

Synthesis, Structure, Spectroscopy, and Reactivity of Half-Open Rhodocenium and Iridocenium with Oxodienyl Ligands

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Received June 19, 2002

The syntheses of the oxopentadienyl complex $[\text{Cp}^*\text{Rh}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{BF}_4]$ (**6**) and the iridaoxabenzene $[\text{Cp}^*\text{IrAg}_2(\mu^2\text{-OPF}_2\text{O})_2(1,5\text{-}\eta\text{-CHC}(\text{CMe}_3)\text{CHC}(\text{CMe}_3)\text{O})]$ (**9**) are reported. Compound **9** is an organometallic polymer, formed in competition with complex $[(\text{Cp}^*\text{Ir})_2(\mu^2\text{-OPF}_2\text{O})_3][\text{PF}_6]$ (**8**). Treatment of $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) with lithium 2-methyl-4-oxopentadienide produces $\text{Cp}^*\text{M}(\text{Cl})[\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}]$ ($\text{M} = \text{Ir}, \text{7}; \text{Rh}, \text{10}$). ^1H and ^{13}C NMR, as well as IR spectra, indicate that the ligand acts as an η^3 -oxodienyl group with an exo-syn conformation. The addition of phosphines, PR_3 ($\text{R} = \text{Ph}, \text{Me}$ or $\text{PR}_3 = \text{PPh}_2$), in acetone to compound $[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{PF}_6]$ (**1**) led to the formation of isomers $[\text{Cp}^*\text{Ir}(1,5\text{-}\eta\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{L})][\text{PF}_6]$ [$\text{L} = \text{PMe}_3$, **11**; PPh_3 , **15**] and $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{L})][\text{PF}_6]$ [$\text{L} = \text{PMe}_3$, **12**; PPh_2 , **14**; PPh_3 , **16**]. The 1,5- η and the η^3 isomers are the kinetic and thermodynamic products, respectively. The addition of phosphines PR_3 ($\text{R} = \text{Me}, \text{Ph}$) in methylene chloride to compound **6** led to the formation of compounds $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{L})][\text{BF}_4]$ [$\text{L} = \text{PMe}_3$, **18**; PPh_3 , **20**]. Compounds **18**, **20**, and $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_2)][\text{OTf}]$ (**21**) can also be obtained by adding the corresponding phosphine to compound **10**, followed by the addition of AgOTf . The addition at room temperature of acetonitrile to compound **1** led to the formation of $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{NCMe})][\text{PF}_6]$ (**22**), with an exo-anti conformation of the oxodienyl ligand. Facile dissociation of MeCN became evident. The exo-anti isomer structure of **22** has unequivocally been established by an X-ray diffraction study. The analogous rhodium exo-syn isomer $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{NCMe})][\text{BF}_4]$ (**23**) has been established by ^1H and ^{13}C NMR spectroscopy. Exo-anti and exo-syn preferences have been established for all synthesized rhodium and iridium compounds. Compounds **1** and **6** did not suffer oxidative addition with SnCl_4 and I_2 . With I_2 the bridged iodine compounds $[(\text{Cp}^*\text{M})_2(\mu^2\text{-I})_3][\text{X}]$ ($\text{M} = \text{Ir}, \text{X} = \text{PF}_6$, **25**; $\text{M} = \text{Rh}, \text{X} = \text{BF}_4$, **26**) were obtained. Crystal structures for iridium compounds **1**, **9**, **22**, and **25** and rhodium compounds **6**, **10**, **18**, and $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{H}_2\text{O})][\text{BF}_4]$ (**24**) are described.

Introduction

Interest in the chemistry of cationic half-open rhodocene- or iridium-containing oxodienyl ligands has received additional impetus after the study of the neutral half-open ruthenocene analogous complexes.¹

Maitlis and co-workers² were the first to describe $[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{PF}_6]$ (**1**) from a serendipitous reaction of the cationic $[\text{Cp}^*\text{Ir}(\text{Me}_2\text{CO})_3]^{2+}$ (**2**)³ with 4-methylpent-3-en-2-one (mesityl oxide), which was formed in situ by a catalyzed aldol condensation. This

was demonstrated when compound **1** was prepared in the presence of mesityl oxide and **2**, in better yields (Scheme 1).

Compound **1** can be slowly converted into the isomer $[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{OH})\text{CH}_2)][\text{PF}_6]$ (**3**) in the presence of acid. There was no evidence for the formation of a rhodium analogue to compound **1**. In contrast to the behavior of iridium compound **2**, when the rhodium acetone solvent complex $[\text{Cp}^*\text{Rh}(\text{Me}_2\text{CO})_3]^{2+}$, **4**, was heated, the PF_6^- ion was partially solvolyzed to PO_2F_2^- , which coordinated in a bridging manner to two Cp^*Rh units, giving a crystalline compound, $[(\text{Cp}^*\text{Rh})_2(\mu^2\text{-OPF}_2\text{O})_3][\text{PF}_6]$ (**5**).⁴

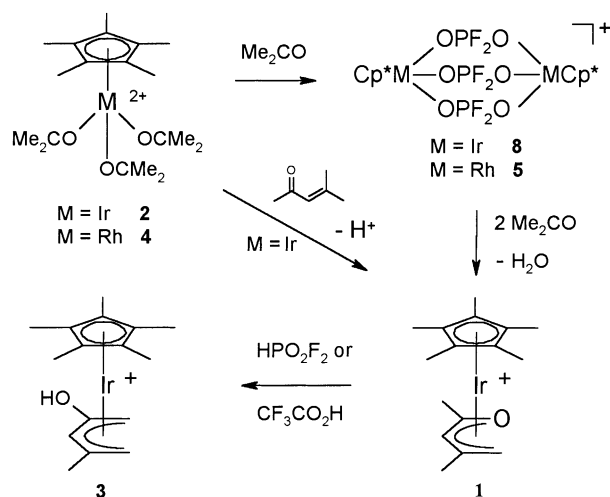
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Scheme 1



In the past, a few acyclic 1-oxopentadienyl transition metal compounds were described as unexpected products from various chemical reactions, affording complexes, such as $[\text{Pd}(\mu\text{-Cl})(\eta^3\text{-CH}(\text{R}^1)\text{CHCH}(\text{R}^2))_2]^{5-}$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Et}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CO}_2\text{Et}$); $\text{Pd}(\text{Cl})(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_3)$,⁶ $\text{Mn}[\eta^5\text{-CH}(\text{R}^1)\text{C}(\text{R}^2)\text{CHC}(\text{R}^3)\text{O}](\text{CO})_3$ ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{CH}_2\text{Ph}$;⁷ $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$;⁸ $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$),⁹ and $\text{Re}(\eta^5\text{-CH}_2\text{CHCHCHO})(\text{CO})(\text{PPh}_3)_2$.¹⁰ More recently, convenient syntheses of oxodienyl complexes of several transition elements have been reported; some examples are $\text{CpFe}(\text{L})(\eta^3\text{-CH}_2\text{CHCHCOMe})$ [$\text{L} = \text{CO}$, PMe_3 , $\text{P}(\text{OMe})_3$],¹¹ $\text{CpRu}(\text{CO})(\eta^3\text{-CH}_2\text{CHCHCHO})$,¹² $\text{Mn}(\eta^3\text{-CH}_2\text{CHCHCOR})(\text{CO})_3$ ($\text{R} = \text{OMe}$, Me), and derivatives, such as $\text{Mn}(\eta^3\text{-CH}_2\text{CHCHCOR})(\text{CO})_3(\text{L})$ [$\text{L} = \text{MeCN}$, Me_2CO , THF , CO] or their phosphine complexes $\text{Mn}(\eta^3\text{-CH}_2\text{CHCHCOR})(\text{CO})_2(\text{PR}_3)$ and $\text{Mn}(\eta^3\text{-CH}_2\text{CHCHCOR})(\text{CO})_3(\text{PR}_3)$ ($\text{PR}_3 = \text{PMe}_3$, PPh_3).¹³ The trimethylsilyloxy-buta-1,3-dienes $\text{Me}_3\text{SiOCH}=\text{CR}^1\text{CH}=\text{CHR}^2$ [$\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$] coordinate to the labile acetonitrile complexes $[(\eta^5\text{-L})\text{Mo}(\text{NCMe})_2(\text{CO})_2][\text{BF}_4]$ ($\text{L} = \text{C}_6\text{H}_7$ or Cp^*) followed by a rapid desilylation, affording the corresponding oxodienyl derivatives $(\eta^5\text{-L})\text{Mo}(\eta^3\text{-CR}^3\text{R}^2\text{CHCR}^1\text{CHO})(\text{CO})_2$ ($\text{R}^3 = \text{H}$, Me) as a mixture of isomers.¹⁴ In 1991, the first homoleptic open ruthenocenes with non-hydrocarbon ligands were published,¹⁵ and a systematic exploration of the synthesis of (heterodienyl)metal complexes has been carried out by Bleeker, using halo-metal-phosphine compounds.¹⁶

Specifically, the anionic oxapentadienide^{17,18} reagents as building blocks have been reported for iridium. The formation of (1,2,5- η - or η^3 -5-oxopentadienyl)iridium complexes,¹⁷ their protonation, or the corresponding protonation of (2,5- η -oxairidacycles) gives iridafuran complexes as the thermodynamic products.¹⁸

As mentioned before, isoelectronic half-open ruthenocenes of the type $\text{Cp}^*\text{Ru}(\eta^5\text{-oxopentadienyl})$ have been prepared and their reactivity has been explored toward oxidative addition or ligand addition reactions.¹

The present studies center on the synthesis and reactivity of $[\text{Cp}^*\text{M}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{X}]$ [$\text{M} = \text{Ir}$, $\text{X} = \text{PF}_6$ (1); $\text{M} = \text{Rh}$, $\text{X} = \text{BF}_4$ (6)] and $[\text{Cp}^*\text{IrAg}_2(\mu^2\text{-OPF}_2\text{O})_2(1,5\text{-}\eta\text{-CHC}(\text{CMe}_3)\text{CHC}(\text{CMe}_3)\text{O})]$ (9). Compounds 1 and 6 and their reactions have been of special interest as part of an effort to understand the reactivity of the oxodienyl ligand. In particular, we would like to compare with neutral isoelectronic $\text{Cp}^*\text{Ru}[\eta^5\text{-CH}_2\text{C}(\text{R})\text{CHC}(\text{R})\text{O}]$ [$\text{R} = \text{Me}$, CMe_3] complexes, which have already been studied in detail.¹

Results and Discussion

Synthesis and Spectroscopy of Oxodienyl Compounds. The iridium-oxodienyl complex $[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_2\text{C}(\text{R})\text{CHC}(\text{R})\text{O})][\text{PF}_6]$ [$\text{R} = \text{Me}$, 1] was most conveniently prepared by replacement of the solvent in the labile tris-acetone derivative 2 by mesityl oxide in 68% (64)² yield.

This salt showed high solubility in chlorinated solvents, acetone or nitromethane, but little in organic solvents less polar than chloroform. While compound 1 is obtained pure, analogue compounds with $\text{R} = \text{Ph}$ or $t\text{-Bu}$ failed to give the η^5 -oxopentadienyl half-open sandwich derivatives. Compound 1 was characterized by its ¹H, ¹³C, and ³¹P NMR spectra (Tables 1 and 2), and the X-ray crystal structure determination was also carried out (Figure 1).

Attempts to use AgPF_6 in the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ and the lithium 2,4-diphenyl-4-oxobutadienide complex were unsuccessful.

Compound 1 can also be obtained at room temperature from $\text{Cp}^*\text{Ir}(\text{Cl})(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})$ (7) in the presence of AgPF_6 within 30 min. However, it is always isolated along with the isomeric hydroxypentadienyl complex $[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{OH})\text{CH}_2)][\text{PF}_6]$ (3), which is the corresponding enol form of compound 1 (Scheme 2). There was no evidence of formation of compound $[(\text{Cp}^*\text{Ir})_2(\mu^2\text{-OPF}_2\text{O})_3][\text{PF}_6]$ (8) (vide infra).²

An analogous synthetic procedure, as described for compound 1, was followed using compound 2 and the corresponding 2,2,5,6,6-pentamethyl-4-hepten-3-one. Instead of the oxopentadienyl analogue, a novel polymeric iridaoxabenzenes complex $[(\text{Cp}^*\text{IrAg}_2(\mu^2\text{-OPF}_2\text{O})_2)(1,5\text{-}\eta\text{-}$

