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Formation of 2-Azaallyl Cobalt(I) Complexes by Csp³–H Bond Activation

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Supporting Information

ABSTRACT: Three novel unsymmetrical η^3 -2-azaallyl cobalt (I) complexes, [(2-PPh₂)C₆H₄]CH=N[CHC₆H₄(4-R)]Co-(PMe₃)₂ (4-6) (R = H (4); Cl (5); and OMe (6)), were synthesized by the reactions of Schiff base ligands [(2-PPh₂)C₆H₄]CH=N[CH₂C₆H₄(4-R)] (1-3) (R = H (1); Cl (2); and OMe (3)) with CoMe(PMe₃)₄ via sp³ C-H bond activation under mild reaction conditions. Complex {[(2-PPh₂)C₆H₄]CH=NCH₃[CHC₆H₄(4-R)]Co(PMe₃)₂}I (7) as an 18e cobalt(III) salt was obtained through the reaction of 4 with iodomethane. The substitution reaction of complex 4 with carbon monoxide afforded the dicarbonyl cobalt(I) complex [(2-PPh₂)C₄H₄]CH[N=CHC₄H₄(4-R)]Co(CO)₂(PMe₂) (8).



 $[(2-PPh_2)C_6H_4]CH[N=CHC_6H_4(4-R)]Co(CO)_2(PMe_3)$ (8). The molecular structures of complexes 4–8 were determined by single crystal X-ray diffraction.

INTRODUCTION

Transition metal π -allyl complexes are of great importance in the areas of organic synthesis and coordination chemistry.^{1–4} Especially, π -allyl palladium(II) complexes have been extensively studied in the allylic sp³ C–H functionalization and some π -allyl palladium(II) intermediates have been isolated and completely characterized.^{5–11} For example, White and coworkers reported the palladium-catalyzed formation of *anti*-2aminooxazoline and *anti*-imidazolidinone from common urea precursors.¹² Other transition metal π -allyl complexes like Mo,^{13,14} Rh,^{15–18} Ni,^{19–21} Ru,^{22,23} Os,^{24,25} Fe,²⁶ Ir,²⁷ and Zr^{28–32} were also reported with the application in the area of catalysis.

As the structurally similar ligands, the chemistry of azaallyl ligands and their transition metal complexes has attracted much interest because of diverse bonding modes with different electronic properties brought by the substitution of the carbon atom in the allyl ligand by the N atom in the azaallyl ligand.^{33–37} It can be concluded from the literature that there are several kinds of the azaallyl ligands and their coordination modes (Scheme 1): (A) N-coordinated enamido mode,^{33,35,36} (B) η^3 -coordinated 1-azaallyl mode,^{38–40} (C) η^3 -coordinated 2-azaallyl mode,^{41–45} and (D) η^3 -coordinated 1,3-diazaallyl mode^{34,46} (Scheme 1).

Generally, there are several methods to prepare azaallyl complexes. The first one is that the lithium salt of the azaallyl ligand was prepared through deprotonation⁴¹ or insertion reaction,^{39,40} and further transmetalation of this lithium salt with a transition metal precursor afforded the final azaallyl

Scheme 1. Kinds of Azaallyl Ligands and Their Coordination Modes



metal complex. The second one is that the azaallyl metal complex was formed by deprotonation of the preformed metal complex using a strong base, such as $\rm KH^{44}$ and $\rm KO^{4}Bu$.⁴⁶ The azaallyl nickel complexes were synthesized by the reaction of the precursor of azaallyl ligand, an organic iodide (RN= C(⁴Bu)-CHR-I), with Ni(cod)₂ via oxidative addition of the C– I bond at the nickel center.³⁸ To the best of our knowledge, no azaallyl transition metal complexes were directly obtained from Csp³-H bond cleavage mediated by transition metals.

In recent years, our group has prepared many Fe, Co, and Ni complexes through C–H activation.^{47–51} In this paper, three Schiff base ligands 1–3 were prepared. Unsymmetrical η^3 -2-azaallyl cobalt(I) complexes 4–6 (C, Scheme 1) were synthesized by the reactions of Schiff base ligands 1–3 with CoMe(PMe₃)₄ via Csp³–H bond activation of the methylene group directly linked to the imine group. These complexes are the first unsymmetrical 2-azaallyl cobalt(I) complexes. 2-Azaallyl cobalt complexes 4–6 were completely characterized

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Figure 1. Molecular structures of complexes 4-6. Hydrogen atoms were omitted for clarity.

