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Practical Synthesis of a PCP-Type Pincer Ligand and Its Metal Complexes

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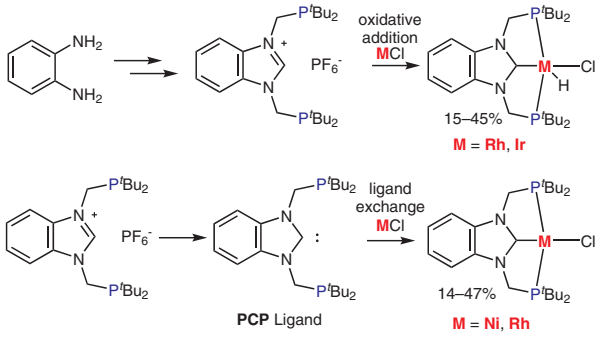

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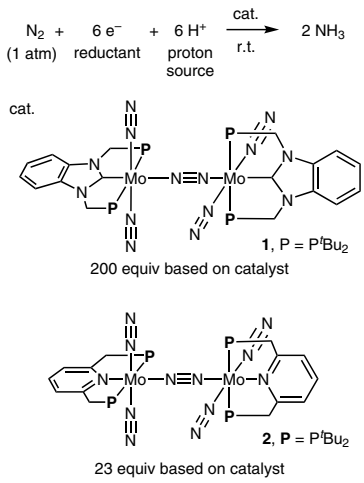
Abstract A synthetic method for N-heterocyclic carbene- and phosphine-based PCP-type pincer ligand is described on a large scale. Some transition-metal complexes bearing the PCP-type pincer ligand are prepared and characterized by X-ray crystal structure analysis.

Key words N-heterocyclic carbene, PCP ligand, phosphine, pincer ligand, transition-metal complexes

Development of catalytic transformations of nitrogen gas in the presence of transition-metal–dinitrogen complexes as catalysts under mild reaction conditions has attracted much attention from viewpoints of inorganic and organometallic chemistry. As effective catalysts toward nitrogen fixation under ambient reaction conditions, we have designed and prepared dinitrogen-bridged dimolybdenum complexes bearing N-heterocyclic carbene- (NHC) and phosphine-based PCP-type pincer ligands (a PCP-type pincer ligand composed of NHC and two phosphines) [{Mo(N_2)$_2$(PCP)}$_2$(μ-N_2)] [**1**; PCP = 1,3-bis(di-*tert*-butylphosphinomethyl)benzimidazol-2-ylidene] (Scheme 1).[1] In this novel nitrogen fixation system, up to 200 equivalents of ammonia were produced based on the catalyst (100 equiv of ammonia based on the molybdenum atom of the catalyst). This was so far the most effective catalytic reduction of nitrogen gas into ammonia under ambient reaction conditions using transition-metal–dinitrogen complexes as catalysts.[2,3] In fact, the catalytic activity of **1** is ca. 10 times higher than that of dinitrogen-bridged dimolybdenum complexes bearing PNP-type pincer ligands such as [{Mo(N_2)$_2$(PNP)}$_2$(μ-N_2)][4] [**2**; PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine], where up to 23 equivalents of ammonia were produced based on the catalyst (Scheme 1).[5,6]

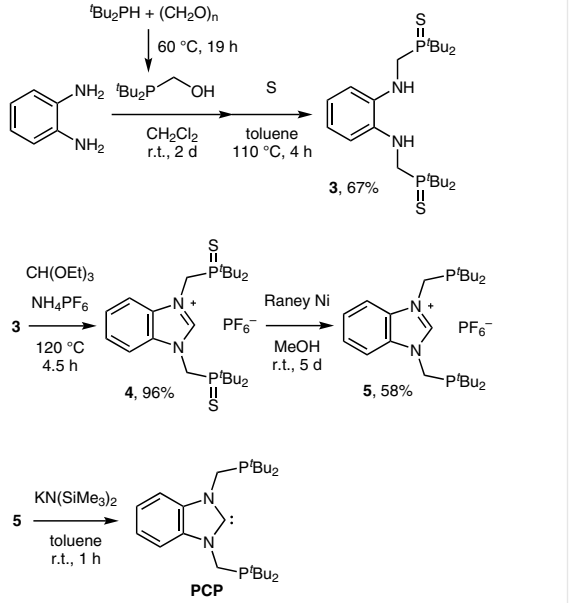


Scheme 1 Molybdenum-catalyzed ammonia formation under ambient reaction conditions

