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Synthesis, Structural Characterization, and Reactivity of the (η^2-Benzoato)iridium(III) Hydride Complex [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)$][$PF_6$]

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mer-$(Me_3P)_3Ir(H)(O_2CC_6H_5)(Cl)$ (**1**) reacts with $Tl[PF_6]$ to form the unusual (η^2-benzoato)iridium(III) hydride complex [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)$][$PF_6$] (**2**). Compound **2** was crystallographically characterized and found to belong to the monoclinic space group $P2_1/n$ with $a = 6.899(2)$ Å, $b = 11.783(3)$ Å, $c = 32.303(8)$ Å, $\beta = 92.89(2)°$, and $V = 2622.7(13)$ Å^3 for $Z = 4$. The Ir–O(1) and Ir–O(2) distances are 2.244(8) and 2.198(8) Å, respectively. The coordinated oxygen–carbon distances are O(1)–C(7) = 1.294(15) Å and O(2)–C(7) = 1.284(15) Å, respectively. Compound **2** reacts with dimethyl acetylenedicarboxylate (DMAD) to yield [*mer*-$(Me_3P)_3Ir\{(MeOC(O)C{=}C(H)(C(O)OMe)\}(\eta^2\text{-}O_2CC_6H_5)$][$PF_6$] (**3**). Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.129(4)$ Å, $b = 17.837(8)$ Å, $c = 16.939(4)$ Å, $\beta = 109.81(2)°$, and $V = 3732(2)$ Å^3 for $Z = 4$. The synthesis and reactivity of **2** are discussed with respect to the nature of the Ir–O linkage.

Introduction

In recent years the study of late transition metal complexes with O-bonded ligands has received significant attention. One reason for this attention is the possibility that the mismatch between the relatively hard character of oxygen-donor ligands and the soft character of late transition metals might lead to new and interesting chemistry. The literature on metal carboxylates is extensive. In 1983, Mehrotra and Bohra reviewed the literature on metal carboxylates.[1] Although further progress has since been made in this field, much less is known about the chemistry of *hydrido* carboxylato metal complexes.[2-4] Kubota and co-workers reported that carbonylation of the bidentate carboxylato complex $IrCl(PPh_3)_2(\eta^2\text{-}OCOR)H$ led to formation of hydrido carbonyl complexes $IrH(CO)(PPh_3)_2Cl(OCOR)$ where the carboxylate ligand is unidentate.[5] Chan, Marder, and co-workers reported that the monodentate carboxylate hydride complex $(Et_3P)_3Ir(H)(Cl)(OCO(CH_2)_2CCCH_3)$ exhibits Lewis acid properties.[6] More recently, Bianchini proposed that the carboxylate group acts as a counterion and then as a nucleophile along the mechanistic pathway for the catalytic addition of benzoic acid to 1-propyne.[7] All of this suggests that the increased electron affinity of O-donor ligands and the versatility of carboxylate anions lead to interesting and unusual chemistry.

We have already reported on the oxidative additions of B–H,[8] C–H,[9] and N–H[10] bonds to Ir(I) in the form of $[Ir(COD)(PMe_3)_3]Cl$ (COD = cyclooctadiene). More recently, we reported that $[Ir(COD)(PMe_3)_3]Cl$ will undergo oxidative addition reactions with the O–H bond of carboxylic acids to yield (η^1-carboxylato)iridium(III) hydride complexes.[11] In this paper, we report our findings on the synthesis and structural characterization of the (η^2-benzoato)iridium(III) hydride [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)$][$PF_6$] (**2**) and the ($\eta^2$-benzoato)iridium(III) vinyl complex [*mer*-$(Me_3P)_3Ir(MeOC(O)C{=}CHC(O)OMe)(\eta^2\text{-}O_2CC_6H_5)$][$PF_6$] (**3**) resulting from reaction of **2** with dimethyl acetylenedicarboxylate (DMAD).

Table I. Crystallographic Data for Complexes **2** and **3**

	2	3
formula	$C_{16}H_{33}F_6IrO_2P_4$	$C_{26}H_{47}F_6Ir_1O_7P_4$
a, Å	6.899(2)	13.129(4)
b, Å	11.783(3)	17.837(8)
c, Å	32.303(8)	16.939(4)
β, °	92.89(2)	109.81(2)
V, Å^3	2622.7(13)	3732(2)
Z	4	4
fw	687.5	901.7
space group	$P2_1/n$	$P2_1/n$
T, °C	25	25
λ, Å	0.710 73	0.710 73
d_{calc}, g cm^{-3}	1.741	1.605
μ, mm^{-1}	5.363	3.798
$F(000)$	1344	1800
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0001F^2$	$\sigma^2(F) + 0.0009F^2$
R, R_w, %[a]	4.71, 5.55	4.05, 4.92

[a] $R = (\sum|F_o - F_c|)/(\sum F_o)$; $R_w = \{[\sum w(|F_o - F_c|)^2]/[\sum w(F_o)^2]\}^{1/2}$.