Table 1. Selected Bond Lengths and Angles of Complexes 4-6

		4	5	6
bond length (Å)	Co1–N1	1.962(5)	1.959(3)	1.961(1)
	Co1-C19	1.999(5)	2.000(3)	1.997(2)
	Co1-C20	2.097(5)	2.082(3)	2.086(2)
	Co1-P1	2.181(2)	1.180(1)	2.1769(6)
	Co1-P2	2.201(2)	2.187(1)	2.1864(5)
	Co1-P3	2.175(2)	2.198(1)	2.1828(5)
	C19-N1	1.419(8)	1.406(5)	1.405(2)
	C20-N1	1.393(6)	1.374(5)	1.385(2)
bond angle (deg)	C19-N1-C20	107.1(4)	107.3(3)	106.8(1)
	C19-Co1-C20	67.0(2)	66.5(2)	66.48(6)
	N1-Co1-C19	42.0(2)	41.6(1)	41.57(6)
	N1-Co1-C20	40.0(2)	39.6(1)	39.87(6)
	N1-C19-C18	114.6(4)	113.4(3)	114.8(1)
	N1-C20-C21	117.8(5)	117.9(3)	118.(1)

by spectroscopic and X-ray diffraction technology. The reactivity of complexes 4-6 has been explored.

RESULTS AND DISCUSSION

Syntheses of 2-Azaallyl Cobalt(I) Complexes. The reaction of Schiff base ligands 1-3 with CoMe(PMe₃)₄ in THF afforded three 18e 2-azaallyl cobalt(I) complexes 4-6 via sp³ C–H bond activation with the elimination of methane (eq 1).



Complexes 4-6 were obtained as red crystals by crystallization from pentane and Et_2O at -10 °C in the yield of 74% (4), 61% (5), and 72% (6), respectively. Complexes 4-6 in the solid state were stable in the air at room temperature for about 3 h, but they quickly decomposed when their solutions were exposed to the air.

In the IR spectra of complexes 4-6, the typical stretching vibrations of the C=N bond in ligands 1-3 disappeared. The signals of the imine-H (9.08 (1), 8.98 (2), and 8.99 (3) ppm) and benzyl-H (4.72 (1), 4.63 (2), and 4.61 (3) ppm) in the free ligands were moved to the upfield region (3.11/2.11 (4), 2.94/2.08 (2), and 3.17/2.14 (3) ppm) in the ¹H NMR spectra of complexes 4-6 because the deprotonation of the ligands and

the back-bonding from the cobalt(I) center to the η^3 -(C-N-C) ligand make the two hydrogen atoms basic. In the ³¹P NMR spectra of complexes **4**–**6**, diphenylphosphanyl signals appear at 72.0 (4), 72.0 (5), and 71.1 (6) ppm, respectively, and trimethylphosphine signals are located at 12.1, 10.8 (4), 11.5, 9.4 (5), and 13.7, 11.3 (6) ppm.

Single crystal X-ray diffraction confirmed the structures of complexes 4-6 (Figure 1). Selected bond lengths and angles of complexes 4-6 are listed in Table 1. The table of selected crystallographic data of complexes 4-6 is in the Supporting Information. With complex 4 as an example, we discuss the molecular structures of complexes 4-6 because the three complexes have the similar structures. As we can see from eq 1, the Csp³-H activation of the free ligand furnished η^3 -azaallyl-(C-N-C) coordination. The averaged N-C bond distances (N1-C19 (1.419(8) Å) and N1-C20 (1.393(6) Å)) explain the delocalization of the four coordinated π -electrons. Both N– C bond distances are comparatively longer than those (1.30 and 1.38 Å) in the 2-azaallyl iron(III) complex.⁴⁴ The angle C19-N1-C20 is $107.1(4)^{\circ}$. Compared with the azaallyl coordination in the literatures,^{41,44} the biggest difference is that Co1 is not in the azaallyl (C19-N1-C20) plane in complex 4, while the metal atoms are in the azaallyl planes in the literatures. If the midpoints of bonds N1-C19 and N1-C20 are regarded as two coordination sites in complex 4, the cobalt atom is centered in a penta-coordinated geometry. The phenyl (C21-C26) and the 2-azaallyl moieties (C19-N1-C20) are in one plane, while the phenyl (C13–C18) is almost perpendicular to the azaallyl moiety. This confirms that phenyl (C21–C26) and 2-azaallyl are conjugated together. The bond

