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Reactions of 3,3-Diphenylcyclopropene with Iridium(I) Complexes: Probing the Mechanism of Cyclopropene Rearrangements at Transition Metal Centers[†]

Robert T. Li,[‡] SonBinh T. Nguyen,[‡] Robert H. Grubbs,[*,‡] and Joseph W. Ziller[§]

Contribution No. 8988 from The Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and the Department of Chemistry, University of California at Irvine, Irvine, California 92717

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Abstract: This paper describes the syntheses and reactivities of a series of $IrCl(CO)(PR_3)_2(\eta^2$-3,3-diphenylcyclopropene) complexes (**1**, $PR_3 = PMe_3$; **2**, $PR_3 = PMe_2Ph$; **3**, $PR_3 = PMePh_2$; **4**, $PR_3 = PEt_3$). NMR spectroscopic data for these complexes and a single crystal X-ray diffraction study of **1** support a trigonal bipyramidal structure where the PR_3 ligands and the olefin lie in the equatorial plane. The equilibrium between free and bound olefin was found to depend on the size of the tertiary phosphine: olefin coordination becomes less favorable as the cone angle of the tertiary phosphine increases. Lability of the olefin moiety was demonstrated by exchange of the olefin in **1** with deuterium-labeled 3,3–diphenylcyclopropene. In the presence of excess $IrCl(CO)(PMe_3)_2$, complex **1** rearranges. Spectroscopic data support the formation of an iridacyclobutene as part of a bimetallic complex where the iridacyclobutene moiety is stabilized by η^2-coordination to $IrCl(CO)(PMe_3)_2$. Mechanistic studies support formation of this bimetallic complex by direct insertion of $IrCl(CO)(PMe_3)_2$ into the C–C σ-bond of the cyclopropene moiety in **1**. Kinetic measurements suggest that this reaction occurs by a second-order process, first order in both $IrCl(CO)(PMe_3)_2$ and **1**. The mechanism of C–C bond insertion was further supported by isotopic-labeling experiments, which demonstrate that the metal in the metallacycle originates from free $IrCl(CO)(PMe_3)_2$.

Transition metal mediated reactions of cyclopropenes are of considerable interest and synthetic utility.[1] In recent years, the rearrangement of cyclopropenes in the presence of transition metal complexes has shown great promise as a method for generating transition metal vinylcarbene complexes. The first syntheses of transition metal vinylcarbene complexes from the rearrangement of cyclopropenes were reported in 1989 for titanocene(II) and zirconocene(II) precursors.[2] More recently, vinylcarbene complexes of later transition metals such as tungsten,[3] rhenium,[4] and ruthenium[5] have been generated from the reactions of 3,3-diphenylcyclopropene with the appropriate precursors.

Despite the synthetic utility of using cyclopropenes as a carbene source, a complete understanding of the mechanism of the rearrangement of cyclopropenes to vinylcarbenes at metal centers remains obscure. Assuming that the transition metal center plays an important role in this arrangement, the ring-opening of cyclopropenes may be envisioned as proceeding through a stepwise sequence of cyclopropene → metal η^2-cyclopropene → metallacyclobutene/metal vinylcarbene. Although the intermediate metal η^2-cyclopropene,[2,3,6] metal vinylcarbene,[2,3,6a,7] and metallacyclobutene[8,9] complexes have been independently synthesized, and the direct conversion of the metal η^2-cyclopropene → metal vinylcarbene has been observed,[3,6a] there has been to our knowledge no report of a metal η^2-cyclopropene → metallacyclobutene conversion.

It has been observed by Johnson and Grubbs that $HgCl_2$ catalyzes the rearrangement of a tungsten(IV) η^2-cyclopropene complex to a tungsten(VI) vinylcarbene complex.[3] This observation bears a striking resemblance to the metal-catalyzed rearrangement of bicyclo[1.1.0]butane to butadiene.[10] Indeed, when the metal η^2-cyclopropene complex is viewed as a metallabicyclo[1.1.0]butane, the similarity is unmistakable (Scheme 1). Given the extensive literature available on the metal-catalyzed rearrangement of bicyclo[1.1.0]butane, this analogy has prompted us to take a closer look at the possibility of a bimolecular mechanism in the formation of metal-vinylcarbenes from metal η^2-cyclopropene complexes.

This paper presents the results of studies of the reaction of 3,3–diphenylcyclopropene with $IrCl(CO)(PR_3)_2$ complexes. Syntheses of Vaska complexes, $IrCl(CO)(PR_3)_2$, were first reported in 1961;[11] their selection as precursors for this study was based

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[†] This paper is respectfully dedicated to the memory of Professor Paul Gassman.

[‡] California Institute of Technology.

[§] University of California at Irvine.

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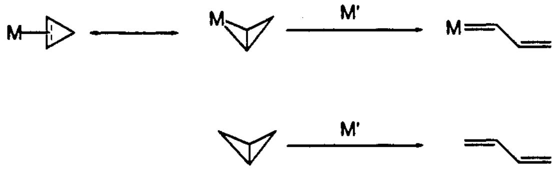
Table 1. Selected NMR and IR Spectral Data for η^2-Cyclopropene Complexes[a]

	^{1}H (t, HC=CH)		^{13}C (q, HC=CH)			
η^2-cyclopropene complex	δ (ppm)	J_{HP} (Hz)	δ (ppm)	J_{HP} (Hz)	^{31}P (δ)	ν_{CO} (cm^{-1})
IrCl(CO)(PMe$_3$)$_2$(HC=CHCPh$_2$)	3.32	6.4	37.07	29.7	−51.2	1985.9
IrCl(CO)(PMe$_2$Ph)$_2$(HC=CHCPh$_2$)	3.40	6.5	38.36	29.3	−38.5	1992.6
IrCl(CO)(PMePh$_2$)$_2$(HC=CHCPh$_2$)	3.47	6.7	38.66	26.7	−21.3	2000.7
IrCl(CO)(PEt$_3$)$_2$(HC=CHCPh$_2$)	3.25	6.3	35.67	33.8	−18.4	1979.3

[a] ^{1}H NMR and ^{31}P NMR spectra were acquired in C$_6$D$_6$, and ^{13}C NMR spectra were acquired in CD$_2$Cl$_2$.

Scheme 1. Comparison of the Metal-Catalyzed Rearrangements of Metal η^2-Cyclopropene Complexes and Bicyclo[1.1.0]butane[3,10]



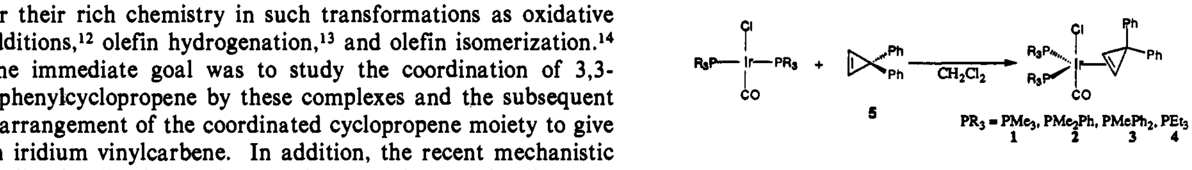
on their coordinative unsaturation, which is in part responsible for their rich chemistry in such transformations as oxidative additions,[12] olefin hydrogenation,[13] and olefin isomerization.[14] The immediate goal was to study the coordination of 3,3-diphenylcyclopropene by these complexes and the subsequent rearrangement of the coordinated cyclopropene moiety to give an iridium vinylcarbene. In addition, the recent mechanistic studies by Hughes and co-workers on the reaction between tetrafluorocyclopropene and the Vaska complex[8a] have led us to anticipate that the use of this metal system could provide some insight into the mechanism of 3,3-diphenylcyclopropene rearrangement to the corresponding vinylcarbene.