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Table 1. ^1H and ^{31}P NMR Data^a for Compounds **1**, **6**, **7**, **9–12**, **14–16**, and **18–23**

compound	H1 anti	H1 syn	H3	H(C5)	H(C6)	Cp*	L	^{31}P
1	3.09, s	4.15, s	6.65, s	2.03, s	2.44, s	2.02, s		−143.7 PF ₆ $J_{\text{PF}} = 714$
6-BF₄	(3.08) ^b 3.52, s	(4.12) 4.38, s	(6.65) 6.13, s	(2.00) 2.01, s	(2.41) 2.41, s	(2.00) 2.02, s		
6-PF₆	3.50, s	4.02, s	6.29, s	1.95, s	2.39, s	1.94, s		−143.5 PF ₆ $J_{\text{PF}} = 715$
7	2.83, s	3.21, s	3.57, s	2.00, s	2.17, s	1.64, s		
9^c		9.61, d 2.5 Hz	6.83, d 2.5 Hz	1.27, s	1.39, s	2.05, s		−13.1 PF ₂ O ₂ $J_{\text{PF}} = 949$
10	3.20, s	3.33, s	3.61, s	2.12, s	2.15, s	1.60, s		
11	n.a.	3.12, td $J = 16.5$ $J \approx 2.0$	6.13, s	1.99, s	2.10, s	1.82, d $J = 1.9$	1.65, d $J = 9.9$	−44.3 PMe ₃ −143.2 PF ₆
12	2.74–2.81, m	2.74–2.81, m	2.74–2.81, m	2.04, s	2.43, s	1.81, d $J = 1.5$	1.63, d $J = 10.3$	−36.4 PMe ₃ −143.2 PF ₆
14 exo-anti	3.10, d $J = 19.3$	3.52, s, br	4.82, s	1.67, s	2.28, s	1.76, d $J = 2.2$	7.2–7.7, 6.49, d $J_{\text{PH}} = 421$	8.8, d $J_{\text{PH}} = 417$ PPh ₂ −143.8PF ₆ −5.9 PPh ₂ −143.8 PF ₆
14 exo-syn	2.08, d $J = 10.6$	3.05, d $J = 2$	2.26, d $J = 15.9$	1.86, s	2.45, s	1.72, d $J = 2.9$	7.07, d $J = 407$ 7.3–7.7, m	−12.9 PPh ₃ −143.1 PF ₆
15	2.90, d $J = 15.8$	4.32, td $J = 16.1$ $J = 1.8$	5.84, s	1.95, s	2.02, s	1.35, d $J = 2.0$	7.3–7.7	−12.9 PPh ₃ −143.1 PF ₆
16	2.16, d $J = 12.6$	3.06, d $J = 1.6$	2.53, d $J = 16.6$	1.99, s	2.40, s	1.51, d $J = 2.2$	7.3–7.6	12.4PPh ₃ −143.1 PF ₆
18	2.18, d $J = 15.0$	2.86, d $J \approx 2.0$	2.60, d $J = 11.7$	2.09, s	2.37, s	1.79, d $J = 3.3$	1.61, dd $J = 9.9, 0.7$	3.05, d $J = 148.8$ PMe ₃
19	2.49, d $J = 12.5$	3.29, m $J = 15.4$	5.98, s	2.09, s	2.16, s	1.32, d $J = 3.3$	7.3–7.7	40.9, d $J = 158.8$ PPh ₃
20	2.16, d $J = 14.0$	3.41, s, br	2.37, d $J = 12.9$	2.01, s	2.31, s	1.48, d $J = 3.5$	7.3–7.6	48.4, d $J = 153.8$ PPh ₃
21	2.09, d $J = 11.4$	3.16, s, br	2.10, d $J = 16.8$	1.93, s	2.32, s	1.68, d $J = 4.5$	7.2–7.7 7.08, d $J = 390$	27.9, d $J = 154$ PPh ₂
22 exo-anti	3.19, s	3.76, s	4.95, s	1.94, s	2.01, s	1.89, s	2.67, s	
22 exo-syn	2.46, s, br	3.37, d $J = 1.2$	3.32, s	2.06, s	2.22, s	1.70, s	1.97, s	
23	2.72, s	3.44, s	3.23, s	2.04, s	2.09, s	1.56, s	1.90, s, br	

^a In CDCl₃. δ values are in ppm and J values in hertz. For numbering, see oxodienyl ligand in any crystal structure figure. ^b Ref 2. ^c In CD₃CN.

CHC(CMe₃)CHC(CMe₃)O)] (**9**) was isolated in 34–65% yield, depending on the experimental conditions (see Experimental Section). Compound **9** is an organometallic polymer, formed in competition with complex **8** (Scheme 3).

The reaction of **2** and the corresponding ketone required 15–30 min at 50 °C, leading to the precipitation of compound **8** in 35–66% yield. From the orange mother liquor, red crystals of **9** were isolated after 3–5 h at room temperature. Yields for compounds **8** and **9** are quite time dependent. After 15 min at 50 °C, compound **8** can be isolated in 66% yield. However, when the reaction was performed for 30 min at the same temperature, **9** is obtained in ~65% yield. Longer reaction times do not improve the yield of compound **9**. The solid state structure of the polymeric compound **9** (Figure 2) is described below in the crystal structure section, and examination of the ^1H NMR spectrum of compound **9** revealed the presence, in solution, of two signals at high frequency, as doublets at $\delta = 9.61$, $^4J_{\text{H-H}} = 2.5$ Hz, and $\delta = 6.81$, $^4J_{\text{H-H}} = 2.5$ Hz. This shifting indicates metal orbital participation in ring π -bonding

and the establishment of a ring current in the metal-laoxabenzene compound **9**. Similar chemical shifts have been reported for the iridapyrylium complex $[\{\text{IrCHC}(\text{Me})\text{CHC}(\text{Me})\text{O}\}(\text{PET}_3)_3][\text{BF}_4]$,¹⁹ other iridathiabenzenes $\text{Cp}^*\text{Ir}[\text{SC}(\text{Me})\text{CHCHC}(\text{Me})]$,²⁰ $[\{\text{IrSCHCHCHCH}\}(\text{PPh}_2\text{-CH}_2)_3\text{CCH}_3][\text{BF}_4]$,²¹ and several related examples of metallathiabenzenes,²² e.g., $\text{Cp}^*\text{Rh}[\text{SCHCHCHCH}]$.²³ The single Cp* signal at $\delta = 2.02$ is unexpectedly broad ($\nu_{1/2} = 11.4$ Hz). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the ring carbons shows resonances at $\delta(\text{CD}_3\text{CN}) = 189.9$ (C4), 101.5 (C3), 171.4 (C2), 140.7 (C1, br, $\nu_{1/2} = \sim 25$ Hz), while those for the iridapyrylium compound $[\{\text{IrCHC}(\text{Me})\text{CHC}(\text{Me})\text{O}\}(\text{PET}_3)_3]^+$ are at $\delta(\text{CD}_2\text{Cl}_2) = 170.7$ (C4), 112.2 (C3), 147.3 (C2), and 162.2 (C1).^{19b} The ^{19}F and ^{31}P NMR ($\delta = 185.7$, d, 950 Hz and -16.2 , t, 950 Hz,

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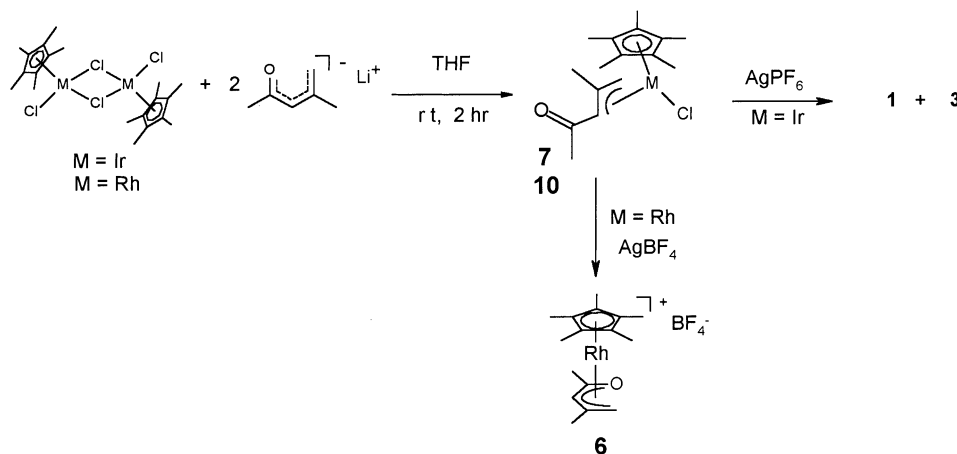
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Table 2. ^{13}C NMR Data^a for Compounds **1**, **6**, **7**, **9–12**, **14–16**, and **18–23**

compound	C1	C2	C3	C4	C5	C6	MeCp*	CCp*	L
1	59.9 (60.3) ^b	111.9 (111.7)	86.3 (86.2)	158.7 (157.2)	22.9 (23.2)	21.6 (21.8)	8.9 (9.2)	96.6 (96.6)	
6	72.3, d	121.5, d	85.2, d	171.4	24.2	22.7	9.6	102.3, d	
BF₄	$J_{\text{RhC}} = 9.1$	$J_{\text{RhC}} = 5.9$	$J_{\text{RhC}} = 4.1$					$J_{\text{RhC}} = 7.9$	
PF₆	72.4, d	121.6, d	85.1, d	172.1	24.5	22.9	9.8	102.4, d	
7	$J_{\text{RhC}} = 9.1$	$J_{\text{RhC}} = 5.9$	$J_{\text{RhC}} = 4.1$					$J_{\text{RhC}} = 7.9$	
9	49.6	97.4	59.5	203.6	31.2	18.7	8.1	93.1	
10	140.7	171.4	101.5	189.8	40.9	38.7	9.6	92.9	
					31.3	28.3			
11	63.8, d	111.8 d	67.9, d	202.4	31.3	18.7	8.6	98.6, d	
	$J_{\text{RhC}} = 9.2$	$J_{\text{RhC}} = 6.1$	$J_{\text{RhC}} = 8.4$					$J_{\text{RhC}} = 6.9$	
12	9.4, d	167.0	121.3	199.2	32.6	27.5	9.9	98.3	17.5, d
	$J_{\text{PC}} = 8.5$								$J_{\text{PC}} = 40.2$
13	37.4, d	92.5, d	46.2, d	202.8	32.3	17.8	9.0	98.5	16.2, d
	$J_{\text{PC}} = 3.8$	$J_{\text{PC}} = 3.0$	$J_{\text{PC}} = 2.6$						$J_{\text{PC}} = 41.2$
14	43.0	93.3	49.2, d	204.4	32.6	22.6	9.3	99.5, d	134.8,
exo-anti			$J_{\text{PC}} = 4.2$					$J_{\text{PC}} = 2.0$	132.8,
									132.1,
14	37.4	94.2	51.0	202.9	32.1	17.3	8.3	98.6	129.3
exo-syn									134.6
									133.6
15	10.9, d	179.7	124.3	202.6	31.3	30.9	9.5	93.4	132.5
	$J_{\text{PC}} = 6.9$								129.8
16	39.4, d	96.1, d	48.8, d	203.0	33.0	17.4	8.6	99.7	134.0,
	$J_{\text{PC}} = 3.3$	$J_{\text{PC}} = 2.7$	$J_{\text{PC}} = 2.6$						131.3,
									128.8,
17									128.3
18	52.0, d	106.8	57.0, d	200.7	31.8	18.5	9.1	102.7, d	135.5,
	$J_{\text{RhC}} = 11.5$		$J_{\text{RhC}} = 9.2$					$J_{\text{RhC}} = 4.7$	134.3,
19	25.8, dd	177.6	123.1	202.9	30.1	29.9	9.0	99.5, d	132.4,
	$J_{\text{RhC}} = 23.6$							$J_{\text{RhC}} = 5.7$	129.6,
	$J_{\text{PC}} = 9.5$								16.0, d
20	54.4, d	109.9	60.0, d	201.2	32.3	18.0	9.0	104.1, d	$J_{\text{PC}} = 33.1$
	$J_{\text{RhC}} = 10.8$		$J_{\text{RhC}} = 10.7$					$J_{\text{RhC}} = 5.3$	134.9
									131.4
21	51.8, dd	107.8, dd	62.1, d	201.5	32.1	18.4	8.9	103.3, dd	129.4
	$J_{\text{RhC}} = 9.6$	$J_{\text{RhC}} = 4.7$	$J_{\text{RhC}} = 8.9$					$J_{\text{RhC}} = 5.0$	128.6
	$J_{\text{PC}} = 4.8$	$J_{\text{PC}} = 2.3$						$J_{\text{PC}} = 1.5$	134.7
22	50.3	99.7	59.0	201.6	30.6	23.4	9.1	95.9	133.4
exo-anti									132.3
23	63.6, d	114.7, d	67.2, d	201.4	31.5	18.1	8.5	100.7, d	129.9
	$J_{\text{RhC}} = 9.3$	$J_{\text{RhC}} = 5.2$	$J_{\text{RhC}} = 8.3$					$J_{\text{RhC}} = 6.2$	8.2
									116.5
									9.6,
									116.7

^a In CDCl_3 . δ values are in ppm and J values in hertz. For numbering, see oxodienyl ligand in any crystal structure figure. ^bRef 2. ^c In CD_3CN .

Scheme 2

respectively) showed the corresponding signals for a POF_2O ligand.

