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Reactions of $[Ir(COD)(PMe_3)_3]Cl$ with Benzene, Pyridine, Furan, and Thiophene: C–H Cleavage vs Ring Opening

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Reactions between $[Ir(COD)(PMe_3)_3]Cl$, **1**, and a number of aromatic hydrocarbons (benzene, pyridine, furan, thiophene, and benzothiophene) were investigated where $[Ir(COD)(PMe_3)_3]Cl$ acts as a convenient source of "$Ir(PMe_3)_3Cl$". Reactions between **1** and benzene, pyridine, and furan lead to the formation of products derived from oxidative addition of a C–H bond. The benzene addition product, **2**, is *mer*-$(Me_3P)_3Ir(H)(Ph)(Cl)$ which crystallized in the monoclinic space group $P2_1/n$ with a = 9.877(2) Å, b = 11.894(3) Å, c = 17.964(5) Å, β = 94.29°, and V = 2104.5(9) Å^3 for Z = 4. The stereochemistry of **2** has the H and Cl trans to each other and the phenyl group trans to PMe_3. NMR evidence indicates that there is hindered rotation about the Ir–phenyl bond. The pyridine addition product, **3**, is *mer*-$(Me_3P)_3Ir(pyr)(H)(Cl)$ which crystallized in the orthorhombic space group *Cmca* with a = 13.340(4) Å, b = 11.999(3) Å, c = 26.315 Å, and V = 4212(2) Å^3 for Z = 8. The stereochemistry of **3** is different from that of **2** in that **3** has pyridine trans to chloride and H trans to PMe_3. The pyridine exclusively adds the C–H bond α to the nitrogen. The furan addition product, **4**, crystallized in the monoclinic space group $P2_1/n$ with a = 9.723(2) Å, b = 11.583(3) Å, c = 17.790(5) Å, β = 94.68(2)°, and V = 1996.7(9) Å^3 for Z = 4. The stereochemistry of **4** is the same as **2**: H trans to Cl and furanyl trans to PMe_3 with the C–H bond α to oxygen being the one that adds. In contrast to the above cases of C–H addition, thiophene reacts via a ring-opening C–S oxidative addition reaction to form *mer*-$(Me_3P)_3\overline{Ir(Cl)\{SC(H){=}C(H)C(H){=}C}(H)\}$, **5a**. The benzothiophene adduct, **5b**, crystallized in the orthorhombic space group $P2_12_12_1$ with a = 11.550(3) Å, b = 13.598(2) Å, c = 14.362(4) Å, and V = 2255.7(9) Å^3 for Z = 4. The stereochemistry of the addition results in C trans to Cl and S trans to PMe_3. The structure and bonding of **5b** is compared with other thiairidametallacycles reported in the literature.

Introduction

The interactions between metals and heteroaromatic compounds have been the subject of much study lately because of their relevance to understanding the chemistry of hydrodesulfurization and hydrodenitrogenation.[1] For the former, reactions between thiophene (or substituted thiophenes) and metal complexes have been extensively examined and over the past several years, and a wealth of coordination modes and reaction patterns for thiophenic molecules have been uncovered.[2–41] While it has been shown that thiophenes can coordinate in a variety of ways to a number of different metal systems, the most in-

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tringuing reaction chemistry has been uncovered in systems containing rhodium and iridium primarily due to the efforts of the Angelici,[2–28] Jones,[29–32] and Rauchfuss[33–41] groups. A common feature in the rhodium and iridium work is the presence of cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligands. Not surprisingly, it has been these same Cp*Rh and Cp*Ir systems that have been well studied for their C–H activation chemistry.[42–55] A common feature here is that both chemistries appear to require an electron-rich, low-valent metal system capable of undergoing oxidative addition reactions. We have been investigating the reaction chemistry of $[Ir(COD)(PMe_3)_3]Cl$,[56,57] 1, which serves as an excellent, stable source of "$Ir(PMe_3)_3Cl$", another electron-rich low-valent metal complex. We found that 1 reacts with benzene (and some substituted benzenes) to yield products derived from the oxidative addition of C–H bonds (equation 1).[58,59] In the course of our studies we began investigating the reactions of $[Ir(COD)(PMe_3)_3]Cl$ and a number of heteroaromatic compounds. Previously, we reported on the reaction between $[Ir(COD)(PMe_3)_3]Cl$ and pyrrolic type molecules and showed that these reactions proceeded via N–H oxidative addition.[60] In this report, we describe reactions between $[Ir(COD)(PMe_3)_3]Cl$ and benzene, pyridine, furan, and thiophene which result in C–H oxidative addition in the cases of benzene, pyridine, and furan and C–S (ring opening) cleavage in the case of thiophenes.

Experimental Section

General Comments. All reactions were carried out on a Schlenk line under an atmosphere of predried nitrogen using air-sensitive procedures and techniques. All drybox manipulations were carried out in a MB-150-M glovebox purchased from Innovative Technologies. The solvents toluene, tetrahydrofuran, ether, pentane, methylene chloride, methylcyclohexane, decalin, *N*-octane, and mesitylene were purchased from either Fisher Scientific or Aldrich Chemical Co. Hydrocarbon solvents were dried using sodium or potassium with benzophenone and were distilled under nitrogen. Methylene chloride was dried over and distilled from P_2O_5. Iridium trichloride trihydrate was either purchased or on loan from Johnson Matthey and used as received. All other chemicals were reagent grade and were used as received. The synthesis of $[Ir(COD)(PMe_3)_3]Cl$ was carried out using a previously reported procedure. ^1H NMR spectra were obtained using either a Bruker WP-270 or WP-200 NMR spectrometer. ^{31}P and ^{13}C NMR spectra were obtained using the Bruker WP-200 NMR spectrometer. Chemical shifts are reported in δ units, using the appropriate deuterated solvent peak as a reference relative to tetramethylsilane. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Synthesis of *mer*-$(Me_3P)_3Ir(H)(Ph)Cl$. A thick-wall, screw-capped reaction tube equipped with a stir bar and septum was charged with dry $[Ir(COD)(PMe_3)_3]Cl$ (5 g, 8.87 mmol) under nitrogen in a drybox. The reaction tube was then connected to a double manifold Schlenk line via a needle. Benzene (35 mL, 0.392 mol) was injected into the reaction tube. With an increased flow of nitrogen, the septum was quickly removed and replaced with a Teflon screw cap and O-ring. This mixture was shaken and then placed in an oil bath at 100 °C for 48 h. As the reaction progressed, the mixture turned red-orange and finally a yellow color with some solids remaining. After the solution was allowed to cool, the cap was replaced with a septum and a needle inserted with flowing nitrogen along with a cannula fitted with a filter paper. The solution was filtered as it was transferred via the cannula to a 100-mL flask under nitrogen. The solvent was removed under vacuum which left a yellow solid behind. The resulting solid was washed with 20 mL of pentane to remove a small amount of a yellow impurity. The remaining solid was dissolved in 2 mL of CH_2Cl_2, and the product was precipitated by the slow addition of pentane. The off-white product was filtered and rinsed with additional pentane (5 mL). The yield was 2.34 g (4.38 mmol (49.4% yield based on $[Ir(COD)(PMe_3)_3]Cl$) of *mer*-$(Me_3P)_3Ir(H)(Ph)Cl$). ^1H NMR (C_6D_6): δ −23.46 ppm (q, J_{P-H} = 4.6 Hz, 1 H, Ir-H), 1.23 (t, J_{P-H} = 2.9, 18 Hz, trans PMe_3), 1.58 (d, J_{P-H} = 7.7 Hz, 9 H, cis PMe_3), 6.7–6.9 (complex set of three pseudotriplets, 3 H, phenyl), 7.39 (pseudotriplet, 1 H, phenyl), 8.15 ppm (pseudotriplet, 1 H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 17.7 (t, J_{P-C} = 79 Hz, mutually trans PMe_3), 21.0 (d, J_{P-C} = 110 Hz, cis PMe_3), 121.5 (s, phenyl), 126.3 (s, phenyl), 126.9 (s, phenyl), 139.3 (s, phenyl), 145.9 (dt, $J_{P(trans)-C}$ = 340 Hz, $J_{P(cis)-C}$ = 60 Hz, ipso carbon of phenyl), 148.5 ppm (s, phenyl). Anal. Calcd for $C_{15}H_{33}ClIrP_3$: C, 33.74; H, 6.23. Found: C, 33.35; H, 6.25.

