Oxidative Addition of O–H Bonds to Iridium(I): Synthesis and Characterization of (Phenolato)- and (Carboxylato)iridium(III) Hydride Complexes

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The reactions of alcohols, phenols, and carboxylic acids with [Ir(COD)$(PMe_3)_3$]Cl are described. Primary and secondary alcohols react with [Ir(COD)$(PMe_3)_3$]Cl to form a complex mixture of hydrido- and carbonylhydridoiridium(III) compounds. The tertiary alcohol *tert*-butyl alcohol reacts with [Ir(COD)$(PMe_3)_3$]Cl to form isobutylene and the iridium(III) product resulting from oxidative addition of H_2O. Phenols react with [Ir(COD)$(PMe_3)_3$]Cl to yield octahedral iridium(III) compounds of the form *mer*-$(Me_3P)_3$Ir(OAr)(H)(Cl). One such compound (Ar = 2,4-dimethylphenyl) was crystallographically characterized and was found to belong to the orthorhombic space group *Pbcn* with a = 13.804(2) Å, b = 16.517(2) Å, c = 22.386(4) Å, V = 5104.0(15) Å^3, and Z = 2. Refinement of 226 least-squares parameters for 3404 reflections ($F > 4\sigma(F)$) led to final R = 0.0425. The Ir–O distance is 2.109(5) Å, and the Ir–O–C angle is 130.4(5)°. One molecule of dichloromethane per two molecules of iridium complex was found in the crystal lattice apparently with C–H···Cl hydrogen bonds formed between the dichloromethane and the chloride of *mer*-$(Me_3P)_3$Ir(OAr)(H)(Cl). Carboxylic acids also react with [Ir(COD)$(PMe_3)_3$]Cl to yield octahedral iridium(III) compounds with the resulting complexes of the form *mer*-$(Me_3P)_3$Ir(OC(O)R)(H)(Cl). Crystals of the (benzoato)iridium hydride complex were found to belong to the orthorhombic space group $P2_12_12_1$ with a = 10.356(3) Å, b = 11.734 Å, c = 19.561(5) Å, V = 2377(1) Å^3, and Z = 4. The Ir–O distance was found to be 2.123(7) Å. Crystals of the (salicylato)iridium hydride compound were found to crystallize in the orthorhombic space group *Pbca* with a = 12.508(5) Å, b = 13.663(3) Å, c = 27.502(6) Å, V = 4700(2) Å^3, and Z = 8. The Ir–O distance was found to be 2.131(6) Å. The structural parameters for these compounds are discussed in terms of the bonding that occurs between iridium(III) and oxygen donor ligands.

Introduction

The study of later transition elements with O-bonded ligands has received significant attention in the last several years. A driving force behind these studies is the possibility that the mismatch between the relatively hard character of the oxygen-donor ligands and the soft character of the metals will lead to new and interesting reaction chemistry. In 1988, Bryndza and Tam reviewed the literature of late-metal alkoxides and amides.[2] Since that time, further progress has been made in this field with most of the M–O–R complexes prepared by metathetical reactions. Much less is known about the chemistry of *hydrido*alkoxymetal complexes, especially the preparation of this type of compound via oxidative addition reactions of O–H to the metal. Bergman reported that the oxidative addition of alcohols to "Cp*Ir(PR_3)" proceeded differently depending on solvent with C–H addition occurring in neat alcohol[3] while O–H addition occurred in liquid xenon.[4] Otsuka and co-workers investigated the oxidative addition of the O–H bond of water to several complexes of rhodium and platinum,[5] and Milstein and co-workers have reported on the addition of water to iridium.[6] Marder and Milstein investigated the oxidative addition of unsaturated carboxylic acids to rhodium and iridium.[7] Recently, Trogler and colleagues reported on their efforts in synthesizing hydrido phenoxy complexes of nickel(II), palladium(II), and platinum(II).[8] All of this body of work points to very unusual chemistry when O-donor ligands are attached to the later transition metals.

We have been actively exploring the oxidative addition reactions of a variety of substrates with iridium(I) in the form of [Ir(COD)$(PMe_3)_3$]Cl (COD = 1,5-cyclooctadiene).[10] We have already reported that this complex will react with B–H bonds,[11] C–H bonds,[12] and N–H bonds.[13] In this paper, we will report our findings on the reactions between [Ir(COD)$(PMe_3)_3$]Cl and O–H bonds from alcohols, phenols, and carboxylic acids focusing on the synthesis and structural characterization of the phenoxyiridium hydride and (carboxylato)iridium hydride complexes which result from those reactions.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of prepurified nitrogen. All solvents were dried by the appropriate procedure and distilled under a nitrogen atmosphere prior to use. Air sensitive solids were stored and manipulated in a M. G. Braun inert-atmosphere box. Conventional glass vessels were used for all reactions, and standard Schlenk line techniques were employed. $IrCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey. [Ir(COD)$(PMe_3)_3$]Cl and [Ir(COD)$(PMe_3)_3$][BF_4] were synthesized using previously published procedures.[10]

The ^1H NMR spectra were obtained on either a Bruker WP270SY or a WP200SY instrument and referenced to TMS via a solvent resonance.

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The ^{31}P NMR spectra were obtained on a Bruker WP200SY (81 MHz) instrument and referenced either to an internal or external standard of 85% H_3PO_4. ^{13}C NMR spectra were obtained on a Bruker WP200SY (at 50 MHz), a Bruker WP270SY (at 67 MHz), or a Varian Unity 400 instrument (at 100 MHz) and referenced to a solvent resonance. In general, resonances for quaternary carbon atoms for all new complexes were not observed. FT-IR spectra were obtained on a Nicolet 5DX W/C instrument. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. GC analyses were performed on a Hewlett-Packard 5840 gas chromatograph using 30-ft stainless steel columns packed with SE-30 packing.

Synthesis of *mer*-$(Me_3P)_3Ir(OC_6H_5)(H)(Cl)$ (2a). A 10-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.485 g (0.860 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) and 0.107 g (1.14 mmol, 1.3 equiv) of phenol under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line, and 3.00 mL of mesitylene was added by syringe. The flask was then heated at 60 °C for 3 h. At completion, the mesitylene solution was filtered and the collected white solids were recrystallized from CH_2Cl_2 by addition of diethyl ether. The white solids were dried under reduced pressure to yield 0.390 g (0.709 mmol) of *mer*-$(Me_3P)_3Ir(OC_6H_5)(H)(Cl)$ (83% yield based on amount of $[Ir(COD)(PMe_3)_3]Cl$) identified on the basis of the following data:

Anal. Calcd for $C_{15}H_{33}ClP_3IrO\cdot 0.5\ CH_2Cl_2$: C, 32.40; H, 5.97. Found: C, 32.21; H, 5.69. ^1H NMR (acetone-d_6): δ −21.00 (dt, J_{P-H} = 22 Hz, 13 Hz, 1H, Ir–H), 1.49 (vt, J_{P-H} = 3.8 Hz, 18H, trans PMe_3), 1.71 (d, J_{P-H} = 10.2 Hz, cis PMe_3), 6.18–6.24 (m, 1H, phenyl), 6.64–6.67 (m, 2H, phenyl), 6.85–6.91 ppm (m, 2H, phenyl). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −49.12 (t, J_{P-P} = 21 Hz, 1P, cis PMe_3), −29.49 (d, J_{P-P} = 21 Hz, 2P, trans PMe_3).