Experimental Section

General Procedures. 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. Conventional glass vessels were used, and standard Schlenk line techniques were employed. $IrCl_3\cdot 3H_2O$ was purchased from Johnson Matthey. *mer*-$(Me_3P)_3Ir(H)(O_2CC_6H_5)(Cl)$ was prepared as described previously.[11]

The ^1H NMR spectra were obtained on either a Bruker WP270SY (270 MHz) or a WP200SY (200 MHz) instrument and referenced either to a solvent resonance or to TMS. The ^{31}P NMR spectra were obtained on a Bruker WP200SY (81 MHz) instrument and referenced to an external standard of 85% H_3PO_4. ^{13}C NMR spectra were obtained on a Bruker WP200SY (50 MHz) instrument and referenced to a solvent resonance. FT-IR spectra were obtained on a Nicolet 5DX W/C instrument. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

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Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for **2** and **3**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
				Compound **2**					
Ir(1)	8188(1)	6486(1)	1268(1)	41(1)					
P(1)	7639(5)	4714(3)	959(1)	62(1)	C(7)	6941(19)	7417(9)	574(4)	53(5)
C(11)	9345(29)	4504(13)	567(6)	138(10)	C(1)	6276(20)	7932(9)	181(4)	59(5)
C(12)	5377(22)	4545(12)	665(5)	102(7)	C(2)	7573(23)	8031(11)	−132(4)	76(6)
C(13)	7918(20)	3423(10)	1252(5)	86(7)	C(3)	6991(31)	8496(12)	−510(5)	97(8)
P(2)	6898(5)	6038(3)	1867(1)	51(1)	C(4)	5122(35)	8863(13)	−562(6)	108(9)
C(21)	6419(22)	7184(12)	2207(4)	86(6)	C(5)	3830(27)	8734(11)	−283(5)	84(7)
C(22)	8152(22)	5041(13)	2196(4)	96(7)	C(6)	4420(22)	8255(11)	101(5)	76(6)
C(23)	4509(18)	5424(11)	1776(5)	84(6)	P(4)	2922(5)	1932(3)	1848(1)	62(1)
P(3)	9489(5)	8237(2)	1470(1)	49(1)	F(1)	3106(14)	2684(8)	1443(3)	107(4)
C(31)	11214(25)	8692(13)	1108(5)	103(8)	F(2)	4928(14)	2418(9)	2024(3)	124(5)
C(32)	10838(21)	8373(11)	1964(4)	79(6)	F(3)	2738(15)	1207(7)	2259(3)	119(5)
C(33)	7806(22)	9414(11)	1463(6)	104(7)	F(4)	939(15)	1475(7)	1680(5)	146(6)
O(1)	5794(11)	7298(6)	876(3)	55(3)	F(5)	3908(17)	911(9)	1644(4)	146(6)
O(2)	8687(12)	7050(7)	633(2)	60(3)	F(6)	1836(15)	2947(8)	2049(3)	124(5)
				Compound **3**					
Ir(1)	1554(1)	7194(1)	2892(1)	41(1)	C(1A)	665(6)	6402(4)	2101(4)	46(3)
P(1)	1096(2)	6687(1)	4025(1)	56(1)	C(2A)	917(7)	5733(4)	1889(5)	57(3)
C(11)	−29(8)	7184(6)	4173(7)	84(5)	C(3A)	144(7)	5211(4)	1318(5)	57(3)
C(12)	2164(8)	6761(6)	5041(5)	82(4)	C(4A)	−14(8)	4057(5)	598(6)	79(4)
C(13)	656(7)	5722(4)	3945(5)	66(4)	C(5A)	−482(6)	6655(4)	1697(5)	50(3)
P(2)	3117(2)	6549(1)	3207(1)	54(1)	C(6A)	−2230(7)	6630(7)	1787(6)	90(5)
C(21)	3268(7)	5636(5)	3724(6)	76(4)	O(3)	−820(5)	5285(3)	1021(4)	76(3)
C(22)	3682(7)	6351(6)	2399(6)	76(4)	O(4)	658(5)	4613(3)	1156(4)	72(3)
C(23)	4145(7)	7130(5)	3942(6)	68(4)	O(5)	−802(5)	7011(3)	1053(4)	65(2)
P(3)	1776(2)	7856(1)	1748(1)	52(1)	O(6)	−1091(5)	6469(3)	2161(3)	65(2)
C(31)	1712(9)	7330(5)	821(5)	75(4)	P(4)	7878(2)	711(2)	814(2)	71(1)
C(32)	742(7)	8555(5)	1335(5)	71(4)	F(1)	8556(14)	717(10)	1672(7)	304(11)
C(33)	2996(8)	8415(5)	2017(6)	77(4)	F(2)	7008(12)	766(10)	1105(13)	331(15)
O(1)	418(4)	8096(3)	2901(3)	53(2)	F(3)	8798(11)	756(11)	550(11)	298(13)
O(2)	2122(4)	8188(3)	3669(3)	47(2)	F(4)	7364(15)	691(8)	−101(6)	300(11)
C(7)	1182(6)	8479(4)	3422(5)	48(3)	F(5)	7924(17)	1537(6)	767(9)	302(14)
C(1)	998(6)	9214(4)	3749(5)	49(3)	F(6)	7770(13)	−103(5)	801(7)	243(10)
C(2)	1795(8)	9532(5)	4414(5)	65(4)	O(1T)	4316(14)	1796(12)	7711(20)	386(21)
C(3)	1616(10)	10206(6)	4721(7)	87(5)	C(1T)	3572(22)	2029(12)	7118(19)	246(26)
C(4)	635(11)	10557(6)	4370(8)	95(6)	C(2T)	2742(20)	1462(16)	6999(14)	219(17)
C(5)	−162(10)	10260(6)	3698(8)	91(5)	C(3T)	3175(20)	884(12)	7521(17)	226(19)
C(6)	16(7)	9566(5)	3373(6)	66(4)	C(4T)	4270(15)	1093(13)	7944(14)	203(14)