Synthesis of *mer*-$(Me_3P)_3Ir(C_5H_4N)(H)Cl$. A thick-wall, screw-capped reaction tube equipped with a stir bar and septum was charged with $[Ir(COD)(PMe_3)_3]Cl$ (290 mg, 0.51 mmol) under nitrogen in a drybox. The reaction tube was then connected to a double manifold Schlenk line, and 5 mL of methylcyclohexane was added along with 0.45 mL (0.43 mol) of pyridine. The septum was replaced with a Teflon screw cap with an O-ring. The slurry was stirred and placed in an oil bath at 110 °C for 48 h. The solution was allowed to cool and was transferred via cannula to a 50-mL flask under nitrogen. The solvent was removed under vacuum leaving a lemon yellow solid. A minimum of methylene chloride (2 mL) was added to dissolve the solid, and the product was precipitated by the slow addition of pentane (20 mL). A light tan product was collected by filtration and rinsed with additional pentane (5 mL). This yielded 0.146 g (0.273 mmol, 53% based on $[Ir(COD)(PMe_3)_3]Cl$) of *mer*-$(Me_3P_3)Ir(C_5H_4N)(H)Cl$. ^1H NMR ($CDCl_3$): δ −10.73 (dt, trans J_{P-H} = 153.5 Hz, cis J_{P-H} = 19.8 Hz, 1 H, Ir-H), 1.39 (t, J_{P-H} = 3.38 Hz, 18 H, trans PMe_3), 1.50 (d, J_{P-H} = 7.99 Hz, 9 H, cis PMe_3), 6.48 (br t, J = 5.69 Hz, 1 H, pyridyl), 6.71 (t d, J = 7.36, 2.15 Hz, 1 H, pyridyl), 7.36 (br d, J = 7.89 Hz, 1 H, pyridiyl), 7.98 ppm (br d, J = 2.7 Hz, 1 H, pyridyl). ^{13}C NMR ($CDCl_3$): δ 16.4 (d, J_{P-C} = 106.3 Hz, cis PMe_3), 17.7 (t, J_{P-C} = 70.3 Hz, trans PMe_3), 114.7, 132.0, 141.6, and 147.0 ppm (all s, pyridyl). (One quaternary carbon not observed). ^{31}P NMR ($CDCl_3$): δ −38.2 (d, J = 54 Hz, cis PMe_3), −48.7 ppm (t, J = 54 Hz, trans PMe_3). Anal. Calcd for $C_{14}H_{32}ClIrNP_3$: C, 31.43; H, 6.04. Found: C, 31.94; H, 6.10.

Synthesis of *mer*-$(Me_3P)_3Ir(H)(C_4H_3O)Cl$. A thick-wall, screw-capped reaction tube equipped with a stir bar and septum was charged with $[Ir(COD)(PMe_3)_3]Cl$ (1.025 g, 1.82 mmol) under nitrogen in a drybox. The reaction tube was then connected to a double manifold Schlenk line via a needle inserted in the septum. Methylcyclohexane (3 mL) was added along with 2.63 mL (36.2

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mmol) of furan. The septum was quickly replaced with a Teflon screw cap fitted with an O-ring. The mixture was shaken well and placed in an oil bath at 100 °C for 24 h. The solution was allowed to cool before the Teflon screw cap was replaced with a septum containing a needle with flowing nitrogen and a cannula fitted with filter paper. The brown-yellow solution was filtered as it was transferred by the cannula to a 100-mL flask under nitrogen. The solution was stripped under vacuum leaving a brown product. The material was redissolved using methylene chloride (4 mL), and the product was precipitated by the slow addition of pentane (20 mL) which gave a brown oil. The solvent was again stripped, and the residue was redissolved using methylene chloride (4 mL). The product was precipitated out by the slow addition of diethyl ether (20 mL) producing an off-white solid. This yielded 482 mg (0.920 mmol, 51% based on [Ir(COD)(PMe$_3$)$_3$]Cl) of *mer*-(Me$_3$P)$_3$Ir(H)(C$_4$H$_3$O)Cl. ^{1}H NMR (CDCl$_3$): δ −22.96 (q, J_{P-H} = 21.4 Hz, 1 H, Ir-H), 1.28 (t, J_{P-H} = 4.76 Hz, 18 H, trans PMe$_3$), 1.55 (d, J_{P-H} = 11.0 Hz, 9 H, cis PMe$_3$), 6.16, 6.21, and 7.53 ppm (m, 3 H, furyl). ^{13}C NMR (CD$_2$Cl$_2$): δ 17.6 (t, J_{P-C} = 18.6 Hz, 19 H, trans PMe$_3$), 19.5 (d, J_{P-C} = 30.6 Hz, 9H, cis PMe$_3$), 110.6, 114.6, and 142.4 ppm (all s, furyl) (One quaternary carbon not observed). ^{31}P NMR (CD$_2$Cl$_2$): δ −36.5 (d, J = 57.2 Hz, cis PMe$_3$), −50.7 (t, J = 57.2 Hz, trans PMe$_3$). Anal. Calcd for C$_{13}$H$_{31}$ClIrOP$_3$: C, 29.8; H, 5.96. Found: C, 29.79; H, 5.82.

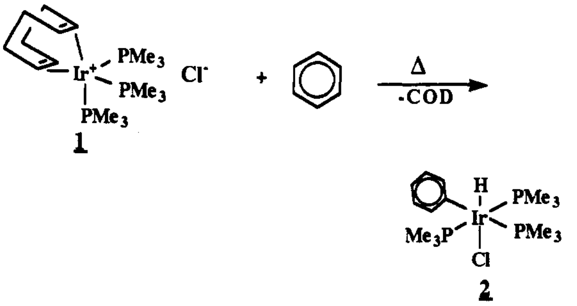
Synthesis of *mer*-(Me$_3$P)$_3$Ir(SC$_4$H$_4$)Cl. A thick-wall, screw-capped reaction tube, equipped with a stir bar and septum, was charged with [Ir(COD)(PMe$_3$)$_3$]Cl (500 mg, 0.887 mmol) under nitrogen in a drybox. The reaction tube was then connected to a double-manifold Schlenk line, and methylcyclohexane (5 mL) and thiophene (3 mL, 38.01 mmol) were injected into the reaction tube. The septum was replaced with a Teflon screw cap with an O-ring. The mixture was shaken well and placed in an oil bath at 80 °C for 24 h. The brown solution was allowed to cool before a Teflon screw cap was replaced with a septum containing a needle with flowing nitrogen and a cannula fitted with a filter paper. The brown solution was filtered as it was transferred via the cannula to a 50-mL flask under nitrogen. Pentane (15 mL) was slowly added to the mixture. A peach-colored product precipitated out. This was filtered and rinsed with additional pentane (5 mL) yielding 210 mg (0.389 mmol, 44% based on [Ir(COD)(PMe$_3$)$_3$]Cl) of *mer*-(Me$_3$P)$_3$Ir(SC$_4$H$_3$)Cl. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.45 (t, J_{P-H} = 3.55 Hz, 18 H, PMe$_3$), 1.63 (d, J_{P-H} = 9.20 Hz, 9 H, PMe$_3$), 5.71 (d d, J_{H-H} = 9.93, 9.07 Hz, 1 H), 5.92 (d d, J_{H-H} = 10.03, 10.06 Hz, 1 H), 6.42 (m, 1 H), and 7.27 ppm (br t, J = 11.94 Hz, 1H) from the thiometallacycle. ^{13}C NMR (CD$_2$Cl$_2$): δ 12.26 (t, J_{P-C} = 73.14 Hz, trans PMe$_3$), 15.55 (d, J_{P-C} = 135.46 Hz, cis PMe$_3$), 113.12 (q, J_{P-C} = 34.8 Hz), and 121.66, 121.94, and 124.97 ppm (s, thiophene). ^{31}P NMR (CD$_2$Cl$_2$) δ −44.17 (t, J = 53.08 Hz, trans PMe$_3$), −35.13 ppm (d, J = 52.62 Hz, cis PMe$_3$). Anal. Calcd for C$_{13}$H$_{31}$IrClP$_3$S: C, 28.90, H, 5.80. Found: C, 28.83, H, 5.53.

