Iridium-Promoted Reactions of Carbon−Carbon Bonds. Skeletal Rearrangement of a Vinylcyclopropene during Iridacyclohexadiene Formation and Subsequent Isomerization of Iridacyclohexadienes via α,α′-Substituent Migrations

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Abstract: On treatment with $[Ir(PMe_3)_2(acac)]$ at room temperature, 1,2,3-triphenyl-3-vinylcyclopropene undergoes ring opening accompanied by rearrangement to give, instead of the expected 1,2,3-triphenyliridacyclohexadiene complex, a crystallographically characterized 1,2,4-triphenyliridacyclohexadiene complex containing *cis*-phosphine ligands. Studies with ^2H- and doubly ^{13}C-labeled vinylcyclopropenes, the syntheses and characterization of which are also reported, show that this process involves a rearrangement of the carbon skeleton and not a substituent shift. The corresponding 1,2-diphenyl-3-vinylcyclopropene undergoes iridacyclohexadiene formation without any rearrangement. On heating at 90 °C, each iridacycle converts to its corresponding isomer containing *trans*-phosphine ligands without any skeletal or substituent rearrangement of the metallacycle, as evidenced by absence of change in the labeling pattern. At higher temperatures, further rearrangement occurs in the case of each metallacycle, which does not alter the metallacyclohexadiene backbone, but rather exchanges the substituents of the α and α′ carbon atoms. This rearrangement is shown to occur even when there is no driving force due to relief of steric effects. Mechanisms for each rearrangement are proposed and discussed.

Introduction

The ring opening of vinylcyclopropenes by transition metal complexes to give metallacyclohexadienes and related compounds is now well-established.[2−15] Metallacyclohexadienes are compounds of considerable interest, yet few isolated examples exist, and their reaction chemistry is poorly defined. They have been invoked as key intermediates in the Dötz reaction,[16] and iridacyclohexadiene species, obtained by a different route,[17] were shown to undergo a facile deprotonation at the α-carbon to afford the first examples of iridabenzene complexes, leading to an extensive chemistry for these compounds.[18−29] The first isolable examples of metallacyclohexadiene complexes of general structure **1** and their related η^3-pentadienediyl relatives **2** were obtained from the ring-opening reactions of 3-vinyl-1-

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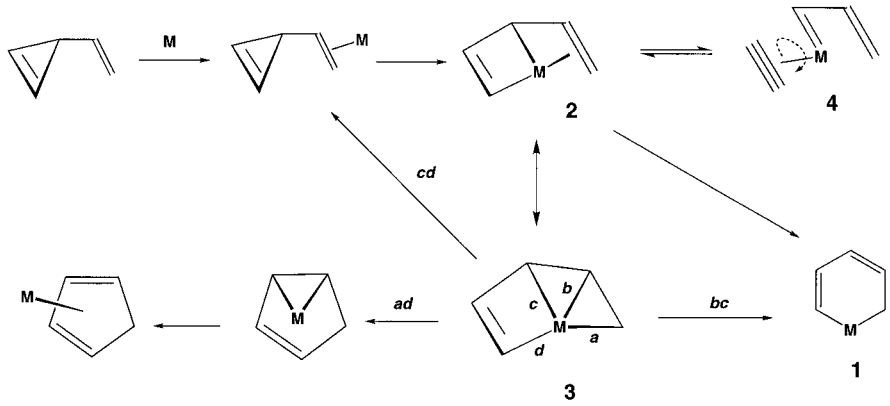
Scheme 1



cyclopropenes with low valent transition metal complexes, as shown in Scheme 1.[6] The reaction can be thought of as occurring via initial coordination of the alkene, followed by insertion of the metal into one of the flanking C−C σ-bonds of the cyclopropene ring. Canonical form **3** is a valid resonance structure of **2**, and much of the known chemistry of these compounds can be rationalized in terms of reductive elimination/oxidative addition of C−C bonds using **3** as shown in Scheme 1. For example, reductive elimination of bonds *cd* affords the vinylcyclopropene complex, elimination of bonds *bc* yields a metallacyclohexadiene, and coupling of bonds *ad* generates a coordinated cyclopentadiene; examples of all these reactions have been observed previously.[2−15] We believe this model is useful for understanding the chemistry described in this paper, in which we describe other skeletal contortions and substituent gymnastics observed in these systems.

Skeletal rearrangements have been observed previously during the reactions of vinylcyclopropenes with transition metal complexes. Various vinylcyclopropenes and cyclopropenyl ketones have been observed to undergo skeletal rearrangements in the presence of Rh(I) and Rh(II) en route to furans, cyclopentadienes, and carbonylation products.[10,11] In the transition-metal-catalyzed ring opening and carbonylation of cyclopropenyl ketones, both Liebeskind[10] and Padwa[11] have observed a skeletal rearrangement in which the carbons presumed adjacent to the metal exchange positions. This exchange was ascribed to fragmentation of the ligand into an acetylene and a ketocarbene over the course of the ring closure; rotation of the η^2-alkyne in an intermediate like **4** (Scheme 1) affords the observed rearrangement. Liebeskind has observed that the substituents on the organic substrate greatly affect whether the rearrangement is observed,[10] while Padwa has noted that the nature of the metal−ligand combination also exerts a strong influence.[11]

We have recently reported that the ring opening of 1,2-diphenyl-3-vinyl-1-cyclopropene **5** (Chart 1) with the rhodium fragment $[RhCl(PMe_3)_2]$ unexpectedly proceeds via a skeletal rearrangement during the kinetically controlled ring-opening process, to give a mixture of **6** and **7**.[9] Here we report that an iridium(I)-promoted reaction of **5** to give an iridacyclohexadiene does not proceed with any skeletal rearrangement but that 1,2,3-triphenylvinylcyclopropene **8** undergoes a previously unobserved skeletal rearrangement during ring opening at room temperature. However, both the kinetically formed iridacyclohexadienes undergo ring substituent migrations on subsequent heating. Part of this work has been communicated previously.[15]

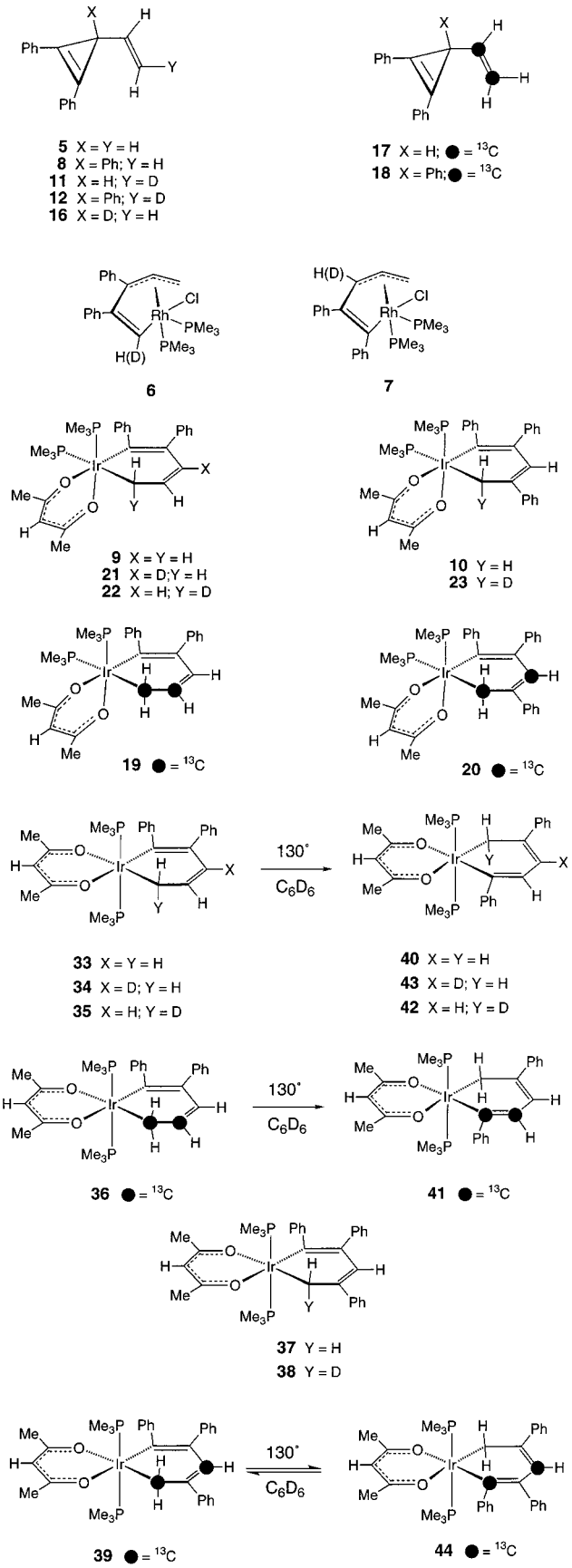
Results and Discussion

Observation of the Low Temperature Rearrangement. Room-temperature reaction of the 16-electron Ir(I) complex $[Ir(acac)(PMe_3)_2]$ (acac = acetylacetonate) with **5** affords the iridacyclohexadiene complex **9** as a single stereoisomer. This and isotopic labeling results described below clearly show that there is no skeletal rearrangement of the type previously observed in Rh(I) chemistry. In contrast, the corresponding triphenylvinylcyclopropene **8** reacts at room temperature with $[Ir(acac)(PMe_3)_2]$ to form a single product whose phenyl groups are clearly no longer on contiguous carbon atoms. This reaction works equally well when the $[Ir(acac)(PMe_3)_2]$ is prepared and isolated ahead of time, or when it is prepared in situ from PMe_3 and $[Ir(acac)(C_2H_4)_2]$. NMR spectra of the product suggested structure **10**, which was confirmed by a single crystal X-ray diffraction study. An ORTEP diagram is presented in Figure 1; crystal data collection and refinement parameters for the structure are presented in Table 1, and selected bond distances and angles, in Table 2. The octahedral geometry around the iridium is relatively unremarkable, with the exception of the difference in the Ir−PMe_3 bond lengths. At 2.409(2) Å, the bond to the equatorial phosphine P(1) is slightly longer than a typical Ir(III)−PMe_3 bond (2.30−2.38 Å),[30] while the bond to the axial phosphine P(2) is significantly shorter (2.219(2) Å). Although Ir(III)−PMe_3 bonds are known to be strongly subject to the influence of the ligand trans to it,[30] to our knowledge, only $[Ir(C_5H_5)(Cl)(Me)(PMe_3)]$ has a comparably short Ir(III)−PMe_3 bond distance (2.228 Å).[30a] The near perpendicularity of the bond angles around the iridium also suggests that this difference arises from the trans influence of the other ligands in the coordination sphere, rather than from steric factors.

