P═PMe$_3$ in THF, and Eind-BPEP (**7**) was obtained in 97% yield. This product was contaminated with a small amount of Mes*-PH$_2$, which could not be removed by repeated chromatographic purifications. Accordingly, compound **7** was identified by NMR spectroscopy and mass spectrometry and used for complex formation without further purification. The $^{31}P\{^1H\}$ NMR spectrum displayed two singlet signals at δ_P 285.8 and 275.2, consistent with the unsymmetrical structure of **7** having different substituents on phosphorus atoms.

Synthesis of Eind-BPEP Complexes 8 and 9. Eind-BPEP (**7**) was coordinated with rhodium and iridium chlorides by the reactions with $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ and $[Ir(\mu\text{-}Cl)(\eta^2\text{-}coe)_2]_2$, respectively (Scheme 3). Both reactions took place instantly at room temperature to give [RhCl(Eind-BPEP)] (**8**) and [IrCl(Eind-BPEP)] (**9**) quantitatively, as confirmed by NMR spectroscopy.

Scheme 3



The $^{31}P\{^1H\}$ NMR spectrum of rhodium complex **8** displayed two sets of doublets of doublets at δ_P 239.2 ($^2J_{PP}$ = 519 Hz, $^1J_{RhP}$ = 207 Hz) and δ_P 231.2 ($^2J_{PP}$ = 519 Hz, $^1J_{RhP}$ = 204 Hz), which were assigned to Mes*-P═CH and Eind-P═CH groups, respectively, referring to the chemical shifts of [RhCl(BPEP)] (δ_P 242.4)[11] and [RhCl(Eind-PPEP)] (**10**; δ_P 230.5). Similarly, complex **9** showed two sets of doublets at δ_P 249.3 and 237.2 ($^2J_{PP}$ = 560 Hz), assignable to Mes*-P═CH and Eind-P═CH groups, respectively. The large $^2J_{PP}$ couplings are consistent with the trans arrangement of two phosphorus atoms. Moreover, the $^1J_{RhP}$ values of **8** are reasonable for a Rh(I) complex.

Complexes **8** and **9** were isolated as crystalline solids, suitable for X-ray diffraction analysis, in 60 and 84% yields, respectively. Figure 1 shows the crystal structures, which are superimposable with one another. Both complexes adopt a square-planar geometry around the metal: ∑(Rh) = 360.1°, ∑(Ir) = 360.0°. The Eind-BPEP ligand adopts meridional coordination, and the chlorido ligand occupies the fourth coordination site. The

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

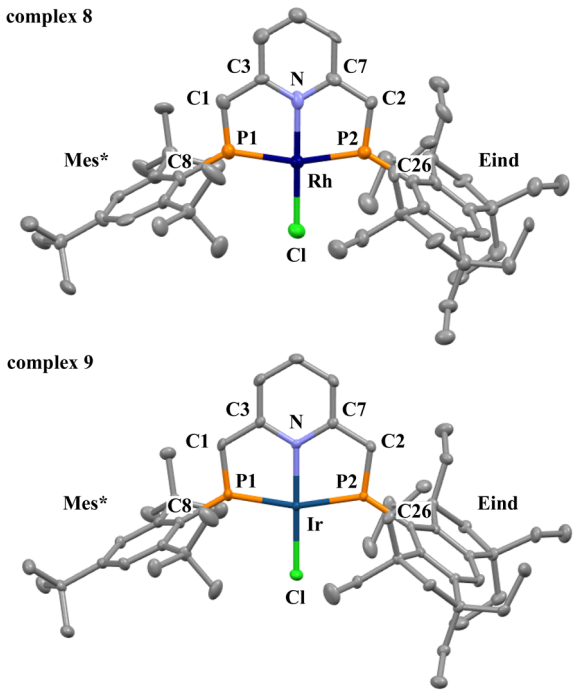


Figure 1. Molecular structures of [RhCl(Eind-BPEP)] (**8**) and [IrCl(Eind-BPEP)] (**9**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): complex **8**, Rh−P1 2.243(3), Rh−P2 2.205(3), Rh−N 2.061(9), Rh−Cl 2.318(3), P1−C1 1.646(10), P2−C2 1.668(10), C1−C3 1.465(13), C2−C7 1.436(13), P1−Rh−P2 161.83(10), N−Rh−Cl 178.3(2), C1−P1−C8 112.8(5), C2−P2−C26 113.5(5); complex **9**, Ir−P1 2.2349(9), Ir−P2 2.2128(8), Ir−N 2.047(3), Ir−Cl 2.3099(9), P1−C1 1.671(3), P2−C2 1.673(3), C1−C3 1.446(5), C2−C7 1.441(4), P1−Ir−P2 161.32(3), N−Ir−Cl 177.73(8), C1−P1−C8 113.37(16), C2−P2−C26 114.40(16).

Mes* and Eind groups are oriented nearly perpendicular to the coordination plane. The C2−P2−C26(Eind) and C1−P1−C8(Mes*) bond angles are comparable to each other for both complexes. The P1−C1 and P2−C2 bond lengths in **8** (1.646(10) and 1.668(10) Å) and in **9** (1.671(3) and 1.673(3) Å) are typical of P=C double bonds. The Rh−P1, Rh−P2, Rh−N, and Rh−Cl lengths of **8** are comparable to those of [RhCl(BPEP)].[11] Moreover, the Ir−P1, Ir−P2, Ir−N, and Ir−Cl lengths of **9** are nearly the same as those of [IrCl(BPEP)].[3c]

Synthesis of Eind-PPEP Complexes 10 and 11. Complexes **8** and **9** were converted to [RhCl(Eind-PPEP)] (**10**) and [IrCl(Eind-PPEP)] (**11**) by C−H addition/cyclization of the Mes*-P=CH group, respectively (Scheme 3). Although **8** and **9** have very similar structures, their reactivities were significantly different from each other. Heating iridium complex **9** in toluene at 70 °C overnight led to quantitative formation of **11**; the reactivity was comparable to that of [IrCl(BPEP)] (**1**) in Scheme 1.[3d] In contrast, rhodium complex **8** was stable at this temperature and converted to **10** by heating at 140 °C for 2 days in a sealed tube.

Complexes **10** and **11** were isolated in quantitative yields and identified by NMR spectroscopy and elemental analysis. The $^{31}P\{^{1}H\}$ NMR spectrum of **10** exhibited two sets of doublets of doublets at δ_P 230.5 ($^{2}J_{PP}$ = 461 Hz, $^{1}J_{RhP}$ = 183 Hz) and δ_P 26.0 ($^{2}J_{PP}$ = 461 Hz, $^{1}J_{RhP}$ = 168 Hz); the chemical shifts are consistent with the unsymmetrical structure of PPEP bearing phosphaethenyl and phospholanylmethyl groups. Likewise, complex **11** displayed two sets of doublets at δ_P 232.7 and 25.4 ($^{2}J_{PP}$ = 480 Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum.

The occurrence of C−H addition/cyclization giving a phospholanylmethyl group was supported by the appearance of benzylic proton and carbon signals in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra: complex **10**, δ_H 4.32 (dd, $^{2}J_{HH}$ = 18.4 Hz, $^{2}J_{PH}$ = 9.6 Hz, 1H), 4.10 (dd, $^{2}J_{HH}$ = 18.4 Hz, $^{2}J_{PH}$ = 9.7 Hz, 1H) and δ_C 50.6 (s, $^{1}J_{PC}$ = 18 Hz); complex **11**, δ_H 4.02 (dd, $^{2}J_{HH}$ = 18.8 Hz, $^{2}J_{PH}$ = 9.9 Hz, 1H), 4.01 (dd, $^{2}J_{HH}$ = 18.8 Hz, $^{2}J_{PH}$ = 10.2 Hz, 1H) and δ_C 51.1 (s, $^{1}J_{PC}$ = 26 Hz). Two benzylic protons are diastereotopic with each other, showing two sets of signals with a large $^{2}J_{HH}$ coupling (ca. 18 Hz). This signal pattern is consistent with the structure of Eind-PPEP having a chiral phospholanylmethyl group.

Synthesis of Dearomatized Eind-PPEP* Complexes 12 and 13. Treatment of Eind-PPEP complexes **10** and **11** with $K[N(SiMe_3)_2]$ (1 equiv) in THF at room temperature resulted in deprotonation at the benzylic position to give the dearomatized complexes K[RhCl(Eind-PPEP*)] (K[**12**]) and K[IrCl(Eind-PPEP*)] (K[**13**]), respectively. Similarly, complexes **10** and **11** reacted with *t*BuOK in THF in the presence of 18-crown-6 (18C6) to form [K(18C6)][**12**] and [K(18C6)][**13**], respectively. The anionic parts showed the same NMR spectrum irrespective of the kind of counterion. Since the crown ether adducts were easily crystallized in high yields (both 80%), [K(18C6)][**12**] and [K(18C6)][**13**] were characterized by NMR and X-ray analysis in detail.