Synthesis of *mer*-(Me$_3$P)$_3$Ir(SC$_8$H$_6$)Cl. A thick-wall, screw-capped reaction tube equipped with a stir bar and septum was charged with dry [Ir(COD)(PMe$_3$)$_3$]Cl (250 mg, 0.444 mmol) under nitrogen in a drybox. The reaction tube was connected to a double-manifold Schlenk line via a needle. A solution of benzothiophene (0.298 g) in methylcyclohexane (10 mL) was injected by syringe. The septum was replaced with a Teflon screw cap and O-ring, and the mixture was mixed well. The tube was placed in an oil bath at 100 °C for 24 h. Once cooled, the solution was transferred to a 100-mL flask by the use of a cannula fitted with filter paper. The solvent was removed by vacuum leaving a yellow product behind. The material was redissolved in methylene chloride (5 mL) and was precipitated by the slow addition of dry ethyl ether (20 mL). The solids were collected by filtration and rinsed with ethyl ether (10 mL) leaving a light yellow solid. The yield was 0.151 g (0.256 mmol, 57.6% based on [Ir(COD)(PMe$_3$)$_3$]Cl) of *mer*-(Me$_3$P)$_3$Ir(SC$_8$H$_6$)Cl. ^{1}H NMR (CDCl$_3$): δ 1.43 (t, J_{P-H} = 3.51 Hz), 1.67 (d, J_{P-H} = 9.10 Hz, 9 H, cis PMe$_3$), 6.70–6.79 (m, 1 H, thiometallacycle), 6.82–6.95 (m, 3 H, phenyl), 7.21–7.32 (m, 1 H, thiometallacycle), 7.41 ppm (br d, 1 H phenyl). ^{13}C NMR (CDCl$_3$): δ 12.60 (t, J_{P-C} = 73.66 Hz, trans PMe$_3$), 15.53 (d, J_{P-C} = 134.38 Hz, cis PMe$_3$), 114.83 (q, J_{P-C} = 32.2 Hz, thiometallacycle), 120.60, 125.21, 129.70, 129.80, 129.94, 130.73, and 138.20 ppm (s, aromatic). ^{31}P (CD$_2$Cl$_2$): δ −38.60 (d, J = 52.55 Hz, cis PMe$_3$), −44.47 ppm (t, J = 52.66 Hz, trans PMe$_3$).

X-ray Diffraction Studies. All structural determinations were carried out at room temperature on a Siemens R3/mv single-crystal diffractometer system utilizing graphite-monochromated Mo Kα radiation and scintillation detection. In all four cases (structures **2**, **3**, **4**, **5b**), the same general procedure was followed. All crystals were grown from methylene chloride/pentane mixtures, and the crystals were mounted on a thin glass fiber. A random search routine was used to collect 30 reflections (15° < 2θ < 30°) which were accurately centered and used for the determination of the unit cell parameters. Following data collection, an empirical absorption correction was applied to the data based on a series of 4 scans, and the structures were solved using the SHELXTL plus package of programs on a microvax computer.[61] The structures were solved using direct methods routines and refined using full-matrix least-squares refinement of the non-hydrogen atoms. Hydrogen atoms were placed at calculated positions. Table I lists the full experimental details for the data collection and refinement for the X-ray structures of compounds **2**, **3**, **4**, and **5b**.

Results

Benzene. Some time ago, we discovered that a thermal reaction takes place between [Ir(COD)(PMe$_3$)$_3$]Cl, **1**, and benzene to yield *mer*-(Me$_3$P)$_3$Ir(H)(Ph)(Cl), **2** (eq 1).[58]



(1)

While we are uncertain as to the exact mechanism of the reaction, it is clear that [Ir(COD)(PMe$_3$)$_3$]Cl is acting as a convenient source of Ir(PMe$_3$)$_3$Cl for the oxidative addition of a C–H bond. In our initial paper, we reported that temperatures of around 150 °C were required for the reaction depicted in eq 1 to take place. In fact, milder conditions of T = 80–100 °C are sufficient for this transformation. Although Ir(cyclooctene)(PMe$_3$)$_3$Cl[62] is a more reactive source of Ir(PMe$_3$)$_3$Cl, we find that [Ir(COD)(PMe$_3$)$_3$]Cl is a more robust compound and can be synthesized in higher yields.

The NMR spectral data for *mer*-(Me$_3$P)$_3$Ir(H)(Ph)(Cl) is consistent with an octahedral arrangement of ligands about the iridium with the PMe$_3$ groups placed in a meridional grouping: a virtual triplet at δ 1.23 ppm for the mutually trans phosphorus methyls and a doublet at δ 1.58 ppm for the cis phosphorus methyls. The resonance for the hydride occurs at δ −23.5 ppm and is a quartet indicating the hydride is cis to all three PMe$_3$ ligands. The ^{13}C and ^{31}P spectra are also consistent with this assignment. The NMR spectral data for the phenyl ligand are worth comment. In the ^{1}H NMR spectrum, while there is some

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[61] Sheldrick, G. M. *SHELXTL*-Plus, Siemens Corp., Madison WI, 1990.

[62] Herskovitz, T. *Inorg. Synth.* **1982**, *21*, 99–102.

Table I. Structure Determination Summary and Crystallographic Data for Complexes 2, 3, 4, and 5b

	2	3	4	5b
formula	$C_{15}H_{33}Cl_1Ir_1P_3$	$C_{14}H_{32}Cl_1Ir_1N_1P_3$	$C_{13}H_{31}Cl_1Ir_1OP_3$	$C_{17}H_{33}Cl_1Ir_1P_3S_1$
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic
space gp	$P2_1/n$	*Cmca*	$P2_1/n$	$P2_12_12_1$
a, Å	9.877 (2)	13.340 (4)	9.723 (2)	11.550 (3)
b, Å	11.894 (3)	11.999(3)	11.583 (3)	13.598 (2)
c, Å	17.964 (5)	26.315(9)	17.790 (5)	14.362 (4)
β (γ)	94.29 (2)	90.00	94.68 (2)	90.00
V, Å^3	2104.5 (9)	4212 (2)	1996.7 (9)	2255.7 (9)
Z	4	8	4	4
fw	534.0	534.0	523.9	590.1
d_{calcd}, g cm^{-3}	1.685	1.684	1.743	1.737
μ, mm^{-1}	6.666	6.662	7.027	63.14
F(000)	1048	2088	1024	1160
2θ range	3.5–55°	3.5–55°	3.5–50.0°	3.5–55°
scan type	Wyckoff	Wyckoff	Wyckoff	Wyckoff
scan speed, deg min^{-1}	variable; 3.97–19.53	variable; 3–19.53	variable; 3.97–19.53	variable; 3.97–19.53
standard reflns	2 every 300 reflections	3 every 300 reflections	3 every 300 reflections	3 every 300 reflections
index ranges	$-12 < h < 0, 0 < k < 15, -23 < l < 23$	$-3 < h < 14, 0 < k < 15, -28 < l < 14$	$0 < h < 11, -13 < k < 13, -21 < l < 21$	$-14 < h < 0, 0 < k < 17, -18 < l < 0$
independent reflns	4791	1522	3512	2916
obsd reflns	3331 ($F > 4\sigma(F)$)	1267 ($F > 3\sigma(F)$)	3194 ($F > 3.0\sigma(F)$)	2681 ($F > 3.0\sigma(F)$)
absorpn correct	semiempirical	semiempirical	semiempirical	semiempirical
min/max transmission	0.4013/0.9882	0.6209/0.9949	0.2788/0.5956	0.5527/0.9008
soln	direct methods	direct methods	direct methods	direct methods
refinement method	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
extinction correct, χ	0.000 19(3)	0.000 050(7)	0.000 022(3)	0.000 24(2)
$F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$				
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0010F^2$	$\sigma^2(F) + 0.0008F^2$	$\sigma^2(F) + 0.0008F^2$	$\sigma^2(F) + 0.0002F^2$
no. of params. refined	186	107	176	209
R, *wR*, %	3.86, 4.39	2.19, 3.26	2.88, 3.90	270, 274
goodness of fit	0.92	0.93	1.09	1.05
largest and mean Δ/σ	0.391, 0.012	0.002, 0.000	0.004, 0.001	0.002, 0.000
data-to-parameter ratio	17.9:1	11.8:1	18.1:1	12.8:1
largest peak, hole, e Å^{-3}	1.13, –0.93	0.43, –0.39	1.15, –0.96	1.24, –0.62