Here we report that 3,3-diphenylcyclopropene reacts with IrCl(CO)(PR$_3$)$_2$ precursors to afford stable η^2-olefin complexes. Among the PR$_3$ derivatives investigated, the equilibrium between free and bound 3,3-diphenylcyclopropene depends on the steric bulk of the tertiary phosphine: the smaller the cone angle of the tertiary phosphine, the more the equilibrium favors bound 3,3-diphenylcyclopropene. Furthermore, the IrCl(CO)(PMe$_3$)$_2$(η^2-3,3-diphenylcyclopropene) complex rearranges to a bimetallic iridacyclobutene in the presence of excess IrCl(CO)(PMe$_3$)$_2$.

Results and Discussion

Synthesis and Structure of IrCl(CO)(PR$_3$)$_2$(η^2-3,3-Diphenylcyclopropene) Complexes. Stable olefin adducts of the Vaska complex, IrCl(CO)(PR$_3$)$_2$, are fairly rare. Although ethylene[15] and cyclohexene[16] adducts of the Vaska complex have been prepared they are unstable and easily lose olefin to revert back to the parent complex. To date, the only stable olefin adducts of Vaska complexes have been derived from electron-poor olefins such as tetracyanoethylene,[16,17] fumaronitrile,[17] maleic anhydride,[16] and tetrafluoroethylene.[18] There are also examples of stable adducts of the Vaska complex with electron-poor alkynes.[16] The fact that Vaska complexes form stable π-complexes with relatively-electron-poor olefins might best be understood when the Ir–olefin complex is viewed as a donor–acceptor complex (i.e. the Vaska complex is a better donor to electron-poor olefins than more electron-rich π-substrates).[19] In this section, we report the synthesis, characterization, and molecular structure of a stable Vaska-type olefin complex and comment on the ability of the Vaska complex to coordinate olefins as a function of the steric bulk of the phosphine ligands.

The reaction of 3,3-diphenylcyclopropene with IrCl(CO)(PMe$_3$)$_2$ in a minimum amount of CH$_2$Cl$_2$ produced the olefin complex IrCl(CO)(PMe$_3$)$_2$(η^2-3,3-diphenylcyclopropene), **1**, in high yield (eq 1). The product was readily recrystallized from a



(1)

mixture of CH$_2$Cl$_2$/hexane to afford white crystals in high yield. Analogs of **1**, where PR$_3$ = PMe$_2$Ph (**2**), PMePh$_2$ (**3**), and PEt$_3$ (**4**), were synthesized similarly.

Spectroscopic data for the IrCl(CO)(PR$_3$)$_2$(η^2-3,3-diphenylcyclopropene) complexes are consistent with a trigonal bipyramidal arrangement of the ligands around the metal center. Notable features in the ^{1}H NMR spectrum of **1** (PR$_3$ = PMe$_3$) are a distorted doublet at 1.25 ppm due to the methyl protons of the cis tertiary phosphine ligands and a triplet at 3.32 ppm (J_{HP} = 6.4 Hz) due to coupling of the olefinic protons to the two phosphines. Key resonances in the ^{13}C NMR spectrum of **1** are a triplet at 17.7 ppm (J_{CP} = 15.5 Hz) due to overlapping doublets of the PMe$_3$ carbons and a pseudoquintet at 37.1 ppm (J_{CP} = 29.7 Hz, J_{CH} = 220.9 Hz) due to overlapping triplets of the olefinic carbons. This J_{CH} coupling constant is similar to that observed for the bridgehead carbon of bicyclo[1.1.0]butane (205 Hz)[20] and for the η^2 olefinic carbons in [W](η^2-3,3-diphenylcyclopropene) complexes (194–195 Hz),[3] suggesting a significant amount of s character in the C–H bond-forming hybrid orbital that is on the coordinated cyclopropene olefinic carbon of **1** (42%).[21] The ^{31}P NMR spectrum of **1** exhibits only a singlet at −51.2 ppm, and its IR spectrum shows a characteristic ν_{CO} stretching frequency at 1985.9 cm^{-1}, significantly lower than that observed for IrCl(CO)(PPh$_3$)$_2$(η^2-cyclohexene) (ν_{CO} = 2040 cm^{-1}).[16] Table 1 summarizes selected NMR and IR data for complexes **1-4**.

The structure of **1** was confirmed with an X-ray crystallographic study. An ORTEP of this complex is shown in Figure 1 and selected bond distances and angles are given in Table 2. The Ir–C bonds (2.116(6) and 2.118(6) Å) are within normal

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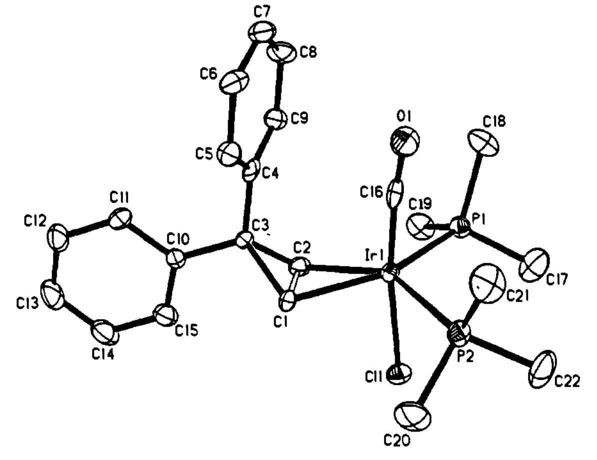

Figure 1. An ORTEP drawing of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene). Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

	Bond Distances		
Ir(1)–Cl(1)	2.442(2)	Ir(1)–P(1)	2.345(2)
Ir(1)–P(2)	2.340(2)	Ir(1)–C(1)	2.116(6)
Ir(1)–C(2)	2.118(6)	Ir(1)–C(16)	1.824(6)
O(1)–C(16)	1.156(8)	C(1)–C(2)	1.445(9)
C(1)–C(3)	1.528(8)	C(2)–C(3)	1.514(8)
C(3)–C(4)	1.497(8)	C(3)–C(10)	1.508(8)
	Bond Angles		
Cl(1)–Ir(1)–P(1)	86.5(1)	Cl(1)–Ir(1)–P(2)	85.2(1)
P(1)–Ir(1)–P(2)	108.6(1)	Cl(1)–Ir(1)–C(1)	85.6(2)
P(1)–Ir(1)–C(1)	142.0(2)	P(2)–Ir(1)–C(1)	107.6(2)
Cl(1)–Ir(1)–C(2)	82.5(2)	P(1)–Ir(1)–C(2)	102.2(2)
P(2)–Ir(1)–C(2)	145.9(2)	C(1)–Ir(1)–C(2)	39.9(2)
Cl(1)–Ir(1)–C(16)	172.5(2)	P(1)–Ir(1)–C(16)	91.1(2)
P(2)–Ir(1)–C(16)	88.9(2)	C(1)–Ir(1)–C(16)	100.6(2)
C(2)–Ir(1)–C(16)	104.9(2)	Ir(1)–C(1)–C(3)	108.9(4)
Ir(1)–C(1)–C(2)	70.1(3)	Ir(1)–C(2)–C(1)	70.0(3)
C(2)–C(1)–C(3)	61.1(4)	C(1)–C(2)–C(3)	62.2(4)
Ir(1)–C(2)–C(3)	109.4(4)	C(1)–C(4)–C(4)	123.1(5)
C(1)–C(3)–C(2)	56.7(4)	C(1)–C(3)–C(10)	113.4(5)
C(2)–C(3)–C(4)	119.9(5)	C(4)–C(3)–C(10)	115.4(4)
C(2)–C(3)–C(10)	115.7(5)	C(3)–C(4)–C(9)	120.0(5)
C(3)–C(4)–C(5)	121.4(5)		

