Oxapentadienyl-Iridium-Phosphine Chemistry.[1] Synthesis of Oxygen-Containing Iridacycles via C-H Bond Activation[2]

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The reactions of $(Cl)Ir(PR_3)_3$ (R = Me, Et) with potassium oxapentadienide, potassium 4-methyl-5-oxapentadienide, and potassium 2,4-dimethyl-5-oxapentadienide have been investigated. Treatment of $(Cl)Ir(PMe_3)_3$ with potassium oxapentadienide initially produces ((1,2,5-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (**1**), which rapidly rearranges to ((1,2,3-η)-5-oxapentadienyl)-$Ir(PMe_3)_3$ (**2a**). When refluxed in tetrahydrofuran, **2a** undergoes metal-centered activation of the aldehydic C—H bond (C4—H) to produce the iridacyclopentenone complex *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PMe_3)_3(H)$ (**3**). Treatment of $(Cl)Ir(PEt_3)_3$ with potassium oxapentadienide yields the iridapyran complex *mer*-$\overline{CH{=}CH—CH{=}CH—O—Ir}(PEt_3)_3(H)$ (**4**) via activation of a C—H bond on the C-terminus (C1) of an O-bound η^1-oxapentadienyl ligand. Upon stirring in tetrahydrofuran solution, **4** gradually converts to the iridacyclopentenone complex *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PEt_3)_3(H)$ (**5**). Treatment of $(Cl)Ir(PMe_3)_3$ with potassium 4-methyl-5-oxapentadienide produces ((1,2,5-η)-4-methyl-5-oxapentadienyl)$Ir(PMe_3)_3$ (**6**). However, upon refluxing in tetrahydrofuran, this species undergoes C—H bond activation at C2 of the 4-methyl-5-oxapentadienyl ligand, generating the iridaoxacyclopentene derivative *mer*-$CH_2{=}\overline{C—CH{=}C(Me)—O—Ir}(PMe_3)_3(H)$ (**7**). Treatment of $(Cl)Ir(PEt_3)_3$ with potassium 4-methyl-5-oxapentadienide initially produces the 4-methyliridapyran complex *mer*-$\overline{CH{=}CH—CH{=}C(Me)—O—Ir}(PEt_3)_3(H)$ (**8**) via C1—H bond activation, but in refluxing tetrahydrofuran this species isomerizes to the PEt_3 analogue of **7**, *mer*-$CH_2{=}\overline{C—CH{=}C(Me)—O—Ir}(PEt_3)_3(H)$ (**9**). Finally, treatment of $(Cl)Ir(PMe_3)_3$ or $(Cl)Ir(PEt_3)_3$ with potassium 2,4-dimethyl-5-oxapentadienide, followed by stirring for several days in tetrahydrofuran at room temperature, leads cleanly to the production of the 2,4-dimethyliridapyran complexes *mer*-$\overline{CH{=}C(Me)—CH{=}C(Me)—O—Ir}(PR_3)_3(H)$ ($PR_3 = PMe_3$, **10**; $PR_3 = PEt_3$, **11**). These species undergo no further rearrangements, even upon refluxing in tetrahydrofuran. Molecular structures of ((1,2,3-η)-5-oxapentadienyl)$Ir(PMe_2Ph)_3$ (**2b**), *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PEt_3)_3(H)$ (**5**), and *mer*-$CH_2{=}\overline{C—CH{=}C(Me)—O—Ir}(PEt_3)_3(H)$ (**9**) have been determined by single-crystal X-ray diffraction studies. Crystal structure data for these compounds are as follows: **2b**, triclinic, $P\bar{1}$, $a = 9.506$ (2) Å, $b = 17.219$ (4) Å, $c = 18.546$ (5) Å, $\alpha = 111.14$ (2)°, $\beta = 97.62$ (2)°, $\gamma = 91.49$ (2)°, $V = 2797.4$ (12) Å^3, $Z = 4$, $R = 0.034$ for 6227 reflections with $I > 3\sigma(I)$; **5**, orthorhombic, $Pna2_1$, $a = 15.271$ (4) Å, $b = 11.401$ (3) Å, $c = 15.473$ (4) Å, $R = 0.025$ for 3363 reflections with $I > 3\sigma(I)$; **9**, triclinic, $P\bar{1}$, $a = 9.396$ (2) Å, $b = 10.742$ (2) Å, $c = 15.725$ (5) Å, $\alpha = 77.88$ (2)°, $\beta = 77.52$ (2)°, $\gamma = 68.09$ (2)°, $V = 1423.0$ (6) Å^3, $Z = 2$, $R = 0.018$ for 4299 reflections with $I > 3\sigma(I)$.

Introduction

During the past decade, the chemistry of metal complexes containing the acyclic pentadienyl group has been extensively investigated.[3] Through these studies, it has become evident that pentadienyl is a highly versatile ligand, capable of interacting with metal centers in a variety of hapticities and geometries. In addition, interconversion between these various bonding modes can give rise to interesting dynamic behavior and enhanced reactivity.

In contrast to (pentadienyl)metal chemistry, relatively little effort has been directed toward synthesizing (heteropentadienyl)metal complexes, i.e., species in which one carbon atom of the pentadienyl chain has been replaced by a heteroatom. Like their all-carbon counterparts, heteropentadienyl ligands have the *potential* to bond to metals in a wide variety of modes. However, little is currently known about the relative energetics of these modes. In order to address this issue, we have begun a systematic exploration of the synthesis of (heteropentadienyl)metal complexes, using halo-metal-phosphine

(1) Pentadienyl-Metal-Phosphine Chemistry. 25. Previous papers in this series include: (a) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740. (b) Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, Jr., T. W.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391.

(2) Metallacyclohexadiene and Metallabenzene Chemistry. 8. Previous papers in this series include: (a) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740. (b) Bleeke, J. R.; Bass, L.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213.

(3) For leading reviews, see: (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1251. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

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compounds and anionic heteropentadienide reagents as our building blocks.

Our initial studies have focused on electron-rich heteropentadienyl–iridium (I)–phosphine complexes because these species have a propensity to undergo C–H bond activation, generating novel metallacyclic products.[4] In this paper, we describe the reactions of $(Cl)Ir(PR_3)_3$ (R = Me and Et) precursors with potassium oxapentadienide, potassium 4-methyl-5-oxapentadienide, and potassium 2,4-dimethyl-5-oxapentadienide, which yield (oxapentadienyl)$Ir(PR_3)_3$ complexes as kinetic products. However, these initially-formed species undergo intramolecular, iridium-centered C–H bond activation to produce five- and six-membered iridacycles as the thermodynamic products. The site of C–H bond activation is strongly influenced by the location of the methyl substituents on the oxapentadienyl backbone; hence, these reactions can be *directed* toward a particular metallacyclic product by choosing the appropriate oxapentadienide reagent.

Results and Discussion

A. Oxapentadienide Reagents. While a variety of synthetic approaches to (oxapentadienyl)metal complexes have been explored over the years,[5] *anionic* oxapentadienide reagents have not previously been employed to introduce oxapentadienyl ligands onto transition metal centers. These reagents promise to provide a new general route to (oxapentadienyl)metal complexes via nucleophilic displacement of anionic ligands from metal precursors.

Potassium oxapentadienide, first reported by Heiszwolf and Kloosterziel[6] in 1967, can be readily synthesized by deprotonating crotonaldehyde with potassium amide in liquid ammonia. Analogous treatment of 3-penten-2-one and mesityl oxide with potassium amide in liquid ammonia generates potassium 4-methyl-5-oxapentadienide and potassium 2,4-dimethyl-5-oxapentadienide, respectively, in good yield. All of these reagents can be isolated as microcrystalline powders and have good solubility in tetrahydrofuran. Although quite air-sensitive, they are stable under inert atmosphere for many days.

B. Reaction of $(Cl)Ir(PMe_3)_3$ with Potassium Oxapentadienide. As shown in Scheme I, treatment of $(Cl)Ir(PMe_3)_3$[7] with potassium oxapentadienide in tetrahydrofuran yields ((1,2,5-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (1). The initial formation of 1 strongly suggests that the nucleophilic attack on $(Cl)Ir(PMe_3)_3$ involves the *oxygen end* of the oxapentadienide reagent rather than the carbon

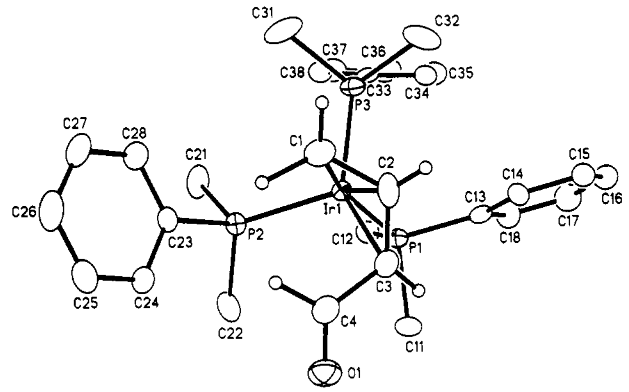
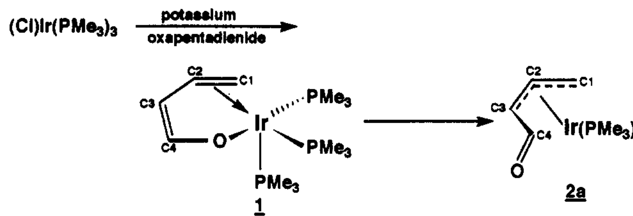


Figure 1. ORTEP drawing of ((1,2,3-η)-5-oxapentadienyl)-$Ir(PMe_2Ph)_3$ (**2b**). This compound crystallizes with two independent molecules in the unit cell. Molecule 1 is shown here.

Scheme I



end.[8] Although the further reactivity of compound 1 precludes its isolation (vide infra), this species has been unambiguously identified from its NMR spectra. Particularly diagnostic are the phosphorus-coupled signals at δ 42.6 and 23.8 in the $^{13}C\{^1H\}$ NMR spectrum, which are due to the metal-coordinated olefin carbons C2 and C1, respectively.[9] The $^{31}P\{^1H\}$ NMR spectrum consists of three doublet-of-doublets patterns.

In solution, 1 quickly (over a period of several hours) rearranges to ((1,2,3-η)-5-oxapentadienyl)$Ir(PMe_3)_3$ (**2a**, Scheme I), in which the oxapentadienyl ligand is bonded in a more-conventional η^3-allyl mode.[10] This transformation probably involves a series of $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization steps (Scheme II). The presence of the free (unbonded) aldehyde group in **2a** is clearly indicated by its ^1H and $^{13}C\{^1H\}$ NMR spectra, which exhibit peaks at δ 7.46 and 173.8 for the aldehyde hydrogen and carbon, respectively. The infrared spectrum shows a characteristic C=O stretch at 1599 cm^{-1}.

Attempts to obtain the X-ray crystal structure of **2a** were stymied by disorder problems. However, crystals of the close analogue ((1,2,3-η)-5-oxapentadienyl)$Ir(PMe_2Ph)_3$ (**2b**) behaved well, and a high-quality structure was obtained (see Figure 1 and Tables I and II). The oxapentadienyl ligand in **2b** is anti and S-shaped; torsional angles C1/C2/C3/C4 and C2/C3/C4/O1 are 19.7 and 179.0°, respectively. As is common for *anti*-η^3-pentadienyl ligands, the aldehyde moiety in **2b** is bent out of the plane of the allyl moiety away from the metal center.[11] Hence, atoms

(4) See, for example, ref 1 and the preliminary account of this work: Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19.

