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Cyclometalation Reactions Involving C−Cl Bond Activation of *ortho*-Chlorinated Substrates with Imine as Anchoring Groups by Cobalt Complexes

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The aldazines ($C_6H_3Cl_2$-2,6)CH=N−NH_2 (**1a**) and ($C_6H_3Cl_2$-2,6)CH=N−N=CH($C_6H_3Cl_2$-2,6) (**1b**) or the Schiff bases ($C_6H_3Cl_2$-2,6)CH=N−CH_3 (**1c**), ($C_6H_3Cl_2$-2,6)CH=N(C_6H_5) (**1d**), and ($C_6H_3Cl_2$-2,6)CH=N($C_{10}H_7$) (**1e**) were obtained by condensation of 2,6-dichlorobenzaldehyde with hydrazine, methylamine, aniline, or α-naphthylamine, respectively. Treatment of **1a**−**1e** with [CoMe(PMe_3)$_4$] resulted in oxidative addition of the C−Cl bond to afford the *ortho*-chelated cobalt(III) complexes [CoClMe(PMe_3)$_2$-{(C_6H_3Cl*ortho*)-CH=N−R}] (**2a**−**2e**). The reaction of **1b**,**1c** with [CoCl(PMe_3)$_3$] delivered the aryl Co(III) complexes **3b**,**3c** containing a [C−Co−Cl] fragment, while Co(II) complexes [CoCl(PMe_3)$_2$((C_6H_3Cl-*ortho*)CH=N−R)] (**3d**,**3e**) were formed through the reaction of **1d** or **1e** with [CoCl(PMe_3)$_3$]. Under similar conditions, the *ortho*-chelated cobalt(III) complex [CoBrCl(PMe_3)$_2$(($C_6H_3Cl_2$-2,6)CH=N−CH_3)] (**4c**) could be isolated via the reaction of [CoBr(PMe_3)$_3$] with **1c**. The crystal and molecular structures of complexes **2a**, **3b**, **3e**, and **4c** were determined by X-ray diffraction.

Introduction

As chloroarenes are widely applied in many fields, the productive activation of the C−Cl bond in chloroarenes is of significant industrial interest. Simultaneously, the disposal of organic wastes containing chloro groups has become a major environmental and social problem, because most of them are toxic and thermally stable, accumulating in the surroundings for a long time. Due to the importance of functionalization or dechlorination of aromatic chlorides, there is currently a great deal of interest in the activation of the comparatively inert C−Cl bond.[1] Several methods have been found to successfully activate a C−Cl bond; however, employing transition-metal complexes apparently seems to be the most promising and efficient approach. There have been many examples of catalytic activation of the C−Cl bond in chloroarenes by palladium,[2–6] nickel,[7] cobalt,[8–11] platinum,[12] and rhodium[13,14] complexes, which are utilized in cross-coupling reactions such as the Heck reaction, the Suzuki coupling, and the Stille coupling. The first key step in all the above-described catalytic reactions is oxidative addition of the C−Cl bond at the electron-rich low-valent transition-metal center. The research of cobalt complexes on this topic was well reviewed by Caubere[15] and Grushin.[16]

Cyclometalation reactions of substrates containing an imine or a pyridyl anchoring group by iron and cobalt complexes

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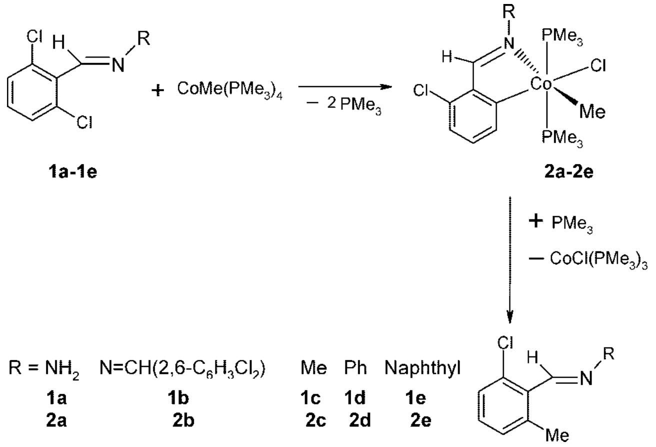
Scheme 1



proceed through intramolecular C−H activation.[17] Recently we have reported cyclometalation reactions involving C−F bond activation at a cobalt(I) center with azine as an anchoring group, which afforded the first complex containing a C−Co−F fragment.[18]

Herein we report on progress in the direction of cyclometalation reactions involving C−Cl bond activation at cobalt(I) centers with azine or imine as prechelate ligands. The new *ortho*-chelated cobalt complexes formed by oxidative addition of an aromatic C−Cl bond were isolated and characterized. C,C-coupling reactions have been observed in reactions of [CoMe(PMe_3)$_4$], while steric crowding in the substrate molecules has a marked effect on reactions of [CoCl(PMe_3)$_3$].