Treatment of $[\text{Cp}^*\text{MCl}_2]_2$ (M = Rh, Ir) with lithium 2-methyl-4-oxopentadienide produces $\text{Cp}^*\text{M}(\text{Cl})[\eta^3\text{-CH}_2\text{C-}$

(Me)CHC(Me)(O)] (M = Ir, **7**; Rh, **10**) in ~20 and 75% yield, respectively (Scheme 2). Compounds **7** and **10** can be recrystallized from diethyl ether/pentane, giving brick-red and yellow crystals. According to ^1H and ^{13}C

Scheme 3

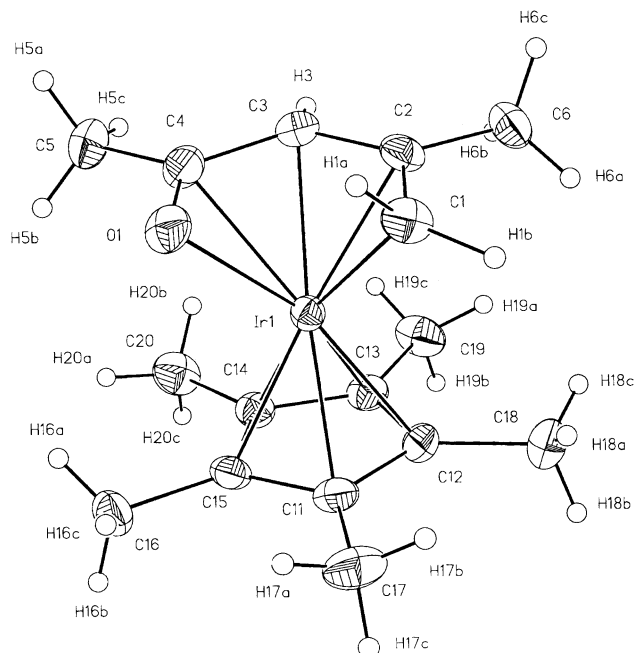
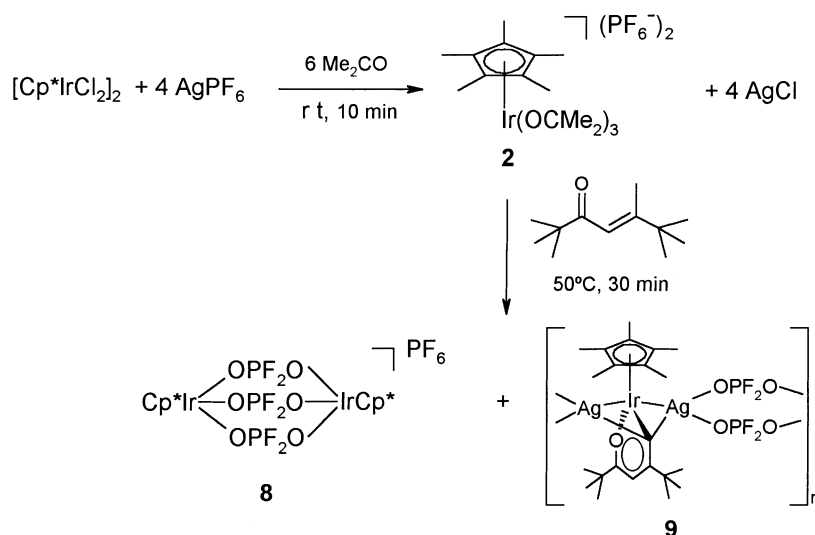


Figure 1. Structure of $[\text{Cp}^*\text{Ir}\{\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}\}]^+[\text{PF}_6]^-$ (**1**).

NMR of both species, as well as GOESY experiments, the oxodienyl ligand in complexes **7** and **10** is W-shaped. The latter compound presents the exo-syn conformation for the oxopentadienyl ligand in the solid state, as determined by X-ray diffraction studies (Figure 3).

Compounds **7** and **10** are quite soluble in diethyl ether, chloroform, or methylene chloride. As described above, their ^1H and ^{13}C NMR, as well as the IR spectra, indicate that the ligand adopts an η^3 -oxodienyl conformation. The syn conformations were indicated by the GOESY experiment, and there are some examples for related pentadienyl²⁴ and oxopentadienyl¹⁷ iridium species. Differentiation of the syn and anti isomers was not possible based on the absence of vicinal coupling constants, but there was evidence of spatial interaction between the H3 and Me(C5) and H1-syn with Me(C6) for **7**.

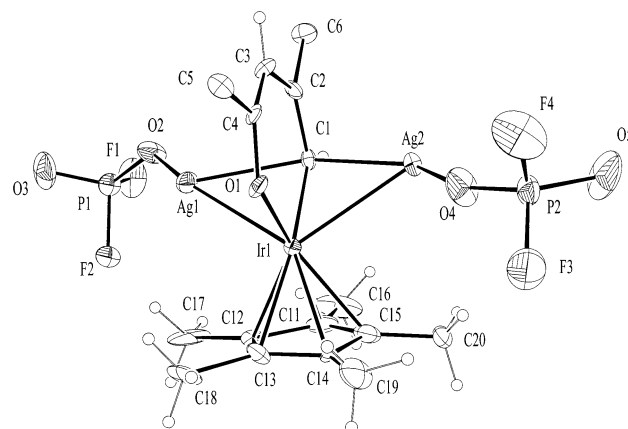


Figure 2. Structure of $[\text{Cp}^*\text{IrAg}_2\{\mu^2\text{-OPF}_2\text{O}\}_2\{1,5\text{-}\eta\text{-CHC}(\text{CMe}_3)\text{CHC}(\text{CMe}_3)\text{O}\}]^+$ (**9**). *tert*-Butyl groups are omitted for clarity.

In solution and in the solid state, the oxodienyl ligand in compound **10** has the exo-syn conformation. The high stability of both oxodienyl ligand conformers in solution was confirmed by an ^1H NMR experiment in which the samples in CDCl_3 were heated at 50°C for 10 and 5 days; there was no evidence for rearrangement of the ligands in **7** and **10**, respectively, suggesting that these isomers are the thermodynamic products (*vide infra*). The $\nu(\text{CO})$ absorption of the unbound carbonyl group of **7** and **10** is observed at 1658 and 1654 cm^{-1} , respectively.

Marked differences in the chemical shift allow the exo and endo isomers to be distinguished for many metal compounds.²⁵ However, in the case of rhodium and iridium there is scarce information in the literature, which was not helpful for the assignment of the preferred isomer, when only one is present.

Similar trends in chemical shifts have been observed for complexes **7** and **10** and the analogous $\text{Cp}^*\text{M}(\eta^3\text{-allyl})\text{X}$ [$\text{M} = \text{Rh}$, $\text{X} = \text{I}$;²⁶ $\text{M} = \text{Ir}$, $\text{X} = \text{Br}$;²⁷ $\text{M} = \text{Rh}$, Ir , $\text{X} = \text{Cl}$;^{28,29}]. Only the exo isomer could be detected for the allylic compounds, as was observed for the oxodienyl derivatives. This is probably because steric factors favor

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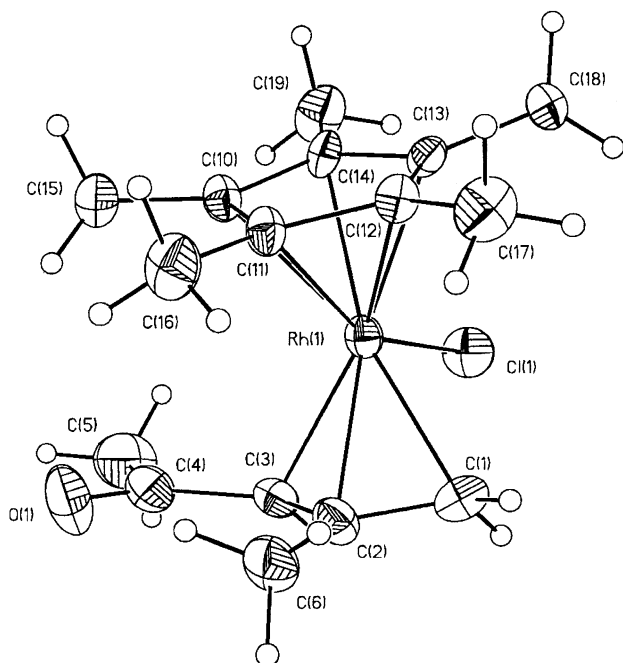


Figure 3. Structure of $[\text{Cp}^*\text{RhCl}\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}\}]\text{ (10)}$.

the isomer with the allylic (C2) carbon pointing away from the Cp^* ligand.

Contrastingly, attempts to prepare the rhodium compound $[\text{Cp}^*\text{Rh}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{PF}_6]$ in a manner similar to that used for **1** were unsuccessful, giving only the solvolysis product $[(\text{Cp}^*\text{Rh})_2(\mu^2\text{-OPF}_2\text{O})_3][\text{PF}_6]$ (**5**) previously reported by Maitlis et al.⁴ However, compound $[\text{Cp}^*\text{Rh}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{BF}_4]$ (**6**) can be synthesized in moderate yield (41%), removing the chloride ion from compound **10** with AgBF_4 . If PF_6^- is used, a mixture of **6** and **5** is obtained in a ratio of 7.5:1. Separation of this mixture was not possible.

Treatment of compound $[\text{Cp}^*\text{Rh}(\text{Me}_2\text{CO})_3][\text{BF}_4]_2$ (**4**)³ with mesityl oxide afforded a yellow-orange solid of the well-known $[\text{Cp}_2\text{Rh}][\text{BF}_4]$ ³⁰ in 50.3% yield. Finally, trying to avoid the presence of acetone and PF_6^- ligands with the Cp^*Rh fragment, $[\text{Cp}^*\text{Rh}(\text{MeCN})_3][\text{BF}_4]_2$ was prepared as starting material, but the MeCN ligands are not labile enough, and there was no displacement of MeCN by mesityl oxide. In the case of $[\text{Cp}^*\text{Rh}(\text{Me}_2\text{CO})_3][\text{OTf}]_2$ (**4-OTf**), the reaction mixture gave evidence of isomerization of the mesityl oxide to the corresponding 4-methylbut-4-en-2-one after 4 h at 50 °C, but this isomerization did not progress any further, even within 2 days at the same temperature. After treatment with 1 equiv of mesityl oxide, most of the recovered product was starting material.

An attempt to prepare compound **6** from **4-BF₄** and lithium oxopentadienide afforded indeed, compound **6**,

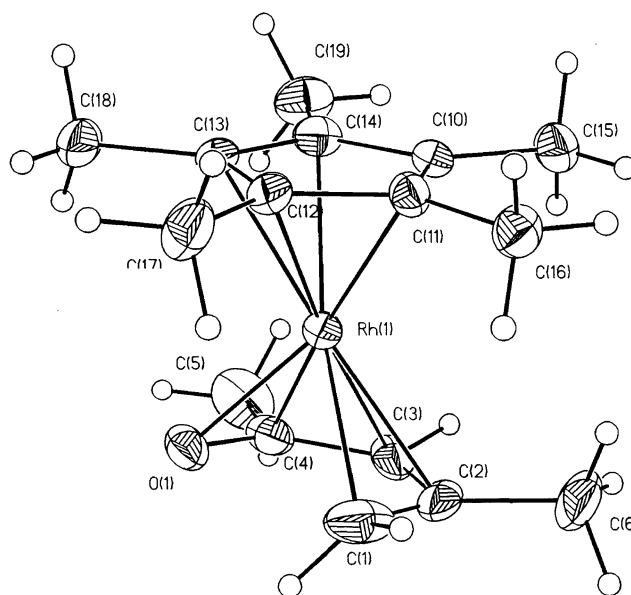


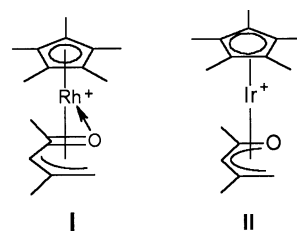
Figure 4. Structure of $[\text{Cp}^*\text{Rh}\{\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}\}][\text{BF}_4]\text{ (6)}$.

but the result depends on the THF/acetone ratio used. This is due to the presence of a lithium complex in THF, which may react with the acetone required for the synthesis of **4-BF₄**. The best synthetic procedure for getting compound **6** is from **10** and AgBF_4 (Scheme 2). The molecular structure of **6** is described in the structural studies section (vide infra) (Figure 4).

¹H and ¹³C NMR data of compound **1** in CDCl_3 can be compared to those reported by Maitlis in $(\text{CD}_3)_2\text{CO}$.²

For comparison, the ¹³C NMR data for both compounds **1** and **6** were obtained in CDCl_3 , and one interesting feature is the extreme high frequency of the rhodium-bound CO carbon atom. In the ¹³C{¹H} NMR spectrum of **6** the signals for carbons C1 ($\delta = 72.3$), C2 ($\delta = 121.5$), and C3 ($\delta = 85.2$) are doublets with $J = 9.1, 5.9$, and 4.1 Hz, respectively. The coupling indicates that C1, C2, and C3 are coordinated to the rhodium atom, while C4 from the group CO showed a singlet at $\delta = 171.4$. For compound **1** the carbon C4 resonates quite differently ($\delta = 158.7$). This indicates that the rhodium derivative experiences a strong inductive effect, and C4 is distinctly the most positively charged carbon. This fact could point to a contribution from a resonance hybrid I in which there is an η^3 -allylic bond, as well as the donation of the electron pair from the oxygen in **6**, while the resonance hybrid II is proposed for **1** (Scheme 4).

Scheme 4



However, on the basis of the X-ray diffraction studies of both compounds (Figures 4 and 1, vide infra), there is a similar interaction of the oxodienyl ligand for **6** and

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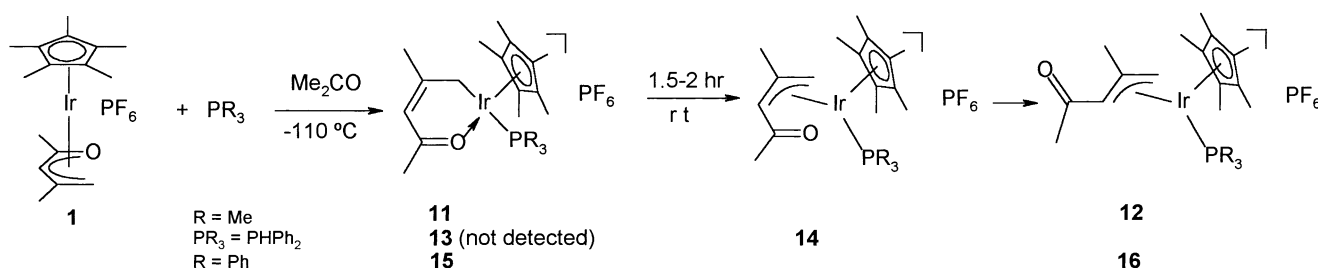
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(30) (a) Gusev, O. V.; Morozova, L. N.; Peganova, T. A.; Petrovskii, P. V.; Ustynyuk, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1994**, 742, 359. (b) Buchholz, D.; Zsolnai, L.; Huttner, G.; Astruc, D. *J. Organomet. Chem.* **2000**, 593, 494.