The $^{31}P\{^{1}H\}$ NMR signals of **12** appeared at δ_P 211.3 ($^{2}J_{PP}$ = 433 Hz, $^{1}J_{RhP}$ = 182 Hz) and δ_P 19.2 ($^{2}J_{PP}$ = 433 Hz, $^{1}J_{RhP}$ = 169 Hz) as two sets of doublets of doublets. These signals were clearly shifted upfield in comparison with the parent complex **10**. Similarly, the signals of iridium complex **13** (δ_P 218.8 and 18.9, $^{2}J_{PP}$ = 458 Hz) appeared at a higher magnetic field in comparison to those of **11**. The presence of a dearomatized pyridine unit in complex **12** was indicated by three characteristic signals of ring protons at δ_H 6.03, 5.92, and 5.49. While the vinylic proton signal of Eind-PPEP* overlapped with a residual proton signal of the solvent (THF-d_8) as confirmed by HMQC experiments, the vinylic carbon signal was observed at δ_C 74.7 (d, $^{1}J_{PC}$ = 51 Hz). On the other hand, the vinylic proton and carbon signals of iridium complex **13** appeared at δ_H 3.89 (virtual triplet, J_{app} = 3.8 Hz) and δ_C 73.1 ($^{1}J_{PC}$ = 64 Hz), respectively.

Figure 2 shows the X-ray structures of [K(18C6)][**12**] and [K(18C6)][**13**], adopting a square-planar configuration around the metals: ∑(Rh) = 360.5°, ∑(Ir) = 360.3°. The Rh−Cl bond length in **12** (2.3382(7) Å) and Ir−Cl bond length in **13** (2.3557(16) Å) are consistent with dative bonding, whereas the Cl and K atoms are significantly distant from each other (2.9570(10) and 2.994(2) Å). Thus, the rhodium and iridium complexes may be described as anionic species bearing electrostatic interactions with the [K(18C6)] cation.

The P1−C1 bonds in **12** (1.751(3) Å) and **13** (1.750(6) Å) are clearly shorter than normal P−C single bonds, whereas the C1−C3 bond lengths (1.383(4) and 1.379(9) Å) are between those expected for single and double bonds. These variations are characteristic of dearomatized PNP-pincer ligands.[5] On the other hand, the P2−C2 bond lengths (1.673(3) and 1.675(6) Å) are typical of P=C double bonds.

Reactions of Dearomatized Eind-PPEP* Complexes with Ammonia. The rhodium and iridium complexes coordinated with Eind-PPEP* were subjected to the reactions with ammonia (1 atm) in THF-d_8 at room temperature

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

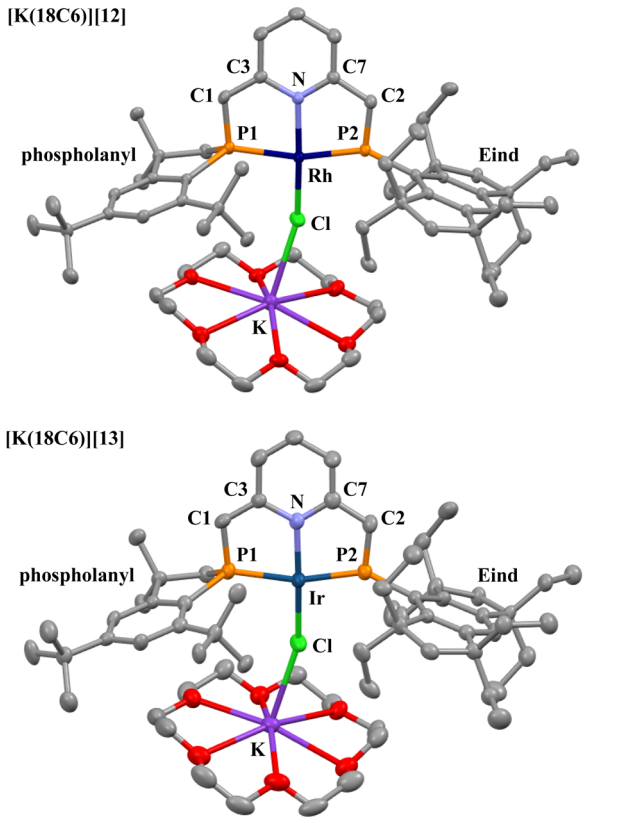
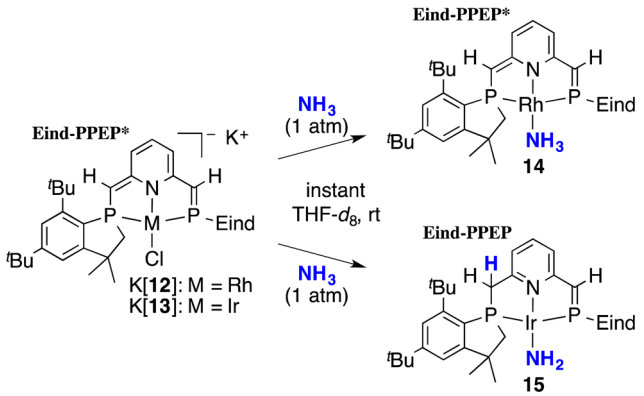


Figure 2. Molecular structures of [K(18-crown-6)][RhCl(Eind-PPEP*)] ([K(18C6)][**12**]) and [K(18-crown-6)][IrCl(Eind-PPEP*)] ([K(18C6)][**13**]) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): complex [K(18C6)][**12**], Rh−P1 2.2800(7), Rh−P2 2.2192(7), Rh−N1 2.067(2), Rh−Cl 2.3382(7), P1−C1 1.751(3), P2−C2 1.673(3), C1−C3 1.383(4), C2−C7 1.437(4), Cl−K 2.9570(10), P1−Rh−P2 162.61(3), N−Rh−Cl 171.32(6); complex [K(18C6)][**13**], Ir−P1 2.2869(16), Ir−P2 2.2174(17), Ir−N 2.068(5), Ir−Cl 2.3557(16), P1−C1 1.750(6), P2−C2 1.675(6), C1−C3 1.379(9), C2−C7 1.434(8), Cl−K 2.994(2), P1−Ir−P2 162.59(6), N−Ir−Cl 172.36(15).

(Scheme 4). Due to the difficulty in separating reaction products from [K(18C6)]Cl, the reactions were conducted with K[MCl(Eind-PPEP*)] (M = Rh, Ir), generated in situ from **10** and **11** by treatment with K[N(SiMe$_3$)$_2$]. The resulting complexes **14** and **15** were isolated in 98 and 99% yields, respectively, and characterized by NMR spectroscopy and elemental analysis.

Scheme 4



The reaction of the rhodium complex K[**12**] with ammonia was instantly completed, to form the ammine complex **14** in almost quantitative yield. Thus, simple displacement of the Cl$^-$ ligand with ammonia took place. The dearomatized pyridine unit was preserved, as indicated by three characteristic signals of ring protons at δ_H 6.04, 5.91, and 5.49 and of a vinylic proton at δ_H 3.48 in the ^{1}H NMR spectrum. A broad signal arising from the ammine ligand was observed at δ_H 2.13. Complex **14** was also examined by X-ray diffraction analysis: see the Supporting Information. While the data quality was insufficient for a detailed discussion of structural parameters (R1 = 0.1458), the existence of a dearomatized pyridine ring with a phosphola-nylmethylidene substituent was evidenced by characteristic P1−C1 (1.74(1) Å) and C1−C3 bond lengths (1.38 Å), which were comparable to those of [K(18C6)][**12**] (1.751(3) and 1.383(4) Å) in Figure 2. Moreover, the P2−C2 bond length (1.65(1) Å) was appropriate for a phosphaalkene unit.

On the other hand, the iridium complex K[**13**] led to metal−ligand cooperative activation of the N−H bond of ammonia, to afford a quantitative yield of parent amido complex **15** bearing an aromatized pyridine ring. The ^{1}H NMR spectrum showed a broad signal assignable to the amido ligand at δ_H 3.95; the chemical shift was similar to that observed for the PPEP amido complex **4** (δ_H 3.82).[3d] The benzylic proton signals appeared at δ_H 4.15 and 4.14 as two sets of doublet of doublets with a large geminal coupling ($^2J_{HH}$ = 20.3 Hz).

Thus, we could observe a dramatic change in the reaction courses depending on the metals. Since both reactions in Scheme 4 were completed instantly at room temperature, it would be reasonable that the distinct change would be mainly due to thermodynamic reasons. We therefore compared the relative stabilities of ammine and amido complexes by DFT calculations. The calculations were performed with the B3LYP-D functional and triple-ζ quality basis sets for the whole molecules without omission of any substituents. Solvent effects (THF) were included by PCM calculations: see the Supporting Information for computational details.