The superiority of **1** over **2** in catalytic nitrogen fixation under mild reaction conditions prompted us to prepare other transition-metal complexes bearing the PCP-type pincer ligand because the use of the PCP-type pincer ligand as an auxiliary ligand to the metal increased the stability of the complexes. In fact, we have separately prepared ruthenium complexes bearing the PCP-type pincer ligand and investigated their catalytic activity toward the formation of imines from reactions of alcohols with amines[7] because Milstein and co-workers reported unique behaviors of ruthenium complexes bearing the PNP-type pincer ligand toward catalytic transformations of organic compounds.[8] These results indicate that transition-metal complexes bearing the PCP-type pincer ligand have a potential to work as more effective catalysts than the corresponding complexes bearing the PNP-type pincer ligand. On the basis of

these research backgrounds, we report here a practical synthetic method for the PCP-type pincer ligand on a large scale. In addition, we report the preparation and characterization of some transition-metal complexes bearing the PCP-type pincer ligand.

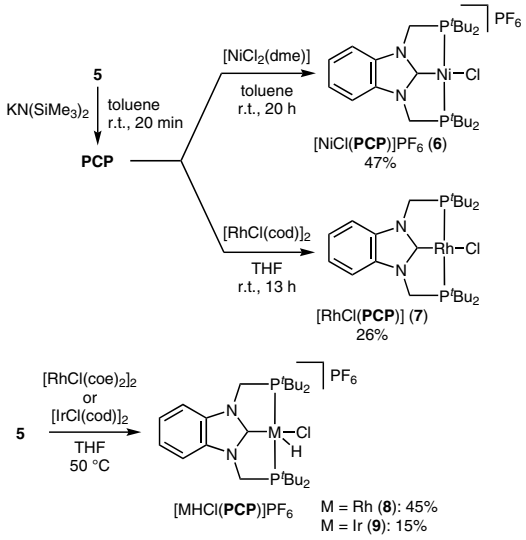
According to the previous method reported by our group,[1] the preparation of the PCP-type pincer ligand (PCP) was carried out on a large scale. Typical results are shown in Scheme 2. First, diamine **3** bearing two di-*tert*-butylphosphinothioylmethyl groups was prepared in 67% (14.56 g) yield from the reaction of *o*-phenylenediamine with 2 equivalents of di-*tert*-butylphosphinomethanol,[9] generated in situ from di-*tert*-butylphosphine and formaldehyde,[10] and further treatment with 2 equivalents of sulfur powder. Then, the reaction of **3** with an excess amount of triethyl orthoformate in the presence of NH_4PF_6 gave the corresponding bis(phosphinesulfide) imidazolium salt **4** in 96% yield.[11] Reduction of the salt **4** with an excess amount of Raney Ni in methanol afforded the corresponding bis(phosphine) imidazolium salt **5** in 58% yield.



Scheme 2 Practical preparation of PCP-type pincer ligand on a large scale

The formation of the corresponding free PCP-type ligand (PCP) was confirmed by deprotonation of the imidazolium salt **5** with 1.4 equivalents of $KN(SiMe_3)_2$. ^1H NMR spectrum of PCP in C_6D_6 indicates the absence of the imidazolium proton. More detailed molecular structures of **4** and **5** were confirmed by X-ray crystal structure analysis. ORTEP drawings of **4** and **5** are shown in Figures S1 and S2 in the Supporting Information.

The complexation of transition-metal complexes with PCP-type pincer ligand was carried out in a similar manner to that used for the synthesis of the molybdenum complex.[1] Reactions of $[NiCl_2(dme)]$ and $[Rh(cod)Cl]_2$ with PCP, generated in situ from **5** with $KN(SiMe_3)_2$, in THF at room temperature for 13–20 hours afforded the corresponding nickel and rhodium complexes bearing the PCP-type ligand $[NiCl(PCP)]PF_6$ (**6**) and [RhCl(PCP)] (**7**) in 47% and 26% isolated yield, respectively (Scheme 3). The ligand exchange with PCP-type pincer ligand proceeded smoothly, in both cases. Complexes **6** and **7** were characterized by NMR spectroscopy. More detailed molecular structures of **6** and **7** were confirmed by X-ray crystal structure analysis. ORTEP drawings of **6** and **7** are shown in Figure 1. The geometry around the nickel (for **6**) and rhodium (for **7**) center is square planar (see Supporting Information for details).