Scheme 5



1. In contrast, unexpectedly short C4–O interatomic distances in the X-ray crystal structures of ruthenium oxodienyl complexes have been found, for which consistent high-frequency-shifted C4 chemical shifts has been detected.³¹

B. Reactions with Phosphine Ligands. Iridium Complexes. The addition of phosphines, PR_3 ($\text{R} = \text{Ph}$, Me or $\text{PR}_3 = \text{PPh}_2$), in acetone to compound **1** led to the formation of compounds **11**–**16** as described in Scheme 5.

The complexes are air-stable in the solid state but oxidize in solution after some time. The reactions generally proceed at low temperature ($-100\text{ }^\circ\text{C}$) and are completed on slow warming to room temperature and then stirring for 2 h at the same temperature. Compounds $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PMe}_3)][\text{PF}_6]$ (**12**) and $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_2)][\text{PF}_6]$ (**14**) were isolated after reducing the volume of acetone and adding diethyl ether. They precipitated as pale yellow solids in 95 and 77% yield, respectively. In the case of PMe_3 if the reaction mixture is immediately evaporated to dryness, after the mixture has attained room temperature the reaction showed by ^{31}P NMR in a CDCl_3 solution clear evidence for the presence of isomer $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PMe}_3)][\text{PF}_6]$ (**11**) as the major compound at $\delta^{31}\text{P} = -44.1$, along with the corresponding signal of **12** at $\delta = -36.4$. After 4 h compound **11** is a minor compound, and after 24 h **11** has been totally consumed with exclusive formation of compound **12**. Compound **11** has been characterized only by the NMR data, while compound **13** was not even detected. According to the ^1H and ^{13}C NMR spectra, compounds **11** and **12** and **14** have the oxodienyl ligand bonded to the iridium atom in a $1,5\text{-}\eta$ and η^3 fashion, respectively. Compound **14** adopts an anti conformation, contrasting with the corresponding exo-syn ruthenium species $[\text{Cp}^*\text{Ru}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_2)]$,¹ whose formation was carried out under cyclohexane refluxing conditions. According to the chemical shifts, compound **12** appears to be the exo-syn isomer. This fact could be explained by the higher reactivity of the basic PMe_3 ligand. The reaction of compound **1** with PPh_3 parallels that of PMe_3 and PPh_2 , but this bulky PPh_3 ligand preferentially stabilizes the compound $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_3)][\text{PF}_6]$ (**15**) (83% yield). After heating 72 h at $40\text{ }^\circ\text{C}$, **15** in CDCl_3 showed evidence of formation of the exo-syn $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_3)][\text{PF}_6]$ (**16**), which was detected by ^1H NMR spectroscopy. However, the reaction is not selective, and there are other products along with compound **16**. In

our hands, the purification of this mixture was not achieved. The ^1H and ^{13}C NMR data of iridium complexes **11**, **12**, and **14**–**16** are summarized in Tables 1 and 2.

Rhodium Complexes. The addition of phosphines PR_3 ($\text{R} = \text{Me}$, Ph) in methylene chloride to compound **6** led to the formation in good yield of $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PMe}_3)][\text{BF}_4]$ (**18**) (83%), and in moderate yield $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_3)][\text{BF}_4]$ (**20**) (54%) as described in Scheme 6. If the reaction mixture, with PPh_3 , is evaporated to dryness after 1 h at room temperature, the ^{31}P NMR spectrum gives evidence of compound **19**, which is totally transformed into compound **20**, after 2 h in methylene chloride. Compounds **18**, **20**, and $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_2)][\text{OTf}]$ (**21**) can also be obtained in 19, 17, and 12% yield, respectively, by adding the corresponding phosphine PR_3 ($\text{R} = \text{Me}$, Ph or $\text{R}_3 = \text{HPh}_2$) in acetone to compound **10**, followed by the addition of AgOTf . A significant improvement in yield is obtained when the AgOTf is added to **10** first, followed by the addition of PPh_2 , affording **21** in ~45% yield. The former synthetic procedure using compound **10**, gave **18**, $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{PPh}_3)][\text{OTf}]$ (**20**), and **21**, along with the corresponding subproducts $\text{Cp}^*\text{RhCl}(\text{PMe}_3)_2$ ³² and an unknown compound with a Cp^* and PPh_3 ligand, tentatively assigned as $\text{Cp}^*\text{RhCl}(\text{OTf})(\text{PPh}_3)$ ³³ and $\text{Cp}^*\text{RhCl}(\text{PPh}_2)_2$ ³⁴. The corresponding ratios are 1:2.7, 4.5:1, and 1:1.1, respectively. However, if compound **21** is prepared by first adding AgOTf to **10**, followed by diphenylphosphine, a 10:1 ratio was observed. In any case, there was no evidence of nucleophilic addition on the oxodienyl fragment.

The ^1H and ^{13}C NMR data for complexes **18**–**21** are summarized in Tables 1 and 2.

^1H NMR data demonstrate the exclusive formation of the exo-syn derivatives **18**, **20**, and **21**, as was also observed for compounds **10** and **23**.

Complex **18** was isolated as an air-stable yellow solid, which after recrystallization from methylene chloride/diethyl ether afforded single crystals, and the exo-syn orientation of the η^3 -oxodienyl was confirmed by X-ray crystallography (Figure 5, vide infra).

(32) Experimental: ^1H (CDCl_3) $\delta = 1.81$, t, 3.3 Hz; 1.65, dd, 5.7, 4.2 Hz; ^{31}P $\delta = 4.18$, d, 132.6 Hz. Reported: ^1H (CD_3NO_2): $\delta = 1.80$, t, 3.2 Hz, Cp^* , 1.70, dd, 0.7, 11 Hz; ^{31}P $\delta = 0.8$, d, 132.5 Hz]. Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450.

(33) $\text{CpRhCl}(\text{OTf})\text{PPh}_3$: ^1H (CDCl_3) $\delta = 1.43$, d, 3.5 Hz, 7.3–7.7, m. ^{31}P $\delta = 32.35$, d, 143.5 Hz. ^{19}F $\delta = -78.68$.

(34) Experimental: ^1H (CDCl_3) $\delta = 1.45$, t, 3.7 Hz, 6.37, d, 412 Hz, 7.3–7.8, m. ^{31}P $\delta = 13.43$, d, 127.5 Hz. Reported: ^1H (CDCl_3) $\delta = 1.45$, t, 3.8 Hz, 6.38, d, 411.1 Hz. ^{31}P $\delta = 13.3$, d, 129.9 Hz]. Esteban, M.; Pequerul, A.; Carmona, D.; Lahoz, F. J.; Marin, A.; Oro, L. A. *J. Organomet. Chem.* **1991**, *402*, 421.

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Scheme 6

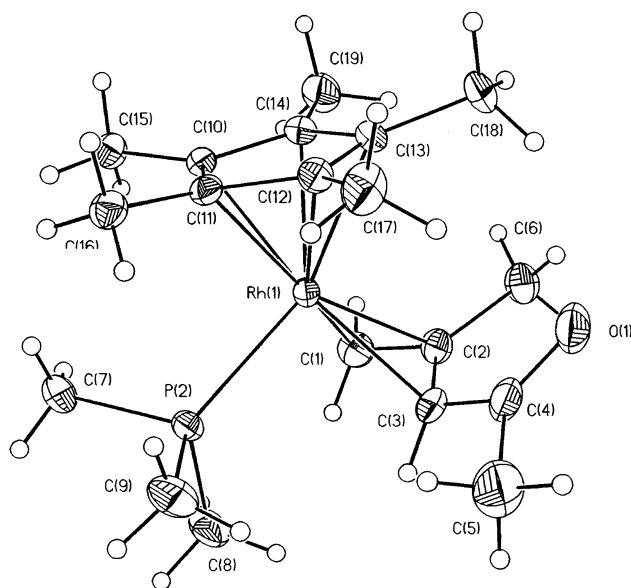
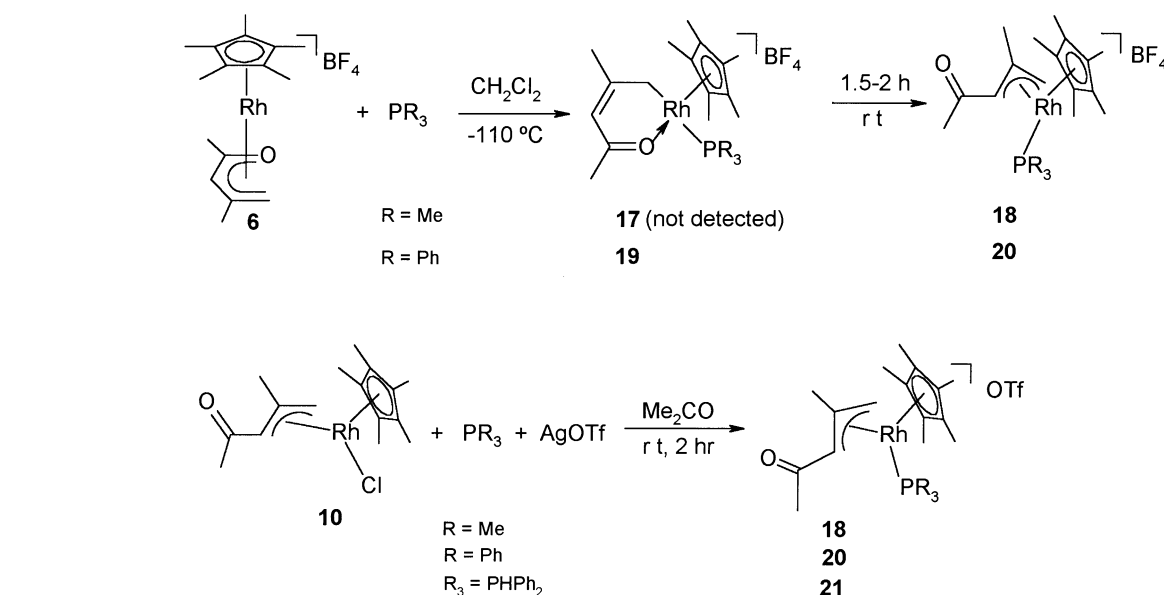


Figure 5. Structure of $[\text{Cp}^*\text{Rh}(\text{PMe}_3)\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}\}][\text{BF}_4]$ (**18**).

Contrasting with the dominant exo-syn geometry of the rhodium-phosphine complexes, as is the case for **21**, the corresponding iridium complex **14** exhibits preferentially in solution an exo-anti (U-shaped) conformation (Scheme 5), without evidence, at room temperature, of the syn (W-shaped) isomer. However, slow conversion from the exo-anti to exo-syn isomer was observed by ^1H NMR spectroscopy, after heating the deuterated chloroform solution of **14** at $50\text{ }^\circ\text{C}$. The ratio of exo-anti to exo-syn isomers after 20, 46, and 88 h was 1:1.1, 1.0:4.5, and 0:1, respectively.

The addition reactions of **1** and **6** (Schemes 5 and 6) generally proceed much faster than those observed for the corresponding neutral complex $\text{Cp}^*\text{Ru}(\eta^2\text{-2,4-dimethyl-}\eta^5\text{-oxopentadienyl})$.¹ The selectivity of rhodium and iridium compounds is evident, and it is interesting to contrast, as far as their conformations are concerned, the strongly preferred exo-syn conformation for rhodium complexes, and the exo-anti for some iridium complexes (vide infra), while for ruthenium analogues both isomers

can be present as a mixture, depending on the reaction conditions.¹

Allylic chemical shifts for compounds such as $[\text{Cp}^*\text{M}(\eta^3\text{-allyl})(\text{L})]^+$ [$\text{M} = \text{Rh}, \text{Ir}, \text{L} = \text{PPh}_3$;^{26,35} $\text{M} = \text{Rh}, \text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{MeCN}, \text{NH}_2\text{Et}$;³⁶ $\text{M} = \text{Rh}, \text{L} = \text{PPh}_3, \text{MeCN}$ and $\text{M} = \text{Rh}, \text{L} = \text{PMe}_3$ ³⁷] do not compare well to the corresponding **14**, **20**, or **21**.

C. Reaction with Acetonitrile and Water Ligands.

The addition at room temperature of acetonitrile to compound **1** led to the formation of exo-anti $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{NCMe})][\text{PF}_6]$ (**22**) as described in Scheme 7. Through ^1H NMR studies of pure compound **22** in CDCl_3 the facile dissociation of MeCN became evident after some minutes, along with the consequent formation of compound **1**.

The exo-anti isomer **22** structure (Figure 6) has unequivocally been established by an X-ray diffraction study, which will be discussed later. The analogous rhodium compound $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{NCMe})][\text{BF}_4]$ (**23**) was also obtained in 55% yield as the exo-syn isomer, resulting from the addition at room temperature of acetonitrile to compound **6** (Scheme 7). There is also dissociation of MeCN from **23**, after 2 days in methylene chloride solution. The higher stability of the rhodium–acetonitrile bond shows that rhodium is a hard atom compared to the soft iridium atom in compound **22**. The higher stability of the MeCN–Rh bond is in agreement with the low reactivity observed for $[\text{Cp}^*\text{Rh}(\text{MeCN})_3][\text{BF}_4]_2$ as described above.

