dicate that the HOMO of the 48-electron precursor should be largely Ru–μ_3-C bonding in character, localized trans to the Ru–L(axial) bonds. The coupling constant to the equatorial ^{31}P nucleus, cis to the Ru–COMe bond, must be too small to be resolved (cf. the ^{31}P–^{13}COMe J_{trans} value of 39 Hz in $H_3Ru_3(COMe)(CO)_6(PPh_3)_3$[18] vs J_{cis} = 3.5 Hz in $H_3Ru_3(COMe)(CO)_7\{(PPh_2)_3CH\}$).

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Supplementary Material Available: Tables of distances and angles, anisotropic thermal parameters, and calculated positions of H atoms for $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_6\{\mu_3\text{-}(PPh_2CH_2)_3CMe\}$ and $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_7\{\mu_2\text{-}(PPh_2)_3CH\}\cdot 1.25CH_2Cl_2$ (14 pages); tables of F_o/F_c values (56 pages). Ordering information is given on any current masthead page.

Pentadienyl–Iridium–Phosphine Chemistry.[1] Survey of the Reactions of Pentadienide Reagents with $ClIrL_3$ Complexes

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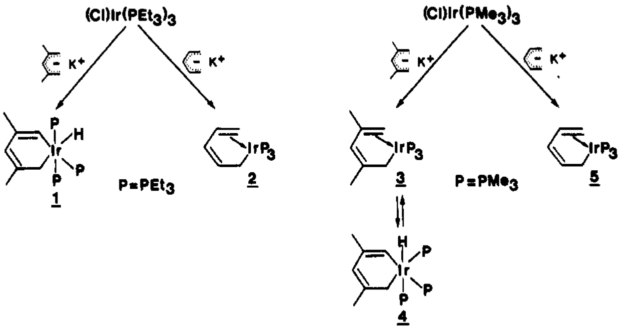
A systematic study of the reactions of four $ClIrL_3$ complexes with pentadienide reagents has been carried out. Treatment of $ClIr(PEt_3)_3$ with potassium pentadienide produces (1,4,5-η-pentadienyl)$Ir(PEt_3)_3$ (2), while the reaction of $ClIr(PMe_3)_3$ with potassium pentadienide yields the analogous trimethylphosphine compound 5. In contrast, treatment of $ClIr(PMe_3)_3$ with potassium 2,4-dimethylpentadienide produces an equilibrium mixture of (1,4,5-η-2,4-dimethylpentadienyl)$Ir(PMe_3)_3$ (3) and the metallacyclohexadiene complex *fac*-$(\overline{IrCH_2C(Me){=}CHC(Me){=}CH})(PMe_3)_3(H)$ (4). The formation of 4 involves the intermediacy of 16e$^-$ (η^1-2,4-dimethylpentadienyl)$Ir(PMe_3)_3$, which intramolecularly activates a C–H bond on the end of the pentadienyl chain. Vaska's complex, $ClIr(PPh_3)_2(CO)$, reacts with potassium 2,4-dimethylpentadienide to produce an equilibrium mixture of (1,4,5-η-2,4-dimethylpentadienyl)$Ir(PPh_3)_2(CO)$ (6) and (1–3-η-2,4-dimethylpentadienyl)$Ir(PPh_3)_2(CO)$ (7). The analogous reaction involving unmethylated pentadienide produces exclusively (1–3-η-pentadienyl)$Ir(PPh_3)_2(CO)$ (8). This species undergoes a dynamic process in solution, which involves shuttling between η^3- and η^1-pentadienyl bonding modes. Treatment of $ClIr(PEt_3)_2(CO)$ with potassium 2,4-dimethylpentadienide yields (1,4,5-η-2,4-dimethylpentadienyl)$Ir(PEt_3)_2(CO)$ (9), while the analogous reaction involving unmethylated pentadienide produces an equilibrium mixture of (1,4,5-η-pentadienyl)$Ir(PEt_3)_2(CO)$ (10) and (1–3-η-pentadienyl)$Ir(PEt_3)_2(CO)$ (11). Molecular structures of compounds 2, 3, 6, and 8 have been determined by single-crystal X-ray diffraction studies. Crystal structure data for these compounds are as follows: 2, monoclinic, $P2_1/c$, a = 15.489 (5) Å, b = 11.453 (5) Å, c = 15.769 (4) Å, β = 101.83 (2)°, V = 2738 (2) Å^3, Z = 4, R = 0.038 for 3572 reflections with $I > 3\sigma(I)$; 3, monoclinic, $P2_1/n$, a = 8.958 (6) Å, b = 20.308 (5) Å, c = 11.970 (5) Å, β = 93.14 (5)°, V = 2174 (2) Å^3, Z = 4, R = 0.037 for 3440 reflections with $I > 3\sigma(I)$; 6, monoclinic, $P2_1/n$, a = 13.518 (5) Å, b = 17.862 (6) Å, c = 15.417 (5) Å, β = 93.59 (3)°, V = 3715 (2) Å^3, Z = 4, R = 0.035 for 5003 reflections with $I > 3\sigma(I)$; 8, monoclinic, $P2_1/c$, a = 17.276 (7) Å, b = 23.038 (8) Å, c = 18.896 (5) Å, β = 111.92 (2)°, V = 6977 (4) Å^3, Z = 8, R = 0.049 for 6353 reflections with $I > 3\sigma(I)$.

Introduction

In an earlier paper,[2] we reported that $ClIr(PEt_3)_3$ reacts with potassium 2,4-dimethylpentadienide to produce a novel iridacyclohexadiene complex, $(\overline{IrCH_2C(Me){=}CHC(Me){=}CH})(PEt_3)_3(H)$ (1). This reaction proceeds through the intermediacy of 16e$^-$ (η^1-2,4-dimethylpentadienyl)$Ir(PEt_3)_3$, which undergoes intramolecular oxidative addition across an sp^2 C–H bond on the dangling terminus of the pentadienyl ligand. Compound 1 is the parent to a large family of unsaturated six-membered metallacycles,[2] including a rare metallabenzene complex $(\overline{Ir{\cdots}CH{\cdots}C(Me){\cdots}CH{\cdots}C(Me){\cdots}CH})(PEt_3)_3$.[3]

Scheme I



In order to probe the generality of this novel synthetic route to unsaturated six-membered metallacycles and to

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† Pew Postdoctoral Fellow.

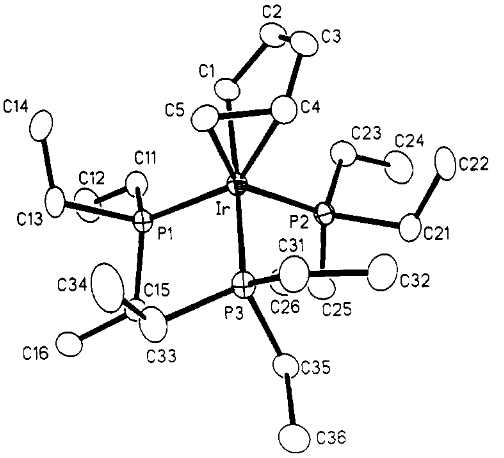

Figure 1. ORTEP drawing of (1,4,5-η-pentadienyl)Ir(PEt$_3$)$_3$ (**2**).

further our understanding of (pentadienyl)iridium chemistry, we have undertaken a systematic study of the reactions of four $\mathrm{ClIrL_3}$ precursors with potassium pentadienide and potassium 2,4-dimethylpentadienide. We have discovered that, in addition to the metallacyclic products described above, these reactions can lead to the production of (1–3-η-pentadienyl)IrL$_3$ and (1,4,5-η-pentadienyl)IrL$_3$ complexes.