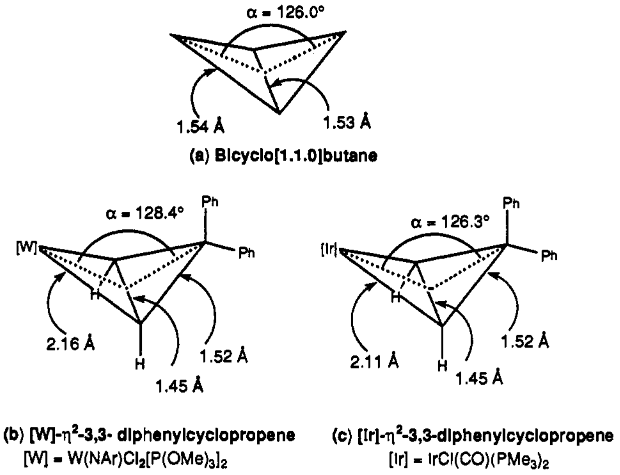

Figure 2. Comparison of the bond lengths and torsion angle of (a) bicyclo[1.1.0]butane,[10] (b) $W(NAr)Cl_2[P(OMe)_3]_2(\eta^2$-3,3–diphenylcyclopropene),[3] and (c) $IrCl(CO)(PMe_3)_2(\eta^2$-3,3–diphenylcyclopropene).[21]

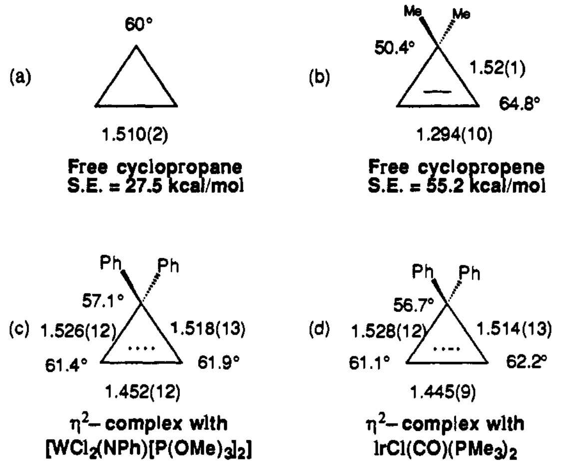

Figure 3. Comparison of the bond lengths and angles of (a) free cyclopropene,[1c] (b) free 3,3-dimethylcyclopropene,[1c] (c) η^2-complex with $[WCl_2(NPh)[P(OMe)_3]_2]$,[3] and (d) η^2-complex with $IrCl(CO)(PMe_3)_2$.

distances,[17] and the cyclopropene C–C bond (1.445(9) Å) is similar to those reported for $[W](\eta^2$-3,3-diphenylcyclopropene) complexes,[3] but slightly smaller than the value obtained from vibrational spectroscopy for bicyclo[1.1.0]butane (1.54 Å) (Figure 2).[22] The arrangement of ligands about the metal center exhibits two distortions from a perfect trigonal bipyramidal geometry. First, the equatorial olefin ligand is puckered out of the plane in a butterfly configuration, where the torsion angle between Ir(1), C(1), C(2), and C(3) is 126.3(4)°, which is remarkably similar to that observed for bicyclo[1.1.0]butane (126.0°)[22] (Figure 2). Second, the two apical ligands, Cl and CO, are bent slightly from perpendicular, away from the olefin ligand. To a first approximation, the metal η^2-cyclopropene moiety resembles a strained bicyclo[1.1.0]butane, a fact which might have important consequences in the ability of **1** to undergo rearrangement (*vide infra*). Similar to that observed in $IrBr(CO)(PPh_3)_2(\eta^2$-tetracyanoethylene),[17] the phosphine ligands in **1** are cis rather than trans. The trans configuration was proposed for adducts of electron-poor olefins with the Vaska complex.[16]

Complexes **1**–**4** are the first stable olefin adducts of the Vaska complex known to date where the olefin is not substituted with electron-withdrawing substituents (*vide supra*). The driving force for formation of the olefin complex is probably derived from the relief of the cyclopropene ring strain (estimated at 57.2 kcal/mol)[23] by coordination to the metal center. The relaxation of cyclopropene ring strain upon coordination to the metal center can be inferred from the crystal structural parameters (Figure 3d). The C–C double bond is lengthened to 1.445(9) Å and the apical angle of the cyclopropene ring is increased to 56.7° compared to that of the uncomplexed cyclopropene (50.4°) (Figure 3b). These observations are consistent with those previously observed by Johnson and Grubbs[3] (Figure 3c).

Also particularly interesting is the observation that olefin complexation to the iridium(I) metal center is affected dramatically by the cone angles of the tertiary phosphines.[24] For example, while the PMe_3 and PMe_2Ph Vaska complexes (in all cases, [Vaska complex] = 3.3 × 10^{-2} M) react with 1.5 equiv of 3,3-diphenylcyclopropene to afford complete conversion to the olefin adducts **1** and **2**, respectively (Table 3, entries 1 and 2), under the same conditions, the $PMePh_2$ the Vaska complex affords only 70% of the olefin complex **3**, and the PPh_3 Vaska complex does not coordinate 3,3-diphenylcyclopropene at all (Table 3, entries 3 and 5). Thus, as the tertiary phosphines become more sterically demanding, coordination of the olefin is inhibited. This effect appears to be determined predominantly by steric rather

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Table 3. Summary of Results Showing the Degree of Complexation of 3,3-Diphenylcyclopropene to $IrCl(CO)(PR_3)_2$ Complexes and the Cone Angles of the Tertiary Phosphines

entry	PR_3	cone angle (deg)[23]	olefin complex/ starting material[a]
1	PMe_3	118	>99/1
2	PMe_2Ph	122	>99/1
3	$PMePh_2$	136	70/30
4	PEt_3	132	40/60
5	PPh_3	145	~0
6	P-*i*-Pr_3	160	~0

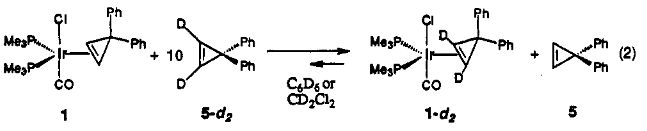
[a] Observed by ^1H NMR upon addition of 1.5 equiv of 3,3-diphenylcyclopropene to a solution of $IrCl(CO)(PR_3)_2$ in CD_2Cl_2 at room temperature.

than electronic factors.[25] When the PEt_3 and P(*i*-Pr)$_3$ Vaska complexes were subjected to the same reaction conditions (PEt_3 and P(*i*-Pr)$_3$ have similar electronic properties, but differ in their steric properties),[24] the PEt_3 Vaska complex reacts with 1.5 equiv of 3,3–diphenylcyclopropene to afford 40% conversion to the olefin complex **4**, while the P(*i*-Pr)$_3$ the Vaska complex does not coordinate 3,3-diphenylcyclopropene (Table 3, entries 4 and 6).

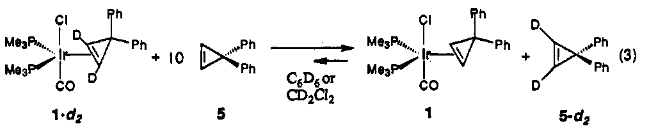
Stability of the η^2-Olefin Complexes and Reversibility of Binding of 3,3–Diphenylcyclopropene. The η^2-3,3-diphenylcyclopropene complexes are stable in solution under inert atmosphere for days without noticeable decomposition and stable indefinitely in the solid phase under inert atmosphere. These complexes also exhibit moderate stability in air. For example, in solution, these olefin complexes can withstand short-term exposure to air (10–12 h) before oxidation to insoluble products is observed. In the solid phase, they are stable in air for several days before oxidation/decomposition is observed (detected as a discoloration of the solid).

Although it has been observed by Johnson and Grubbs[3] that the use of a catalytic amount of $HgCl_2$ or irradiation of the η^2-cyclopropene complexes facilitates the ring opening of metal η^2-cyclopropenes to metal vinylcarbenes in the case of tungsten, an iridium vinylcarbene complex could not be synthesized using these methods. Addition of a catalytic amount of $HgCl_2$ completely decomposed the olefin complex **1** over several days, while irradiation alone at 0 °C caused slow decomposition.