Scheme 3 Preparation of transition-metal complexes bearing a PCP-type pincer ligand

The direct reaction of $[RhCl(coe)_2]_2$ and $[IrCl(cod)]_2$ with imidazolium salt **5** in THF at 50 °C gave the corresponding cationic complexes $[RhHCl(PCP)]PF_6$ (**8**) and $[IrHCl(PCP)]PF_6$ (**9**) in 45% and 15% isolated yield, respectively. Complexes **8**

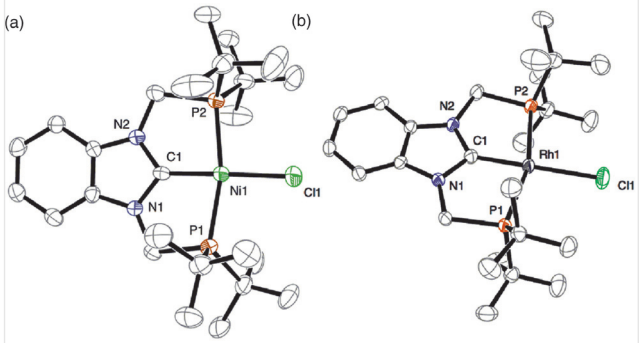


Figure 1 ORTEP drawings of (a) the cationic part of $[NiCl(PCP)]PF_6$ (**6**) and (b) [RhCl(PCP)] (**7**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

and **9** were characterized by NMR spectroscopy. In ^{1}H NMR spectrum, the hydride peaks of complexes **8** and **9** were observed as doublet of triplets at –26.25 ppm with $^1J_{Rh-H}$ = 46.4 Hz and $^2J_{P-H}$ = 10.4 Hz and triplet at –39.42 ppm with $^2J_{P-H}$ = 11.2 Hz, respectively. In sharp contrast to the formation of **6** and **7** via the ligand exchange with PCP-type pincer ligand, oxidative addition of imidazolium salt **5** to the rhodium(I) and iridium(I) complexes occurred to form the rhodium(III) and iridium(III) complexes. A similar oxidative addition of imidazolium salt to $[IrCl(cod)]_2$ was previously reported to prepare the corresponding iridium complex with the higher oxidation state.[12] Detailed molecular structures of **8** and **9** were confirmed by X-ray crystal structure analysis. ORTEP drawings of **8** and **9** are shown in Figure 2. The geometry around the rhodium and iridium centers is square pyramidal with the hydride ligand in the apical position (see Supporting Information for details).

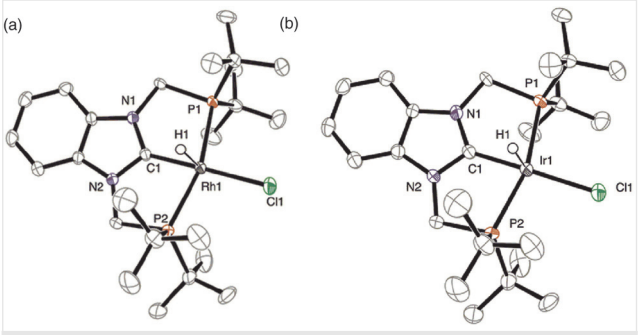


Figure 2 ORTEP drawings of the cationic part of (a) $[RhHCl(PCP)]PF_6$ (**8**) and (b) $[IrHCl(PCP)]PF_6$ (**9**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms except for H1's are omitted for clarity.

In summary, we have reported a practical synthetic method for the PCP-type pincer ligand on a large scale. Some transition-metal complexes bearing the PCP-type pincer ligand have been prepared and characterized by X-ray crystal structure analysis. We believe that the synthetic method of the PCP-type pincer ligand and its complexes provides useful information for readers of this paper. Further investigation including the catalytic activity of the complexes is currently in progress in our laboratory.

^{1}H NMR (270 MHz), ^{31}P{^{1}H} NMR (109 MHz), and ^{13}C{^{1}H} NMR (68 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvents, and spectra were referenced to residual solvent [^{1}H, ^{13}C{^{1}H}] or external standard [^{31}P{^{1}H}: H_3PO_4]. The NMR spectra of compounds **6**, **8**, and **9** were recorded on a JEOL JNM-ECS 400 spectrometer. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo. Melting points were measured on a Standford Research System OptiMelt.