It is interesting to compare the isomerization of **14** in CDCl_3 (vide supra) and **22** in CD_3CN . **14** is totally transformed from the exo-anti to the exo-syn complex (Table 1), while **22** under similar conditions afforded, after 20, 46, and 88 h, an exo-anti:exo-syn ratio of 1:3.8; 1:4, and 1:4 (Table 1). The last results suggest an exo-

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Scheme 7

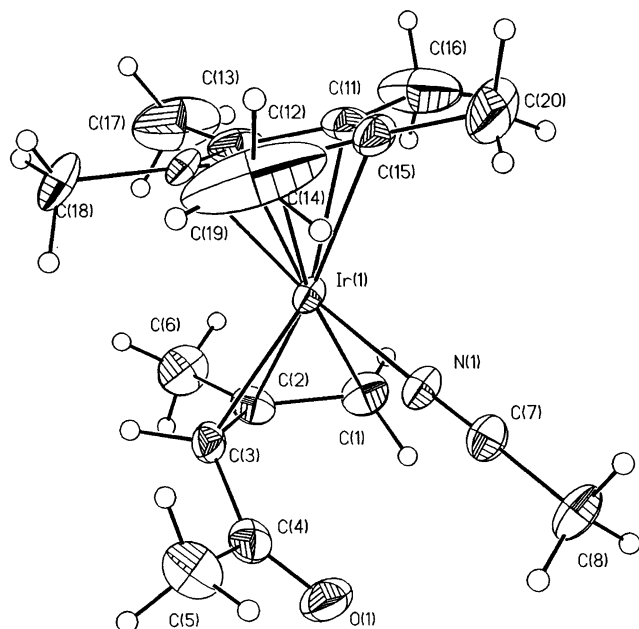
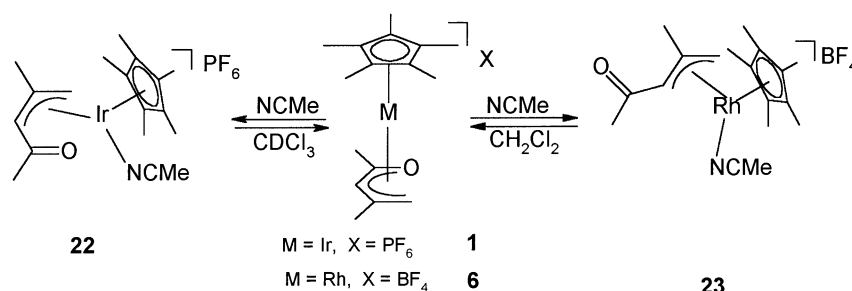


Figure 6. Structure of $[\text{Cp}^*\text{Ir}(\text{NCMe})\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}\}][\text{PF}_6]$ (**22**).

anti, exo-syn equilibrium, favored by the presence of acetonitrile in compound **22**.

The orientation of the allylic moiety with respect to the other ligands has been studied for different allylic derivatives, such as $[\text{Cp}^*\text{M}(\eta^3\text{-allyl})(\text{CO})]^+$ [$\text{M} = \text{Rh}, \text{Ir}$; $\text{Cp}^* = \text{Cp}$,³⁸ Cp^*]³⁹ and $[\text{Cp}^*\text{Ir}(\eta^3\text{-allyl})(\eta^2\text{-CH}_2\text{CH}_2)]^+$.⁴⁰ A detailed study on the stereochemistry of metal-allyl cationic complexes²⁵ and theoretical studies of the interconversion between endo and exo η^3 -allyl for $[\text{CpIr}(\eta^3\text{-allyl})\text{PH}_3]^+$ ⁴¹ has also been reported.

When recrystallization of complex **6** was carried out in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, red crystals of the η^3 -oxodienyl complex $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})(\text{H}_2\text{O})][\text{BF}_4]$ (**24**) were obtained, according to an X-ray diffraction study. Traces of water may have come from the diethyl ether or from methylene chloride, producing serendipitously the new complex **24** (Figure 7).

The cationic structure in the solid state and in solution afforded evidence of an exo-syn isomer. ¹H NMR data of the crystals afforded the spectrum of compound **6** along with a broad signal at 3.05 ppm.

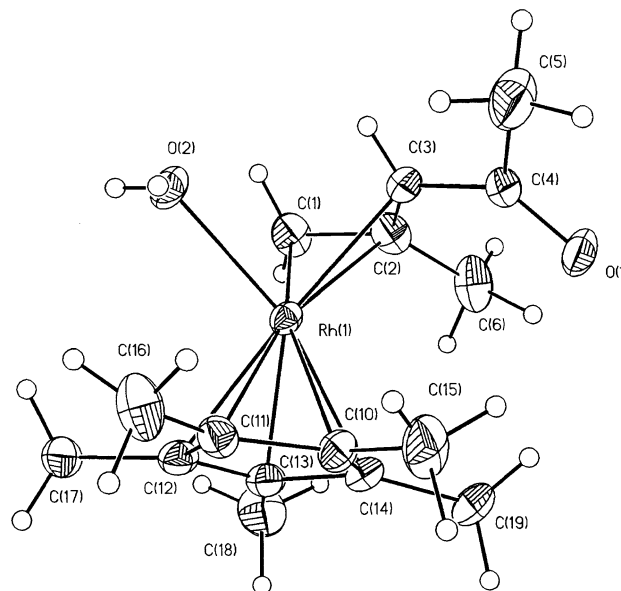


Figure 7. Structure of $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}\}][\text{BF}_4]$ (**24**).

Attempts to synthesize **24** from **6** and $\text{CDCl}_3/\text{H}_2\text{O}$ did not give spectroscopic evidence of reaction, even after 20 days at room temperature. **6** and D_2O affords deuterated **24**.

D. Attempted Oxidative Addition Reactions. Few examples exist of organometallic compounds of late transition metals in high oxidation states. Comparison with high-valent complexes of early transition metals suggests that such compounds, especially those of groups 8, 9, and 10, might be expected to possess unique properties and reactivities. Recently, we studied η^5 -oxopentadienyl ruthenium complexes that were found to undergo oxidative addition of SnCl_4 , I_2 , and O_2 , yielding $\text{Cp}^*\text{Ru}^{(\text{IV})}(\eta^3\text{-oxopentadienyl})(\text{X}_1)(\text{X}_2)$ derivatives readily.¹ Maitlis and co-workers demonstrated the accessibility of pentamethylcyclopentadienyl-substituted organoiridium(V)⁴² and organorhodium(V)⁴³ complexes. Other examples reported in the literature are Cp^*IrH_4 ⁴⁴ and $\text{Cp}^*\text{Ir}(\eta^2\text{-2,5-Me}_2\text{-thiophene})(\text{H})_2$.⁴⁵ As part of continuing studies of the synthesis and reactivity of oxodienyl iridium and rhodium complexes, we decided to

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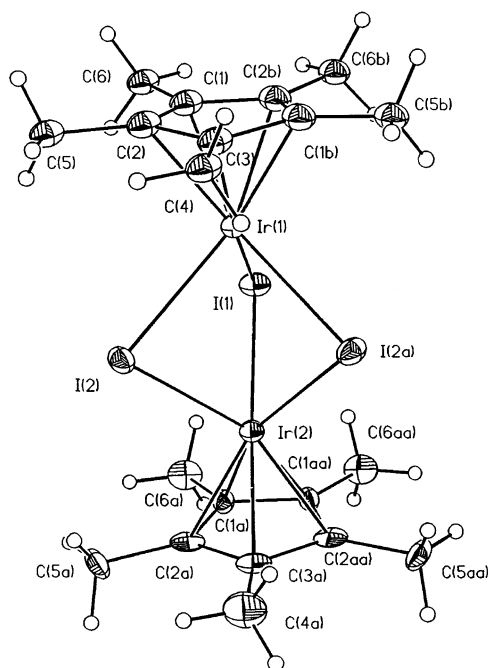
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Table 3. Crystal Data for Iridium Compounds **1**, **9**, **22**, and **25**

	1	9	22	25
mol wt	C ₁₆ H ₂₄ OPF ₆ Ir 569.52	C ₂₂ H ₃₅ Ag ₂ F ₄ IrO ₅ P ₂ 925.38	C ₂₀ H ₃₀ ON ₂ PF ₆ Ir 651.63	C ₂₀ H ₃₀ PF ₆ I ₃ Ir ₂ 1180.51
cryst syst	<i>P</i> ₂ / ₁ / <i>c</i>	<i>P</i> ₂ / ₁ / <i>c</i>	<i>P</i> ₂ / ₁ / <i>m</i>	<i>P</i> ₂ / ₁ / <i>m</i>
<i>a</i> (Å)	7.9485(3)	9.92200(10)	14.5537(10)	9.944(2)
<i>b</i> (Å)	16.5894(7)	14.2738(2)	9.3674(10)	12.134(2)
<i>c</i> (Å)	14.8760(7)	20.6115(4)	18.6867(10)	11.663(2)
α (deg)	90	90	90.0	90.0
β (deg)	101.9300(10)	90	103.392(10)	95.43(3)
γ (deg)	90	90	90.0	90.0
<i>V</i> (Å ³)	1919.19(14)	2919.10(8)	2478.3(3)	1400.9(4)
<i>Z</i>	4	4	2	2
cryst size (mm)	0.25 × 0.17 × 0.08	0.15 × 0.15 × 0.3	0.6 × 0.6 × 0.6	0.51 × 0.45 × 0.32
<i>D</i> _{calc} (g cm ⁻³)	1.971	2.106	1.746	2.799
limit 2 θ (deg)	6.84–54.88	3.48–58.18	4.90–60.66	5.66–49.92
ranges <i>h</i> , <i>k</i> , <i>l</i>	–10 ≤ <i>h</i> ≤ 10 0 ≤ <i>k</i> ≤ 21 0 ≤ <i>l</i> ≤ 19	–8 ≤ <i>h</i> ≤ 13 –18 ≤ <i>k</i> ≤ 18 –25 ≤ <i>l</i> ≤ 25	–20 ≤ <i>h</i> ≤ 18 0 ≤ <i>k</i> ≤ 12 0 ≤ <i>l</i> ≤ 25	–11 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 14 0 ≤ <i>l</i> ≤ 13
total no. data	4316	16 896	6464	5229
total no. unique data	4316	5699	6284	2391
total no. obsd data, <i>F</i> > 4 σ (<i>F</i>)		5195	3988	2253
final R1	0.0422	0.0288	0.0556	0.0849
final wR2	0.0996	0.0697	0.1250	0.2302
no. variables	212	364	198	135
GOF	1.041	1.151	1.188	1.072

Figure 8. Structure of [(Cp*Ir)₂(μ-I)₃][PF₆] (**25**).

explore the possibility of forming species in higher oxidation states. However, all attempted reactions of compounds **1** and **6** with SnCl₄ and I₂ afforded Cp*Ir(III) and Cp*Rh(III) species, losing in all cases the oxodienyl ligand. This behavior contrasts with the chemistry observed for the isoelectronic Cp*Ru(IV) complexes.¹

Treatment of **1** with an acetone solution of iodine or 1 M solution of SnCl₄ in heptane at –110 and –78 °C gives orange solids in 71 and 79% yield of [(Cp*Ir)₂(μ²-I)₃][PF₆] (**25**) (Figure 8) and the well-known dimer [(Cp*IrCl)(μ²-Cl)]₂, respectively. ¹H NMR experiments in Me₂CO-*d*₆ of both reactions show in the case of I₂ that in the initial reaction there is only evidence for the formation of **25**, while in the case of SnCl₄ there is evidence of an intermediate, which was not isolated and which may correspond to an η³-oxodienyl species, but is consumed later, giving only mesityl oxide and the dimer [(Cp*IrCl)(μ²-Cl)]₂.

Analogous treatment of **6** with an acetone solution of iodine afforded [(Cp*Rh)₂(μ²-I)₃][BF₄] (**26**). Similar chloride- and hydroxide-bridged complexes are known, e.g., [(Cp*M)₂(μ²-X)₃]⁺ [M = Rh, X = Cl;⁴⁶ OH;^{46,47} M = Ir, X = OH⁴⁷].

E. Structural Studies. Crystal data for iridium compounds **1**, **9**, **22**, and **25** and rhodium compounds **6**, **10**, **18**, and **24** are provided in Tables 3 and 6, respectively. The structures **1** and **6** are presented in Figures 1 and 4. These are generally similar to those of related species.¹ Some relevant data are provided in Tables 4 and 7.

The solid state structures of the η³-oxodienyl derivatives **10**, **18**, **22**, and **24** are presented in Figures 3, 5, 6, and 7, respectively, while various bonding parameters for iridium or rhodium compounds are contained in Tables 4 and 7, respectively.

The solid state structure of the oxairidabenzene compound **9** is presented in Figure 2, and bonding parameters are given in Table 5.

The crystalline structure of the complex [(Cp*Ir)₂(μ²-I)₃][PF₆] (**25**) is presented in Figure 8, and selected bonding parameters are given in Table 8.

