C-Cl Bond Activation of *ortho*-Chlorinated Imine with Iron Complexes in Low Oxidation States

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The ortho-chelated iron(II) complexes [FeCl(PMe₃)₃((C₆H₃Cl-ortho)CH=N-R)] (R = Me, Ph) (**3**, **4**) and [FeCl(PMe₃)₃(C₆H₄-CH=N-R)] (R = Ph, *n*-Bu) (**7**, **8**) were prepared through oxidative addition of the C-Cl bond of ortho-chlorinated imine using iron(0) complexes, [Fe(PMe₃)₄]. The reactions of **3**, **4**, and **8** with CO delivered the carbonyl Fe(II) complexes **9**–**11**. A one-pot reaction of [FeMe₂(PMe₃)₄] with (C₆H₃Cl₂-2,6)CH=N-Ph in CO atmosphere resulted in carbonyl Fe(II) complexes [FeMe(CO)(PMe₃)₂-((C₆H₃Cl-ortho)CH=N-Ph)] (**12**). The crystal and molecular structures of complexes **3**, **4**, **7**–**9**, and **12** were determined by X-ray diffraction.

Introduction

In the past few years aromatic carbon—halogen bond activation at transition metal centers has been proven to be a useful tool in synthetic organic chemistry. When compared with the reactive and expensive iodo- and bromoarenes, as well as both costly and inert fluoroarenes, chloroarenes are certainly the most attractive aryl halides for synthetic applications on an industrial scale. Due to the importance of functionalization or dechlorination of aromatic chlorides, there is currently a great deal of interest in the activation of the C–Cl bond, which has been found comparatively inert.¹ There have been some examples of catalytic activation of the carbon—chlorine bond and carbon—carbon coupling of chloroarenes by palladium,^{2–4} nickel,⁵ cobalt,^{6–8} and iron⁹ complexes such as the Heck reaction, Suzuki coupling, and Stille coupling.

Recently we have reported cyclometalation reactions involving C–Cl bond activation at a $cobalt(I)^{6c}$ (eq 1) and $nickel(0)^{5g}$

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(eq 2) center with imine as an anchoring group. In the case of nickel(0) complexes, a series of bis(isoindolinone)s were formed through carbonylative cyclization and dimerization of phenylimine.



Here we report on our new progress in the direction of cyclometalation reactions involving C–Cl bond activation at iron centers with imine as prechelate ligands. The new *ortho*chelated iron complexes formed by oxidative addition of an

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Figure 1. Molecular structure of **3** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (deg): N1–Fe1 2.024(2), Fe1–C6 1.951(2), Fe1–P3 2.2435(9), Fe1–P1 2.2504(8), Fe1–P2 2.2647(8), Fe1–Cl2 2.3977(8); C7–N1–Fe1 114.86(16), C8–N1–Fe1 129.31(17), C6–Fe1–N1 81.55(9), C6–Fe1–P3 95.58(7), N1–Fe1–P3 176.96(6), C6–Fe1–P1 93.14(7), N1–Fe1–P1 89.38(6), P3–Fe1–P1 91.77(3), C6–Fe1–P2 91.95(7), N1–Fe1–P2 88.19(6), P3–Fe1–P2 90.93(3), P1–Fe1–P2 173.99(3), C6–Fe1–Cl2 170.60(7), N1–Fe1–Cl2 89.10(6), P3–Fe1–Cl2 93.75(3), P1–Fe1–Cl2 87.72(3), P2–Fe1–Cl2 86.74(3).

aromatic C–Cl bond were isolated and characterized. The reaction with CO resulted in only substituted carbonyl iron(II) complexes; no C,C-coupling reactions have been observed in compration with the case of nickel(0) complex.^{5g}

Results and Discussion

1. Reaction of $Fe(PMe_3)_4$ with the Dichlorinated Imine Ligands Derived from 2,6-Dichlorobenzaldehyde. The reaction of Schiff bases 1 and 2 (R = CH₃, 1; Ph, 2) by reaction with Fe(PMe₃)₄ afforded the six-coordinate Fe(II) complex 3 and 4 via C-Cl bond activation (eq 3).



Crystallization at -27 °C afforded a wine crystalloid **3** and purple **4** in pentane, respectively. In the infrared spectra of complexes **3** and **4**, the characteristic ν (C=N) bands are found at 1564 and 1595 cm⁻¹. Compared with those of the free imine ligands (ν (C=N) = 1622-1655 cm⁻¹), the evident red shift indicates the coordination of the imine N-donor. The expected five-membered metallocycles have been confirmed by X-ray crystallography.