All manipulations were carried out under an atmosphere of N_2 by using standard Schlenk techniques or glovebox techniques, unless otherwise stated. Solvents were dried by general methods, and degassed before use. All reagents including *o*-phenylenediamine and *t*-Bu_2PH (10% solution in hexane) were commercially available.

Diamine 3

Compound **3** was prepared according to literature methods.[1,9] Hexane was removed from a 10% di-*tert*-butylphosphine (*t*-Bu_2PH) solution in hexane (130 g, 88.9 mmol). To a four-necked flask were added *t*-Bu_2PH and paraformaldehyde (2.67 g, 88.9 mmol) and the contents were stirred at 60 °C for 19 h. To the resulting reaction mixture was added a solution of *o*-phenylenediamine (4.81 g, 44.5 mmol) in CH_2Cl_2 (80 mL) and stirred at r.t. for 2 days. The solvent was removed under vacuum and the solid was dissolved in toluene (250 mL). To the solution was added elemental sulfur (2.85 g, 88.9 mmol) and the mixture was stirred at 120 °C for 4 h. The solvent was removed from the mixture and purified by column chromatography (CH_2Cl_2) to give **3** as a white solid (14.56 g, 29.8 mmol, 67%); mp 183.0 °C (decomp.).

^{1}H NMR ($CDCl_3$): δ = 6.84–6.79 (m, 2 H, ArH), 6.72–6.67 (m, 2 H, ArH), 4.61–4.54 (m, 2 H, NH), 3.36 (dd, $^2J_{P-H}$ = 5.4 Hz, $^3J_{N-H}$ = 6.5 Hz, 4 H, NCH_2P), 1.40 [d, $^3J_{P-H}$ = 15.1 Hz, 36 H, 2 × P(*t*-$C_4H_9)_2$].

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 138.0 (d, $^3J_{P-C}$ = 10.6 Hz, NC=CH), 119.4 (s, CH_{Ar}), 111.6 (s, CH_{Ar}), 37.6 (d, $^1J_{P-C}$ = 40.7 Hz, NCH_2P), 36.0 [d, $^1J_{P-C}$ = 46.2 Hz, $PC(CH_3)_3$], 27.6 [d, $^2J_{P-C}$ = 1.1 Hz, $PC(CH_3)_3$].

^{31}P{^{1}H} NMR ($CDCl_3$): δ = 78.3 [s, P(*t*-$C_4H_9)_2$].

Bis(phosphinesulfide) Imidazolium Salt 4

A mixture of **3** (14.40 g, 29.5 mmol), NH_4PF_6 (4.81 g, 29.5 mmol), and $CH(OEt)_3$ (190 mL, 1.14 mol) was stirred at 120 °C for 4.5 h. The volatiles were removed under vacuum. The resultant solid was washed with CH_2Cl_2/Et_2O (2:5 v/v, 240 mL) and Et_2O. The solid was dried under vacuum to give **4** as a white solid (18.24 g, 28.3 mmol, 96%); mp 230.8 °C (decomp.). Crystals suitable for X-ray analysis were prepared by recrystallizing from CH_2Cl_2/Et_2O.

^{1}H NMR ($CDCl_3$): δ = 9.88 (s, 1 H, NCH=N), 7.96–7.91 (m, 2 H, ArH), 7.64–7.61 (m, 2 H, ArH), 4.94 (d, $^2J_{P-H}$ = 3.0 Hz, 4 H, NCH_2P), 1.41 [d, $^3J_{P-H}$ = 15.7 Hz, 36 H, 2 × P(*t*-$C_4H_9)_2$].

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 143.3 (s, NCH=N), 131.3 (s, C_{Ar}), 127.3 (s, CH_{Ar}), 113.8 (s, CH_{Ar}), 40.2 (d, $^1J_{P-C}$ = 32.3 Hz, NCH_2P), 38.9 [d, $^1J_{P-C}$ = 39.0 Hz, $PC(CH_3)_3$], 27.5 [s, $PC(CH_3)_3$].