[a] *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) for **2** and **3**

	Compound **2**		
Ir(1)–P(1)	2.336(3)	C(7)–C(1)	1.460(17)
Ir(1)–P(2)	2.233(3)	C(1)–C(2)	1.389(20)
Ir(1)–P(3)	2.330(3)	C(1)–C(6)	1.349(20)
Ir(1)–O(1)	2.244(8)	C(2)–C(3)	1.381(21)
Ir(1)–O(2)	2.198(8)	C(3)–C(4)	1.362(31)
Ir(1)–C(7)	2.601(12)	C(4)–C(5)	1.308(28)
O(1)–C(7)	1.294(15)	C(5)–C(6)	1.403(21)
O(2)–C(7)	1.284(15)		
	Compound **3**		
Ir(1)–P(1)	2.377(3)	C(3)–C(4)	1.373(17)
Ir(1)–P(2)	2.255(2)	C(4)–C(5)	1.365(15)
Ir(1)–P(3)	2.369(3)	C(5)–C(6)	1.405(15)
Ir(1)–O(1)	2.197(5)	C(1A)–C(2A)	1.320(11)
Ir(1)–O(2)	2.183(5)	C(1A)–C(5A)	1.498(10)
Ir(1)–C(7)	2.568(8)	C(2A)–C(3A)	1.471(11)
Ir(1)–C(1A)	2.024(7)	C(3A)–O(3)	1.200(11)
O(2)–C(7)	1.273(9)	C(3A)–O(4)	1.339(11)
O(1)–C(7)	1.285(8)	C(4A)–O(4)	1.447(10)
C(7)–C(1)	1.475(11)	C(5A)–O(5)	1.208(9)
C(1)–C(2)	1.373(10)	C(5A)–O(6)	1.339(11)
C(1)–C(6)	1.381(11)	C(6A)–O(6)	1.442(10)
C(2)–C(3)	1.362(14)		

Synthesis of [*mer*-$(Me_3P)_3Ir(\eta^2$-O2CC6H5)(H)][PF6] (2). A 10-mL one-necked side-armed flask, equipped with a magnetic stir bar and a septum, was charged with 0.400 g (0.692 mmol) of *mer*-$(Me_3P)_3Ir(H)(O_2CC_6H_5)(Cl)$ and 0.252 g (0.90 mmol, 1.3 equiv) of Tl[PF_6] under N_2 in a drybox. The flask was then connected to a double-manifold Schlenk line, and 6 mL of CH_2Cl_2 was added by syringe. The flask was then fitted with a reflux column equipped with a nitrogen inlet connected to the Schlenk line. The reaction mixture was stirred magnetically and heated to reflux. The solution gradually turned light red, and after 3 h at reflux, a pinkish-white precipitate was observed in a clear solution. The precipitate was removed by filtration, and the methylene chloride solution was stripped under reduced pressure to give pinkish-white solids which were dried under reduced pressure to yield 0.375 g (0.546 mmol) of [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)][PF_6]$ (**2**) (79% 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 $C_{16}H_{33}P_4IrF_6O_2$: C, 27.95; H, 4.84. Found: C, 28.47; H, 4.88. ^1H NMR (CD_2Cl_2): δ −27.34 (dt, J_{P-H} = 25 Hz, 16 Hz, 1H, Ir–H), 1.58 (vt, sep = 3.6 Hz, 18H, trans PMe_3), 1.79 (d, J_{P-H} = 11 Hz, cis PMe_3), 7.43–7.51 (m, 2H, meta protons, phenyl ring), 7.57–7.65 (m, 1H, para proton, phenyl ring), 7.93–7.96 (m, 2H, ortho protons, phenyl ring). ^{31}P NMR (CD_2Cl_2): δ −40.86 (t, J_{P-P} = 17 Hz, 1P, cis PMe_3), −21.11 (d, J_{P-P} = 17 Hz, 2P, trans PMe_3). ^{13}C NMR (acetone-d_6): δ 15.21 (t, J_{C-P} = 18.6 Hz, 6C, trans PMe_3), 20.06 (d, J_{C-P} = 43 Hz, 3C, cis PMe_3), 129.1 (s, 2C, meta carbons, phenyl ring), 129.4 (s, 2C, ortho carbons, phenyl ring), 134.1 (s, 1C, para carbon, phenyl ring).