In the crystal structures of complexes **3** and **4** (Figures 1 and 2) the iron atom is centered in an octahedron geometry with one N atom, one Cl atom, one C atom, and three P atoms. The

chelating ligand is coordinated by a N atom and a C atom, forming a five-membered metallacycle. The sum of internal bond angles (540°) of this five-membered chelating ring indicates planarity. Typically, the Cl atom is *trans*-oriented to the phenyl-C atom because of mutual *trans* influence. Two *trans*trimethylphosphine ligands slightly lean toward the Cl atom because of steric effects. The bulky imino phenyl group of complex **4** makes the angle P2–Fe1–Cl1 (82.57(3)°) significantly smaller than that in complex **3** (P3–Fe1–Cl2 93.75(3)°). In addition, due to the electron-donating property and the conjugation effect of the phenyl group, the Fe1–P3 bond (2.2435(9) Å) in complex **3** is shorter than the Fe1–P2 bond (2.2771(8) Å) in complex **4**.

2. Reaction of Fe(PMe₃)₄ with the Monochlorinated Imine Ligands Derived from 2-Chlorobenzaldehyde. Treatment of imine ligands 5 and 6 (R = Ph, 5; R = *n*-Bu, 6) with 1 equiv of Fe(PMe₃)₄ afforded complexes 7 and 8 (eq 4).



Crystallization at -4 °C resulted in purple crystals of 7 in diethyl ether and dark red crystals of 8 in pentane. In complexes 7 and 8 the iron atom is located at the center of an octahedral geometry (Figures 3 and 4). The molecular structure of 7 is close to that of complex 4.



Figure 2. Molecular structure of **4** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (deg): N1–Fe1 2.050(2), Fe1–C1 1.957(3), Fe1–P3 2.2435(9), Fe1–P1 2.2710(10), Fe1–P2 2.2771(8), Fe1–Cl1 2.3960(8); C7–N1–Fe1 113.61(18), C8–N1–Fe1 132.61(18), C1–Fe1–N1 81.62(10), C1–Fe1–P3 85.93(9), N1–Fe1–P3 88.50(7), C1–Fe1–P1 87.06(9), N1–Fe1–P1 88.63(7), P3–Fe1–P1 172.75(3), C1–Fe1–P2 102.61(8), N1–Fe1–P2 175.77(7), P3–Fe1–P2 91.72(3), P1–Fe1–P2 91.63(3), C1–Fe1–Cl1 174.62(8), N1–Fe1–Cl1 93.20(7), P3–Fe1–Cl1 92.48(3), P1–Fe1–Cl1 94.34(3), P2–Fe1–Cl1 82.57(3).



Figure 3. Molecular structure of **7** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (deg): Fe–C1 1.957(3), Fe–N1 2.058(2), Fe–P3 2.2563(9), Fe–P1 2.2698(9), Fe–P2 2.2822(9), Fe–C1 2.3938(8), N1–C7 1.298(4), N1–C8 1.440(4); C1–Fe–N1 81.56(11), C1–Fe–P3 86.25(9), N1–Fe–P3 88.37(7), C1–Fe–P1 86.60(9), N1–Fe–P1 88.20(7), P3–Fe–P1 172.46(4), C1–Fe–P2 102.95(9), N1–Fe–P2 175.49(7), P3–Fe–P2 92.04(4), P1–Fe–P2 91.90(4), C1–Fe–Cl 173.93(9), N1–Fe–Cl 92.60(7), P3–Fe–Cl 91.99(4), P1–Fe–Cl 94.88(4), P2–Fe–Cl 82.91(3).

A conceivable reaction pathway may be described as follows: The first step is the substitution of one trimethylphosphine by the imine N atom. The C–Cl bond activation is realized through oxidative addition with the support of a chelating effect. The reaction in eq 4 is slower than the reaction in eq 3 because the strong electron-withdrawing ability of the second Cl atom weakens the first C–Cl bond.

3. Reaction of Complexes 3, 4, and 8 with CO. Stirring a solution of 3 or 4 in CO atmosphere gave rise to complex 9 or 10 (eq 5). The reactions was complete within a few minutes. The crystals of complex 9 could be obtained with evaporation of solvent in air. Under the same conditions

complex **11** was isolated from the reaction of complex **8** with carbon monoxide (eq 6).



In the molecular structure of complex **9** (Figure 5), the iron atom is coordinated with one five-membered chelating [C,N]-ligand, two trimethylphosphine molecules, one chlorine atom, and one carbonyl ligand in a disordered octahedron. Complexes **9** and **10** are very stable in air. In comparison with the reaction of Ni(PMe₃)₄ with analogous Schiff base complexes,^{5g} only the substituted products were produced instead of the coupling products.