^{31}P{^{1}H} NMR ($CDCl_3$): δ = 78.4 [s, P(*t*-$C_4H_9)_2$], –144.7 (sept, $^1J_{P-F}$ = 711 Hz, PF_6).

Bis(phosphine) Imidazolium Salt 5

A suspension of **4** (6.65 g, 10.3 mmol) and Raney Ni (100 g) in MeOH (110 mL) was stirred at r.t. for 5 days. The supernatant was collected and the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (4 × 15 mL), and filtered through Celite. The solvent was removed under vacuum. The resulting solid was washed with Et_2O (10 mL) and then dried under vacuum to give **5** as a yellow solid (3.48 g, 5.99 mmol, 58%); mp 145.7 °C (decomp.). Crystals suitable for X-ray analysis were prepared by recrystallizing from CH_2Cl_2/Et_2O.

^{1}H NMR ($CDCl_3$): δ = 9.46 (s, 1 H, NCH=N), 7.98–7.95 (m, 2 H, ArH), 7.64–7.61 (m, 2 H, ArH), 4.61 (s, 4 H, NCH_2P), 1.19 [d, $^3J_{P-H}$ = 11.6 Hz, 36 H, 2 × P(*t*-$C_4H_9)_2$].

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 141.9 (t, $^3J_{P-C}$ = 11.2 Hz, NCH=N), 132.0 (s, CH_{Ar}), 127.1 (s, CH_{Ar}), 114.2 (d, $^3J_{P-C}$ = 5.6 Hz, NC=CH), 42.6 (d, $^1J_{P-C}$ = 30.1 Hz, NCH_2P), 32.2 [d, $^1J_{P-C}$ = 20.1 Hz, $PC(CH_3)_3$], 29.2 [d, $^2J_{P-C}$ = 13.4 Hz, $PC(CH_3)_3$].

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 24.3 [s, $P(t\text{-}C_4H_9)_2$], –144.6 (sept, $^1J_{P-F}$ = 712 Hz, PF_6).

Generation of PCP

To a mixture of **5** (36.3 mg, 0.063 mmol) and $KN(SiMe_3)_2$ (17.3 mg, 0.087 mmol) was added toluene (3 mL) and the resulting suspension was stirred for 1 h at r.t. The suspension was filtered through Celite and the filter cake was washed with toluene (2 × 1 mL). The solvent of the combined solution was removed under vacuum to obtain a pale brown solid. The obtained PCP was used in the subsequent reactions without further purification.

^1H NMR (C_6D_6): δ = 7.92–7.87 (m, 2 H, ArH), 7.15–7.11 (m, 2 H, ArH), 4.71 (d, $^2J_{P-H}$ = 3.0 Hz, 4 H, NCH_2P), 1.14 [d, $^3J_{P-H}$ = 10.5 Hz, 36 H, 2 × $P(t\text{-}C_4H_9)_2$].

$^{31}P\{^1H\}$ NMR (C_6D_6): δ = 14.5 [s, $P(t\text{-}C_4H_9)_2$].

[NiCl(PCP)]PF_6 (6)

A mixture of **5** (58.6 mg, 0.101 mmol) and $KN(SiMe_3)_2$ (26.4 mg, 0.132 mmol) in toluene (8 mL) was stirred at r.t. for 20 min. To the suspension was added [$NiCl_2$(dme)] (20.7 mg, 0.094 mmol) and the resulting suspension was stirred at r.t. for 20 h. The suspension was filtered and the solid was washed with Et_2O (2 × 5 mL). The solid was recrystallized from CH_2Cl_2/hexane to afford [NiCl(PCP)]PF_6 as yellow crystals (29.6 mg, 0.044 mmol, 47%); mp 255.4 °C (decomp.).

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.66 (br s, 2 H, ArH), 7.57 (br s, 2 H, ArH), 4.45 (s, 4 H, NCH_2P), 1.58 [pseudo t, $^3J_{P-H}$ = 7.0 Hz, 36 H, 2 × $P(t\text{-}C_4H_9)_2$].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ = 80.8 [s, $P(t\text{-}C_4H_9)_2$], –144.0 (sept, $^1J_{P-F}$ = 734 Hz, PF_6).

Anal. Calcd for $C_{25}H_{44}ClF_6N_2NiP_3$: C, 44.57; H, 6.58; N, 4.16. Found: C, 44.31; H, 6.79; N, 4.36.