Results and Discussion

A. Reaction of ClIr(PEt$_3$)$_3$ with Potassium Pentadienide. As we reported earlier, treatment of ClIr(PEt$_3$)$_3$ with potassium 2,4-dimethylpentadienide leads cleanly to the production of the iridacyclohexadiene complex, $(\overline{\mathrm{IrCH_2C(Me){=}CHC(Me){=}CH}})(\mathrm{PEt_3})_3(\mathrm{H})$ (**1**).[2] The initial product of this reaction is the *fac* isomer, which slowly (24 h) converts to the more thermodynamically stable *mer* isomer. In contrast, we now report that treatment of ClIr(PEt$_3$)$_3$ with *unmethylated* pentadienide produces (1,4,5-η-pentadienyl)Ir(PEt$_3$)$_3$ (**2**) (see Scheme I) in essentially quantitative yield. An ORTEP drawing of the molecular structure of **2** is shown in Figure 1; selected bond distances and angles are given in Table I. The 1,4,5-η-pentadienyl bonding mode, which involves localized metal–alkyl and metal–olefin coordination, is relatively rare. To our knowledge, the only other pentadienyl complexes that exhibit this type of bonding are (η^5-C$_5$H$_5$)$_2$Ta(2,3-dimethylpentadienyl) and (η^5-C$_5$H$_5$)$_2$Ta(2,4-dimethylpentadienyl).[4]

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (1,4,5-η-Pentadienyl)Ir(PEt$_3$)$_3$ (2)

Bond Distances

Ir-P(1)	2.319 (3)	Ir-C(5)	2.112 (12)
Ir-P(2)	2.333 (3)	C(1)-C(2)	1.502 (19)
Ir-P(3)	2.339 (3)	C(2)-C(3)	1.329 (20)
Ir-C(1)	2.161 (11)	C(3)-C(4)	1.489 (17)
Ir-C(4)	2.139 (12)	C(4)-C(5)	1.454 (17)

Bond Angles

P(1)-Ir-P(2)	103.6 (1)	P(2)-Ir-C(5)	144.9 (4)
P(1)-Ir-P(3)	95.4 (1)	P(3)-Ir-C(5)	88.4 (3)
P(2)-Ir-P(3)	97.7 (1)	C(1)-Ir-C(5)	81.9 (5)
P(1)-Ir-C(1)	88.2 (3)	C(4)-Ir-C(5)	40.0 (5)
P(2)-Ir-C(1)	90.1 (3)	Ir-C(1)-C(2)	110.1 (8)
P(3)-Ir-C(1)	170.4 (3)	C(1)-C(2)-C(3)	118.0 (11)
P(1)-Ir-C(4)	148.5 (3)	C(2)-C(3)-C(4)	117.5 (12)
P(2)-Ir-C(4)	104.9 (3)	Ir-C(4)-C(3)	110.0 (9)
P(3)-Ir-C(4)	93.9 (3)	Ir-C(4)-C(5)	69.0 (7)
C(1)-Ir-C(4)	78.5 (5)	C(3)-C(4)-C(5)	115.7 (9)
P(1)-Ir-C(5)	110.3 (3)	Ir-C(5)-C(4)	71.0 (7)

Compound **2** can perhaps best be viewed as a distorted octahedron in which the six coordination sites are occupied by C(1), C(4), and C(5) of the pentadienyl ligand and the three PEt$_3$ phosphorus atoms. Of course, the geometry is distorted because of the rigidity of the pentadienyl ligand. The σ-bonded carbon atom, C(1), lies approximately trans to P(3) and cis to P(1) and P(2). The π-bonded carbons C(4) and C(5) lie approximately in the Ir–P(1)–P(2) plane[5] and experience substantial back-bonding as evidenced by the relatively long C(4)–C(5) distance of 1.454 (17) Å. In fact, the Ir–C(4)–C(5) interaction approximates a metallacyclopropane in which the iridium center is formally oxidized to Ir(III). Hence, the stability of the 1,4,5-η-pentadienyl bonding mode in **2** may result, in part, from the stability of d^6 Ir(III) in an octahedral coordination geometry.

The ^{13}C{^{1}H} NMR spectrum of **2** exhibits the pattern of resonances that is characteristic of the 1,4,5-η-pentadienyl bonding mode. Uncomplexed carbon atoms C(3) and C(2) resonate far downfield at δ 143.5 and 133.9, respectively. π-complexed atoms C(4) and C(5) resonate at δ 36.6 and 20.9, respectively, and appear as doublets due to phosphorus coupling. Finally, σ-bonded carbon atom C(1) resonates far upfield at δ 10.1 and appears as a doublet of triplets, coupled strongly to the trans phosphorus and weakly to the two cis phosphorus atoms. All three phosphorus atoms are inequivalent and appear as a second-order ABC pattern in the ^{31}P{^{1}H} NMR spectrum. The signals show no tendency to coalesce upon heating to 80 °C.

B. Reactions of ClIr(PMe$_3$)$_3$ with Potassium 2,4-Dimethylpentadienide and Potassium Pentadienide. Treatment of ClIr(PMe$_3$)$_3$ with potassium 2,4-dimethylpentadienide produces an equilibrium mixture of (1,4,5-η-2,4-dimethylpentadienyl)Ir(PMe$_3$)$_3$ (**3**) and the metallacyclohexadiene complex, *fac*-$(\overline{\mathrm{IrCH_2C(Me){=}CHC(Me){=}CH}})(\mathrm{PMe_3})_3(\mathrm{H})$ (**4**) (see Scheme I). Interconversion between **3** and **4** probably involves the intermediacy of (η^1-2,4-dimethylpentadienyl)Ir(PMe$_3$)$_3$. The iridium center in this 16e$^-$ species can either coordinate the terminal double bond of the pentadienyl (producing **3**) or oxidatively add across a C–H bond on the end of the η^1-pentadienyl (producing **4**). Unlike its PEt$_3$ analogue, compound **4** does not isomerize from the *fac* to the *mer* geometry, apparently because of reduced steric strain in the *fac* geometry. In benzene at room temperature (20 °C), the equilibrium mixture slightly favors the metallacyclohexadiene complex (**4**:**3** = 1.15:1). However, the position of the equilibrium can be pushed further toward the metallacycle by refluxing the mixture for short periods of time in polar solvents (e.g., acetone) and can be pushed toward the 1,4,5-η-pentadienyl complex by refluxing in nonpolar solvents (e.g., pentane). These isomerically enriched so-

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[1] Pentadienyl-Metal-Phosphine Chemistry. 23. For recent papers in this series, see: (a) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19. (b) Bleeke, J. R.; Wittenbrink, R. J. *J. Organomet. Chem.* **1991**, *405*, 121. (c) Bleeke, J. R.; Wittenbrink, R. J.; Clayton, Jr., T. W.; Chiang, M. Y. *J. Am. Chem. Soc.* **1990**, *112*, 6539.

[2] (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113.

[3] Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118.

[4] Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 8703.

[5] The mean deviation of atoms from the Ir–P(1)–P(2)–C(4)–C(5) plane is 0.071 Å.

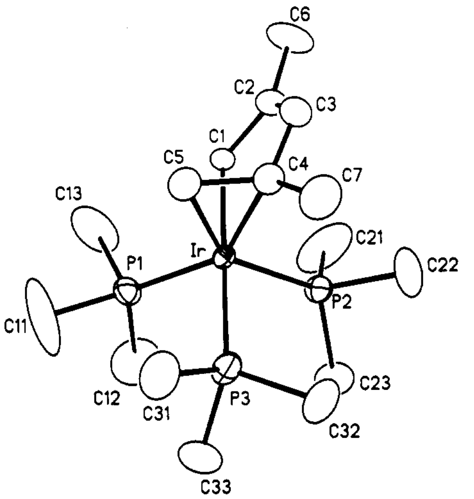


Figure 2. ORTEP drawing of (1,4,5-η-2,4-dimethylpentadienyl)Ir(PMe_3)$_3$ (**3**).

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (1,4,5-η-2,4-Dimethylpentadienyl)Ir(PMe_3)$_3$ (3)

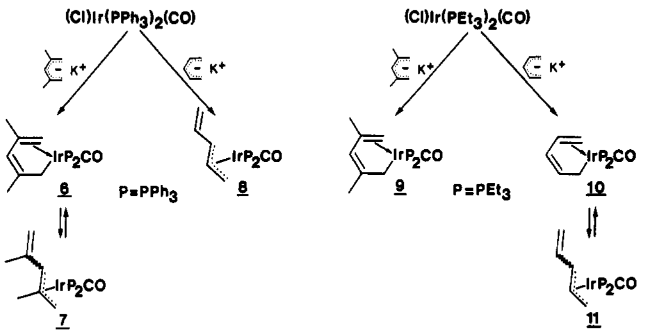
	Bond Distances		
Ir–P(1)	2.291 (3)	C(1)–C(2)	1.469 (13)
Ir–P(2)	2.288 (2)	C(2)–C(3)	1.334 (14)
Ir–P(3)	2.323 (3)	C(2)–C(6)	1.506 (13)
Ir–Cl(1)	2.127 (8)	C(3)–C(4)	1.480 (14)
Ir–C(4)	2.160 (8)	C(4)–C(5)	1.465 (12)
Ir–C(5)	2.130 (8)	C(4)–C(7)	1.495 (13)
	Bond Angles		
P(1)–Ir–P(2)	105.0 (1)	C(4)–Ir–C(5)	39.9 (3)
P(1)–Ir–P(3)	95.0 (1)	Ir–C(1)–C(2)	112.9 (6)
P(2)–Ir–P(3)	94.6 (1)	C(1)–C(2)–C(3)	115.2 (8)
P(1)–Ir–C(1)	88.7 (3)	C(1)–C(2)–C(6)	122.0 (9)
P(2)–Ir–C(1)	87.9 (2)	C(3)–C(2)–C(6)	122.8 (10)
P(3)–Ir–C(1)	174.8 (2)	C(2)–C(3)–C(4)	119.7 (9)
P(1)–Ir–C(4)	146.3 (2)	Ir–C(4)–C(3)	108.9 (6)
P(2)–Ir–C(4)	105.2 (2)	Ir–C(4)–C(5)	68.9 (5)
P(3)–Ir–C(4)	97.1 (2)	C(3)–C(4)–C(5)	115.4 (8)
C(1)–Ir–C(4)	77.9 (3)	Ir–C(4)–C(7)	125.7 (7)
P(1)–Ir–C(5)	108.0 (3)	C(3)–C(4)–C(7)	113.2 (8)
P(2)–Ir–C(5)	145.0 (3)	C(5)–C(4)–C(7)	118.0 (8)
P(3)–Ir–C(5)	93.8 (2)	Ir–C(5)–C(4)	71.1 (4)
C(1)–Ir–C(5)	81.6 (3)		