(5) (a) Parshall, G. W.; Wilkinson, G. *Inorg. Chem.* **1962**, *1*, 896. (b) Tsuji, J.; Imamura, S.; Kiji, J. *J. Am. Chem. Soc.* **1964**, *86*, 4491. (c) Bannister, W. D.; Green, M.; Haszeldine, R. N. *J. Chem. Soc. A* **1966**, 194. (d) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1968**, 109. (e) Bennett, R. L.; Bruce, M. I. *Aust. J. Chem.* **1975**, *28*, 1141. (f) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319. (g) Baudry, D.; Daran, J.-C.; Dromzee, Y.; Ephritikhine, M.; Felkin, H.; Jeannine, Y.; Janusz, Z. *J. Chem. Soc., Chem. Commun.* **1983**, 813. (h) Cheng, M.-H.; Wu, Y.-J.; Wang, S.-L.; Liu, R.-S. *J. Organomet. Chem.* **1989**, *373*, 119. (i) Cheng, M.-H.; Cheng, C.-Y.; Wang, S.-L.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 1853. (j) Benyunes, S. A.; Day, J. P.; Green, M.; Al-Saadoon, A. W.; Waring, T. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1416. (k) Benyunes, S. A.; Binelli, A.; Green, M.; Grimshire, M. J. *J. Chem. Soc., Dalton Trans.* **1991**, 895. (l) Schmidt, T.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1427. (m) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1992**, *11*, 1686.

(6) Heiszwolf, G. J.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 807.

(7) Produced in situ by reacting $[(cyclooctene)_2IrCl]_2$ with 6 equiv of PMe_3 in tetrahydrofuran.

(8) Bergman has shown that $XRhL_3$ complexes react with potassium enolates ("oxaallyls") to produce O-bound enolate complexes of rhodium in nearly quantitative yield: Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938.

(9) Very similar signals are observed for the metal-coordinated olefin carbons in the pentadienyl analogue of 1, ((1,2,5-η)-pentadienyl)$Ir(PMe_3)_3$,[1b] and in the thiapentadienyl analogue of 1, ((1,2,5-η)-5-thiapentadienyl)$Ir(PMe_3)_3$.[1a]

(10) For other examples of ((1,2,3-η)-5-oxapentadienyl)metal complexes, see refs 5a–d,h–k.

Scheme II

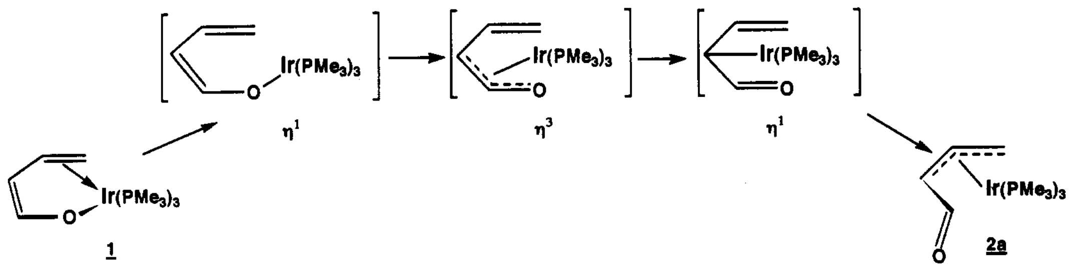


Table I. Atomic Coordinates (×10⁴) with Estimated Standard Deviations for Non-Hydrogen Atoms in ((1,2,3-η)-5-Oxapentadienyl)Ir(PMe₂Ph)₃ (2b)[a]

molecule 1				molecule 2			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ir1	3519 (1)	6312 (1)	2595 (1)	Ir2	127 (1)	1278 (1)	2534 (1)
P1	1912 (2)	7293 (1)	2691 (1)	P4	1811 (2)	2299 (1)	2636 (1)
P2	5035 (3)	6989 (1)	3758 (1)	P5	−675 (3)	1918 (1)	3723 (1)
P3	4554 (3)	6512 (2)	1649 (2)	P6	−1471 (3)	1485 (2)	1627 (2)
O1	1799 (9)	5788 (6)	4074 (5)	O2	2663 (9)	761 (5)	3990 (5)
C1	4263 (12)	5074 (6)	2301 (7)	C71	−774 (11)	13 (6)	2192 (7)
C2	2722 (11)	5062 (5)	2111 (6)	C72	646 (12)	35 (5)	1993 (6)
C3	1955 (10)	5394 (6)	2738 (6)	C73	1743 (11)	408 (5)	2650 (7)
C4	2478 (12)	5508 (6)	3530 (7)	C74	1679 (13)	470 (7)	3437 (7)
C11	664 (11)	7331 (7)	3374 (6)	C41	3455 (10)	2354 (7)	3295 (6)
C12	2519 (10)	8381 (5)	3016 (6)	C42	1381 (10)	3388 (5)	2989 (5)
C13	637 (9)	7124 (6)	1803 (5)	C43	2599 (9)	2212 (5)	1753 (5)
C14	278 (10)	6321 (6)	1279 (5)	C44	2540 (10)	1430 (6)	1154 (6)
C15	−683 (11)	6163 (7)	594 (6)	C45	3171 (11)	1350 (7)	506 (6)
C16	−1282 (11)	6799 (9)	438 (7)	C46	3851 (10)	2019 (7)	435 (6)
C17	−958 (12)	7609 (8)	958 (7)	C47	3953 (11)	2774 (6)	1036 (6)
C18	−6 (11)	7770 (7)	1628 (6)	C48	3332 (10)	2871 (6)	1676 (6)
C21	6349 (10)	7821 (6)	3836 (7)	C51	693 (11)	2436 (6)	4569 (5)
C22	4216 (12)	7513 (7)	4606 (6)	C52	−1889 (12)	2756 (6)	3847 (6)
C23	6172 (9)	6299 (5)	4082 (5)	C53	−1677 (9)	1208 (5)	4045 (5)
C24	5840 (10)	6006 (6)	4651 (6)	C54	−3064 (10)	943 (6)	3727 (6)
C25	6719 (12)	5470 (7)	4875 (6)	C55	−3827 (12)	412 (7)	3975 (7)
C26	7891 (13)	5230 (7)	4555 (7)	C56	−3184 (14)	158 (6)	4550 (7)
C27	8224 (11)	5508 (7)	3992 (7)	C57	−1800 (13)	415 (7)	4863 (7)
C28	7377 (10)	6037 (6)	3747 (6)	C58	−1053 (11)	937 (6)	4620 (6)
C31	6440 (12)	6358 (9)	1689 (9)	C61	−1326 (14)	817 (6)	631 (6)
C32	3862 (15)	5758 (7)	661 (6)	C62	−3325 (11)	1203 (8)	1634 (8)
C33	4500 (9)	7497 (6)	1495 (5)	C63	−1574 (9)	2517 (6)	1552 (5)
C34	3389 (11)	7652 (7)	1018 (6)	C64	−808 (11)	2756 (6)	1084 (6)
C35	3268 (13)	8424 (8)	963 (7)	C65	−840 (13)	3548 (7)	1073 (7)
C36	4261 (13)	9043 (7)	1363 (7)	C66	−1653 (12)	4112 (8)	1520 (7)
C37	5375 (13)	8935 (7)	1833 (7)	C67	−2430 (12)	3895 (7)	1995 (7)
C38	5510 (11)	8155 (7)	1900 (6)	C68	−2406 (10)	3095 (7)	2000 (6)

[a] Compound **2b** crystallized with two independent molecules in the unit cell.

C4 and O1 lie 0.40 and 0.41 Å, respectively, out of the C1/C2/C3 plane. Perhaps the most interesting structural feature of the η^3-oxapentadienyl ligand is the shortness of the bond between C3 and C4 (1.428 (16) and 1.434 (19) Å in the two independent molecules). This short bond distance suggests that despite the coordination of iridium to an allylic moiety, the η^3-oxapentadienyl ligand still retains substantial π-electron delocalization.[12] The C–O distance (1.225 (15) and 1.236 (14) Å in the two independent molecules) is just slightly longer than a "normal" carbon–oxygen double bond (1.20 Å).[13]

At room temperature, compound **2a** undergoes a fluxional process that exchanges the three phosphine ligands, causing the $^{31}P\{^1H\}$ NMR signal to appear as a singlet at 25 °C. However, as the compound is cooled to −80 °C, the exchange process is stopped, and the $^{31}P\{^1H\}$ NMR spectrum decoalesces to three well-separated doublet-of-doublets patterns. The most likely mechanism for this dynamic process is simple rotation of the η^3-oxapentadienyl ligand with respect to the $Ir(PMe_3)_3$ moiety (Scheme III).[14] Under this process, the three phosphine ligands would take turns beneath the "open mouth" of the η^3-oxapentadienyl ligand.

In solution, compound **2a** gradually undergoes metal-centered activation of the aldehydic C—H bond (C4—H) to produce the iridacyclopentenone complex *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PMe_3)_3(H)$ (**3**, Scheme IV).[15] This conversion takes many days in tetrahydrofuran at room temperature but occurs much more rapidly in refluxing tetrahydrofuran. Mechanistically, this reaction probably

(11) See, for example: (a) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026. (b) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422. (c) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Organometallics* **1988**, *7*, 33.

(12) Similar effects have been observed in (*anti*-η^3-pentadienyl)metal complexes: (a) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Organometallics* **1988**, *7*, 33. (b) Lee, G.-H.; Peng, S.-M.; Liu, F.-C.; Mu, D.; Liu, R.-S. *Organometallics* **1989**, *8*, 402.

(13) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; Appendix E (see also references therein).

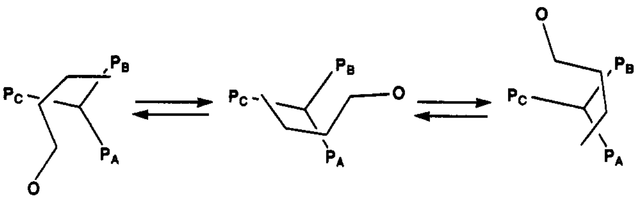
(14) Rotational barriers for η^3-allyl ligands are typically quite low. See: Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, England, 1982; Vol. 3, pp 60–67.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for ((1,2,3-η)-5-Oxapentadienyl)Ir(PMe$_2$Ph)$_3$ (2b)[a]

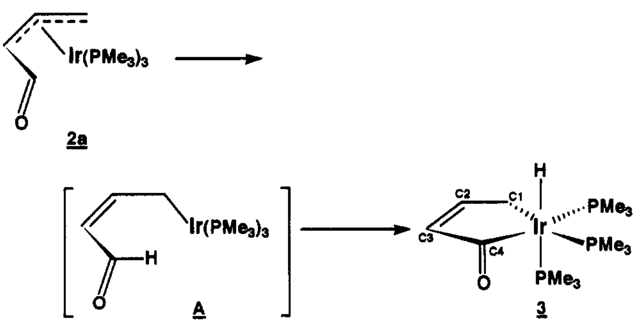
molecule 1		molecule 2	
	Bond Distances		
Ir1–P1	2.282 (2)	Ir2–P4	2.285 (2)
Ir1–P2	2.316 (2)	Ir2–P5	2.323 (2)
Ir1–P3	2.245 (3)	Ir2–P6	2.246 (3)
Ir1–C1	2.164 (10)	Ir2–C71	2.155 (10)
Ir1–C2	2.088 (8)	Ir2–C72	2.113 (9)
Ir1–C3	2.250 (11)	Ir2–C73	2.218 (10)
C1–C2	1.458 (15)	C71–C72	1.449 (16)
C2–C3	1.405 (15)	C72–C73	1.431 (13)
C3–C4	1.428 (16)	C73–C74	1.434 (19)
C4–O1	1.225 (15)	C74–O2	1.236 (14)
	Bond Angles		
P1–Ir1–P2	99.3 (1)	P4–Ir2–P5	98.7 (1)
P1–Ir1–P3	96.7 (1)	P4–Ir2–P6	97.1 (1)
P2–Ir1–P3	106.6 (1)	P5–Ir2–P6	106.1 (1)
P1–Ir1–C1	157.2 (3)	P4–Ir2–C71	155.6 (3)
P2–Ir1–C1	99.1 (3)	P5–Ir2–C71	101.4 (3)
P3–Ir1–C1	90.9 (4)	P6–Ir2–C71	90.6 (3)
P1–Ir1–C2	117.1 (3)	P4–Ir2–C72	116.0 (3)
P2–Ir1–C2	128.2 (3)	P5–Ir2–C72	129.9 (3)
P3–Pr1–C2	104.4 (3)	P6–Ir2–C72	104.4 (3)
P1–Ir1–C3	93.6 (3)	P4–Ir2–C73	93.0 (3)
P2–Ir1–C3	110.4 (3)	P5–Ir2–C73	109.8 (3)
P3–Ir1–C3	139.3 (3)	P6–Ir2–C73	140.7 (3)
C1–Ir1–C2	40.1 (4)	C71–Ir2–C72	39.7 (4)
C1–Ir1–C3	67.3 (4)	C71–Ir2–C73	67.3 (4)
C2–Ir1–C3	37.6 (4)	C72–Ir2–C73	38.5 (4)
C1–C2–C3	117.4 (9)	C71–C72–C73	114.5 (9)
C2–C3–C4	124.4 (9)	C72–C73–C74	125.9 (10)
C3–C4–O1	124.2 (10)	C73–C74–O2	124.9 (12)

[a] Compound **2b** crystallized with two independent molecules in the unit cell.