Results and Discussion

1. Reaction of [CoMe(PMe_3)$_4$] with Aryl Chlorides. Reactions of [CoMe(PMe_3)$_4$] with *ortho*-chlorinated substrates containing imine anchoring groups (**1a**−**1e**) proceed by oxidative addition of the C−Cl bond to give rise to the *ortho*-metalated diorgano cobalt(III) chlorides **2a**−**2d**, respectively. In every reaction [CoCl(PMe_3)$_3$] was found as a byproduct. The formation of the respective methyl arene derivatives via C,C-coupling through reductive elimination was verified by LC-MS analysis (Scheme 1). No spontaneous elimination of chloromethane was observed. It appears that initial coordination of the N-donor should be the key step. With *H*C=N as an anchoring group the oxidative addition reactions proceed smoother, and products are more stable owing to the chelate effect.

The selected IR and NMR data of complexes **2a**−**2e**, **3b**−**3e**, and **4c** were collected in Table 1. Compared with the (C=N) band of **1a**−**1e** (1622–1655 cm^{-1}), a substantial red shift upon coordination of the N-donor atom indicates a weakening of the C=N double bond.

In the ^{13}C NMR spectra, we found that the PMe_3 group gives rise to a virtual triplet signal between 11.6 and 11.9 ppm with the coupling constant $|^1J(PC) + {}^3J(PC)|$ = 25.5–28.5 Hz. The coordinated HC=N group shows a singlet in the region of 167.7–172.6 ppm. All spectroscopic data are compatible with an octahedral configuration around the cobalt atom in solution, consisting of a P−Co−P axis and equatorial coordination of C, C, Cl, and N donor atoms. The crystal structure of complex **2a** was elucidated by an X-ray diffraction analysis.

Table 1. Selected Spectrocopic Data of Complexes 2a−2e, 3b−3e, and 4c

	IR, cm^{-1}			NMR, ppm		
				^{1}H		^{31}P
	ν(C=N)	ν(C=C)	ρ(PMe_3)	PC*H*$_3$,	CoC*H*$_3$	*P*Me$_3$
2a	1591	1564,1531	945	0.86(t)	0.66(m)	5.3(s)
2b	1625,1610	1581,1567	945	0.94(m)	0.64(m)	5.3(s)
2c	1599	1567,1531	945	0.69(m)	0.57(m)	5.2(s)
2d	1599	1567,1531	945	0.96(m)	0.69(m)	9.4(s)
2e	1591	1564,1531	945	0.86(t)	0.52(m)	6.3(s, br)
3b	1624,1615	1568,1558	942	1.07(m)		10.8(s)
3c	1594	1562,1531	940	1.12(m)		−0.9(s)
3d	1596		939			
3e	1592		948			
4c	1592		941	1.17(m)		−1.8(s, br)

The molecular structure of complex **2a** (Figure 1) confirms the octahedral coordination geometry in the crystal. A five-membered metallacycle is formed through the coordination of the N atom of the imine group and the *ortho*-chelated C atom. The sum of internal bond angles (540°) of this chelate ring indicates ideal planarity. Typically, the Cl atom is *trans*-oriented to the phenyl-C atom, which is well understood in terms of mutual *trans*-influence. The bite angle of the chelating ligand [C1−Co1−N1 = 82.41(10)°] is close to that found in a related compound.[13] The two axial trimethylphosphine ligands are slightly displaced [P2−Co1−P1 = 173.90(4)°] toward the Co−Me group for steric reasons. The C=N bond length [N1−C7 = 1.289(3) Å] is comparable with that (1.293(8) Å) in the *ortho*-metalated cobalt(III) fluoride we have recently reported.[18] This can be explained by the strong electron-withdrawing ability of the fluorine atom, which makes the cobalt(III) center more electron-deficient, which strengthens coordination of the N-donor and weakens the C=N bond.