The NMR spectra of **10** jibe with the crystal structure. A small ^1H NMR coupling (3 Hz) between the methine proton (H_9 on C_9) and one of the methylene protons (H_{11a} on C_{11}) is consistent with a W-interaction, although no coupling between H_9 and the other methylene proton (H_{11b}) is observed. In the $^{13}C\{^1H\}$ spectrum, the large coupling between C_{11} and the equatorial phosphine P_1 is consistent with their trans-orientation;[17,18,31] this coupling is also observed in diphenyl compound

(30) (a) For the structure of $[Ir(C_5H_5)(Cl)(Me)(PMe_3)]$, see: Foo, T.; Bergman, R. G. *Organometallics* **1992**, *11*, 1801−1810. (b) Examples of other compounds can be found in: Deeming, A. J.; Doherty, S.; Marshall, J. E. *Polyhedron* **1991**, *10*, 1857−1864. Einstein, F. W. B.; Yan, X.; Sutton, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *C47*, 1957−1976. (d) Knorr, J. R.; Merola J. S. *Organometallics* **1990**, *9*, 3008−3010. Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O. *J. Chem. Soc., Dalton Trans.* **1990**, 1429−1432. Behr, A.; Hertweck, E.; Herrmann, W. A.; Keim, W.; Kipshagen, W. *J. Chem. Soc.* **1986**, 1262−1263. Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387−6389. Kaner, R. B.; Kouvetakis, J.; Mayorga, S. G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 500−501. Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223−1230. Kalck, P.; Bonnet, J. J.; Poilblanc, R. *J. Am. Chem. Soc.* **1982**, *104*, 3069−3077. Nolte, M. J.; Singleton, E.; Van der Stok, E. *J. Chem. Soc., Chem. Commun* **1978**, 973−974. Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237−2242.

Chart 1



9. Clearly, to establish whether the molecular gymnastics involved in the formation of **10** occurred by a skeletal reorganization or a substituent shift, a number of isotopically labeled vinylcyclopropenes were required.

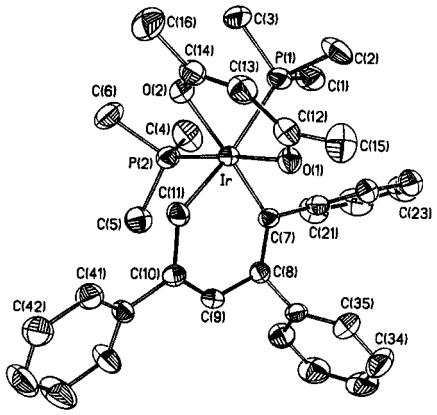


Figure 1. Molecular structure of **10** with thermal ellipsoids at 50% probability level.

Preparation of Isotopically Labeled Vinylcyclopropenes. To aid in elucidating the mechanism for this (and subsequent) rearrangement(s), a number of ^{2}H- and doubly ^{13}C-labeled vinylcyclopropenes were prepared. trans-Deuterated vinylcyclopropenes **11** and **12** were prepared by coupling the appropriate cyclopropenyl cations with trans-deuterated vinyllithium and magnesium bromide, as shown in Scheme 2. The starting bis-(tributylstannyl)ethylene **13** has been prepared by two routes in the literature. Corey's preparation,[32] in which (tributylstannyl)chloroacetylene, prepared from dichloroethylene, is hydrostannylated and reduced, is convenient on the small scale reported, but the low yield (typically 30−40% overall) and the need for 3 equiv of tin reagent make this procedure less desirable on a larger scale. Bottaro's preparation,[33] which quenches acetylide anion with tributyl tin chloride and then hydrostannylates the resulting stannylacetylene, on the other hand, requires only 2 equiv of tin and is more convenient on a large scale.

Sequential exchanges of lithium for tin on **13** provide trans-deuterated vinyllithium **14**. Minimal yields of the vinylcyclopropenes are obtained when the lithiate is used to couple with cyclopropenyl cations. The lithiate can be converted to a Grignard reagent **15**, however, by the addition of magnesium bromide−ether complex,[34] which allows the preparation of the phenyl-substituted vinylcyclopropenes **11** and **12** in reasonable yields. Presumably, the more strongly reducing lithiate causes the cyclopropenyl cation to be reduced to a greater extent than does the more covalent magnesium bromide.

The ring-deuterated vinylcyclopropene, **16**, was prepared by coupling of vinyl Grignard reagent with deuteriodiphenylcyclopropenyl fluoroborate, which was prepared identically to its protic analogue[35,36] by the addition of phenylchlorocarbene to 1-deuteriophenylacetylene,[37] as shown in Scheme 3.

Doubly ^{13}C-labeled di- and triphenylvinylcyclopropenes **17** and **18** were likewise prepared from labeled vinylmagnesium bromide, which had in turn been prepared from a labeled vinyltin precursor, as shown in Scheme 3. Smolin has prepared tributyl-

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Table 1. Crystal Data Collection and Refinement Parameters for **10**

(a) Crystal Parameters

formula	$C_{34}H_{42}O_2P_2Ir$	V, Å^3	3274(2)
cryst system	monoclinic	Z	4
space group	$P21/c$	d_{calc}, 9 cm^{-1}	1.49
a, Å	15.532(3)	μ, cm^{-1}	44 5
b, Å	12.425(3)	cryst size, mm	0.34 × 0.34 × 0.34
c, Å	17.547(7)	cryst color	yellow
β, deg	104.77(3)		

(b) Data Collection

diffractometer	Nicolet R3M/μ	scan speed (deg min^{-1})	variable, 5−20
radiation	Mo Kα (λ = 0.71073 Å)	rflns collected	6985
monochromator	graphite	indpdnt data	6442
scan technique	Wyckoff	indpdnt data ≥ 5$\sigma(F_o)$	4478
28 scan range, deg	4−52	std rflns	3 stds/197 rflns
data collected	$\pm h, +k, +l$	decay	< 1%

(c) Refinement

$R(F)$, X	3.55	GOF	0.973
w$R(F)$, %	3.71	data/parameter	13.5
$\Delta(\rho)$, e Å^{-3}	1.22 (near Ir)	(Δ/σ), final	0.007

Table 2. Selected Bond Distances and Angles for **10**

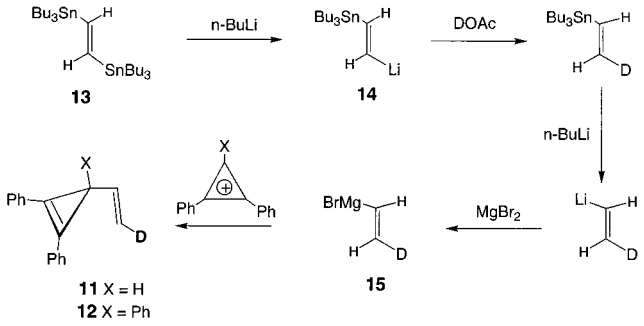
(a) Bond Distances (Å)

Ir−P(1)	2.409(2)	O(2)−C(14)	1.256(9)
Ir−P(2)	2.219(2)	C(7)−C(8)	1.364(8)
Ir−O(1)	2.125(4)	C(8)−C(9)	1.466(9)
Ir−O(2)	2.161(4)	C(9)−C(10)	1.329(8)
Ir−C(7)	2.023(5)	C(10-C(11)	1.496(8)
Ir−C(11)	2.111(7)	C(12)−C(13)	1.385(9)
P(1)−C⟨avg⟩	1.824(8)	C(12)−C(15)	1.506(11)
P(2)−C⟨avg⟩	1.806(8)	C(13)−C(14)	1.406(11)
O(1)−C(12)	1.276(8)	C(14)−C(16)	1.526(10)

(b) Bond Angles (deg)

P(1)−Ir−P(2)	96.2(1)	C(7)−Ir−C(10)	91.7(2)
P(1)−Ir−O(l)	88.4(1)	Ir−P(1)−C(l)	126.8(3)
P(2)−Ir−O(1)	175.5(1)	Ir−P(1)−C(2)	114.2(3)
P(1)−Ir−O(2)	84.7(1)	Ir−P(2)−C(4)	119.5(3)
P(2)−Ir−O(2)	92.0(1)	Ir−P(2)−C(5)	117.5(3)
O(1)−Ir−O(2)	88.5(2)	Ir−P(2)−C(6)	112.8(3)
P(1)−Ir−C(7)	100.5(2)	Ir−O(1)−C(l2)	124.8(4)
P(2)−Ir−C(7)	90.9(2)	Ir−O(2)−C(14)	124.3(4)
O(1)−Ir−C(7)	88.2(2)	Ir−C(7)−C(8)	125.7(5)
O(2)−Ir−C(7)	173.7(2)	C(7)−C(8)−C(9)	125.6(5)
P(1)−Ir−C(11)	166.3(2)	C(8)−C(9)−C(10)	128.6(5)
P(2)−Ir−C(11)	89.9(2)	C(9)−C(10)−C(11)	122.4(6)
O(1)−Ir−C(11)	85.6(2)	Ir−C(11)−C(10)	122.5(5)
O(2)−Ir−C(11)	82.8(2)		

Scheme 2



vinyltin by hydrostannylation of unlabeled acetylene,[38] but the expense of [$^{13}C_2$]acetylene renders the 2-fold excess of acetylene necessitated by this procedure undesirable for the labeled reaction. Using a stoichiometric amount of acetylene and a lower pressure (5 vs 10 atm), a reasonable yield (70%) of the labeled vinyltin was obtained. The use of still lower pressures (2 atm),

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Scheme 3

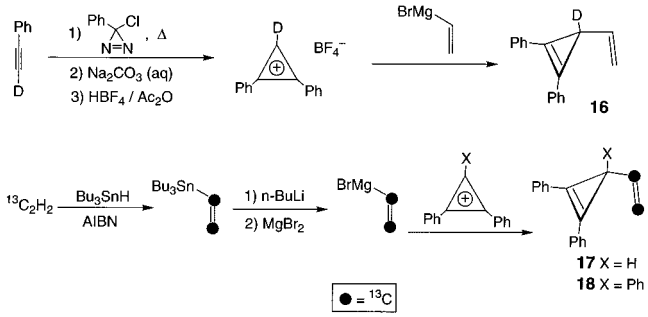
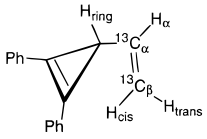


Table 3. Calculated Chemical Shifts (ppm) and Coupling Constants (Hz) for Diphenyl[$^{13}C_2$]vinylcyclopropene **17**



	δ	Cβ	H_{ring}	Hα	H_{cis}	H_{trans}
Cα	143.77	68.9	8.7	151.9	-3.2	-0.3
Cβ	112.27		2.8	0.1	153.6	158.3
H_{ring}	2.81			7.8	0.2	-0.2
Hα	5.67				16.7	10.1
H_{cis}	5.38					1.9
H_{trans}	5.00					

which would be desirable for safety, led to a drastic reduction in product formation. An unexpected side product formed in these lower pressure reactions was *trans*-bis(tributylstannyl)-ethylene. The subsequent formation of the ^{13}C-labeled Grignard reagents from the labeled vinyltin and the coupling to di- and triphenylcyclopropenyl cations proceeded uneventfully. The products were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and spectral simulations[39] generated the couplings presented in Table 3. In its ^{1}H and ^{13}C NMR spectra, the diphenyl vinylcyclopropene **17** shows slight second-order effects for its six coupled nuclei.