Reaction between [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)][PF_6]$ (2) and Dimethyl Acetylenedicarboxylate (DMAD). A screw-capped, glass-walled pressure tube, equipped with a magnetic stir bar and a septum, was charged with 0.200 g (~0.29 mmol) of [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)][PF_6]$ (**2**) under N_2 in a drybox. A 39-μL portion (~0.32 mmol, 1.1 equiv) of DMAD was added by syringe, followed by 2 mL of acetone. The reaction mixture was heated at 70 °C for 24 h. At completion, the yellow acetone solution was stripped under reduced pressure to give light-brown solids. The solids were washed with pentane (10 mL) and dried under reduced pressure to yield 0.197 g (0.24 mmol) of [*mer*-$(Me_3P)_3Ir\{C(CO_2Me){=}C(H)(CO_2Me)\}(\eta^2\text{-}O_2CC_6H_5)][PF_6]$(**3**) (82% yield based on amount of [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)][PF_6]$) identified on the basis of the following data. Anal. Calcd for $C_{22}H_{39}P_4IrF_6O_6$: C, 31.85; H, 4.74. Found: C, 31.59; H, 4.69. ^1H NMR (acetone-d_6): δ 1.61 (vt,

Table IV. Selected Bond Angles (deg) for 2 and 3

Compound 2			
P(1)–Ir(1)–P(2)	95.5(1)	Ir(1)–O(2)–C(7)	92.9(7)
P(1)–Ir(1)–P(3)	164.3(1)	Ir(1)–C(7)–O(1)	59.6(6)
P(2)–Ir(1)–P(3)	97.6(1)	Ir(1)–C(7)–O(2)	57.6(6)
P(1)–Ir(1)–O(1)	92.4(2)	O(1)–C(7)–O(2)	117.2(10)
P(2)–Ir(1)–O(1)	106.0(2)	Ir(1)–C(7)–C(1)	178.9(10)
P(3)–Ir(1)–O(1)	92.4(2)	O(1)–C(7)–C(1)	121.5(11)
P(1)–Ir(1)–O(2)	84.3(2)	O(2)–C(7)–C(1)	121.4(11)
P(2)–Ir(1)–O(2)	165.3(2)	C(7)–C(1)–C(2)	118.8(12)
P(3)–Ir(1)–O(2)	85.2(2)	C(7)–C(1)–C(6)	122.6(13)
O(1)–Ir(1)–O(2)	59.4(3)	C(2)–C(1)–C(6)	118.4(12)
P(1)–Ir(1)–C(7)	88.2(3)	C(1)–C(2)–C(3)	120.6(15)
P(2)–Ir(1)–C(7)	135.8(3)	C(2)–C(3)–C(4)	117.7(17)
P(3)–Ir(1)–C(7)	88.5(3)	C(3)–C(4)–C(5)	123.5(17)
O(1)–Ir(1)–C(7)	29.8(4)	C(4)–C(5)–C(6)	118.6(17)
O(2)–Ir(1)–C(7)	29.5(4)	C(1)–C(6)–C(5)	120.9(14)
Ir(1)–O(1)–C(7)	90.6(7)		
Compound 3			
P(1)–Ir(1)–P(2)	94.2(1)	O(1)–C(7)–O(2)	116.9(7)
P(1)–Ir(1)–P(3)	170.1(1)	Ir(1)–C(7)–C(1)	178.2(5)
P(2)–Ir(1)–P(3)	95.4(1)	O(1)–C(7)–C(1)	122.8(7)
P(1)–Ir(1)–O(1)	85.1(2)	O(2)–C(7)–C(1)	120.2(6)
P(2)–Ir(1)–O(1)	159.7(1)	C(7)–C(1)–C(2)	119.9(7)
P(3)–Ir(1)–O(1)	85.0(2)	C(7)–C(1)–C(6)	118.5(6)
P(1)–Ir(1)–O(2)	87.2(2)	C(2)–C(1)–C(6)	121.6(8)
P(2)–Ir(1)–O(2)	100.0(1)	C(1)–C(2)–C(3)	119.7(8)
P(3)–Ir(1)–O(2)	88.7(2)	C(2)–C(3)–C(4)	119.7(9)
O(1)–Ir(1)–O(2)	59.7(2)	C(3)–C(4)–C(5)	121.7(11)
P(1)–Ir(1)–C(7)	85.8(2)	C(4)–C(5)–C(6)	119.1(10)
P(2)–Ir(1)–C(7)	129.7(2)	C(1)–C(6)–C(5)	118.2(8)
P(3)–Ir(1)–C(7)	86.1(2)	Ir(1)–C(1A)–C(2A)	132.1(5)
O(1)–Ir(1)–C(7)	30.0(2)	Ir(1)–C(1A)–C(5A)	110.8(5)
O(2)–Ir(1)–C(7)	29.7(2)	C(2A)–C(1A)–C(5A)	117.1(6)
P(1)–Ir(1)–C(1A)	91.2(2)	C(1A)–C(2A)–C(3A)	124.7(7)
P(2)–Ir(1)–C(1A)	94.3(2)	C(2A)–C(3A)–O(3)	126.9(8)
P(3)–Ir(1)–C(1A)	90.5(2)	C(2A)–C(3A)–O(4)	110.8(7)
O(1)–Ir(1)–C(1A)	106.0(2)	O(3)–C(3A)–O(4)	122.3(7)
O(2)–Ir(1)–C(1A)	165.7(2)	C(1A)–C(5A)–O(5)	124.0(8)
C(7)–Ir(1)–C(1A)	136.1(3)	C(1A)–C(5A)–O(6)	111.4(6)
Ir(1)–O(1)–C(7)	91.2(4)	O(5)–C(5A)–O(6)	124.5(7)
Ir(1)–O(2)–C(7)	92.2(4)	C(3A)–O(4)–C(4A)	116.3(7)
Ir(1)–C(7)–O(1)	58.8(4)	C(5A)–O(6)–C(6A)	115.4(7)
Ir(1)–C(7)–O(2)	58.1(4)		