Synthesis of *mer*-$(Me_3P)_3Ir(OC_7H_7)(H)(Cl)$ (2b). A 10.0-mL one-necked side-armed flask, equipped with a magnetic stir bar and septum, was charged with 0.200 g (0.355 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line. A 3.00-mL volume of dry mesitylene was added by syringe followed by 56 μL (0.532 mmol, 1.5 equiv) of *p*-cresol. The flask was then heated at 66 °C for 20 h. At completion, the mesitylene solution was filtered and the white solids collected were washed with diethyl ether (3 × 5 mL). The white solids were recrystallized from CH_2Cl_2/diethyl ether and dried under reduced pressure to yield 0.087 g (0.154 mmol) of *mer*-$(Me_3P)_3Ir(OC_7H_7)(H)(Cl)$ (44% yield based on amount of $[Ir(COD)(PMe_3)_3]Cl$) identified on the basis of the following data:

Anal. Calcd for $C_{16}H_{35}ClP_3IrO\cdot 0.5CH_2Cl_2$: C, 32.68; H, 5.98. Found: C, 32.45; H, 5.63. ^1H NMR ($CDCl_3$): δ −20.27 (dt, J_{P-H} = 22 Hz, Hz, 1H, Ir–H), 1.51 (vt, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.66 (d, J_{P-H} = 9.9 Hz, cis PMe_3), 2.16 (s, 3H, ring CH_3), 6.69–6.83 ppm (m, 4H, ring protons). ^{31}P NMR ($CDCl_3$): δ −50.32 (t, J_{P-P} = 20 Hz, 1P, cis PMe_3), −30.47 ppm (d, J_{P-P} = 20 Hz, 2P, trans PMe_3). ^{13}C NMR (CD_2Cl_2): δ 15.96 (vt, J_{C-P} = 18.4 Hz, 6C, trans PMe_3), 21.08 (d, J_{C-P} = 40 Hz, 3C, cis PMe_3), 20.27 (s, 1C, CH_3), 119.3 (s, 2C, meta carbons, OC_7H_7), 129.7 ppm (s, 2C, ortho carbons, OC_7H_7).

Synthesis of *mer*-$(Me_3P)_3Ir(OC_8H_9)(H)(Cl)$ (2c). A 10.0-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.200 g (0.355 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) and 0.065 g (0.532 mmol, 1.5 equiv) of 3,5-dimethylphenol under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line. A 6-mL volume of dry mesitylene was added by syringe. The flask was then heated at 60 °C for 20 h. At completion, the mesitylene solution was filtered and the white solids collected were recrystallized from CH_2Cl_2 and diethyl ether and then dried under reduced pressure to yield 0.085 g (0.147 mmol) of *mer*-$(Me_3P)_3Ir(OC_8H_9)(H)(Cl)$ (42% yield based on amount of $[Ir(COD)(PMe_3)_3]Cl$) identified on the basis of the following data:

Anal. Calcd for $C_{16}H_{35}ClP_3IrO\cdot 0.5CH_2Cl_2$: C, 33.87; H, 6.17. Found: C, 33.77; H, 6.28. ^1H NMR (CD_2Cl_2): δ −21.33 (dt, J_{P-H} = 22 Hz, 9 Hz, 1H, Ir–H), 1.47 (vt, J_{P-H} = 3.8 Hz, 18H, trans PMe_3), 1.65 (d, J_{P-H} = 10 Hz, cis PMe_3), 2.13 (s, 6H, ring CH_3's), 6.02 (s, 1H, para H, OC_8H_9), 6.32 ppm (s, 2H, ortho protons, OC_8H_9). ^{31}P NMR (CD_2Cl_2): δ −50.25 (t, J_{P-P} = 19.8 Hz, 1P, cis PMe_3), −30.29 (d, J_{P-P} = 19.8 Hz, 2P, trans PMe_3). ^{13}C NMR (acetone-d_6): δ 15.71 (vt, J_{C-P} = 18.3 Hz, 6C, trans PMe_3), 20.99 (d, J_{C-P} = 40.4 Hz, 3C, cis PMe_3), 21.71 (s, 2C, methyl groups), 115.2 (s, 1C, para carbon, OC_7H_7), 117.8 ppm (s, 2C, ortho carbons, OC_7H_7).

Reaction between Phenol and $[Ir(COD)(PMe_3)_3])[BF_4]$. An NMR tube was charged with 20 mg (0.033 mmol) of $[Ir(COD)(PMe_3)_3][BF_4]$ along with 0.5 mL of benzene-d_6 and 7 mg of phenol. The tube was sealed and heated at 70 °C for a period of 3 days. ^1H NMR analysis at the end of that time showed one extremely weak set of resonances attributable to a hydride species with the bulk of the resonances due to starting $[Ir(COD)(PMe_3)_3][BF_4]$. Under the same conditions, $[Ir(COD)(PMe_3)_3]Cl$ reacts with phenol to yield **2a** in a much shorter period of time (see above). Preparative scale reactions between phenol and $[Ir(COD)(PMe_3)_3][BF_4]$ gave the same result as the NMR tube experiment.

Reaction between Benzyl Alcohol and $[Ir(COD)(PMe_3)_3]Cl$. A 10.0-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.090 g (0.16 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line. A 3.0-mL volume of dry mesitylene and 22 μL of benzyl alcohol were added by syringe. The flask was then heated at 90 °C for 15 h. At completion, the mesitylene solution was stripped under reduced pressure to yield a yellow oil. ^1H NMR analysis of this oil revealed multiple resonances in the hydride region of the spectrum from δ −10 to −30 ppm with multiplicities indicative of both mono- and dihydride complexes.

Reaction between $[Ir(COD)(PMe_3)_3]Cl$ and *tert*-Butyl Alcohol. A 10.0-mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 0.200 g (0.355 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line. A 200.0-μL volume (6 equiv) of *tert*-butyl alcohol was added along with 3.0 mL of mesitylene by syringe. The flask was then heated at ~70 °C for 4 h. At completion, the mesitylene solution was filtered to remove some white solids and the mesitylene was removed from the filtrate under reduced pressure to yield a yellow-orange oil. The yellow oil was dissolved in CH_2Cl_2 (~0.500 mL), and diethyl ether was used to precipitate a thick dark orange oil. The oil was dried under reduced pressure and identified as *mer*-$(Me_3P)_3Ir(OH)(H)(Cl)$ by comparison of its NMR spectra with those of the material prepared from H_2O (see below). In a spearate experiment, 20 mg of $[Ir(COD)(PMe_3)_3]Cl$ was dissolved in 0.5 mL of benzene-d_6 along with 3.7 μL of *tert*-butyl alcohol in an NMR tube. The tube was sealed and heated at 80 °C for 16 h. ^1H NMR analysis at the end of the reaction time indicated a sharp singlet at δ 1.6 consistent with the presence of isobutylene. The sample was also subject to GC analysis, and the presence of a peak with the same retention time as that of an authentic sample of isobutylene confirmed the formation of isobutylene in this reaction.

Synthesis of *mer*-$(Me_3P)_3Ir(OH)(H)(Cl)$. A 10.0-mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 0.200 g (0.355 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line. A 15.0-μL volume (0.710 mmol, 2 equiv) of water was added along with 5.00 mL of mesitylene by syringe. The flask was then heated at ~90 °C for 20 h. At completion, the mesitylene solution was filtered and the solution was concentrated to a yellow oil. The yellow oil was dissolved in CH_2Cl_2 (~0.500 mL), and pentane was used to precipitate a thick brownish oil. The brown oil was dried under reduced pressure to yield 0.060 g (0.127 mmol) of *mer*-$(Me_3P)_3Ir(OH)(H)(Cl)$ (~36% yield based on amount of $[Ir(COD)(PMe_3)_3]Cl$) identified on the basis of the following data:

^1H NMR (acetone-d_6): δ −22.24 (dt, J_{P-H} = 19 Hz, 14.5 Hz, 1H, Ir–H), 1.67 (vt, J_{P-H} = 3.8 Hz, 18H, trans PMe_3), 1.73 ppm (d, J_{P-H} = 10.5 Hz, cis PMe_3). ^{31}P NMR (CD_2Cl_2): δ −41.66 (t, J_{P-P} = 25 Hz, 1P, cis PMe_3), −37.91 ppm (d, J_{P-P} = 22 Hz, 2P, trans PMe_3).