Ring-Opening Reactions with Labeled Vinylcyclopropenes. Using doubly ^{13}C-labeled diphenylvinylcyclopropene **17** as the substrate, ^{1}H NMR spectra of the product **19** showed

(39) Simulated NMR spectra were generated using LAOCOON III: Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 4863−4869.

Table 4. Geminal Proton/Phosphine Couplings and NOE Results for **10**[a]

		NOE to			
	δ[b]	$(PMe_3)_{ax}$	$(PMe_3)_{eq}$	$J_{HP(ax)}$[c]	$J_{HP(eq)}$[c]
H_{5a}	4.42[d]	n.o.	n.o.	9.4	3.0
H_{5b}	2.81	+	n.o.	7.6	5.6

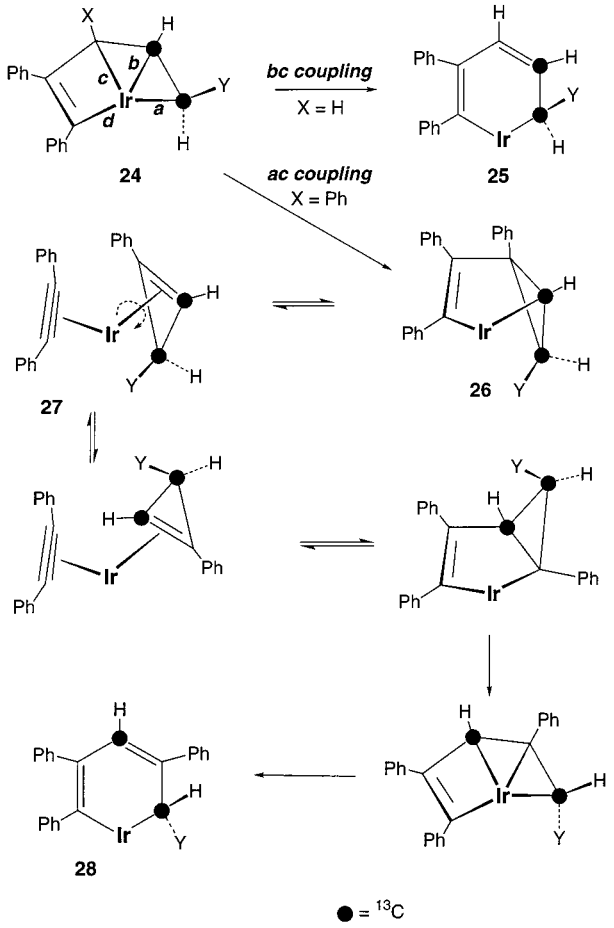
[a] ax, axial; eq, equatorial; n.o., not observed. [b] In ppm relative to TMS (C_6D_6). [c] In Hz. [d] Resonance which disappears in deuterated compound **23**.

that the labeled carbons remained in the methylene and methine groups and that the labeled carbons were adjacent, with a large $^1J_{CC} = 41$ Hz. Typical one-bond carbon−carbon couplings fall in the ranges 35−40 Hz (sp^3-sp^3), 40−55 Hz (sp^3-sp^2), 55−70 Hz (sp^2-sp^2), and 155−170 Hz (sp−sp); two- and three-bond couplings are generally <10 Hz.[40] In contrast, reaction of the doubly labeled triphenyl compound **18** afforded the rearranged product **20**, in which the labeled carbons remained in the methylene and methine groups, but were no longer adjacent as indicated by a much smaller $^2J_{CC} = 3.0$ Hz.[40] This result conclusively demonstrates that the rearrangement in the formation of **20** (and **10**) is indeed skeletal and is not due to substituent migrations on a fixed carbon framework. That no rearrangement of any type occurs in the diphenyl system is confirmed by reaction using ring-deuterated vinylcyclopropene **16**, which afforded a single isotopomer **21** with the deuterium label in the position shown adjacent to the phenyl groups.

Repetition of these reactions using trans-deuterated vinylcyclopropenes **11** and **12** gave in each case clean conversion to single isotopomers of the resultant metallacyclohexadienes **21** and **23**, respectively. No intermediates could be observed during NMR monitoring of the evolving reaction systems. Thus, stereochemical information is retained at both the metal and at the methylene carbon over the course of the reaction, *whether skeletal rearrangement occurs or not*! The position of the deuterium on the metallacycle face opposite (anti to) the axial phosphine was established by NOE experiments on the protic material. For example, NOE difference spectra (Table 4) of **10** showed that the position which remains undeuterated in **23** is syn to the axial phosphine P_1. Although too small to be conclusive in themselves, the different couplings of the two geminal protons to the axial phosphine accord with this assignment: a larger coupling constant is observed to the proton assigned anti to the axial phosphine than to the corresponding syn proton.

We have been able to devise two mechanisms by which the observed skeletal rearrangement can be accomplished. Other rearrangements of the type observed previously for Rh-promoted rearrangements of vinylcyclopropenes[9] can be excluded, since they cannot give rise to the observed carbon reorganization. Each path invokes an initial intermediate **24**, analogous to structure **3** (Scheme 1) discussed previously, with subsequent chemistry evolving from it. It is clear that in order to accommodate intermediate **24**, only three other ligands can be bound to iridium. We propose that the acac ligand becomes monodentate at this stage, as phosphine dissociation must give the metallacyclohexadiene isomers with PMe_3 ligands mutually trans, as shown later. In the first mechanism, illustrated in Scheme 4, the exchange of carbons and their appended groups occurs by rotation of a cyclopropene bearing both. Initial reaction of the vinylcyclopropene to give intermediate **24** followed by elimination of bonds *bc* affords unrearranged metallacyclohexadiene

Scheme 4



25. However, if formation of **24** is followed by reductive elimination of bonds *ac* with retention of configuration at each carbon to give **26**, reversible retrocyclization of **26** affords the alkyne−cyclopropene species **27**. Rotation of the cyclopropene as shown, followed by reconnection of the carbon−carbon bonds and subsequent ring opening (the microscopic reverse of the original *ac* coupling with retention of configuration at each carbon atom), affords the correct carbon disposition in the resultant metallacyclohexadiene **28**. When X = Ph, a driving force exists to alleviate steric strain between phenyl groups; when X = H (or D), no rearrangement occurs. It is noteworthy that reaction of diazoalkanes with metallacyclopentadiene complexes is known to afford cyclopentadienes;[41] cyclopropanation of one of the metallacyclopentadiene double bonds would afford an analogue of **26**, and the eventual cyclopentadiene may arise from collapse of this compound to the analogue of **24**, followed by *ad* coupling to give the cyclopentadiene, a reaction which we have demonstrated previously.[12] The coupling of alkynes with three carbon fragments to afford metallacyclohexadiene intermediates has also been noted in the literature.[42]

Appealing as this pathway might be, it suffers from a potentially fatal flaw. If we assume that intermediate **24** is formed regardless of whether X is Ph or H and that the vinylcyclopropene approaches iridium to give **24** in the same stereochemical sense in either case, Scheme 4 predicts that the labeled atom Y (deuterium) should appear on opposite faces of the metallacyclohexadiene product **25** or **28**, depending on

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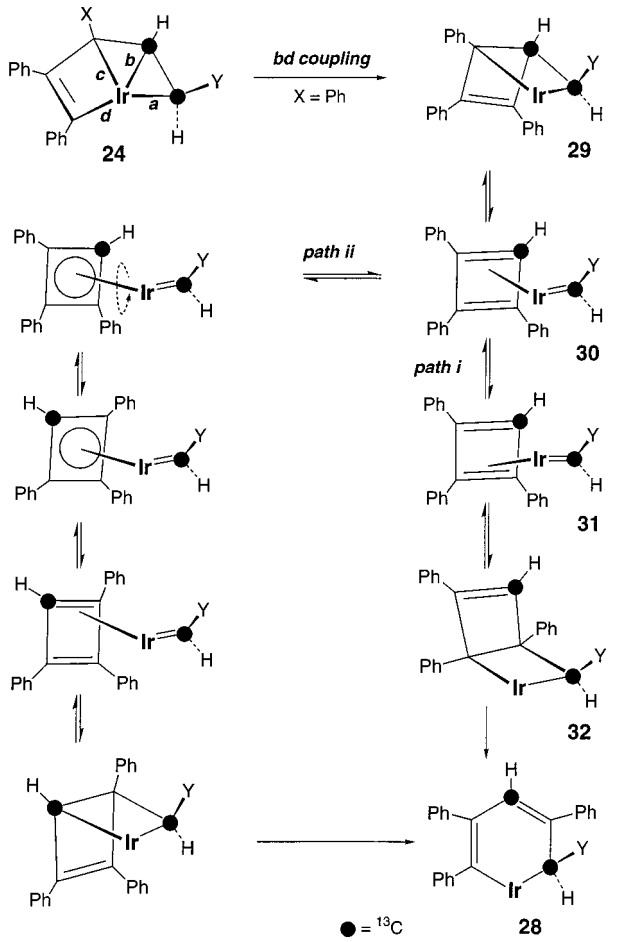
(41) O'Connor, J. M.; Pu, L.; Rheingold, A. L.; Uhrhammer, R.; Johnson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1889−91.

(42) Albright, T. A.; Clemens, P. R.; Hughes, R. P.; Hunton, D. E.; Margerum, L. D. *J. Am. Chem. Soc.* **1982**, *104*, 5369−79.

Scheme 5



whether the cyclopropene rearrangement occurs or not, i.e., if the labeled carbons maintain their contiguity, Y must point up in **25**, in the sense shown; if the labeled carbons become disconnected by the mechanism shown in Scheme 4, label Y must point down in **28**. The NOE results indicate that the deuterium label in the CHD group is on the same side of the metallacycle, regardless of whether skeletal reorganization has occurred. So, either the mechanism in Scheme 4 is flawed, or the vinylcyclopropene adopts two different approaches to iridium in the initial binding and ring opening. We note that the stereochemistry of cyclopropane ring formation and opening has been assumed here to occur with retention of configuration at carbon, effectively corresponding to a disrotatory opening and closure of the type demonstrated previously for other palladium-promoted methylenecyclopropane ring openings.[42] Whatever the stereochemistry might be, in fact, as long as closure and opening of the ring are the microscopic reverse of each other, substituent Y must switch ring faces as a result.