overlap, it can be seen that all five protons are inequivalent giving rise to five separate signals. The inequivalence of the two sides of the phenyl ligand is even more clearly seen in the ^{13}C NMR spectrum. The carbon atom directly bonded to the iridium is observed as a doublet of triplets due to phosphorus–carbon coupling, and the other five aromatic carbon resonances are observed as five separate singlets. This suggests that there is hindered rotation about the iridium–carbon bond leading to the observed inequivalencies. An attempt was made to measure the barrier to rotation via variable-temperature NMR but, up to a temperature of 120 °C, there was no evidence for rotation, showing that the barrier is very high.

Hindered rotation about metal–phenyl bonds has been reported before for a number of metal systems with varying explanations as to the cause (electronic vs steric) of the rotation barrier.[63,64] The single-crystal X-ray structure of 2 was carried out both to confirm the proposed structure as well as to determine if there were any apparent interactions which would be responsible for the high rotation barrier. The molecular structure of 2 is depicted in Figure 1 and confirms the structure assigned by spectroscopy. A select listing of bond lengths and angles can be found in Table II. Further comment on the structural parameters of 2 will be made below in comparing the various structures reported in this paper.

Pyridine. The reaction between pyridine and [Ir(COD)(PMe$_3$)$_3$]Cl proceeds to yield a C–H addition product 3, but with a stereochemistry different from that of the benzene product 2 (eq 2). The different stereochemistry is most evident in the ^1H NMR spectrum where the hydride resonance is displayed as a doublet of triplets at δ –10.83 ppm with a large coupling to a trans phosphorus of 154 Hz and a smaller coupling to the cis phosphines of 20 Hz, clearly indicating that the hydride is in the plane

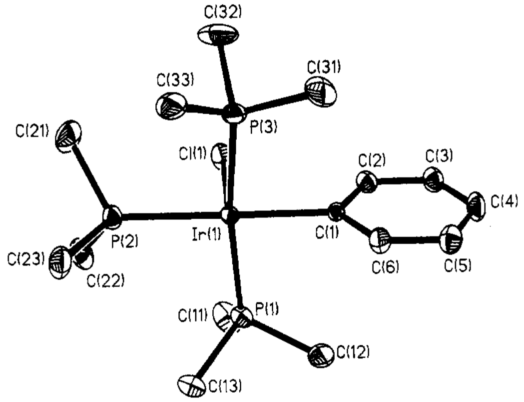
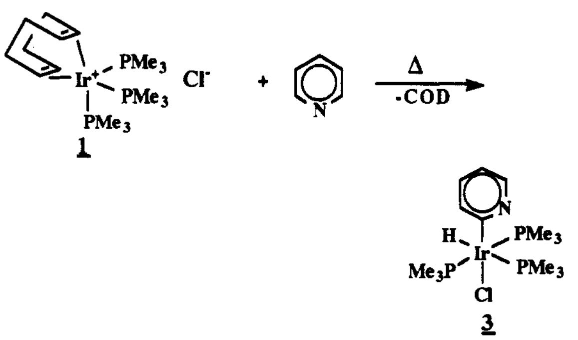


Figure 1. Molecular structure of *mer*-(Me$_3$P)$_3$Ir(H)(C$_6$H$_5$)(Cl), 2, showing the atom-numbering scheme.



(2)

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(63) Probitts, E. J.; Saunders, D. R.; Stone, M. H.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1167–1173.

(64) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376–2388.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2

	x	*y*	*z*	*U*(eq)
Ir(1)	283(1)	8151(1)	8746(1)	33(1)
P(1)	−775(2)	7385(2)	9735(1)	45(1)
P(2)	−1750(2)	8691(2)	8089(1)	53(1)
P(3)	1640(3)	9110(2)	7961(1)	52(1)
Cl(1)	79(3)	6406(2)	7962(2)	67(1)
C(1)	2119(7)	7615(6)	9326(4)	31(2)
C(2)	2715(9)	6596(7)	9166(5)	48(3)
C(3)	3926(9)	6248(8)	9545(5)	55(3)
C(4)	4572(9)	6918(8)	10 086(6)	64(3)
C(5)	3996(10)	7922(8)	10 261(6)	60(3)
C(6)	2815(9)	8272(7)	9874(5)	50(3)
C(11)	−1638(11)	6041(8)	9599(7)	88(5)
C(12)	282(11)	7099(9)	10 588(5)	74(4)
C(13)	−2045(10)	8271(7)	10 124(6)	63(4)
C(21)	−1761(12)	8813(11)	7081(5)	91(5)
C(22)	−3210(10)	7737(10)	8127(7)	84(5)
C(23)	−2464(11)	10 036(8)	8339(6)	79(4)
C(31)	3386(10)	9337(11)	8312(7)	100(6)
C(32)	1891(15)	8513(10)	7070(7)	109(6)
C(33)	1132(11)	10 551(8)	7732(6)	73(4)

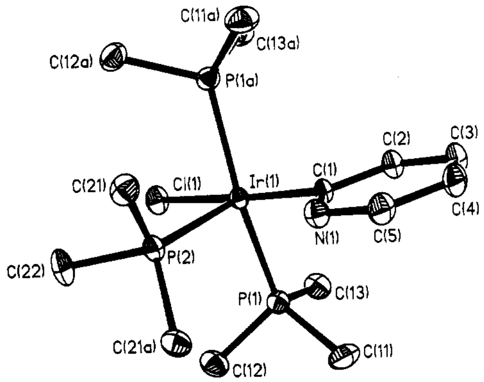


Figure 2. Molecular structure of *mer*-$(Me_3P)_3Ir(C_5H_4N)(H)(Cl)$, **3**, showing the atom-numbering scheme.

of the meridional PMe_3 ligands. Both ^1H and ^{13}C NMR spectra would seem to show that only one type of C–H bond on the pyridine ring is attacked by iridium since there is a single isomer formed and it is most likely that it is the C–H bond α to the nitrogen which has added to the iridium. Again, we have no information concerning the mechanism of this reaction, but this result seems to suggest that coordination of the pyridine nitrogen lone pair may play a role in directing the addition and also inducing an isomer different from that observed in the benzene addition to form.

Confirmation of this structure came from a single-crystal X-ray structure determination. The molecular structure of 3 is shown in Figure 2, and a select listing of bond lengths and angles for 3 can be found in Table II. In this structure, the molecule lies on a mirror plane which means that all of the atoms of the pyridyl ligand, the iridium, the chlorine, the hydride, and one PMe_3 ligand must lie on that plane. The remaining two PMe_3 ligands are related to each other via reflection through that mirror plane. The assignment of the nitrogen atom position is not unambiguous: there may be disorder of the nitrogen over the two sites ortho to the metal. However, if there is restricted rotation of the 2-pyridyl group, the solid-state structure will persist in solution and the presence of two different "rotamers" would be detected by ^1H or ^{13}C NMR spectroscopy. The nitrogen was placed at the position indicated following an examination of a fourier difference map which suggested residual electron density at around 1 Å from the other ring atoms but not at the one designated as nitrogen.