lutions yield spectroscopically pure crystalline samples of **4** and **3**, respectively, upon workup.

The molecular structure of **3** has been determined by single-crystal X-ray diffraction and is shown in Figure 2. Selected bond distances and angles are reported in Table II. The structure of **3** bears a strong resemblance to that of **2**. Once again, the coordination geometry is probably best described as a distorted octahedron in which C(1), C(4), C(5), P(1), P(2), and P(3) occupy the six coordination sites. C(1) lies directly trans to P(3) (C(1)–Ir–P(3) = 174.9 (2)°), an orientation that gives rise to very strong carbon–phosphorus coupling in the $^{13}C\{^1H\}$ NMR spectrum ($J_{C(1)-P}$ = 71.0 Hz).

Metallacycle **4** exhibits NMR spectra that very closely resemble those of *fac*-($\overline{IrCH_2C(Me)=CHC(Me)=CH}$)($PEt_3$)$_3$(H), which we reported earlier.[2] Particularly diagnostic is the $^{13}C\{^1H\}$ NMR spectrum, which shows four downfield peaks between δ 120 and 145 for C(2), C(3), C(4), and C(5). C(5) is a broadly spaced doublet (J = 81.8 Hz) due to strong trans carbon-phosphorus coupling. Ring carbon atom C(1) (the methylene carbon) appears far upfield (δ −3.0) and is a broadly spaced doublet (J = 71.8 Hz) due to trans carbon–phosphorus coupling. The metal–hydride in **4** resonates at δ −11.27 in the ^1H NMR spectrum and is a doublet (J = 160.3 Hz) of triplets (J = 20.9 Hz), confirming the *fac* orientation of the phosphines. The three PMe_3 ligands are all inequivalent and give rise to a complicated second-order ABC pattern in the $^{31}P\{^1H\}$ NMR spectrum.

Scheme II



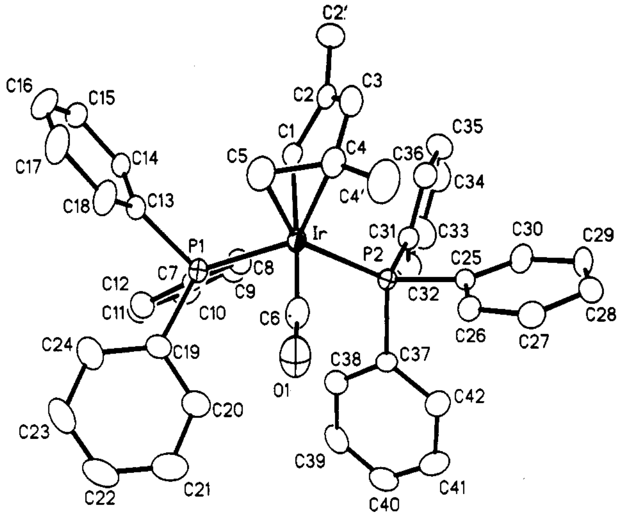


Figure 3. ORTEP drawing of (1,4,5-η-2,4-dimethylpentadienyl)Ir(PPh_3)$_2$(CO). (**6**).

Treatment of ClIr(PMe_3)$_3$ with unmethylated pentadienide cleanly produces (1,4,5-η-pentadienyl)Ir(PMe_3)$_3$ (**5**) (see Scheme I). As in the reaction of ClIr(PEt_3)$_3$ with potassium pentadienide, no metallacyclic products can be detected.

C. Reactions of ClIr(PPh_3)$_2$(CO) with Potassium 2,4-Dimethylpentadienide and Potassium Pentadienide. When Vaska's complex, ClIr(PPh_3)$_2$(CO), is treated with potassium 2,4-dimethylpentadienide, no metallacyclic products are observed. This is perhaps not surprising, given the relative electron-poorness of the IrL_3 fragment in this case. Instead, an equilibrium mixture of (1,4,5-η-2,4-dimethylpentadienyl)Ir(PPh_3)$_2$(CO) (**6**) and (1–3-η-2,4-dimethylpentadienyl)Ir(PPh_3)$_2$(CO) (**7**) is obtained (see Scheme II). Interconversion between **6** and **7** probably involves the intermediacy of (η^1-2,4-dimethylpentadienyl)Ir(PPh_3)$_2$(CO). The iridium center in this 16e$^-$ species can coordinate the terminal double bond (producing **6**) or the internal double bond (producing **7**). At 20 °C in methylene chloride, the 1–3-η-2,4-dimethylpentadienyl compound predominates slightly (**7**:**6** = 1.5:1), but it is the 1,4,5-η-dimethylpentadienyl isomer that crystallizes from THF/pentane by using the slow diffusion technique.

The molecular structure of compound **6**, determined by a single-crystal X-ray diffraction study, is shown in Figure 3. Selected bond distances and angles are reported in Table III. As with compounds **2** and **3**, the coordination

Table III. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (1,4,5-η-2,4-Dimethylpentadienyl)Ir(PPh$_3$)$_2$(CO) (6)

	Bond Distances		
Ir–P(1)	2.336 (2)	C(1)–C(2)	1.506 (10)
Ir–P(2)	2.359 (2)	C(2)–C(2′)	1.519 (13)
Ir–C(1)	2.143 (7)	C(2)–C(3)	1.309 (13)
Ir–C(4)	2.214 (8)	C(3)–C(4)	1.484 (12)
Ir–C(5)	2.141 (7)	C(4)–C(4′)	1.498 (12)
Ir–C(6)	1.886 (7)	C(4)–C(5)	1.430 (11)
	Bond Angles		
P(1)–Ir–P(2)	115.2 (1)	C(5)–Ir–C(6)	87.2 (3)
P(1)–Ir–C(1)	88.1 (2)	Ir–C(1)–C(2)	110.7 (5)
P(2)–Ir–C(1)	92.9 (2)	C(1)–C(2)–C(2′)	117.2 (7)
P(1)–Ir–C(4)	137.1 (2)	C(1)–C(2)–C(3)	118.8 (7)
P(2)–Ir–C(4)	106.4 (2)	C(2′)–C(2)–C(3)	124.0 (8)
C(1)–Ir–C(4)	79.4 (3)	C(2)–C(3)–C(4)	119.9 (7)
P(1)–Ir–C(5)	100.1 (2)	Ir–C(4)–C(3)	107.9 (5)
P(2)–Ir–C(5)	144.5 (2)	Ir–C(4)–C(4′)	120.8 (6)
C(1)–Ir–C(5)	84.2 (3)	C(3)–C(4)–C(4′)	116.4 (7)
C(4)–Ir–C(5)	38.3 (3)	Ir–C(4)–C(5)	68.1 (4)
P(1)–Ir–C(6)	94.3 (2)	C(3)–C(4)–C(5)	114.3 (7)
P(2)–Ir–C(6)	93.5 (2)	C(4′)–C(4)–C(5)	120.1 (7)
C(1)–Ir–C(6)	171.4 (3)	Ir–C(5)–C(4)	73.6 (4)
C(4)–Ir–C(6)	93.2 (3)		

Scheme III

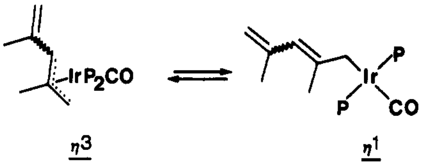


Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (*syn*-1-3-η-Pentadienyl)Ir(PPh$_3$)$_2$(CO) (8)[a]