As a result, it was found that the rhodium ammine complex **14** (Rh^{NH3}) is more stable than the amido complex [Rh(NH$_2$)(Eind-PPEP)] (Rh^{NH2}) (eq 1); in contrast, the iridium ammine complex [Ir(NH$_3$)(Eind-PPEP*)] (Ir^{NH3}) is less stable than the amido complex **15** (Ir^{NH2}) (eq 2). The energy differences between two species (ΔG_{298} = −2.4 and +2.2 kcal/mol) correspond to the ratios Rh^{NH3}/Rh^{NH2} = 58/1 and Ir^{NH3}/Ir^{NH2} = 1/41, respectively. Thus, while the energy differences are somewhat smaller than those expected for the experimental observations showing selective formation of either complex, the tendencies were reproduced by DFT calculations.

$$[Rh(NH_3)(Eind\text{-}PPEP^*)] > [Rh(NH_2)(Eind\text{-}PPEP)]$$
$$\Delta G_{298}([Rh^{NH3}]-[Rh^{NH2}]) = -2.4\ \text{kcal/mol} \quad (1)$$

$$[Ir(NH_3)(Eind\text{-}PPEP^*)] < [Ir(NH_2)(Eind\text{-}PPEP)]$$
$$\Delta G_{298}([Ir^{NH3}]-[Ir^{NH2}]) = +2.2\ \text{kcal/mol} \quad (2)$$

CONCLUSION

In this study, we could synthesize a novel PNP-pincer type phosphaalkene ligand (Eind-PPEP) that functions as a

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

noninnocent ligand on transition metals. Unlike PPEP, bearing Mes* as a steric protecting group of the P═C bond, Eind-PPEP protected by a fused-ring bulky Eind group was sufficiently stable against C−H addition/cyclization even on a Rh(I) center. Therefore, we could compare the reactivity of K[MCl(Eind-PPEP*)] (M = Rh, Ir) toward ammonia and found a dramatic change in the reaction courses depending on the metals. It is worth noting that the reactivity of the iridium complex K[**13**] toward N−H bond cleavage of ammonia is comparable to that of the PPEP* complex K[**3b**]. This observation indicates that, while the Eind group seems sterically more demanding than the Mes* group, the highly reactive nature of the dearomatized phosphaalkene complex toward metal−ligand cooperative activation is successfully preserved after structural modification using Eind. At present, we are synthesizing various late-transition-metal complexes with Eind-PPEP and Eind-PPEP* ligands. Those results, including their reaction chemistry, will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a nitrogen atmosphere using a glovebox and Schlenk techniques. Eind-PCl_2 was prepared as previously reported.[10] The other chemicals were obtained from commercial sources. NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in δ (ppm), referenced to ^1H (residual) and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of 85% H_3PO_4 as an external standard. The assignments of ^{13}C signals are based on HMQC experiments. Elemental analysis was performed by ICR Analytical Laboratory, Kyoto University.

Synthesis of Eind-BPEP (7). *Synthesis of* ***6****.* To a mixture of zinc dust (348 mg, 5.3 mmol) and Eind-PCl_2 (300 mg, 0.62 mmol) in THF (4 mL) was added a 1.0 M THF solution of PMe_3 (1.5 mL, 1.5 mmol) at room temperature. After it was stirred for 1 h, the reaction mixture was added dropwise to a THF solution (6 mL) of **5** (86 mg, 0.64 mmol) by a cannula at 0 °C over 10 min. The mixture was stirred at room temperature for 6 h, and solvent was removed under reduced pressure. The residue was suspended in hexane (600 mL) and the suspension filtered through a Celite pad to remove zinc dust, $ZnCl_2$, and Me_3PO. The filtrate was concentrated to half volume and purified by gel filtration using 1,2-dihydroxy-3-propoxypropyl-modified silica gel with hexane as the eluent to afford **6** as a pale yellow powder (241 mg, 0.45 mmol, 74%).

Data for **6** are as follows. ^1H NMR (C_6D_6, 25 °C): δ 10.05 (s, 1H, C*H*O), 9.21 (d, $^2J_{PH}$ = 25.5 Hz, 1H, EindP═C*H*), 7.48 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Py), 7.31 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Py), 6.88 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Py), 6.86 (s, 1H, *p*-Eind), 2.11−2.02 (m, 4H, 2 × CH_2CH$_3$), 1.98−1.89 (m, 4H, 2 × CH_2CH$_3$), 1.78 (s, 4H, 2 × CH_2), 1.76−1.58 (m, 8H, 4 × CH_2CH$_3$), 0.90 (t, $^3J_{HH}$ = 7.4 Hz, 12H, 4 × CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 193.3 (s, CHO), 180.3 (d, $^1J_{PC}$ = 36 Hz, EindP═CH), 158.8 (d, J_{PC} = 15 Hz), 153.9 (s), 150.7 (d, J_{PC} = 3 Hz), 150.2 (s), 137.8 (s), 136.3 (d, $^1J_{PC}$ = 48 Hz, *ipso*-Eind), 124.3 (d, J_{PC} = 18 Hz), 121.5 (s, *p*-Eind), 120.1 (d, J_{PC} = 6 Hz), 53.7 (s), 49.0 (s), 42.9 (s, CH_2), 34.4 (br s, CH_2CH_3), 33.7 (br s, CH_2CH_3), 10.1 (s, CH_2CH_3), 9.8 (s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 284.2 (s). Anal. Calcd for $C_{35}H_{50}NOP$: C, 79.05; H, 9.48; N, 2.63. Found: C, 79.10; H, 9.62; N, 2.65.

Synthesis of ***7****.* To a mixture of zinc dust (235 mg, 3.6 mmol) and Mes*-PCl_2 (119 mg, 0.33 mmol) in THF (3.5 mL) was added a 1.0 M THF solution of PMe_3 (0.9 mL, 0.9 mmol) at room temperature. After it was stirred for 3 h, the reaction mixture was added dropwise to a THF solution (7 mL) of **6** (174 mg, 0.33 mmol) by a cannula at 0 °C. The mixture was stirred at room temperature for 6 h, and volatiles were removed under reduced pressure. The residue was suspended in hexane (30 mL) and the suspension filtered through a Celite pad to remove zinc dust, $ZnCl_2$, and Me_3PO. The filtrate was concentrated to dryness under reduced pressure to afford Eind-BPEP (**7**) as a yellow solid (259 mg, 0.32 mmol, 97%). The crude product was purified by column chromatography using deactivated neutral alumina and hexane as the eluent to remove a small amount of Mes*PH_2 formed by decomposition of the phospha-Wittig reagent (Mes*P═PMe_3).

Data for **7** are as follows. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.86 (d, $^2J_{PH}$ = 25.6 Hz, 1H, EindP═C*H*), 8.13 (d, $^2J_{PH}$ = 25.3 Hz, 1H, Mes*P═C*H*), 7.58 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 7.55 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 7.45 (s, 2H, *m*-Mes*), 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py), 6.73 (s, 1H, *p*-Eind), 1.91−1.76 (m, 8H, 4 × CH_2CH$_3$), 1.81 (s, 4H, 2 × CH_2), 1.74−1.55 (m, 8H, 4 × CH_2CH$_3$), 1.53 (s, 18H, *o*-^{t}Bu), 1.36 (s, 9H, *p*-^{t}Bu), 0.85 (t, $^3J_{HH}$ = 7.4 Hz, 12H, 4 × CH$_2$CH_3), 0.77 (t, $^3J_{HH}$ = 7.4 Hz, 12H, 4 × CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 181.8 (d, $^1J_{PC}$ = 34 Hz, EindP═CH), 175.9 (d, $^1J_{PC}$ = 35 Hz, Mes*P═CH), 158.7 (d, J_{PC} = 28 Hz), 158.6 (d, J_{PC} = 27 Hz), 154.7 (s), 150.6 (s), 150.4 (s), 150.0 (s), 139.6 (d, $^1J_{PC}$ = 54 Hz, *ipso*-Ar), 137.3 (s), 136.3 (d, $^1J_{PC}$ = 48 Hz, *ipso*-Ar), 122.6 (s, *m*-Mes*), 121.3 (s, *p*-Eind), 119.8 (t, J_{PC} = 18 Hz), 119.7 (t, J_{PC} = 17 Hz), 53.6 (s), 48.8 (s), 42.7 (s, CH_2), 38.8 (s), 35.6 (s), 34.4 (d, $^4J_{PC}$ = 7 Hz, *o*-C(CH$_3$)$_3$), 34.1 (br, CH_2CH_3), 33.5 (br, CH_2CH_3), 31.8 (s, *p*-C(CH$_3$)$_3$), 10.0 (s, CH_2CH_3), 9.6 (s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 285.8 (s), 275.2 (s). HRMS (APCI): calcd for $C_{53}H_{79}NP_2$, 792.5761 ([M + H]$^+$); found, 792.5774.

Synthesis of Eind-BPEP Complexes 8 and 9. A typical synthetic procedure is described for [RhCl(Eind-BPEP)] (**8**). The complex [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ (26 mg, 0.067 mmol) was suspended in THF (2 mL), and a solution (1 mL) of Eind-BPEP (122 mg, 0.15 mmol) in THF (1 mL) was added at room temperature. The mixture instantly changed into a greenish brown solution. The solution was stirred for 30 min and concentrated under reduced pressure. Addition of Et_2O (0.5 mL) led to the formation of a dark green crystalline solid of **8**, which was collected by filtration, washed with Et_2O (0.3 mL × 5), and dried under vacuum (75 mg, 0.080 mmol, 60%). The complex [IrCl(Eind-BPEP)] (**9**) was similarly prepared from [Ir(μ-Cl)(coe)$_2$]$_2$ and isolated as a greenish brown crystalline solid (84%).