sep = 4.3 Hz, 18H, trans PMe$_3$), 1.96 (d, J_{P-H} = 11 Hz, cis PMe$_3$), 3.61 (s, 3H, OCH$_3$), 3.85 (s, 3H, OCH$_3$), 5.49 (br s, 1H, vinyl proton), 7.43 –7.62 (m, 2H, meta protons, phenyl ring), 7.70–7.77 (m, 1H, para proton, phenyl ring), 8.02–8.08 (m, 2H, ortho protons, phenyl ring). ^{31}P NMR (acetone-d_6): δ –41.36 (t, J_{P-P} = 18 Hz, 1P, cis PMe$_3$), –21.71 (d, J_{P-P} = 18 Hz, 2P, trans PMe$_3$). ^{13}C NMR (acetone-d_6): δ 12.39 (t, J_{C-P} = 18.4 Hz, 6C, trans PMe$_3$), 16.05 (d, J_{C-P} = 43 Hz, 3C, cis PMe$_3$), 51.33 (s, 1C, OCH$_3$), 51.81 (s, 1C, OCH$_3$), 122.9 (br s, 1C, vinyl carbon), 129.5 (s, 2C, meta carbons, phenyl ring), 129.8 (s, 2C, ortho carbons, phenyl ring), 135.2 (s, 1C, para carbon, phenyl ring).

Reactions between [*mer*-(Me$_3$P)$_3$Ir(H)(O$_2$CC$_6$H$_5$)(H)] (1) and Alkynes. Several exploratory reactions were examined between *mer*-(Me$_3$P)$_3$Ir(H)(O$_2$CC$_6$H$_5$)(Cl) and alkynes (DMAD, (trimethylsilyl)acetylene, bis(trimethylsilyl)acetylene, and *tert*-(butylacetylene) in acetone-d_6. In all cases, there was ^{1}H NMR evidence for the formation of a vinyliridium complex. However, none of the reactions were clean, with the PMe$_3$ region of the ^{1}H NMR spectrum displaying multiple resonances, suggesting the presence of at least three species.

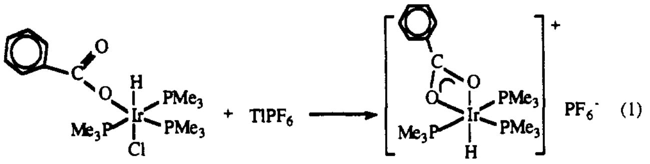
X-ray Structural Determinations. The X-ray crystal structures were determined using a Siemens R3m/v automated diffractometer equipped with a graphite monochromator. Data collections were performed at room temperature using Mo radiation (λ = 0.710 73 Å). In all cases, a random search routine was used 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.[12] Further experimental details for each structural determination can be found in Table I. For both compounds a listing of atomic positional parameters can be found in Table II, a selected listing of bond lengths can be found in Table III, and a selected listing of bond angles can be found in Table IV.

Compound 2. Crystals suitable for diffraction were grown by allowing a layer of pentane to diffuse into a solution of 2 in acetone. A clear, irregular prism of 2c with approximate dimensions 0.2 × 0.2 × 0.4 mm was chosen for data collection. Unit cell parameters indicated that the structure belonged to a monoclinic 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 $P2_1/n$, 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 3. Crystals suitable for diffraction were grown by allowing a layer of pentane to diffuse into a solution of 3 in tetrahydrofuran. A clear, irregular "chunk" of 3 with approximate dimensions 0.4 × 0.4 × 0.4 mm was cleaved from a larger mass and used for data collection. Unit cell parameters indicated that the structure belonged to a monoclinic 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 $P2_1/n$, and the structure was successfully solved and refined in that space group. A molecule of tetrahydrofuran was found to cocrystallize with 3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and were not refined.