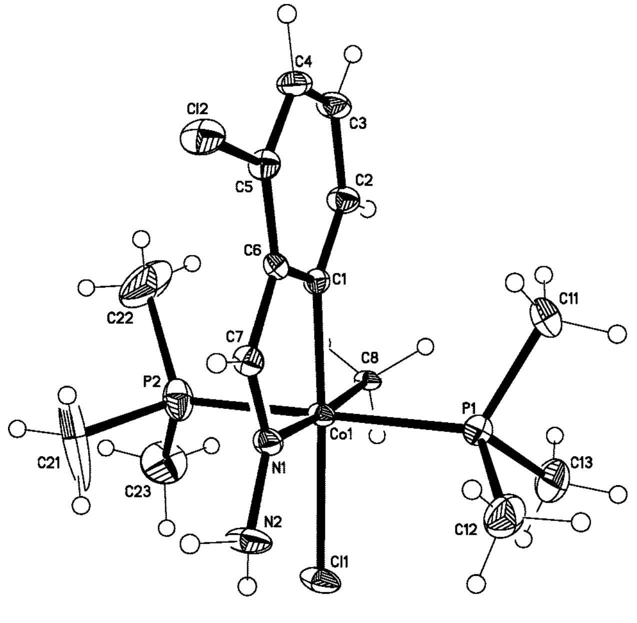


Figure 1. Molecular structure of **2a**. Selected bond distances (Å) and angles (deg): Co1−C1 1.913(3), Co1−N1 1.991(2), Co1−C8 2.044(2), N1−C7 1.289(3), Co1−Cl1 2.3679(8), Co1−P2 2.2161(9), Co1−P1 2.176(9); C1−Co1−N1 82.41(10), C8−Co1−Cl1 93.33(8), P2−Co1−P1 173.90(4), N1−C7−C6 113.8(2), C1−C6−C7 115.1(2), C6−C1−Co1 112.66(19), C7−N1−Co1 115.98(19).

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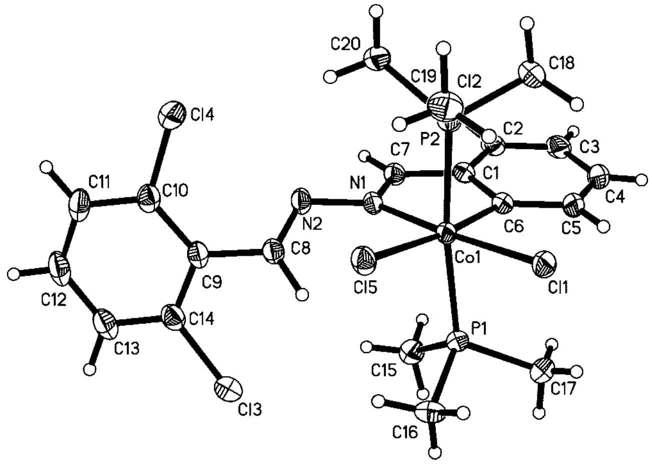
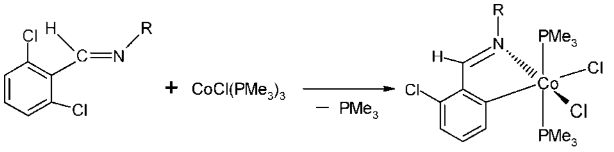


Figure 2. Molecular structure of **3b**. Selected bond distances (Å) and angles (deg): C7−N1 1.313(3), C8−N2 1.204(3), C1−C7 1.394(3), C8−C9 1.441(3), Co1−C6 1.944(2), Co1−N1 1.9997(18), Co1−Cl1 2.2885(7), Co1−P2 2.3377(9), Co1−P1 2.3392(8), Co1−Cl5 2.3748(8), C6−Co1−N1 79.12(8), N1−C7−C1 114.2(2), C7−N1−Co1 117.79(14), C1−C6−Co1 114.68(15), C7−C1−C6 113.58(19), P2−Co1−P1 172.89(2).

2. Reaction of CoX(PMe$_3$)$_3$ (X = Cl, Br) with Aryl Chlorides. When [CoCl(PMe$_3$)$_3$] was used instead of [CoMe(PMe$_3$)$_4$] in reactions with **1b** or **1c** in THF with stirring for 18 h at room temperature, a similar oxidative addition reaction also happened. *ortho*-Metalated cobalt(III) chloride **3b** or **3c** (eq 1) was formed. Complexes **3b** and **3c** were isolated by crystallization from diethyl ether at −27 °C. Both complexes are stable under ambient condition and can be handled in the air for at least 2 h. Under argon, decomposition begins above 120 °C.



1b-1c **3b-3c**

(1)

In the ^{13}C NMR spectrum, the PMe$_3$ group gives rise to a pseudotriplet resonance at 12.7 ppm (**3b**) or at 12.3 ppm (**3c**) with coupling constants $^1J(PC) + {}^3J(PC) = 29.2$ or 25.5 Hz, respectively. The spectroscopic data are in line with an octahedral configuration around the cobalt atom with two *trans*-oriented trimethylphosphine ligands and a five-membered chelate ring [C, C, C, N, Co].