To accommodate this awkward fact, we are obliged to propose the more complicated mechanism outlined in Scheme 5, in which retrocyclization to give an alkylidene−cyclobutadiene intermediate is required. A similar initial ring opening of the vinylcyclopropene gives intermediate **24**. Coupling of bonds *bd* as shown would give the "Dewar cyclohexadiene" **29**. Retrocyclization of **29** into cyclobutadiene and carbene fragments would give **30**. Two paths may then exchange the hydrogen and phenyl substituents: following path i, the metal would slide across the face of the cyclobutadiene to coordinate the other double bond, giving **31**. Reinsertion of the carbene group leads to **32**, and ring-opening produces rearranged product **28**. Alternatively, the skeletal rearrangement may occur by a 90° rotation (and formal bond isomerization) of the cyclobutadiene in **30**, as shown in path ii. Similar reinsertion and ring opening leads to the appropriately rearranged product **28**. The retrocyclization/cyclization sequence to give a cyclobutadiene and a carbene and their recombination is reminiscent of the accepted mechanism for olefin metathesis.[44] Provided that no rotation occurs about the iridium−carbon double bond during the rearrangement, this mechanism allows for the label Y to maintain its spatial location relative to other ligands on the metal, while accommodating the presence or absence of skeletal rearrangement in the remainder of the carbon framework. The driving force for this mechanism is less easy to appreciate, however, since relief of steric interactions does not come into play until the very end of the sequence. This mechanism also requires that in path ii the cyclobutadiene ligand in **30** rotates only by 90°, and not by 180°, to obtain the single observed product.

However, while the required conspiracy of circumstances in Scheme 5 seems improbable, we have been unable to devise an alternative reaction pathway that accommodates both the observed carbon and deuterium labeling patterns.

Substituent Shifts in Metallacyclohexadienes. On heating at 90 °C in benzene solution, each of the metallacyclohexadiene complexes with PMe_3 ligands originally cis rearranged smoothly to the corresponding trans-isomers **33**−**39**. No scrambling of isotopic labels was observed in any system under these conditions; for example, rearrangement of **19** afforded **36**, in which the ^{13}C-labels in the product remained adjacent ($^1J_{CC}$ = 40 Hz) and the corresponding ^{1}H resonances showed one-bond couplings to the labeled carbons (CH, $^1J_{CH}$ = 148 Hz; CH_2, $^1J_{CH}$ = 123, 124 Hz). Similar to Bleeke's observations,[17,18,31] the ^{13}C NMR resonance for the sp^3 ring carbons of *trans*-phosphine compounds all appear far upfield (ca. −10 ppm), whereas those of the corresponding cis compounds appear at ca. 20 ppm. We assume that dissociation of PMe_3 followed by recombination is responsible for this change in stereochemistry at the metal, but we have done no experiments to verify this. The most important conclusion is that stereochemical change at the metal by ligand loss of some type does not result in any rearrangement of the skeleton or the substituent pattern of the metallacyclohexadienes.

However, further heating of the iridacyclohexadienes to 130 °C revealed yet another rearrangement process. Under these conditions, complex **33** yields a new isomer **40**, in which the two phenyl groups occupy positions 1 and 4 on the iridacyclohexadiene ring. The molecular structure of **40** has been confirmed in a previously reported single-crystal X-ray diffraction study.[15] The nature of this novel rearrangement can be clearly defined using the available series of isotopically labeled analogues. Transformation of the doubly ^{13}C-labeled iridacycle **36** yields **40**, in which the labeled carbons are still adjacent, but in which the CH_2 carbon atom is *unlabeled*; one labeled carbon has a single H atom directly bound, and the other bears no hydrogens. The absence of a triplet $^2J_{CH}$ or $^3J_{CH}$ also demonstrates that neither labeled carbon is α or β to the CH_2. Given the known substitution pattern from the X-ray structure of **40**,[15] these observations are consistent only with the presence of ^{13}C labels in **41** at positions 1 (CPh) and 2 (CH) in the

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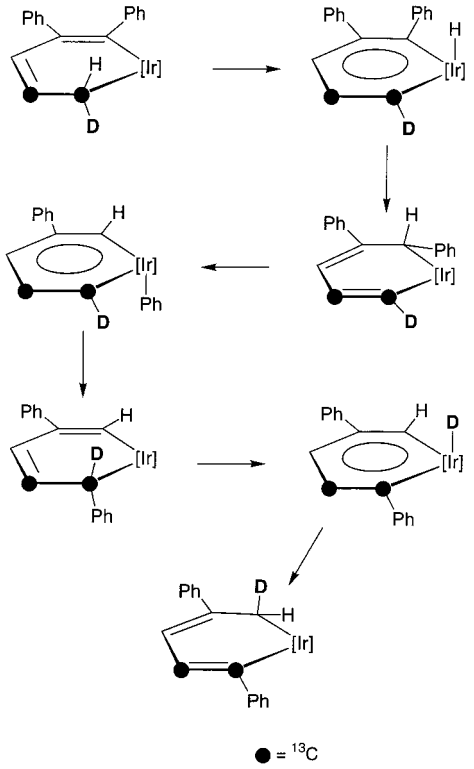
(44) For examples, see: Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−52. Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449−492. Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808−7809. Schrock, R. R. *Science* **1983**, *219*, 13−18.

Scheme 6



metallacyclic ring. Rearrangement of monodeuteriomethylene complex **35** to **42** occurs with preservation of the CHD group, implying that the rearrangement is intramolecular, and the corresponding conversion of **34** to **43** confirms that the deuterium at position 3 is not involved in any migrations.

These labeling experiments clearly demonstrate that this rearrangement is not a skeletal transformation of the metallacycle but must involve an interchange of substituents between the two carbon atoms directly bonded to iridium, perhaps driven by relief of steric repulsion between adjacent phenyl groups. An attractive mechanism involves a sequence of α-elimination/addition reactions, via iridabenzene intermediates, to accomplish the observed transformation, as shown in Scheme 6. Reversible migrations of H from α-carbon positions to metals are well-known,[45] as are iridabenzene species,[20,29] but the unprecedented step required by this mechanism is transfer of a phenyl substituent from one α-carbon to the other. While we have no direct evidence that this process occurs via an iridium−phenyl intermediate, we note the well-precedented migrations of phenyl, and other carbon substituents, from coordinated tertiary phosphorus centers to transition metals.[46] Such an intermediate presumably requires dissociation of a phosphine, or one arm of the acac ligand, to free up the required coordination sites. An example of a phenyl migration from silicon to platinum has also been reported.[47] These results demonstrate that analogous migrations from ligated carbon atoms may also be feasible, but we must note that our data do not exclude the possibility that the subsistent migrations occur by [1,5] sigmatropic shifts of the hydrogen and the phenyl substituents instead of by their traversal across the metal. Although phenyl migrations are less common than hydrogen migrations, examples of overall [1,2], [1,3], [1,5], and [1,7] phenyl migrations have been reported.[48]

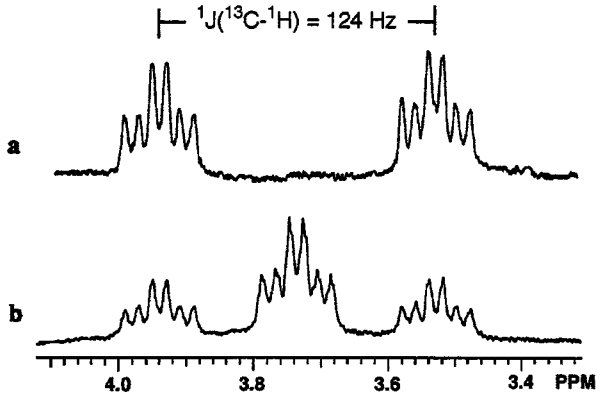


Figure 2. ^{1}H NMR resonances for the CH_2 group of **39** and **44**: (a) before heating, the sample is all isotopomer **39**; (b) after 30 h at 120 °C it is a 1:1 mixture of **39:44**.

While some driving force for the rearrangement of the diphenylmetallacyclohexadiene ligands can arise from relief of steric repulsions between the initially adjacent phenyl groups, the same argument is clearly not valid for the triphenyl analogues. Barring any isotope effects, the corresponding substituent rearrangement of **37** is a degenerate automerization whose availability is revealed using the doubly labeled compound **39**, which on heating does indeed undergo the same substituent migration process. Figure 2 shows the ^{1}H NMR spectrum of the CH_2 protons of doubly ^{13}C labeled **39**; the entire population of geminal protons showed the expected one-bond ^{13}C−H coupling of 124 Hz. As the sample was held at 120 °C, the fraction of protons with this coupling dropped steadily, until a 1:1 mixture of **39** and **44** was obtained after 30 h. This rearrangement presumably occurs by the same mechanism proposed for the diphenyl compounds (Scheme 6) and demonstrates that relief of steric strain between adjacent substituents is not required for such rearrangements to occur, since ΔG for the triphenyl case must be zero.

Conclusions

In summary, the ring opening of triphenylvinylcyclopropenes by $[Ir(PMe_3)_2(acac)]$ has been shown to involve a skeletal rearrangement possibly through a cyclobutadiene−carbene

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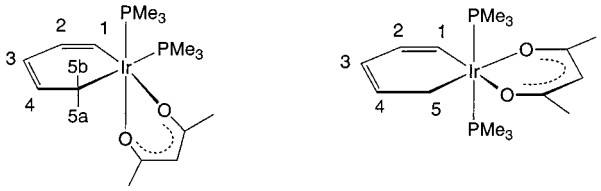

Figure 3. Numbering scheme used for the ^{1}H and ^{13}C NMR data of metallacyclohexadienes.

complex en route to iridacyclohexadienes. In contrast, this rearrangement is not observed with the analogous diphenyl compounds. On heating, iridacyclohexadienes with *cis*-phosphines convert to their *trans*-phosphine isomers, which on further heating undergo a different rearrangement, in which the geminal α-hydrogens and α′-phenyl group exchange on an unaltered cyclic framework.

Experimental Section

General Procedures. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over Aquasorb. Hydrocarbon reaction solvents and ethers were distilled under nitrogen from benzophenone ketyl, and halogenated solvents and methanol, from CaH_2, 4 Å molecular sieves, or 10% Na/Pb alloy. Aromatic and unsaturated components of 35−65 °C petroleum ether were removed before distillation by prolonged standing over H_2SO_4 (concentrated), followed by washing with Na_2CO_3 (10% aqueous). ^{1}H and ^{1}H{^{31}P} (300 MHz), ^{2}H{^{1}H} (46.1 MHz), ^{13}C and ^{13}C{^{1}H} (75.4 MHz), ^{119}Sn{^{1}H} (112 MHz), and ^{31}P {^{1}H} (121 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of either TMS (^{1}H, ^{2}H, and ^{13}C NMR, referenced to the solvent), neat Me_4Sn (^{119}Sn, referenced to external neat Bu_4Sn: −12.0 ppm), or external 85% H_3PO_4 (^{31}P NMR). Metallacyclohexadiene resonances are assigned using the numbering scheme of Figure 3; H_{5a} and H_{5b} are respectively on the opposite and the same face of the ring as the axial phosphine. Coupling constants are reported in hertz; tin satellites are reported using the notation "J_{117Sn}/J_{119Sn}". IR spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer. Melting points of samples in capillaries sealed under vacuum were obtained using a Thomas-Hoover device, and are uncorrected. Elemental analyses were performed by Spang (Eagle Harbor, MI).

n-Butyllithium (2.5 M in hexanes), vinylmagnesium bromide (1 M in THF), deuterioacetic acid, and tributyltin hydride were purchased from Aldrich; azobis(isobutyronitrile) (AIBN) was from Alfa, acetylene-$^{13}C_2$ was from Cambridge Isotope Laboratories, and trimethylphosphine was from Strem. 1,2-Diphenyl-3-vinylcyclopropene[35] (**5**), 1,2,3-triphenyl-3-vinylcyclopropene[49] (**8**), *trans*-Bis(tributylstannyl)ethylene[32,33] (**13**), triphenylcyclopropenyl bromide,[50] diphenylcyclopropenyl fluoroborate,[36,51] β-deuteriophenylacetylene,[37] $MgBr_2$/ether complex,[52] $[Ir(C_8H_{14})_2Cl]_2$ (C_8H_{14} = *cis*-cyclooctene),[53] and $[Ir(C_2H_4)_2(acac)]$[54] were prepared by literature routes. Tl(acac) (acac = acetylacetonate) was sublimed before use.