Data for **8** are as follows. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.66 (dd, $^2J_{PH}$ = 17.5 Hz, $^3J_{RhH}$ = 3.6 Hz, 1H, EindP═C*H*), 7.59 (d, $^4J_{PH}$ = 2.5 Hz, 2H, *m*-Mes*), 7.28−7.23 (m, 1H, Py), 7.19 (dd, $^2J_{PH}$ = 18.1 Hz, $^3J_{RhH}$ = 3.6 Hz, 1H, Mes*P═C*H*), 6.91 (d, $^5J_{PH}$ = 3.3 Hz, 1H, *p*-Eind), 6.72−6.68 (m, 2H, Py), 2.39−2.24 (m, 4H, 2 × CH_2CH$_3$), 2.18−2.11 (m, 2H, CH_2CH$_3$), 1.97−1.88 (m, 2H, CH_2CH$_3$), 1.93 (d, $^2J_{HH}$ = 14.0 Hz, 2H, CH_2), 1.84 (d, $^2J_{HH}$ = 14.0 Hz, 2H, CH_2), 1.74 (s, 18H, *o*-^{t}Bu), 1.72−1.52 (m, 8H, 4 × CH_2CH$_3$), 1.38 (s, 9H, *p*-^{t}Bu), 0.90 (t, $^3J_{HH}$ = 7.4 Hz, 6H, 2 × CH$_2$CH_3), 0.85 (t, $^3J_{HH}$ = 7.4 Hz, 6H, 2 × CH$_2$CH_3), 0.83 (t, $^3J_{HH}$ = 7.6 Hz, 6H, 2 × CH$_2$CH_3), 0.77 (t, $^3J_{HH}$ = 7.3 Hz, 6H, 2 × CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 168.5 (d, J_{PC} = 8 Hz), 157.2 (s), 153.7 (d, J_{PC} = 2 Hz), 153.3 (s), 151.0 (s), 150.9 (s), 149.3 (dd, $^1J_{PC}$ = 36 Hz, $^2J_{RhC}$ = 4 Hz, EindP═CH), 148.1 (dd, $^1J_{PC}$ = 36 Hz, $^2J_{RhC}$ = 4 Hz, Mes*P═CH), 134.4 (s), 126.8−126.4 (m, *ipso*-Ar), 124.3−123.9 (m, *ipso*-Ar), 123.7 (d, $^4J_{PC}$ = 2 Hz, *p*-Eind), 123.4 (d, $^3J_{PC}$ = 7 Hz, *m*-Mes*), 114.6 (t, J_{PC} = 8 Hz, J_{RhC} = 8 Hz), 114.3 (t, J_{PC} = 8 Hz, J_{RhC} = 8 Hz), 54.2 (s), 48.8 (s), 43.0 (s, CH_2), 39.5 (s), 35.9(s), 35.0 (d, $^4J_{PC}$ = 2 Hz, CH_2CH_3), 34.8 (d, $^4J_{PC}$ = 2 Hz, *o*-C(CH$_3$)$_3$), 34.4 (s, CH_2CH_3), 33.7 (s, CH_2CH_3), 33.5 (s, CH_2CH_3), 31.6 (s, *p*-C(CH$_3$)$_3$), 10.5 (s, CH_2CH_3), 10.4 (s, CH_2CH_3), 9.6 (s, 2 × CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 239.2 (dd, $^2J_{PP}$ = 519 Hz, $^1J_{RhP}$ = 207 Hz), 231.2 (dd, $^2J_{PP}$ = 519 Hz, $^1J_{RhP}$ = 204 Hz). Anal. Calcd for $C_{53}H_{79}ClNP_2Rh$: C, 68.41; H, 8.56; N, 1.51. Found: C, 68.32; H, 8.65; N, 1.65.

Data for **9** are as follows. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.96 (dd, $^2J_{PH}$ = 13.3 Hz, $^4J_{PH}$ = 5.4 Hz, 1H, EindP═C*H*), 8.50 (dd, $^2J_{PH}$ = 14.1 Hz, $^4J_{PH}$ = 5.1 Hz, 1H, Mes*P═C*H*), 7.79−7.74 (m, 1H, Py), 7.65 (d, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-Mes*), 7.05−7.03 (m, 1H, Py), 7.00−6.98 (m, 1H, Py), 6.95 (d, $^5J_{PH}$ = 1.7 Hz, 1H, *p*-Eind), 2.35−2.24 (m. 4H, 2 × CH_2CH$_3$), 2.14−2.06 (m, 2H, CH_2CH$_3$), 1.94 (d, $^2J_{HH}$ = 14.0 Hz, 2H, CH_2), 1.94−1.81 (m, 2H, CH_2CH$_3$), 1.85 (d, $^2J_{HH}$ = 14.0 Hz, 2H, CH_2), 1.79−1.58 (m, 8H, 4 × CH_2CH$_3$), 1.72 (s, 18H, *o*-^{t}Bu), 1.41 (s, 9H, *p*-^{t}Bu), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 6H, 2 × CH$_2$CH_3), 0.862 (t, $^3J_{HH}$ = 7.2 Hz, 6H, 2 × CH$_2$CH_3), 0.857 (t, $^3J_{HH}$ = 7.2 Hz, 6H, 2 × CH$_2$CH_3),

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

0.71 (t, $^3J_{HH}$ = 7.3 Hz, 6H, 2 × CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 174.6 (dd, J_{PC} = 9 and 4 Hz), 157.4 (vt, J_{app} = 2 Hz), 154.0 (d, J_{PC} = 2 Hz), 153.3 (s), 151.2 (s), 151.1 (s), 143.2 (d, $^1J_{PC}$ = 53 Hz, Mes*P═CH), 142.6 (d, $^1J_{PC}$ = 53 Hz, EindP═CH), 135.8 (vt, J_{app} = 3 Hz, Py), 127.3 (d, $^1J_{PC}$ = 21 Hz, *ipso*-Ar), 124.5 (dd, $^1J_{PC}$ = 21 Hz, $^3J_{PC}$ = 5 Hz, *ipso*-Ar), 124.0 (d, $^4J_{PC}$ = 3 Hz, *p*-Eind), 123.5 (d, $^3J_{PC}$ = 8 Hz, *m*-Mes*), 108.0 (dd, J_{PC} = 7 and 6 Hz), 107.8 (dd, J_{PC} = 7 and 6 Hz), 54.3 (s), 48.7 (s), 43.0 (s, CH_2), 39.5 (s), 36.0 (s), 34.6 (s, CH_2CH_3), 34.4 (d, $^4J_{PC}$ = 1 Hz, *o*- $C(CH_3)_3$), 33.9 (s, CH_2CH_3), 33.6 (s, 2 × CH_2CH_3), 31.6 (s, *p*-$C(CH_3)_3$), 10.5 (s, CH_2CH_3), 10.3 (s, CH_2CH_3), 9.6 (s, 2 × CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 249.3 (d, $^2J_{PP}$ = 560 Hz), 237.2 (d, $^2J_{PP}$ = 560 Hz). Anal. Calcd for $C_{53}H_{79}ClNP_2Ir$: C, 62.42; H, 7.81; N, 1.37. Found: C, 62.28; H, 7.88; N, 1.32.

Synthesis of Eind-PPEP Complexes 10 and 11. The complex [RhCl(Eind-BPEP)] (**8**; 14 mg, 0.015 mmol) was dissolved in toluene-d_8 (0.6 mL) and heated at 140 °C for 2 days in a sealed NMR sample tube. The solution gradually changed from dark green to dark red. ^1H and $^{31}P\{^1H\}$ NMR analysis revealed the complete conversion of **8** to **10**. The solution was filtered through a Celite pad to remove a small amount of black solids and concentrated to dryness to give a dark red crystalline solid of **10** (14 mg, 100%), which was analytically pure. The iridium Eind-PPEP complex **11** was prepared by heating a toluene solution of **9** at 70 °C for 10 h and isolated as a pure brown crystalline solid in quantitative yield.