The coordination of 3,3-diphenylcyclopropene to the iridium(I) center was found to be reversible in the sense that the coordinated olefin will exchange with excess 3,3–diphenylcyclopropene. Reaction of **1** with 10 equiv of 3,3-diphenylcyclopropene-*1,2-d$_2$*, **5–*d$_2$***, resulted in complete exchange of the olefin ligand in **1** with **5–*d$_2$*** (eq 2). Conversely, the reaction of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene-*1,2-d$_2$*) (**1–*d$_2$***) with 10 equiv of 3,3-diphenylcyclopropene resulted in exclusive formation of **1** (eq 3). The exchange of olefin was found to be 2.5 times faster in C_6D_6 than in CH_2Cl_2 (as described in the Experimental Section). Reaction of **1** with 1 equiv of various electron-deficient olefins such as tetracyanoethylene and dimethylmaleate also results in complete substitution of the olefin moiety.[26] These electron-deficient olefins are bound to the iridium metal center preferrentially over 3,3-diphenylcyclopropene in the sense that the reaction of $IrCl(CO)(PMe_3)_2(\eta^2$-Y), where Y is either tetracyanoethylene or dimethylmaleate, with up to 20 equiv of 3,3-diphenylcyclopropene does not form **1**. However, reaction of **1** with other cyclic olefins such as norbornene, cyclooctene, cyclopentene, and cyclohexene does not result in any exchange of the olefin moiety.[27]



(2)



(3)

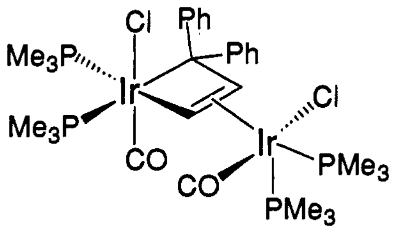
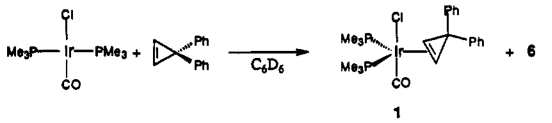
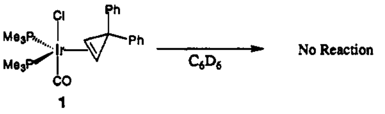

6

Figure 4. Proposed structure of **6**.

Further Reaction of the η^2-3,3-Diphenylcyclopropene Complex 1. When $IrCl(CO)(PMe_3)_2$ reacts with less than 1 equiv of 3,3-diphenylcyclopropene in C_6D_6, two products were observed, one of which was the η^2-olefin complex **1**, the other being a new product **6** (eq 4). Increasing the molar ratio of $IrCl(CO)(PMe_3)_2$ to 3,3-diphenylcyclopropene in the reaction resulted in a decrease of **1** and an increase in the formation of **6**. Formation of **6** was maximized (i.e. complete disappearance of **1**) when this molar ratio was at least 4/1. We hypothesized that the generation of **6** proceeded through the intermediacy of the η^2-olefin complex **1**, which then reacted further with another molecule of $IrCl(CO)(PMe_3)_2$. To examine this hypothesis, two simultaneous reactions were carried out: in one case, the olefin complex **1** was dissolved in C_6D_6 and allowed it to stand on its own (eq 5); in the second case, 1 equiv of $IrCl(CO)(PMe_3)_2$ was added to a C_6D_6 solution of **1** (eq 6). Only in the second case was **6** formed.



(4)



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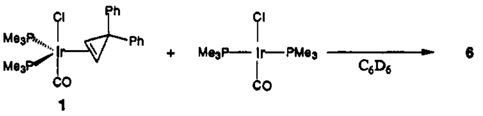

(6)

The formation of **6** directly correlated with the disappearance of **1** and thus appeared to involve the intermediacy of **1**. The available spectroscopic data (*vide infra*) suggest that **6** is an iridacyclobutene that is stabilized by coordination in an η^2 fashion to another molecule of $IrCl(CO)(PMe_3)_2$. The proposed structure of **6** is shown in Figure 4.

The formation of a metallacyclobutene from the metal-mediated rearrangement of cyclopropenes has precedence in the literature. Hughes and co-workers[8] reported that tetrafluorocyclopropenes react with $IrCl(CO)(PR_3)_2$ and Pt(II) complexes to afford metallacyclobutene complexes. However, these workers apparently did not observe the formation of an η^2-olefin complex

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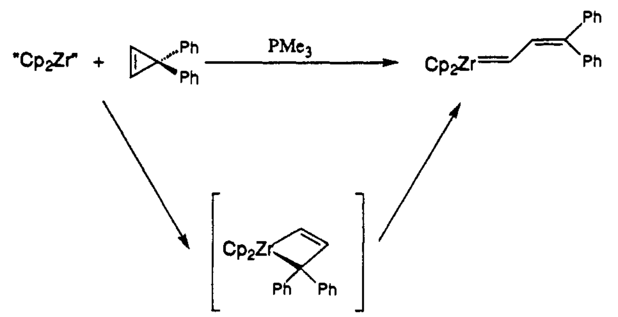
(25) PMe_3 > PMe_2Ph > $PMePh_2$ > PPh_3 in electron donating capability; see also ref 24.

(26) Observed by ^1H and ^{31}P NMR upon addition of 1 equiv of tetracyanoethylene or dimethylmaleate to a solution of **1** in C_6D_6.

(27) Observed by ^1H and ^{31}P NMR upon addition of 20 equiv of either norbornene, cyclooctene, cyclopentene, or cyclohexene to a solution of **1** in C_6D_6.

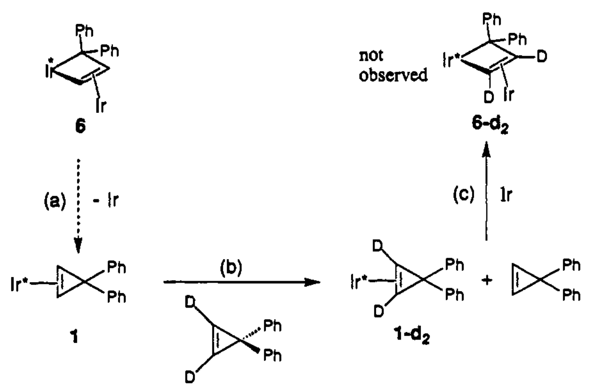
Scheme 2. Proposed Metallacyclobutene Intermediate in the Metal-Mediated Rearrangement of 3,3-Diphenylcyclopropene to Vinylcarbenes[9]



as an intermediate. Binger and co-workers observed that 1,2-diphenylcyclopropene reacts with a zirconocene(II) precursor to form a metallacyclobutene complex.[9] This observation led Binger to propose that the ring-opening of 3,3-diphenylcyclopropenes to vinylcarbenes at transition metal centers proceeded to a metallacyclobutene through direct σ bond insertion (Scheme 2), although this type of intermediate has not been observed during the formation of metal vinylcarbene complexes from 3,3-diphenylcyclopropene.