Tributyl[$^{13}C_2$]vinyltin. The labeled vinyltin was prepared by a modification of Smolin's procedure.[38] A solution of AIBN (26.6 mg) in benzene (10 mL) was frozen in a 100 mL heavy-walled reaction tube. Tributyltin hydride (6.0 mL, 22 mmol, 1 equiv) was introduced, then the system was evacuated and acetylene-$^{13}C_2$ (500 mL at STP, 22.3 mmol, 1 equiv) was condensed into the tube. The tube was sealed (Youngs O-ring valve), and its contents were allowed to thaw (***CAUTION:*** *PRESSURE BUILD-UP!)* and then heated to 80 °C while being agitated on a Parr hydrogenator for 30 min. Hydroquinone (10 mg) was added to the cooled mixture, and the product was distilled to give 4.96 g (70%) labeled vinyltin (bp: 50−52 °C, 0.04 mmHg). ^{1}H NMR ($CDCl_3$): δ 6.43 (dddd, 1H, J_{HH} = 20.3, 13.6, J_{CH} = 144.0, 4.3, H_α), 6.14 (dddd, 1H, J_{HH} = 14.1, 3.7, J_{CH} = 153.8, 5.2, H_{trans}), 5.63 (dddd, 1H, J_{HH} = 20.6, 3.8, J_{CH} = 155, 1.4, H_{cis}), 0.75−1.60 (m, 27H, Bu). ^{13}C NMR ($CDCl_3$): δ 139.31 (ddd, J_{CC} = 59.1, J_{CH} = 144.5, 5.0, J_{SnC} = 355.8/372.1 C_α), 133.62 (dddd, J_{CC} = 59.0, J_{CH} = 154.4, 152.4, 4.8, C_β). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ −119.6 (d, J_{SnC} = 371.9).

***trans*-3-(β-Deuteriovinyl)-1,2-diphenyl-1-cyclopropene, 11.** *n*-Butyllithium (3.6 mL, 2.3 M in hexanes, 8.3 mmol, 1.0 equiv) was added to a −78 °C solution of bis(tributylstannyl)ethylene (4.4 mL, 8.2 mmol, 1.0 equiv) in THF (60 mL). After stirring for 1.5 h at −78 °C, the yellow solution was quenched with DOAc (0.48 mL, 8.2 mmol, 1.0 equiv), and a second equivalent of BuLi (3.6 mL) was added. The yellow solution was stirred 1.5 h at −78 °C, then treated with $MgBr_2$/ether complex (3.8 mL, 10.0 mmol, 1.2 equiv) and allowed to warm to room temperature with stirring. The straw-colored solution was cooled back to −78 °C and added to a −78 °C slurry of 1,2-diphenyl-1-cyclopropenyl fluoroborate (1.49 g, 5.36 mmol, 0.65 equiv) in THF (60 mL). The mixture was stirred for 8 h at room temperature, to give an orange solution, and quenched with aqueous ammonium chloride (90 mL, 20%), and the layers were separated. The aqueous layer was extracted with ether (3 × 30 mL); the combined organic layers were washed with water (3 × 50 mL) and brine (1 × 10 mL). Drying over $MgSO_4$ and evaporation gave an orange oil which was passed through a flash chromatography column[55] (5 × 30 cm SiO_2) with hexanes (2 L). Bu_4Sn eluted first, followed by the vinylcyclopropene. Evaporation gave **11** (570 mg, 48%) as a cloudy white oil. ^{1}H NMR ($CDCl_3$): δ 7.23−7.80 (m, 10H, Ph), 5.64 (dd, 1H, J = 17.0, 7.8, H_α), 5.33 (d, 1H, J = 17.4, H_{cis}), 2.78 (d, 1H, J = 7.8, H_{ring}). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 5.07 (D_{trans}).

3-Deutero-1,2-diphenyl-3-vinyl-1-cyclopropene, 16. β-Deuteriophenylacetylene was converted to deuteriodiphenylcyclopropenyl fluoroborate, which was alkylated to give diphenylvinylcyclopropene **16**, in a manner analogous to the preparation of the protic vinylcyclopropene **5**.[35,49] **16**: white crystals from ether, mp: 32−32.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.19−7.71 (m, 10H, Ph), 5.64 (dd, 1H, J_{HH} = 17.2, 10.1, H_α), 5.34 (dd, 1H, J_{HH} = 17.0, 1.7, H_{trans}), 4.96 (dd, 1H, J_{HH} = 10.2, 1.8, H_{cis}). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 2.76 (s, D_{ring}).

1,2,3-Triphenyl-3-[$^{13}C_2$]vinyl-1-cyclopropene, 18. *n*-Butyllithium (2.3 mL, 2.4 M (hexanes), 5.6 mmol, 1 equiv) was added to a −78 °C solution of tributyl[$^{13}C_2$]vinyltin (1.80 g, 5.64 mmol, 1 equiv) in THF (50 mL). After standing for 1 h at −78 °C, the yellow solution was treated with magnesium bromide/ether complex (2.6 mL, 7.0 mmol, 1.2 equiv) and allowed to warm to room temperature. After stirring for 15 min at room temperature, the colorless solution was cooled to −78 °C and added to a −78 °C suspension of 1,2,3-triphenylcyclopropenyl bromide (0.991 g, 2.87 mmol, 0.5 equiv) in THF (50 mL). The mixture was allowed to warm to room temperature and was stirred for 6 h, giving a pale yellow solution. The reaction mixture was quenched with aqueous ammonium chloride (40 mL, 20%), and the layers were separated. The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic layers were washed with water (3 × 25 mL) and brine (2 × 10 mL) and then dried over $MgSO_4$. Flash chromatography[55] (3 × 27 cm SiO_2, 2 L hexanes) of the orange oil obtained on solvent removal gave Bu_4Sn followed by the vinylcyclopropene. Evaporation of the fractions containing the vinylcyclopropene afforded **18** as soapy white crystals (326 mg, 38%). ^{1}H NMR (C_6D_6): δ 6.95−7.75 (m, 15 H, Ph), 6.70 (ddd, 1H, J_{HH} = 17.2, 10.4, J_{CH} = 151.9, H_α), 5.33 (dddd, 1H, J_{HH} = 17.2, 1.6, J_{CH} = 153.9, 3.3, H_{cis}), 5.12 (ddd, 1H, J_{HH} = 10.3, 1.5, J_{CH} = 158.6, H_{trans}). ^{13}C NMR (C_6D_6): δ 142.37 (ddd, J_{CC} = 70.5, J_{CH} = 152.1, 2.4, C_α), 114.60 (ddd, J_{CC} = 70.4, J_{CH} = 158.4, 154.2, C_β).

***trans*-3-(β-Deuteriovinyl)-1,2,3-triphenyl-1-cyclopropene, 12.** *n*-Butyllithium (4.6 mL, 2.81 M (hexanes), 13 mmol, 1 equiv) was added

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to a −78 °C solution of *trans*-bis(tributylstannyl)ethylene (7.0 mL, 13 mmol, 1.0 equiv) in THF (90 mL). The resulting pale yellow solution was stirred for 1 h at −78 °C and then quenched with DOAc (0.75 mL, 13 mmol, 1 equiv) and warmed to room temperature. The colorless mixture was cooled back to −78 °C and treated with a second equivalent of BuLi (4.6 mL, 13 mmol). After stirring for 1 h at −78 °C, the yellow mixture was treated with $MgBr_2$/ether complex (6.0 mL, 16 mmol, 1.2 equiv) and allowed to warm to room temperature, giving a clear yellow solution. The solution was added to a −78 °C slurry of 1,2,3-triphenylcyclopropenyl bromide (2.26 g, 6.56 mmol, 0.5 equiv) in THF (90 mL), warmed to room temperature, and stirred 8 h to give a pale yellow solution. The reaction was quenched with aqueous ammonium chloride (100 mL, 20%), and the layers were separated. The aqueous layer was extracted with ether (3 × 50 mL); the combined organic layers were washed with water (3 × 50 mL) and brine (2 × 10 mL). Drying over $MgSO_4$ and evaporation left a yellow oil, which was purified by flash chromatography[55] (SiO_2, 5 × 16 cm). Elution with hexanes (2.5 L) gave Bu_4Sn, followed by the desired vinylcyclopropene (1.00 g, 50% soapy white crystals after evaporation). ^{1}H NMR (C_6D_6): δ 6.98−7.68 (m, 15 H, Ph), 6.70 (d, 1H, J = 17.2, H_α), 5.32 (d, 1H, J = 17.3, H_{cis}). ^{2}H{^{1}H} NMR (C_6H_6): δ 5.14 (br, D_{trans}).