Crystals of **3b** were obtained from diethyl ether and were analyzed by X-ray diffraction. The molecular structure of **3b** is shown in Figure 2. The cobalt atom attains an octahedral coordination with two *cis*-chloro ligands (Cl1−Co1−Cl5 = 86.87(3)°), opposite to the planar [*C:N*]-chelate ring of a diazine ligand with the bite angle C6−Co1−N1 = 79.12(8)°. The two axial trimethylphosphine ligands are slightly displaced (P2−Co1−P1=172.89(2)°) toward the midpoint Cl1−Cl5 by the bulky diazine ligand. The C=N bond length with the coordinated nitrogen, C7−N1 (1.313(3) Å), is longer than that of the uncoordinated C=N, C8−N2 (1.204(3) Å), indicating significant bond weakening upon coordination of the nitrogen donor atom. C1−C7 (1.394(3) Å) is shorter than C8−C9 (1.441(3) Å), which could be due to back-donation from the cobalt atom into the π^*-orbital of the ligand and a considerable conjugation in the cobaltocycle. The sum of internal bond angles (539.3°) indicates planarity of the chelating ring. The longer bond Co1−Cl5 (2.3748(8) Å), when compared with Co1−Cl1 (2.2885(7) Å), reflects the stronger *trans*-influence of the carbon atom (C6) than that of the nitrogen atom (N1).

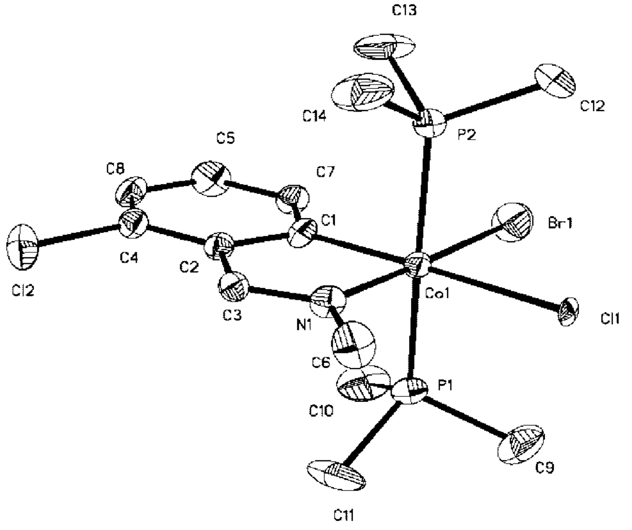
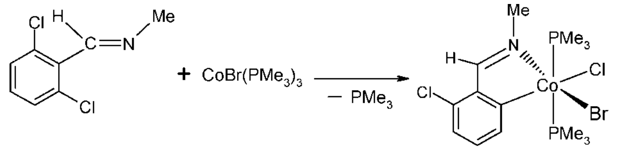


Figure 3. Molecular structure of **4c**. Selected bond distances (Å) and angles (deg): Co1−C1 1.925(10), Co1−N1 1.929(9), Co1−P2 2.255(3), Co1−P1 2.259(3), Co1−Br1 2.3941(18), Co1−Cl1 2.420(2), N1−C3 1.295(13); C1−Co1−N1 82.5(4), C3−N1−Co1 116.1(7), N1−C3−C2 114.9(9), C1−C2−C3 112.4(8), C2−C1−Co1 114.0(7), P2−Co1−P1 173.09(12).

The reaction of [CoBr(PMe$_3$)$_3$] with **1c** under similar conditions afforded a violet-red solution. Complex **4c** could be isolated from diethyl ether at −27 °C as violet-red crystals suitable for X-ray diffraction analysis (eq 2). The other possible isomer with the position exchange of Cl/Br atoms was not found.



1c **4c**

(2)

An X-ray diffraction study reveals that complex **4c** attains a molecular structure (Figure 3) that is closely related with that of complex **3b**. The bite angle C1−Co1−N1 = 82.9(2)° almost matches that in **2a** (82.41(10)°), while both bite angles are substantially larger than that in complex **3b** (79.12(8)°).

Reactions of [CoCl(PMe$_3$)$_3$] with **1d**,**1e** did not afford the expected Co(III) complexes according to eq 1 or 2, but formed aryl Co(II) chloride **3d** or **3e**, while [CoCl$_2$(PMe$_3$)$_3$] was isolated as a second fraction of crystals and identified through the comparation of the IR data with those in the literature[19] (Scheme 2). Complexes **3d** and **3e** are paramagnetic and were characterized by elemental analysis and IR.