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distances Co1–C19 (1.999(5) Å) and Co1–C20 (2.097(5) Å) are in the normal region of the cobalt(I)–carbon lengths.⁵² Co1–N1 (1.962(5) Å) is comparable with that of the cobalt– N_{imine} distance.⁵³

Reaction of 2-Azaallyl Cobalt(I) Complex 4 with Iodomethane. The combination of complex 4 and iodomethane afforded the diorganocobalt(III) complex 7 as yellow crystals (eq 2). In this process, the oxidative addition of Me-I at the cobalt(I) center furnished the 18e cobalt(III) coordination cation via C,N-coupling. In the IR spectrum of complex 7, the signals of ν (C==C) and ρ (PMe₃) appeared at 1593 and 952 cm⁻¹, respectively. In the ¹H NMR spectrum of complex 7, the methyl group connected to the nitrogen atom was registered at 3.25 ppm. The two hydrogens (NC-*H*) were found at 3.01 and 2.79 ppm, respectively. In the ³¹P NMR spectrum of complex 7, the diphenylphosphanyl signal appeared at 73.1 ppm and PMe₃ signals appeared at 18.9 and 10.1 ppm.



The molecular structure of complex 7 was determined by single crystal X-diffraction (Figure 2). The cobalt atom is



Figure 2. Molecular structure of complex 7. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–C20 1.47(10), N1–C19 1.44(10), N1–C21 1.42(10), N1–Co1 1.90(6), Co1–C19 1.98(7), Co1–C21 2.06(8), Co1–P1 2.22(2), Co1–P2 2.25(2), Co1–P3 2.21(2); N1–Co1–C21 41.8(3), N1–Co1–C19 43.6(3), N1–Co1–P1 104.2(2), P1–Co1–P3 105.52(9), P3–Co1–C21 99.5(2), C19–Co1–P2 162.1(2).

situated in the center of a strongly distorted octahedron owing to the coordination of the (C-N-C) moiety. The angles between Co–P bonds are deviated from 90° (P1–Co1–P2 98.79(8)°, P1–Co1–P3 105.51(8)°, and P2–Co1–P3 98.30(8)°). C19–N1–C21 (106.1(6)°) indicates that N1 is an amine-N (sp³-hybridized) and has a tetrahedral geometry. The phenyl (C22–C27) and the moiety (C19–N1–C21) are in one plane, while the phenyl (C13–C18) is in the plane of the chelate ring (Co1–P1–C13–C18–C19). The sum of the inner angles of the five-membered chelate ring is 538.1° (C19– Co1–P1 85.1(2)°, Co1–P1–C13 101.9(3)°, P1–C13–C18 114.0(6)°, C13–C18–C19 117.1(7)°, and C18–C19–Co1 120.0(5)°). This implies that the five atoms of the chelate ring are not completely in one plane. The bond distances N1–C19 (1.44(1) Å) and N1–C21 (1.42(1) Å) are a little bit shorter than the normal C–N bond (N1–C20 1.47(1) Å). The coordination bonds (N1–C01 1.895(7) Å, C01–C19 1.975(8) Å, C01–C21 2.055(9) Å) are in the normal ranges of the corresponding bonds.

However, complex 4 did not react with EtBr, C_6Cl_6 , and CO_2 under the normal reaction conditions. Complex 4 in the presence of HCl decomposed into the free Schiff base ligand 1 and CoCl(PMe₃)₃ as violet crystals (eq 3). Both ligand 1 and CoCl(PMe₃)₃ were confirmed by spectroscopic methods. In addition, complex 4 could not catalyze the hydrosilylation of aldehydes and ketones.