Data for **10** are as follows. ^1H NMR (THF-d_8, 25 °C): δ 8.06 (dd, $^2J_{PH}$ = 17.0 Hz, $^3J_{RhH}$ = 3.6 Hz, 1H, EindP═C*H*), 7.58 (br t, $^3J_{HH}$ = 7.7 Hz, 1H, Py), 7.46 (dd, $^4J_{PH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar), 7.27 (d, $^4J_{HH}$ = 1.7 Hz, 1H, Ar), 7.13−7.10 (m, 1H, Py), 7.02 (br d, $^3J_{HH}$ = 6.4 Hz, 1H, Py), 6.92 (s, 1H, *p*-Eind), 4.32 (dd, $^2J_{HH}$ = 18.4 Hz, $^2J_{PH}$ = 9.6 Hz, 1H, PyCH_2P), 4.10 (dd, $^2J_{HH}$ = 18.4 Hz, $^2J_{PH}$ = 9.7 Hz, 1H, PyCH_2P), 2.83−2.71 (m, 2H, PCH_2 + CH_2CH$_3$), 2.57−2.47 (m, 1H, CH_2CH$_3$), 2.36 (dd, $^2J_{HH}$ = 14.8 Hz, $^2J_{PH}$ = 2.1 Hz, 1H, PCH_2), 2.25−2.14 (m, 3H, CH_2CH$_3$), 2.06−1.93 (m, 4H, CH_2CH$_3$ + CH_2), 1.89−1.83 (m, 3H, CH_2CH$_3$ + CH_2), 1.79−1.58 (m, 8H, 4 × CH_2CH$_3$), 1.53 (s, 9H, ^{t}Bu), 1.51 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.35 (s, 9H, ^{t}Bu), 0.93 (t, $^3J_{HH}$ = 6.8 Hz, 6H, 2 × CH_2CH_3), 0.90−0.82 (m, 12H, 4 × CH_2CH_3), 0.82−0.75 (m, 6H, 2 × CH_2CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): δ 166.3 (d, J_{PC} = 10 Hz), 164.0 (d, J_{PC} = 10 Hz), 160.1 (dd, J_{PC} = 11 and 5 Hz), 154.9 (d, J_{PC} = 2 Hz), 154.7 (d, J_{PC} = 11 Hz), 153.3 (d, J_{PC} = 2 Hz), 153.0 (s), 150.8 (d, J_{PC} = 6 Hz), 150.7 (d, J_{PC} = 6 Hz), 149.0 (dd, $^1J_{PC}$ = 32 Hz, $^2J_{RhC}$ = 3 Hz, EindP═CH), 132.5 (s), 129.3−129.0 (m), 128.6 (dt, J_{RhC} = 19 Hz, J_{PC} = 19 and 7 Hz), 123.9 (d, $^3J_{PC}$ = 8 Hz, Ar), 123.2 (s, *p*-Eind), 120.8 (d, J_{PC} = 25 Hz), 119.6 (d, $^3J_{PC}$ = 8 Hz, Ar), 118.9 (dd, J_{PC} = 13 and 8 Hz), 54.9 (s), 54.7 (s), 50.6 (d, $^1J_{PC}$ = 18 Hz, PyCH_2P), 49.21 (s), 43.18 (s), 45.4−45.2 (m), 43.7 (s, CH_2), 43.6 (s, CH_2), 42.3 (d, $^1J_{PC}$ = 27 Hz, PCH_2), 38.3 (s), 36.1 (s), 35.5 (s, CH_2CH_3), 35.3 (s, CH_2CH_3), 35.1 (d, $^4J_{PC}$ = 3 Hz, CH_2CH_3), 34.8 (s, CH_2CH_3), 34.7 (s, CH_2CH_3), 34.6 (d, $^4J_{PC}$ = 2 Hz, CH_2CH_3), 33.8 (d, $^4J_{PC}$ = 3 Hz, $C(CH_3)_3$), 33.7 (s, CH_3), 33.3 (s, CH_2CH_3), 33.2 (s, CH_2CH_3), 32.1 (d, $^3J_{PC}$ = 9 Hz, CH_3), 31.9 (s, $C(CH_3)_3$), 11.02 (s, CH_2CH_3), 10.99 (s, CH_2CH_3), 10.7 (s, CH_2CH_3), 10.6 (s, CH_2CH_3), 9.8 (s, 4 × CH_2CH_3). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): δ 230.5 (dd, $^2J_{PP}$ = 461 Hz, $^1J_{RhP}$ = 183 Hz), 26.0 (dd, $^2J_{PP}$ = 461 Hz, $^1J_{RhP}$ = 168 Hz). Anal. Calcd for $C_{53}H_{79}ClNP_2Rh$: C, 68.41; H, 8.56; N, 1.51. Found: C, 68.68; H, 8.83; N, 1.73.

Data for **11** are as follows. ^1H NMR (THF-d_8, 25 °C): δ 8.94 (dd, $^2J_{PH}$ = 12.7 Hz, $^4J_{PH}$ = 4.1 Hz, 1H, EindP═C*H*), 7.99 (td, $^3J_{HH}$ = 7.6 Hz, $^5J_{PH}$ = 1.7 Hz, 1 H, Py), 7.47 (dd, $^4J_{PH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar), 7.30 (d, $^4J_{HH}$ = 1.7 Hz, 1H, Ar), 6.96 (br d, $^3J_{HH}$ = 7.2 Hz, 1H, Py), 6.95 (s, 1H, *p*-Eind), 6.90 (br d, $^3J_{HH}$ = 7.6 Hz, 1H, Py), 4.02 (dd, $^2J_{HH}$ = 18.8 Hz, $^2J_{PH}$ = 9.9 Hz, 1H, PyCH_2P), 4.01 (dd, $^2J_{HH}$ = 18.8 Hz, $^2J_{PH}$ = 10.2 Hz, 1H, PyCH_2P), 2.81−2.69 (m, 2H, PCH_2 + CH_2CH$_3$), 2.63−2.51 (m, 1H, CH_2CH$_3$), 2.38 (dd, $^2J_{HH}$ = 14.8 Hz, $^2J_{PH}$ = 3.1 Hz, 1H, PCH_2), 2.32−2.18 (m, 3H, CH_2CH$_3$), 2.16−2.09 (m, 1H, CH_2CH$_3$), 2.07−2.00 (m, 1H, CH_2CH$_3$), 1.95 (d, $^2J_{HH}$ = 13.9 Hz, 2H, CH_2), 1.86 (d, $^2J_{HH}$ = 13.9 Hz, 1H, CH_2), 1.85 (d, $^2J_{HH}$ = 13.9 Hz, 1H, CH_2), 1.91−1.63 (m, 9H, CH_2CH$_3$), 1.51 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.42 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu), 0.95−0.76 (m, 24H, 8 × CH_2CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): δ 168.0 (d, J_{PC} = 7 Hz), 167.3 (dd, J_{PC} = 6 and 3 Hz), 160.4 (dd, J_{PC} = 14 and 5 Hz), 154.9 (d, J_{PC} = 2 Hz), 154.8 (d, J_{PC} = 10 Hz), 152.7 (d, J_{PC} = 2 Hz), 152.5 (s), 150.9 (d, J_{PC} = 7 Hz), 150.8 (d, J_{PC} = 10 Hz), 143.9 (d, $^1J_{PC}$ = 47 Hz, EindP═CH), 130.9 (s), 128.9 (dd, J_{PC} = 20 and 4 Hz), 126.9 (dd, 37 and 6 Hz), 124.0 (d, $^3J_{PC}$ = 9 Hz, Ar), 123.4 (d, $^4J_{PC}$ = 2 Hz, *p*-Eind), 121.6 (d, J_{PC} = 25 Hz), 119.6 (d, $^3J_{PC}$ = 9 Hz, Ar), 118.2 (dd, J_{PC} = 12 and 8 Hz), 54.8 (s), 54.7 (s), 51.1 (d, $^1J_{PC}$ = 26 Hz, PyCH_2P), 49.0 (s), 48.9 (s), 44.5 (vt, J_{app} = 4 Hz), 43.7 (s, CH_2), 43.6 (s, CH_2), 40.8 (d, $^1J_{PC}$ = 34 Hz, PCH_2), 38.1 (s), 36.0 (s), 34.8 (s, CH_2CH_3), 34.6 (s, CH_2CH_3), 34.52 (s, CH_2CH_3), 34.47 (s, CH_2CH_3), 34.4 (s, CH_2CH_3), 34.1 (s, CH_2CH_3), 33.7 (s, CH_3), 33.6 (d, $^4J_{PC}$ = 2 Hz, $C(CH_3)_3$), 33.4 (s, CH_2CH_3), 33.3 (s, CH_2CH_3), 31.9 (s, CH_3), 31.8 (s, $C(CH_3)_3$), 10.90 (s, CH_2CH_3), 10.86 (s, CH_2CH_3), 10.6 (s, CH_2CH_3), 10.5 (s, CH_2CH_3), 9.8 (s, 2 × CH_2CH_3), 9.7 (s, 2 × CH_2CH_3). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): δ 232.7 (d, $^2J_{PP}$ = 480 Hz), 25.4 (d, $^2J_{PP}$ = 480 Hz). Anal. Calcd for $C_{53}H_{79}ClNP_2Ir$: C, 62.42; H, 7.81; N, 1.37. Found: C, 62.23; H, 7.86; N, 1.24.

Synthesis of Eind-PPEP* Complexes 12 and 13. A solution of ^{t}BuOK (6.7 mg, 0.060 mmol) and 18-crown-6 (16 mg, 0.060 mmol) in THF (1 mL) was added to a THF solution (1 mL) of **10** (56 mg, 0.060 mmol). The solution instantly changed from dark red to dark greenish brown. After 20 min at room temperature, the complete conversion of **10** was confirmed by $^{31}P\{^1H\}$ NMR analysis. The solvent was removed under reduced pressure, and Et_2O (0.3 mL) was added to the residue, affording dark brown crystals of [K(18C6)][RhCl(Eind-PPEP*)] ([K(18C6)][**12**]). The supernatant was removed by decantation, and the crystalline soild was washed with Et_2O (0.3 mL × 5) and dried under vacuum (59 mg, 0.048 mmol, 80%). The complex [K(18C6)][IrCl(Eind-PPEP*)] ([K(18C6)][**13**]) was similarly prepared from **11** as dark green crystals (80%).