	Molecule 1		
	Bond Distances		
Ir(1)–P(1)	2.296 (3)	Ir(1)–C(6)	1.872 (12)
Ir(1)–P(2)	2.353 (4)	C(1)–C(2)	1.445 (21)
Ir(1)–C(1)	2.193 (11)	C(2)–C(3)	1.453 (18)
Ir(1)–C(2)	2.120 (15)	C(3)–C(4)	1.508 (20)
Ir(1)–C(3)	2.217 (14)	C(4)–C(5)	1.348 (19)
	Bond Angles		
P(1)–Ir(1)–P(2)	107.3 (1)	C(1)–Ir(1)–C(6)	149.3 (7)
P(1)–Ir(1)–C(1)	89.8 (3)	C(2)–Ir(1)–C(6)	111.1 (6)
P(2)–Ir(1)–C(1)	100.1 (4)	C(3)–Ir(1)–C(6)	95.4 (5)
P(1)–Ir(1)–C(2)	110.3 (4)	Ir(1)–C(1)–C(2)	67.7 (7)
P(2)–Ir(1)–C(2)	121.7 (4)	Ir(1)–C(2)–C(1)	73.2 (8)
C(1)–Ir(1)–C(2)	39.1 (5)	Ir(1)–C(2)–C(3)	74.1 (8)
P(1)–Ir(1)–C(3)	149.4 (4)	C(1)–C(2)–C(3)	110.6 (13)
P(2)–Ir(1)–C(3)	95.1 (4)	Ir(1)–C(3)–C(2)	66.9 (8)
C(1)–Ir(1)–C(3)	65.4 (5)	Ir(1)–C(3)–C(4)	119.1 (8)
C(2)–Ir(1)–C(3)	39.1 (5)	C(2)–C(3)–C(4)	117.2 (13)
P(1)–Ir(1)–C(6)	98.3 (4)	C(3)–C(4)–C(5)	124.0 (14)
P(2)–Ir(1)–C(6)	105.5 (5)		
	Molecule 2		
	Bond Distances		
Ir(2)–P(1′)	2.292 (3)	Ir(2)–C(6′)	1.898 (13)
Ir(2)–P(2′)	2.345 (4)	C(1′)–C(2′)	1.453 (25)
Ir(2)–C(1′)	2.234 (12)	C(2′)–C(3′)	1.459 (19)
Ir(2)–C(2′)	2.100 (15)	C(3′)–C(4′)	1.477 (24)
Ir(2)–C(3′)	2.206 (15)	C(4′)–C(5′)	1.337 (25)
	Bond Angles		
P(1′)-Ir(2)–P(2′)	114.9 (1)	C(1′)–Ir(2)–C(6′)	151.0 (7)
P(1′)–Ir(2)–C(1′)	90.9 (4)	C(2′)–Ir(2)–C(6′)	112.8 (7)
P(2′)–Ir(2)–C(1′)	98.5 (4)	C(3′)–Ir(2)–C(6′)	95.8 (6)
P(1′)–Ir(2)–C(2′)	105.9 (4)	Ir(2)–C(1′)–C(2′)	65.5 (7)
P(2′)–Ir(2)–C(2′)	121.1 (5)	Ir(2)–C(2′)–C(1′)	75.5 (9)
C(1′)–Ir(2)–C(2′)	39.0 (7)	Ir(2)–C(2′)–C(3′)	74.2 (9)
P(1′)–Ir(2)–C(3′)	144.5 (4)	C(1′)–C(2′)–C(3′)	112.2 (15)
P(2′)–Ir(2)–C(3′)	95.7 (4)	Ir(2)–C(3′)–C(2′)	66.3 (8)
C(1′)–Ir(2)–C(3′)	65.9 (5)	Ir(2)–C(3′)–C(4′)	117.9 (9)
C(2′)–Ir(2)–C(3′)	39.5 (5)	C(2′)–C(3′)–C(4′)	118.6 (15)
P(1′)–Ir(2)–C(6′)	92.8 (4)	C(3′)–C(4′)–C(5′)	123.2 (16)
P(2′)–Ir(2)–C(6′)	105.9 (5)		

[a] This compound crystallized with two independent molecules in the asymmetric unit. Only molecule 1 is pictured in Figure 4.

geometry of 6 is probably best described as a distorted octahedron. The carbonyl ligand resides trans to σ-donating carbon C(1) of the pentadienyl group. The phosphine ligands lie approximately in the plane containing the iridium atom and the π-olefin component of the 2,4-dimethylpentadienyl ligand (C(4)–C(5)). This orientation allows back-bonding of electrons from the phosphines into π* orbitals on the olefin. As a result, the C(4)–C(5) bond distance (1.430 (11) Å) is considerably lengthened over that of a normal carbon–carbon double bond; however, it is not quite as long as the C(4)–C(5) bonds in the more electron-rich molecules 2 and 3.

Clean NMR spectra of 6 (without interference from isomeric compound 7) can be obtained by dissolving crystals of 6 in cold CD$_2$Cl$_2$ and recording the spectra at −40 °C. The ^{13}C{^{1}H} NMR spectrum of 6 closely resembles that of the other 1,4,5-η-pentadienyl complexes described earlier. The one difference is that C(1) is not strongly coupled to phosphorus, because it resides trans to a carbonyl ligand in 6. The ^{31}P{^{1}H} NMR spectrum is a second-order AB pattern. As the temperature of the sample is raised to 20 °C, peaks due to (1-3-η-2,4-dimethylpentadienyl)Ir(PPh$_3$)$_2$(CO) (7) begin to grow in, until ultimately the equilibrium mixture is obtained. The ^{13}C{^{1}H} NMR spectrum of 7 shows five well-separated resonances for the five pentadienyl carbons at δ 148.1 (C(4)), 110.5 (C(5)), 79.3 (C(2)), 56.6 (C(3)), and 36.5 (C(1)). The peak positions are similar to those observed in other (1-3-η-pentadienyl)metal complexes.[6] The ^{31}P{^{1}H} NMR spectrum of 7 is a broad hump at 20 °C, which decoalesces into the expected pair of doublets at about −20 °C. We believe that the fluxional process responsible for the broad ^{31}P resonance at room temperature is a pentadienyl ligand shift from η^3 to η^1 (see Scheme III).[7] This process would create mirror-plane symmetry in the molecule, making the two PPh$_3$ ligands equivalent. The free energy of activation (ΔG^*) for this process, determined from the coalescence temperature and the peak separation of the phosphine ^{31}P NMR signals at the stopped-exchange limit, is approximately 13 kcal/mol.

Treatment of Vaska's complex, ClIr(PPh$_3$)$_2$(CO), with unmethylated pentadienide cleanly produces (1-3-η-pentadienyl)Ir(PPh$_3$)$_2$(CO) (8) in high yield. No 1,4,5-η-pentadienyl or metallacyclic products can be detected. The molecular structure of 8, derived from a single-crystal X-ray diffraction study, is shown in Figure 4; selected bond distances and angles are given in Table IV. The pentadienyl ligand adopts the syn (W-shaped) geometry with torsional angles of 176.6 and 156.7° for C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5), respectively. As with other syn-1-3-η-pentadienyl structures,[6] C(1), C(2), C(3), and C(4) are essentially coplanar, while C(5) resides 0.42 Å out of the plane away from the iridium atom. The open

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[6] See, for example, the following: (a) Bleeke, J. R.; Hays, M. K. *Organometallics* **1984**, *3*, 506. (b) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422. (c) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1985**, *4*, 194. (d) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026. (e) Lush, S.-F.; Liu, R.-S. *Organometallics* **1986**, *5*, 1908. (f) Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Organometallics* **1986**, *5*, 2378.

[7] Shifts of this type has been observed in other (pentadienyl)metal(phosphine) complexes. See, for example: Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588.

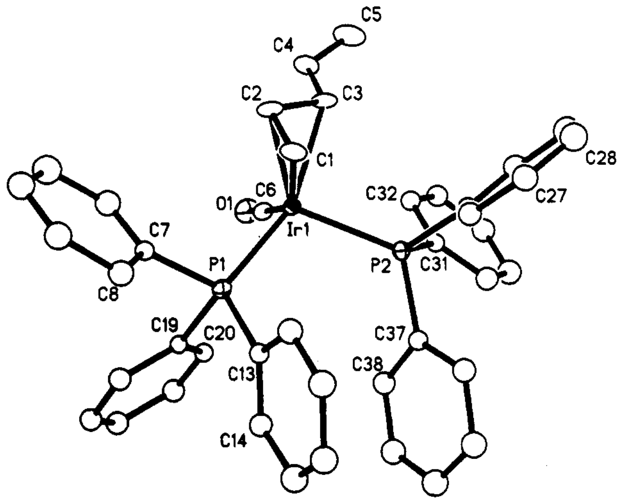

Figure 4. ORTEP drawing of (*syn*-1-3-η-pentadienyl)Ir(PPh_3)$_2$(CO) (**8**).