Results

Heating a methylene chloride solution of *mer*-(Me$_3$P)$_3$Ir(H)(O$_2$CC$_6$H$_5$)(Cl) (1)[11] with 1 equiv of Tl[PF$_6$] at reflux for 4 h results in the formation of a precipitate of TlCl and a clear solution. Filtration followed by solvent removal produces [*mer*-(Me$_3$P)$_3$Ir(η^2-O$_2$CC$_6$H$_5$)(H)][PF$_6$] (2) in 79% yield (eq 1). This



1 2 (1)

octahedral hydridoiridium(III) η^2-benzoato complex was characterized as follows: Both the ^{1}H and the ^{31}P NMR spectra clearly indicate a meridional arrangement of the three PMe$_3$ ligands around the iridium. In the ^{1}H NMR spectrum, a virtual triplet at δ 1.58 ppm (J_{P-H} = 3.6 Hz) and a doublet at δ 1.79 ppm (J_{P-H} = 11 Hz) arising from the phosphorus methyl hydrogens are observed. A triplet at δ –40.86 ppm (J_{P-P} = 17 Hz) and a doublet at δ –21.11 ppm (J_{P-P} = 17 Hz) observed in the ^{31}P NMR spectrum further corroborate this geometry assignment. The appearance of a hydride resonance as an overlapping doublet of triplets at δ –27.34 ppm in the ^{1}H NMR spectrum indicates the presence of a hydride on the iridium and that the hydride is cis to all three PMe$_3$ ligands. In the aromatic region of the spectrum, a complex multiplet for the benzoate protons is found at δ 7.43–7.96 ppm. That the benzoate ligand is attached to the iridium in a bidentate (chelating) fashion was deduced from an examination of the positions of the asymmetric (υ_{as}) and symmetric (υ_s) stretching frequencies of the carboxylate group in the IR spectrum (υ_{as} = 1510 cm^{-1} and υ_s = 1428 cm^{-1}). Furthermore, the value of the separation between the asymmetric and symmetric stretch, $\Delta\upsilon$ (= 82), is consistent with η^2 coordination of the carboxylate group. Low $\Delta\upsilon$ values are generally considered indicative of chelating groups.[13,14] The ^{13}C NMR data are also consistent with this structure.

A single-crystal X-ray diffraction study provided definitive characterization of 2, and the resulting structure is shown in Figure 1. The solid-state structure of 2 confirmed the structure

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

[13] Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

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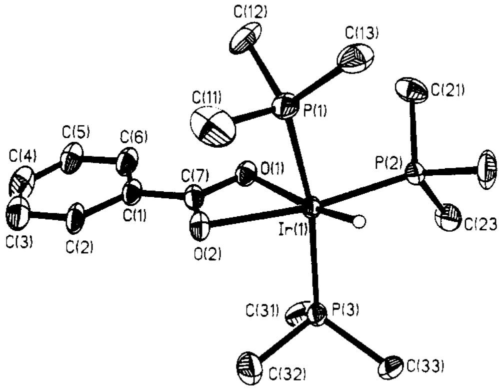
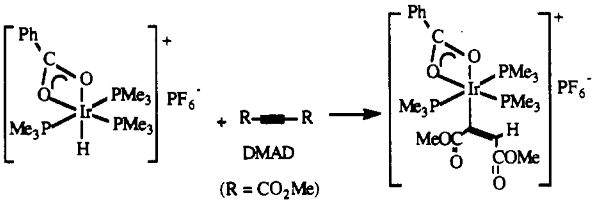


Figure 1. Molecular structure of [*mer*-$(Me_3P)_3Ir(H)(\eta^2\text{-}O_2CC_6H_5)]^+$ (cation of **2**) showing the atom-labeling scheme.

assigned by spectroscopy: an octahedral arrangement of ligands about the iridium with the three PMe_3 groups in a meridional arrangement and the benzoate group coordinated bidentately to iridium. The Ir–O(1) (the oxygen atom trans to the hydride) and Ir–O(2) (the oxygen atom trans to PMe_3) distances of 2.244(8) and 2.198(8) Å, respectively, are comparable to those found in the related complex $Ru(\eta^2\text{-}CO_2Me)H(PPh_3)_3$.[15] Two of the Ir–P distances [Ir–P(1) = 2.336(3) Å and Ir–P(3) = 2.330(3) Å] are appreciably longer than the third [Ir–P(2) = 2.233(3) Å]. The two PMe_3 groups associated with the longer Ir–P bonds are approximately trans to each other [P(1)–Ir(1)–P(3) = 164.3(1)°]. The coordinated oxygen–carbon distances of O(1)–C(7) = 1.294(15) Å and O(2)–C(7) = 1.284(15) Å are similar, which indicates an equal contribution to the η^2 coordination by both ends of the carboxylate group.