Synthesis of *mer*-$(Me_3P)_3Ir(O_2CCH_3)(H)(Cl)$ (3a). A 25.0-mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 0.500 g (0.885 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1a**) under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line, and 4.00 mL of dry mesitylene was added by syringe followed by 76.0 μL (1.24 mmol, 1.4 equiv) of acetic acid. The reaction mixture was heated at ~100 °C for 22 h. At completion, a colorless heterogeneous mixture was observed. The mesitylene was stripped off under reduced pressure to give a light-brown oil. The oil was dissolved in 0.500 mL of THF, and some solids were filtered off. A 5.00-mL volume of diethyl ether was used to recrystallize creamy-white solids. The THF/diethyl ether solution was filtered, and the solids were dried under reduced pressure to yield 0.166 g (0.322 mmol) of *mer*-$(Me_3P)_3Ir(O_2CCH_3)(H)(Cl)$ (36% yield based on amount of $[Ir(COD)(PMe_3)_3]Cl$) identified on the basis of the following data:

Anal. Calcd for $C_{11}H_{31}ClP_3IrO_2$: C, 25.58; H, 6.05. Found: C, 25.38; H, 6.02. ^1H NMR (acetone-d_6): δ −20.87 (dt, J_{P-H} = 22 Hz, 13 Hz, 1H, Ir–H), 1.53 (vt, J_{P-H} = 3.8 Hz, 18H, trans PMe_3), 1.66 (d, J_{P-H} = 10.2 Hz, cis PMe_3), 1.82 ppm (s, 3H, O_2CCH_3). ^{31}P NMR (acetone-

Table I. Crystallographic Data for Complexes **2c**, **3b**, and **4a**

	2c	**3b**	**4a**
chem formula	$C_{17.5}H_{38}Cl_2IrOP_3$	$C_{16}H_{33}ClIrO_2P_3$	$C_{16}H_{33}ClIrO_3P_3$
a, Å	13.804(2)	10.356(3)	12.508(5)
b, Å	16.517(2)	11.734(4)	13.663(3)
c, Å	22.386(4)	19.561(5)	27.502(6)
V, Å^3	5104.0(15)	2377.0(12)	4700(2)
Z	8	4	8
fw	620.5	578.0	594.0
space group	*Pbcn*	$P2_12_12_1$	*Pbca*
T, °C	25	25	25
λ, Å	0.710 73	0.710 73	0.710 73
d_{calc}, g cm^{-3}	1.615	1.615	1.679
μ, mm^{-1}	5.614	5.914	5.987
min/max transm	0.3037/0.8316	0.4911/0.8715	0.0000/0.8921
R, R_w, %	4.25, 5.32	3.36, 4.36	5.13, 5.26
goodness-of-fit	1.39	1.28	1.58

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **2c**, **3b**, and **4a**

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Compound **2c**									
Ir(1)	2131(1)	1394(1)	1040(1)	32(1)	Cl(1)	2116(2)	2297(1)	1936(1)	51(1)
P(1)	473(2)	1607(1)	956(1)	44(1)	O(1)	2243(3)	2490(3)	561(2)	41(2)
C(11)	–259(7)	1439(6)	1613(5)	70(4)	C(1)	2187(5)	2633(5)	–20(4)	40(2)
C(12)	–147(7)	1044(6)	375(4)	71(4)	C(2)	2239(6)	3452(5)	–188(4)	48(3)
C(13)	184(6)	2651(5)	779(4)	63(3)	C(3)	2180(6)	3678(5)	–802(4)	45(3)
P(2)	2022(22)	226(1)	1538(1)	45(1)	C(3A)	2244(8)	4554(6)	–957(5)	76(4)
C(21)	1954(8)	293(6)	2352(4)	87(5)	C(4)	2066(6)	3087(5)	–1239(4)	47(3)
C(22)	998(8)	–425(6)	1357(6)	94(5)	C(5)	2007(6)	2274(6)	–1069(3)	49(3)
C(23)	2990(7)	–498(5)	1444(5)	68(4)	C(5A)	1829(8)	1652(6)	–1540(4)	73(4)
P(3)	3817(2)	1431(1)	1054(1)	48(1)	C(6)	2070(5)	2050(5)	–466(3)	44(3)
C(31)	4449(6)	775(6)	528(5)	79(4)	Cl(2)	9361(2)	4141(2)	1989(1)	99(1)
C(32)	4263(7)	2407(6)	860(5)	74(4)	C(50)	10000	3550(7)	2500	93(7)
C(33)	4418(7)	1276(6)	1760(4)	74(4)					
Compound **3b**									
Ir(1)	8027(1)	3176(1)	3330(1)	37(1)	C(33)	5755(18)	2012(13)	2158(8)	90(6)
P(1)	9443(3)	3183(3)	4252(1)	46(1)	Cl(1)	6743(3)	1682(3)	3935(2)	61(1)
C(11)	9996(13)	1816(11)	4555(7)	71(5)	O(1)	6962(8)	4421(5)	3879(3)	45(2)
C(12)	8689(12)	3721(12)	5028(6)	63(4)	O(2)	8374(10)	5818(7)	3731(6)	88(4)
C(13)	10915(11)	4021(11)	4207(6)	62(4)	C(1)	6380(12)	6258(10)	4237(6)	50(4)
P(2)	9213(4)	2039(3)	2671(2)	61(1)	C(2)	5275(17)	5857(13)	4543(8)	91(6)
C(21)	8878(18)	532(11)	2733(10)	105(7)	C(3)	4430(20)	6600(16)	4828(10)	133(10)
C(22)	9114(20)	2277(17)	1772(6)	101(7)	C(4)	4757(23)	7774(16)	4826(9)	107(8)
C(23)	10968(15)	2132(15)	2772(9)	95(6)	C(5)	5783(18)	8202(14)	4525(8)	86(6)
P(3)	6314(3)	3308(3)	2569(2)	61(1)	C(6)	6615(15)	7412(11)	4223(7)	67(5)
C(31)	4822(15)	3725(17)	3029(10)	104(7)	C(7)	7295(12)	5464(9)	3894(5)	51(4)
C(32)	6446(19)	4349(13)	1892(7)	97(7)					
Compound **4a**									
Ir(1)	642(1)	2709(1)	3746(1)	39(1)	C(5)	–1247(11)	–2165(8)	3813(3)	61(4)
Cl(1)	2449(2)	2086(2)	3509(1)	58(1)	C(6)	–271(10)	–1790(8)	3716(4)	63(4)
P(1)	–17(3)	2631(2)	2958(1)	65(1)	C(7)	–109(9)	–794(7)	3743(4)	55(4)
P(2)	1234(2)	4251(2)	3682(1)	55(1)	C(11)	906(13)	2316(14)	2497(5)	156(11)
P(3)	1007(2)	2569(2)	4573(1)	52(1)	C(12)	–685(12)	3659(11)	2701(5)	143(9)
O(1)	154(5)	1215(4)	3780(2)	47(2)	C(13)	–1019(13)	1755(13)	2865(5)	157(10)
O(2)	–1504(6)	1434(5)	4075(3)	74(3)	C(21)	2231(11)	4657(9)	4125(5)	98(6)
C(1)	–759(8)	893(7)	3916(4)	50(4)	C(22)	278(10)	5207(8)	3721(5)	105(7)
C(2)	–927(8)	–167(7)	3880(3)	45(3)	C(23)	1963(10)	4534(8)	3136(4)	83(5)
O(3)	–2742(6)	–23(6)	4163(4)	99(4)	C(31)	2380(9)	2555(8)	4774(4)	75(5)
C(3)	–1917(9)	–578(8)	3998(4)	62(4)	C(32)	534(10)	1453(9)	4839(4)	84(5)
C(4)	–2086(9)	–1577(8)	3943(4)	61(4)	C(33)	378(10)	3447(9)	4971(4)	85(6)

d_6): δ –47.90 (t, J_{P-P} = 22 Hz, 1P, cis PMe_3), –30.16 ppm (d, J_{P-P} = 21 Hz, 2P, trans PMe_3). ^{13}C NMR (acetone-d_6): δ 15.74 (vt, J_{C-P} = 18 Hz, 6C, trans PMe_3), 20.65 (d, J_{C-P} = 42 Hz, 3C, cis PMe_3), 23.04 ppm (s, 1C, O_2CCH_3).