Scheme III



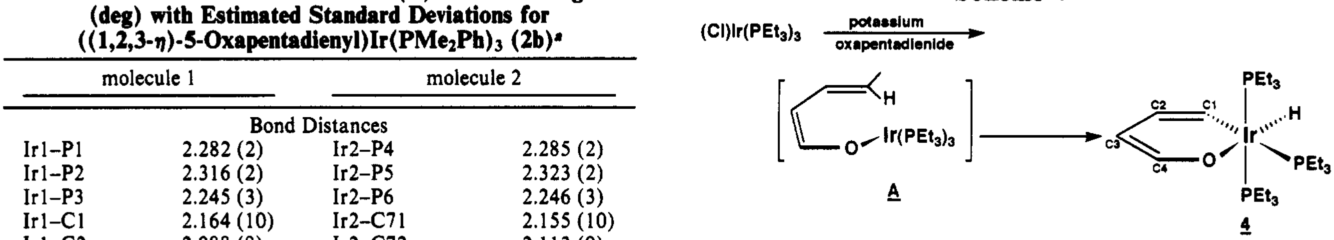
Scheme IV



involves the 16e η^1-oxapentadienyl species (A, Scheme IV) as the key intermediate.[16]

The facial arrangement of the phosphine ligands in **3** is clear from the $^{31}P\{^1H\}$ NMR spectrum, which exhibits three separate signals for the three inequivalent phosphines. In the $^{13}C\{^1H\}$ NMR spectrum, olefin carbons C2 and C3 resonate far downfield (at δ 161.6 and 152.1, respectively), while the signal for methylene carbon C1 appears at δ 10.2 and is a doublet of triplets, due to strong coupling (J = 65.5 Hz) to the trans phosphorus and much weaker coupling (J = 4.3 Hz) to the two cis ^{31}P nuclei. The hydride ligand also resides trans to a phosphine ligand

Scheme V



and exhibits a characteristically strong trans H–P coupling (J_{H-P} = 128.9 Hz). Its chemical shift position in the ^1H NMR is δ −11.19.[17]

C. Reaction of (Cl)Ir(PEt$_3$)$_3$ with Potassium Oxapentadienide. As shown in Scheme V, treatment of (Cl)-Ir(PEt$_3$)$_3$[18] with potassium oxapentadienide yields the iridapyran complex *mer*-CH=CH—CH=CH—O—Ir-(PEt$_3$)$_3$(H) (**4**).[19] Although no intermediates are observed by NMR, this reaction probably proceeds through the 16e oxygen-bound η^1-oxapentadienyl species (A, Scheme V), which can undergo intramolecular oxidative addition across the sp^2 C—H bond on the chain terminus (C1—H). The X-ray crystal structure of **4**, which we reported earlier,[4] exhibits an essentially planar six-membered ring with alternating C—C bond lengths. The ring C—O bond, formally a carbon—oxygen single bond, is unusually short (1.317 (6) Å) and may reflect some participation by an oxygen lone pair in ring π-bonding. The sum of the internal angles in the six-membered ring is 719.7°, very close to the theoretical value of 720°. However, in order to compensate for the relatively small O—Ir—C1 angle (90.7°) which is dictated by the long Ir—O and Ir—C1 bonds, the other five internal angles expand to values greater than 120° (range = 122.3–129.6°; average = 125.8°).[20] These expanded internal angles introduce substantial strain into the ring system.

Compound **4** adopts an octahedral coordination geometry in which the hydride ligand resides cis to C1 (the carbon to which it was originally bonded) and trans to the ring oxygen atom. The phosphines fill the remaining coordination sites, adopting a *mer* arrangement. Due to the planarity of the metallacycle, the two trans-diaxial phosphines are equivalent and give rise to a doublet in the $^{31}P\{^1H\}$ NMR spectrum, while the unique equatorial phosphine appears as a triplet.

(15) For other examples of complexes containing the metallacyclopentenone ring skeleton, see: (a) Huffman, M. A.; Liesbeskind, L. S.; Pennington, W. T., Jr. *Organometallics* **1990**, *9*, 2194. (b) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368. (c) Navarre, D.; Rudler, H.; Daran, J. C. *J. Organomet. Chem.* **1986**, *314*, C34. (d) Cotton, F. A.; Troup, J. M.; Billups, W. E.; Lin, L. P.; Smith, C. V. *J. Organomet. Chem.* **1975**, *102*, 345.

(16) Similar $\eta^3 \rightarrow \eta^1$ isomerizations are common in (allyl)metal chemistry: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 175–181.

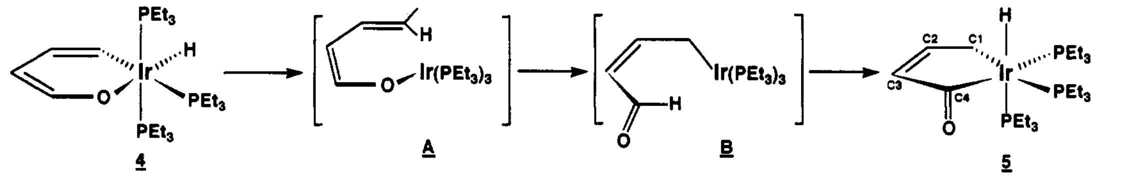
(17) The structure of **3** has been confirmed by X-ray crystallography: see ref 4.

(18) Produced in situ by reacting [(cyclooctene)$_2$IrCl]$_2$ with 6 equiv of PEt$_3$ in tetrahydrofuran.

(19) The metallapyran ring skeleton is extremely rare. For a recent report of a zirconium-based metallapyran, see: Erker, G.; Petrenz, R. *J. Chem. Soc., Chem. Commun.* **1989**, 345. Related to these complexes are the cyclometalated *o*-phenylphenoxide systems to Rothwell. See, for example: (a) Kerschner, J. L.; Rothwell, I. P.; Hoffman, J. C.; Streib, W. E. *Organometallics* **1988**, *7*, 1871. (b) Steffey, B. D.; Chamberlain, L. R.; Chesnut, R. W.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1419.

(20) Even the formally sp^3 oxygen center exhibits an internal angle (Ir–O–C4) of 122.3°.

Scheme VI



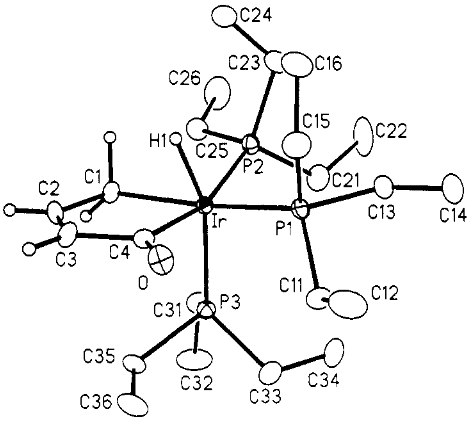


Figure 2. ORTEP drawing of *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PEt_3)_3(H)$ (5).

In the $^{13}C\{^1H\}$ NMR spectrum of 4, C1 gives rise to a doublet-of-triplets pattern at δ 117.3. As in compound 3 (vide supra), the strong doublet coupling (J = 76.9 Hz) is due to the trans phosphorus atom, while the weaker triplet coupling (J = 16.4 Hz) is due to the two cis ^{31}P nuclei. The remaining ring carbons, C2, C3, and C4, resonate at δ 122.4, 99.7, and 149.6, respectively, in the $^{13}C\{^1H\}$ NMR spectrum. These chemical shifts reflect the distribution of charge in the ring. C4, which resides α to the oxygen atom, experiences a strong inductive effect and is the most positive ring carbon. On the other hand, C3 is the most negative ring carbon due to resonance effects involving the oxygen lone pairs.[21] In the ^1H NMR, the hydride ligand resonates at δ −24.94, far upfield from the hydride position in 3 (δ −11.19). This high field shift apparently results from the hydride's trans relationship to the electronegative oxygen center in 4.

When stirred in tetrahydrofuran solution, compound 4 very slowly converts to the iridacyclopentenone complex *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PEt_3)_3(H)$ (5). At room temperature, this conversion takes several days. Although no intermediates can be detected, we propose that this reaction proceeds via a series of steps closely analogous to those outlined above for the tris(PMe_3) system. As shown in Scheme VI, hydride migration back to C1 would produce oxygen-bound η^1-oxapentadienyl species A. Isomerization to carbon-bound η^1-oxapentadienyl species B (via a series of $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ shifts), followed by oxidative addition of the aldehydic C—H bond, would yield the observed iridacycle 5.