Reaction of 2-Azaallyl Cobalt(I) Complex 4 with Carbon Monoxide. A THF solution of complex 4 was stirred under 1 bar of carbon monoxide atmosphere for 24 h to afford complex 8 (eq 4). After extraction and crystallization, complex 8 was isolated as yellow crystals. In the IR spectrum of complex 8, two strong signals of two terminal carbonyl ligands were registered at 1899 and 1956 cm⁻¹. However, the signal of ρ (PMe₃) appeared at 950 cm⁻¹. In addition, a signal of the PMe₃ ligand appeared at 0.77 ppm in the ¹H NMR spectrum and 30.6 ppm in the ³¹P NMR spectrum. The diphenylphosphanyl signal was found at 66.5 ppm in the ³¹P NMR spectrum. In the ¹H NMR spectrum, the benzyl-H was recorded at 6.59 ppm because of the influence of the negatively charged benzylcarbon atom while the imine-H was registered at 8.69 ppm.



Single crystal X-ray diffraction confirmed the molecular structure of complex 8 (Figure 3). The 2-azaallyl coordination



Figure 3. Molecular structure of complex **8**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1-C21 1.437(2), N1-C22 1.280(2), Co1-C21 2.0824(19), Co1-C1 1.746(2), Co1-C2 1.750(2), Co1-P1 2.2006(5), Co1-P2 2.1945(6), O1-C1 1.149(3), O2-C2 1.150(2); C21-Co1-P2 176.44(5), C1-Co1-P1 114.66(7), C1-Co1-C2 120.97(10), C2-Co1-P1 123.40(7).

mode in complex 4 was destroyed because of the strong coordination between the cobalt(I) center and the carbonyl ligands caused by the strong π -backbonding. There is only cobalt-C_{benzyl} coordination among the three atoms of the (C-N-C) moiety. The imine function with the phenyl group orientates toward the direction away from the cobalt center. The distance from the cobalt center to the nitrogen atom (2.923 Å) indicates that there is no bonding interaction between them. The distances N1–C22 (1.280(2) Å) and N1–C21 (1.437(2) Å) explain that the former is a C=N double bond and the latter is a C–N single bond.

CONCLUSIONS

In conclusion, three unsymmetrical η^3 -2-azaallyl cobalt(I) complexes **4**-**6** were synthesized through sp³ C-H bond activation under a mild condition without additives. A diorganocobalt(III) coordination cation 7 could be obtained from the reaction of complex **4** with iodomethane via C,N-coupling. In the presence of HCl, complex **4** decomposed to the free ligand **1** and CoCl(PMe₃)₃. A penta-coordinate dicarbonylcobalt(I) complex **8** was isolated by the reaction of complex **4** with carbon monoxide. The molecular structures of **4**-**8** were determined by single crystal X-ray diffraction.

EXPERIMENTAL SECTION

General Procedures and Materials. Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by distillation from Na-benzophenone under nitrogen before use. $CoMe(PMe_3)_4$,⁵⁴o-diphenylphosphinobenzaldehyde,⁵⁵and the Schiff base ligand 1⁵⁶ were prepared by the literature methods. Infrared spectra (4000–400 cm⁻¹), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. ¹H, ³¹P, and ¹³C {H} NMR spectra (300, 121.5, and 75 MHz, respectively) were recorded on a Bruker Avance 300 spectrometer with C₆D₆ or CDCl₃ as the solvent without an internal reference at room temperature. The ¹³C and ³¹P NMR resonances were obtained with broad-band proton decoupling. Elemental analyses were carried out on an ElementarVario ELIII. Melting points were measured in capillaries sealed under nitrogen and are uncorrected.

Synthesis of Ligand 2. Chlorobenzylamine (2.43 g, 17.24 mmol) was added to a solution of *o*-diphenylphosphinobenzaldehyde (5.00 g, 17.24 mmol) in 10 mL of methanol. The mixed solution was stirred for 10 min. Ligand **2** was afforded by the crystallization in methanol at -10 °C, yield 6.76 g (16.38 mmol, 95%). IR (Nujol mull, cm⁻¹): 1581 ν (C=C), 1640 ν (C=N). ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.88 (d, ⁴J_{P,H} = 6.0 Hz, 1H, -HC=N), 8.03–6.84 (m, 18H, Ar-H), 4.63 (s, 2H, CH₂). ³¹P NMR (121.5 MHz, CDCl₃, 298 K, ppm): -13.31 (s). ¹³C NMR (75 MHz, C₆D₆, 298 K, ppm): 160.9 (m, CH=N), 139.2 (C_{Ar}), 137.4 (C_{Ar}), 134.2 (C_{Ar}), 132.5 (C_{Ar}), 129.3 (C_{Ar}), 128.6 (C_{Ar}), 127.8 (C_{Ar}), 64.3 (s, benzyl-C).