A mechanism of formation is proposed in Scheme 2. With the nitrogen atom of the imine function serving as anchoring group, an oxdative addition of the C−Cl bond to the cobalt center occurs, affording intermediate aryl Co(III) complexes that are similar to **3b** and **3c**. Owing to the electron-withdrawing effect of the phenyl or naphthyl group, the Co(III) intermediates

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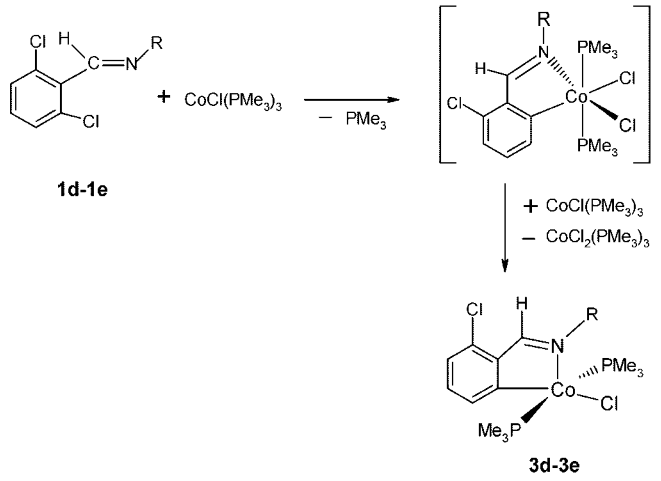
Scheme 2



are readily reduced by [CoCl(PMe_3)$_3$] to afford the pentacoordinate Co(II) complexes **3d**,**3e**. Our efforts to isolate the Co(III) intermediates were not successful.

By recrystallization from pentane at 4 °C brown-red prisms of **3e** were obtained, which proved suitable for X-ray diffraction analysis. The molecular geometry is shown in Figure 4. It can be described as a distorted square-pyramidal coordination of a cobalt(II) center with the N atom in the apical position. The angles N1−Co1−P1 (98.23(4)°) and N1−Co1−P2 (97.33(4)°) are larger than 90° because the bulky naphthyl ring is almost in plane with atoms [N1, P1, P2] and perpendicular to the five-membered chelate ring. This metallacycle with the internal bond angles (539.9°) is perpendicular to the square coordination plane.

Conclusion

Reactions of *ortho*-chlorinated aromatic compounds bearing imine as anchoring groups with [CoMe(PMe_3)$_4$], [CoCl(PMe_3)$_3$], or [CoBr(PMe_3)$_3$] were investigated. By activation of the C−Cl bond novel *ortho*-chelated cobalt(III) complexes were obtained. Thermally stable crystalline materials were isolated and structurally characterized. Likely routes of formation are in accord with the notion that intially the N-donor function is coordinated to the cobalt center, folowed by activation of the C−Cl bond and oxidative addition. In the reactions of CoMe(PMe_3)$_4$, the aryl Co(III) complexes (**2a**−**2e**) show a trend to undergo subsequent reductive elimination accompanied by C,C-coupling to give monochlorinated arene derivatives. Reactions of **1b** or **1c** with [CoCl(PMe_3)$_3$] or [CoBr(PMe_3)$_3$] afforded *ortho*-metalated cobalt(III) chlorides (**3b**, **3c**, and **4c**), while Co(II) complexes (**3d** and **3e**) were formed by reactions of [CoCl(PMe_3)$_3$] with reactants containing bulky groups.

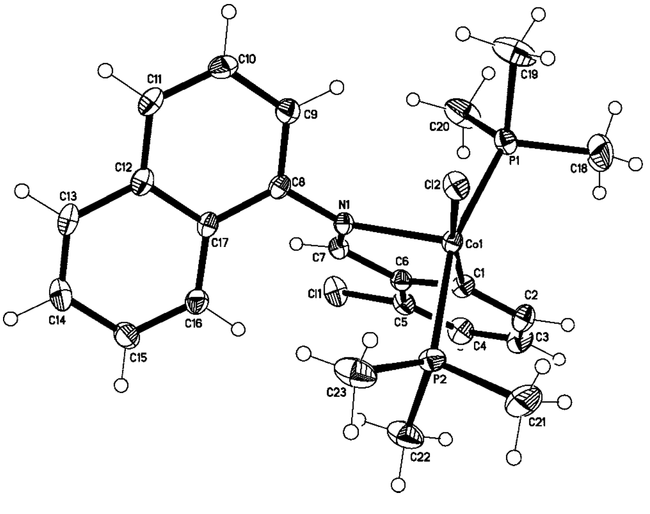


Figure 4. Molecular structure of **3e**. Selected bond distances (Å) and angles (deg): Co1−C1 1.9046(15), Co1−N1 2.0770(13), Co1−P2 2.2235(5), Co1−P1 2.2337(5), Co1−Cl2 2.2826(5), N1−C7 1.2964(19); C1−Co1−N1 82.90(6), N1−Co1−P1 98.23(4), N1−Co1−P2 97.33(4), N1−Co1−C1 82.90(6), N1−Co1−Cl2 105.09(4), P2−Co1−P1 163.13(18), N1−C7−C6 116.74(13), C1−C6−C7 115.46(13), C6−C1−Co1 113.15(11), C7−N1−Co1 111.66(10).