The structure of 5 has been confirmed by X-ray crystallography (see Figure 2 and Tables III and IV). The coordination geometry of the compound is octahedral, with the three phosphine ligands situated in a facial arrangement. The five-membered ring is essentially planar and shows the expected alternation in C–C bond lengths. The sum of the internal angles around the ring is 539.9°, very close to the theoretical value of 540°. Unlike 4 (vide supra), most of the internal angles in 5 closely approximate their ideal values; only C3–C4–Ir deviates significantly from the ideal (112.6° vs a theoretical value of 120°). This reduction in ring strain is probably a major driving force for the conversion of 4 to 5. The hydride ligand, which was located in the electron difference maps but not refined, lies at a position 1.462 Å from the iridium center. It bends

Table III. Atomic Coordinates (×10⁴) with Estimated Standard Deviations for Non-Hydrogen Atoms in *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PEt_3)_3(H)$ (5)

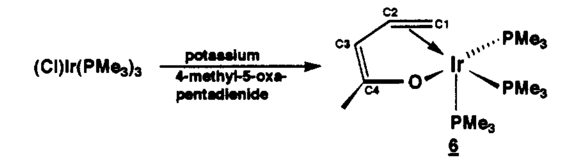
atom	x	y	z
Ir	7746 (1)	8741 (1)	0
P1	6671 (2)	9488 (2)	−922 (2)
P2	8766 (1)	10311 (2)	−68 (3)
P3	7156 (1)	9064 (2)	1391 (1)
O	6448 (4)	6901 (6)	−497 (4)
C1	8718 (6)	7678 (8)	618 (6)
C2	8415 (6)	6430 (7)	607 (6)
C3	7664 (6)	6153 (8)	239 (6)
C4	7137 (5)	7136 (7)	−135 (7)
C11	5524 (6)	9250 (9)	−564 (6)
C12	4841 (7)	8917 (12)	−1232 (8)
C13	6683 (7)	11059 (9)	−1176 (7)
C14	5978 (9)	11557 (12)	−1781 (10)
C15	6672 (7)	8816 (10)	−2007 (6)
C16	7473 (7)	9074 (12)	−2551 (7)
C21	8416 (8)	11795 (9)	329 (8)
C22	8769 (8)	12881 (8)	−76 (13)
C23	9214 (7)	10621 (9)	−1133 (7)
C24	9728 (7)	9639 (10)	−1513 (7)
C25	9785 (6)	10077 (9)	550 (7)
C26	10496 (7)	10948 (10)	511 (10)
C31	7925 (6)	9748 (10)	2165 (6)
C32	7656 (8)	9903 (14)	3093 (7)
C33	6136 (7)	9871 (10)	1608 (6)
C34	6169 (11)	11160 (10)	1411 (10)
C35	6892 (6)	7704 (9)	1997 (6)
C36	6045 (7)	7094 (10)	1718 (7)

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for *fac*-$\overline{CH_2—CH{=}CH—C(O)—Ir}(PEt_3)_3(H)$ (5)

Bond Distances			
Ir–P1	2.336 (2)	C1–C2	1.496 (12)
Ir–P2	2.376 (2)	C2–C3	1.319 (13)
Ir–P3	2.363 (2)	C3–C4	1.496 (12)
Ir–C1	2.141 (9)	C4–O	1.223 (10)
Ir–C4	2.062 (8)		
Bond Angles			
P1–Ir–P2	99.1 (1)	Ir–C1–C2	108.5 (6)
P1–Ir–P3	103.4 (1)	C1–C2–C3	120.1 (8)
P2–Ir–P3	100.0 (1)	C2–C3–C4	117.0 (8)
P1–Ir–C1	165.1 (2)	C3–C4–O	118.4 (7)
P1–Ir–C4	86.8 (2)	C3–C4–Ir	112.6 (6)
P2–Ir–C1	89.5 (2)	O–C4–Ir	129.0 (6)
P2–Ir–C4	163.6 (2)		
P3–Ir–C1	86.9 (2)		
P3–Ir–C4	93.4 (3)		
C1–Ir–C4	81.7 (3)		

(21) For a discussion of inductive effects vs resonance effects, see: Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1973; pp 358–368.

Scheme VII



toward the ring (and away from the bulky phosphines), making a P3–Ir–H angle of 155.0°.

D. Reaction of (Cl)Ir(PMe$_3$)$_3$ with Potassium 4-Methyl-5-oxapentadienide. As shown in Scheme VII, treatment of (Cl)Ir(PMe$_3$)$_3$[7] with potassium 4-methyl-5-oxapentadienide produces ((1,2,5-η)-4-methyl-5-oxapentadienyl)Ir(PMe$_3$)$_3$ (**6**). Unlike its unmethylated analogue (compound **1**), **6** is stable enough to be isolated and fully characterized. In the ^{13}C{^{1}H} NMR spectrum of **6**, uncoordinated carbons C4 and C3 appear in the downfield region at δ 164.0 and 103.6, respectively. Coordinated carbons C2 and C1 resonate upfield at δ 40.9 and 23.5, respectively, and are doublets due to phosphorus coupling. The ^{31}P{^{1}H} NMR spectrum exhibits three doublet-of-doublets patterns, as expected for the three inequivalent PMe$_3$ ligands.

Upon stirring in tetrahydrofuran, **6** gradually undergoes intramolecular C—H bond activation. Since the 4-methyl-5-oxapentadienyl ligand is methylated at C4, activation at this site is prevented. Instead, activation occurs at C1 and C2, with the ultimate thermodynamic product being the C2 activation product *mer*-CH$_2$=C—CH=C(Me)—O—Ir(PMe$_3$)$_3$(H) (**7**, Scheme VIII).

NMR monitoring of the reaction solution during the conversion of **6** to **7** shows the presence of ((1,2,3-η)-4-methyl-5-oxapentadienyl)Ir(PMe$_3$)$_3$ (A, Scheme VIII), together with two *kinetic* C—H bond activation products, the *mer*-iridapyran complex, *mer*-CH=CH—CH=C(Me)—O—Ir(PMe$_3$)$_3$(H) (B, Scheme VIII), and the *fac*-iridaoxacyclopentene complex, *fac*-CH$_2$=C—CH=C(Me)—O—Ir(PMe$_3$)$_3$(H) (C, Scheme VIII). Species B and C, which arise from C1—H and C2—H activation, respectively, exhibit very characteristic signals in the hydride and downfield regions of the ^{1}H NMR spectrum.[22] However, these signals gradually disappear as B and C are converted to the thermodynamically-favored *mer* isomer of the five-membered ring compound **7**.[23]

In the ^{13}C{^{1}H} NMR spectrum of **7**, C4 appears farthest downfield (δ 173.8), followed by C2 (δ 162.0), C3 (δ 113.2), and C1 (δ 107.1). As discussed earlier for compound **4**, these shifts reflect the charge distribution in the metallacycle; C4 is the most positive carbon, while exocyclic carbon C1 is the most negative.[24] C2 exhibits the characteristic doublet-of-triplets pattern, due to its strong coupling to the trans phosphorus and weaker coupling to the two cis ^{31}P nuclei. In the ^{1}H NMR spectrum, the hydride ligand resonates at δ −22.95 and is a triplet of doublets (J = 18.6 Hz, 11.0 Hz) due to phosphorus coupling. Compound **7** possesses mirror plane symmetry; hence, the trans-diaxial phosphines are equivalent and appear as a doublet in the ^{31}P{^{1}H} NMR spectrum, while the unique equatorial phosphine appears as a triplet.

E. Reaction of (Cl)Ir(PEt$_3$)$_3$ with Potassium 4-Methyl-5-oxapentadienide. As shown in Scheme IX, treatment of (Cl)Ir(PEt$_3$)$_3$[18] with potassium 4-methyl-5-oxapentadienide generates the 4-methyliridapyran complex *mer*-CH=CH—CH=C(Me)—O—Ir(PEt$_3$)$_3$(H) (**8**). This reaction parallels that of (Cl)Ir(PEt$_3$)$_3$ with unmethylated oxapentadienide (cf., Scheme V), and the NMR spectra of **8** bear a close resemblance to those of the unmethylated iridapyran, **4**. Upon stirring in tetrahydrofuran, **8** is gradually converted to the iridaoxacyclopentene complex *mer*-CH$_2$=C—CH=C(Me)—O—Ir(PEt$_3$)$_3$(H) (**9**, Scheme X). While the conversion proceeds slowly at room temperature, it is complete in 2 h in refluxing THF. Mechanistically, this reaction probably involves hydride migration back to C1, generating the oxygen-bound η^1-4-methyl-5-oxapentadienyl species A (see Scheme X). Rotation about C2—C3 then places the C2—H bond into a position where it is activated by the iridium center, generating **9**.

The solid-state structure of **9** has been confirmed by single-crystal X-ray diffraction (see Figure 3 and Tables V and VI). As expected, the phosphines adopt a meridional geometry, while the hydride (which was located and refined) resides in the ring plane, cis to C2 and trans to O. The metallacycle is planar to within 0.01 Å and exhibits the expected alternation in C–C bond lengths. One surprise is the shortness of the C4–O bond, which is formally a carbon–oxygen single bond (1.322 (6) Å).[13] As in **4** (vide supra), this shortness may reflect some participation by an oxygen lone pair in ring π-bonding. Ring strain in **9** is less severe than in the six-membered ring of **4**. The sum of the five internal angles in the ring is 539.9° (theoretical value = 540°), with internal angle Ir–C2–C3 showing the only significant deviation from its ideal value (108.0° vs ideal of 120°). The NMR spectra of **9** closely resemble those of **7**, its tris(PMe$_3$) analogue.

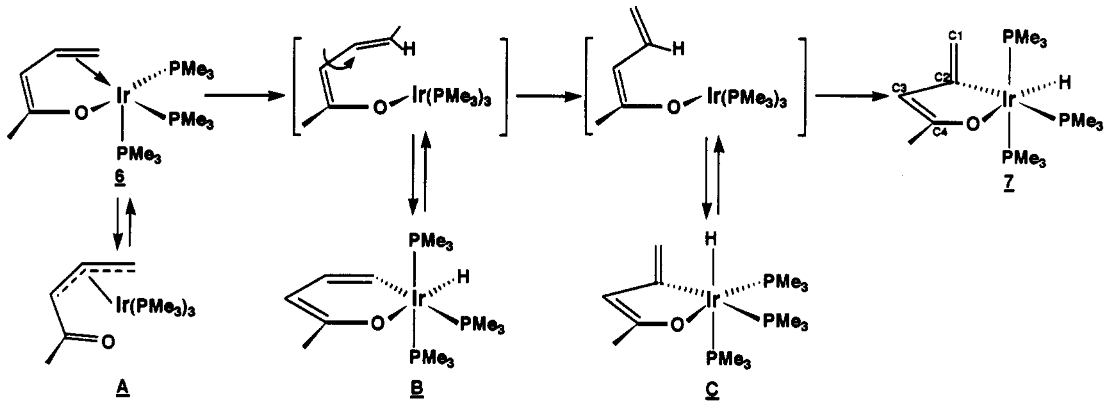
F. Reactions of (Cl)Ir(PMe$_3$)$_3$ and (Cl)Ir(PEt$_3$)$_3$ with Potassium 2,4-Dimethyl-5-oxapentadienide. As shown in Scheme XI, treatment of (Cl)Ir(PMe$_3$)$_3$[7] with potassium 2,4-dimethyl-5-oxapentadienide in THF leads ultimately to the production of the dimethyliridapyran complex *mer*-CH=C(Me)—CH=C(Me)—O—Ir(PMe$_3$)$_3$-(H) (**10**). In this system, C—H bond activation at both C2 and C4 is prevented by the presence of methyl groups, so the six-membered iridacycle is the thermodynamic product. NMR monitoring of the reaction indicates that the oxapentadienide salt reacts quickly with the iridium precursor, producing a complex mixture of oxapentadienyl-containing iridium species. From the NMR spectra of the mixture, the major species present appear to be ((1,2,5-η)-2,4-dimethyl-5-oxapentadienyl)Ir(PMe$_3$)$_3$ (A, Scheme

(22) (a) ^{1}H NMR of *mer*-CH=CH—CH=C(Me)—O—Ir(PMe$_3$)$_3$(H) (B, Scheme VIII) (C$_6$D$_6$, 22 °C, selected peaks): δ 7.05 (m, 1, H2), 6.80 (m, 1, H1), 4.86 (d, 1, H3), −23.9 (t of d, J_{H-P} = 18.0, 9.0 Hz, 1, Ir—H). (b) ^{1}H NMR of *fac*-CH$_2$=C—CH=C(Me)—O—Ir(PMe$_3$)$_3$(H) (C, Scheme VIII) (C$_6$D$_6$, 22 °C, selected peaks): δ 5.74 (br d, 1, H1), 5.55 (d, 1, H3), 4.32 (m, 1, H1), −10.12 (d of t, J_{H-P} = 160.4, 20.5 Hz, 1, Ir—H).