The bonding of the oxodienyl ligands in **1** and **6** appears similar, while the respective values for C_{*n*}–C_{*n*+1} (*n* = 1–3) and M–C(1–4) are comparatively longer, because of weak π-back-bonding, than those for ruthenium analogous species,¹ while M–O bonds are quite similar (~2.163 Å). The corresponding atom distances for **1** and **6** (Tables 4 and 7) reflect a significant charge effect of the cationic iridium and rhodium complexes, as the values for the ligand atoms (C1–C4) are lengthened, while the bonds to O1 do not experience significant lengthening. The O1–C4 distance in **6** is slightly shorter [1.293(9) Å] than in **1** [1.312(10) Å] and the analogous neutral Cp*Ru(2,4-dimethyl-η⁵-oxopentadienyl) [1.348(11) Å].¹

In general the structural parameters for the species **10**, **18**, and **24** correspond fairly closely to each other and also to the neutral compound Cp*Ru[η³-CH₂C(Me)-CHC(Me)O](PPh₃),¹ despite the fact that the last one is

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1 and 22

1		22		1		22	
Bond Distances							
Ir–C1	2.175(8)	2.212(9)	C11–C12	1.4227(19)	C11–C16	1.481(18)	
Ir–C2	2.204(7)	2.182(9)	C14–C15	1.4228(19)		1.425(17)	
Ir–C3	2.222(7)	2.183(9)	C11–C15	1.4227(19)	C12–C13	1.411(16)	
Ir–C4	2.245(8)		C15–C16	1.512(2)	C12–C17	1.503(17)	
Ir–C11	2.173(3)	2.224(10)	C11–C17	1.512(2)	C13–C14	1.460(17)	
Ir–C12	2.171(3)	2.180(10)	C12–C18	1.512(2)	C13–C18	1.494(16)	
Ir–C13	2.192(3)	2.193(9)	C13–C19	1.512(2)	C14–C19	1.498(18)	
Ir–C14	2.206(3)	2.183(9)	C14–C20	1.512(2)	C7–N1	1.119(12)	
Ir–C15	2.194(3)	2.182(10)	Ir–O1	2.159(6)	Ir–N1	2.045(7)	
C1–C2	1.412(11)	1.439(14)	O1–C4	1.312(10)		1.222(12)	
C2–C3	1.434(11)	1.445(14)	F1–P1	1.498(10)	F1–P2	1.491(12)	
C3–C4	1.443(11)	1.478(14)	F2–P1	1.529(9)	F2–P2	1.556(13)	
C4–C5	1.484(11)	1.485(17)	F3–P1	1.510(8)	F3–P2	1.570(10)	
C2–C6	1.509(12)	1.521(14)	F4–P1	1.476(11)	F4–P2	1.492(12)	
C–C(Cp*)	1.4227(11)	1.416(16)	F5–P1	1.540(8)	F5–P2	1.431(13)	
C–Me(Cp*)	1.512(2)	1.497(17)	F6–P1	1.459(10)	F6–P2	1.513(12)	
Bond Angles							
C1–C2–C3	121.7(8)	118.3(9)	C4–C3–Ir	72.0(4)		111.8(6)	
C1–C2–C6	120.3(7)	120.5(10)	C1–C2–Ir	70.1(4)		72.1(5)	
C2–C3–C4	124.6(7)	125.2(9)	C3–C2–Ir	71.8(4)		70.7(5)	
C3–C2–C6	117.3(7)	120.9(10)	C6–C2–Ir	123.3(6)		122.3(7)	
C3–C4–C5	120.6(7)	116.9(10)	C5–C4–Ir	131.0(6)	N1–Ir–C14	96.5(4)	
O1–C4–C3	118.6(7)	123.2(10)			N1–C7–C8	176.8(11)	
O1–C4–C5	120.8(8)	119.9(11)			N1–Ir–C2	104.3(3)	
O1–C4–Ir	69.1(4)				N1–Ir–C1	84.6(4)	

Table 5. Bond Lengths (Å) and Angles (deg) for Compound 9

Bond Lengths			
Ir–O1	1.998(3)	Ir1–Ag1	2.7670(7)
Ir–C1	2.000(4)	Ir1–Ag2	2.7708(7)
Ir–C12	2.142(6)	Ir1–C11	2.146(4)
Ir–C13	2.150(7)	Ir1–C14	2.297(6)
Ir–C15	2.228(9)	Ag1–O2	2.278(6)
P1–F1	1.534(4)	Ag2–O4	2.379(7)
P1–F2	1.530(4)	Ag1–O5A	2.116(7)
P2–F3	1.528(4)	Ag1–C1	2.455(9)
P2–F4	1.517(5)	Ag2–C1	2.296(9)
C1–C2	1.417(5)	P1–O2	1.469(6)
C2–C3	1.412(5)	P1–O3	1.418(8)
C3–C4	1.389(5)	P2–O4	1.372(7)
C4–C5	1.535(5)	P2–O5	1.487(8)
C2–C6	1.553(5)	C5–C25	1.533(6)
O1–C4	1.309(5)	C6–C23	1.512(11)
C11–C16	1.518(8)	C12–C13	1.452(10)
C13–C14	1.373(8)	C12–C17	1.581(11)
Bond Angles			
O1–Ir–C1	88.15(3)	O1–Ir–Ag2	84.64(19)
O1–Ir–C12	132.1(3)	C1–Ir–Ag2	54.7(3)
O1–Ir–C11	168.18(15)	C11–Ir–Ag2	101.8(5)
O1–Ir–C13	103.2(2)	C1–Ag1–Ir	44.53(10)
C1–Ir–C13	162.5(3)	O1–Ir–Ag2	84.64(19)
C1–Ir–C12	123.3(3)	C12–Ir–Ag2	142.16(18)
C1–Ir–C11	103.67(16)	C15–Ir–Ag2	83.8(2)
C12–Ir–C13	39.6(3)	O1–C4–C3	123.3(4)
O1–Ir–C15	136.4(4)	C1–C2–C3	123.1(3)
C1–Ir–C14	153.2(3)	C3–C4–C5	122.8(3)
C12–Ir–C15	63.7(2)	C1–C2–C6	119.5(3)
Ir–C1–Ag1	76.0(2)	O4–Ag2–Ir	101.19(17)
Ir–C1–Ag2	80.0(2)	O3–P1–F1	101.5(5)
C2–C1–Ir	127.5(3)	F2–P1–F1	98.9(3)
C2–C1–Ag1	89.8(6)	O4–P2–F4	106.6(5)
C2–C1–Ag2	94.9(6)	F4–P2–F3	98.0(3)
Ag1–Ir–Ag2	113.056(13)	O2–Ag1–Ir	146.43(16)

a Ru(II) species, while others are Rh(III). Each complex contains an η^3 -oxodienyl ligand as an exo-syn isomer, contrasting with the crystalline structure of the cationic Ir(III) complex **22**, which contains an η^3 -oxodienyl ligand in an exo-anti conformation. The bonding parameters within the oxodienyl ligands are quite similar independently of their conformations, except for the terminal

C1–C2 [1.439(14) Å] and Ir–C1 [2.212(9) Å] distances for **22**, which are longer than those of the corresponding exo-syn [Cp* $\text{Ru}(\eta^3\text{-oxodienyl})(\text{PPh}_3)$] [1.407(5), 2.189(3) Å] and rhodium complex **24** [1.400(6), 2.164(4) Å]. The η^3 -oxodienyl ligand for the rhodium and iridium compounds coordinates preferentially through carbon atoms rather than through an oxoallyl, as observed for the soft Ru(II) analogue derivatives.¹ The average C=O distance is 1.221 Å. Typical bond distances for Ir–NCMe (2.045 Å) were observed for compound **22** and [Ir₂(COD)₂-(NCMe)(Tcbiim)] (Tcbiim = 4,4',5,5'-tetracyano-2,2'-biimidazole) [2.044(12) Å]⁴⁸ and Rh–O (2.187(3) Å) for **24**, similar to that found for [Cp*Rh(Me₂CO)₂(OH)]⁺₃₁ (2.180(4) Å) and shorter and longer than those for [Cp*Rh(H₂O)₃]²⁺ [2.213(8), 2.131(8), and 2.137(8) Å].⁴⁹ The substituents L = Cl, PMe₃, and H₂O for **10**, **18**, and **24** are opposite the carbonyl group, while for L = MeCN in **22** it is on the same side of the C=O group. This arrangement is in accord with the exo-syn and exo-anti conformations of the oxodienyl ligands in each case.

The solid state study of compound **9** shows disorder in one of the *tert*-butyl groups with an occupancy of 50:50. The structure confirms the metallabenzene structure with an Ir(III) center. This inorganic polymer is bridging the Ir and C1 through the dimer [Ag(O₂PF₂)₂]₂. The structure has two planar rings, the Cp* and the iridabenzene, which are perpendicular (93.7°) to each other. In the six-membered ring, the interior angle at Ir is 88.15(13)°, and that at O is 131.9(2)°; the interior angles at the four carbons range from 122.8(3)° to 125.2(4)°. The six-membered ring is nearly planar, with no atom deviating by more than 0.079 Å from the best mean plane. Bond distances also suggest that the ring can be represented as an aromatic system. The bond length of Ir–C1 (2.000(4) Å) is similar to those for iridabenzene [2.024(8) and 1.985(8) Å]⁵⁰ and shorter

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Table 6. Crystal Data for Rhodium Compounds 6, 10, 18, and 24

	6	10	18	24
	C ₁₆ H ₂₄ BF ₄ ORh	C ₁₆ H ₂₄ OCIRh	C ₁₉ H ₃₃ OPBF ₄ Rh	C ₁₆ H ₂₆ O ₂ BF ₄ Rh
mol wt	422.07	370.71	498.14	440.09
cryst syst	P2 ₂ 12 ₁	P2 ₁ /n	P1	P2 ₁ /c
<i>a</i> (Å)	7.3972(3)	7.260(5)	9.1825(2)	10.8608(4)
<i>b</i> (Å)	14.5614(6)	27.038(5)	10.4846(2)	12.3331(4)
<i>c</i> (Å)	16.4645(7)	9.010(5)	12.3365(3)	14.5758(5)
α (deg)	90	90	97.9940(10)	90
β (deg)	90	113.498(5)	97.4550(10)	107.076(2)
γ (deg)	90	90	98.5480(10)	90
<i>V</i> (Å ³)	1773.45(13)	1622.0(15)	1149.29(4)	1866.32(11)
<i>Z</i>	4	4	2	4
cryst size (mm)	0.1 × 0.08 × 0.03	0.45 × 0.39 × 0.25	0.5 × 0.2 × 0.05	0.1 × 0.05 × 0.1
<i>D</i> _{calc} (g cm ⁻³)	1.581	1.518	1.439	1.566
limit 2 θ (deg)	7.40–59.94	5.78–53.86	4.78–54.94	6.02–55.00
ranges <i>h</i> , <i>k</i> , <i>l</i>	–9 ≤ <i>h</i> ≤ 9 –18 ≤ <i>k</i> ≤ 16 –21 ≤ <i>l</i> ≤ 21	0 ≤ <i>h</i> ≤ 9 0 ≤ <i>k</i> ≤ 34 –11 ≤ <i>l</i> ≤ 10	–11 ≤ <i>h</i> ≤ 11 –13 ≤ <i>k</i> ≤ 11 –15 ≤ <i>l</i> ≤ 16	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 16 –18 ≤ <i>l</i> ≤ 18
total no. data	12 580	4041	8889	23 814
total no. unique data	4031	3945	5231	4258
total no. obsd data, <i>F</i> > 4 σ (<i>F</i>)	3096	2189	4822	2887
final R1	0.0573	0.0631	0.0395	0.0432
final wR2	0.1275	0.1691	0.1072	0.0839
no. variables	178	172	271	248
GOF	1.040	1.429	1.146	1.038

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Compounds 6, 10, 18, and 24

	6		10		18		24
			Bond Lengths				
Rh–O1	2.162(5)	Rh–Cl	2.422(3)	Rh–P2	2.3352(7)	Rh–O2	2.187(3)
Rh–C1	2.188(8)		2.189(12)		2.190(3)		2.164(4)
Rh–C2	2.221(7)		2.173(12)		2.160(3)		2.186(5)
Rh–C3	2.194(7)		2.193(11)		2.206(3)		2.197(5)
Rh–C4	2.244(8)						
Rh–C10	2.172(3)		2.242(12)		2.201(3)		2.217(4)
Rh–C11	2.154(3)		2.185(11)		2.220(3)		2.191(4)
Rh–C12	2.152(3)		2.210(12)		2.242(3)		2.171(4)
Rh–C13	2.168(3)		2.161(12)		2.258(3)		2.155(4)
Rh–C14	2.180(3)		2.208(12)		2.228(3)		2.151(4)
O1–C4	1.293(9)		1.221(17)		1.222(5)		1.222(5)
C1–C2	1.391(14)		1.394(17)		1.401(5)		1.400(6)
C2–C3	1.431(14)		1.435(16)		1.423(5)		1.423(6)
C3–C4	1.438(12)		1.469(18)		1.484(5)		1.462(6)
C4–C5	1.486(12)		1.51(2)		1.498(6)		1.496(7)
C2–C6	1.488(12)		1.509(16)		1.515(5)		1.507(7)
C–C(Cp*)	1.4216(17)		1.421(15)		1.4324(4)		1.4242(6)
C–Me(Cp*)	1.5112(18)		1.504(15)		1.4968(4)		1.5032(6)
B1–F4	1.305 ^a (14)				1.288(9)		1.368(6)
B1–F2	1.369(17)				1.296(6)		1.351(6)
B1–F3					1.358(6)		1.361(6)
			Bond Angles				
C1–C2–C3	120.5(7)		115.0(11)		116.5(3)		115.3(4)
C3–C2–C6	117.4(11)		124.9(11)		124.5(3)		124.1(4)
C2–C3–C4	125.1(8)		125.6(12)		125.4(3)		127.3(4)
C1–C2–C6	121.0(11)		120.1(11)		119.0(3)		120.4(5)
C1–C2–Rh	70.3(5)		72.0(7)		72.35(18)		70.4(3)
C3–C2–Rh	70.1(4)		71.6(6)		72.71(17)		71.5(3)
C4–C3–Rh	73.0(4)		114.9(9)		116.0(2)		118.4(3)
C6–C2–Rh	122.9(5)		122.9(10)		123.7(2)		123.8(4)
C2–C3–Rh	72.1(5)		70.1(7)		69.26(17)		70.6(3)
O1–C4–C3	119.3(7)		125.7(14)		123.8(3)		123.9(4)
O1–C4–C5	121.5(8)		121.2(15)		119.7(4)		119.6(4)
C2–Rh–C3	37.8(4)		38.4(4)		38.03(14)		37.88(17)
C1–Rh–C3	68.0(4)		66.0(5)		66.22(14)		66.27(18)
		C1–Rh–Cl	85.2(4)	C1–Rh–P2	88.13(9)	C1–Rh–O2	82.48(18)
		C2–Rh–Cl	104.8(4)	C2–Rh–P2	107.29(9)	C2–Rh–O2	101.04(17)