"mouth" of the metal-bound allyl moiety faces one of the PPh_3 ligands, while the other PPh_3 ligand and the carbonyl ligand reside under the allyl edges. The smaller carbonyl ligand lies under the vinyl-substituted side of the allyl moiety, probably for steric reasons.

As with compound **7**, the $^{31}P\{^1H\}$ NMR spectrum of **8** indicates that a relatively low-energy fluxional process is occurring in solution. At 20 °C the spectrum consists of a single broad signal, which, upon cooling to −60 °C, decoalesces and ultimately sharpens to a well-separated pair of doublets. Likewise in the ^1H NMR spectrum, the two protons on C(1) (H(1)$_{syn}$ and H(1)$_{anti}$) appear as a single broad resonance at 20 °C but decoalesce and reappear as well-separated signals at −60 °C. As with compound **7**, we believe that the dynamic process responsible for this behavior is a $\eta^3 \rightleftarrows \eta^1$ pentadienyl ligand shift (cf., Scheme III). As discussed above, this process would create mirror-plane symmetry, making the two phosphine ligands and the two hydrogens on C(1) equivalent. Using the coalescence temperatures and the peak separations of the coalescing signals (P(1)/P(2) and H(1)$_{syn}$/H(1)$_{anti}$) at the stopped-exchange limit, we have calculated a free energy of activation, ΔG^*, of approximately 11.5 kcal/mol for this process.

D. Reactions of ClIr(PEt_3)$_2$(CO) with Potassium 2,4-Dimethylpentadienide and Potassium Pentadienide. Treatment of ClIr(PEt_3)$_2$(CO), the triethylphosphine analogue of Vaska's complex, with potassium 2,4-dimethylpentadienide produces (1,4,5-η-2,4-dimethylpentadienyl)Ir(PEt_3)$_2$(CO) (**9**) (see Scheme II) in high yield. No 1-3-η-2,4-dimethylpentadienyl or metallacyclic products can be detected in the crude reaction mixtures. As expected, the NMR spectra of **9** closely resemble those of its PPh_3 analogue, **6**. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to C(1) is not strongly phosphorus-coupled, indicating that C(1) lies trans to the carbonyl ligand (as in **6**).

Finally, treatment of ClIr(PEt_3)$_2$(CO) with unmethylated pentadienide produces an equilibrium mixture of (1,4,5-η-pentadienyl)Ir(PEt_3)$_2$(CO) (**10**) and (1-3-η-pentadienyl)Ir(PEt_3)$_2$(CO) (**11**). At 20 °C in methylene chloride, compounds **10** and **11** are present in an approximate ratio of 2:1. The $^{31}P\{^1H\}$ NMR spectrum of the mixture of 20 °C consists of a second-order AB pattern for **10** and a broad singlet for **11**. As the sample is cooled, the broad singlet due to **11** continues to broaden until at −80 °C it disappears into the baseline. We are unable to observe the stopped-exchange limiting spectrum, indicating that the $\eta^3 \rightleftarrows \eta^1$ pentadienyl fluxional process in this system has a substantially lower barrier than in the PPh_3-containing systems discussed earlier (compounds **7** and **8**). This lower barrier probably results from the fact that the PEt_3 ligands are better electron donors than PPh_3 ligands and can, therefore, stabilize the 16e$^-$ (η^1-pentadienyl)IrL_3 intermediate more effectively.

Conclusion

From this survey of the reactions of a series of ClIrL_3 complexes with pentadienide reagents, the following conclusions can be drawn.

(1) Within the electron-rich (pentadienyl)Ir(PR_3)$_3$ systems (Scheme I), two types of reaction products are observed: metallacyclohexadienes and (1,4,5-η-pentadienyl)Ir(PR_3)$_3$ complexes. Methylation of the pentadienyl ligand in the 2- and 4-positions promotes metallacycle formation, probably by sterically destabilizing the π component of the 1,4,5-η-pentadienyl bonding mode. π-bond dissociation produces the key 16e$^-$ (η^1-pentadienyl)Ir(PR_3)$_3$ intermediate through which metallacycle formation proceeds.

(2) Introduction of just one electron-withdrawing carbonyl ligand onto the iridium center completely shuts down the metallacycle-forming reaction.

(3) The carbonyl-containing systems [(pentadienyl)Ir(PR_3)$_2$CO] are, in general, more prone to exhibit the 1-3-η-pentadienyl bonding mode than are the all-phosphine [(pentadienyl)Ir(PR_3)$_3$] systems (cf., Scheme II vs Scheme I). This may be a result of the fact that the 1,4,5-η-bonding mode is stabilized by strong π back-bonding into the π^* orbitals of the olefin moiety and is, therefore, a particularly favorable mode for very electron-rich systems.

(4) The formation of 1-3-η-pentadienyl products vs 1,4,5-η-pentadienyl products in the carbonyl-containing systems is favored by (a) more sterically demanding phosphine ligands and (b) the unmethylated pentadienyl ligand. The preference for the 1-3-η-bonding mode in complexes containing larger phosphine ligands probably derives from the fact that the 1,4,5-η-bonding mode is sterically more demanding; in the 1-3-η mode, the vinyl or isopropenyl substituent on the allyl moiety can swing out of the way of the rest of the molecule. The apparent preference of the 2,4-dimethylpentadienyl ligand for the 1,4,5-η (vs 1-3-η) bonding mode may result from the fact that the methyl substituents point away from each other in the U-shaped 1,4,5-η mode. In contrast, the methyl substituents in a W-shaped *syn*-1-3-η-2,4-dimethylpentadienyl ligand experience some steric contact.

(5) Finally, the 1-3-η-pentadienyl complexes undergo a dynamic process in solution, which involves shuttling between η^3- and η^1-pentadienyl bonding modes. The barrier for this process is lowered by electron-donating ligands that can stabilize the 16e$^-$ η^1-pentadienyl intermediate.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres drybox or by standard vacuum or Schlenk techniques. Solvents were stored under nitrogen after being distilled from appropriate drying agents. ClIr(PEt_3)$_3$ and ClIr(PMe_3)$_3$ were produced in situ via the reactions of [(cyclooctene)$_2$IrCl]$_2$[8] with 6 equiv of PEt_3 and PMe_3, respectively. Vaska's complex, ClIr(PPh_3)$_2$(CO),[9] and its triethylphosphine analogue, ClIr-

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[8] 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.

[9] Vrieze, K.; Collman, J. P.; Sears, C. T., Jr.; Kubota, M. In *Inorganic Syntheses*; Jolly, W. L., Ed.; McGraw-Hill: New York, 1968; Vol. 11, pp 101–104.

(PEt$_3$)$_2$(CO),[10] were prepared by literature routes. Potassium 2,4-dimethylpentadienide–tetrahydrofuran and potassium pentadienide–tetrahydrofuran were prepared by the method of Yasuda and Nakamura.[11]

NMR experiments were performed on a Varian XL-300 spectrometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra are referenced to tetramethylsilane, while ^{31}P spectra are referenced to H$_3$PO$_4$. Probe temperature were calibrated by using the temperature dependence for the frequency separation of the ^{1}H resonances of the methyl and hydroxyl groups of neat methanol below ambient temperatures and the ^{1}H resonances of the methylene and hydroxyl groups of neat ethylene glycol above ambient temperatures. In general, ^{1}H connectivities were determined from ^{1}H–^{1}H shift-correlated (COSY) 2D spectra; ^{1}H and ^{13}C peak assignments were made by using ^{13}C gated-decoupled spectra and ^{13}C-^{1}H shift-correlated (HETCOR) 2D spectra.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. High-resolution mass spectra were obtained with a VG-ZAB-3F mass spectrometer operated in the double-focusing mode, and data were processed with an associated VG-11-250 data system.