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Literature methods were used in the preparation of *N*,*N*′-bis(2,6-dichlorobenzylidene)hydrazine,[20] methyltetrakis(trimethylphosphine)cobalt(I),[21] chlorotris(trimethylphosphine)cobalt(I), and bromotris(trimethylphosphine)cobalt(I).[22] Schiff bases were obtained by condensation of 2,6-dichlorobenzaldehyde with amines. The other chemicals were used as purchased. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ^1H, ^{13}C, and ^{31}P NMR (300, 75, and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broadband proton decoupling. Elemental analyses were carried out on an Elementar Vario EL III. Melting points were measured in capillaries sealed under argon and are uncorrected. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

Synthesis of 2a. A solution of 0.44 g (1.16 mmol) of [CoMe(PMe_3)$_4$] in 30 mL of pentane was combined with a solution of **1a** 0.21 g (1.14 mmol) in pentane (20 mL) at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned red-brown in color. After filtering, the red solid residue was extracted with diethyl ether (60 mL). Repeated recrystallization from diethyl ether at 4 °C yielded orange single crystals suitable for X-ray structure analysis. Yield: 0.19 g (42.0%). Dec > 120 °C. Anal. Calcd for $C_{14}H_{27}Cl_2CoN_2P_2$ (415.15 g/mol): C, 40.47; H, 6.55; N, 6.74. Found: C, 40.78; H, 6.80; N, 6.57. IR (Nujol): 1591 ν(C=N), 1564, 1531 ν(C=C), 945 ρ(PMe_3) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 296 K): δ 0.66 (m, 3H, CH_3), 0.86 (t, $^2J(PH) + {}^4J(PH) = 7.8$ Hz, 18H, PCH_3), 6.33 (s, 2H, NH_2), 6.74−7.07 (m, 3H, Ar-*H*), 7.97(s, 1H, CH=N). ^{13}C NMR (75 MHz, C_6D_6, 296 K): δ 11.6 (t, $^1J(PC) + {}^3J(PC) = 26.6$ Hz, PCH_3), 121.7 s, 126.3 s, 127.6 s, 136.2 s, 141.3 s, 145.5 s. ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 5.3 s.

Complexes **2b**−**2e** were synthesized according to the method given above for **2a**.

Synthesis of 2b. Yield: 36%. Dec > 135 °C. Anal. Calcd for $C_{21}H_{29}Cl_4CoN_2P_2$ (572.33 g/mol): C, 44.07; H, 5.11; N, 4.89. Found: C, 44.58; H, 5.30; N, 4.57. IR (Nujol): 1625, 1610 ν(C=N), 1581, 1567 ν(C=C), 945 ρ(PMe_3) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 296 K): δ 0.64 (m, 3H, CH_3), 0.94 (m, 18H, PCH_3), 6.50−7.00 (m, 6H, Ar-*H*), 9.45 (s, 1H, C*H*=N), 10.46 (s, 1H, CH=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 5.3 s.

Synthesis of 2c. Yield: 61%. Dec > 120 °C. Anal. Calcd for $C_{15}H_{28}Cl_2CoNP_2$ (414.17 g/mol): C, 43.50; H, 6.81; N, 3.38. Found: C, 43.78; H, 6.80; N, 3.57. IR (Nujol): 1599 ν(C=N), 1567, 1531 ν(C=C), 945 ρ(PMe_3) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 296 K):

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Table 2. Crystallographis Data for Complexes 2a, 3b, 3e, and 4c