Reactions between the η^1-benzoate complex, **1**, and most alkynes, while usually providing some evidence for vinyl formation (through insertion reactions), were not clean and did not yield any clearly definable products. On the other hand, heating an acetone solution of [*mer*-$(Me_3P)_3Ir(\eta^2\text{-}O_2CC_6H_5)(H)][PF_6]$ (**2**) with dimethyl acetylenedicarboxylate (DMAD) at 70 °C for 24 h resulted in the formation of [*mer*-$(Me_3P)_3Ir\{C(CO_2Me){=}C(H)(CO_2Me)\}(\eta^2\text{-}O_2CC_6H_5)][PF_6]$ (**3**) in 82% yield after workup (eq 2). As in the case of **2**, a meridional arrangement of the three PMe_3 ligands can be deduced for **3** from the presence of a virtual triplet at δ 1.61 ppm ($J_{P\text{-}H}$ = 4.3 Hz) and a doublet at δ 1.96 ppm ($J_{P\text{-}H}$ = 11 Hz) in ^1H NMR spectrum for the phosphorus methyls. That DMAD had inserted into the Ir–H bond was deduced as follows: First, the DMAD methyl groups show up as two singlets at δ 3.61 and 3.85 ppm. Second, a vinyl resonance shows up at δ 5.49 ppm as a broad singlet, the broadness due to weak coupling to the three cis phosphorus atoms. Finally, there is no hydride signal in the spectrum. In the aromatic region of the spectrum, a complex multiplet for the benzoate protons appears at δ 7.50–8.06 ppm. ^{31}P and ^{13}C NMR spectra are also consistent with this structure.



(2)

2 **3**

Final confirmation of the structure of **3** came from single-crystal X-ray diffraction. The solid-state structure of **3** confirmed the structure assigned by spectroscopy: an octahedral arrangement of ligands about the iridium with the three PMe_3 groups in a meridional arrangement, the benzoate group coordinated bidentately to iridium, and the sixth coordination site filled by the vinyl ligand Figure 2. The Ir–O(1) and Ir–O(2) distances of 2.197(5) and 2.183(5) Å, respectively, and the Ir–C(7) distance of 2.568(8) Å (carboxylate group carbon) are significantly shorter than those found for **2**. The Ir–C(1A) (vinyl carbon) distance is 2.024(7) Å. Two of the Ir–P distances [Ir–P(1) = 2.377(3) Å and Ir–P(3) = 2.369(3) Å] are appreciably longer than the third [Ir–P(2) = 2.255(2) Å]. The two PMe_3 groups associated with the longer Ir–P bonds are approximately trans to each other [P(1)–Ir(1)–P(3) = 170.1(1)°]. The coordinated oxygen–carbon distances of O(1)–C(7) = 1.285(8) Å and O(2)–C(7) = 1.273(8) Å are similar to those found for complex **2**. A molecule of tetrahydrofuran was found to cocrystallize with **3**, but there appeared to be no significant interaction between THF and the complex.

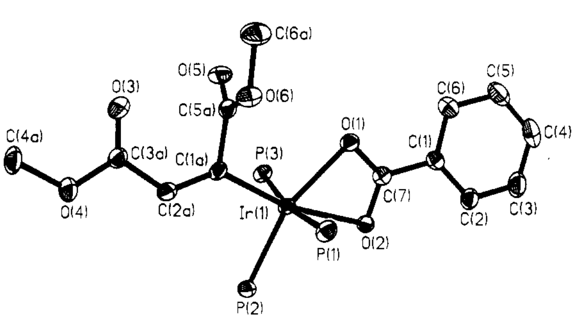


Figure 2. Molecular structure of [*mer*-$(Me_3P)_3Ir\{C(CO_2Me){=}C(H)(CO_2Me)\}(\eta^2\text{-}O_2CC_6H_5)]^+$ (cation of **3**) showing the atom-labeling scheme. Carbon atoms of phosphorus have been omitted for clarity.

Discussion

Reactivity. Previously, we reported that the phenyliridium hydride compound obtained from C–H addition will undergo reactions with alkynes upon removal of the chlorine as Cl^- with Tl^+.[9] We also reported that hydrido compounds obtained from N–H addition only sluggishly react with Tl^+.[10] As a matter of fact, for the N–Ir–H system, decomposition reactions were initiated upon chloride removal. We believe that the reaction of the (η^1-carboxylato)iridium(III) hydride complex (**1**) with Tl^+ to yield **2** proceeded cleanly because (i) the benzoate ligand assists chloride removal via lone pair interactions between the coordinated oxygen atom and iridium and (ii) the benzoate ligand then traps the unsaturated, pentacoordinate, 16e⁻ intermediate resulting from chloride loss with a lone pair on the uncoordinated oxygen atom.