Dynamic NMR Studies. Determination of $\Delta G^\ddagger$. For each exchange process, NMR spectra were recorded over a range of temperatures, including the stopped-exchange-limiting temperature and the coalescence temperature. The exchange rate constant, k_c, at the coalescence temperature was calculated by using the formula

$$k_c = \frac{\pi(\Delta\nu)}{2^{1/2}}$$

where $\Delta\nu$ is the difference in frequency between the two exchanging sites in the stopped-exchange limit.[12] This exchange rate constant was then used to determine the free energy of activation, $\Delta G^\ddagger$, at the coalescence temperature, T_c, from the Eyring equation

$$k = \frac{k'}{h} T e^{-\Delta G^\ddagger/RT}$$

where k' = Boltzmann's constant, h = Planck's constant, and R = ideal gas constant.[13]

Synthesis of (1,4,5-η-Pentadienyl)Ir(PEt$_3$)$_3$ (2). Triethylphosphine (0.40 g, 3.4×10^{-3} mol) was added dropwise to a cold (0 °C) solution of [(cyclooctene)$_2$IrCl]$_2$ (0.50 g, 5.6×10^{-4} mol) in 25 mL of tetrahydrofuran (THF). After the mixture was stirred for about 1 h, potassium pentadienide–tetrahydrofuran (0.20 g, 1.1×10^{-3} mol) in 15 mL of THF was added dropwise. The resulting orange solution was warmed to room temperature and stirred overnight. After removal of the volatiles under vacuum, pentane was added and the solution was filtered through Celite. The pentane solution was concentrated and cooled to -30 °C, causing yellow-brown crystals of 2 to form (0.43 g; 63% yield). Anal. Calcd for C$_{23}$H$_{52}$IrP$_3$: C, 45.00; H, 8.56. Found: C, 44.65; H, 8.26.

^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.44 (s, 1 H(3)), 5.50 (s, 1, H(2)), 2.62 (s, 1, H(4)), 2.02 (s, 1, H(5)), 1.85–1.20 (m, 18, PEt$_3$ CH$_2$'s), 1.08–0.78 (m, 27, PEt$_3$ CH$_3$'s). H(1)'s and one H(5) are obscured.

^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C): δ 143.5 (d, $J_{\text{C-P}}$ = 13.2 Hz, C(3)), 133.9 (d, $J_{\text{C-P}}$ = 12.8 Hz, C(2)), 36.6 (d, $J_{\text{C-P}}$ = 25.2 Hz, C(4)), 22.4 (m, PEt$_3$ CH$_2$'s), 21.5 (m, PEt$_3$ CH$_2$'s), 20.9 (d, $J_{\text{C-P}}$ = 28.2 Hz, C(5)), 19.1 (d, $J_{\text{C-P}}$ = 21.0 Hz, PEt$_3$ CH$_2$'s), 10.1 (d of t, partially obscured, C(1)), 9.3 (m, PEt$_3$ CH$_3$'s).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C): a second-order pattern; δ -29.1 (dd, $J_{\text{P-P}} \approx$ 50 Hz, 14 Hz, 1), -29.6 (dd, $J_{\text{P-P}} \approx$ 50 Hz, 14 Hz, 1), -32.3 (t, $J_{\text{P-P}} \approx$ 14 Hz, 1).

Synthesis of (1,4,5-η-2,4-Dimethylpentadienyl)Ir(PMe$_3$)$_3$ (3) and *fac*-($\overline{\mathrm{IrCH_2C(Me){=}CHC(Me){=}C}}$H)(PMe$_3$)$_3$(H) (4). Trimethylphosphine (0.92 g, 1.2×10^{-2} mol) was added to a solution of [(cyclooctene)$_2$IrCl]$_2$ (1.8 g, 2.0×10^{-3} mol) in 100 mL of pentane. The solution was cooled to -78 °C, and potassium 2,4-dimethylpentadienide–tetrahydrofuran (0.82 g, 4.0×10^{-3} mol) in 50 mL of THF was added dropwise with stirring. The resulting opaque yellow mixture was warmed slowly to room temperature to give a cloudy amber solution. After removal of the volatiles under vacuum, the yellow residue was extracted into pentane and filtered through Celite. Removal of the pentane produced 1.75 g of a light yellow power containing isomeric compounds 3 and 4 (85% yield). Anal. Calcd for C$_{16}$H$_{38}$IrP$_3$: C, 37.26; H, 7.44. Found: C, 37.21; H, 7.42.

Isolation of (1,4,5-η-2,4-Dimethylpentadienyl)Ir(PMe$_3$)$_3$ (3). Approximately 1.0 g of the mixture described above was refluxed in 50 mL of pentane for 30 min. Partial removal of the pentane solvent in vacuo resulted in precipitation of a small quantity of unconverted compound 4. Decantation of the mother liquor, followed by further removal of pentane in vacuo, then yielded 3 as lemon yellow microcrystals. Recrystallization from pentane at -30 °C gave clear yellow plates of pure 3.

^{1}H NMR (C$_6$D$_6$, 6 °C): δ 6.03 (s, 1, H(3)), 2.08 (br m, 1, H(5)), 1.99 (s, 3, pentadienyl CH$_3$), 1.95 (d, J = 9.0 Hz, 3, pentadienyl CH$_3$), 1.87 (br m, 1, H(1)), 1.78 (q, J = 7.5 Hz, 1, H(5)), 1.27 (d, $J_{\text{H-P}}$ = 7.1 Hz, 9, PMe$_3$ CH$_3$'s), 1.20 (d, $J_{\text{H-P}}$ = 6.5 Hz, 9, PMe$_3$ CH$_3$'s), ~1.10 (partially obscured, H(1)), 1.09 (d, $J_{\text{H-P}}$ = 6.2 Hz, 9, PMe$_3$ CH$_3$'s).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 6 °C): δ 143.8 (s, C(3)), 140.2 (d, $J_{\text{C-P}}$ = 13.4 Hz, C(2)), 43.6 (d, $J_{\text{C-P}}$ = 37.1 Hz, C(4)), 29.6 (s, pentadienyl CH$_3$), 29.1 (d, partially obscured, C(5)), 22.3 (d, $J_{\text{C-P}}$ = 19.9 Hz, PMe$_3$ CH$_3$'s), 21.8 (d, $J_{\text{C-P}}$ = 5.7 Hz, pentadienyl CH$_3$), 21.4 (d, $J_{\text{C-P}}$ = 19.9 Hz, PMe$_3$ CH$_3$'s), 16.5 (br d, $J_{\text{C-P}}$ = 71.0 Hz, C(1)).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 6 °C): δ -53.4 (dd, $J_{\text{P-P}}$ = 41.8 Hz, 18.3 Hz, 1), -58.7 (complex m, 2).

Isolation of *fac*-($\overline{\mathrm{IrCH_2C(Me){=}CHC(Me){=}C}}$H)(PMe$_3$)$_3$(H) (4). Approximately 1.0 g of the mixture described above was refluxed in 50 mL of acetone for 30 min. The acetone was removed in vacuo, and the residue was dissolved in pentane. Partial removal of the pentane solution in vacuo resulted in the precipitation of yellow-orange blocks of 4. These blocks were filtered out and recrystallized from pentane at -30 °C.

In the following spectra, the ring carbons are numbered by starting at the methylene (CH$_2$) end.

^{1}H NMR (C$_6$D$_6$, 6 °C): δ 6.77 (d of t, $J_{\text{H-P}}$ = 16.1 Hz, 5.9 Hz, 1, H(5)), 5.86 (s, 1, H(3)), 2.55 (br m, 1, H(1)), 2.40 (d, J = 2.3 Hz, 3, ring CH$_3$), 2.25 (br m, 1, H(1)), 2.21 (s, 3, ring CH$_3$), 1.18 (d, $J_{\text{H-P}}$ = 6.9 Hz, 9, PMe$_3$ CH$_3$'s), 1.13 (d, $J_{\text{H-P}}$ = 7.2 Hz, 9, PMe$_3$ CH$_3$'s), 1.05 (d, $J_{\text{H-P}}$ = 6.6 Hz, 9, PMe$_3$ CH$_3$'s), -11.27 (d of t, $J_{\text{H-P}}$ = 160.3 Hz, 20.9 Hz, 1, Ir–H).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 6 °C): δ 140.5, 130.2 (s's, C(4)/C(2)), 128.1 (s, C(3)), 121.6 (br d, $J_{\text{C-P}}$ = 81.8 Hz, C(5)), 29.0 (d, $J_{\text{C-P}}$ = 9.6 Hz, ring CH$_3$), 28.0 (d, $J_{\text{C-P}}$ = 7.2 Hz, ring CH$_3$), 21.2 (d, $J_{\text{C-P}}$ = 27.7 Hz, PMe$_3$ CH$_3$'s), 20.6 (d, $J_{\text{C-P}}$ = 26.5 Hz, PMe$_3$ CH$_3$'s), 17.0 (d, $J_{\text{C-P}}$ = 23.5 Hz, PMe$_3$ CH$_3$'s), -3.0 (br d, $J_{\text{C-P}}$ = 71.8 Hz, C(1)).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 6 °C): δ -57.3 (complex m, 3).