Spectroscopic Data for 6. Analysis by NMR spectroscopy supports a bimetallic structure for compound **6**. The ^{1}H NMR spectrum of **6** shows, for example, that the olefinic protons are inequivalent and highly coupled. One olefinic proton appears as an imperfect sextet at 2.62 ppm; the other olefinic proton appears as an imperfect septet at 4.23 ppm (Figure 5a). Homonuclear decoupling showed that these protons were coupled only to each other and to no other protons. Irradiation of the multiplet at 2.62 ppm collapsed the septet at 4.22 ppm into a sextet, while irradiation of the multiplet at 4.22 ppm collapsed the sextet at 2.62 ppm into a quintet (Figure 5b). The remainder of the complex coupling pattern probably results from ^{31}P coupling. These results are suggestive of a bimetallic structure since a single bis-phosphine metal center cannot produce such a highly coupled spectrum.[28] Other key features of the ^{1}H NMR spectrum are doublets at 1.01 (J_{HP} = 9.0 Hz) and 1.19 ppm (J_{HP} = 10.5 Hz). These resonances probably correspond to the protons of inequivalent PMe$_3$ ligands of the metal bearing the metallacycle. The PMe$_3$ protons of the second metal appear as a doublet at 1.3 ppm, which suggests a cis arrangement of the tertiary phosphines on the second metal center. The ^{31}P NMR spectrum in C$_6$D$_6$ shows four resonances corresponding to the four inequivalent phosphine ligands. These include two doublets at −56.1 and −46.2 ppm (J_{PP} = 17.5 Hz), probably corresponding to the tertiary phosphine ligands on the metal bearing the metallacycle, and two broad singlets at −14.5 and −38.3 ppm, probably corresponding to the tertiary phosphines on the other metal center. Key features of the {^{1}H}^{13}C NMR spectrum of **6** are assigned as follows: doublet of quartets at 14.1 ppm (J_{CP} = 95.5 Hz, $J_{CP'}$ = 6.7 Hz, J_{CH} = 391.8 Hz), corresponding to the olefinic carbon closest to the metal center which is coupled to four phosphines; a doublet of triplets at 66.0 ppm (J_{CP} = 37.6 Hz, $J_{CP'}$ = 4.2 Hz, J_{CH} = 168.9 Hz), corresponding to the olefinic β-carbon which is coupled to three phosphines; two doublets at 14.9 ppm (J_{CP} = 15.1 Hz) and 15.2 ppm (J_{CP} = 18.4 Hz), corresponding to the PMe$_3$ carbons at the metal center bearing the metallacycle; two doublets at 17.6 and 17.8 ppm (J_{CP} = 15.5 Hz), corresponding to the PMe$_3$ carbons of the other metal center; one doublet at 146.6 ppm (J_{CP} = 4.1 Hz), corresponding to the C$_{ipso}$ of one phenyl ring; and another doublet at 147.7 ppm (J_{CP} = 2.4 Hz) corresponding to the C$_{ipso'}$ of the other phenyl ring. Noteworthy is the fact that the ipso carbons of the phenyl rings are coupled to the phosphines, which suggests their proximity to the metal center and further supports the metallacyclobutene structure **6**. The IR spectrum of this compound exhibits two CO stretches: ν_{CO} = 2004.2 and 1944.8 cm^{-1} consistent with the presence of two inequivalent carbonyl groups and, perhaps, two iridium centers in different oxidation states.

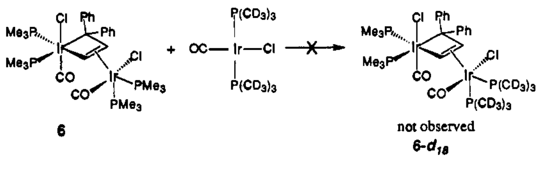
Scheme 3. Possible Pathway for the Formation of **6**-d_2[a]



[a] Given that steps b and c are known to occur, step a does not occur since there is no observable deuterium incorporation into complex **6** upon treatment of **6** with 3,3-diphenylcyclopropene-*1,2*-d_2.

Stability and Irreversible Formation of 6. Compound **6** is unstable in both C$_6$D$_6$ and CD$_2$Cl$_2$ and attempts to isolate it have not been successful. At low concentrations (ca. 10^{-3} M) in either C$_6$D$_6$ or CD$_2$Cl$_2$, **6** is stable for 12–20 h. At higher concentrations (ca. 10^{-1} M in the same solvents), however, **6** decomposes within several hours. It is quite stable in the solid phase, but attempts to purify it by recrystallization have so far been unsuccessful.

Furthermore, the addition of 1,2-dideuterio-3,3-diphenylcyclopropene, **5**-d_2, to a solution of **6** does not lead to exchange of the hydrocarbon moiety. Given the fact that olefin complexation in **1** is reversible, this suggests that **6** does not revert back to **1**, thus, the formation of **6** from **1** is apparently irreversible (Scheme 3). Also, it appears that complexation of the iridacyclobutene to the second metal center is irreversible. Addition of labeled Vaska's complex IrCl(CO)[P(CD$_3$)$_3$]$_2$ to a solution of **6** does not lead to exchange of the metal centers (eq 7).



(7)

Kinetics of the Rearrangement of 1 to 6. The progress of the reaction between **1** and IrCl(CO)(PMe$_3$)$_2$ to yield **6** was monitored by ^{1}H NMR spectroscopy in both C$_6$D$_6$ and CD$_2$Cl$_2$ (as described in the Experimental Section). This rearrangement was examined by varying the initial concentration of IrCl(CO)(PMe$_3$)$_2$. The reaction exhibited clean second-order kinetics at room temperature (Tables 4 and 5).[29] This rearrangement does not appear to exhibit any solvent effect in the two solvents examined. Analysis of the data suggest that the second order rate constant (k$_2$) is approximately the same in both CD$_2$Cl$_2$ and C$_6$D$_6$.

Mechanism of the Rearrangement and Isotopic Labeling Studies. There are at least two possible pathways for the formation of **6** from the reaction of **1** with IrCl(CO)(PMe$_3$)$_2$ as illustrated in Scheme 4. It should be possible to distinguish between these two pathways by labeling one of the two metal centers involved. If the reaction proceeds through a vinylcarbene intermediate

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[28] Line-shape analysis using the LAOCOON simulation program developed by Professor John D. Roberts of the California Institute of Technology showed that the coupling patterns of the olefinic protons must involve more than two ^{31}P nuclei. The precise line shape could not be simulated.

[29] Atkins, P. W. *Physical Chemistry*; W. H. Freeman & Co.: New York, 1986; pp 695–696.