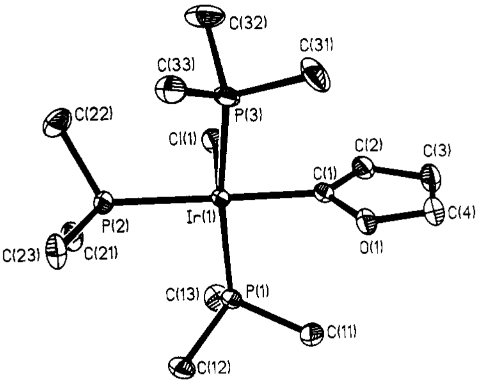
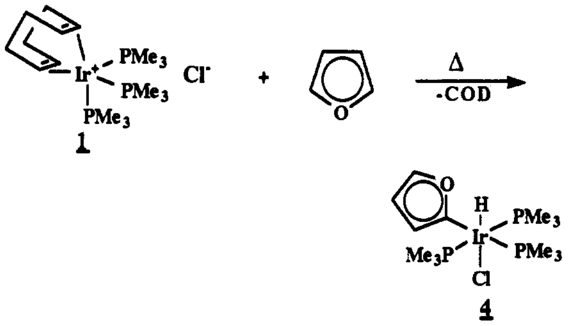


Figure 3. Molecular structure of *mer*-$(Me_3P)_3Ir(H)(C_4H_3O)(Cl)$, **4**, showing the atom-numbering scheme.

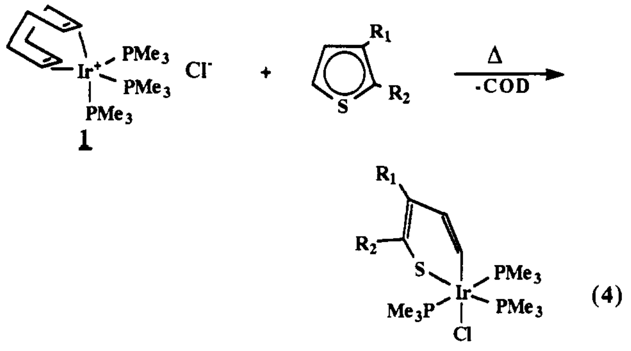
Furan. Furan adds to [Ir(COD)(PMe3)3]Cl to yield a furanyl iridium hydride complex 4 (eq 3). In this case, we observed the same product stereochemistry as that found for benzene: hydride cis to the three PMe_3 ligands and carbon trans to a PMe_3 group. Evidence for this comes from ^1H NMR spectroscopy where the hydride resonance is displayed as a quartet at −23 ppm with coupling to the three cis phosphorus atoms of around 21 Hz. The PMe_3 ligands give rise to signals due to the phosphorus methyls at 1.28 ppm (triplet) and 1.55 ppm (doublet) indicating a meridional arrangement of the phosphines. As in the case of pyridine, both ^1H and ^{13}C NMR data show the presence of one isomer suggesting that only one type of C–H bond has added, and we believe that this is the C–H bond α- to the oxygen.



(3)

Confirmation for this structure was obtained from the results of a single-crystal X-ray structural determination. The molecular structure of 4 is displayed in Figure 3, and a select listing of bond lengths and angles for 4 can be found in Table II. The placement of the oxygen atom in the furan ring was based on bond lengths around the ring.

Thiophene. In contrast to its reaction with furan, [Ir(COD)(PMe3)3]Cl reacts with thiophene and benzothiophene at 80 °C not to yield C–H addition products but to yield ring-opened products derived from C–S addition to iridium (eq 4). In the case of thiophene, the resulting product, **5a**, displays resonances in the ^1H NMR spectrum at δ 1.45 ppm (triplet) and 1.63 ppm (doublet) for the phosphorus methyls, again consistent with a meridional arrangement of the PMe_3 ligands. The absence of a hydride resonance in the regions 0 to −30 ppm in conspicuous. Multiplets for each of the ring C–H bonds were observed at δ 5.71, 5.92, 6.42, and 7.27 ppm. The presence of a carbon atom directly bound to iridium was indicated in the ^{13}C NMR spectrum where a resonance at



5a: $R_1 = R_2 = H$
5b: $R_1 + R_2 = C_4H_4$

δ 113 ppm was observed as a quartet due to coupling to three PMe_3 groups oriented cis to the carbon. Other carbon resonances for the ring system were found as singlets at δ 121.7, 121.9, and 125 ppm.

Similar spectral evidence was found for the benzothiophene adduct, **5b**, but the exact regiochemistry of the C–S cleavage was not directly determinable from this evidence. A single-crystal X-ray structural determination was carried out, and the resulting molecular structure is displayed in Figure 4, while a select listing of bond lengths and angles for **5b** can be found in Table III. The structural study confirmed that **5b** was indeed the product of ring-opening C–S bond cleavage and that the ring system has sulfur trans to a PMe_3 group in that plane of the meridional PMe_3 ligands and carbon cis to the three PMe_3 ligands. The structure also shows that ring cleavage occurred at the C–S bond away from the fused benzene ring.

Discussion

C–H Additions. The oxidative addition of aromatic C–H bonds has been observed in a number of systems, but the most common occurrences have been in rhodium and iridium chemistry.[42–55] The most detailed studies for these systems come from the laboratories of Bergman (primarily iridium)[42–50] and Jones (primarily rhodium).[51–55] The bulk of these studies have been carried out with Cp*ML systems. Both Jones and Bergman have shown the arylmetal hydride complexes are thermodynamically more stable than alkylmetal hydride complexes, and our ability to isolate the aryliridium hydride complexes in this work after reaction at temperature of around 100 °C speaks for the stability of our compounds.

We have carried out no investigations into the mechanism of the C–H addition step, so we do not know that exact sequence of steps that must take place in the reaction, such as COD loss, C–H addition, chloride attack. However, it is clear that the nature of the aromatic group and of the individual C–H bonds in the aromatic group play an important role in determining the specific course of the reaction. Benzene leads to an adduct with the phenyl ring trans to phosphorus and a hydride cis to chloride. Furan also gives a product with this same stereochemistry. On the other hand, pyridine results in the formation of a product with the opposite sense of C–H addition: H trans to PMe_3 and C trans to Cl. It is tempting to speculate that this is controlled in some fashion by coordination of the nitrogen lone pair to iridium along the addition pathway. It is known that furan is a very poor ligand through oxygen, so there is no influence of the oxygen lone pairs and furan leads to a product of the same stereochemistry as that found for benzene.