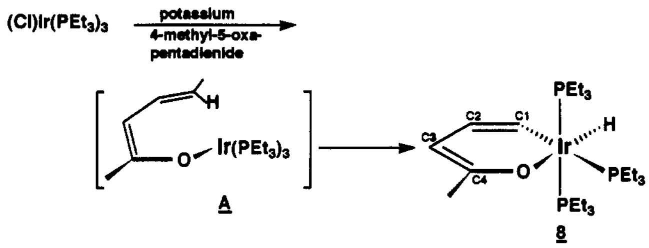
(23) The metallaoxacyclopentene ring skeleton with an exocyclic double bond at the α-ring carbon is quite rare. See: (a) Hermann, W. A.; Steffl, I.; Ziegler, M. L.; Weidenhammer, K. *Chem. Ber.* **1979**, *112*, 1731. (b) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergmann, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (c) Strecker, B.; Zeier, B.; Schulz, M.; Wolf, J.; Werner, H. *Chem. Ber.* **1990**, *123*, 1787.

(24) This distribution of charge is consistent with the observation that protonation of **7** occurs cleanly at the exocyclic methylene carbon, C1: Bleeke, J. R.; New, P. R. To be published.

Scheme VIII



Scheme IX



XI), ((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)Ir(PMe_3)$_3$ (B, Scheme XI), and *fac*-CH=C(Me)—CH=C(Me)—O—Ir(PMe_3)$_3$(H) (C, Scheme XI),[25] as well as **10**. However, over the course of several days, all of the NMR peaks except for those due to **10** gradually decrease in intensity and finally disappear altogether. Compound **10** is then isolated in good yield.

Treatment of (Cl)Ir(PEt_3)$_3$[18] with potassium 2,4-dimethyl-5-oxapentadienide in THF also leads to the generation of a dimethyliridapyran complex *mer*-CH=C(Me)—CH=C(Me)—O—Ir(PEt_3)$_3$(H) (**11**, Scheme XII). NMR monitoring of the reaction in this case indicates a slower reaction of oxapentadienide with the iridium precursor and an absence of intermediate (oxapentadienyl)iridium species. Hence, NMR spectra taken during the course of the reaction exhibit *only* the peaks due to unreacted (Cl)Ir(PEt_3)$_3$ and those due to the final product, *mer*-CH=C(Me)—CH=C(Me)—O—Ir(PEt_3)$_3$(H) (**11**).

The NMR spectra of **10** and **11** are very similar to those described earlier for iridapyrans **4** and **8**. In each case, the $^{31}P\{^1H\}$ NMR spectrum consists of a doublet and a triplet, indicating a *mer* arrangement of the phosphines and a planar metallacycle. In the ^1H NMR, the hydride appears at high field (δ −23.74 in **10** and δ −24.46 in **11**), due to its trans relationship to the electronegative oxygen center, and exhibits rather weak H–P coupling ($J_{H-P} < 30$ Hz), as a result of its cis orientation to the three phosphines. In the $^{13}C\{^1H\}$ NMR spectra of both **10** and **11**, ring carbon C1 gives rise to the characteristic doublet-of-triplets pattern. The strong doublet coupling (J = 76.5 Hz for **10** and 75.3 Hz for **11**) is due to the trans phosphorus atom, while the weaker triplet coupling is due to the two cis ^{31}P nuclei. In both **10** and **11**, the most downfield ring carbon atom is C4, followed by C2, C1, and C3, suggesting that C4 is the most positive ring carbon while C3 is the most negative.[26]

Unlike compounds **4** and **8**, compounds **10** and **11** undergo no further rearrangements, even upon refluxing in tetrahydrofuran.

Conclusion

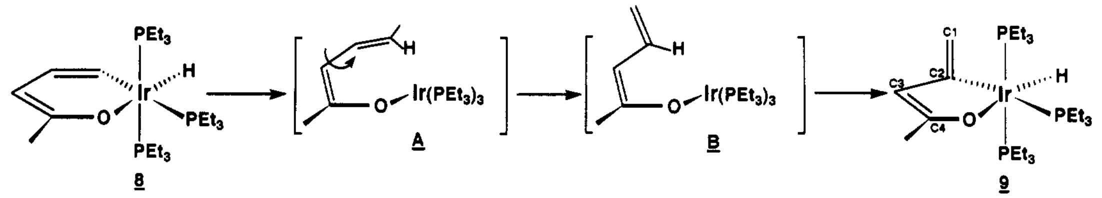
The reactions of (Cl)Ir(PR_3)$_3$ (P = PMe_3 and PEt_3) reagents with potassium oxapentadienide, potassium 4-methyl-5-oxapentadienide, and potassium 2,4-dimethyl-5-oxapentadienide have been investigated. In the PMe_3 systems, the *kinetically*-formed products are (η^3-oxapentadienyl)Ir(PMe_3)$_3$ complexes. Species containing two different η^3 bonding modes, the (1,2,5-η)-5-oxapentadienyl mode and the (1,2,3-η)-5-oxapentadienyl mode, have been characterized. In contrast, the *kinetic* products in the PEt_3 systems are iridaoxacyclohexadiene (iridapyran) complexes, generated via C–H bond activation on the oxapentadienyl C-terminus. Apparently, the steric bulk of the PEt_3 ligands destabilizes the interaction between iridium and the oxapentadienyl π-bonds, allowing oxidative addition to occur from 16e (η^1-oxapentadienyl)Ir(PEt_3)$_3$ intermediates.

Although the kinetic products differ in the PMe_3 and PEt_3 systems, the final *thermodynamic* products are identical (see Scheme XIII). In each case, metallacycles are obtained via C–H bond activation, and the *site* of activation is determined by the pattern of methyl substitution on the oxapentadienyl chain. In the unmethylated oxapentadienyl reaction systems, iridacyclopentenones are generated via activation of the aldehydic hydrogen on the carbon adjacent to oxygen (C4). These reactions appear to be driven by the favorable thermodynamics of forming five-membered rings and carbon–oxygen double bonds. In the 4-methyl-5-oxapentadienyl systems, the carbon adjacent to oxygen bears a methyl group. Therefore, aldehydic bond activation is shut down and C–H activation occurs instead at C2, generating iridaoxacyclopentene derivatives. Again, in this case, the stability of five-membered rings (as compared to six-membered rings) appears to be an important driving force. Finally, in the 2,4-dimethyloxapentadienyl systems, activation at both C2 and C4 is prevented by the presence

(25) The ^1H NMR spectrum of *fac*-CH=C(Me)—CH=C(Me)—O—Ir(PMe_3)$_3$(H) (C, Scheme XI) is very characteristic. ^1H NMR (C_6D_6, 22 °C, selected peaks): δ 6.38 (br m, 1, H1), 4.95 (s, 1, H3), −9.60 (d of t, J_{H-P} = 195, 20 Hz, 1, Ir—H).

(26) Consistent with this charge distribution is the observation that protonation of **10** or **11** occurs cleanly at C3: Bleeke, J. R.; Haile, T. To be published.

Scheme X



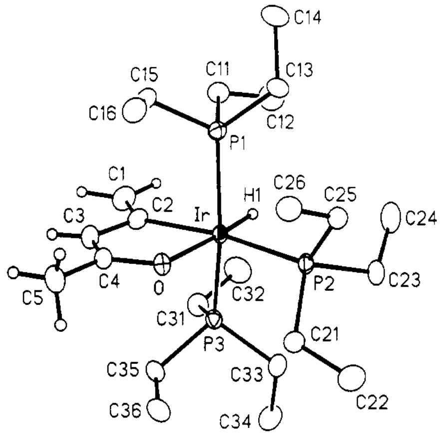


Figure 3. ORTEP drawing of *mer*-CH_2=C—CH=C-(Me)—O—Ir($(PEt_3)_3$)(H) (9).

Table V. Atomic Coordinates (×10[4]) with Estimated Standard Deviations for Non-Hydrogen Atoms in *mer*-CH_2=C—CH=C(Me)—O-Ir($(PEt_3)_3$)(H) (9)

atom	*x*	*y*	*z*
Ir	1491 (1)	2662 (1)	2652 (1)
P1	−490 (1)	4244 (1)	3436 (1)
P2	100 (1)	2195 (1)	1755 (1)
P3	3748 (1)	828 (1)	2398 (1)
O	2071 (3)	4067 (2)	1547 (2)
C1	3359 (6)	2992 (5)	3986 (3)
C2	2927 (4)	3291 (4)	3198 (3)
C3	3481 (5)	4264 (4)	2517 (3)
C4	3002 (4)	4609 (4)	1731 (3)
C5	3441 (5)	5607 (5)	996 (3)
C11	−559 (5)	3738 (4)	4628 (2)
C12	−1037 (6)	2522 (5)	5014 (3)
C13	−2543 (4)	4676 (4)	3328 (3)
C14	−3747 (5)	5600 (5)	3948 (3)
C15	−303 (5)	5915 (4)	3316 (2)
C16	−580 (5)	6779 (4)	2436 (3)
C21	1195 (4)	2020 (4)	644 (2)
C22	609 (6)	1517 (6)	7 (3)
C23	−431 (4)	651 (4)	2103 (3)
C24	−1333 (6)	593 (5)	3017 (3)
C25	−1764 (4)	3411 (3)	1455 (2)
C26	−1686 (4)	4784 (4)	988 (3)
C31	4678 (5)	−19 (4)	3382 (3)
C32	3712 (6)	−608 (5)	4137 (3)
C33	3652 (4)	−643 (4)	2013 (3)
C34	5150 (5)	−1799 (4)	1821 (4)
C35	5401 (5)	1182 (4)	1664 (3)
C36	5256 (5)	1596 (5)	702 (3)

of methyl groups. Therefore, C–H activation occurs at the C-terminus of the 2,4-dimethyl-5-oxapentadienyl chain (C1), producing the six-membered ring compounds, the iridapyrans.

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere, using either glovebox or double-manifold Schlenk techniques. Solvents were stored under nitrogen after being distilled from the appropriate drying agents. Diethyl ether and tetrahydrofuran were dried over sodium/benzophenone, pentane was dried over calcium hydride, and acetone was dried over magnesium sulfate. The following reagents were used as obtained from the supplier indicated: anhydrous ammonia (Matheson), potassium (Aldrich), crotonaldehyde (Aldrich), mesityl oxide (Aldrich), $IrCl_3 \cdot 3H_2O$ (Johnson-Matthey), cyclooctene (Aldrich), trimethylphosphine (Strem), dimethylphenylphosphine (Strem), and triethylphosphine (Strem). 3-Penten-2-one was obtained as a mixture with mesityl oxide (65:35) from Aldrich and was separated on a silica gel column using diethyl ether/pentane as the eluant. Potassium oxapentadienide[6] and [(cyclooctene)$_2$IrCl]$_2$[27] were prepared using literature procedures.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for *mer*-CH_2=C—CH=C(Me)—O-Ir($(PEt_3)_3$)(H) (9)

Bond Distances			
Ir–P1	2.323 (1)	C1–C2	1.326 (7)
Ir–P2	2.352 (1)	C2–C3	1.484 (6)
Ir–P3	2.321 (1)	C3–C4	1.338 (6)
Ir–C2	2.107 (5)	C4–C5	1.503 (6)
Ir–O	2.167 (2)	C4–O	1.322 (6)
Ir–H1	1.473 (35)		
Bond Angles			
P1–Ir–P2	101.1 (1)	Ir–C2–C1	132.6 (4)
P1–Ir–P3	158.0 (1)	Ir–C2–C3	108.0 (3)
P2–Ir–P3	95.9 (1)	C1–C2–C3	119.4 (5)
P1–Ir–C2	83.2 (1)	C2–C3–C4	119.7 (5)
P1–Ir–O	97.7 (1)	C3–C4–C5	124.9 (5)
P1–Ir–H1	81.4 (12)	C3–C4–O	120.6 (4)
P2–Ir–C2	167.6 (1)	C4–O–Ir	111.5 (2)
P2–Ir–O	87.7 (1)	C5–C4–O	114.4 (4)
P2–Ir–H1	96.1 (18)		
P3–Ir–C2	83.0 (1)		
P3–Ir–O	96.6 (1)		
P3–Ir–H1	83.2 (12)		
C2–Ir–H1	96.1 (18)		
O–Ir–H1	176.2 (17)		
C2–Ir–O	80.1 (1)		