Synthesis of *mer*-$(Me_3P)_3Ir(O_2CC_6H_5)(H)(Cl)$ (3b). A 250-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 2.80 g (4.96 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) and 0.790 g (6.45 mmol, 1.3 equiv) of benzoic acid under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line, and 120 mL of dry mesitylene was added by syringe. The reaction mixture was heated at 60 °C for 23 h. At completion, a yellow heterogeneous mixture was observed. The mesitylene suspension was concentrated to ~5.00 mL under reduced pressure, and brownish-yellow solids were observed and collected by filtration. The solids were dissolved in 6.00 mL of CH_2Cl_2, and 6 mL of pentane was added to precipitate a small amount of a brown solid. The CH_2Cl_2/pentane solution was filtered into a 50.0-mL flask and stripped to give cream-colored solids which were washed with a 20.0-mL pentane/2.00-mL THF solution. The solids were dried under reduced pressure to yield 2.09 g (3.62 mmol) of *mer*-$(Me_3P)_3Ir(O_2CC_6H_5)(H)(Cl)$ (73% based on amount of $[Ir(COD)(PMe_3)_3]Cl$) identified on the basis of the following data:

Anal. Calcd for $C_{16}H_{33}ClP_3IrO_2$: C, 33.25; H, 5.75. Found: C, 33.78; H, 5.67. ^{1}H NMR (acetone-d_6): δ –20.55 (dt, J_{P-H} = 22 Hz, 13 Hz, 1H, Ir–H), 1.53 (vt, J_{P-H} = 3.7 Hz, 18H, trans PMe_3), 1.72 (d, J_{P-H} = 10.3 Hz, cis PMe_3), 7.28–7.58 (m, 3H, meta and para protons, phenyl ring), 8.00–8.06 ppm (m, 2H, ortho protons, phenyl ring). ^{31}P NMR (acetone-d_6): δ –47.45 (t, J_{P-P} = 21 Hz, 1P, cis PMe_3), –29.72 ppm (d, J_{P-P} = 21 Hz, 2P, trans PMe_3). ^{13}C NMR (CD_2Cl_2): δ 16.08 (vt, J_{C-P} = 18 Hz, 6C, trans PMe_3), 20.82 (d, J_{C-P} = 41 Hz, 3C, cis PMe_3), 128.0 (s, 2C, meta carbons, phenyl ring), 130.3 (s, 2C, ortho carbons, phenyl ring), 130.4 ppm (s, 1C, para carbon, phenyl ring). IR (CH_2Cl_2): $\nu_{as}(COO^-)$ = 1614 cm^{-1} and $\nu_s(COO^-)$ = 1345 cm^{-1}.

Synthesis of *mer*-$(Me_3P)_3Ir(O_2CC_6H_4OH)(H)(Cl)$ (4a). A 100-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.250 g (0.44 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1a**) and 0.090 g (0.66 mmol, 1.5 equiv) of salicylic acid under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line, and 20 mL of dry THF was added by syringe. The flask was then fitted with a reflux condenser attached to a N_2 inlet, and the reaction mixture was heated and stirred at 60 °C for 8 h. At the end of the reaction, the initial white suspension became a clear solution. The solvent was removed under vacuum, and the resulting white solids were washed with 10 mL of ether to remove any excess salicylic acid. The solids were then reprecipitated from 4 mL of THF by the addition of 20 mL of pentane, and the solids were collected and dried under vacuum. This procedure yielded 0.220 g (0.37 mmol, 85% yield based on $[Ir(COD)(PMe_3)_3]Cl$) of *mer*-$(Me_3P)_3Ir(O_2CC_6H_4OH)(H)(Cl)$, identified on the basis of the following information:

Anal. Calcd for $C_{16}H_{33}ClP_3IrO_3$: C, 32.40; H, 5.43. Found: C, 32.44; H, 5.49. ^1H NMR ($CDCl_3$): δ −20.82 (dt, J_{P-H} = 22 Hz, 13 Hz, 1H, Ir–H), 1.55 (vt, J_{P-H} = 3.5 Hz, 18H, trans PMe_3), 1.69 (d, J_{P-H} = 10.2 Hz, 9H, cis PMe_3), 6.76 (t, 1H, para to OH), 6.87 (d, 1H, ortho to OH), 7.28 (t, 1H, meta to OH), 7.97 (d, 1H, ortho to COOIr), 12.90 ppm (br s, 1H, OH). ^{31}P NMR ($CDCl_3$): δ −47.38 (t, J_{P-P} = 52 Hz, 1P, cis PMe_3), −30.42 ppm (d, J_{P-P} = 52 Hz, 2P, trans PMe_3). ^{13}C NMR ($CDCl_3$): δ 15.85 (vt, J_{C-P} = 19 Hz, 6C, trans PMe_3), 20.42 (dt, J_{C-P} = 42 Hz; 3 Hz, 3C, cis PMe_3), 116.46 (s), 118.06 (s), 131.59 (s), 133.01 (s) (aromatic C–H carbons; quaternary C were not observed), and 161 ppm (br s, COOIr).

Synthesis of *mer*-$(Me_3P)_3Ir(O_2CC_{10}H_6OH)(H)(Cl)$ (4b). A 100-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.140 g (0.25 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ (**1**) and 0.070 g (0.38 mmol, 1.5 equiv) of 3-hydroxy-2-naphthoic acid under N_2 in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line, and 20 mL of dry THF was added by syringe. The flask was then fitted with a reflux condenser attached to a N_2 inlet, and the reaction mixture was heated and stirred at 60 °C for 8 h. By the end of the reaction time, the initial white suspension had become a clear solution. The solvent was reduced to 2 mL, and 15 mL of ether was added to precipitate 0.120 g (0.18 mmol, 72% yield based on $[Ir(COD)(PMe_3)_3]Cl$) of *mer*-$(Me_3P)_3Ir(O_2CC_{10}H_6OH)(H)(Cl)$ (**4b**), identified on the basis of the following information:

Anal. Calcd for $C_{20}H_{35}ClP_3IrO_3$: C, 37.30; H, 5.48. Found: C, 37.34; H, 5.47. ^1H NMR ($CDCl_3$): δ −20.73 (dt, J_{P-H} = 22 Hz, 10 Hz, 1H, Ir–H), 1.61 (vt, J_{P-H} = 3.6 Hz, 18H, trans PMe_3), 1.74 (d, J_{P-H} = 10.2 Hz, 9H, cis PMe_3), 7.23 (s), 7.29 (t), 7.42 (t), 7.66 (d), 7.85 (d), 8.60 (s0 (all aromatic protons) and 10.80 ppm (s, 1H, O–H). ^{31}P NMR ($CDCl_3$): δ −47.26 (t, J_{P-P} = 52 Hz, 1P, cis PMe_3), −30.32 ppm (d, J_{P-P} = 52 Hz, 2P, trans PMe_3). ^{13}C NMR ($CDCl_3$): δ 16.06 (vt, J_{C-P} = 17.9 Hz, 6C, trans PMe_3), 20.56 (d, J_{C-P} = 41 Hz, 3C, cis PMe_3), six singlets at 115.6, 116.2, 131.4, 133.0, 148.7, and 172.8 for aromatic C–H carbons.

Reaction between $Ir(O_2CC_6H_5)(H)(PMe_3)_3(Cl)$ (2a) and Trimethylphosphine. A 10.0-mL one-necked, side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.210 g (0.363 mmol) of *mer*-$(Me_3P)_3Ir(H)(O_2CC_6H_5)(Cl)$, **2a**, under N_2 in a drybox. The flask was then connected to a double-manifold Schlenk line. A 4.0-mL volume of CH_2Cl_2 was added by syringe followed by 42.0 μL (0.399 mmol, 1.1 equiv) of trimethylphosphine. The solution was stirred magnetically at room temperature for 3.5 h. At completion, a yellowish solution was observed. The CH_2Cl_2 solution was concentrated to 0.5 mL, and 4.0 mL of diethyl ether was used to crystallize white solids. The white solids were dried under reduced pressure to yield 0.210 g (0.321 mmol) of $[(Me_3P)_4Ir(H)(O_2CC_6H_5)]Cl$ (88.4% yield based on amount of *mer*-$(Me_3P)_3Ir(H)(O_2CC_6H_5)(Cl)$, identified on the basis of the following data:

Anal. Calcd for $C_{19}H_{42}P_4IrClO_2$: C, 34.89; H, 6.47. Found: C, 34.58; H, 6.48. ^1H NMR (CD_2Cl_2): δ −10.33 (d of q, $J_{P-H_{trans}}$ = 149 Hz, $J_{P-H_{cis}}$ = 18.7 Hz, 1H, Ir–H), 1.66 (vt, J_{P-H} ≈ 3.5 Hz, 18H, trans PMe_3), 1.73 (d, J_{P-H} = 8 Hz, cis PMe_3), 1.90 (d, J_{P-H} = 10.1 Hz, cis PMe_3), 7.33–7.44 (m, 3H, meta and para protons, phenyl ring), 7.88–7.91 (m, 2H, ortho protons, phenyl ring). ^{31}P NMR (CD_2Cl_2): β −41.21 (t, J_{P-P} = 19 Hz, 2P, trans PMe_3), −47.67 (dt, J_{P-P} = 10 Hz, 20 Hz, 1P, cis PMe_3), −53.52 (dt, J_{P-P} = 10 Hz, 19 Hz, 1P, cis PMe_3). ^{13}C NMR (CD_2Cl_2): δ 18.32 (d, J_{C-P} = 29.1 Hz, 3C, PMe_3), 20.28 (t, J_{C-P} = 19.5 Hz, 6C, trans PMe_3), 23.29 (d, J_{C-P} = 42.3 Hz, 3C, PMe_3), 130.0 (s, 2C, meta carbons, phenyl ring), 131.3 (s, 2C, ortho carbons, phenyl ring), 134.7 (s, 1C, para carbon, phenyl ring).