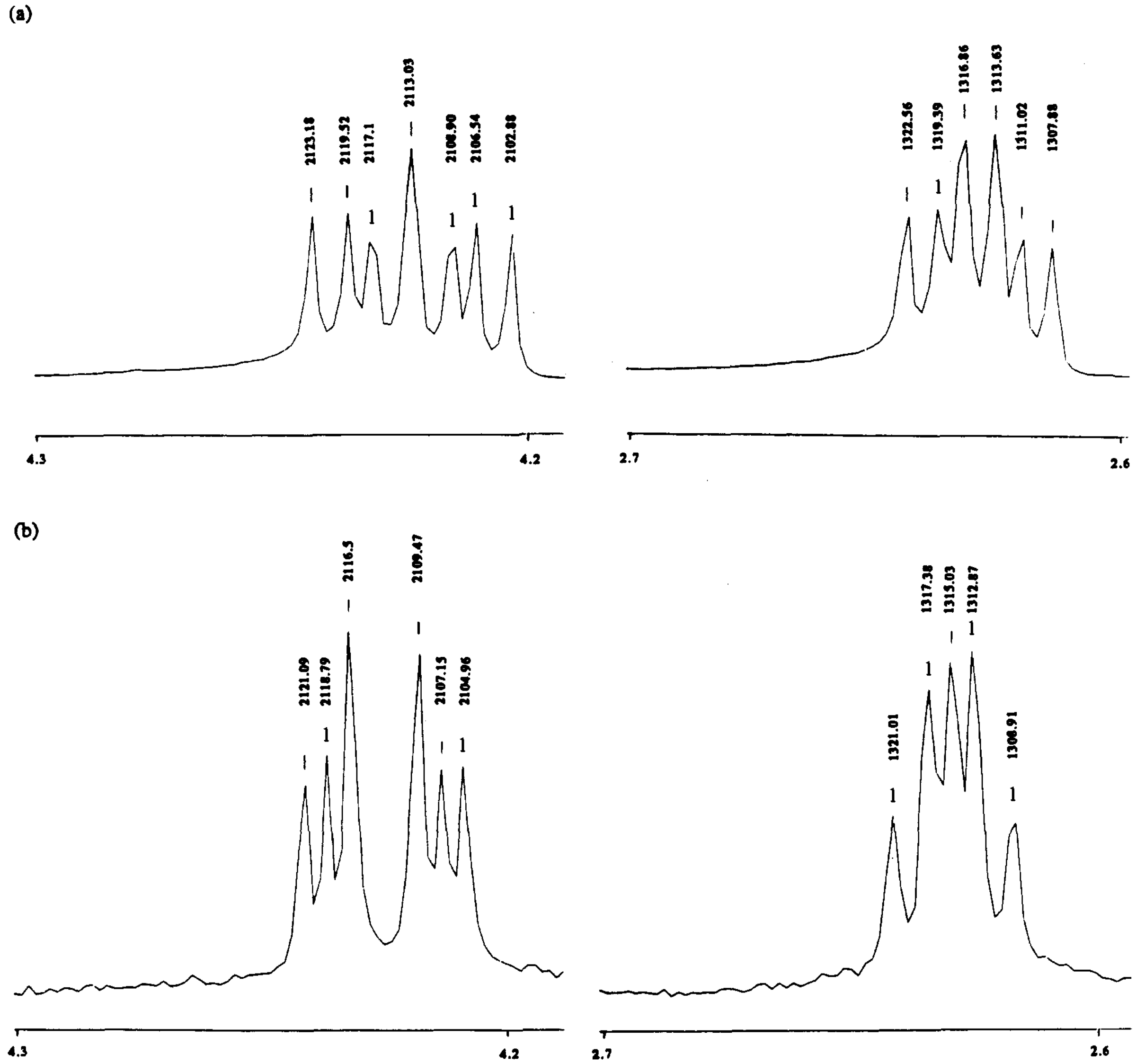


Figure 5. (a) 500 MHz ^{1}H NMR spectra of the olefinic protons at δ 2.62 and 4.23. (b) 500 MHz ^{1}H NMR spectra of the proton-decoupled olefinic protons at δ 2.62 after irradiation at δ 4.23 and the proton-decoupled olefinic proton at δ 4.23 after irradiation at δ 2.62. Chemical shift data are provided in Hz on top of each peak.

Table 4. Kinetic Parameters for the Reaction of **1** with $IrCl(CO)(PMe_3)_2$ in C_6D_6 Including [**1**], $[IrCl(CO)(PMe_3)_2]$, and the Second-Order Rate Constant (k_2)

$10^2[IrCl(CO)(PMe_3)_2]$ (M)	$10^2[IrCl(CO)(PMe_3)_2$(3,3-diphenylcyclopropene)] (M)	10^3k_2 ($M^{-1}\ s^{-1}$)[a]
1.17 ± 0.02	1.67 ± 0.03	8.29 ± 1.32
1.67 ± 0.03	1.67 ± 0.03	8.54 ± 1.36
3.33 ± 0.05	1.67 ± 0.03	10.6 ± 1.46
6.67 ± 0.09	1.67 ± 0.03	10.1 ± 1.54
9.72 ± 0.14	1.67 ± 0.03	7.07 ± 1.60
3.33 ± 0.05	3.33 ± 0.05	6.90 ± 1.52
6.67 ± 0.09	3.33 ± 0.05	7.82 ± 1.61
10.0 ± 0.2	3.33 ± 0.05	8.53 ± 1.68
13.3 ± 0.2	3.33 ± 0.05	7.26 ± 1.72

[a] $k_2t = 1/\{B_o - A_o\}\ \ln\{A_o(B_o - X)/(A_o - X)B_o\}$,[29] where A_o is the starting concentration of **1**, B_o is the starting concentration of $IrCl(CO)(PMe_3)_2$, and X is the concentration of **6** at time *t*.

Table 5. Kinetic Parameters for the Reaction of **1** with $IrCl(CO)(PMe_3)_2$ in CD_2Cl_2 Including [**1**], $[IrCl(CO)(PMe_3)_2]$, and the Second-Order Rate Constant (k_2)

$10^2[IrCl(CO)(PMe_3)_2]$	$10^2[IrCl(CO)(PMe_3)_2$(3,3-diphenylcyclopropene)] (M)	10^3k_2 ($M^{-1}\ s^{-1}$)[a]
1.67 ± 0.03	1.67 ± 0.03	6.73 ± 1.32
3.33 ± 0.05	1.67 ± 0.03	7.07 ± 1.40
6.67 ± 0.09	1.67 ± 0.03	7.83 ± 1.47
9.72 ± 0.14	1.67 ± 0.03	7.52 ± 1.53

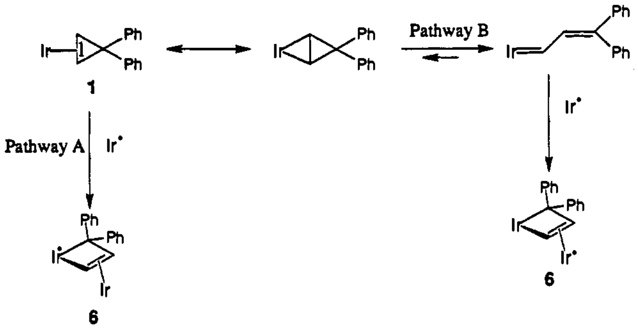
[a] $k_2t = 1/\{B_o-A_o\}\ln\{A_o(B_o-X)/(A_o-X)_{Bo}\}$,[29] where A_o is the starting concentration of **1**, B_o is the starting concentration of $IrCl(CO)(PMe_3)_2$, and X is the concentration of **6** at time *t*.

(pathway B), then the metallacycle should contain the metal originally found in **1**. If, however, the reaction occurs by direct insertion of $IrCl(CO)(PMe_3)_2$ into the C–C bond of the cyclopropene ring in **1** (pathway A), then the metallacycle should contain the metal that participates in the σ-bond insertion.

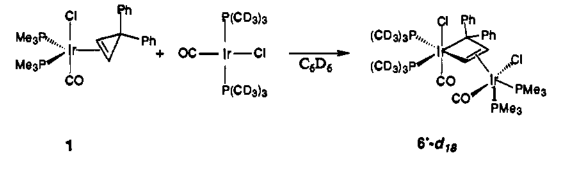
We chose to distinguish the metal centers by using perdeuteriotrimethylphosphine on one metal center and unlabeled trimethylphosphine on the other. Thus, in one experiment $IrCl(CO)(PMe_3)_2$(3,3-diphenylcyclopropene) was reacted with $IrCl(CO)(P[CD_3]_3)_2$ (eq 8), and in the other, $IrCl(CO)(P[CD_3]_3)_2$(3,3–diphenylcyclopropene) was reacted with $IrCl(CO)(PMe_3)_2$ (eq 9).

Previous analysis of the ^{1}H NMR spectrum of **6** established that the resonances for the PMe_3 protons of the metal bearing the metallacycle were shifted approximately 0.2 ppm from the PMe_3 protons of the metal coordinated to the iridacyclobutene. Thus, we could establish the origin of the two metals in **6** (i.e., which metal comes from **1** and which metal comes from free

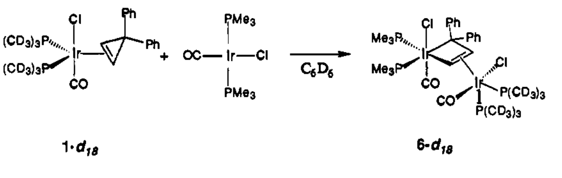
Scheme 4. Two Possible Pathways for the Formation of **6**



$IrCl(CO)(PMe_3)_2$). In addition, by integrating both PMe_3 resonances relative to the olefinic resonances, we could establish the isotopic "cleanliness" of the reactions.