4. One-Pot Reaction of $FeMe_2(PMe_3)_4$ with Ligand 5 in CO Atmosphere. Reactions of $Fe(Me_2)(PMe_3)_4$ with ligand 5 in a CO atmosphere did not afford the expected complex 13 via C–Cl activation according to Scheme 1, but formed complex 12 through C–H activation and cyclometalation. At the same time, an expected insertion of CO into the Fe–Me bond did not occur; only a simple substitution of a trimethylphosphine ligand by CO was observed. Although the bond energy of the C–H bond (435 kJ mol⁻¹) is significantly higher than that of the C–Cl bond (351 kJ mol⁻¹), complex 12 was obtained as a

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Figure 4. Molecular structure of 8 (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (deg): Fe1–C1 1.9590(18), Fe1–N1 2.0075(15), Fe1–P3 2.0075(15), Fe1–P3 2.2543(7), Fe1–P1 2.2661(7), Fe1–P2 2.2714(7), Fe1–Cl1 2.4208(7), N1–C7 1.277(2), N1–C8 1.480(2); C1–Fe1–N1 81.77(7), C1–Fe1–P3 86.02(6), N1–Fe1–P3 87.62(5), P3–Fe1–P1 171.05(2), C1–Fe1–P2 104.13(6), N1–Fe1–P2 174.09(5), P3–Fe1–P2 92.62(3), P1–Fe1–P2 91.90(3), C1–Fe1–Cl1 173.45(5), N1–Fe1–Cl1 91.70(5), P2–Fe1–Cl1 82.40(2), P3–Fe1–Cl1 94.30(3), C7–N1–C8 119.90(16), C7–N1–Fe1 114.89(13).



Figure 5. Molecular structure of **9** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (deg): Fe1-C1 1.759(12), Fe1-C2 1.967(8), Fe1-N1 1.999(8), Fe1-P2 2.234(3), Fe1-P1 2.272(3), Fe1-Cl1 2.384(2), O1-C1 1.086(13), C8-N1 1.318(12), C9-N1 1.478(10); C1-Fe1-C2 95.6(4), C2-Fe1-N1 81.7(3), N1-Fe1-Cl1 93.0(2), C1-Fe1-Cl1 89.8(3), P2-Fe1-P1 176.82(12), C2-Fe1-Cl1 174.0(3), C1-Fe1-N1 176.2(4), P1-Fe1-Cl1 87.23(10), C9-N1-Fe1 127.1(6).

kinetic product of C–H activation. An attempt to isolate the possible intermediate $14\ \mbox{was}$ not successful.

In the infrared spectra of complex 12, the characteristic $\nu(C \equiv O)$ band is found at 1907 cm⁻¹. The proton resonances of the Fe-CH₃ were recorded at -0.77 ppm.

The iron atom has an octahedral geometry and is coordinated with the carbonyl ligand *trans*-oriented to the imine N atom (Figure 6). The chelating ligand with the N atom as the an-



Figure 6. Molecular structure of **12** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (deg): Fe1-C1 1.726(3), Fe1-C8 1.979(3), Fe1-C21 2.183(3), Fe1-P2 2.2446(9), Fe1-P1 2.2500(9), O1-C1 1.154(4), N1-C14 1.300(4), N1-C15 1.443(3), N1-Fe1 2.063(2); C1-Fe1-C8 94.57(14), C8-Fe1-N1 80.83(10), N1-Fe1-C21 95.84(10), C1-Fe1-C21 88.77(14), C1-Fe1-P1 91.90(10), C8-Fe1-P1 90.91(7), O1-C1-Fe1 178.5(3),N1-C14-C13118.3(2),C8-C13-C14112.7(2),C13-C8-Fe1 114.42(19), C14-N1-Fe1 113.80(17).

Scheme 1



choring group forms a five-membered metallacyle where the sum of internal bond angles (540.05°) indicates planarity.

Conclusion

Reactions of mono- and di-*ortho*-cholorinated compounds (1, 2, 5, and 6) containing imine as anchoring groups with $Fe(PMe_3)_4$ delivered cyclometalated complexes (3, 4, 7, and 8) in octahedral coordination geometry via the C-Cl bond activation. The novel stable *ortho*-chelated iron complexes were characterized by spectroscopic methods. Only simple substitution products 9–11 were observed in the reactions of complexes 3, 4, and 8 with CO. No insertion and/or reductive elimination were found in these reactions. The one-pot reaction of prechelate ligand 5 with FeMe₂(PMe₃)₄ in CO atmosphere interestingly afforded the C-H activation product 12 instead of the C-Cl bond activation product. The structures of complexes 3, 4, 7–9, and 12 were determined by X-ray diffraction.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive material.