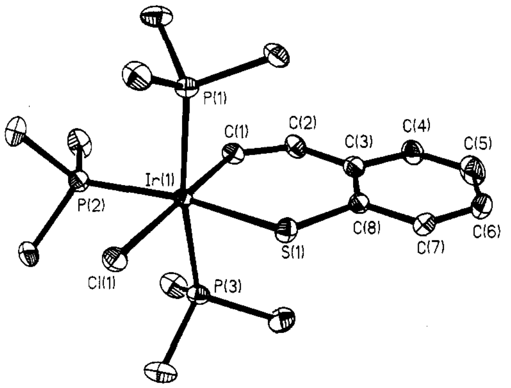


Figure 4. Molecular structure of *mer*-$(Me_3P)_3Ir(C_8H_6S)(Cl)$, **5b**, showing the atom-numbering scheme.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 3

	x	*y*	*z*	*U*(eq)
Ir(1)	0	–60(1)	1235(1)	34(1)
P(1)	1710(1)	–240(1)	1150(1)	45(1)
C(11)	2456(5)	997(5)	1031(3)	74(3)
C(12)	2373(5)	–911(5)	1666(2)	69(2)
C(13)	2037(4)	–1125(5)	617(2)	65(2)
P(2)	0	659(2)	2073(1)	42(1)
C(21)	–1051(4)	1528(4)	2266(2)	59(2)
C(22)	0	–405(6)	2576(3)	71(3)
Cl(1)	0	–2070(2)	1504(1)	60(1)
N(1)	0	2405(5)	1224(2)	48(3)
C(1)	0	1488(6)	921(3)	37(2)
C(2)	0	1669(7)	398(3)	52(3)
C(3)	0	2707(8)	186(3)	64(3)
C(4)	0	3614(7)	504(3)	64(3)
C(5)	0	3431(6)	1016(3)	56(3)

In terms of the point of attack on the aromatic ring, the nature of the aromatic group has a marked effect. In benzene, with six equivalent C–H bonds, C–H addition of any of the C–H bonds obviously leads to the same product. However, in the case of pyridine there are three different types of C–H bonds and in the case of furan there are two. Yet, in both of these latter cases we only observe one product isomer indicating a clear preference for one of the C–H bonds. Both spectroscopic and crystallographic evidence support the finding that both furan and pyridine react with a C–H bond α to the heteroatom. For both heteroaromatics, the heteroatom makes the proton on the carbon α to the heteroatom more acidic. Since acidity of the C–H proton seems to play an important role in C–H oxidative addition reactions, it is not surprising that it is the most acidic proton which adds.

Over the last several years, a number of catalytic and photocatalytic systems have been described for the insertion of alkynes and alkenes into C–H bonds of aromatic compounds.[65–68] In one such study, Yamazaki and Hong[68] investigated the high-temperature reactions between alkynes and aromatics catalyzed by $Rh_4(CO)_{12}$. It is interesting to note from their study that reactions with furan led exclusively to products derived from insertion into the C–H bond α to the oxygen. This is the same regioselectivity as we have seen for the C–H addition to iridium.

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(65) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782–6.
(66) Tanaka, M. *Chemtech* **1989**, *19*, 59.
(67) Tokunaga, Y.; Sakakura, T.; Tanaka, M. *J. Mol. Catal.* **1989**, *56*, 305–314.
(68) Yamazaki, H.; Hong, P. *J. Mol. Catal.* **1983**, *21*, 133–150.

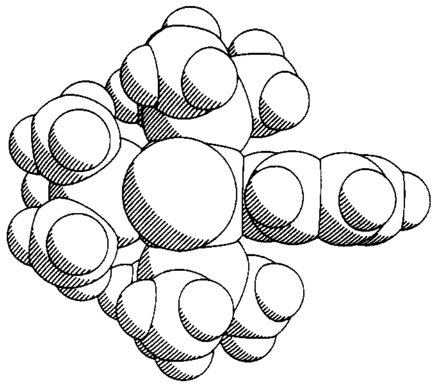

Figure 5. Space-filling plot of *mer*-(Me$_3$P)$_3$Ir(H)(C$_6$H$_5$)(Cl), **2**, looking down the Cl–Ir bond.

Hindered Rotation of Phenyl Ligand. The very high barrier to rotation for the phenyl ligand in **2** was very intriguing. While there were no significant inter- or intramolecular interactions that would explain the high barrier to rotation for the phenyl ligand in **2**, the crystal structure did provide some insight into the reason for the barrier. An examination of a space-filling plot of **2** (Figure 5) shows that the phenyl ring sits in a pocket defined by the flanking PMe$_3$ groups. Attempts to rotate the phenyl ligand (using either CPK models or simple molecular modeling programs) result in the phenyl group coming into contact with the PMe$_3$ ligands. A rotation of the phenyl ring correlated with PMe$_3$ rotation is not possible because of the meridional arrangement of the three PMe$_3$ groups: in effect, we have an "odd number of gears" situation in which moving one PMe$_3$ ligand out of the way forces the second to move in turn forcing the third to move in a way opposite to that required for a correlated rotation. While we have no experimental evidence either for or against any electronic factors, we believe that the high rotation barrier is easily explained based solely on the steric requirements of the system. Some years ago, Mawby[63] and co-workers reported on the synthesis of a number of arylruthenium complexes of the form Ru(CO)(C$_6$H$_4$X)YL$_2$L′ where L = PR$_3$, L′ = CO, PR$_3$, CNR and Y = halide with the aryl group flanked by two cis PR$_3$ groups. These workers also observed hindered rotation about the metal–aryl bond and ascribed this to electronic effects, namely π backbonding into the empty π^* orbitals of the aryl group. They came to this conclusion based on two major points: (1) the crystal structure of one compound "revealed no steric reasons for this barrier," and (2) there was a dramatic effect on the barrier to rotation upon changing the ligand trans to the aryl group. As in the case of the iridium complex reported here, a space-filling model does indeed show that the aryl ring in the ruthenium complex is rather restricted by the pocket described by the flanking PR$_3$ groups. Moreover, if the ligand trans to the aryl group is small, it may allow for the PR$_3$ ligands cis to the aryl group to rotate out of the way when the aryl group rotates. However, if, as in the iridium complex reported here, the trans ligand does not accomodate free rotation, then the whole system is fixed and the rotation barrier is large. In the Mawby work, a CO in the trans position yielded a complex with a relatively low rotation barrier, while a trans PMe$_2$Ph resulted in a complex with a very high rotation barrier. While π backbonding effects cannot be ruled out, we believed the ruthenium aryl results can be explained on steric reasons. Jones has also investigated hindered aryl ligand rotation in a series of Cp*Rh(X)(Aryl)(PMe$_3$) complexes and also reached the conclusion that the barrier to rotation in the Cp*Rh complexes is steric in nature.[64]

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 4

	x	*y*	*z*	*U*(eq)
Ir(1)	257(1)	3174(1)	3775(1)	36(1)
Cl(1)	187(2)	1310(1)	3067(1)	67(1)
P(1)	–823(1)	2440(1)	4786(1)	45(1)
P(2)	–1809(1)	3676(1)	3100(1)	49(1)
P(3)	1627(2)	4115(1)	2963(1)	54(1)
C(1)	2083(5)	2670(4)	4356(3)	44(2)
C(2)	2884(6)	1712(5)	4348(4)	60(2)
C(3)	4047(7)	1864(6)	4880(4)	76(3)
C(4)	3920(6)	2899(7)	5201(4)	72(2)
O(1)	2722(4)	3417(3)	4889(2)	59(1)
C(11)	299(6)	2268(7)	5642(3)	70(2)
C(12)	–2182(7)	3302(5)	5134(4)	65(2)
C(13)	–1602(7)	1011(5)	4681(4)	76(2)
C(21)	–3230(6)	2667(6)	3134(4)	71(2)
C(22)	–1821(8)	3780(8)	2076(3)	91(3)
C(23)	–2569(6)	5048(5)	3348(4)	73(2)
C(31)	3390(6)	4331(7)	3332(5)	99(3)
C(32)	1853(10)	3476(7)	2050(5)	104(4)
C(33)	1157(7)	5588(5)	2715(3)	66(2)

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 5b

	x	*y*	*z*	*U*(eq)
Ir(1)	2669(1)	3373(1)	7302(1)	32(1)
P(1)	2188(2)	4510(1)	6143(1)	46(1)
P(2)	4113(2)	2659(2)	6421(2)	45(1)
P(3)	2797(2)	2209(1)	8517(1)	41(1)
Cl(1)	4271(2)	4392(1)	7958(1)	49(1)
S(1)	1464(2)	4317(1)	8300(1)	45(1)
C(1)	1347(6)	2550(5)	6835 (5)	42(2)
C(2)	227 (6)	2579(6)	7023(5)	47(3)
C(3)	–441(6)	3208(6)	7649(6)	47(2)
C(4)	–1654(7)	3049(6)	7670(7)	61(3)
C(5)	–2348(8)	3619(8)	8219(7)	80(4)
C(6)	–1909(8)	4357(7)	8752(7)	71(4)
C(7)	–760(7)	4542(6)	8738(6)	53(3)
C(8)	–3(6)	3974(6)	8203(5)	41(2)
C(11)	3100(9)	5595(6)	6045(6)	72(4)
C(12)	737(8)	5063(7)	6215(6)	73(4)
C(13)	2115(8)	4002(7)	4972(5)	70(3)
C(21)	5277(7)	2091(7)	7049(6)	63(3)
C(22)	4997(7)	3503(6)	5733(6)	66(3)
C(23)	3695(8)	1711(6)	5577(6)	71(3)
C(31)	2922(9)	926(5)	8183(7)	71(4)
C(32)	3955(7)	2409(7)	9356(6)	63(3)
C(33)	1534(7)	2129(6)	9252(5)	56(3)