Synthesis of Ligand 3. Methoxybenzylamine (2.36 g, 17.24 mmol) was added to a solution of *o*-diphenylphosphinobenzaldehyde (5.00 g, 17.24 mmol) in 10 mL of methanol. The solution was stirred for 10 min. Ligand 3 was afforded by the crystallization in methanol at $-10 \,^{\circ}$ C, yield 6.56 g (16.03 mmol, 93%). IR (Nujol mull, cm⁻¹): 1612 ν (C=C), 1633 ν (C=N). ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): 8.99 (d, ⁴J_{P,H} = 3.0 Hz, 1H, -HC=N), 8.06-6.73 (m, 18H, Ar-H), 4.61(s, 2H, CH₂), 3.78 (s, 3H, -OCH₃). ³¹P NMR (121.5 MHz, CDCl₃, 298 K, ppm): $-13.85 \,$ (s). ¹³C NMR (75 MHz, C₆D₆, 298 K, ppm): 160.2 (m, CH=N), 158.5 (C_{Ar}), 139.4 (C_{Ar}), 136.3 (C_{Ar}), 133.1 (C_{Ar}), 130.3 (C_{Ar}), 128.9 (C_{Ar}), 127.7 (C_{Ar}), 113.8 (C_{Ar}), 64.5 (s, benzyl-C), 55.29 (s, OCH₃).

Synthesis of Complex 4. A solution of ligand 1 (0.62 g, 1.60 mmol) in THF (30 mL) was added to a solution of CoMe- $(PMe_3)_4(0.62 \text{ g}, 1.60 \text{ mmol})$ in THF (30 mL) at -78 °C. The reaction mixture was warmed to 25 °C and stirred for 24 h to get a red

solution. THF was removed under reduced pressure. The residue was extracted with pentane (60 mL) and diethyl ether (60 mL) in turn to give a red solution. Complex 4 was obtained as red crystals from the *n*-pentane solution and diethyl ether solution at -10 °C, yield 0.71 g (1.21 mmol, 74%). m.p.: 160–162 °C, $C_{32}H_{39}CoNP_3$ (589.51 g/mol): calcd. C 65.20, H 6.67, N 2.38; found C 65.55, H 7.03, N 2.12. IR (Nujol mull, cm⁻¹): 1583 ν (C==C), 934 ρ (PMe₃). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): 8.60–7.12 (m, 19H, Ar-H), 3.11 (m, 1H, azaallyl-H), 2.14 (d, *J* = 21.0 Hz, 1H, azaallyl-H),1.13 (d, ²*J*_{P,H} = 6.0 Hz, 9H, PMe₃), 0.77 (d, ²*J*_{P,H} = 9.0 Hz, 9H, PMe₃). ³¹P NMR (121.5 MHz, C₆D₆, 298 K, ppm): 72.04 (m, 1P, PPh₂), 12.10 (s, 1P, PMe₃), 10.83 (m, 1P, PMe₃). ¹³C NMR (75 MHz, C₆D₆, 298 K, ppm): 154.0 (C_{Ar}), 147.8 (C_{Ar}), 141.8 (C_{Ar}), 138.2 (C_{Ar}), 132.9 (C_{Ar}), 131.8 (C_{Ar}), 123.6 (C_{Ar}), 73.7 (azaallyl-C), 65.2 (azaallyl-C), 21.2 (m, P(CH₃)₃), 19.7 (m, P(CH₃)₃).