1,2-Diphenyl-3-[$^{13}C_2$]vinyl-1-cyclopropene, 17. A −78 °C solution of [$^{13}C_2$]vinyltributyltin (2.01 g, 6.30 mmol) in THF (50 mL) was treated with *n*-butyllithium (2.6 mL, 2.43 M in hexanes, 6.3 mmol, 1.0 equiv). After stirring for 1.5 h at −78 °C, the yellow mixture was treated with $MgBr_2/Et_2O$ complex (2.9 mL, 8.1 mmol, 1.3 equiv) and warmed to room temperature, giving a colorless solution. The mixture was cooled to −78 °C and added dropwise to a −78 °C suspension of diphenylcyclopropenyl fluoroborate (1.14 g, 4.09 mmol, 0.65 equiv) in THF (50 mL) The cloudy mixture was warmed to room temperature, stirred for 9 h to give a yellow solution, and then quenched with aqueous NH_4Cl (20 mL, 20%). The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic layers were washed with water (3 × 25 mL) and brine (2 × 10 mL). The extracts were dried over $MgSO_4$ and evaporated, giving an orange oil, which was purified by flash chromatography[55] (3 × 33 cm silica, 400 mL petroleum ether). Removal of the solvent under vacuum yielded **17** (707 mg, 78%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.32−7.76 (m, 10H, Ph), 5.67 (dddd, 1H, J_{HH} = 17.2, 10.1, 7.8, J_{CH} = 152.2, H_α), 5.38 (dddd, 1H, J_{HH} = 17.1, 1.9, J_{CH} = 153.8, 3.3, H_{cis}), 5.00 (ddd, 1H, J_{HH} = 10.2, 1.8, J_{CH} = 158.4, H_{trans}), 2.80 (ddd, 1H, J_{HH} = 7.8, J_{CH} = 8.7, 3.2, H_{ring}). ^{13}C NMR ($CDCl_3$): δ 143.77 (dddd, J_{CC} = 69.0, J_{CH} = 152.2, 8.8, 3.3, C_α), 112.26 (dddd, J_{CC} = 68.3, J_{CH} = 153.6, 158.2, 3.2, C_β). Note that both the ^{1}H and ^{13}C NMR spectra for this compound show slight second-order effects; the coupling constants reported are averages of the values observed, and accord well with the absolute value of those obtained by simulation.[39]

[Ir(PMe$_3$)$_2$(acac)]. [IrCl(C_8H_{14})$_2$]$_2$ (537 mg, 1.20 mmol Ir) was stirred for 2 h with Tl(acac) (361 mg, 1.19 mmol, 1.0 equiv) in methylene chloride (10 mL) at room temperature. The resultant mustard yellow suspension was evaporated to dryness and extracted with petroleum ether until no more yellow color was discharged (6 × 10 mL). The extracts were filtered through Celite and diluted to 90 mL. A solution of PMe_3 (0.25 mL, 2.5 mmol, 2.0 equiv) in petroleum ether (30 mL) was added dropwise to the diluted extracts over 20 min with vigorous stirring, causing the mixture to darken slightly and to grow turbid. After stirring overnight, the orange mixture was passed through Celite, concentrated to 3 mL, and cooled slowly to −78 °C. The solid which precipitated was isolated, rinsed with petroleum ether (1 mL), and dried under vacuum, to give [Ir(PMe$_3$)$_2$(acac)] as dark orange crystals (388 mg, 78%). This solid decomposes rapidly in air. Calculated for $C_{11}H_{25}O_2P_2Ir$: 29.79% C, 5.69% H. Found: 29.36% C, 5.88% H. ^{1}H NMR (C_6D_6): δ 5.39 (s, 1H, CH), 1.64 (s, 6H, acac Me), 1.38 (filled d, 18 H, J_{obs} = 9.4, PMe_3). ^{13}C NMR (C_6D_6): δ 181.01 (quint, J_{CH} = 5.0, CO), 102.04 (d(sept), J_{CH} = 155.9, 2.4, CH), 27.81 (qdt, J_{CH} = 126.1, 3.8, J_{CP} = 3.1, acac Me), 18.83 (br q, J_{CH} = 127.1, PMe_3). In the ^{13}C{^{1}H} NMR spectrum, the PMe_3 peak appears as a five-line AA′X pattern, which may be simulated with J_{CP} = 45, $J_{CP'}$ = 0, and $J_{PP'}$ = 17.[39] IR (KBr, cm^{-1}): 1576 s, 1515 s, 1397 s, 973 s, 947 s.

Protic Compounds *cis*- and *trans*-Acetylacetonato(1,5-η-1,2-diphenyl-1,3-pentadienediyl)bis(trimethylphosphine)iridium(III), 9 and 33, and *trans*-acetylacetonato(1,5-η-1,4-diphenyl-1,3-pentadienediyl)bis(trimethylphosphine)iridium(III), 40. (a) General Procedure. An orange solution of [Ir(PMe$_3$)$_2$(acac)] (29 mg, 66 μmol) and diphenylvinylcyclopropene **5** (15 mg, 69 μmol, 1.0 equiv) in C_6D_6 (0.6 mL) was freeze−pump−thaw degassed and sealed in an NMR tube under vacuum. After standing for 3 d at room temperature, the sample had converted entirely to **9**. The sample was then heated at 95 °C for 33 h, giving a red solution containing **33**. Further heating at 120 °C for 45 h gave **40**.

9: ^{1}H NMR (C_6D_6): δ 6.52−7.89 (m, 10 H, Ph), 6.41 (dd, 1H, J_{HH} = 10.0, 3.0, H_3), 6.03 (dddd, 1H, J_{HH} = 9.3, 6.3, 3.2, J_{HP} = 16.3, H_4), 5.06 (s, 1H, acac CH), 3.97 (dddt, 1H, J_{HH} = 16.7, 3.2, 3.2, J_{HP} = 9.2, 3.8, H_{5a}), 2.46 (dq, 1H, J_{HH} = 16.1, 6.3, J_{HP} = 6.3, 6.3, H_{5b}), 1.76 (s, 3H, acac Me), 1.67 (s, 3H, acac Me), 1.32 (d, 9H, J_{HP} = 10.6, axial PMe_3), 0.59 (d, 9H, J_{HP} = 7.4, equatorial PMe_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −37.2 (d, J_{PP} = 7.0, equatorial PMe_3), −42.9 (d, J_{PP} = 6.8, axial PMe_3). IR (KBr, cm^{-1}): 2914 m, 1584 s, 1515 s, 960 s, 947 s.

33: ^{1}H NMR (C_6D_6): δ 6.63−7.95 (m, 10H, Ph), 6.41 (dt, 1H, J_{HH} = 10.4, 1.9, H_3), 5.42 (dt, ^{1}H, J_{HH} = 10.4, 4.6, H_4), 4.90 (s, 1H, acac CH), 3.37 (ddt, 2H, J_{HH} = 4.2, 2.0, J_{HP} = 13.5, H_5), 1.59 (s, 3H, acac Me), 1.43 (s, 3H, acac Me) 1.06 (virtual t, 18 H, J_{HPobs} = 3.5). ^{31}P{^{1}H} NMR (C_6D_6): −25.76 (s, PMe_3).

40: ^{1}H NMR (C_6D_6): δ 6.85−7.84 (m, 10H, Ph), 6.70 (dt, 1H, J_{HH} = 6.5, 1.4, H_3), 6.59 (dt, 1H, J_{HH} = 6.9, J_{HP} = 2.3, H_2), 4.96 (s, 1H, acac CH), 3.69 (td, 2H, J_{HH} = 1.4, J_{HP} = 13.1, H_5), 1.61 (s, 1H, acac Me), 1.56 (s, 1H, acac Me), 0.97 (virtual t, 18 H, J_{HPobs} = 3.4, PMe_3). ^{13}C NMR (C_6D_6): δ 185.32 (s, acac CO), 184.88 (s, acac CO), 154.84 (s, C_4 or C_{ipso}), 145.62 (s, C_4 or C_{ipso}), J_{CH} = 144, J_{CP} = 2, C_3), 140.51 (tdd, J_{CH} = 8, 2, J_{CP} = 10, C_1), 134.87 (s, C_4 or C_{ipso}), 130.13 (dt, J_{CH} = 148, J_{CP} = 4, C_2), 129.28 (dt, J_{CH} = 144, J_{CP} = 2, C_3), 128.75 (dt, J_{CH} = 153, 7, C_{meta}), 128.23 (dd, J_{HH} = 142, 9, C_{ortho}), 126.62 (dd, J_{CH} = 154, 9, C_{ortho}), 125.58 (dt, J_{CH} = 156, 8, C_{meta}), 125.26 (dt, J_{CH} = 152, 7, C_{para}), 124.26 (dt, J_{CH} = 151, 8, C_{para}), 100.69 (d J_{CH} = 155, acac CH), 28.15 (q, J_{CH} = 127, acac Me), 27.85 (q, J_{CH} = 126.6, acac Me), 10.78 (qt, J_{CH} = 130, J_{CP} = 16, PMe_3), −10.27 (tt, J_{CH} = 128, J_{CP} = 6, C_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −29.46 (s, PMe_3).

(b) Isolation of 33. [Ir(PMe$_3$)$_2$(acac)] (0.169 g, 0.381 mmol) and **5** (0.083 g, 0.381 mmol) were placed in a nitrogen-purged 50 mL Schlenk flask which was then equipped with a reflux condenser. The reaction vessel was purged again and C_6H_6 (30 mL) was added. The resultant bright yellow solution was refluxed overnight with little color change. Removal of solvent in vacuo gave a yellow-brown oil. The oil was extracted with 3 mL of diethyl ether/petroleum ether (2/1) and the extract brought to dryness. The dried extract was dissolved in 5 mL of refluxing petroleum ether, filtered, and concentrated to 2 mL. Cooling to −20 °C gave 30 mg of **33** as dark yellow crystals. A second crop of crystals (30 mg) was isolated from the mother liquor in a similar manner (yield, 24%). ^{1}H, ^{31}P NMR identical to those reported above. ^{13}C{^{1}H} NMR ($CDCl_3$, selected J_{CH} values and multiplicities included in square brackets): δ 185.67 (s, acac CO), [quint, $^2J_{CH}$ = 5]); 184.24 (s, acac CO, [quint, $^2J_{CH}$ = 5]), 135.04 (s, C_3, [d, J_{CH} = 147]), 133.83 (virtual t, J_{CP} = 9.8, C_1), 134.18 (virtual t, J_{CP} = 3.8, C_4), 128.75 (br s, C_4, [d, J_{CH} = 147]), 151.16, 148.71, 129.81, 126.64, 125.10, 123.22, 122.33, (s, phenyl C's), 100.43 (s, acac CH, [d, $^1J_{CH}$ = 154]), 27.95 (s, acac CH_3 [qd, $^1J_{CH}$ = 126, $^3J_{CH}$ = 2]), 27.74 (s, acac CH_3 [qd, $^1J_{CH}$ = 126, $^3J_{CH}$ = 2]), 10.93 (virtual t, J_{CP} = 16.4, PMe_3, [q, J_{CH} = 129 Hz]), −10.20 (virtual t, J_{PC} = 6.2, C_5, [t, J_{CH} = 127 Hz]). Calculated for $C_{28}H_{39}O_2P_2Ir$: 50.81% C, 5.95% H. Found: 50.80% C, 6.06% H.

(c) Isolation of 40. An orange solution of [Ir(PMe$_3$)$_2$(acac)] (38 mg, 86 μmol) and diphenylvinylcyclopropene **5** (19 μL, 19 mg, 86 mmol, 1.0 equiv) in C_6D_6 (0.3 mL) was heated at 125 °C for 28 h, by which time conversion to **40** was complete. The sample was evaporated, and crystals suitable for diffraction were grown by slow evaporation of an ether solution. Mp: 138−140 °C. ^{1}H NMR data were identical to those reported above.

Geminally Deuterated *cis*- and *trans*-Acetylacetonato(1,5-η-5-deutero-1,2-diphenyl-1,3-pentadienediyl)bis(trimethylphosphine)iridium(III), 22 and 35, and *trans*-Acetylacetonato(1,5-η-5-deutero-1,4-diphenyl-1,3-pentadienediyl)bis(trimethylphosphine)iridium(III), 42. A solution of [Ir(PMe$_3$)$_2$(acac)] (18 mg, 20 μmol/sample) and *trans*-deuterated diphenylvinylcyclopropene **11** (9.4 mg,

21 μmol/sample, 1.0 equiv) in benzene (1.4 mL) was loaded equally into two NMR tubes. The contents of one tube was freeze-dried and dissolved in C_6D_6 (0.7 mL), then both tubes were freeze−pump−thaw degassed and sealed under vacuum. The tubes were heated as described for the protic compounds above (procedure a), with similar observations.