	2a	3b	3e	4c
empirical formula	$C_{14}H_{27}Cl_2CoN_2P_2$	$C_{20}H_{26}Cl_5CoN_2P_2$	$C_{23}H_{29}Cl_2CoNP_2$	$C_{14}H_{25}BrCl_2CoNP_2$
fw	415.15	592.55	511.24	479.03
cryst dimens, mm^3	0.35 × 0.23 × 0.13	0.35 × 0.23 × 0.13	0.48 × 0.45 × 0.39	0.25 × 0.20 × 0.19
temp, K	120(2)	150(2)	120(2)	273(2)
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	*Pbca*	*P*2(1)/*c*	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
a, Å	10.4280(12)	10.646(2)	8.8928(13)	8.7058(5)
b, Å	14.2733(17)	17.194 (3)	15.554(2)	10.7403(5)
c, Å	26.233(3)	14.953(3)	18.083(3)	22.1671(13)
α, deg	90	90	90	90
β, deg	90	101.15(3)	90	90
γ, deg	90	90	90	90
V, Å^3	3904.5(8)	2685.4(9)	2495.1(6)	2072.7(2)
Z	8	4	4	4
D_c, g cm^{-3}	1.412	1.412	1.361	1.535
no. of rflns collected	32 793	16 363	19 103	9281
no. of indep rflns	4653	5646	5956	3650
R_{int}	0.1090	0.0520	0.0205	0.0304
θ_{max}, deg	27.87	28.53	27.87	25.00
R_1 ($I > 2\sigma(I)$)	0.0471	0.0471	0.0228	0.0683
wR_2 (all data)	0.0943	0.0943	0.0599	0.2204

δ 0.57 (m, 3H, C*H*$_3$), 0.69 (m, 18H, PC*H*$_3$), 3.42 (s, 3H, N-C*H*$_3$), 6.66–7.07 (m, 3H, Ar-*H*), 8.57(s, 1H, CH=N). ^{13}C NMR (75 MHz, C_6D_6, 296 K): δ 11.9 (t, ^1J(PC) + ^3J(PC) = 25.5 Hz, PCH$_3$), 121.5 s, 123.1 s, 127.1 s, 130.7 s, 136.5 s, 142.3 s, Ar; 167.7 s, *C*H=N. ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 5.2 s.

Synthesis of 2d. Yield: 37%. Dec > 120 °C. Anal. Calcd for $C_{20}H_{30}Cl_2CoNP_2$ (476.24 g/mol): C, 50.44; H, 6.35; N, 2.94. Found: C, 50.98; H, 6.56; N, 2.57. IR (Nujol): 1599 (C=N), 1567, 1531 (C=C), 945 (PMe$_3$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 0.69 (m, 3H, C*H*$_3$), 0.96 (m, 18H, PC*H*$_3$), 6.65–7.74 (m, 8H, Ar-*H*), 8.15(s, 1H, C*H*=N). ^{13}C NMR (75 MHz, C_6D_6, 296 K): δ 12.6 (t, ^1J(PC) + ^3J(PC)) = 28.5 Hz, P*C*H$_3$), 124.9 s, 126.5 s, 127.1 s, 127.7 s, 128.3 s, 129.6 s, 137.7 s, 138.9 s, 145.1 s, 149.5 s; 172.6 (s, *C*H=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 9.4 s.

Synthesis of 2e. Yield: 34%. Dec > 110 °C. Anal. Calcd for $C_{24}H_{32}Cl_2CoNP_2$ (526.30 g/mol): C, 54.77; H, 6.13; N, 2.66. Found: C, 54.98; H, 6.30; N, 2.57. IR (Nujol): 1591 (C=N), 1564, 1531 (C=C), 945 (PMe$_3$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 0.52 (m, 3H, C*H*$_3$), 0.86 (t, ^2J(PH) +^4J(PH) = 7.2 Hz, 18H, PC*H*$_3$), 6.77–8.53 (m, 10H, Ar-*H*), 9.31 (s, 1H, C*H*=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 6.3 s (br).

Synthesis of 3b. Chlorotris(trimethylphosphane)cobalt(I) (0.83 g, 2.57 mmol) was dissolved in 40 mL of THF. To this solution was added **1b** (0.89 g, 2.57 mmol) in 20 mL of THF at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned violet-red. The filtrate was evaporated in vacuo, and the residue was extracted with pentane (60 mL) and diethyl ether (60 mL), respectively. Crystallization from diethyl ether at −27 °C afforded complex **3b** as brown-red crystals suitable for X-ray diffraction analysis. Yield: 0.64 g (41.8%). Dec > 120 °C. Anal. Calcd for $C_{20}H_{26}Cl_5CoN_2P_2$(592.55 g/mol): C, 40.54; H, 4.42; N, 4.72. Found: C, 40.76; H, 4.60; N, 4.57. IR (Nujol): 1624, 1615 (C=N), 1568, 1558 (C=C), 942 (PMe$_3$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 296 K): δ 1.07 (m, 18H, PC*H*$_3$), 6.42−8.15 (m, 6H, Ar-*H*), 8.39 (s, 1H, C8*H*=N2), 9.28 (s, 1H, C7*H*=N1). ^{13}C NMR (75 MHz, C_6D_6, 296 K): δ 12.7 (t, ^1J(PC) + ^3J(PC)) = 29.2 Hz, P*C*H$_3$), 123.8 s, 125.6 s, 127.6 s, 128.0 s, 129.2 s, 129.6 s, 131.2 s, 136.0 s, 137.8 s, 139.1 s, 140.2 s; 166.6 s, 177.2 s (*C*H=N). ^{31}P NMR (121 MHz, C_6D_6, 300 K): δ 10.8 s.