Synthesis of Complex 5. A solution of ligand 2 (0.67 g, 1.61 mmol) in THF (30 mL) was added to a solution of CoMe(PMe₃)₄ (0.61 g, 1.61 mmol) in THF (30 mL) at -78 °C. The reaction mixture was warmed to 25 °C and stirred for 24 h to get a red solution. THF was removed under reduced pressure. The residue was extracted with pentane (60 mL) and diethyl ether (60 mL) in turn to give a red solution. Complex 5 was obtained as red crystals from the *n*-pentane solution and diethyl ether solution at -10 °C, yield 0.61 g (0.97 mmol, 61%). m.p.: 154–157 °C, C₃₂H₃₈ClCoNP₃ (623.96 g/mol): calcd. C 61.60, H 6.14, N 2.24; found C 62.01, H 6.02, N 2.41. IR (Nujol mull, cm⁻¹): 1578 ν(C=C), 950 ρ(PMe₃). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): 8.40-7.13 (m, 18H, Ar-H), 2.95 (m, 1H, azaallyl-H), 2.12 (d, J = 18.0 Hz, 1H, azaallyl-H), 1.12 (d, ${}^{2}J_{P,H} = 6.0$ Hz, 9H, PMe₃), 0.71 (d, ${}^{2}J_{P,H}$ = 9.0 Hz, 9H, PMe₃). ${}^{31}P$ NMR (121.5 MHz, C₆D₆, 298 K, ppm): 72.0 (m, 1P, PPh₂), 10.2 (m, 2P, PMe₃). ¹³C NMR (75 MHz, C₆D₆, 298 K, ppm): 154.3 (C_{Ar}), 146.7 (C_{Ar}), 141.6 (C_{Ar}), 137.8 (C_{Ar}), 132.9 (C_{Ar}), 131.7 (C_{Ar}), 126.9 (C_{Ar}), 73.4 (azaallyl-C), 63.6 (azaallyl-C), 21.1 (m, P(CH₃)₃), 19.7 (m, P(CH₃)₃).

Synthesis of Complex 6. A solution of ligand 3 (0.65 g, 1.58 mmol) in THF (30 mL) was added to a solution of CoMe(PMe₃)₄ (0.60 g, 1.58 mmol) in THF (30 mL) at -78 °C. The reaction mixture was warmed to 25 °C and stirred for 24 h to get a red solution. THF was removed under reduced pressure. The residue was extracted with pentane (60 mL) and diethyl ether (60 mL) in turn to give a red solution. Complex 6 was obtained as red crystals from the *n*-pentane solution and diethyl ether solution at -10 °C, yield 0.71 g (1.14 mmol, 72%). m.p.: 166-169 °C, C₃₃H₄₁CoNOP₃ (619.54 g/mol): calcd. C 63.98, H 6.67, N 2.26; found C 64.34, H 6.29, N 2.39. IR (Nujol mull, cm⁻¹): 1579 ν (C=C), 947 ρ (PMe₃). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): 8.54-6.92 (m, 18H, Ar-H), 3.41 (s, 3H, OCH₃), 3.16 (m, 1H, azaallyl-*H*), 2.18 (d, J = 21.0 Hz, 1H, azaallyl-*H*), 1.16 (d, ${}^{2}J_{P,H} =$ 6.0 Hz, 9H, PMe₃), 0.81 (d, ${}^{2}J_{P,H} = 6.0$ Hz, 9H, PMe₃). ${}^{31}P$ NMR (121.5 MHz, C₆D₆, 298 K, ppm): 71.1 (m, 1P, PPh₂), 13.7 (s, 1P, PMe₃), 11.3 (m, 1P, PMe₃). ${}^{13}C$ NMR (75 MHz, C₆D₆, 298 K, ppm): 154.8 (C_{Ar}), 142.1 (C_{Ar}), 141.0 (C_{Ar}), 139.7 (C_{Ar}), 133.0 (C_{Ar}), 131.8 (C_{Ar}), 126.7 (C_{Ar}), 73.6 (azaallyl-C), 65.3 (azaallyl-C), 54.5 (OCH₃), 21.2 (m, $P(CH_3)_3$), 19.8 (m, $P(CH_3)_3$).