(8)

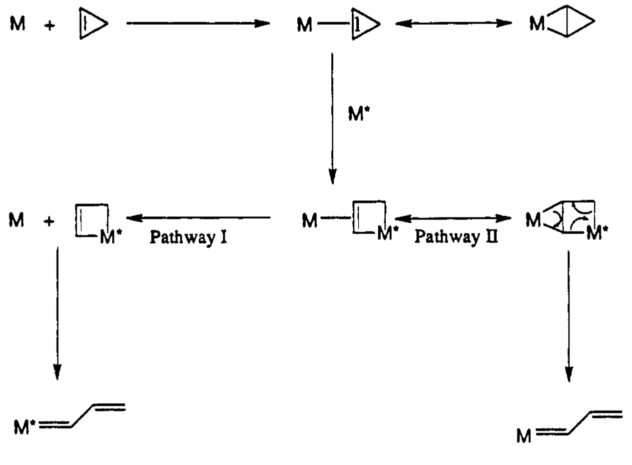


(9)

For both reactions (eqs 8 and 9), the metal from free $IrCl(CO)(PR_3)_2$ was found to be in 88% of the metallacycle metal centers. Consequently, 12% of the metallacycle metal centers were found to contain the metal originally in **1**. These results establish that the predominant pathway for the formation of **6** involves σ-bond activation of the cyclopropene moiety in **1** by $IrCl(CO)(PR_3)_2$ (i.e., pathway A in Scheme 4).

A Proposed Bimetallic Pathway for the Ring Opening of Cyclopropenes to Vinylcarbenes. On the basis of the preceding observations, a scheme for the bimetallic metal-mediated ring opening of metal η^2-cyclopropenes to metallacyclobutenes/metal vinylcarbenes is proposed (Scheme 5). First, the metal and cyclopropene react to form an η^2-olefin complex. This η^2-olefin complex undergoes subsequent reaction with another metal (M^*), which inserts into the C–C σ-bond to form a bimetallic metallacyclobutene complex. This complex can then rearrange further by several pathways. One pathway involves the dissociation of the metal M to form an isolated metallacyclobutene complex, which can rearrange on its own to a vinylcarbene (pathway I). The bimetallic complex can also rearrange on its own to a vinylcarbene—a pathway that uses the second metal (M^*) as a catalyst (pathway II). In the case presented here, however, the iridium vinylcarbene complex seems to be less stable than the bimetallic iridium metallacyclobutene complex, and thus rearrangement of the metallacyclobutene to the metal vinylcarbene is not observed. This observation can be rationalized if we consider the carbene moiety to be a neutral ligand. Assuming a constant ancillary ligand environment, rearrangement of the metallacyclobutene moiety would result in a 5-coordinate, 18-electron iridium(I) carbene complex, an inherently unstable species.[19] On the other hand, the metallacyclobutene configuration is preferred because it is formally an 18-electron complex of iridium(III), which can coordinate six ligands and adopt an octahedral geometry.

Scheme 5. Possible Pathways for the Metal-Mediated Rearrangement of Cyclopropenes to Vinylcarbenes



Group VIII metal complexes have long been known to catalyze the rearrangement of bicyclo[1.1.0]butane to butadiene.[30] In these reactions, it has been proposed that the first step involves the activation of a side $C_{methylene}$–$C_{methine}$ σ-bond.[31] This proposal is analogous to our proposed mechanistic scheme where one metal center is part of the bicyclobutane and the other metal center functions as a catalyst for the rearrangement. The similarity between the rearrangement of metal-η^2-cyclopropene complexes and that of bicyclo[1.1.0]butane is striking where the metal center in the η^2-cyclopropene complex behaves much like one of the methylene carbons in bicyclo[1.1.0]butane.

An additional example of the bimetallic pathway depicted in Scheme 5 may be inferred from recent work in our laboratory. Using the metal η^2-cyclopropene/bicyclobutane analogy, Johnson and Grubbs succesfully catalyzed the formation of tungsten vinylcarbenes from tungsten η^2-3,3-diphenylcyclopropene complexes with $HgCl_2$.[3,32] There, the Hg^{2+} can be viewed to function as M^*. In a related paper, Swager and Grubbs have used both Hg^{2+} and Ag^+ to catalyze the isomerization of the bicylobutane rings in polybenzvalene to 1,3-dienes.[33] Although we are certain that a bimetallic path such as that shown in Scheme 5 is possible in the metal-mediated ring opening of cyclopropenes to metallacyclobutenes/metal vinylcarbenes, it is only one route among the many mechanistic pathways that exist. Depending on the metal center, ligand environment, and reaction conditions, the mechanism for this transformation may vary from system to system.

Conclusions

To summarize, $IrCl(CO)(PR_3)_2$ complexes react with 3,3-diphenylcyclopropene to afford stable η^2-olefin complexes. The binding of the olefin is reversible and depends on the steric bulk of the tertiary phosphine: complexation of the olefin becomes less favorable as the size of the tertiary phosphine increases. Addition of another equivalent of $IrCl(CO)(PMe_3)_2$ to the olefin complex **1** produces a bimetallic iridacyclobutene, where the iridacyclobutene moiety is stabilized by coordination in an η^2 fashion to a second metal center. Kinetic measurements show this rearrangement to be a second order process. Isotopic labeling studies suggest that formation of the bimetallic iridacyclobutene proceeds by a mechanism involving C–C bond activation of the

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(30) (a) Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7748–7756. (b) Gassman, P. G.; Meyer, G. R.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7741–7748.

(31) (a) Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7733–7740. (b) Gassman, P. G.; Atkins, T. J.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 1812–1813.

(32) Johnson, L. K. Ph.D. Thesis, California Institute of Technology, 1992.

(33) Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973–2974.

olefin moiety in **1** by free $IrCl(CO)(PMe_3)_2$. This study provides further evidence that a bimetallic C–C activation pathway is one possible mechanism in the metal-catalyzed ring opening of cyclopropenes to metallacyclobutenes/metal vinylcarbenes.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3–11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. NMR experiments were also prepared inside a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz ^{1}H; 22.53 MHz ^{13}C; 34.82 MHz ^{31}P, ^{7}Li external lock, ^{31}P NMR data referenced to external H_3PO_4 where PPh_3 has a chemical shift at −5.4 ppm), or a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer.

Materials. Hexane was stirred over concentrated H_2SO_4, dried successively over $MgSO_4$ and CaH_2, and then transferred onto sodium benzophenone ketyl solubilized with tetraglyme. *n*-Butyl ether and benzene were distilled or vacuum transferred from sodium benzophenone ketyl. Methylene chloride was stirred over either CaH_2 or P_2O_5, distilled under argon, and degassed by three continuous freeze–pump–thaw cycles. Methylene chloride-d_2 was dried over CaH_2, vacuum transferred, and then degassed by three continuous freeze–pump–thaw cycles. Benzene-d_6 was dried over sodium benzophenone ketyl and then vacuum transferred. $[Ir(COD)Cl]_2$[34] and $IrCl(CO)(PR_3)_2$[35] were prepared according to literature procedures. 3,3-Diphenylcyclopropene was prepared following a procedure by Moore.[36] The following chemicals were obtained from commercial sources and used as received: dimethyl sulfoxide-d_6 (Cambridge Isotopes); *t*-BuOK, Mg turnings, and iodomethane-d_3 (Aldrich Chemical Co.); silica gel, diethyl ether, and hexane (EM Science).

$IrCl(CO)(PMe_3)_2(\eta^2$-3,3-diphenylcyclopropene) (1). In a typical reaction, a 50 mL Schlenk flask equipped with a magnetic stirbar was charged with $IrCl(CO)(PMe_3)_2$ (1.0 g, 2.4 mmol) inside a nitrogen-filled drybox. Methylene chloride (10 mL) was added to dissolve the complex. 3,3-Diphenylcyclopropene (0.69 g, 1.5 equiv) in CH_2Cl_2 (2 mL) was then added to the solution via cannula. The reaction was allowed to stir under argon at room temperature for 2 h. Hexane (20 mL) was added to the solution which was then cooled to −30 °C for 24 h upon which white crystals of the product formed. The supernatant was cannula filtered away while the mixture was kept cold. The remaining crystals were washed with ice-cold hexane (2 × 10 mL) and dried under vacuum overnight. Yield = 1.1–1.3 g (75–90%). ^{1}H NMR (C_6D_6): δ 1.25 (pseudodoublet, $IrP(CH_3)_3$, $J_{HP} = 6.6$ Hz), 3.32 (t, $HC{=}CH$, $J_{HP} = 6.4$ Hz). ^{31}P NMR (C_6D_6): δ −51.2 (s). ^{13}C NMR (CD_2Cl_2): δ 17.7 (t, $IrP(CH_3)_3$, $J_{CP} = 15.5$ Hz), 37.1 (quintet (overlapping triplets), $HC{=}CH$, $J_{CP} = 29.7$ Hz), 64.3 (s, $M(C{=}CC)$, 165.9 (t, $M(CO)$, $J_{CP} = 8.9$ Hz). IR (C_6H_6): $\nu_{CO} = 1985.9$ cm.$^{-1}$ Anal. Calcd for $C_{22}H_{30}ClIrOP_2$: C, 44.03; H, 5.04. Found: C, 43.94; H, 5.05.