22: ^{1}H NMR (C_6D_6): δ 6.74−7.86 (m, 10H, Ph), 6.44 (d, 1H, J_{HH} = 10.0, H_3), 6.04 (ddd, 1H, J_{HH} = 10.1, 6.3, J_{HP} = 16.0, H_4), 5.06 (s, 1H, acac CH), 2.45 (br d, 1H, J_{HH} = 6.6, H_{5b}), 1.72 (s, 3H, acac Me), 2.63 (s, 3H, acac Me), 1.28 (d, 9H, J_{HP} = 10.7, axial PMe_3), 0.56 (d, 9H, J_{HP} = 7.2, equatorial PMe_3). ^{2}H{^{1}H} NMR (C_6H_6): δ 3.92 (br, D_{5a}). **35:** ^{1}H NMR (C_6D_6): δ 6.72−7.74 (m, 10H, Ph), 6.42 (dd, 1H, J_{HH} = 10.4, 2.2 H_3), 5.41 (ddd, 1H, J_{HH} = 10.5, 4.4, J_{HP} = 0.8, H_4), 4.90 (s, 1H, acac CH), 3.34 (m, 1H, H_5), 1.60 (s, 3H, acac Me), 1.42 (s, 3H, acac Me), 1.06 (m, 18H, PMe_3). ^{2}H{^{1}H} NMR (C_6H_6): 3.32 (br, D_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −25.54 (s, PMe_3), −25.87 (s, PMe_3).

42: ^{1}H NMR (C_6D_6): 6.82−7.88 (m, 10H, Ph), 6.71 (dd, 1H, J_{HH} = 6.9, 1.5, H_3), 6.61 (dd, 1H, J_{HH} = 6.9, J_{HP} = 2.4, H_2), 4.95 (s, 1H, acac CH), 3.67 (apparent tdd, 1H, J_{HH} = 1.5, J_{HPobs} = 12.4, 5.3, H_5), 1.62 (s, 3H, acac Me), 1.56 (s, 3H, acac Me), 0.97 (m, 18H, PMe_3). ^{2}H{^{1}H} NMR (C_6H_6): δ 3.62 (br, D_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −26.47 (br s, PMe_3).

Ring-Deuterated Isomers *cis*- and *trans*-Acetylacetonato(1,5-η-3-deutero-1,2-diphenyl-1,3-pentadienediyl)bis(trimethylphosphine)-iridium(III), 21 and 34. A solution of [Ir(PMe_3)$_2$(acac)] (6.4 mg, 14 μmol) and **16** (3.8 mg, 17 μmol, 1.2 equiv) in C_6D_6 (1 mL) was sealed in an NMR tube under vacuum. The yellow solution darkened slightly as **21** formed over 3 d at room temperature. After ^{1}H and ^{31}P NMR spectra were obtained, the sample was evaporated and redissolved in C_6H_6 for ^{2}H NMR. ^{1}H NMR (C_6D_6): δ 6.55−7.87 (m, 10 H, Ph), 6.08 (ddd, 1H, J_{HH} = 6.2, 3.1, J_{HP} = 16.2, H_4), 5.10 (s, 1H, acac CH), 4.02 (ddt, 1H, J_{HH} = 16.6, 2.9, J_{HP} = 9.0, 2.9, H_{5a}), 2.52 (ddt, 1H, J_{HH} = 16.7, 6.2, J_{HP} = 7.4, 6.2, H_{5b}), 1.75 (s, 3H, acac Me), 1.67 (s, 3H, acac Me), 1.32 (d, 9H, J_{HP} = 10.4, axial PMe_3), 0.59 (d, 9H, J_{HP} = 7.4, equatorial PMe_3). ^{2}H{^{1}H} NMR (C_6H_6): δ 6.42 (br, D_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −36.60 (d, 1P, J_{PP} = 6.8, equatorial PMe_3), −42.38 (d, 1P, J_{PP} = 7.0, axial PMe_3).

The NMR sample of **21** was evaporated, redissolved in C_6D_6 (0.5 mL), and sealed under vacuum. After 16 h at 80 °C, ^{1}H and ^{31}P NMR showed the sample to be completely converted to **34**. The sample was evaporated and redissolved in C_6H_6 for ^{2}H NMR. ^{1}H NMR (C_6D_6): δ 6.73−7.76 (m, 10 H, Ph), 5.49 (m, 1H, H_4), 4.92 (s, 1H, acac CH), 3.43 (td, 2H, J_{HH} = 4.4, J_{HP} = 13.5, H_5), 1.63 (s, 3H, acac Me), 1.47 (s, 3H, acac Me), 1.10 (virtual t, 18H, J_{HPobs} = 3.3, PMe_3). ^{2}H{^{1}H} NMR (C_6H_6): δ 6.39 (br, D_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −25.42 (s, PMe3).

The NMR sample of **34** was evaporated, redissolved in C_6D_6 (0.5 mL), and sealed under vacuum. After 12 d at 80 °C, no evidence of deuterium scrambling was observed by ^{1}H or (after evaporation and dissolution in C_6H_6) ^{2}H NMR.

Ring-Deuterated Isomer *trans*-Acetylacetonato(1,5-η-3-deutero-1,4-diphenyl-1,3-pentadienediyl)bis(trimethylphosphine)iridium-(III), 43. An NMR sample was prepared as described for the protic compound **40** above (procedure b), with the substitution of ring-deuterated **34** for the protic ligand. After heating, the sample was opened, evaporated, and redissolved in C_6H_6 for ^{1}H NMR. ^{1}H NMR (C_6D_6): δ 6.80−7.88 (m, 10 H, Ph), 6.63 (t, 1H, J_{HP} = 2.3, H_2), 5.01 (s, 1H, acac CH), 3.71 (t, 2H, J_{HP} = 13.1, H_5), 1.65 (s, 3H, acac Me), 1.60 (s, 3H, acac Me), 1.00 (virtual t, 18H, J_{HPobs} = 3.6, PMe_3). ^{2}H-{^{1}H} NMR (C_6H_6): δ 6.73 (br, D_3). ^{31}P NMR identical to that of the unlabeled complex.

^{13}C-Labeled Isomers *cis*- and *trans*-Acetylacetonato(1,5-η-1,2-diphenyl-1,3-[4,5-$^{13}C_2$]pentadienediyl)bis(trimethylphosphine)iridium-(III), 19 and 36, and *trans*-Acetylacetonato(1,5-η-1,4-diphenyl-1,3-[1,2-$^{13}C_2$]pentadienediyl)bis(trimethylphosphine)iridium(III), 41. An NMR sample was prepared from [Ir(PMe_3)$_2$(acac)] and ^{13}C-labeled **17** as described for the unlabeled compounds (procedure a). On standing at room temperature and on subsequent heating, the sample underwent the changes noted for the unlabeled compounds.

19: ^{1}H NMR (C_6D_6): δ 6.54−7.89(m, 10H, Ph), 6.46 (td, 1H, J_{CH} = 10.1, J_{HH} = 2.7, 10.1, H_3), 6.08 (dm, 1H, J_{CH} = 148, H_4), 5.10 (s, 1H, acac CH), 4.01 (dm, 1H, J_{CH} = 123, H_{5a}), 2.50 (dm, 1H, J_{CH} = 124, H_{5b}), 1.76 (s, 3H, acac Me), 1.66 (s, 3H, acac Me), 1.32 (d, 9H, J_{HP} = 10.6, axial PMe_3), 0.59 (d, 9H, J_{HP} = 7.2, equatorial PMe_3). ^{13}C NMR (C_6D_6): δ 131.50 (ddtdd, J_{CC} = 40.8, J_{CP} = 3.2, 1.4, J_{CH} = 146.9, 8.8, C_4), 18.93 (tdddd, J_{CC} = 40.8, J_{CP} = 90.5, 7.2, J_{CH} = 123.1, 9.2, C_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −36.81 (dd, J_{PP} = 7.0, J_{CP} = 90.5, 3.1, equatorial PMe_3), −42.56 (t, J_{PP} = J_{CP} = 7.2, axial PMe_3).

36: ^{1}H NMR (C_6D_6): δ 6.75−7.89 (m, 10H, Ph), 6.45 (tt, 1H, J_{HH} = 10.8, 2.2, J_{CH} = 10.8, H_3), 5.46 (dm, 1H, J_{CH} = 142, H_4), 4.93 (s, 1H, acac CH), 3.41 (dm, 2H, J_{CH} = 122, H_5), 1.63 (s, 3H, acac Me), 1.47 (s, 3H, acac Me), 1.10 (virtual t, 18H, J_{HPobs} = 3.4, PMe_3). ^{13}C NMR (C_6D_6): 129.52 (br ddt, J_{CH} = 146.5, J_{CC} = 40.4, J_{CP} = 2.4, C_4), −9.69 (tdt, J_{CH} = 123.6, 6.7, J_{CC} = 40.3, J_{CP} = 6.1, C_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −25.57 (dd, J_{CP} = 6.1, 2.4, PMe_3).

41: ^{1}H NMR (C_6D_6): δ 6.79−7.89 (m, 10H, Ph), 6.75 (br t, 1H, J_{HH} = J_{CH} = 7.9, H_3), 6.63 (ddq, 1H, J_{HH} = 6.9, J_{CH} = 146.7, 2.3, J_{HP} = 2.3, H_2), 4.99 (s, 1H, acac CH), 3.72 (tq, 2H, J_{HH} = J_{CH} = 2.1, J_{HP} = 13.2, H_5), 1.65 (s, 3H, acac Me), 1.60 (s, 3H, acac Me), 1.00 (virtual t, 18H, J_{HPobs} = 3.6, PMe_3). ^{13}C NMR (C_6D_6): δ 140.51 (dtdd, J_{CC} = 63.1, J_{CH} = 8.4, 1.9, J_{CP} = 9.9, C_1), 130.20 (ddt, J_{CC} = 63.0, J_{CH} = 146.9, J_{CP} = 3.6, C_2). ^{31}P{^{1}H} NMR (C_6D_6): δ −24.85 (dd, J_{CP} = 9.9, 3.6, PMe_3).

Protic Compounds *cis*- and *trans*-(Acetylacetonato)bis(trimethylphosphine)(1,5-η-1,2,4-triphenyl-1,3-pentadienediyl)-iridium(III), 10 and 37. (a) General Procedure. An orange solution of [Ir(PMe_3)$_2$(acac)] (24 mg, 54 μmol) and triphenylvinylcyclopropene **8** (17 mg, 57 μmol, 1.1 equiv) in C_6D_6 (0.5 mL) was loaded into an NMR tube, freeze−pump−thaw degassed, and sealed under vacuum. After 2 d at room temperature, conversion to **10** was complete. The sample was then heated for 35 h at 100 °C, during which time **37** was formed.