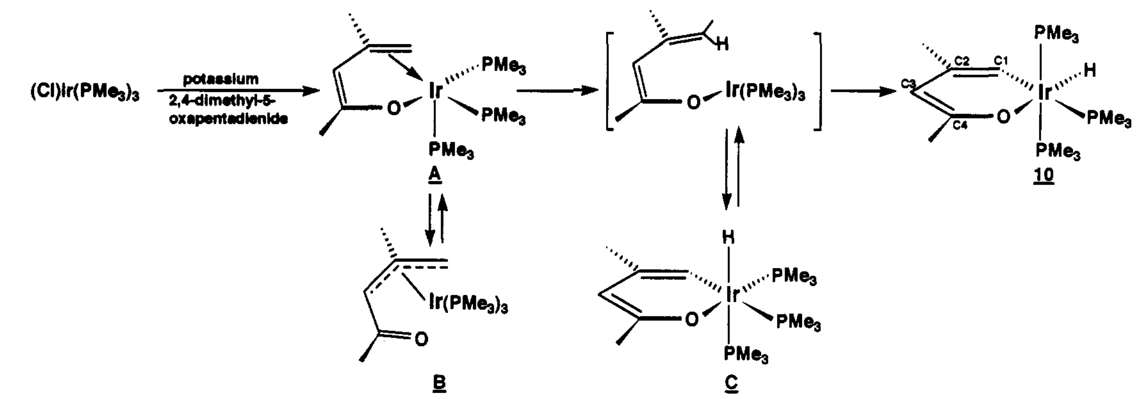
NMR experiments were performed on a Varian XL-300 NMR spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz). ^1H and ^{13}C spectra were referenced to tetramethylsilane, while ^{31}P spectra were referenced to external H_3PO_4. In general, ^1H connectivities were determined from COSY (^1H–^1H correlation spectroscopy) spectra; HMQC (^1H-detected multiple quantum coherence) and APT (attached proton test) experiments aided in assigning some of the ^1H and ^{13}C peaks. Note: In all of the NMR spectra, carbon atoms and associated hydrogens are numbered by *starting* at the end of the chain *opposite oxygen*.

The infrared spectra were recorded on a Perkin-Elmer 283B or a Mattson Polaris FT IR spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

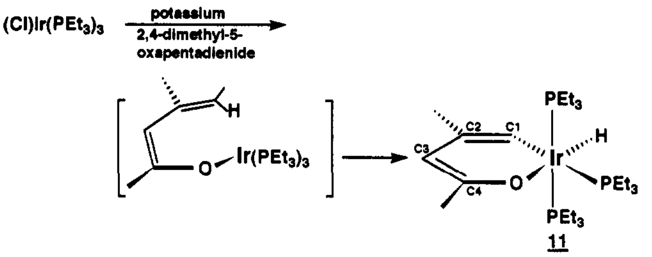
Synthesis of Potassium 4-Methyl-5-oxapentadienide. To 250 mL of liquid ammonia at −78 °C, a small piece of potassium metal was added. After the appearance of a blue color, a few crystals of ferric nitrate (~0.1 g) were added, followed by small pieces of potassium until a total of 2.1 g (0.055 mol) had been added. After stirring this mixture for 2 h at −78 °C, 3-penten-

(27) Herde, J. L.; Lambert, J. C.; Senoff, C. V. In *Inorganic Syntheses*; Parshall, G. W., Ed.; McGraw-Hill: New York, 1974; Vol. 15, pp 18–20.

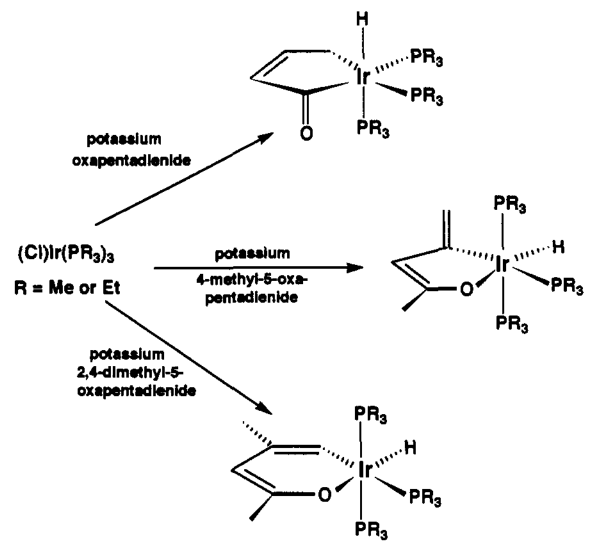
Scheme XI



Scheme XII



Scheme XIII



2-one (3.1 g, 0.037 mol) was added dropwise over a period of 30 min. The resultant solution was then stirred at −78 °C for an additional 2 h and slowly warmed to room temperature, during which time the ammonia evaporated off. To complete the removal of ammonia, the residue was placed under vacuum for 15 min. The dark-colored residue was then extracted with tetrahydrofuran; the resulting yellow-brown solution was filtered through Celite and its volume was reduced under vacuum. Addition of pentane caused potassium 4-methyl-5-oxapentadienide to precipitate as a yellow powder. Yield: 3.6 g, 80%. Two isomers in an approximate 2.2:1 ratio were observed.

^{1}H NMR (C_4D_8O, 22 °C): major isomer δ 6.60 (m, 1, H2), 4.60 (d, J = 11.2 Hz, 1, H3), 4.28 (d, J = 17.1 Hz, 1, $H1_{anti}$), 3.96 (d, J = 10.5 Hz, 1, $H1_{syn}$), 1.64 (s, 3, CH_3); minor isomer δ 6.42 (m, 1, H2), 4.66 (d, J = 11.6 Hz, 1, H3), 4.09 (d, J = 16.7 Hz, 1, $H1_{anti}$), 3.76 (J = 11.2 Hz, 1, $H1_{syn}$), 1.74 (s, 3, CH_3). $^{13}C\{^1H\}$ NMR (C_4D_8O, 22 °C): major isomer δ 169.5 (s, C4), 136.1 (s, C2), 96.3 (s, C3), 95.1 (s, C1), 22.2 (s, CH_3); minor isomer δ 170.8 (s, C4), 139.7 (s, C2), 96.7 (s, C3), 93.6 (s, C1), 23.2 (s, CH_3).

Synthesis of Potassium 2,4-Dimethyl-5-oxapentadienide. A similar procedure to that described above was employed. Potassium (2.7 g, 0.069 mol) was added to 250 mL of liquid NH_3, and mesityl oxide (5.0 g, 0.051 mol) was then added dropwise over 30 min. Workup produced potassium 2,4-dimethyl-5-oxapentadienide (6.2 g, 90%) as a dark brown crystalline solid.

^{1}H NMR (C_4D_8O, 22 °C): δ 5.29 (s, 1, H3), 4.07 (s, 2, H1's), 1.67 (s, 3, CH_3), 1.59 (s, 3, CH_3). $^{13}C\{^1H\}$ NMR (C_4D_8O, 22 °C): δ 172.4 (s, C4), 145.2 (s, C2), 95.6 (s, C1), 93.0 (s, C3), 29.0 (s, CH_3), 27.0 (s, CH_3).

Synthesis of ((1,2,5-η)-5-Oxapentadienyl)Ir(PMe$_3$)$_3$ (1). Trimethylphosphine (0.26 g, 3.4 mmol) was added dropwise to a cold (−78 °C) stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.50 g, 0.56 mmol) in tetrahydrofuran. The resultant solution was stirred for 20 min before dropwise addition of potassium oxapentadienide (0.22 g, 2.0 mmol) in 10 mL of tetrahydrofuran. After stirring at −78 °C for 30 min, the light yellow solution was warmed to 0 °C. The tetrahydrofuran solvent was removed under vacuum, and the residue was extracted with pentane. Removal of the pentane solvent under vacuum produced a light yellow residue of 1 mixed with some ((1,2,3-η)-5-oxapentadienyl)Ir(PMe$_3$)$_3$ (**2a**). Yield of mixture: 0.38 g, 70%.

^{1}H NMR (C_6D_6, 22 °C): δ 6.58 (m, 1, H4), 5.08 (m, 1, H3), 3.10 (m, 1, H2), 1.76 (m, 2, H1's), 1.32 (m, 18, PMe$_3$'s), 1.01 (m, 9, PMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 157.7 (d, $J_{C\text{-}P}$ = 13.4 Hz, C4), 108.8 (s, C3), 42.6 (d, $J_{C\text{-}P}$ = 33.2 Hz, C2), 23.8 (d, $J_{C\text{-}P}$ = 37.4 Hz, C1), 20.2 (m, PMe$_3$'s), 19.2 (d, $J_{C\text{-}P}$ = 37.2 Hz, PMe$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ −41.1 (dd, $J_{P\text{-}P}$ = 47.4, 10.6 Hz, 1), −44.3 (dd, $J_{P\text{-}P}$ = 14.6, 10.6 Hz, 1), −47.7 (dd, $J_{P\text{-}P}$ = 47.4, 14.6 Hz, 1).

Synthesis of ((1,2,3-η)-5-Oxapentadienyl)Ir(PMe$_3$)$_3$ (2a). Trimethylphosphine (0.26 g, 3.4 mmol) was added dropwise to a cold (−78 °C) stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.50 g, 0.56 mmol) in THF. Potassium oxapentadienide (0.22 g, 2.0 mmol) in 10 mL of THF was then added dropwise. After the mixture was warmed to room temperature and stirred overnight (to allow conversion of 1 to **2a**), the volatiles were removed under vacuum and the residue was extracted with pentane. Concentration of the pentane extract, followed by cooling to −30 °C, produced pure yellow crystals of **2a**. Yield: 0.33 g, 60%. Anal. Calcd for $C_{13}H_{32}OIrP_3$: C, 31.89; H, 6.60. Found: C, 32.31; H, 6.81.

^{1}H NMR (C_6D_6, 22 °C): δ 7.46 (d, J_{H-H} = 8.7 Hz, 1, H4), 4.32 (m, H2), 4.10 (m, H3), 1.16 (br s, 27, PMe$_3$'s), 0.71 (m, 2, H1's). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 173.8 (s, C4), 62.2 (d, J_{C-P} = 2.7 Hz, C3), 53.1 (s, C2), 22.8 (filled-in d, J_{C-P} = 33.8 Hz, PMe$_3$'s), 17.3 (q, J_{C-P} = 8.3 Hz, C1). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ −54.3 (s). At low temperature, this singlet decoalesces to three dd patterns: $^{31}P\{^1H\}$ NMR ($CD_3C(O)CD_3$, −80 °C): δ −45.5 (dd, J_{P-P} = 43.9, 15.1 Hz, 1), −51.1 (dd, J_{P-P} = 23.1, 15.1 Hz, 1), −55.5 (dd, J_{P-P} = 43.9, 23.1 Hz, 1). IR (toluene, 22 °C): 1599 cm^{-1} (C=O stretch).

Synthesis of ((1,2,3-η)-5-Oxapentadienyl)Ir(PMe$_2$Ph)$_3$ (2b). Dimethylphenylphosphine (0.46 g, 3.4 mmol) was added dropwise to a cold (−78 °C) stirred solution of [(cyclooctene)$_2$IrCl]$_2$ (0.50 g, 0.56 mmol) in THF. Potassium oxapentadienide (0.22 g, 2.0 mmol) in 15 mL of THF was then added dropwise. After the mixture was warmed to room temperature and stirred for 2 h, the solvent was removed under vacuum and the residue was extracted with pentane. The concentrated pentane solution was cooled to -30 °C to obtain yellow crystals of **2b**. Yield: 0.52 g, 69%. Anal. Calcd for $C_{28}H_{38}IrOP_3$: C, 49.76; H, 5.68. Found: C, 49.48; H, 5.74.