Comparison of Aryliridium Hydride Structures. Having a number of octahedral iridium(III) aryl hydride structures in hand gives us an opportunity to try to assess subtle electronic differences in the various aromatic ligands via their effect on the ground-state structures of the molecules. In the series of compounds described in this paper (and including some information from previous reports from our group) there is a large variation in ligand set and geometries such that a complete analogous series for bond comparison purposes is not available. Nevertheless, there are some intriguing pieces of information in the data at hand. The shortest iridium–carbon bonds seen in these compounds are those found in complex **3** [2.032(7) Å] and complex **5** [2.009(7) Å]. In these two complexes, the C is trans to chloride in contrast with the other two complexes where C is trans to PMe$_3$. It is generally recognized that chloride is a weaker trans influence ligand than PMe$_3$, so the longer bonds being those trans to PMe$_3$ may reflect the stronger trans influence of that ligand.

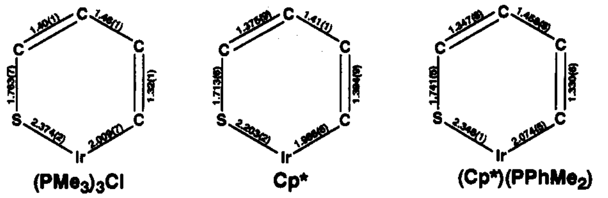

Figure 6. Comparison of bond lengths in various metallathiairidacyclohexanes.

Table VI. Selected Bond Distances and Angles for 2–4

	compd 2	compd 3	compd 4
A. bond distances (Å)			
Ir–C	2.120(7)	2.032(7)	2.065(5)
Ir–P(1)	2.314(2)	2.303(2)	2.317(1)
Ir–P(2)	2.343(2)	2.368(2)	2.328(1)
Ir–P(3)	2.316(3)	2.303(2)	2.315(2)
Ir–Cl	2.507(3)	2.514(2)	2.497(2)
B. bond angles (deg)			
P(1)–Ir(2)–P(2)	94.3(1)	97.2(1)	93.8(1)
P(1)–Ir(1)–P(3)	167.4(1)	164.5(1)	167.7(1)
P(2)–Ir(1)–P(3)	94.1(1)	97.2(1)	94.4(1)
P(1)–Ir(1)–Cl(1)	94.8(1)	86.4(1)	94.5(1)
P(2)–Ir(1)–Cl(1)	85.1(1)	95.0(1)	88.3(1)
P(3)–Ir(1)–Cl(1)	95.3(1)	86.4(1)	94.9(1)
P(1)–Ir(1)–C(1)	85.6(2)	92.7(1)	86.2(1)
P(2)–Ir(1)–C(1)	178.3(2)	92.6(2)	178.0(1)
P(3)–Ir(1)–C(1)	86.3(2)	92.7(1)	86.0(1)
Cl(1)–Ir(1)–C(1)	93.3(2)	172.4(2)	89.7(1)

Table VII. Selected Bond Distances and Angles for 5b

A. Bond Distances (Å)			
Ir(1)–P(1)	2.340(2)	C(2)–C(3)	1.461(11)
Ir(1)–P(2)	2.308(2)	C(3)–C(4)	1.418(10)
Ir(1)–P(3)	2.360(2)	C(3)–C(8)	1.404(11)
Ir(1)–Cl(1)	2.496(2)	C(4)–C(5)	1.366(13)
Ir(1)–S(1)	2.374(2)	C(5)–C(6)	1.361(14)
Ir(1)–C(1)	2.009(7)	C(6)–C(7)	1.350(13)
S(1)–C(8)	1.763(7)	C(7)–C(8)	1.398(11)
C(1)–C(2)	1.323(10)		
B. Bond Angles (deg)			
P(1)–Ir(1)–P(2)	93.4(1)	S(1)–Ir(1)–C(1)	93.3(2)
P(1)–Ir(1)–P(3)	169.8(1)	Ir(1)–S(1)–C(8)	111.8(3)
P(2)–Ir(1)–P(3)	94.4(1)	Ir(1)–C(1)–C(2)	131.2(6)
P(1)–Ir(1)–Cl(1)	94.5(1)	C(1)–C(2)–C(3)	131.3(7)
P(2)–Ir(1)–Cl(1)	84.5(1)	C(2)–C(3)–C(4)	116.5(7)
P(3)–Ir(1)–Cl(1)	92.7(1)	C(2)–C(3)–C(8)	126.3(6)
P(1)–Ir(1)–S(1)	86.2(1)	C(4)–C(3)–C(8)	117.2(7)
P(2)–Ir(1)–S(1)	169.1(1)	C(3)–C(4)–C(5)	120.4(8)
P(3)–Ir(1)–S(1)	87.3(1)	C(4)–C(5)–C(6)	121.7(8)
Cl(1)–Ir(1)–S(1)	84.6(1)	C(5)–C(6)–C(7)	119.7(9)
P(1)–Ir(1)–C(1)	87.1(2)	C(6)–C(7)–C(8)	121.4(8)
P(2)–Ir(1)–C(1)	97.5(2)	S(1)–C(8)–C(3)	126.0(5)
P(3)–Ir(1)–C(1)	85.4(2)	S(1)–C(8)–C(7)	114.3(6)
Cl(1)–Ir(1)–C(1)	177.3(2)	C(3)–C(8)–C(7)	119.7(6)

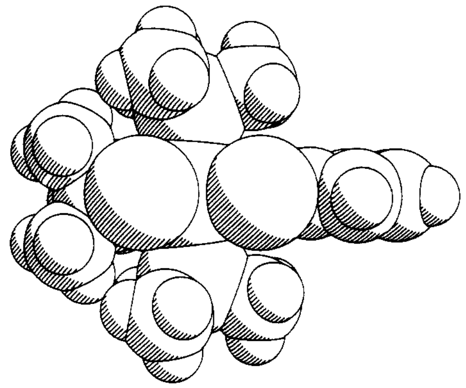

Figure 7. Space-filling plot of *mer*-$(Me_3P)_3Ir(C_8H_6S)(Cl)$, **5b**, viewed down the Cl-Ir bond.

The more interesting comparison is between compounds **2** and **4** since the both compounds have exactly the same geometry: aryl group trans to PMe_3 and hydride trans to Cl. In this case, there is a significant difference in Ir–C bond distances with the Ir–phenyl bond distance (2.120(7) Å) being larger than the Ir–furanyl distance (2.065(7) Å). There may be two factors involved in the shorter Ir–furanyl distance. The first factor may be based in sterics: the angles about carbon in the furanyl group are such that the ring is "pulled-back" away from the metal and there is less of a problem in bringing the furanyl group close the metal when compared with the phenyl ligand. This can be most easily seen by looking at the nonbonded contacts for these aryl groups and other ligands on the metal. The only real contact of importance in either of these systems is the ortho C–H···Cl interaction for each of the ring systems. In the case of the furanyl group, this ortho H···Cl distance is 2.82 Å while for the phenyl ring this same parameter has a value of 2.56 Å. Clearly, the phenyl ring hydrogens are being forced into close proximity to the chlorine which may force some lengthening of the Ir–C bond. The second factor may be an electronic one: due to inductive effects, it would be expected that the carbon in the furanyl ring is more electronegative than that in the phenyl ring resulting in a stronger Ir–C bond for the furanyl compound. A more electronegative carbon on the iridium would also be expected to result in a stronger Ir–Cl interaction based solely on inductive effects, and this is what is observed: for the complex **2**, the Ir–Cl distance is 2.507(3) Å, while for complex **3** the Ir–Cl distance is 2.497(2) Å. These differences are not large, and they are in the same direction as would be expected based on the steric arguments described above, so it is impossible to separate steric from electronic effects in this case.