Compound **2** is a coordinatively-saturated, 18e⁻ iridium(III) complex yet appears to be reactive with organic unsaturates. In fact, much cleaner reaction chemistry is observed between **2** and alkynes than is found with **1** and alkynes: reaction between **2** and DMAD led to a product resulting from insertion of the carbon–carbon triple bond into the Ir–H bond, which we could isolate and structurally characterize. This may be due in part to the fact that the carboxylate ligand, through a hapticity change from η^2 to η^1, could allow for a low-energy path for obtaining coordinative unsaturation. Displacement of one of the benzoate ligand oxygen atoms (η^2 to η^1 shift) would generate an unsaturated, pentacoordinate, 16e⁻ Ir(III) intermediate, which can then be trapped by DMAD. Displacement of one of the benzoate ligand oxygen atoms is consistent with a recent report by Marder et al. that the carboxylate moiety of the iridium–α,ω-alkynoic acid complex $Ir(\eta^1\text{-}CO_2(CH_2)_2CCR)H(PEt_3)_3Cl$ was displaced from the iridium metal center by the acetylenic moiety.[6] Insertion of DMAD into the Ir–H bond and then reattachment of the displaced oxygen atom to the iridium (η^1 to η^2 shift) would result in the formation of **3** (Scheme I). Since one end of the benzoate stays tethered to the iridium at all times, a more stable system results when compared with one that must totally dissociate benzoate for reaction to occur.

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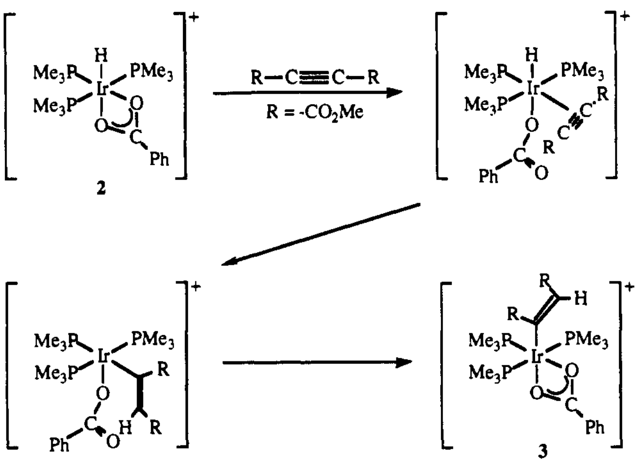
Scheme I



Recently, a fair amount of attention has been directed toward the study of metal complexes with indenyl ligands because of the ability of the indenyl group to open up a coordination site on the metal through η^5 to η^3 shift.[16] The hapticity shift of the carboxylate ligand could be utilized in a similar way: the carboxylate could be a "spectator" ligand, opening and closing to allow small molecules to bind to the metal and facilitate catalysis of reactions such as hydrogenation and oligomerization. It is interesting to note that some active hydrogenation catalysts based on ruthenium[17] and rhodium[18] were found to contain η^2-carboxylate ligands. However, it is important to note that the carboxylate may not stay a simple spectator: the carboxylate could become involved as one of the reagents such as in the addition of carboxylic acids to alkynes to form vinyl esters. Chan, Marder, and coworkers[6] as well as Bianchini and co-workers[7] have demonstrated the catalytic addition of carboxylic acids to alkynes. We are continuing our studies into the reactivity of complexes **1** and **2** as well as analogs of those compounds We have discovered that both **1** and **2** can also act as catalyst precursors for the addition of benzoic acid to alkynes and we will report on the details of our studies in that area in a the future.

η^2-Carboxylate Structures. Both **2** and **3** are pseudooctahedral iridium(III) complexes which contain η^2-benzoate ligands. The structures of the benzoate ligand in both complexes are identical within the errors of measurement. Both C–O distances as well as the O–C–O angle for the two compounds are the same, suggesting that there is little perturbation of the "free" benzoate structure upon complexation. Bond angles about iridium are also remarkably similar for both complexes. The Ir–P bond distances in **3** are slightly elongated when compared with those in **2**, a feature that may be explained by increased steric interactions between the vinyl group on **3** and the phosphine ligands. The only real significant difference between the two structures is the Ir–O bond distance for the oxygen trans to H in **2** versus the oxygen trans to vinyl in **3**: 2.244(8) Å for **2** and 2.183(5) Å for **3**. This is in keeping with an expected large trans influence of the hydride ligand. The Ir–O distances for **2** and **3** for the oxygen trans to PMe$_3$ are identical for both compounds: 2.198(8) Å for **2** and 2.197(5) Å for **3**. The bond distances and angles for both **2** and **3** are in close agreement with those fund for an η^2-acetate complex of ruthenium.[15]

Conclusions

Initial experiments to explore the reactivity of **2** suggest that the Ir–O linkage allows facile generation of an open coordination site at the metal center. The inherent mismatch between the soft character of iridium and the relatively hard character of the oxygen atom of the benzoate ligand, as well as the versatility of the carboxylate ligand to bind the iridium in a unidentate or chelate mode, apparently facilitates this process. We are continuing our investigations into the reactivity of both (η^1-carboxylato)iridium(III) hydride and (η^2-carboxylato)iridium(III) hydride complexes, especially toward unsaturated molecules, with special attention directed toward understanding how the nature of the Ir–O linkage affects the reactivity of these complexes.

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Supplementary Material Available: Listings of the structural determination summaries, bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates for **2** and **3** (9 pages). Ordering information is given on any current masthead page.

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