^{1}H NMR (C_6D_6, 22 °C): δ 7.40 (d, J_{H-H} = 8.0 Hz, 1, H4), 7.2–7.0 (m, 15, phenyl H's), 4.38–4.31 (m, 2, H2 and H3), 1.50 (s, 9, PMe_2-Ph CH_3's), 1.38 (s, 9, PMe_2Ph CH_3's), 0.57 (m, 2 H1's). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 177.3 (s, C4), 129.9 (m, phenyl C's), 128.0 (m, phenyl C's), 61.4 (s, C3), 59.5 (s, C2), 22.2 (m, C1), 21.9 (filled-in d, J_{C-P} = 36.5 Hz, PMe_2Ph CH_3's), 19.3 (filled-in d, J_{C-P} = 33.2 Hz, PMe_2Ph CH_3's). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ -39.5 (s).

Synthesis of *fac*-CH₂—CH═CH—C(O)—Ir(PMe₃)₃(H) (3). A tetrahydrofuran solution of **2a** (0.12 g, 0.24 mmol) was refluxed under nitrogen for 24 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum. The resulting residue was extracted with pentane and filtered. The pentane extract was reduced in volume, treated with several drops of acetone, and cooled to -30 °C to produce very light yellow crystals of **3**. Yield: 0.096 g, 80%. Anal. Calcd for $C_{13}H_{32}IrOP_3$: C, 31.89; H, 6.60. Found: C, 32.04; H, 6.66.

^{1}H NMR (C_6D_6, 22 °C): δ 7.36 (br m, 1, H2), 6.18 (s, 1, H3), 2.91 (br d, J = 19.8 Hz, 1, H1), 1.86 (br m, 1, H1), 1.48 (d, J_{H-P} = 8.3 Hz, 9, PMe_3), 1.07 (d, J_{H-P} = 7.1 Hz, 9, PMe_3), 0.99 (d, J_{H-P} = 7.9 Hz, 9, PMe_3), -11.19 (d of t, J_{H-P} = 128.9, 19.1 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 161.6 (d, J_{C-P} = 5.9 Hz, C2), 152.1 (d, J_{C-P} = 24.0 Hz, C3), 21.9 (overlapping d's, PMe_3's), 17.6 (d, J_{C-P} = 23.2 Hz, PMe_3), 10.2 (d of t, J_{C-P} = 65.5, 4.3 Hz, C1). Note: the quaternary carbon C4 was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ -51.2 (m, 1), -55.1 (m, 1), -61.9 (m, 1).

Synthesis of *mer*-CH═CH—CH═CH—O—Ir(PEt₃)₃(H) (4). Triethylphosphine (0.40 g, 3.4 mmol) was added dropwise to a cold (0 °C) stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.50 g, 0.56 mmol) in 15 mL of tetrahydrofuran (THF). Potassium oxapentadienide (0.22 g, 2.0 mmol) in 15 mL of THF was then added dropwise. The solution was warmed to room temperature and stirred overnight, before removal of the THF solvent. **4** was extracted from the resulting residue with pentane and crystallized at -30 °C from a concentrated pentane solution containing several drops of acetone; yield (orange crystals) 0.55 g, 80%. Anal. Calcd for $C_{22}H_{50}IrOP_3$: C, 42.90; H, 8.20. Found: C, 42.97; H, 8.21.

^{1}H NMR (C_6D_6, 22 °C): δ 6.92 (br s, 2, H2 and H4), 6.80 (br s, 1, H1), 4.87 (t, J = 6.0 Hz, 1, H3), 2.01–1.57 (m, 18, PEt_3 CH_2's), 1.08–0.75 (m, 27, PEt_3 CH_3's), -24.94 (t of d, J_{H-P} = 28.0, 16.7 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 149.6 (s, C4), 122.4 (s, C2), 117.3 (d of t, J_{C-P} = 76.9, 16.4 Hz, C1), 99.7 (s, C3), 20.0 (d, J_{C-P} = 21.9 Hz, equatorial PEt_3 CH_2's), 17.2 (virtual t, J_{C-P} = 31.3 Hz, axial PEt_3 CH_2's), 8.5, 8.3 (s's, PEt_3 CH_3's). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ -7.7 (d, J_{P-P} = 16.8 Hz, 2, axial PEt_3's), -19.8 (t, J_{P-P} = 16.8 Hz, 1, equatorial PEt_3).

Synthesis of *fac*-CH₂—CH═CH—C(O)—Ir(PEt₃)₃(H) (5). A tetrahydrofuran solution of **4** (0.35 g, 0.57 mmol) was stirred at room temperature for 72 h. After removal of the solvent under vacuum, the residue was extracted with pentane. The resulting yellow solution was filtered, reduced in volume, treated with several drops of acetone, and cooled to -30 °C to produce yellow crystals of **5**. Yield: 0.23 g, 65%. Anal. Calcd for $C_{22}H_{50}IrOP_3$: C, 42.90; H, 8.20. Found: C, 42.86; H, 8.19.

^{1}H NMR (C_6D_6, 22 °C): δ 7.28 (br s, 1, H2), 6.10 (s, 1, H3), 2.83 (d, J_{H-P} = 19.1 Hz, 1, H1), 1.81 (m, 18, PEt_3 CH_2's), 1.20 (m, 27, PEt_3 CH_3's), -12.32 (d of t, J_{H-P} = 125.1, 19.0 Hz, 1, Ir—H). Note: one H1 signal is obscured by the PEt_3 peaks. $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 161.6 (d, J_{C-P} = 3.6 Hz, C2), 152.3 (d, J_{C-P} = 24.0 Hz, C3), 20.2 (m, PEt_3 CH_2's), 9.5 (partially obscured d, C1), 9.0 (m, PEt_3 CH_3's). Note: the quaternary carbon C4 was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ -21.5 (m, 1), -32.9 (m, 1), -34.6 (m, 1).

Synthesis of ((1,2,5-η)-4-Methyl-5-oxapentadienyl)Ir(PMe₃)₃ (6). Trimethylphosphine (0.10 g, 1.3 mmol) was added to a solution of [(cyclooctene)$_2$IrCl]$_2$ (0.20 g, 0.22 mmol) in tetrahydrofuran. After stirring for 5 min, the volatiles were removed under vacuum, and the residue was redissolved in tetrahydrofuran and cooled to 0 °C. Potassium 4-methyl-5-oxapentadienide (0.068 g, 0.56 mmol) in tetrahydrofuran was added dropwise, and the resulting reaction mixture was warmed to room temperature and stirred for 2 h. After removal of the THF solvent under vacuum, the residue was extracted with pentane. The resulting solution was filtered through Celite and evacuated to dryness. Yield of **6**: 0.15 g, 68%. Anal. Calcd for $C_{14}H_{34}IrOP_3$: C, 33.39; H, 6.82. Found: C, 33.08; H, 6.70.

^{1}H NMR (C_6D_6, 22 °C): δ 5.18 (m, 1, H3), 3.09 (m, 1, H2), 2.06 (s, 3, CH_3), 1.92 (m, 1, H1), 1.74 (m, 1, H1), 1.36 (d, J_{H-P} = 7.3 Hz, 9, PMe_3), 1.31 (d, J_{H-P} = 8.0 Hz, 9, PMe_3), 0.90 (d, J_{H-P} = 8.5 Hz, 9, PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 164.0 (d, J_{C-P} = 13.2 Hz, C4), 103.9 (s, C3), 40.9 (d, J_{C-P} = 33.6 Hz, C2), 23.5 (d, J_{C-P} = 36.1 Hz, C1), 20.2 (m, PMe_3's), 19.3 (s, CH_3), 19.1 (d, J_{C-P} = 37.1 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ -39.6 (dd, J_{P-P} = 50.7, 10.2 Hz, 1), -44.8 (dd, J_{P-P} = 14.1, 10.2 Hz, 1), -48.2 (dd, J_{P-P} = 50.7, 14.1 Hz, 1).

Synthesis of *mer*-CH₂═C—CH═C(Me)—O—Ir(PMe₃)₃(H) (7). Trimethylphosphine (0.10 g, 1.3 mmol) was added to a solution of [(cyclooctene)$_2$IrCl]$_2$ (0.20 g, 0.22 mmol) in tetrahydrofuran. After stirring for 5 min, the volatiles were removed under vacuum, and the residue was redissolved in 75 mL of tetrahydrofuran. After cooling to 0 °C, potassium 4-methyl-5-oxapentadienide (0.081 g, 0.66 mmol) in 30 mL of tetrahydrofuran was added dropwise. The solution was then refluxed for 24 h. After removal of the THF solvent under vacuum, the residue was extracted with pentane. The resulting solution was filtered through Celite and evacuated to dryness. Yield of **7**: 0.10 g, 45%. Anal. Calcd for $C_{14}H_{34}IrOP_3$: C, 33.39; H, 6.82. Found: C, 33.08; H, 6.90.

^{1}H NMR (C_6D_6, 22 °C): δ 6.15 (br d, 1, H1), 5.45 (d, J_{H-P} = 6.2 Hz, 1, H3), 4.72 (m, 1, H1), 2.12 (s, 3, CH_3), 1.4–1.1 (m, 27, PMe_3's), -22.95 (t of d, J_{H-P} = 18.6, 11.0 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 173.8 (s, C4), 162.0 (d of t, J_{C-P} = 74.8, 12.8 Hz, C2), 113.2 (s, 1, C3), 107.1 (s, C1), 20.5 (d, J_{C-P} = 23.4 Hz, equatorial PMe_3), 20.1 (partially obscured s, CH_3), 17.6 (virtual t, J_{C-P} = 36.3 Hz, axial PMe_3's). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ -41.2 (d, J_{P-P} = 19.9 Hz, 2, axial PMe_3's), -50.0 (t, J_{P-P} = 19.9 Hz, 1, equatorial PMe_3).

Synthesis of *mer*-CH═CH—CH═C(Me)—O—Ir(PEt₃)₃(H) (8). Triethylphosphine (0.40 g, 3.4 mmol) was added to a solution of [(cyclooctene)$_2$IrCl]$_2$ (0.50 g, 0.56 mmol) in tetrahydrofuran. After stirring for 5 min, the volatiles were removed under vacuum, and the residue was redissolved in 75 mL of tetrahydrofuran. After cooling to 0 °C, potassium 4-methyl-5-oxapentadienide (0.21 g, 1.7 mmol) in 30 mL of THF was added dropwise. The solution was then warmed to room temperature and stirred overnight. After removal of the THF solvent under vacuum, the residue was extracted with pentane. The resulting solution was filtered through Celite, reduced in volume, and cooled to -30 °C, producing yellow crystals of **8**. Yield: 0.51 g, 73%. Anal. Calcd for $C_{23}H_{52}IrOP_3$: C, 43.85; H, 8.34. Found: C, 42.79; H, 8.31.