^a F1–B1.

than iridacyclohexadienes [2.161(11), 2.127(8), and 2.143(7) Å].⁵¹ Considering the planar, delocalized bonding indicated by the X-ray results and the aromatic characteristics of the NMR spectrum, complex **9** is reasonably described as a metallaheterobenzene derivative, best described as an “iridaoxabenzene”, analogous to the “iridathiabenzene” described by Angelici.²⁰ Bond

distances between Ag1 and Ag2 with C1 are 2.455(9) and 2.296(9) Å, respectively. These values are an indication of the π nature of the silver–carbon bond, as has been previously observed in other silver compounds.⁵² To our knowledge, the only reported type of similar ring is the iridapyrylium complex [IrCHC(Me)–CHC(Me)O](PEt₃)₃]⁺,¹⁹ but the crystal structure has not

Table 8. Selected Bond Lengths (Å) and Angles (deg) for Compound 25

Bond Lengths			
Ir1–C1	2.122(18)	Ir2–C1A	2.145(16)
Ir1–C2	2.185(19)	Ir2–C2A	2.160(16)
Ir1–C3	2.15(3)	Ir2–C3A	2.14(2)
Ir1–I1	2.7264(19)	C1–C2	1.40(3)
Ir1–I2	2.7257(13)	C2–C3	1.47(2)
P1–F1	1.58(2)	C3–C4	1.44(4)
P1–F2	1.550(16)	C1–C6	1.52(3)
P1–F3	1.571(19)	C2–C5	1.48(3)
P1–F4	1.586(17)	C3–C4	1.44(4)
Ir2–I1	2.7288(17)		
Ir2–I2	2.7273(13)		
Bond Angles			
C1A–Ir1–C1	38.4(12)	C1–Ir1–I1	100.5(5)
C1–Ir1–C3	65.5(8)	C1–Ir1–I2	120.2(6)
C1–Ir1–C2A	64.2(8)	Ir1–I1–Ir2	81.05(5)
C3–Ir1–C2	39.6(6)	Ir1–I2–Ir2	81.09(4)
C2A–Ir2–I1	131.5(5)	I2–Ir2–I1	82.87(4)

been published. The difluorophosphate rhodium structure of $[\text{Rh}_2(\text{Cp})_2(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-AgOPF}_2\text{O})]$ has been published.⁵³

The single-crystal X-ray structure determination of $[(\text{Cp}^*\text{Ir})_2(\mu^2\text{-I})_3][\text{PF}_6]$ (**25**) shows bond lengths and angles similar to those previously reported for $[(\text{Cp}^*\text{Ir})_2\text{I}_6]$ ⁵⁴ and $[(\text{Cp}^*\text{Ir})_2\text{I}_4]$.⁵⁵ Each iridium atom has a distorted octahedral coordination with a Cp^* occupying three coordination sites and three iodine atoms surrounding the cationic Ir(III).

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (hexane and pentane with CaH_2 , diethyl ether and THF with Na/benzophenone, CH_2Cl_2 , CHCl_3 , and CH_3NO_2 with CaCl_2 , acetone with K_2CO_3 , benzene and toluene with Na, CH_3CN with P_2O_5) and distilled under nitrogen prior to use. Compounds $[\text{Cp}^*\text{MCl}_2]_2$ [$\text{M} = \text{Rh}, \text{Ir}$]^{3b} and 2,2,5,6,6-pentamethyl-4-hepten-3-one,⁵⁶ were prepared according to literature procedures. All other chemicals were used as purchased from Sigma-Aldrich, Strem Chemicals, Merck, J. T. Baker, Isotec, and Cambridge Isotopes. Elemental analyses were performed by Robertson Microлит Laboratories, Inc., Madison, NJ, and Desert Analytics, Tucson, AZ. Solution IR spectra were recorded on a Perkin-Elmer 6FPC-FT spectrophotometer using KBr or a CHCl_3 solution in NaCl plates. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on JEOL GSX-270, JEOL Eclipse+400 MHz, or Bruker 300 MHz spectrometers in deoxygenated, deuterated solvents. NMR chemical shifts are reported relative to TMS and ^{31}P NMR chemical shifts relative to 85% H_3PO_4 . Mass spectra were obtained at Washington University, St. Louis, MO. Melting

points were determined using a Mel-Temp apparatus and are not corrected.

Synthesis of $[\text{Cp}^*\text{Ir}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{PF}_6]$ (1**).** To an acetone solution (10 mL) containing 200 mg of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.25 mmol) at room temperature was added AgPF_6 (253 mg, 1.0 mmol) previously weighed in a drybox and dissolved in acetone (3 mL). The solution was stirred for 15 min under nitrogen atmosphere, and AgCl was then filtered. The addition resulted in a change in color from orange to yellow. To the filtered yellow solution, mesityl oxide (70 μL , 0.6 mmol) was added. The solution was then warmed to 50 °C and stirred for 30 min. Afterward, the yellow solution was allowed to cool to room temperature, the solvent was reduced, and diethyl ether was added, precipitating compound **1** as a yellow powder, which can be crystallized in chloroform/diethyl ether. **1** was obtained in 68% yield (192 mg, 0.337 mmol) and decomposes at ~174 °C, without melting. X-ray quality crystals were obtained by diffusion crystallization with nitromethane/diethyl ether. Spectroscopic and physical properties have been previously reported.²

Attempted Synthesis of Compound 6. Synthesis of $[(\text{Cp}^*\text{Rh})_2(\mu^2\text{-OPF}_2\text{O})_3][\text{PF}_6]$ (5**).** To an acetone solution (10 mL) containing 100 mg of $[\text{Cp}^*\text{RhCl}_2]_2$ (0.162 mmol) at room temperature was added AgPF_6 (163 mg, 0.648 mmol) previously weighed in a drybox and dissolved in acetone (3 mL). The solution was stirred for 15 min under nitrogen atmosphere, and AgCl was then filtered. The addition resulted in a change in color from brick-red to yellow. To the filtered yellow solution was added mesityl oxide (44 μL , 0.38 mmol). The solution was then warmed to 50 °C and stirred for 40 min. Afterward, the yellow solution was allowed to cool to room temperature, the solvent was reduced, and diethyl ether was added, precipitating compound **5** as an orange-yellow powder in 92% yield (138 mg, 0.149 mmol). Mp: 219–221 °C. Spectroscopic and crystallographic data and physical properties have been previously reported.^{2,4}

Synthesis of $[\text{Cp}^*\text{Rh}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})][\text{X}]$ [$\text{X} = \text{PF}_6, \text{BF}_4$] (6**).** To a CH_2Cl_2 solution (5 mL) containing 150 mg of compound **10** (0.40 mmol) at room temperature was added AgPF_6 (102 mg, 0.40 mmol) in 2 mL of CH_2Cl_2 . The addition resulted in a change in color from dark brown to yellow and then red-brown. The amber suspension was stirred at room temperature for 30 min and was then filtered. After reducing the volume of the volatiles, diethyl ether (20 mL) was added and the yellow-greenish solid that precipitated was purified by fast chromatography through Celatom FW-50 (2 cm \times 10 cm), eluting with CH_2Cl_2 . Attempts to purify with CH_2Cl_2 /diethyl ether (0.5/20 mL) afforded compound **6-PF₆** mixed with **5** as a bright yellow powder (88 mg) in a ratio of 7.5:1, respectively. The synthesis of **6-BF₄** was carried out similarly as described for **6-PF₆**, using AgBF_4 (80 mg, 0.40 mmol), and 69 mg (0.163 mmol, 40.8%) was isolated. Mp: 137–139 °C. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{BF}_4\text{ORh}$: C, 45.53; H, 5.73. Found: C, 45.83, H, 5.98. MS: 335(100) [$\text{M} - \text{BF}_4^+$], 237(10).

Synthesis of $\text{Cp}^*\text{IrCl}[\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}]$ (7**).** Under a nitrogen atmosphere, a $n\text{-BuLi}$ (0.32 mL, 1.6 M, 0.5 mmol) solution was added to a cold (–78 °C) THF solution (1.0 mL) of diisopropylamine (70 μL , 0.5 mmol). The solution was stirred with slow warming to room temperature. After 15 min the solution was cooled to –78 °C, and mesityl oxide (57 μL , 0.5 mmol) was added dropwise. The solution was then warmed to room temperature and stirred for 1 h, after which a light yellow solution was observed. The resulting (oxopentadienyl)-lithium salt was slowly added dropwise to a cold (–110 °C) solution of $[\text{Cp}^*\text{IrCl}_2]_2$ (200 mg, 0.25 mmol) in 4.0 mL of THF. After the solution was warmed to room temperature and stirred for 2 h, the volatiles were removed under vacuum. Compound **7** was then extracted from the remaining residue with diethyl ether, and the resulting solution was concentrated and then chromatographed on a neutral Al_2O_3 (1.0 \times 15 cm) column with diethyl ether as the eluant. A yellow band was

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eluted. The solvent was removed in vacuo, and the crude product was crystallized from diethyl ether/pentane at -20°C to give 47 mg (0.1 mmol, 20%) of **7** as yellow crystals. Mp: $156-160^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{ClOIr}$: C, 41.77; H, 5.25. Found: C, 42.03, H, 5.36. MS: 425(100) $[\text{M} - \text{Cl}^+]$, 363(16). IR (CHCl_3 , cm^{-1}): 1658 ($\text{C}=\text{O}$).

Synthesis of $[(\text{Cp}^*\text{Ir})_2(\mu^2\text{-OPF}_2\text{O})_3][\text{PF}_6]$ (8**) and $\text{Cp}^*\text{IrAg}_2(\mu^2\text{-OPF}_2\text{O})_2[\eta^{1,1}\text{-CHC}(\text{Me}_3)\text{CHC}(\text{Me}_3)\text{O}]$ (**9**).** To an acetone solution (10 mL) containing 200 mg of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.25 mmol) at room temperature was added AgPF_6 (253 mg, 1.0 mmol) previously weighed in a drybox. The addition resulted in a change in color from orange to yellow. The solution was stirred for 15 min under nitrogen atmosphere, and AgCl was then filtered. To the yellow filtrate was added dropwise 2,2,5,6,6-pentamethyl-4-hepten-3-one (0.12 mL, 0.6 mmol). The solution was then warmed to 50°C and stirred for 15 min. Afterward, the amber solution was allowed to cool to room temperature, the solvent was reduced, and diethyl ether was added, precipitating compound **8** as a pale yellow powder in 66% yield (168 mg, 0.165 mmol). Mp: $173-175^{\circ}\text{C}$, decomp. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{F}_{12}\text{O}_6\text{P}_4\text{Ir}_2$: C, 21.78; H, 2.74. Found: C, 22.64, H, 2.88. MS: 957(65) $[\text{M} - \text{PF}_6^+]$, 751(100), 701(60), 687(35), 671(30), 664(22).

The remaining orange solution after a couple of hours at room temperature afforded compound **9** as dark red crystals in 65% yield (134 mg, 0.164 mmol). Mp: $167-171^{\circ}\text{C}$. Crystals suitable for X-ray analysis were obtained directly at room temperature. Anal. Calcd for $\text{C}_{22}\text{H}_{35}\text{Ag}_2\text{F}_4\text{IrO}_5\text{P}_2$: C, 28.55; H, 3.81. Found: C, 27.98, H, 3.70. MS: 929 $[\text{M}]^+$ (2.5), 835 (5), 615 (35), 505 (10), 1124 (100). HRMS: 929.2936. IR (KBr, cm^{-1}): 1530 ($\text{C}=\text{O}$), 1316 ($\text{P}=\text{O}$); 837 ($\text{P}-\text{F}$).

Synthesis of $\text{Cp}^*\text{RhCl}[\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O}]$ (10**).** Under a nitrogen atmosphere, a *n*-BuLi (1.0 mL, 1.6 M, 1.62 mmol) solution was added to a cold (-78°C) THF solution (2.0 mL) of diisopropylamine (0.25 mL, 1.62 mmol). The solution was stirred with slow warming to room temperature. After 15 min the solution was cooled to -78°C and mesityl oxide (0.18 mL, 1.62 mmol) was added dropwise. The solution was then warmed to room temperature and stirred for 1 h, after which a light yellow solution was observed. The resulting (oxopentadienyl)lithium salt was slowly added dropwise to a cold (-110°C) solution of $[\text{Cp}^*\text{RhCl}_2]_2$ (500 mg, 0.81 mmol) in 5.0 mL of THF. After the solution was warmed to room temperature and stirred for 2 h, the volatiles were removed under vacuum. Compound **10** was then extracted from the remaining residue with diethyl ether, and the resulting brick-red solution was concentrated and then chromatographed on neutral Al_2O_3 (1.0 \times 20 cm) column with diethyl ether as the eluant. A brick-red band was collected. The solvent was removed in vacuo, and the crude product was crystallized from diethyl ether/pentane at -10° to give 449 mg (1.21 mmol, 74.8%) of **10** as brick-red crystals that decompose at 105°C . Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{ClORh}$: C, 51.84; H, 6.52. Found: C, 52.46, H, 6.53. MS: 370(13) $[\text{M}^+]$, 335(100) $[\text{M} - \text{Cl}^+]$, 273(84), 237(46). IR (CHCl_3 , cm^{-1}): 1654 ($\text{C}=\text{O}$).

Synthesis of $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{PMe}_3][\text{PF}_6]$ (12**).** To an acetone solution (10 mL) containing 100 mg of compound **1** (0.175 mmol) at -110°C was added PMe_3 (20 μL , 0.19 mmol). The addition resulted in a change in color from amber to light yellow and then amber. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 2 h and then filtered. After removal of the volatiles, the oily residue was dissolved in a minimum amount of acetone, and diethyl ether was added, giving a pale yellow precipitate in 95% yield (108 mg, 0.167 mmol). Mp: $202-205^{\circ}\text{C}$. IR (CHCl_3 , cm^{-1}): 1674 ($\text{C}=\text{O}$). LR/ESI: 501 (100) $[\text{M} - \text{PF}_6]^+$, 446 (10), 425 (5), 278 (5).