Table III. Selected Bond Lengths (Å) and Angles (deg) for **2c**, **3b**, and **4a**

	Bond Lengths for **2c**		
Ir(1)–P(1)	2.324(2)	Ir(1)–O(1)	2.109(5)
Ir(1)–P(2)	2.234(2)	O(1)–C(1)	1.324(9)
Ir(1)–P(3)	2.327(2)	Cl(2)–C(50)	1.744(8)
Ir(1)–Cl(1)	2.499(2)		
	Bond Angles for **2c**		
P(1)–Ir(1)–P(2)	96.0(1)	P(1)–Ir(1)–O(1)	84.3(1)
P(1)–Ir(1)–P(3)	169.1(1)	P(2)–Ir(1)–O(1)	179.3(1)
P(2)–Ir(1)–P(3)	94.8(1)	P(3)–Ir(1)–O(1)	84.9(1)
P(1)–Ir(1)–Cl(1)	88.0(1)	Cl(1)–Ir(1)–O(1)	84.0(1)
P(2)–Ir(1)–Cl(1)	96.6(1)	Ir(1)–O(1)–C(1)	130.4(5)
P(3)–Ir(1)–Cl(1)	89.0(1)		
	Bond Lenghts for **3b**		
Ir(1)–P(1)	2.324(3)	Ir(1)–O(1)	2.123(7)
Ir(1)–P(2)	2.224(4)	O(1)–C(7)	1.271(12)
Ir(1)–P(3)	2.320(3)	O(2)–C(7)	1.234(15)
Ir(1)–Cl(1)	2.499(3)	C(1)–C(7)	1.489(16)
	Bond Angles for **3b**		
P(1)–Ir(1)–P(2)	95.9(1)	P(2)–Ir(1)–O(1)	173.2(2)
P(1)–Ir(1)–P(3)	168.4(1)	P(3)–Ir(1)–O(1)	83.2(2)
P(2)–Ir(1)–P(3)	95.2(1)	Cl(1)–Ir(1)–O(1)	88.1(2)
P(1)–Ir(1)–Cl(1)	88.3(1)	Ir(1)–O(1)–C(7)	122.2(7)
P(2)–Ir(1)–Cl(1)	98.5(1)	O(1)–C(7)–O(2)	124.3(11)
P(3)–Ir(1)–Cl(1)	86.8(1)	O(1)–C(7)–C(1)	116.1(10)
P(1)–Ir(1)–O(1)	86.1(2)	O(2)–C(7)–C(1)	118.8(10)
	Bond Lengths for **4a**		
Ir(1)–Cl(1)	2.502(3)	Ir(1)–O(1)	2.131(6)
Ir(1)–P(1)	2.321(3)	O(1)–C(1)	1.281(12)
Ir(1)–P(2)	2.241(3)	O(2)–C(1)	1.266(12)
Ir(1)–P(3)	2.329(3)	C(1)–C(2)	1.467(14)
	Bond Angles for **4a**		
Cl(1)–Ir(1)–P(1)	93.5(1)	P(1)–Ir(1)–O(1)	84.0(2)
Cl(1)–Ir(1)–P(2)	90.0(1)	P(2)–Ir(1)–O(1)	176.6(2)
P(1)–Ir(1)–P(2)	95.0(1)	P(3)–Ir(1)–O(1)	86.2(2)
Cl(1)–Ir(1)–P(3)	92.9(1)	Ir(1)–O(1)–C(1)	126.7(6)
P(1)–Ir(1)–P(3)	168.0(1)	O(1)–C(1)–O(2)	123.8(9)
P(2)–Ir(1)–P(3)	95.1(1)	O(1)–C(1)–C(2)	116.6(9)
Cl(1)–Ir(1)–O(1)	86.8(2)	O(2)–C(1)–C(2)	119.7(9)

X-ray Structural Determinations. The X-ray crystal structures were determined using a Siemens R3m/v automated diffractometer equipped with a graphite monochromator. Data collections were performed at room temperature using MO radiation (λ = 0.710 73 Å). In all cases, a random search routine was used to find 30 reflections which were centered and used to determine the unit cell parameters. Structure solutions and least-squares refinement were performed on a DEC Microvax II computer with SHELXTL PLUS software. Further experimental details for each structural determination can be found in Table I. For all three compounds (**2c**, **3b**, **4a**), a listing of atomic positional parameters can be found in Table II, while a selected listing of bond lengths and angles can be found in Table III.

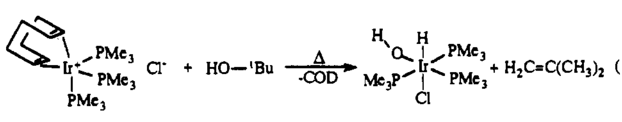
Compound 2c. Crystals suitable for diffraction were grown by allowing a layer of diethyl ether to diffuse into a solution of **2c** in dichloromethane. A clear, rectangular prism of **2c** with approximate dimensions 0.3 × 0.5 × 0.8 mm was chosen for data collection. Unit cell parameters indicated that the structure belonged to an orthorhombic space group, and data collection was carried out accordingly. An empirical absorption correction was carried out based on a series of ψ scans. Systematic absences were consistent for the space group *Pbcn*, and the structure was successfully solved and refined in that space group. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and were not refined.

Compound 3b. Crystals suitable for diffraction were grown by allowing a layer of diethyl ether to diffuse into a solution of **3** in dichloromethane. A clear, irregular crystalline fragment of **3b** with approximate dimensions 0.3 × 0.3 × 0.3 mm was cleaved from a larger mass and used for data collection. Unit cell parameters indicated that the structure belonged to an orthorhombic space group, and the data collection was carried out accordingly. An empirical absorption correction was carried out on a series of ψ scans. Systematic absences were consistent for the space group $P2_12_12_1$, and the structure was successfully solved and refined in that space group. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and were not refined.

Compound 4a. Crystals suitable for diffraction were grown by allowing a layer of pentane to diffuse into a solution of **4a** in THF. Unusual, pyramid-shaped crystals grew in this manner. A crystal with approximate dimensions at the base of 0.3 × 0.4 × 0.4 mm was chosen for this study. Unit cell parameters indicated that the structure belonged to an orthorhombic space group, and the data collection was carried out accordingly. An empirical absorption correction was carried out based on a series of ψ scans. Systematic absences were consistent for the space group *Pbca*, and the structure was successfully solved and refined in that space group. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and were not refined.