[RhCl(PCP)] (7)

A mixture of **5** (57.9 mg, 0.100 mmol) and $KN(SiMe_3)_2$ (27.9 mg, 0.140 mmol) in toluene (4 mL) was stirred at r.t. for 20 min. The suspension was filtered through Celite and the solvent was removed under vacuum. The residue was dissolved in THF (4 mL) and the solution was added to another solution of $[RhCl(cod)]_2$ (24.6 mg, 0.050 mmol) in THF (4 mL) and stirred at r.t. for 13 h. The solvent was removed under vacuum and the resulting solid was washed with hexane (3 × 3 mL). The residue was recrystallized from THF/hexane to afford [RhCl(PCP)] as yellow crystals (15.0 mg, 0.026 mmol, 26%); mp 283.7 °C (decomp.).

^1H NMR (C_6D_6): δ = 7.00–6.97 (m, 2 H, ArH), 6.68–6.65 (m, 2 H, ArH), 3.51 (s, 4 H, NCH_2P), 1.41 [pseudo t, $^3J_{P-H}$ = 6.5 Hz, 36 H, 2 × $P(t\text{-}C_4H_9)_2$].

$^{31}P\{^1H\}$ NMR (C_6D_6): δ = 82.6 [d, $^1J_{P-Rh}$ = 157 Hz, $P(t\text{-}C_4H_9)_2$].

Anal. Calcd for $C_{25}H_{44}ClN_2P_2Rh$: C, 52.41; H, 7.74; N, 4.89. Found: C, 52.46; H, 7.80; N, 4.89.

[RhHCl(PCP)]PF_6 (8)

A mixture of **5** (58.1 mg, 0.100 mmol) and $[RhCl(coe)_2]_2$ (35.6 mg, 0.050 mmol) in THF (3 mL) was stirred at 50 °C for 1 h. The suspension was filtered and the resulting solid was recrystallized from CH_2Cl_2/hexane to afford [RhHCl(PCP)]PF_6 as yellow crystals (32.2 mg, 0.045 mmol, 45%); mp 196.7 °C (decomp.).

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.75–7.72 (m, 2 H, ArH), 7.58–7.55 (m, 2 H, ArH), 4.63 (dd, $^2J_{P-H}$ = 14.0 Hz, $^3J_{Rh-H}$ = 44.0 Hz, 4 H, NCH_2P), 1.48 [pseudo d, $^2J_{P-H}$ = 6.8 Hz, 36 H, 2 × $P(t\text{-}C_4H_9)_2$], –26.25 (dt, $^1J_{Rh-H}$ = 46.4 Hz, $^2J_{P-H}$ = 10.4 Hz, 1 H, RhH).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ = 83.8 [d, $^1J_{P-Rh}$ = 105 Hz, $P(t\text{-}C_4H_9)_2$], –144.1 (sept, $^1J_{P-F}$ = 712 Hz, PF_6).

Anal. Calcd for $C_{25}H_{45}ClF_6N_2P_3Rh$: C, 41.77; H, 6.31; N, 3.90. Found: C, 41.75; H, 6.21; N, 4.11.

[IrHCl(PCP)]PF_6 (9)

A mixture of **5** (58.0 mg, 0.100 mmol) and $[IrCl(cod)]_2$ (33.2 mg, 0.049 mmol) in THF (10 mL) was stirred at 50 °C for 30 h. The suspension was filtered and the resulting solid was recrystallized from CH_2Cl_2/hexane to afford [IrHCl(PCP)]PF_6 as orange crystals (11.7 mg, 0.014 mmol, 15%); mp 250.2 °C (decomp.).

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.71–7.67 (m, 2 H, ArH), 7.51–7.48 (m, 2 H, ArH), 4.67–4.51 (m, 4 H, NCH_2P), 1.49–1.43 [m, 36 H, 2 × $P(t\text{-}C_4H_9)_2$], –39.42 (t, $^2J_{P-H}$ = 11.2 Hz, 1 H, IrH).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ = 76.8 [s, $P(t\text{-}C_4H_9)_2$], –144.0 (sept, $^1J_{P-F}$ = 711 Hz, PF_6).

Anal. Calcd for $C_{25}H_{45}ClF_6IrN_2P_3$: C, 37.15; H, 5.61; N, 3.47. Found: C, 37.15; H, 5.23; N, 3.45.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1589153.

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