10: ^{1}H NMR (C_6D_6): δ 6.59−7.86 (m, 15H, Ph), 6.83 (dd, 1H, J_{HH} = 3.0, 1.2, H_3), 5.15 (s, 1H, acac CH), 4.42 (ddt, 1H, J_{HH} = 15.9, 3.0, J_{HP} = 9.4, 3.0, H_{5a}), 2.81 (ddd, 1H, J_{HH} = 16.1, J_{HP} = 7.6, 5.6, H_{5b}), 1.78 (s, 3H, acac Me), 1.68 (s, 3H, acac Me), 1.27 (d, 9H, J_{HP} = 10.1, axial PMe_3), 0.59 (d, 9H, J_{HP} = 7.4, equatorial PMe_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −35.88 (d, J_{PP} = 8.2, axial PMe_3), −42.76 (d, J_{PP} = 8.1, equatorial PMe_3).

37: ^{1}H NMR (C_6D_6): δ 6.85−7.81 (m, 15H, Ph), 6.79 (t, 1H, J_{HH} = 1.4, H_3), 4.92 (s, 1H, acac CH), 3.71 (dt, 2H, J_{HH} = 1.4, J_{HP} = 12.3, H_5), 1.61 (s, 3H, acac Me), 1.47 (s, 3H, acac Me), 1.02 (virtual t, 18H, J_{HPobs} = 3.5, PMe_3). ^{13}C NMR ($CDCl_3$): δ 185.70 (s, acac CO), 184.91 (s, acac CO), 138.12 (t, J_{CP} = 11.3, C_1), 135.20 (d, J_{CH} = 149.8, C_3), 100.70 (d, J_{CH} = 154.3, acac CH), 27.86 (q, J_{CH} = 130.3, acac Me), 27.73 (q, J_{CH} = 130.3, acac Me), 10.79 (qt, J_{CH} = 128.4, J_{CP} = 16.3, PMe_3), −8.81 (tt, J_{CH} = 110.8, J_{CP} = 6.3, C_5). Other resonances could not be assigned unambiguously. ^{31}P{^{1}H} NMR (C_6D_6): δ −25.91 (s, PMe_3).

(b) Preparation of 10 from [Ir(C_2H_4)$_2$(acac)]. Solid triphenylvinylcyclopropene **8** (0.148 g, 0.504 mmol) was added to a solution of [Ir(C_2H_4)$_2$(acac)] (0.175 g, 0.504 mmol) in THF (20 mL) at −70 °C, followed by the addition of PMe_3 (0.103 mL, 1.01 mmol). The orange color was partially bleached, and the mixture was allowed to come to room temperature. Removal of solvent in vacuo from the resultant orange solution yielded an orange-red oil. The oil was washed with hexanes (2 × 5 mL) and recrystallized at −78 °C from THF/hexanes (1/20), yielding a yellow solid. ^{1}H and ^{31}P NMR spectra were identical to those reported above. ^{13}C{^{1}H}NMR ($CDCl_3$, selected CH multiplicities and coupling constants in square brackets): δ 183.42 (s, acac CO), 182.51 (d, J_{CP} = 1.8, acac CO), 100.00 (s, [d, 155.4], acac CH), 28.53 (d, J_{CP} = 6.3, [q, 127.0], acac CH_3), 28.42 (s, [q, 126.5], acac CH_3), 19.43 (dd, J_{HP} = 91.9, J_{HP} = 7.4,[t, ∼124], C_5), 15.51(dd, J_{HP} = 39.4, J_{HP} = 3.4, [q, 128.6], PMe_3), 14.73 (d, J_{CP} = 20.9, [q, 128.7], PMe_3); other resonances due to phenyl and ring carbons were not unambiguously assigned.

(c) Preparation of 10 from [Ir(PMe_3)$_2$(acac)]. The reaction of [Ir-(PMe_3)$_2$(acac)] (0.058 g, 0.131 mmol) with triphenylvinylcyclopropene (0.040 g, 0.136 mmol) in benzene (10 mL) yielded an identical product after stirring overnight and recrystallization from petroleum ether/ether (0.033 g, 43% yield). Single crystals were obtained from this sample.

Crystal Structure Determination of 10. A crystal of **10** was attached to a fine glass fiber with epoxy cement. On the basis of

systematic absences, **10** was determined to crystallize in monoclinic $P2_1/c$. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $20° \leq 2\theta \leq 26°$. An empirical absorption correction was applied where six parameters are employed to define a pseudoellipsoid. The structure was solved via heavy-atom methods which located Ir. Remaining non-hydrogen atoms were located from subsequent difference Fourier synthesis and were refined anisotropically. Phenyl carbon atoms were fixed to fit rigid hexagons. Hydrogen atom positions were calculated ($d_{CH} = 0.96$ Å, $U = 1.2$ times the isotropic equivalent for the carbon to which it was attached). All computer programs used in the crystal data collection and refinement are contained in Shelxtl (version 5.1) (G. Sheldrick, Nicolet XRD, Madison, WI). Crystal data collection parameters and selected bond distances and angles are provided in Tables 1 and 2; additional crystallographic data is available as Supporting Information.

Geminally Deuterated Isomers *cis*- and *trans*-Acetylacetonato-(1,5-η-5-deutero-1,2,4-triphenyl-1,3-pentadienediyl)bis(trimethylphosphine)iridium(III), 23 and 38. A solution of [Ir(PMe_3)$_2$(acac)] (20.5 mg, 23 μmol/sample) and **12** (13.7 mg, 23 μmol/sample, 1.0 equiv) in benzene (1.4 mL) was loaded equally into two NMR tubes. One sample was freeze-dried and redissolved in C_6D_6 (0.7 mL). The samples were then freeze−pump−thaw degassed and sealed under vacuum. Treatment as described for the protic compounds above (procedure a) gave **23** followed by **38**. The C_6D_6 sample was then heated at 120, 140, and 150 °C with only slight decomposition, but decomposed extensively after 24 h at 165 °C.

23: ^{1}H NMR (C_6D_6): δ 6.70−7.84 (m, 15H, Ph), 6.80 (d, 1H, $J_{HH} = 1.4$, H_3), 5.11 (s, 1H, acac CH), 2.76 (dd, 1H, $J_{HP} = 7.7$, 5.5, H_{5b}), 1.75 (s, 3H, acac Me), 1.64 (s, 3H, acac Me), 1.23 (d, 9H, $J_{HP} = 10.3$, axial PMe_3), 0.56 (d, 9H, $J_{HP} = 7.2$, equatorial PMe_3). ^{2}H{^{1}H} NMR (C_6H_6): δ 4.34 (br, D_{5a}).

38: ^{1}H NMR (C_6D_6): δ 6.65−7.77 (m, 15 H, Ph), 6.80 (d, 1H, $J_{HH} = 1.4$, H_3), 4.92 (s, 3H, acac CH), 3.70 (br t, 1H, $J_{HP} = 12.3$, H_5), 1.60 (s, 3H, acac Me), 1.47 (s, 3H, acac CH), 1.02 (m, 18H, PMe_3). ^{2}H-{^{1}H} NMR (C_6H_6): δ 3.66 (br, D_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −26.05 (s, PMe_3), −26.08 (s, PMe_3).

^{13}C-Labeled Compounds *cis*- and *trans*-Acetylacetonato(1,5-η-1,2,4-triphenyl-1,3-[3,5-$^{13}C_2$]pentadienediyl)bis(trimethylphosphine)-iridium(III), 20 and 39, and Automerization of 39 to *trans*-Acetylacetonato(1,5-η-1,2,4-triphenyl-1,3-[1,3-$^{13}C_2$]pentadienediyl)-bis(trimethylphosphine)iridium(III), 44. An NMR sample of **20** was prepared from [Ir(PMe_3)$_2$(acac)] and ^{13}C-labeled triphenylvinylcyclopropene **18**, as described for the unlabeled compound above. Over the course of 30 h at 100 °C, **39** was formed with no scrambling of the ^{13}C labels. The sample was then heated at 125 °C for 40 h, during which time the labels scrambled to give a 1:1 mixture of **39** and **44**. The NMR sample was opened, evaporated, and redissolved in a minimum of toluene. Passage through a Florisil column (1 × 23 cm, −60 °C under N_2, 1:6 ether/toluene) gave a yellow eluate. Evaporation of the eluate and recrystallization from petroleum ether gave clean product as a 1:1 mixture of isotopomers **39** and **44**.

20: ^{1}H NMR (C_6D_6): δ 6.58−7.81 (m, 15H, Ph), 6.81 (d, 1H, $J_{CH} = 148$, H_3), 5.15 (s, 1H, acac CH), 4.41 (dm, 1H, $J_{CH} = 126$, H_{5a}), 2.80 (dm, 1H, $J_{CH} = 124$, J_{5b}), 1.78 (s, 3H, acac Me), 1.68 (s, 3H, acac Me), 1.27 (d, 9H, $J_{HP} = 10.4$, axial PMe_3), 0.89 (d, 9H, $J_{HP} = 7.3$, equatorial PMe_3). ^{13}C NMR (C_6D_6): δ 133.10 (dt, $J_{CC} = 2.9$, $J_{CH} = 148.4$, $J_{CP} = 2.9$, C_3), 20.77 (tddd $J_{CC} = 3.2$, $J_{CH} = 124.1$, $J_{CP} = 92.1$, 7.3, C_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −36.71 (ddd $J_{PP} = 7.7$, $J_{CP} = 92.0$, 2.7, equatorial PMe_3), −43.67 (t, $J_{PP} = J_{CP} = 7.5$, axial PMe_3).

39: ^{1}H NMR (C_6D_6): δ 6.95−7.79 (m, 15H, Ph), 6.83 (br dd, 1H, $J_{CH} = 145.1$, 8.5, H_3), 5.26 (s, 1H, acac CH), 3.73 (dtdd, 2H, $J_{HH} = 0.6$, $J_{CH} = 123.7$, 6.6, $J_{HP} = 12.4$, H_5), 1.64 (s, 3H, acac Me), 1.50 (s, 3H, acac Me), 1.05 (virtual t, 18H, $J_{HPobs} = 3.4$, PMe_3). ^{13}C NMR (C_6D_6): δ 135.24 (ddt, $J_{CC} = 3.1$, $J_{CH} = 145.2$, $J_{CP} = 1.6$, C_3), −8.82 (tdtd, $J_{CC} = 2.9$, $J_{CH} = 123.7$, 8.9, $J_{HP} = 6.1$, C_5). ^{31}P{^{1}H} NMR (C_6D_6): δ −26.08 (dd, $J_{CP} = 5.7$, 1.9, PMe_3).

44: ^{1}H NMR and ^{31}P NMR: identical to the spectra of **39** except for the absence of the 124 Hz carbon coupling to the geminal hydrogens. ^{13}C{^{1}H} NMR (C_6D_6): δ 138.02 (t, $J_{CP} = 10.0$, C_1), 135.24 (m, C_3).

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Supporting Information Available: Atomic coordinates and isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters for **10** (PDF). This material is available free of charge via the Internet at http://www.pubs.acs.org.

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