Data for [K(18C6)][**12**] are as follows. ^1H NMR (THF-d_8, 25 °C): δ 7.52 (dd, $^2J_{PH}$ = 16.3 Hz, $^3J_{RhH}$ = 2.7 Hz, 1H, EindP═C*H*), 7.27 (dd, $^4J_{PH}$ = 3.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, Ar), 7.08 (d, $^4J_{HH}$ = 1.4 Hz, 1H, Ar), 6.74 (s, 1H, *p*-Eind), 6.03 (m, 1H, Py), 5.92 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 2.8 Hz, 1H, Py), 5.49 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{PH}$ = 3.9 Hz, 1H, Py), 3.56 (vt, 1H, Py═C*H*P), 3.53 (s, 24H, 18-crown-6), 3.11−3.03 (m, 1H, CH_2CH$_3$), 2.74−2.70 (m, 1H, CH_2CH$_3$), 2.46 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 4.0 Hz, 1H, PCH_2), 2.33−2.19 (m, 4H, 2 × CH_2CH$_3$), 2.10−1.94 (m, 2H, CH_2CH$_3$), 1.88 (d, $^2J_{HH}$ = 13.6 Hz, 2H, CH_2), 1.82 (d, $^2J_{HH}$ = 13.6 Hz, 1H, CH_2), 1.80 (d, $^2J_{HH}$ = 13.6 Hz, 1H, CH_2), 1.71 (s, 9H, ^{t}Bu), 1.71−1.54 (m, 9H, 4 × CH_2CH$_3$ + PCH_2), 1.42 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.31 (s, 9H, ^{t}Bu), 0.91 (t, $^3J_{HH}$ = 7.3 Hz, 6H, 2 × CH_2CH_3), 0.87−0.77 (m, 18H, 6 × CH_2CH_3). The coupling constant for the vinylic proton at δ 3.56 was obscured due to the overlap with a residual signal of THF-d_8. $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): δ 173.5 (dd, J_{PC} = 25 Hz, J_{RhC} = 3 Hz), 163.6 (d, J_{PC} = 10 Hz), 158.6 (dd, J_{PC} = 10 and 5 Hz), 153.8 (d, J_{PC} = 10 Hz), 152.45 (s), 152.41 (s), 150.5 (d, J_{PC} = 2 Hz), 149.7 (d, $^1J_{PC}$ = 33 Hz, EindP═CH), 149.4 (d, J_{PC} = 4 Hz), 149.1 (d, J_{PC} = 5 Hz), 136.7−136.5 (br d, J_{PC} = 25 Hz), 132.8 (ddd, J_{PC} = 29 and 20 Hz, J_{RhC} = 7 Hz), 129.4 (vt, J_{app} = 3 Hz), 121.1 (d, $^3J_{PC}$ = 7 Hz, Ar), 120.8 (s, *p*-Eind), 117.6 (d, $^3J_{PC}$ = 7 Hz, Ar), 109.3 (dd, J_{PC} = 21 and 10 Hz), 100.4 (d, J_{PC} = 28 Hz), 74.7 (d, $^1J_{PC}$ = 51 Hz, Py═C*H*P), 71.0 (s, 18-crwon-6), 54.4 (s), 54.2 (s), 48.34 (s), 48.30 (s), 43.7 (d, $^1J_{PC}$ = 27 Hz, PCH_2), 43.8−43.7 (m), 43.6 (s, CH_2), 43.5 (s, CH_2), 38.6 (s), 35.3 (s), 34.7 (s, CH_2CH_3), 34.6 (s, CH_2CH_3), 34.5 (s, CH_2CH_3), 34.4 (s, CH_2CH_3), 34.03 (s, $C(CH_3)_3$), 34.00 (s, CH_3), 33.97 (s, CH_2CH_3), 33.7 (d, $^4J_{PC}$ = 3 Hz, CH_2CH_3), 32.9 (s, CH_2CH_3), 32.8 (s, CH_2CH_3), 32.3 (d, $^3J_{PC}$ = 8 Hz, CH_3), 31.8 (s, $C(CH_3)_3$), 11.0 (s, CH_2CH_3), 10.9 (s, CH_2CH_3), 10.4 (s, CH_2CH_3), 10.3 (s, CH_2CH_3), 9.5 (s, 2 × CH_2CH_3), 9.4 (s, 2 × CH_2CH_3). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): δ 211.3 (dd, $^2J_{PP}$ = 433 Hz, $^1J_{RhP}$ = 182 Hz), 19.2 (dd, $^2J_{PP}$ = 433 Hz, $^1J_{RhP}$ = 169 Hz). Anal. Calcd for $C_{65}H_{102}ClKNO_6P_2Rh$: C, 63.32; H, 8.34; N, 1.14. Found: C, 63.04; H, 8.54; N, 1.08.

Data for [K(18C6)][**13**] are as follows. ^1H NMR (THF-d_8, 25 °C): δ 8.90 (dd, $^2J_{PH}$ = 11.7 Hz, $^4J_{PH}$ = 3.6 Hz, 1H, EindP═C*H*), 7.27 (dd, $^4J_{PH}$ = 3.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar), 7.12 (d, $^4J_{HH}$ = 1.7 Hz, 1H, Ar),

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

6.76 (s, 1H, *p*-Eind), 6.13 (dd, $^3J_{HH}$ = 8.1 and 6.8 Hz, 1H, Py), 6.06−6.03 (m, 2H, Py), 3.89 (vt, J_{app} = 3.8 Hz, Py=C*H*P), 3.53 (s, 24H, 18-crown-6), 3.23−3.14 (m, 1H, CH_2CH$_3$), 2.90−2.81 (m, 1H, CH_2CH$_3$), 2.37 (br dd, $^1J_{HH}$ = 13.6 Hz, $^2J_{PH}$ = 7.2 Hz, 1H, PCH_2), 2.32−2.17 (m, 4H, 2 × CH_2CH$_3$), 2.03−1.93 (m, 2H, CH_2CH$_3$), 1.88 (d, $^2J_{HH}$ = 13.8 Hz, 2H, CH_2), 1.81 (d, $^2J_{HH}$ = 13.8 Hz, 1H, CH_2), 1.80 (d, $^2J_{HH}$ = 13.8 Hz, 1H, CH_2), 1.71−1.57 (m, 9H, CH_2CH$_3$ + PCH_2), 1.55 (s, 9H, ^{t}Bu), 1.47 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.32 (s, 9H, ^{t}Bu), 0.92−0.77 (m, 24H, 8 × CH$_2$CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 177.4 (d, J_{PC} = 20 Hz), 167.4 (dd, J_{PC} = 8 and 3 Hz), 159.0 (dd, J_{PC} = 13 and 5 Hz), 154.0 (d, J_{PC} = 9 Hz), 152.5 (s), 150.71 (s), 150.69 (s), 149.7 (d, J_{PC} = 5 Hz), 149.4 (d, J_{PC} = 6 Hz), 141.9 (d, $^1J_{PC}$ = 48 Hz, EindP=CH), 135.8 (dd, J_{PC} = 34 and 5 Hz), 133.8 (dd, J_{PC} = 22 and 17 Hz), 130.7 (s), 122.3 (d, $^3J_{PC}$ = 7 Hz, Ar), 121.2 (s, *p*-Eind), 117.8 (d, $^3J_{PC}$ = 8 Hz, Ar), 105.9 (dd, J_{PC} = 18 and 8 Hz), 98.6 (d, J_{PC} = 26 Hz), 73.1 (d, $^1J_{PC}$ = 64 Hz, Py=CHP), 71.1 (s, 18-crown-6), 54.5 (s), 54.3 (s), 48.3 (s), 48.2 (s), 43.9 (s, CH_2), 43.7 (s, CH_2), 43.3 (br s), 43.1 (d, $^1J_{PC}$ = 29 Hz, PCH_2), 38.5 (s), 35.4 (s), 34.44 (s, CH_2CH$_3$), 34.43 (s, CH_2CH$_3$), 34.35 (s, CH_2CH$_3$), 34.34 (s, CH_2CH$_3$), 34.2 (d, $^4J_{PC}$ = 2 Hz, C(CH_3)$_3$), 34.1 (s, CH_3), 33.9 (br s, CH_2CH$_3$), 33.2 (br s, CH_2CH$_3$), 33.1 (s, CH_2CH$_3$), 32.9 (s, CH_2CH$_3$), 32.4 (d, $^3J_{PC}$ = 9 Hz, CH_3), 31.8 (s, C(CH_3)$_3$), 11.02 (s, CH_2CH$_3$), 10.98 (s, CH_2CH$_3$), 10.5 (s, CH_2CH$_3$), 10.4 (s, CH_2CH$_3$), 9.6 (s, 2 × CH_2CH$_3$), 9.5 (s, 2 × CH_2CH$_3$). ^{31}P{^{1}H} NMR (THF-d_8, 25 °C): δ 218.8 (d, $^2J_{PP}$ = 458 Hz), 18.9 (d, $^2J_{PP}$ = 458 Hz). Anal. Calcd for $C_{65}H_{102}ClIrKNO_6P_2$: C, 59.04; H, 7.78; N, 1.06. Found: C, 58.64; H, 8.00; N, 1.22.