 Table 1. Crystallographic Data for Complexes 3, 4, 7, 8, 9, and 12

	3	4	7	8	9	12
empirical formula	C ₁₇ H ₃₄ C ₁₂ FeNP ₃	C22H36C12FeNP3	C22H37ClFeNP3	C20H41ClFeNP3	C15H25Cl2FeNOP2	C21H31ClFeNOP2
fw	472.13	534.2	499.8	481.8	424.06	466.71
cryst syst	monoclinic	noclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	P2(1)/n	P2(1)/n	P2(1)/n	P2(1)/n	$P_{na}2$ (1)	$P\overline{1}$
a, Å	8.6000(17)	8.6390(17)	8.9303(10)	897(2)	30.994(6)	8.8720(18)
<i>b</i> , Å	28.838(6)	34.588 (7)	33.154(3)	9.878(8)	8.5930(17)	9.0070(18)
<i>c</i> , Å	9.1660(18)	9.5210(19)	9.7044(9)	9.545(3)	29.837(6)	15.555(3)
α, deg	90	90	90	90	90	86.41(3)
β , deg	93.01(3)	98.14(3)	99.450(6)	96.349(4)	90	75.14(3)
γ , deg	90	90	90	90	90	74.43(3)
V, Å ³	2270.1(8)	2816.3(10)	2834.3(5)	2521.6(12)	7947(3)	1157.3(4)
Z	4	4	4	2	16	2
$D_{\rm c}$, g cm ⁻³	1.381	1.373	1.251	2.065	1.424	1.339
no. of rflns collec	10 050	13 744	22 090	14 874	34 481	4253
no. of indep rflns	5206	5952	5944	5645	14 372	3424
R _{int}	0.0403	0.0543	0.0235	0.0430	0.0765	0.0411
$\theta_{\rm max}$, deg	31.79	27.14	27.55	27.53	27.11	27.02
$R_1 (I > 2\sigma (I))$	0.0356	0.0532	0.0443	0.0323	0.0858	0.0385
wR_{2} (all data)	0.1358	0.1595	0 1469	0.0760	0.2173	0 1243

Solvents were dried by known procedures and distilled under nitrogen before use. Corresponding Schiff base complexes of 2,6-dichlorobenzaldehyde and 2-chlorobenzaldehyde were prepared by refluxing mixtures of chlorobenzaldehyde and amine in alcohol solution. Infrared spectra (4000–400 cm⁻¹), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ¹H and ³¹P NMR (300 and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ³¹P NMR resonances were obtained with broadband proton decoupling. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

Synthesis of 3. A solution of Fe(PMe₃)₄ (1.35 g, 3.75 mmol) in 30 mL of pentane was combined with a solution of 1 (0.7 g, 3.72 mmol) in pentane (20 mL) at -80 °C. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. During this period, the reaction mixture turned black-red. At this point the solution was filtered. Crystallization at -27 °C afforded black-red microcrystals of 3: yield 0.54 g (30.0%). IR (Nujol, cm⁻¹): 1564 ν (C=N), 1578 ν (C=C), 942 ν (PMe₃). ³¹P NMR (C₆D₆, 297 K, ppm): δ 11.4 (d, ²*J*(PP) = 58 Hz, 2P), 14.7 (t, ²*J*(PP) = 52 Hz, 1P).

Synthesis of 4. A sample of 1.07 g (2.97 mmol) of Fe(PMe₃)₄ and 0.74 g (2.96 mmol) of **2** in 50 mL of pentane after 6 h at room temperature formed a purple solution. Then the solution was filtered. Crystallization at -27 °C afforded black-red microcrystals of **5**. Yield: 0.63 g (40%). IR (Nujol, cm⁻¹): 1565 ν (C=C), 1595 ν (C=N), 944 ν (PMe₃).

Synthesis of 7. A solution of 0.80 g (2.22 mmol) of Fe(PMe₃)₄ in 30 mL of diethyl ether was combined with a solution of complex **5** (0.48 g, 2.23 mmol) in 30 mL of diethyl ether at -80 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. Dark purple crystals of **7** were afforded at -27 °C after filtering. Yield: 0.75 g (67%). IR (Nujol, cm⁻¹): 1574 ν (C=N), 1558 ν (C=C), 940 ν (PMe₃).