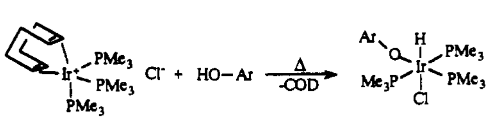
Results

Oxidative Addition of Alcohols. We began our investigation into the oxidative addition reactions of O–H bonds to [Ir(COD)(PMe$_3$)$_3$]Cl by carrying out the reaction with primary alcohols such as methanol or benzyl alcohol. Unfortunately, [Ir(COD)(PMe$_3$)$_3$]Cl requires moderate temperatures (60–80 °C) for reactions to take place, presumably because COD must be displaced in the reaction. At these temperatures, we observed a complicated variety of products from the reactions of the primary alcohols. Analysis of the product mixture by ^{1}H NMR spectroscopy revealed numerous resonances attributable to hydride species, while infrared analysis indicated the presence of several carbonyl-containing species. For example, reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and benzyl alcohol resulted in a product mixture with three major sets of resonances that could be assigned to hydrides along with several minor sets. Since it seemed reasonable that this complexity resulted from further reactions beyond the O–H addition stage (β-hydrogen elimination, decarbonylation), we next examined the reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and *tert*-butyl alcohol. The product from O–H addition of *tert*-butyl alcohol would not contain β-hydrogens, and so further reaction should be blocked. Surprisingly, reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and *tert*-butyl alcohol resulted in the formation of a hydroxyiridium hydride complex and isobutylene (eq 1). The hydroxyiridium hydride complex *mer*-(Me$_3$P)$_3$Ir(OH)(H)(Cl) could also be prepared directly by the reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and water. The formation of this product in the reaction depicted in eq 1 was *not* the result of adventitious water in the *tert*-butyl alcohol since the isobutylene formed in the reaction was trapped and identified on the basis of NMR and GC data. We are continuing to study this reaction and will report on its details in due course.



(1)

Oxidative Addition of Phenols. Since alcohols did not produce clean O–H addition products, we turned our attention to the addition reactions of phenols with the belief that these additions would proceed without complicating side reactions. Indeed, this is the case and reaction of phenol with [Ir(COD)(PMe$_3$)$_3$]Cl proceeds cleanly to give a good yield of the expected product from O–H oxidative addition, *mer*-(Me$_3$P)$_3$Ir(OPh)(H)(Cl), **2a** (eq 2). Other phenolic compounds such as *p*-cresol and 3,5-dimethylphenol also reacted cleanly with [Ir(COD)(PMe$_3$)$_3$]Cl to yield phenoxyiridium hydride complexes, but yields were not optimized.



(2)

2a: Ar = phenyl
2b: Ar = *p*-cresyl
2c: Ar = 3,5-dimethylphenyl

The characterization of the octahedral phenoxyiridium(III) hydride complexes was fairly straightforward using NMR spectroscopy. For example, for the phenol addition product, that the PMe$_3$ ligands occupy a meridional arrangement about the iridium can clearly be seen in the ^{1}H NMR spectrum where a doublet appears at δ 1.71 ppm and a virtual triplet appears at δ 1.49 ppm arising from the phosphorus methyl hydrogens. Corroborating data were found for this geometry assignment in the ^{31}P NMR spectrum. Furthermore, the presence of the aromatic group could be determined from the resonances from δ 6.18–6.91 ppm in the ^{1}H NMR spectrum. Finally, the presence of a hydride ligand on the iridium could be determined from the appearance of a hydride resonance at δ −21.00 ppm. That this resonance appears as an overlapping doublet of triplets is evidence that the hydride is cis to all three PMe$_3$ groups.

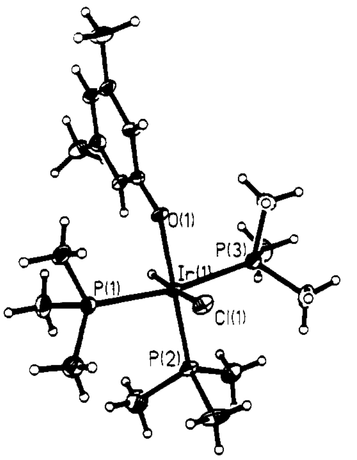


Figure 1. Molecular structure of **2c** showing thermal ellipsoids and the labeling scheme.

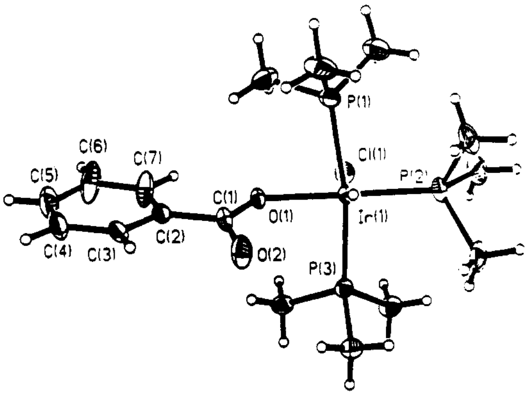
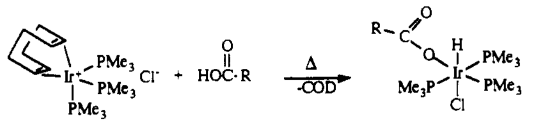


Figure 2. Molecular structure of **3b** showing thermal ellipsoids and the labeling scheme.

Final confirmation of the structure of the phenoxyiridium hydride complexes came from single-crystal X-ray diffraction. In this case, the most suitable crystals were obtained for the 3,5-dimethylphenoxy complex, **2c**. Compound **2c** shows a distorted octahedral geometry with the three PMe$_3$ ligands occupying meridional positions with the 3,5-dimethylphenoxy group occupying a site in the same place. This leaves the H and Cl ligands trans to each other (Figure 1). The geometry is somewhat disorted from an idealized octahedron, but the distortions are not particularly severe. The largest deviation is for the P(1)–Ir(1)–P(3) angle of 169.1(1) due to the PMe$_3$ groups tilting toward the hydride. The Ir–O distance of 2.109(5) Å is experimentally the same as those found in other crystallographically characterized Ir–O compounds with similar trans ligands.[6] The relatively short Ir–P bond distance for the PMe$_3$ trans to the 3,5-dimethylphenol group (2.234(2) Å) compared to those for the mutually trans PMe$_3$ ligands (2.324(2) and 2.327(2) Å) shows that 3,5-dimethylphenol is a relatively weak trans influence ligand and is weaker than PMe$_3$. The hydride in this compound was located but not refined. The Ir–Cl bond length of 2.499(2) Å is quite long, presumably due to the strong trans influence of the hydride. The Ir–O–C(1) bond is nonlinear with an angle of 130.4(5)°. The aryl ring is on the same side of iridium as the hydride ligand. While an alternative conformation with the C_6 ring on the same side as the chloride is possible, it appears that this conformation is unfavorable because of steric interactions between chloride and the hydrogens of the aryl ring.

Compound **2c** crystallizes with 0.5 equiv of dichloromethane per molecule of **2c**. The position of the CH_2Cl_2 in the crystal lattice is such that the idealized positions for the hydrogen atoms point directly at a chlorine atom in **2c**. This may suggest that there is C–H···Cl hydrogen bonding occurring in this instance. C, H analysis and ^{1}H NMR spectra of analytical samples of **2a** and **2b** also indicated the presence of 0.5 mol of CH_2Cl_2/mol of iridium complex.

Oxidative Addition of Carboxylic Acids. The O–H bond of carboxylic acids will also add cleanly to $[Ir(COD)(PMe_3)_3]Cl$ to yield (carboxylato)iridium hydride complexes (eq 3). These



(3)

3a: R = methyl
3b: R = phenyl

(carboxylato)iridium hydride complexes could also be characterized unambiguously using NMR spectroscopy. The structures of the (carboxylato)iridium hydride complexes and the phenoxyiridium hydride complexes are similar and so are their spectra. In the case of the benzoic acid addition product, **3a**, for example, a meridional arrangement of the PMe_3 ligands can be deduced from the presence of a doublet at δ 1.72 ppm and a virtual triplet at δ 1.53 ppm in the ^{1}H NMR spectrum for the phosphorus methyls. In the aromatic region, a complex multiplet for the benzoate protons is found at δ 7.28–7.58 ppm. Finally, a resonance at δ −20.55 ppm which appears as two overlapping triplets indicates that the hydride is cis to all three PMe_3 ligands. ^{31}P and ^{13}C NMR spectra are also consistent with this structure.