Reactions of Eind-PPEP* Complexes with Ammonia. A THF-d_8 solution (0.3 mL) of K[N(SiMe$_3$)$_2$] (2.0 mg, 0.010 mmol) was added to a THF-d_8 solution (0.3 mL) of **10** (9.3 mg, 0.010 mmol) at room temperature in an NMR sample tube. The solution instantly changed from dark red to dark greenish brown. After 30 min at room temperature, the complete conversion of **10** to K[**12**] was confirmed by ^{1}H and ^{31}P{^{1}H} NMR analysis. The resulting solution was degassed by freeze−pump−thaw cycles (three times) and charged with an anhydrous NH_3 gas (1 atm). The solution turned reddish brown. Volatile materials were removed under reduced pressure, and the residue was dissolved in hexane (1 mL) and filtered through a glass fiber filter to remove KCl. The filtrate was concentrated to dryness under reduced pressure to give a reddish brown crystalline solid of [Rh(NH_3)(Eind-PPEP*)] (**14**; 9.0 mg, 98%). Complex **14** was gradually degraded upon drying under reduced pressure, probably due to dissociation of the ammine ligand. Therefore, the complex did not give a satisfactory elemental analysis, and its composition was confirmed by HRMS analysis and NMR spectroscopy.

Complex K[**13**] was similarly prepared from **11** and K[N(SiMe$_3$)$_2$] in THF-d_8; this solution was treated with NH_3 (1 atm) at room temperature. The reaction was instantly completed, and [Ir(NH_2)(Eind-PPEP)] (**15**) was isolated as a dark green crystalline solid (99%).

Data for **14** are as follows. ^{1}H NMR (THF-d_8, 25 °C): δ 7.64 (dd, $^2J_{PH}$ = 17.4 Hz, $^3J_{RhH}$ = 2.9 Hz, 1H, EindP=C*H*), 7.38 (dd, $^4J_{PH}$ = 4.1 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, Ar), 7.18 (d, $^4J_{HH}$ = 1.8 Hz, 1H, Ar), 6.85 (s, 1H, *p*-Eind), 6.04 (m, 1H, Py), 5.91 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 4.7 Hz, 1H, Py), 5.49 (t, $^3J_{HH}$ = 5.7 Hz, $^4J_{PH}$ = 5.7 Hz, 1H, Py), 3.48 (br d, $^2J_{PH}$ = 3.9 Hz, 1H, Py=C*H*P), 2.89−2.80 (m, 1H, CH_2CH$_3$), 2.68−2.58 (m, 1H, CH_2CH$_3$), 2.34−2.23 (m, 4H, 2 × CH_2CH$_3$), 2.13 (br, 3H, NH_3), 2.09−2.01 (m, 3H, PCH_2 + CH_2CH$_3$), 1.89 (br s, 4H, 2 × CH_2), 1.79 (s, 9H, ^{t}Bu), 1.78 (dd, $^1J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 4.6 Hz, 1H, PCH_2), 1.70−1.49 (m, 8H, 4 × CH_2CH$_3$), 1.42 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.32 (s, 9H, ^{t}Bu), 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 6H, 2 × CH$_2$CH_3), 0.85 (t, $^3J_{HH}$ = 7.2 Hz, 12H, 4 × CH$_2$CH_3), 0.81−0.75 (m, 6H, 2 × CH$_2$CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 173.6 (dd, J_{PC} = 24 Hz, J_{RhC} = 3 Hz), 162.8 (br d, J_{PC} = 10 Hz), 159.5 (dd, J_{PC} = 12 and 4 Hz), 156.3 (d, $^1J_{PC}$ = 37 Hz, EindP=CH), 154.0 (d, J_{PC} = 10 Hz), 152.7 (s), 152.3 (d, J_{PC} = 1 Hz), 152.0 (s), 150.6 (d, J_{PC} = 5 Hz), 150.5 (d, J_{PC} = 5 Hz), 134.4 (br d, J_{PC} = 30 Hz), 130.9 (vt, J_{app} = 5 Hz), 130.2−129.8 (m), 123.0 (d, $^3J_{PC}$ = 7 Hz, Ar), 122.2 (s, *p*-Eind), 118.7 (d, $^3J_{PC}$ = 7 Hz, Ar), 113.4 (dd, J_{PC} = 21 and 12 Hz), 103.5 (d, J_{PC} = 33 Hz), 74.0 (d, $^1J_{PC}$ = 54 Hz, Py=CHP), 54.4 (s), 54.3 (s), 48.59 (s), 48.57 (s), 44.2−44.1 (m), 43.4 (s, CH_2), 43.3 (d, $^1J_{PC}$ = 28 Hz, PCH_2), 43.2 (s, CH_2), 38.5 (s), 35.5 (s), 35.0 (s, CH_2CH$_3$), 34.7 (s, CH_2CH$_3$), 34.1 (s, 2 × CH_2CH$_3$), 33.9 (d, $^4J_{PC}$ = 4 Hz, CH_2CH$_3$), 33.7 (d, $^4J_{PC}$ = 3 Hz, C(CH_3)$_3$), 33.5 (d, $^4J_{PC}$ = 4 Hz, CH_2CH$_3$), 33.4 (s, CH_3), 33.18 (s, CH_2CH$_3$), 33.15 (s, CH_2CH$_3$), 32.1 (d, $^3J_{PC}$ = 8 Hz, CH_3), 31.7 (s, C(CH_3)$_3$), 10.7 (s, CH_2CH$_3$), 10.31 (s, CH_2CH$_3$), 10.25 (s, CH_2CH$_3$), 10.2 (s, CH_2CH$_3$), 9.5 (s, 2 × CH_2CH$_3$), 9.4 (s, 2 × CH_2CH$_3$). ^{31}P{^{1}H} NMR (THF-d_8, 25 °C): δ 215.2 (dd, $^2J_{PP}$ = 368 Hz, $^1J_{RhP}$ = 177 Hz), 16.4 (dd, $^2J_{PP}$ = 368 Hz, $^1J_{RhP}$ = 167 Hz). HRMS (ESI): calcd for $C_{53}H_{81}N_2P_2Rh$, 910.4925 ([M]$^+$); found, 910.4936.

Data for **15** are as follows. ^{1}H NMR (THF-d_8, 25 °C): δ 8.72 (dd, $^2J_{PH}$ = 7.5 Hz, $^4J_{PH}$ = 3.4 Hz, 1H, EindP=C*H*), 7.63 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, $^5J_{PH}$ = 3.0 Hz, 1H, Py), 7.45 (dd, $^4J_{PH}$ = 4.5 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.30 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 6.95 (s, 1H, *p*-Eind), 6.88 (br d, $^3J_{HH}$ = 8.0 Hz, 1H, Py), 6.69 (br d, $^3J_{HH}$ = 6.8 Hz, 1H, Py), 4.15 (dd, $^2J_{HH}$ = 20.3 Hz, $^2J_{PH}$ = 10.7 Hz, 1H, PyCH_2P), 4.14 (dd, $^2J_{HH}$ = 20.3 Hz, $^2J_{PH}$ = 10.2 Hz, 1H, PyCH_2P), 3.95 (br, 2H, NH_2), 2.98−2.89 (m, 1H, CH_2CH$_3$), 2.77−2.68 (m, 1H, CH_2CH$_3$), 2.63 (dd, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 4.0 Hz, 1H, PCH_2), 2.40 (dt, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 3.7 Hz, 1H, PCH_2), 2.24−1.93 (m, 6H, 3 × CH_2CH$_3$), 1.90−1.88 (m, 4H, 2 × CH_2), 1.86−1.60 (m, 8H, 4 × CH_2CH$_3$), 1.53 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.38 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu), 0.95−0.67 (m, 24H, 8 × CH$_2$CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 163.5 (dd, J_{PC} = 6 and 2 Hz), 161.0 (dd, J_{PC} = 7 and 3 Hz), 159.8 (dd, J_{PC} = 14 and 5 Hz), 155.2 (d, J_{PC} = 10 Hz), 154.3 (d, J_{PC} = 2 Hz), 151.0 (s), 150.9 (s), 150.3 (d, J_{PC} = 7 Hz), 150.1 (d, J_{PC} = 7 Hz), 135.1 (d, $^1J_{PC}$ = 43 Hz, EindP=CH), 131.1 (d, J_{PC} = 18 Hz), 125.5 (dd, J_{PC} = 32 and 5 Hz), 123.7 (d, $^3J_{PC}$ = 8 Hz, Ar), 123.2 (vt, J_{app} = 3 Hz), 122.8 (d, J_{PC} = 25 Hz), 122.6 (d, $^4J_{PC}$ = 2 Hz, *p*-Eind), 119.1 (d, $^3J_{PC}$ = 8 Hz, Ar), 113.3 (dd, J_{PC} = 13 and 4 Hz), 54.7 (s), 54.6 (s), 50.0 (d, $^1J_{PC}$ = 29 Hz, PyCH$_2$P), 48.35 (s), 48.34 (s), 44.0 (t, J_{PC} = 4 Hz), 43.6 (s, CH_2), 43.4 (s, CH_2), 43.2 (d, $^1J_{PC}$ = 34 Hz, PCH_2), 38.2 (s), 35.7 (s), 34.3 (s, CH_2CH$_3$), 34.23 (s, CH_2CH$_3$), 34.15 (s, CH_2CH$_3$), 34.07 (s, CH_2CH$_3$), 33.7 (s, CH_3), 33.2 (s, CH_2CH$_3$), 33.14 (s, CH_2CH$_3$), 33.06 (d, $^4J_{PC}$ = 2 Hz, C(CH_3)$_3$), 32.3 (s, CH_2CH$_3$), 32.2 (s, CH_2CH$_3$), 31.6 (s, C(CH_3)$_3$), 31.5 (s, CH_3), 10.5 (s, CH_2CH$_3$), 10.43 (s, CH_2CH$_3$), 10.37 (s, CH_2CH$_3$), 10.3 (s, CH_2CH$_3$), 9.52 (s, 2 × CH_2CH$_3$), 9.49 (s, 2 × CH_2CH$_3$). ^{31}P{^{1}H} NMR (THF-d_8, 25 °C): δ 173.6 (d, $^2J_{PP}$ = 468 Hz), 26.4 (d, $^2J_{PP}$ = 468 Hz). Anal. Calcd for $C_{53}H_{81}N_2P_2Ir$: C, 63.63; H, 8.16; N, 2.80. Found: C, 63.35; H, 8.24; N, 2.55.