Synthesis of Complex 7. A solution of complex 4 (0.48 g, 0.81 mmol) in THF (20 mL) was added to a solution of iodomethane (0.12 g, 0.81 mmol) in THF (20 mL) at -78 °C. The reaction mixture was warmed to 25 °C and stirred for 24 h to give a muddy orange solution. The muddy solution was filtered to give a clear orange solution. The residue was extracted with THF (180 mL) to give a clear orange solution. Complex 7 was obtained as orange crystals from the THF solution at -10° C, yield 0.33 g (0.46 mmol, 56%). m.p.: 201–203 °C, C33H42CoINP3 (731.45 g/mol): calcd. C 54.19, H 5.79, N 1.91; found C 53.85, H 6.17, N 2.00. IR (Nujol mull, cm⁻¹): 1593 ν (C=C), 952 ρ(PMe₃). ¹H NMR (300 MHz, CO(CD₃), 298 K, ppm): 8.03-7.06 (m, 19H, Ph-H),3.25 (d, J = 3.0 Hz, 3H, $-CH_3$), 3.01 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H, NCH), 2.79 (s, 1H, NCH), 1.13 (d, ${}^{2}J_{P,H} = 6.0$ Hz, 9H, PMe_3), 1.04 (d, ${}^2J_{P.H}$ = 6.0 Hz, 9H, PMe_3). ${}^{31}P$ NMR (121.5 MHz, CO(CD₃), 298 K, ppm): 73.1 (m, 1P, PPh₂), 18.9 (m, 1P, PMe₃), 10.1 (s, 1P, PMe₃). ¹³C NMR (75 MHz, C₆D₆, 298 K, ppm): 138.1 (C_{Ar}), 137.9 (C_{Ar}), 136.0 (C_{Ar}), 134.5 (C_{Ar}), 133.0 (C_{Ar}), 131.8 (C_{Ar}), 72.4 (C-N), 44.4 (CH_3) , 23.7 $(m, P(CH_3)_3)$, 22.8 $(m, P(CH_3)_3)$.

Synthesis of Complex 8. A solution of complex 4 (0.59 g, 1.00 mmol) in THF (40 mL) was stirred in the atmosphere of carbon monoxide for 24 h at 25 °C to give a light yellow solution. The THF was removed under reduced pressure. The residue was extracted with pentane (60 mL) and diethyl ether (60 mL) in turn to give a light yellow solution. Complex 8 was obtained as yellow crystals from the npentane solution and diethyl ether solution at -10 °C, yield 0.32 g (0.59 mmol, 59%). m.p.: 146–147 °C, $C_{31}H_{30}CoNO_{2}P_{2}$ (569.11 g/ mol): calcd. C 65.38, H 5.31, N 2.46; found C 65.67, H 5.52, N 2.56. IR (Nujol mull, cm⁻¹): 1956, 1899 ν (C=O), 1611 ν (C=N), 950 ρ(PMe₃). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): 8.69 (s, 1H, CH=N), 8.20-7.03 (m, 19H, Ar-H), 6.59 (s, 1H, benzyl-H) 0.77 (d, ${}^{2}J_{P,H}$ = 9.0 Hz, 9H, PMe₃). ³¹P NMR (121.5 MHz, C₆D₆, 298 K, ppm): 66.5 (d, ${}^{2}J_{P,P}$ = 30.4 Hz, 1P, PPh₂), 30.6 (d, ${}^{2}J$ = 41.3, 1P, PMe₃). ${}^{13}C$ NMR (75 MHz, C₆D₆, 298 K, ppm): 162.3 (m, CH=N), 152.2 (C_{Ar}), 138.7 (C_{Ar}), 133.8 (C_{Ar}), 130.1 (C_{Ar}), 125.8 (C_{Ar}), 125.0 (C_{Ar}), 69.1 (benzyl-C), 19.5 (dd, ${}^{1}J_{P,C} = 27.0$ Hz, ${}^{3}J_{P,C} = 4.5$ Hz, P(CH₃)₃).

X-ray Crystal Structure Determinations. Single crystal X-ray diffraction data of the complexes 4–8 were collected on a STOE STADIVARI Cu or Stoe IPDS2 diffractometer. Using Olex2,⁵⁷ the structure was solved with the ShelXS⁵⁸ structure solution program using Direct Methods and refined with the ShelXL⁵⁹ refinement package using Least Squares minimization. CCDC-1505636 (4), -1505637 (5), -1505638 (6), -1505639 (7), and -1514772 (8) contain supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00884.

Table of selected crystallographic data and original IR, ¹H NMR, ¹³C NMR, and ³¹P NMR spectra of the compounds (PDF) Crystallographic data (CIF)

Crystanographic data (Chr)

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Notes

The authors declare no competing financial interest.

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