Thiophene. We have isolated no thienyliridium hydride complexes from the reaction between $[Ir(COD)(PMe_3)_3]Cl$ and thiophene but, rather, the thiairidametallacycle pictured in Figure 4. To our knowledge, this is the third occurrence of this ring-opening reaction in a discrete molecular system: the other two reports were by Angelici[13] and Jones.[32] Both of the previous reports involved C–S cleavage of thiophene and substituted thiophenes on Cp* rhodium and iridium complexes. Jones found that when $Cp^*Rh(PMe_3)(Ph)(H)$ was heated along with thiophene, the C–S cleavage product was formed in high yield and a crystal structure was obtained on the 2,4-dimethyl analog. Angelici's group found that a two-electron reduction of $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ (Me_2T = dimethylthiophene) resulted in the formation of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ which, upon treatment with alumina, then underwent insertion of the iridium into the C–S bond yielding an iridathiametallacycle. A particularly interesting feature of the Angelici complex is that the metallacycle seems best formulated as an iridathiabenzene: It is planar, and bond lengths and angles suggest a high degree of delocalization. The Jones complex, on the other hand, differs (in addition to having rhodium vs iridium) in the addition of another ligand on the metal. The Jones metallacycle is nonplanar and appears to have quite localized bonding. Addition of phosphines to the Angelici compound converts them into direct iridium analogues of the Jones complex, and they now appear to have nonplanar metallacycles with localized bonding.[10]

Complexes **5a** and **5b** reported in this study differ from the earlier reports in that they are not based on a Cp*-

Table VIII. Comparison of Chemical Shift Data for Thiairidametallacycles

	Cp*Ir(SCCC)	$(Cl)(PMe_3)_3Ir(SCCCC)$	Cp*Ir{SCCCC}(PR_3)	$(H)(PEt_3)_3Ir(SCCCC)$
^1H:				
H1	9.35	7.27	n/a	7.18
H2	7.83	6.42	5.38	6.43
H3	7.64	5.92	5.82	5.79
H4	n/a	5.71	n/a	5.70
^{13}C:				
C1	182.8	113.1	not specifically	121.1
C2	128.1	121.7	assigned: all in	122.6
C3	126.2	122.7	121–136 ppm	122.8
C4	137.2	124.9	region	122.7

C1 is carbon attached to iridium; H1 is attached to C1.

based system. Nevertheless, it is clear that a C–S oxidative addition occurs in the reaction between $[Ir(COD)(PMe_3)_3]$-Cl and thiophene to yield a metallacycle similar to those reported by Jones and Angelici. However, there are some interesting structural features of **5b** which make it unlike either one of the previously reported metallacycles. Figure 6 shows some selected structural parameters for the metallacycle core of Cp*Ir{SC(Me)=CHCH=C(Me)}, Cp*Ir(PMe_2Ph){SC(Me)=CHCH=C(Me)} and complex **5b**. Angelici has argued that the metallacycle in CP*Ir-{SC(Me)=CHCH=C(Me)} is best viewed as an iridathiabenzene: in the absence of delocalization of the structure, the iridium is only a 16e–center. Structural support for this view is taken from the equal C–C bond lengths in the ring, the rather short Ir–C bond distance, and the planarity of the C_4SIr ring. When an additional 2e–donor is added to the iridium forming Cp*Ir(PMe_2-Ph){SC(Me)=CHCH=C(Me)}, a more localized structure results with irregular C–C bonds, a long Ir–C bond, and a nonplanar ring. It is not necessary to invoke a delocalized structure for **5a** or **5b** on the basis of electronic count: the iridium in **5a** and **5b** is an 18e–center with a localized structure, and the irregular C–C bond lengths in **5b** would seem to support a localized structure. However, the Ir–C bond length is intermediate between that of Cp*Ir{SC-(Me)=CHCH=C(Me)} and that of Cp*Ir(PMe_2Ph){SC-(Me)=CHCH=C(Me)}, making a determination of the order of the Ir–C bond ambiguous. In addition, the metallacycle in **5b** is planar: the mean deviation from the plane defined by atoms Ir1, C1, C2, C3, C8, and S1 is only 0.010 Å. (The entire ring system comprised C1, C2, C3, C4, C5, C6, C7, C8, S1, and Ir1 is planar with a mean deviation of only 0.016 Å from planarity.)

A partial explanation for the planarity of the metallacycle in **5b** may come from an examination of the steric congestion about the iridium. We have already seen that sterics may be responsible for the hindered rotation about the Ir–C bond in the phenyl complex **2**, and a similar phenomenon may be holding the metallacycle in **5b** planar. Figure 7 is a space-filling representation of **5b** looking parallel to the metallacycle, and it is apparent that the pocket defined by the PMe_3 ligands leaves little room for the ring system. The sulfur atom represents a rather "soft" site for deformations, and the steric forces here may be sufficient to force the ring system to be planar even though it is not a benzenoid system.

Very recently, Bleeke et al. reported on the synthesis of a similar metallacycle,[69] HIr(SCH=CH—CH—CH)-$(PEt_3)_3$, which differs from **5a** in the replacement of PEt_3 for PMe_3 and the replacement of H for Cl (and the relative stereochemistry of the C and S termini of the metallacycle are reversed). The Bleeke complex was synthesized by the reaction between potassium thiapentadienide and ClIr-$(PEt_3)_3$. (When $ClIr(PMe_3)_3$ was used, the reaction stopped at an η^3-thiapentadienyl complex.) Although HIr(SCH=CHCH=CH)$(PEt_3)_3$ was not isolated as a pure compound, the full complement of NMR spectroscopic data was obtained. Table VIII compares both ^1H and ^{13}C NMR data for the ring systems in **5a**, Cp*Ir{SC(Me)=CHCH=C(Me)}, Cp*Ir(PMe_2Ph){SC(Me)=CHCH=C(Me)}, and HIr(SCH=CHCH=CH)$(PEt_3)_3$. It is clear that the chemical shift parameters for the iridathiabenzene complex, Cp*Ir{SC(Me)=CHCH=C(Me)}, are markedly different from those for the other metallacycles, especially with respect to the notably downfield chemical shifts of H1 (δ 9.35 ppm) and C1 (δ 182.8 ppm). As Angelici has pointed out, these parameters may be the best indicator of delocalized bonding in the ring systems especially since our work shows that a localized system can still be planar.

Conclusions. We have demonstrated that [Ir(COD)-$(PMe_3)_3]Cl$ acts as a convenient, stable source of $Ir(PMe_3)_3$-Cl for a variety of oxidative addition reactions. We have discovered that reaction with a number of aromatic and heteroaromatic compounds react via C–H oxidative addition to form aryliridium hydride complexes whose geometries are determined in part by the nature of the heterocycle. In the case of thiophene, C–H addition is not observed, but C–S addition to form a thiairidametallacycle is seen instead. We have previously reported on two examples of the reaction chemistry of *mer*-$(Me_3P)_3Ir(H)$-(Ph)Cl), **2**, with alkynes. We will report in the future on the reactions of complexes **3**–**5** since it appears that the presence of a heteroatom in these systems profoundly affects the chemistry of these complexes.

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Supplementary Material Available: Tables of experimental details for the crystal structure determinations of complexes **2**, **3**, **4**, and **5b** and tables of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **2**, **3**, **4**, and **5b** (15 pages). Ordering information is given on any current masthead page.

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[69] Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* 1992, *11*, 2740–2743.