Synthesis of 8. Fe(PMe₃)₄ (0.80 g, 2.22 mmol) dissolved in 30 mL of pentane was combined with a solution of complex **6** (0.44 g, 2.25 mmol) in 40 mL of pentane at room temperature and stirred for 12 h. The filtrate was kept at -27 °C to afford red crystals of **10**. Yield: 0.64 g (60%). IR (Nujol, cm⁻¹): 1596 ν (C=N), 1572 ν (C=C), 941 ν (PMe₃). ¹H NMR (C₆D₆, 298 K, ppm): δ 0.96 (m, 27H, PCH₃), 1.25 (m, 3H, CH₃), 1.37 (m, 2H, CH₂), 1.70 (m, 2H, CH₂), 3.79 (m, 2H, CH₂), 6.90–7.55 (m, 4H, Ar-H), 7.97 (s, 1H, CH=N). ³¹P NMR (121 MHz, C₆D₆, 298 K, ppm): δ 12.8 (s).

Synthesis of 9. 3 (0.20 g, 0.42 mmol) was dissolved in pentane. Stirring the solution in an atmosphere of CO resulted in a red solution in a few minutes. The solution was filtered after 2 h. Crystallization at $-27 \,^{\circ}$ C afforded a red deposition of 9. Yield: 0.17 g (98%). IR (Nujol, cm⁻¹): 1912 ν (C=O), 1567 ν (C=C), 1593 ν (C=N), 944 ν (PMe₃). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): δ 0.90 (m, 18H, PCH₃), 3.48 (s, 3H, CH₃), 6.63–7.75 (m, 3H, Ar-H), 8.70 (s, 1H, CH=N). ³¹P NMR (121 MHz, C₆D₆, 298 K, ppm): δ 27.2 (s).

Synthesis of 10. 4 (0.30 g, 0.56 mmol) was dissolved in pentane. Stirring the solution in an atmosphere of CO resulted in a green solution after 1 h. The filtrate was kept at -27 °C to afford purple crystals of 10. Yield: 0.16 g (60%). IR (Nujol, cm⁻¹): 1917 ν (C=O). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): δ 0.98 (m, 18H, PCH₃), 6.64–7.85 (m, 8H, Ar-H), 9.05 (s, 1H, CH=N). ³¹P NMR (121 MHz, C₆D₆, 298 K, ppm): δ 25.3 (s).

Synthesis of 11. A solution of complex **8** (0.50 g 1.04 mmol) in 50 mL of pentane was stirred in an atmosphere of CO for 12 h. The filtrate was kept at -27 °C to afford red crystals of **11**. Yield: 0.26 g (58%). IR (Nujol, cm⁻¹): 1903 ν (C=O), 1599 ν (C=N), 1577 ν (C=C), 947 ν (PMe₃). ¹H NMR (300 MHz, C₆D₆, 298 K, ppm): δ 1.37 (m, 2H, CH₂), 1.68 (m, 2H, CH₂), 3.84 (m, 2H, N-CH₂), 6.73-7.47 (m, 4H, Ar-H), 8.46 (s, br, 1H, CH=N).

Synthesis of 12. A solution of FeMe₂(PMe₃)₄ (1.00 g, 4.47 mmol) in 30 mL of pentane was combined with a solution of **7** (0.97 g, 4.50 mmol) in pentane (30 mL) at -80 °C. The reaction mixture was allowed to warm to room temperature. The reaction mixture turned blue after a few minutes. After 5 h, stirring the solution in an atmosphere of CO resulted in a green solution in a few minutes. Crystallization at -27 °C afforded green microcrystals of **12**. Yield: 0.21 g (10%). IR (Nujol, cm⁻¹): 1907 ν (C=O), 1566 ν (C=C), 946 ν (PMe₃). ¹H NMR (300 MHz, CDCl₃, 298 K, ppm): δ -0.76 (m, 3H, Fe-CH₃), 0.89 (m, 18H, PCH₃), 6.73-7.90 (m, 8H, Ar-H), 8.75 (s, br, 1H, CH=N). ³¹P NMR (121 MHz, CDCl₃, 294 K, ppm): δ 19.4 (s).

X-ray Structure Determinations. Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystallographic data for complexes **3**, **4**, **7**–**9**, and **12** are summarized in Table 1. 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-11783 (**3**), CCDC-11784(**4**), CCDC-679219(**7**), CCDC-679220 (**8**), CCDC-679221 (**9**), and CCDC-702986 (**12**) 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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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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