Synthesis of (1,4,5-η-Pentadienyl)Ir(PMe$_3$)$_3$ (5). A procedure analogous to that described for compound 2 was employed. Treatment of [(cyclooctene)$_2$IrCl]$_2$ (0.50 g, 5.6×10^{-4} mol) with trimethylphosphine (0.26 g, 3.4×10^{-3} mol) and potassium pentadienide–tetrahydrofuran (0.20 g, 1.1×10^{-3} mol) produced 0.29 g of yellow crystalline 5 (54% yield). Anal. Calcd for C$_{14}$H$_{34}$IrP$_3$: C, 34.48; H, 7.04. Found: C, 34.65; H, 7.00.

^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.70 (s, 1 H(3)), 5.77 (br s, 1, H(2)), 2.45 (br s, 1, H(4)), 1.86, 1.42 (br s's, 4, H(1)'s and H(5)'s), 1.26 (d, $J_{\text{H-P}}$ = 7.2 Hz, 18, PMe$_3$ CH$_3$'s), 0.98 (d, $J_{\text{H-P}}$ = 7.4 Hz, 9, PMe$_3$ CH$_3$'s).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C): δ 143.9 (m, C(3)), 134.8 (d, $J_{\text{C-P}}$ = 18 Hz, C(2)), 38.9 (d, $J_{\text{C-P}}$ = 34 Hz, C(4)), 23.5 (d, $J_{\text{C-P}}$ = 34 Hz, C(5)), 22.0 (m, PMe$_3$ CH$_3$'s), 18.7 (m, PMe$_3$ CH$_3$'s), 11.3 (br d, $J_{\text{C-P}}$ = 79 Hz, C(1)).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 22 °C): δ -54.1 (t, $J_{\text{P-P}} \approx$ 15 Hz, 1), -54.8 (dd, $J_{\text{P-P}} \approx$ 51 Hz, 15 Hz, 1), -55.8 (dd, $J_{\text{P-P}} \approx$ 51 Hz, 15 Hz, 1).

Synthesis of (1,4,5-η-2,4-Dimethylpentadienyl)Ir(PPh$_3$)$_2$(CO) (6) and (1-3-η-2,4-Dimethylpentadienyl)Ir(PPh$_3$)$_2$(CO) (7). *trans*-ClIr(PPh$_3$)$_2$(CO) (1.0 g, 1.3×10^{-3} mol) was added to 25 mL of THF, and the solution was cooled to ~-20 °C in an

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Table V. X-ray Diffraction Structure Summary

	2	3	6	8
Crystal Parameters and Data Collection Summary				
formula	$C_{23}H_{52}IrP_3$	$C_{16}H_{38}IrP_3$	$C_{44}H_{41}IrOP_2$	$C_{42}H_{37}IrOP_2$
fw	613.8	515.6	839.9	811.9
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	15.489 (5)	8.958 (6)	13.518 (5)	17.276 (7)
b, Å	11.453 (5)	20.308 (5)	17.862 (6)	23.038 (8)
c, Å	15.769 (4)	11.970 (5)	15.417 (5)	18.896 (5)
α, deg	90.0	90.0	90.0	90.0
β, deg	101.83 (2)	93.14 (5)	93.59 (3)	111.92 (2)
γ, deg	90.0	90.0	90.0	90.0
V, Å^3	2738 (2)	2174 (2)	3715 (2)	6977 (4)
Z	4	4	4	8
cryst dimens, mm	0.30 × 0.50 × 0.90	0.50 × 0.58 × 0.70	0.25 × 0.30 × 0.63	0.15 × 0.40 × 0.40
cryst color	yellow-brown	yellow	yellow	yellow
d_{calcd}, g/cm^3	1.489	1.575	1.502	1.546
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
scan type	θ:2θ	θ2:θ	θ:2θ	Wyckoff
scan rate, deg/min in ω	variable; 4.19–9.77	variable; 2.44–14.65	variable; 4.19–9.77	fixed; 9.77
scan range	1.20° plus Kα separation	1.20° plus Kα separation	1.20° plus Kα separation	0.60°
2θ range, deg	3.5–55.0	3.5–55.0	3.5–55.0	3.5–50.0
data collcd	h (0→20)	h (0→11)	h (0→17)	h (0→20)
	k (0→14)	k (0→25)	k (0→23)	k (0→27)
	l (-20→20)	l (-15→15)	l (-20→20)	l (-22→20)
tot. decay	9.1%	none obsd	none obsd	none obsd
Treatment of Intensity Data and Refinement Summary				
no. of data collcd	7814	5462	9300	13098
no. of unique data	6287	5002	8509	12310
no. of data with $I > 3\sigma(I)$	3572	3440	5003	6353
Mo Kα linear abs coeff, cm^{-1}	50.38	63.29	36.96	39.33
abs corr applied	semiempirical	semiempirical	semiempirical	semiempirical
data to param ratio	13.5:1	18.9:1	11.5:1	13.5:1
R^a	0.0381	0.0367	0.0346	0.0490
$R_w{}^a$	0.0426^b	0.0437^c	0.0413^d	0.0526^e
GOF^f	3.33	1.25	0.97	1.17

[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] Unit weight. [c] $w = [\sigma^2(F_o) + 0.0007(F_o)^2]^{-1}$. [d] $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1}$. [e] $w = [\sigma^2(F_o) + 0.0006(F_o)^2]^{-1}$. [f] GOF $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$.

acetone/ice bath. Potassium 2,4-dimethylpentadienide–tetrahydrofuran (0.26 g, 1.3 × 10^{-3} mol) in 15 mL of THF was added dropwise with stirring over 40 min. Although considerable undissolved solid remained at -20 °C, all of the solid dissolved upon warming to room temperature, producing a yellow solution with a greenish tint. After the solution was stirred for 4 h at room temperature, the volatiles were removed under vacuum, leaving an oily residue. The oily residue was extracted with pentane, filtered through Celite, and dried in vacuo several times. This procedure yielded a white solid with a faint yellow/green tint, which contained both 6 and 7. Pale yellow/green crystals of pure 6 (0.87 g) were obtained by slow diffusion of pentane into a concentrated solution of the crude powder in THF over a period of about 2 weeks (80% yield). Anal. Calcd for $C_{44}H_{41}IrOP_2$: C, 62.91; H, 4.93. Found: C, 63.10; H, 4.95. NMR spectra of pure 6 were obtained by dissolving crystals of 6 in CD_2Cl_2 at -40 °C and recording the spectra at this temperature.

^{1}H NMR (CD_2Cl_2, -40 °C): δ 7.26–7.08 (m's, 30, phenyl H's), 5.39 (s, 1, H(3)), 2.37 (m, 1, H(5)), 1.70 (m, 1, H(5)), 1.32 (s, 3, pentadienyl CH_3), 1.11 (m, 4, H(1) and pentadienyl CH_3), 0.09 (m, 1, H(1)).

^{13}C{^{1}H} NMR (CD_2Cl_2, -40 °C): δ 179.2 (s, carbonyl C), 143.3 (d, J_{C-P} = 12 Hz, C(2)), 138.2 (s, C(3)), 136.6–127.5 (m's, phenyl C's), 61.5 (d, J = 24 Hz, C(4)), 37.7 (d, J = 22 Hz, C(5)), 24.4 (s, pentadienyl CH_3), 22.2 (m, C(1)), 21.9 (s, pentadienyl CH_3).

^{31}P{^{1}H} NMR (CD_2Cl_2, -40 °C): second-order AB multiplet centered at δ 3.5.

^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 4.1 (d, J_{P-P} = 50 Hz, 1), 2.3 (d, J_{P-P} = 50 Hz, 1).

As a solution of 6 was warmed to room temperature, isomeric compound 7 gradually formed. At 20 °C in CD_2Cl_2, the equilibrium ratio of 7 to 6 was approximately 1.5:1. From this mixture, the following NMR resonances due to 7 were obtained.

^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.36–7.18 (m's, 30, phenyl H's), 4.86–4.83 (m, 2, H(5)'s), 2.01 (s, 3, pentadienyl CH_3), 1.90 (s, 3, pentadienyl CH_3), 1.8–1.2 (m's, 3, H(3) and H(1)'s).

^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 186.9 (s, carbonyl C), 148.1 (s, C(4)), 137.6–127.9 (m's, phenyl C's), 110.5 (s, C(5)), 79.3 (s, C(2)), 56.6 (s, C(3)), 36.5 (s, C(1)), 23.3 (s, pentadienyl CH_3), 19.5 (s, pentadienyl CH_3).