Synthesis of $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{PPh}_2][\text{PF}_6]$ (14**).** To an acetone solution (10 mL) containing 100 mg of compound **1** (0.175 mmol) at -110°C was added PPh_2 (32 μL , 0.18 mmol). The addition resulted in a change in color

from amber to light yellow and then bright yellow. The solution was allowed to warm slowly to room temperature and was stirred for 1.5 h and then filtered. After removal of the volatiles, the oily residue was dissolved in a minimum amount of acetone, and diethyl ether was added, giving a pale yellow precipitate in 77% yield (102 mg, 0.135 mmol). Mp: $118-120^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{28}\text{H}_{35}\text{F}_6\text{IrOP}_2$: C, 44.50; H, 4.66. Found: C, 44.29, H, 4.40. MS: 611(100) $[\text{M} - \text{PF}_6^+]$, 513(63), 425(35). IR (CHCl_3 , cm^{-1}): 1666 ($\text{C}=\text{O}$).

Synthesis of $[\text{Cp}^*\text{Ir}(1,5\text{-}\eta\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{PPh}_3][\text{PF}_6]$ (15**).** To an acetone solution (10 mL) containing 100 mg of compound **1** (0.175 mmol) at -78°C was added PPh_3 (50.0 mg, 0.19 mmol) in acetone (2 mL). The addition resulted in a change in color from amber to orange-yellow. The solution was allowed to warm slowly to room temperature and was stirred for 2 h and then filtered. After removal of the volatiles, the oily residue was washed with pentane (2 \times 20 mL). The yellow solid was dissolved in a minimum amount of acetone, and diethyl ether was added, affording a yellow precipitate in 83% yield (122 mg, 0.146 mmol). Mp: $163-165^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{34}\text{H}_{39}\text{F}_6\text{IrOP}_2$: C, 49.09; H, 4.72. Found: C, 49.16, H, 4.62. MS: 687(42) $[\text{M} - \text{PF}_6^+]$, 589(52), 425(73). IR (CHCl_3 , cm^{-1}): 1620 ($\text{C}=\text{O}$).

Synthesis of $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{PMe}_3][\text{X}]$ ($\text{X} = \text{BF}_4$, OTf) (18**).** To a CH_2Cl_2 solution (10 mL) containing 100 mg of compound **6-BF₄** (0.237 mmol) at -110°C was added PMe_3 (27 μL , 0.26 mmol). The addition resulted in a change in color from orange to yellow and then amber. The solution was allowed to warm slowly to room temperature and was stirred for 2 h and then filtered. After removal of the volatiles, the oily residue was washed with pentane (3 \times 10 mL) and diethyl ether (2 \times 10 mL). The orange-yellow solid was dissolved in a minimum amount of CH_2Cl_2 and purified by chromatography on a Celatom FW-50 column (1 \times 10 cm) using methylene chloride as eluent. Evaporation of the solvent under vacuum afforded a yellow compound **18-BF₄** in 83% yield (101 mg, 0.197 mmol). Mp: $124-127^{\circ}\text{C}$, decomp. Anal. Calcd for $\text{C}_{19}\text{H}_{33}\text{OPBF}_4\text{Rh}$: C, 45.81; H, 6.67. Found: C, 45.92, H, 6.57. MS: 411(100) $[\text{M} - \text{BF}_4^+]$. IR (CHCl_3 , cm^{-1}): 1670 ($\text{C}=\text{O}$).

Compound **18-OTf** was obtained from an acetone solution (10 mL) containing 100 mg of compound **10** (0.269 mmol) at -110°C . PMe_3 (31 μL , 0.295 mmol) was added, the reaction mixture was allowed to warm slowly to room temperature, and AgOTf (69 mg, 0.269 mmol) was added previously dissolved in acetone (2 mL), stirred for 2 h, and then filtered. After removal of the volatiles, the oily residue was recrystallized from chloroform/diethyl ether, affording an orange-yellow solid (29 mg) as a mixture of **18** and $[\text{Cp}^*\text{RhCl}(\text{PMe}_3)_2]^+ \text{ } ^{32}$ in a ratio of 1:2.7, respectively.

Synthesis of $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{PPh}_3][\text{X}]$ ($\text{X} = \text{BF}_4$, OTf) (20**).** To a CH_2Cl_2 solution (10 mL) containing 100 mg of compound **6-BF₄** (0.237 mmol) at -110°C was added PPh_3 (62 mg, 0.237 mmol), dissolved in CH_2Cl_2 (2 mL). The addition resulted in a change in color from orange to red and then yellow. The solution was allowed to warm slowly to room temperature and was stirred for 3 h and then filtered. After removal of the volatiles, the oily residue was washed with pentane (3 \times 10 mL) and dissolved in a minimum amount of methylene chloride, and addition of diethyl ether afforded a yellow compound **20-BF₄** in 53.6% yield (87 mg, 0.127 mmol). Mp: $119-121^{\circ}\text{C}$. MS: 597(100) $[\text{M} - \text{BF}_4^+]$, 695(10), 433(5). IR (CHCl_3 , cm^{-1}): 1670 ($\text{C}=\text{O}$).

Compound **20-OTf** was obtained from an acetone solution (10 mL) containing 100 mg of compound **10** (0.269 mmol) at -110°C . PPh_3 (71 mg, 0.269 mmol) in acetone (2 mL) was added. The reaction mixture was allowed to warm slowly to room temperature, and AgOTf (69 mg, 0.269 mmol) was added previously dissolved in acetone (2 mL). The amber solution was stirred for 2 h and then filtered. After removal of the volatiles, the oily residue was washed with pentane (3 \times 10

mL) and recrystallized from chloroform/diethyl ether, affording a yellow solid (34 mg) as a mixture of compound **20** and $\text{Cp}^*\text{RhCl}(\text{OTf})(\text{PPh}_3)^{33}$ in a 4.5:1 ratio, respectively.

Synthesis of $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{PPh}_2][\text{OTf}]$ (21**).** The synthesis was carried out similarly as described for **18-OTf** (vide supra), using PPh_2 (51 μL , 0.295 mmol). After removal of the volatiles, the orange-yellow oily solid was dissolved in a minimum amount of acetone, and diethyl ether was added, precipitating a yellow solid that is a mixture (21.6 mg) of compound **21** and $[\text{Cp}^*\text{RhCl}(\text{PPh}_2)_2]^+$ (ratio 1:1.1, respectively). Also compound **21-OTf** was obtained from an acetone solution (10 mL) containing 100 mg of compound **10** (0.269 mmol) at -110°C , and AgOTf (69 mg, 0.269 mmol) was added previously dissolved in acetone (2 mL). The reaction mixture was allowed to warm slowly to room temperature and then stirred for 30 min. The yellow solution was cooled again to -110°C , and 31 μL (0.295 mmol) of PPh_2 was added. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 2 h and filtered. After removal of the volatiles, the oily residue was recrystallized from acetone/diethyl ether, affording an orange-yellow solid that is a mixture of **21** and $[\text{Cp}^*\text{RhCl}(\text{PPh}_2)_2]^+$ (82 mg) in a ratio of 10:1.

Synthesis of $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{MeCN}][\text{PF}_6]$ (22**).** A MeCN solution (10 mL) containing 100 mg of compound **1** (0.175 mmol) was stirred for 1 h at room temperature. The volume of the yellow solution was reduced to ~ 0.5 mL, and diethyl ether was added (20 mL), giving a pale yellow precipitate of **22** in 66% yield (70 mg, 0.12 mmol). Mp: $97\text{--}99^\circ\text{C}$. Crystals suitable for X-ray analysis were deposited at -10°C from acetonitrile solutions. Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{F}_6\text{IrNOP}\cdot\text{MeCN}$: C, 36.86; H, 4.64. Found: C, 36.47; H, 4.68. MS: 467(4) $[\text{M} - \text{PF}_6^+]$, 425(42), 313 (40). IR (CHCl_3 , cm^{-1}): 1677 (C=O).

Synthesis of $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{MeCN}][\text{BF}_4]$ (23**).** The synthesis was carried out similarly as described for **22** (vide supra), using compound **6** (50 mg, 0.12 mmol). A yellow precipitate in 55% yield (30.5 mg, 0.065 mmol) was isolated. Mp: $109\text{--}111^\circ\text{C}$. Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{BF}_4\text{NORh}$: C, 46.68; H, 5.87. Found: C, 46.61; H, 5.63. MS: 376 (<1) $[\text{M} - \text{BF}_4^+]$, 355(100). IR (CHCl_3 , cm^{-1}): 1665 (C=O).

Synthesis of $[\text{Cp}^*\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{H}_2\text{O}][\text{BF}_4]$ (24**).** Compound **24** was obtained from a CH_2Cl_2 solution (0.5 mL) containing 53 mg of compound **6** (0.13 mmol). Diethyl ether (20 mL) was added separately for a crystallization under slow diffusion of the ether on the CH_2Cl_2 solution. Recrystallization at -10°C during 2 days yielded a few red crystals, without a melting point.

Synthesis of $[(\text{Cp}^*\text{Ir})_2(\mu^2\text{-I})_3][\text{PF}_6]$ (25**).** To an acetone solution (10 mL) containing 100 mg of compound **1** (0.175 mmol) at -110°C was added I_2 (44 mg, 0.175 mmol) in acetone (2 mL). The addition resulted in a change in color from amber to brown and then orange. The orange solution was allowed to warm slowly to room temperature and was stirred for 1 h and then filtered. After removal of the volatiles, the oily residue was washed with pentane (2×20 mL) and diethyl ether (1×10 mL). The red solid was dissolved in the minimum amount of nitromethane, and diethyl ether was added, affording an orange precipitate in 71% yield (74 mg, 0.062 mmol), which decomposed at 155°C . Red crystals suitable for X-ray analysis were deposited after slow diffusion of diethyl ether

into a saturated nitromethane solution. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{F}_6\text{I}_3\text{Ir}_2\text{P}$: C, 20.34; H, 2.56. Found: C, 20.47; H, 2.43. MS: 1035(100) $[\text{M} - \text{PF}_6^+]$, 954(10), 908(28).

Synthesis of $[(\text{Cp}^*\text{Rh})_2(\mu^2\text{-I})_3][\text{BF}_4]$ (26**).** The synthesis was carried out similarly as described for **25** (vide supra), using **6-BF₄** (25 mg, 0.06 mmol) and 11.5 mg (0.05 mmol) of I_2 in acetone (2 mL). A red-brown precipitate in 78% yield (22 mg, 0.023 mmol) was isolated. It does not melt until 230°C . MS: 856.9 $[\text{M} - \text{BF}_4^+]$.

Synthesis of $[\text{Cp}^*\text{IrCl}(\mu^2\text{-Cl})_2]$. To an acetone solution (10 mL) containing 100 mg of compound **1** (0.175 mmol) at -78°C was added a heptane solution of SnCl_4 (1 M, 0.35 mL, 0.35 mmol). The addition resulted in a change in color from amber to light yellow and then yellow-brown. The yellow-brown solution was allowed to warm slowly to room temperature and was stirred for 1 h and then filtered. After removal of the volatiles, the oily residue was washed with pentane (3×10 mL) and diethyl ether (1×10 mL). The light yellow solid was dissolved in a minimum amount of nitromethane, and diethyl ether was added, affording an orange precipitate in 79% yield (55 mg, 0.069 mmol), which did not melt below 230°C . Spectroscopic data and physical properties have been previously reported.^{3b}

Synthesis of $[\text{Cp}^*_2\text{Rh}][\text{BF}_4]$. To an acetone solution (10 mL) containing 200 mg of $[\text{Cp}^*\text{RhCl}_2]_2$ (0.32 mmol) at room temperature was added AgBF_4 (252 mg, 1.3 mmol) in acetone (3 mL). The solution was stirred for 15 min under nitrogen atmosphere and AgCl was then filtered. To the yellow filtrate was added dropwise mesityl oxide (90 μL , 0.78 mmol). The solution was then warmed to 50°C and stirred for 105 min. Afterward, the yellow solution was allowed to cool to room temperature, the solvent was reduced, and diethyl ether was added, precipitating $[\text{Cp}^*_2\text{Rh}][\text{BF}_4]$ as a yellow-orange powder in 53% yield (153 mg, 0.34 mmol), which did not melt below 230°C . Spectroscopic and crystallographic data and physical properties have been previously reported.¹⁹

X-ray Structure Determination for **1, **6**, **9**, **10**, **18**, **22**, **24**, and **25**.** Crystal data and experimental details are given in Tables 3 and 6. X-ray data were collected on Enraf-Nonius four-circle or Siemens diffractometers using graphite-monochromated Mo K α ($\lambda = 0.7107 \text{ \AA}$) radiation. Final positional parameters are available as Supporting Information.

Acknowledgment. M.A.P.S. would like to thank Conacyt for financial support through the project 26352-E, as well as for the X-ray diffractometer (No. F0084), and Washington University Mass Spectrometry Research Resource (NIH, No. P41RR0954) for recording some of the mass spectra. I.I.R.S. thanks also Conacyt for a scholarship. Thanks to Marco Antonio Leyva and Ma. Esther Sánchez Castro for helping us with some X-ray diffraction studies. We would like to thank Prof. Peter M. Maitlis for crystallographic data of compound $[\text{Cp}^*\text{Rh}]_2(\mu^2\text{-OPO}_2\text{F}_2)$ and interesting comments.

Supporting Information Available: X-ray complementary data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020400Q