Definitive structural information for **3b** was obtained from a single-crystal X-ray diffraction study, and the resulting structure can be seen in Figure 2. The solid-state structure of **3b** confirmed the assignment made using spectroscopic data: an octahedral arrangement of ligands about the iridium with the three PMe_3 groups in a meridional arrangement and the benzoate group coordinated unidentate to iridium and trans to PMe_3. The Ir–O(1) bond length of 2.123(7) Å is comparable to the Ir–O(1) distance of 2.109(5) Å found for the 3,5-dimethylphenol complex, **2c**. The relatively short Ir–P distance for the PMe_3 trans to the benzoate (2.224(4) Å) compared to those for the mutually trans PMe_3 ligands (2.324(3) and 2.320(3) Å) shows that benzoate (like 3,5-dimethylphenol) is a relatively weak trans influence ligand and is weaker than PMe_3. The Ir–Cl bond distance of 2.499(3) Å is essentially identical to that found for the 3,5-dimethylphenol complex, **2c** (2.499(2) Å). The coordinated oxygen–carbon bond [O(1)–C(7) = 1.271(12) Å] is longer than the uncoordinated oxygen–carbon bond [O(2)–C(7) = 1.234(15) Å] but not significantly so. The infrared spectrum for **3b** contains bands for the carboxylate C=O stretch at 1614 and 1424 cm^{-1} (ν_s and ν_{as}).

Oxidative Addition of Salicylic Acid. Reaction between $[Ir(COD)(PMe_3)_3]Cl$ and salicylic acid was then investigated since salicylic acid contains both a carboxylate group and a phenolic group. Reaction between $[Ir(COD)(PMe_3)_3]Cl$ and salicylic acid proceeded cleanly in THF at 60 °C to yield **4a**, a complex resulting from oxidative addition of the carboxylic acid O–H bond, in 85%

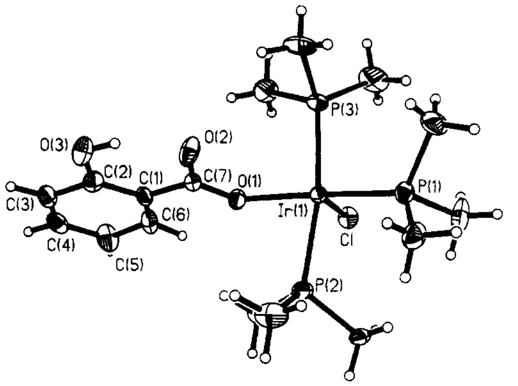
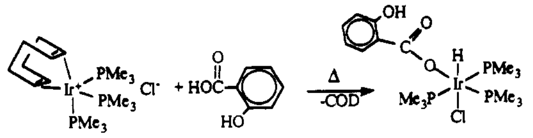


Figure 3. Molecular structure of **4a** showing thermal ellipsoids and the labeling scheme.

yield (eq 4). A similar complex resulted from addition of 2-hydroxynaphthoic acid.



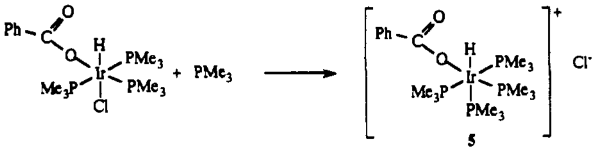
(4)

4a

Complexes **4a,b** were completely characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. In the case of the salicylic acid adduct, **4a**, the ^{1}H NMR spectrum displays a virtual triplet at δ 1.55 ppm and a doublet at 1.69 ppm indicative of the meridional arrangement of PMe_3 ligands that we have seen for all of the complexes formed thus far. In the aromatic region of the ^{1}H NMR spectrum for **4a**, there are four distinct resonances at δ 6.76 (triplet), 6.87 (doublet), 7.28 (triplet), and 7.97 ppm (doublet) which were assigned to the aromatic ring protons. The proton attached to the hydroxy group gives rise to a broad singlet resonance at δ 12.90 ppm. Finally, the hydride on iridium gives rise to a peak at −20.83 ppm as a set of overlapping triplets which shows the hydride to be cis to all three phosphines. In all, this structure would appear to be identical to that of the benzoate complex.

Indeed the single-crystal X-ray structure of **4a** is quite similar to that of the benzoic acid adduct, **3b** (Figure 3): an octahedral arrangement of ligands about the iridium with the three PMe_3 groups in a meridional arrangement and the salicylate group coordinated unidentate to iridium and trans to PMe_3. The Ir–O(1) bond length of 2.131(6) Å is comparable to the other two Ir–O distances reported in this paper. The relatively short Ir–P distance for the PMe_3 trans to the salicylate group (2.241(3) Å) compared to those for the mutually trans PMe_3 ligands (2.321(3) and 2.329(3) Å) shows that salicylate is not a strong trans influence ligand. The Ir–Cl bond distance of 2.502(3) Å is essentially identical to that found for the other two compounds. The coordinated oxygen–carbon bond [O(1)–C(1) = 1.281(12) Å] is longer than the uncoordinated oxygen–carbon bond [O(2)–C(7) = 1.266(12) Å] but not significantly so.

Reactions. While a detailed discussion of the reaction chemistry of these O–Ir–H complexes will be the focus of a future paper, some preliminary results on reactions of these compounds bear mentioning here. Reaction between **2a** and nucleophilies such as PMe_3 did not produce any isolable products, but NMR evidence suggested that heterolytic cleavage of the Ir–OPh bond takes place readily. Reaction between **3b** and PMe_3 proceeded quite cleanly to yield an ionic product, **5**, derived not from benzoate dissociation but from chloride dissociation (eq 5). Support for



(5)

this structure comes from ^1H, ^{13}C, and ^{31}P NMR spectroscopy and well as from infrared data, where the symmetric and asymmetric carboxylates stretches occur at 1640 and 1329 cm^{-1}, respectively.

Discussion

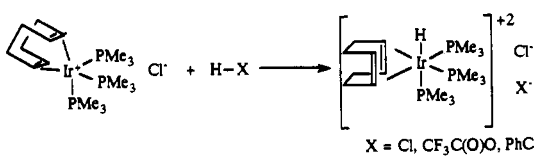
Syntheses. Metal alkoxide complexes have long been the subject of study in numerous research groups. Initially, the bulk of the work on metal alkoxides centered on the complexes of the early transition metals. Recently, interest has developed in the chemistry of the later transition metal alkoxides. Bryndza has developed the chemistry of Pt alkoxides and has carried out mechanistic studies on some of the fundamental reactions of these complexes.[2] Atwood has investigated some chemistry of a series of iridium alkoxide compounds and found some interesting carbonylation reactions which may involve dissociated alkoxide as an intermediate. He also showed that iridium alkoxide compounds can be induced to take part in carbon–oxygen bond-forming reactions.[14]

The bulk of the previous chemistry of metal alkoxide complexes has typically involved preparation of these compounds via metathetical reactions. Very little is known about the formation of alkoxide complexes, especially alkoxy *hydride* complexes, via the oxidative addition reactions of O–H bonds to transition metals. Bergman initially reported the synthesis of Cp*Ir(PPh$_3$)(H)(OCH$_2$CH$_3$) via ethoxide attack on Cp*Ir(PPh$_3$)(H)(Cl).[3] The initial efforts to determine if the O–H bond would add to the intermediate formed by photolysis of Cp*Ir(PMe$_3$)H$_2$ yielded only the products resulting from C–H bond addition.[4a] However, a more recent report showed that the same reaction carried out in liquid xenon yielded the ethoxyiridium hydride complex, presumably from the oxidative addition of the O–H bond.[4b] The addition of an O–H bond from water to form hydroxy hydride complexes has been reported for iridium by Milstein et al.[6] and for platinum by Otsuka et al.[5] Recently, Trogler has reported on the chemistry of hydrido phenoxo complexes of Ni, Pd, and Pt, which, in some cases, were synthesized via oxidative addition reactions.[8] Braga et al. also discussed the oxidative addition of phenols to Pd.[9] In work most closely related to carboxylic acids, Marder and Chan et al. showed that rhodium could act as a catalyst for the transformation of α,ω-alkynoic acids to alkylidene lactones, and they demonstrated oxidative addition of the carboxylic acid end to an iridium model.[7]

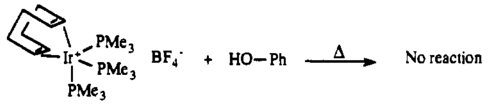
Our results indicate that the oxidative addition of O–H bonds from a variety of substrates (alcohols, phenols, carboxylic acids) to iridium(I) is a general reaction when using [Ir(COD)(PMe$_3$)$_3$]Cl as the source of iridium(I). [Ir(COD)(PMe$_3$)$_3$]Cl is a stable, convenient source of iridium(I): it is air stable and thermally stable and is made in very high yield from [Ir(COD)Cl]$_2$.[10] In order to induce reactions, however, moderate temperatures are required and the actual product observed from ROH additions depends on the further reactions available to the system at the reaction conditions employed. Thus far, only phenols and carboxylic acids lead to stable products based on simple oxidative addition. In the case of aliphatic alcohols with hydrogens on carbon β to oxygen, while oxidative addition to form an alkoxyiridium intermediate probably occurs, further reaction via β-hydride elimination results in the formation of a variety of hydridoiridium species with evidence that some of those complexes contain carbon monoxide. The possibilities for reactions beyond the O–H addition are all consistent with results found by other groups for late metal alkoxide systems.[2-15]

The most unusual finding encountered when dealing with the reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and alcohols came from the reaction with *tert*-butyl alcohol depicted in eq 1. It was presumed that the product of the O–H addition would be stable because of the absence of β-hydrogens, but a different decomposition pathway was traversed. We are still investigating the mechanism for this dehydration reaction and will report on it in due course.