X-ray Crystal Structure Determination. The intensity data were collected at 103 K on a Rigaku Saturn70 CCD diffractometer with the VariMax Optic, using Mo Kα radiation (λ = 0.71075 Å). The intensity data were corrected for Lorentz and polarization effects and for absorption (multiscan[12]). The structures were solved by direct methods (SHELXS-97)[13] and refined by least-squares calculations on F^2 for all reflections (SHELXL-97),[13] using Yadokari-XG 2009.[14] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and included in calculations without refinement of their parameters. The crystallographic data and a summary of solution and refinement are given in Tables S1 and S2 in the Supporting Information.

Computational Details. DFT calculations were carried out by using the Gaussian 09 program.[15] We adopted the B3LYP-D functional, which is the B3LYP hybrid functional[16] combined with an empirical dispersion correction developed by Grimme.[17] For optimization, we chose SDD for Ir and Rh and 6-31G(d) for the other atoms as basis sets.[18] Systematic vibrational analyses were carried out for all complexes to characterize stationary-point structures. To determine the energy differences, we performed single-point calculations at the optimized geometries using the 6-311+G(d,p) basis set instead of the 6-31G(d) basis set. Solvation effects (THF) were taken into account by using the polarizable continuum model (PCM).[19] Thermal corrections at 298.15 K were applied for evaluating the free energy changes (ΔG_{298}).

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00113.

Characterization and crystal data of **8**, **9**, [K(18C6)][**12**], and [K(18C6)][**13**] and the X-ray structure of **14** (PDF)
Crystallographic data for **8**, **9**, [K(18C6)][**12**], [K(18C6)][**13**], and **14** (CIF)
Cartesian coordinates of the optimized structures (XYZ)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for F.O.: ozawa@scl.kyoto-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by KAKENHI (26288050 (F.O.)) from the JSPS and by a MEXT Grant-in-Aid for Scientific Research on Innovative Areas "Stimuli-responsive Chemical Species" (24109003 (T.M.), 24109014 (K.Y.), and 24109010 (F.O.)). We thank the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant #2015-21), and the MEXT Project of "Integrated Research on Chemical Synthesis" for partial support.

■ REFERENCES

(1) (a) Dugal-Tessier, J.; Conrad, E. D.; Dake, G. R.; Gates, D. P. In *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*; Kamer, P. C. J., van Leeuwen, P. W. N. M., Eds.; Wiley: Chichester, U.K., 2012; Chapter 10. (b) Ozawa, F.; Kawagishi, S.; Ishiyama, T.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1325−1332. (c) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627−681. (d) Müller, C.; Pidko, E. A.; Lutz, M.; Spek, A. L.; Vogt, D. *Chem. - Eur. J.* **2008**, *14*, 8803−8807.

(2) (a) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987. (b) Ozawa, F. *Yuki Gosei Kagaku Kyokaishi* **2009**, *67*, 529−539.

(3) For recent examples, see: (a) Nakajima, Y.; Nakao, Y.; Sakaki, S.; Tamada, Y.; Ono, T.; Ozawa, F. *J. Am. Chem. Soc.* **2010**, *132*, 9934−9936. (b) Nakajima, Y.; Shiraishi, Y.; Tsuchimoto, T.; Ozawa, F. *Chem. Commun.* **2011**, *47*, 6332−6334. (c) Chang, Y.-H.; Nakajima, Y.; Ozawa, F. *Organometallics* **2013**, *32*, 2210−2215. (d) Chang, Y.-H.; Nakajima, Y.; Tanaka, H.; Yoshizawa, K.; Ozawa, F. *J. Am. Chem. Soc.* **2013**, *135*, 11791−11794. (e) Chang, Y.-H.; Nakajima, Y.; Tanaka, H.; Yoshizawa, K.; Ozawa, F. *Organometallics* **2014**, *33*, 715−721. (f) Taguchi, H.; Chang, Y.-H.; Takeuchi, K.; Ozawa, F. *Organometallics* **2015**, *34*, 1589−1596. (g) Chang, Y.-H.; Takeuchi, K.; Wakioka, M.; Ozawa, F. *Organometallics* **2015**, *34*, 1957−1962. (h) Chang, Y.-H; Tanigawa, I.; Taguchi, H.; Takeuchi, K.; Ozawa, F. *Eur. J. Inorg. Chem.* **2016**, *2016*, 754.

(4) For related studies on phosphaalkene complexes, see: (a) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Tetrahedron Lett.* **1992**, *33*, 5071−5074. (b) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935−5943. (c) Ionkin, A. S.; Marshall, W. J. *Heteroat. Chem.* **2002**, *13*, 662−666. (d) Dugal-Tessier, J.; Dake, G. R.; Gates, D. P. *Organometallics* **2007**, *26*, 6481−6486. (e) Orthaber, A.; Belaj, F.; Pietschnig, R. *Inorg. Chim. Acta* **2011**, *374*, 211−215. (f) Ito, S.; Nanko, M.; Mikami, K. *ChemCatChem* **2014**, *6*, 2292−2297.

(5) For recent reviews, see: (a) Gunanathan, C.; Milstein, D. In *Pincer and Pincer-Type Complexes: Application in Organic Synthesis and Catalysis*; Szabó, K. J., Wendt, O. F., Eds.; Wiley-VCH: Weinheim, Germany, 2014; Chapter I. (b) Zell, T.; Milstein, D. *Acc. Chem. Res.* **2015**, *48*, 1979−1994. (c) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024−12087. (d) Khusnutdinova, J. R.; Milstein, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236−12273.

(6) (a) Tsang, C.; Rohrick, C. A.; Saini, T. S.; Patrick, B. O.; Gates, D. P. *Organometallics* **2002**, *21*, 1008−1010. (b) Houdard, R.; Mézailles, N.; Le Goff, X.-F.; Le Floch, P. *Organometallics* **2009**, *28*, 5952−5959.

(7) (a) Matsuo, T.; Tamao, K. *C. R. Chim.* **2010**, *13*, 1104−1110. (b) Matsuo, T.; Tamao, K. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1201−1220. (c) Matsuo, T.; Suzuki, K.; Fukawa, T.; Li, B.; Ito, M.; Shoji, Y.; Otani, T.; Li, L.; Kobayashi, M.; Hachiya, M.; Tahara, Y.; Hashizume, D.; Fukunaga, T.; Fukazawa, A.; Li, Y.; Tsuji, H.; Tamao, K. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1178−1191.

(8) (a) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Tetrahedron Lett.* **1992**, *33*, 5071−5074. (b) Yam, M.; Chong, J. H.; Tsang, C.-W.; Patrick, B. O.; Lam, A. E.; Gates, D. P. *Inorg. Chem.* **2006**, *45*, 5225−5234.

(9) Shah, S.; Protasiewicz, J. D. *Chem. Commun.* **1998**, *3*, 1585−1586.

(10) Li, B.; Tsujimoto, S.; Li, Y.; Tsuji, H.; Tamao, K.; Hashizume, D.; Matsuo, T. *Heteroat. Chem.* **2014**, *25*, 612−618.

(11) Hayashi, A.; Okazaki, M.; Ozawa, F.; Tanaka, R. *Organometallics* **2007**, *26*, 5246−5249.

(12) Blessing, R. H. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1995**, *51*, 33−38.

(13) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Göttingen, Germany, 1997.

(14) Kabuto, C.; Akine, S.; Kwon, E. *Nippon Kessho Gakkaishi* **2009**, *51*, 218−224.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*; Gaussian, Inc., Wallingford, CT, 2009.

(16) (a) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(17) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787−1799.

(18) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222. (d) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem.* **1983**, *4*, 294−301. (e) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654−3665. (f) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. *Theor. Chim. Acta* **1990**, *77*, 123−141.

(19) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3094.

DOI: 10.1021/acs.organomet.6b00113
Organometallics XXXX, XXX, XXX−XXX