Synthesis of 3c. Complex **3c** was prepared according to the method given above for **3b**. Yield: 0.85 g (57.0%). Anal. Calcd for $C_{14}H_{25}Cl_3CoNP_2$ (434.48 g/mol): C, 38.70; H, 5.80; N, 3.22. Found: C, 38.28; H, 6.00; N, 3.51. IR (Nujol): 1594 (C=N), 1562, 1531 (C=C), 940 (PMe$_3$) cm^{-1}. Dec >120 °C. ^{1}H NMR (300 MHz,CDCl$_3$, 296 K): δ 1.12 (m, 18H, PC*H*$_3$), 3.26 (s, 3H, C*H*$_3$), 6.98−7.71 (m, 3H, Ar-*H*), 8.14 (s, 1H, C*H*=N). ^{13}C NMR (75 MHz, CDCl$_3$, 296 K): δ 12.3 (t, ^1J(PC) + ^3J(PC)) = 25.5 Hz), 48.75 s, 123.5 s, 129.9 s, 130.9 s, 138.5 s, 142.3 s; 172.0 (s *C*H=N). ^{31}P NMR (121 MHz, CDCl$_3$, 296 K): δ −0.87 s.

Synthesis of 3d. Chlorotris(trimethylphosphane)cobalt(I) (0.90 g, 2.79 mmol) was dissolved in 40 mL of THF. To this solution was added **1d** (0.69 g, 2.79 mmol) in 20 mL of THF at −80 °C. The mixture was allowed to warm to 20 °C and stirred for 18 h, turning violet-red. This was filtered and the filtrate was evaporated in vacuo. The residue was extracted with pentane (60 mL) and diethyl ether (60 mL), respectively. Crystallization in pentane at −27 °C afforded complex **3c** as brown-red crystals. Yield: 0.33 g (57.0%). Dec > 135 °C. Anal. Calcd for $C_{19}H_{27}Cl_2CoNP_2$ (461.18 g/mol): C, 49.48; H, 5.90; N, 3.04. Found: C, 50.08; H, 5.80; N, 3.27. IR (Nujol): 1596 (C=N), 939 (PMe$_3$) cm^{-1}.

Synthesis of 3e. Complexes **3e** were synthesized according to the method given above for **3d**. Yield: 42%. Dec > 135 °C. Anal. Calcd for $C_{23}H_{29}Cl_2CoNP_2$ (511.24 g/mol): C, 54.04; H, 5.72; N, 2.74. Found: C, 54.24; H, 5.89; N, 2.57. IR (Nujol): 1592 (C=N), 948 (PMe$_3$) cm^{-1}.

Synthesis of 4c. Bromotris(trimethylphosphane)cobalt(I) (0.43 g, 1.17 mmol) was dissolved in 20 mL of THF. To this solution was added **1c** (0.22 g, 1.16 mmol) in 20 mL of THF at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned violet-red. The filtrate was evaporated in vacuo, and the residue was extracted with pentane (40 mL) and diethyl ether (30 mL), respectively. Crystallization in diethyl ether at −27 °C afforded complex **4c** as violet-red crystals suitable for X-ray diffraction analysis. Yield: 0.20 g (35.8%). Dec > 130 °C. Anal. Calcd for $C_{14}H_{25}BrCl_2CoNP_2$ (479.03 g/mol): C, 35.10; H, 5.26; N, 2.92. Found: C, 35.37; H, 5.50; N, 2.77. IR (Nujol): 1592 (C=N) 941 (PMe$_3$) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 296 K): δ 1.17 (m, 18H, PC*H*$_3$), 3.20 (s, 3H, C*H*$_3$), 7.00–7.92 (m, 3H, Ar-*H*), 8.26 (s, 1H, C*H*=N). ^{31}P NMR (121 MHz, CDCl$_3$, 300 K): δ −1.8 (b).

X-ray Structure Determinations. Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic data for complexes **2a**, **3b**, **3e,** and **4c** are summarized in Table 2. The structures were solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

CCDC-667085 (**2a**), CCDC-667084 (**3b**), CCDC-667086 (**3e**) and CCDC-667083 (**4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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