^{1}H NMR (C_6D_6, 22 °C): δ 6.72 (m, 1, H2), 6.48 (m, 1, H1), 4.80 (d, J_{H-H} = 6.9 Hz, 1, H3), 1.90 (s, 3, CH_3), 1.98–1.61 (m's, 18, PEt_3 CH_2's), 1.05–0.90 (m's, 27, PEt_3 CH_3's), -24.64 (t of d, J_{H-P} = 17.1, 10.5 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 154.7 (s, C4), 124.3 (s, C2), 115.8 (d of t, J_{C-P} = 75.5, 16.6 Hz, C1), 95.2 (s, C3), 26.5 (s, CH_3), 20.1 (d, J_{C-P} = 21.4 Hz, equatorial PEt_3 CH_2's), 17.2 (virtual t, J_{C-P} = 31.4 Hz, axial PEt_3 CH_2's), 8.4, 8.3 (s's, PEt_3 CH_3's). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): -7.6 (d, J_{P-P} = 15.6 Hz, 2, axial PEt_3's), -21.0 (t, J_{P-P} = 15.6 Hz, 1, equatorial PEt_3).

Synthesis of *mer*-CH₂═C—CH═C(Me)—O—Ir(PEt₃)₃(H) (9). Triethylphosphine (0.40 g, 3.4 mmol) was added to a solution of [(cyclooctene)$_2$IrCl]$_2$ (0.50 g, 0.56 mmol) in tetrahydrofuran. After stirring for 5 min, the volatiles were removed

Table VII. X-ray Diffraction Structure Summary

	2b	5	9
	Crystal Parameters and Data Collection Summary		
formula	$C_{28}H_{38}IrOP_3$	$C_{22}H_{50}IrOP_3$	$C_{23}H_{52}IrOP_3$
fw	675.7	615.7	629.8
cryst syst	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a, Å	9.506 (2)	15.271 (4)	9.396 (2)
b, Å	17.219 (4)	11.401 (3)	10.742 (2)
c, Å	18.546 (5)	15.473 (4)	15.725 (5)
α, deg	111.14 (2)	90.0	77.88 (2)
β, deg	97.62 (2)	90.0	77.52 (2)
γ, deg	91.49 (2)	90.0	68.09 (2)
V, Å^3	2797.4 (12)	2693.9 (12)	1423.0 (6)
Z	4	4	2
cryst dimens, mm	0.18 × 0.27 × 0.50	0.26 × 0.38 × 0.56	0.25 × 0.40 × 0.40
cryst color and habit	yellow plate	yellow prism	yellow plate
density$_{calcd}$, g/cm^3	1.604	1.518	1.470
radiation, Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
scan type	ω	θ:2θ	θ:2θ
scan rate, deg/min in ω	variable; 4.88–14.65	variable, 4.99–14.65	variable; 4.19–14.65
scan range (ω), deg	1.20	0.6 (plus Kα separation)	1.20 (plus Kα separation)
2θ range, deg	3.5–50.0	3.5–50.0	3.5–50.0
data collcd	*h* 0→11 *k* −20→+20 *l* −22→+21	*h* (−18→0), *k* (−13→0), *l* (−18→0) and (0→18), (0→13), (0→18)	*h* 0→11 *k* −11→+12 *l* −18→+18
total decay	none detected	none detected	none detected
temp, K	295	295	295
	Treatment of Intensity Data and Refinement Summary		
no. of data collcd	10502	5406	5357
no. of unique data	9860	4743	5027
no. of data with $I > 3\sigma(I)$	6227	3363	4299
Mo Kα linear abs coeff, cm^{-1}	49.41	51.44	48.71
abs corrcn applied	semiempirical	semiempirical	semiempirical
data to param ratio	9.9:1	13.8:1	16.2:1
R^a	0.034	0.025	0.018
$R_w{}^a$	0.042[b]	0.031[c]	0.022[d]
GOF[e]	0.85	0.82	0.83

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [b] $w = [\sigma^2(F_o) + 0.0014(F_o)^2]^{-1}$. [c] $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1}$. [d] $w = [\sigma^2(F_o) + 0.0004(F_o)^2]^{-1}$. [e] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{variables})]^{1/2}$.

under vacuum, and the residue was redissolved in 75 mL of THF. After cooling to 0 °C, potassium 4-methyl-5-oxapentadienide (0.21 g, 1.7 mmol) in 30 mL of THF was added dropwise. The solution was then refluxed for 2 h. After cooling, the THF solvent was removed under vacuum and the residue was extracted with pentane. The resulting solution was filtered through Celite and evacuated to dryness. Crude yield: 0.70 g, 100%. Yellow crystals of **9** were obtained by dissolving the crude product in minimal diethyl ether/pentane and cooling to −30 °C overnight. Crystalline yield: 0.30 g, 43%. Anal. Calcd for $C_{23}H_{52}IrOP_3$: C, 43.85; H, 8.34. Found: C, 43.22; H, 8.36.

^{1}H NMR (C_6D_6, 22 °C): δ 6.10 (br d, 1, H1), 5.47 (d, J = 6.6 Hz, 1, H3), 4.59 (m, 1, H1), 2.20 (s, 3, CH_3), 2.10 (m, 6, PEt_3 CH_2's), 1.80 (m, 6, PEt_3 CH_2's), 1.65 (m, 6, PEt_3 CH_2's), 1.0 (m, 27, PEt_3 CH_3's), −23.08 (t of d, J_{H-P} = 18.2, 10.3 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 174.0 (s, C4), 162.0 (d of t, J_{C-P} = 75.4, 14.4 Hz, C2), 113.5 (s, C3), 105.5 (s, C1), 22.7 (s, CH_3), 20.2 (d, J_{C-P} = 20.9 Hz, equatorial PEt_3 CH_2's), 17.2 (virtual t, J_{C-P} = 31.5 Hz, axial PEt_3 CH_2's), 8.4, 8.2 (s's, PEt_3 CH_3's). $^{31}P\{^1H\}$ (C_6D_6, 22 °C): δ −16.2 (d, J_{P-P} = 17.5 Hz, 2, axial PEt_3's), −18.6 (t, J_{P-P} = 17.5 Hz, 1, equatorial PEt_3).

Synthesis of *mer*-CH=C(Me)—CH=C(Me)—O—Ir-(PMe$_3$)$_3$(H) (10). Trimethylphosphine (0.26 g, 3.4 mmol) was added dropwise to a cold (−78 °C) stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.50 g, 0.56 mmol) in 30 mL of THF. Potassium 2,4-dimethyloxapentadienide (0.25 g, 1.9 mmol) in 10 mL of THF was then added, and the resulting solution was warmed to room temperature. After stirring for 72 h, the solvent was removed under vacuum and the residue was extracted with pentane. Filtration of the pentane solution, followed by concentration and cooling to −30 °C, produced orange crystals of **10**. Yield: 0.19 g, 65%. Anal. Calcd for $C_{15}H_{36}IrOP_3$: C, 34.80; H, 7.02. Found: C, 34.44; H, 7.03.

^{1}H NMR (C_6D_6, 22 °C): δ 6.61 (s, 1, H1), 4.72 (s, 1, H3), 2.20 (s, 3, ring CH_3), 2.05 (s, 3, ring CH_3), 1.26 (m, 27, PMe_3 CH_3's), −23.74 (t of d, J_{H-P} = 27.4 Hz, 18.3 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 156.4 (s, C4), 126.0 (d, J_{C-P} = 4.5 Hz, C2), 109.7 (d of t, J_{C-P} = 76.5, 16.1 Hz, C1), 98.8 (s, C3), 29.6 (d, J_{C-P} = 11.3 Hz, ring CH_3), 26.2 (s, ring CH_3), 19.4 (d, J_{C-P} = 24.8 Hz, equatorial PMe_3 CH_3's), 17.2 (virtual t, J_{C-P} = 36.0 Hz, axial PMe_3 CH_3's). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ −35.2 (d, J_{P-P} = 18.8 Hz, 2, axial PMe_3's), −48.5 (t, J_{P-P} = 18.8 Hz, 1, equatorial PMe_3).

Synthesis of *mer*-CH=C(Me)—CH=C(Me)—O—Ir-(PEt$_3$)$_3$(H) (11). Triethylphosphine (0.40 g, 3.4 mmol) was added dropwise to a cold (0 °C) stirred solution of [(cyclooctene)$_2$Ir(Cl)]$_2$ (0.50 g, 0.56 mmol) in 30 mL of THF. Potassium 2,4-dimethyloxapentadienide (0.23 g, 1.7 mmol) in 15 mL of THF was then added dropwise, and the resulting solution was warmed to room temperature. After stirring for 20 h, the solvent was removed under vacuum and the residue was extracted with pentane. After filtering and concentrating the pentane solution, it was cooled to −30 °C to produce orange crystals of **11**. Yield: 0.61 g, 85%. Anal. Calcd for $C_{24}H_{54}IrOP_3$: C, 44.76; H, 8.47. Found: C, 44.49; H, 8.14.

^{1}H NMR (C_6D_6, 22 °C): δ 6.04 (s, 1, H1), 4.70 (s, 1, H3), 2.06 (s, 3, ring CH_3), 1.98 (s, 3, ring CH_3), 1.82–1.60 (m, 18, PEt_3 CH_2's), 1.10–0.88 (m, 27, PEt_3 CH_3's), −24.46 (t of d, J_{H-P} = 28.1, 17.2 Hz, 1, Ir—H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 156.8 (s, C4), 127.4 (s, C2), 108.7 (d of t, J_{C-P} = 75.3, 15.8 Hz, C1), 97.4 (s, C3), 30.0 (d, J_{C-P} = 11.0 Hz, ring CH_3), 26.5 (s, ring CH_3), 20.2 (d, J_{C-P} = 21.7 Hz, equatorial PEt_3 CH_2's), 17.2 (virtual t, J_{C-P} = 31.9 Hz, axial PEt_3 CH_2's), 8.4, 8.2 (s's, PEt_3 CH_3's). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ −7.8 (d, J_{P-P} = 16.2 Hz, 2, axial PEt_3's), −20.3 (t, J_{P-P} = 16.2 Hz, 1, equatorial PEt_3).

X-ray Diffraction Studies of ((1,2,3-η)-5-Oxapentadienyl)-Ir(PMe_2Ph)$_3$ (2b), *fac*-$\overline{CH_2—CH═CH—C(O)—Ir}$($PEt_3$)$_3$(H) (5), and *mer*-$CH_2$═$\overline{C—CH═C(Me)—O—Ir}$($PEt_3$)$_3$(H) (9). Single crystals of **2b**, **5**, and **9** were sealed in glass capillaries under an inert atmosphere. Data were collected at room temperature, using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 100 events as check reflections for crystal deterioration and/or misalignment. All data reduction and refinement were done using the Siemens SHELXTL PLUS package on a Micro VAX II computer.[28] Crystal data and details of data collection and structure analysis are listed in Table VII.

The positions of the iridium atoms in compound **2b** were calculated from a Patterson map; the iridium atom positions in **5** and **9** were determined by direct methods. In each case, remaining non-hydrogen atoms were found by successive full-matrix least-squares refinement and difference Fourier map calculations. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were treated as described below.

In compound **2b**, the hydrogens on the oxapentadienyl group (in both independent molecules) were located and refined positionally. All other hydrogen atoms were placed at idealized positions and assumed the riding model. A common isotropic *U* value for all hydrogens was refined. In compound **5**, H1 (the Ir–H hydrogen) and H1A and H1B (the hydrogens bonded to ring carbon C1) were located and added at those positions but not positionally refined. All other hydrogens were placed at idealized positions and assumed the riding model. A common isotropic *U* value for all hydrogen atoms was refined. In compound **9**, H1 (the Ir–H hydrogen), H1A and H1B (the hydrogens bonded to the exocyclic methylene carbon, C1), and H3 (the hydrogen bonded to ring carbon C3) were located and positionally refined. All other hydrogens were placed at idealized positions and assumed the riding model. A common isotropic *U* value for all hydrogen atoms was refined.

(28) Atomic scattering factors were obtained from the following: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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Supplementary Material Available: Tables of structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **2b**, **5**, and **9** and ORTEP drawings for molecules 1 and 2 of **2b** (28 pages). Ordering information is given on any current masthead page.

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