^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 9.9 (v br).

^{31}P{^{1}H} NMR (CD_2Cl_2, -40 °C): δ 15.0 (d, J_{P-P} = 58 Hz, 1), 6.8 (d, J_{P-P} = 58 Hz, 1).

Synthesis of (1-3-η-Pentadienyl)Ir(PPh_3)$_2$(CO) (8). A procedure analogous to that described for compound 6 was employed. Treatment of *trans*-ClIr(PPh_3)$_2$(CO) (1.0 g, 1.3 × 10^{-3} mol) with potassium pentadienide–tetrahydrofuran (0.23 g, 1.3 × 10^{-3} mol) produced 0.84 g of yellow crystalline 8 (80% yield). Anal. Calcd for $C_{42}H_{37}IrOP_2$: C, 62.12; H, 4.60. Found: C, 61.88; H, 4.64.

^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.20–7.00 (m, 30, phenyl H's), 6.03 (m, 1, H(4)), 4.81 (d, J = 18 Hz, 1, H(5)), 4.75 (d, J = 10 Hz, 1, H(5)), 3.92 (m, 1, H(2)), 2.35 (m, 1, H(3)), 0.53 (br s, 2, H(1)'s). As the sample was cooled to -80 °C, the broad peak at δ 0.53 decoalesced to two peaks: δ 1.05 (m, 1, H(1)$_{syn}$), -0.24 (dd, J = 22 Hz, 6 Hz, 1, H(1)$_{anti}$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 185.0 (s, carbonyl C), 143.9 (s, C(4)), 137.2–128.1 (m's, phenyl C's), 108.9 (s, C(5)), 68.3 (s, C(2)), 55.0 (s, C(3)), 30.6 (s, C(1)).

^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 12.0 (br s).

^{31}P{^{1}H} NMR (CD_2Cl_2, -80 °C): δ 18.9 (d, J_{P-P} = 52 Hz, 1), 7.1 (d, J_{P-P} = 52 Hz, 1).

Synthesis of (1,4,5-η-2,4-Dimethylpentadienyl)Ir(PEt_3)$_2$(CO) (9). *trans*-ClIr(PEt_3)$_2$(CO) (0.50 g, 1.0 × 10^{-3} mol) was dissolved in 10 mL of THF, and the solution was cooled to -78 °C in an acetone/dry-ice bath. Potassium 2,4-dimethylpentadienide–tetrahydrofuran (0.21 g, 1.0 × 10^{-3} mol) in 10 mL of THF was added dropwise with stirring over 40 min. The resulting yellow solution was warmed to room temperature and stirred for 4 h. before removal of the volatiles in vacuo. The oily residue was extracted with pentane and filtered through Celite, producing a very faintly colored yellow/green solution. Cooling to -30 °C produced 0.48 g of large, nearly colorless blocks of **9** (90% yield). Anal. Calcd for $C_{20}H_{41}IrOP_2$: C, 46.12; H, 7.95. Found: C, 45.88; H, 7.63.

^{1}H NMR ($CDCl_3$, 20 °C): δ 5.48 (s, 1, H(3)), 2.11 (d, J = 3.8 Hz, 1, H(5)), 1.83 (d, J = 8 Hz, 3, pentadienyl CH_3), 1.76–1.66 (m, 12, PEt_3 CH_2's), 1.45 (s, 3, pentadienyl CH_3), 1.3–0.8 (m's, 3, H(5) and H(1)'s) 0.99–0.89 (m, 18, PEt_3 CH_3's).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 178.1 (s, carbonyl C), 141.8 (d, J_{C-P} = 14 Hz, C(2)), 139.1 (s, C(3)), 51.2 (d, J_{C-P} = 26 Hz, C(4)), 29.4 (d, J_{C-P} = 22 Hz, C(5)), 28.0 (s, pentadienyl CH_3), 21.8 (s, pentadienyl CH_3), 20.9 (d, J = 22 Hz, PEt_3 CH_2's), 20.0 (d, J = 22 Hz, PEt_3 CH_2's), 10.3 (t, J_{C-P} = 9 Hz, C(1)), 8.1 (s, PEt_3 CH_3's).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ -20.4 (d, J_{P-P} = 53 Hz, 1), -22.0 (d, J_{P-P} = 53 Hz, 1).

Synthesis of (1,4,5-η-Pentadienyl)Ir(PEt_3)$_2$(CO) (10) and (1-3-η-Pentadienyl)Ir(PEt_3)$_2$(CO) (11). A procedure analogous to that described for compound **9** was employed. Treatment of *trans*-ClIr(PEt_3)$_2$(CO) (0.50 g, 1.0 × 10^{-3} mol) with potassium pentadienide–tetrahydrofuran (0.18 g, 1.0 × 10^{-3} mol) produced 0.43 g of a yellow oil containing **10** and **11** in an approximate ratio of 2:1 (88% yield).

MS (high resolution, electron impact, solid probe, 70 eV): calcd for M^+, m/e 522.193, 524.195; found, m/e 522.198, 524.203.

^{1}H NMR (CD_2Cl_2, 20 °C): δ 5.90 (br s, H(2) or H(3) in **10**), 5.15 (br s, H(3) or H(2) in **10**), 3.05 (br s, H(4) in **10**), 2.22 (br s, H(5) in **10**), 1.9–1.2 (br m, PEt_3 CH_2's), 1.0–0.5 (br m, PEt_3 CH_3's). H(1)'s and one H(5) in **10** are obscured. Resonances due to minor isomer **11** were very broad and could not be reliably assigned.

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 185.7, 178.2 (s's, carbonyl C's in **10** and **11**), 145.5 (s, C(4) in **11**), 140.6 (s, C(2) or C(3) in **10**), 135.2 (d, J_{C-P} = 15 Hz, C(3) or C(2) in **10**), 105.2 (s, C(5) in **11**), 60.4 (s, C(2) in **11**), 48.2 (br s, C(3) in **11**), 42.2 (d, J_{C-P} = 24 Hz, C(4) in **10**), 23.3 (d, J_{C-P} = 28 Hz, C(5) in **10**), 22.0–20.0 (m's, PEt_3 CH_2's), 8.9–8.4 (m's, PEt_3 CH_3's), 7.0 (br s, C(1) in **10**). C(1) in **11** is obscured.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ -12.8 (br s, P's in **11**), -18.5 (d, J_{P-P} = 51 Hz, P in **10**), -21.4 (d, J_{P-P} = 51 Hz, P in **10**).

Single-Crystal X-ray Diffraction Studies. Suitable crystals of compounds **2**, **3**, **6**, and **8** were mounted in glass capillaries under inert atmosphere. Data were collected at room temperature on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 50 or 100 events as check reflections for crystal deterioration and/or misalignment. Where necessary, corrections were made for linear decay. All data reduction and refinement were done by using the Siemens SHELXTL PLUS program package on a MicroVAX II computer.[14] Crystal data and details of data collection and structure analysis are summarized in Table V.

In each case, the positions of most of the non-hydrogen atoms were obtained by using direct methods. The structures were completed by successive full-matrix least-squares refinements and difference Fourier map calculations. All non-hydrogen atoms, except for the phenyl carbons in **8**, were refined anisotropically; the phenyl carbons in **8** were refined isotropically.

The hydrogen atoms on the pentadienyl ligand in compound **2** were positionally refined, while all other H's in **2** were placed at idealized positions, riding upon their respective carbon atoms. A common, fixed isotropic thermal parameter was assigned. All of the hydrogen atoms in compound **3** were placed at idealized positions, riding upon their respective carbon atoms. The pentadienyl H's were given a common, fixed isotropic thermal parameter, while a common isotropic temperature factor was refined for all of the other hydrogens. The pentadienyl hydrogens in **6** were located in the difference Fourier maps and their positions were fixed. All other H's in **6** were added at idealized positions, riding upon their respective carbon atoms. A common isotropic thermal parameter was refined. In compound **8**, only the phenyl hydrogens were included in the model. They were placed at idealized positions, riding upon their respective carbon atoms, and a common isotropic temperature factor was refined.

Compound **8** crystallized with two molecules in the asymmetric unit. Only one of these is pictured in Figure 4. An ORTEP drawing of the other molecule and a complete set of structural data are included in the supplementary material.

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Supplementary Material Available: Structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **2**, **3**, **6**, and **8** and ORTEP drawings of the two crystallographically independent molecules of **8** (34 pages); listings of observed and calculated structure factor amplitudes (116 pages). Ordering information is given on any current masthead page.

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