In terms of reactions that led to stable R–O–Ir–H complexes, only those between phenols and carboxylic acids were successful. In all cases, the oxidative addition resulted in iridium complexes with the same general geometry: a meridional arrangements of PMe$_3$ ligands, oxygen trans to the center PMe$_3$, and H and Cl trans to each other. For these more acidic O–H materials, it may well be that the first step in the oxidation addition reaction is protonation of the iridium. Support for this comes from the isolation of the protonated dication from the reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and strong acids (eq 6).[16] Under the reaction conditions, then, the carboxylate of phenoxide as well as the chloride will then undergo a nucleophilic attack upon the iridium displacing the COD and resulting in the final complex. Relevant to this postulate is the fact that, under the same reaction conditions, there is no reaction between [Ir(COD)(PMe$_3$)$_3$][BF$_4$] and phenol underscoring the importance of nucleophilic attack by the chloride ion in driving the reaction to completion (eq 7).



(6)



(7)

Also, since acidity of the O–H proton appears to play a key role in the oxidative addition reaction, it is no surprise that salicylic acid reacts via addition of the carboxylic acid O–H bond rather than the phenolic O–H bond.

Solid-State Structures. There are several interesting features of the solid-state structures of **2c**, **3b**, and **4a** which bear mentioning. These are all octahedral iridium(III) complexes with the same overall geometry. In all three cases, the Ir–P bond distances are the same from compound to compound within experimental error. The Ir–P distance for the PMe$_3$ ligand trans to O would be the one most affected by any changes caused by differences between phenoxide and carboxylate, but these are the same throughout the series. The same is true for the Ir–Cl bond distances: within experimental error they are the same for **2c**, **3b**, and **4a**.

In the case of the carboxylate ligands, the geometry of the carboxylate group is fairly regular. The angles about carbon are all approximately 120°. The two carbon–oxygen bond distances of the carboxylate group are not statistically different. This

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(14) (a) Rees, W. M.; Atwood, J. D. *Organometallics* **1985**, *4*, 402. (b) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179. (c) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390. (d) Bernard, K. A.; Atwood, J. D. *Organometallics* **1987**, *6*, 1133. (e) Bernard, K. A.; Atwood, J. D. *Organometallics* **1988**, *7*, 235. (f) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795. (g) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939.

(15) See, in addition to ref 2: (a) Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101.

(16) Roy, C. P.; Frazier, J. F.; Merola, J. S. Manuscript in preparation.

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suggests that the interaction between iridium and the carboxylate is substantially an electrostatic one with the delocalized form of the carboxylate being largely maintained.

While there have been a number of structurally characterized alkoxo and phenoxo compounds of the later transition metals, most of them have involved metals in their lower oxidation states such as Rh(I), Pd(II), or Pt(II). The most directly comparable complexes in the literature are those reported by Milstein et al. which resulted from addition of water or methanol to $[Ir(PMe_3)_4][PB_6]$.[6] The Ir–P distances for the phosphines cis to oxygen are 2.337(1) Å for $[(Me_3P)_4Ir(H)(OH)]^+$ and 2.336(3) Å for $[(Me_3P)_4Ir(H)(OMe)]^+$ compared with 2.324(2) Å found for **2c**. The longer Ir–P distances in the tetrakis-PMe_3 complexes compared with **2c** are probably the result of having a bulkier, more electron-donating ligand in place of Cl. The Ir–P distance for the phosphine trans to oxygen is also shorter in **2c** (2.234(2) Å) compared with $[(Me_3P)_4Ir(H)(OMe)]^+$ (2.274(3) Å) most likely for the same reason. However, the Ir–O distances for all three compounds are quite similar: 2.109(5) Å for **2c**, 2.119(5) Å for $[(Me_3P)_4Ir(H)(OH)]^+$, and 2.118(8) Å for $[(Me_3P)_4Ir(H)(OMe)]^+$.

Recent reports by Caulton and co-workers on the structures of some iridium(III) alkoxides have appeared in which they discuss the structural differences between the coordinatively unsaturated $IrH_2(OR)(PCy_3)_2$ complex and the coordinatively saturated $IrH_2(OR)CO(PCy_3)_2$ complex ($R = CH_2CF_3$).[16] The Ir–O bond distance in the unsaturated compound is significantly shorter (2.032(10) Å) than the Ir–O distance in the saturated compound (2.169(7) Å). They ascribed this difference to alkoxide π-donation for the unsaturated compound. Compound **2c** provides another example of a structurally characterized iridium(III) complex with an oxygen ligand. Since **2c** is a coordinatively-saturated, 18 e^- complex, it would be predicted that π-bonding from oxygen to iridium may not be significant in this case. The Ir–O distances found for **2c** as well as those previously reported for $[(Me_3P)_4Ir(H)(OMe)]^+$ and $[(Me_3P)_4Ir(H)(OH)]^+$ suggest that π-donation is not important here since the same distances are found for complexes with PMe_3 in place of chloride.

A small feature worthy of some attention is the presence of the dichloromethane in the crystal lattice of **2c**. While the incorporation of solvent molecules into crystal lattices is not an unusual occurrence, examination of the placement of the CH_2Cl_2 shows that, when placed at their calculated positions, each of the C–H bonds points toward a chloride ligand of a molecule of **2c**. The C–H···Cl C–Cl distance is 3.8 Å. While there is significant discussion in the literature concerning C–H···O bonding,[18] there are actually a few reports concerning C–H···Cl hydrogen bonding. Early evidence for C–H···Cl interactions came from a vibrational spectroscopy study of complexes of the type $(Me_4N)_2[MCl_6]$ (M = Pt, Te, Sn) where low-temperature results were explained by the formation of weak C–H···Cl bonds.[19] Recently, calculations on the C–H hydrogen bonding that takes place for C–H···X–I–X^- systems (X = Cl, Br, I) such as found in organic charge-transfer salts have been done.[20] The C–Cl distance found for the C–H···Cl interaction in **2c** comes right at the optimum distance calculated for the H_2C–H···Cl–I–Cl^- interaction and lends credence to the conclusion that a hydrogen bond exists between CH_2Cl_2 and **2c**. These C–H···Cl bonds may actually be more common than the literature would suggest and have gone unnoticed. NMR and analytical data all show that all three of the phenolate complexes synthesized for this study strongly retain CH_2Cl_2 in the ratio of 1 mol of CH_2Cl_2 to 2 mol of the iridium complex.

Conclusions

We continue to develop the chemistry of $[Ir(COD)(PMe_3)_3]Cl$ and show that reactions with O–H bonds to form iridium(III) O–Ir–H complexes are facile. While alcohols with hydrogens on carbon β to the oxygen decompose readily under the reaction conditions, phenols and carboxylic acids react smoothly to give clean products to the type *mer*-$(Me_3P)_3Ir(OR)(H)(Cl)$. The structural information provides data which sheds some light on the nature of bonding between these oxygen ligands and iridium(III). Ultimately, we hope to use this knowledge in developing the chemistry of these complexes with an eye toward uncovering catalysts capable of adding O–H bonds across unsaturates. We are currently exploring that chemistry and will report on that work in the near future.

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Supplementary Material Available: Listings of the structural determination summaries, non-hydrogen atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates for **2c**, **3b**, and **4a** (15 pages). Ordering information is given on any current masthead page.

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