X-ray Diffraction Study of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3–diphenylcyclopropene) (1). A concentrated solution of $IrCl(CO)(PMe_3)_2(\eta^2$-3,3–diphenylcyclopropene), **1**, in dichloromethane (1 mL) was loaded into a 5 mm NMR tube inside a nitrogen-filled drybox, sealed with a rubber septum, and slowly cooled to −20 °C over 24 h upon which a large, pale yellow crystal was obtained. The supernatant was then carefully removed from the tube via pipet. The resulting crystal was transferred quickly into an oil-filled crystallizing dish and cut to ca. 0.20 x 0.33 × 0.40 mm with a razor blade.[37] Next, this crystal was oil-mounted[37] on a glass fiber and transferred to the Syntex $P2_1$ automated four-circle diffractometer which is equipped with a modified LT-1 low temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[38] Intensity data were collected at 163 K using a θ–2θ scan technique with Mo Kα radiation. All 6876 data were corrected for absorption and for Lorentz and polarization effects and are placed on an approximately absolute scale. The difraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ (C_{2h}^5; No. 14) is therefore uniquely defined.

All crystallographic calculations were carried out using either the UCLA Crystallographic Computing Package[39] or the SHELXTL PLUS program set.[40] The analytical scattering factors for neutral atoms were used throughout the analysis;[41a] both real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[41b] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0008(|F_o|)^2$. The structure was solved via an automatic Patterson routine (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C–H) = 0.96$ Å and $U(iso) = 0.06$ Å ^{2}. There is one molecule of dichoromethane present in the assymetric unit. Refinement of positional and thermal paramenters led to convergence with RF = 4.5%; R_{wF} = 5.0% and GOF = 1.26 for 271 variables refined against those 5282 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference Fourier synthesis yielded ρ(max) = 2.63 e Å $^{-3}$ at a distance of 0.96 Å from Ir(1).

$IrCl(CO)(PMe_2Ph)_2(\eta^2$-3,3-diphenylcyclopropene) (2). This compound was synthesized using a procedure similar to that described for the synthesis of **1**. Yield is 70–80%. ^{1}H NMR (C_6D_6): δ 1.47 (pseudodoublet, $IrP(CH_3)(C'H_3)(Ph)$, $J_{CP} = 9.6$ Hz), 1.59 (pseudodoublet, $IrP(CH_3)(C'H_3)(Ph)$, $J_{CP} = 9.0$ Hz), 3.40 (t, $HC{=}CH$, $J_{CP} = 6.5$ Hz). ^{31}P NMR (C_6D_6): δ −38.5 (s). ^{13}C NMR (CD_2Cl_2): δ 17.7 (t, $P(CH_3)_2(Ph)$, $J_{CP} = 17.1$ Hz), 38.4 (quintet (overlapping triplets), $Ir(C{=}CC)$, $J_{CP} = 29.3$ Hz, $J_{CH} = 220.9$ Hz), 167.5 (t, $Ir(CO)$, $J_{CP} = 8.9$ Hz). IR (C_6H_6): $\nu_{CO} = 1992.6$ cm.$^{-1}$ Anal. Calcd for $C_{32}H_{34}ClOP_2Ir$: C, 53.07; H, 4.73. Found: C, 52.85; H, 4.39.

$IrCl(CO)(PMePh_2)_2(\eta^2$-3,3-diphenylcyclopropene) (3). This compound was synthesized using a procedure similar to that described for **1**. The product could not, however, be separated from the starting Vaska complex $IrCl(CO)(PMePh_2)_2$: $IrCl(CO)(PMePh_2)_2$(3,3-diphenylcyclopropene) was isolated in a 7:3 mixture with $IrCl(CO)(PMePh_2)_2$. ^{1}H NMR (C_6D_6): δ 1.92 (pseudodoublet, $IrP(CH_3)(Ph)_2$, $J_{CP} = 9.0$ Hz), 3.47 (t, $HC{=}CH$, $J_{CP} = 6.7$ Hz); ^{31}P NMR (C_6D_6): δ −21.3 (s). ^{13}C NMR (CD_2Cl_2): δ 14.3 (t, $IrP(CH_3)(Ph)_2$, $J_{CP} = 17.1$ Hz), 38.7 (quintet (overlapping triplets), $Ir(C{=}CC)$, $J_{CP} = 26.7$ Hz), 165.4 (t, $Ir(CO)$, $J_{CP} = 8.9$ Hz). IR (C_6H_6): $\nu_{CO} = 2000.7$ cm.$^{-1}$

$IrCl(CO)(PEt_3)_2(\eta^2$-3,3-diphenylcyclopropene) (4). This compound was synthesized using a procedure similar to that described for **1**. The product could not, however, be separated from the starting Vaska complex $IrCl(CO)(PEt_3)_2$: $IrCl(CO)(PEt_3)_2$(3,3-diphenylcyclopropene) was isolated in a 2:5 mixture with $IrCl(CO)(PEt_3)_2$. ^{1}H NMR (C_6D_6): δ 0.89 (m, $IrP(CH_2CH_3)_3$, $J_{HP} = 7.5$ Hz), 1.67 (m, $IrP(CH_2CH_3)_3$, $J_{CP} = 8.1$ Hz), 3.25 (t, $HC{=}CH$, $J_{CP} = 6.3$ Hz). ^{31}P NMR (C_6D_6): δ −18.4 (s). ^{13}C NMR (CH_2Cl_2): δ 8.6 (d, $IrP(CH_2CH_3)_3$, $J_{CP} = 19.5$ Hz), 18.5 (t, $IrP(CH_2CH_3)_3$, $J_{CP} = 14.7$ Hz), 35.7 (q, $HC{=}CH$, $J_{CP} = 33.8$ Hz), 172.8 (t, Ir-CO, $J_{CP} = 11.0$ Hz). IR (C_6H_6): $\nu_{CO} = 1979.3$ cm.$^{-1}$

3,3-Diphenylcyclopropene-*1,2–d₂* (5–d_2). 3,3-Diphenylcyclopropene (1.0 g, 5.2 mmol) and potassium *tert*-butoxide (0.058 g, 0.52 mmol) were dissolved in dimethyl sulfoxide-d_6 (200 mL). The reaction was stirred for 1 h and then quenched with ice-cold D_2O (50 mL). The resulting aqueous slurry was extracted with 2:1 hexane–diethyl ether (5 × 100 mL). The combined extracts were then concentrated using a rotary-evaporator to give a viscous yellowish green liquid which was purified by column chromatography on silica gel using hexane as the eluant. Yield after chromatography = 0.98 g (98%). ^{13}C NMR (CD_2Cl_2): δ 31.7 (s, $C{=}CC$), 113.2 (t, $C{=}CC$, $J_{CD} = 35.4$ Hz), 126.0 (s, C_{ortho}), 128.4 (s, C_{meta} and C_{para}), 147.7 (s, C_{ipso}).

Trimethylphosphine-d_9. The procedure described here represents a modification of a published, large-scale preparation of trimethylphos-

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[37] The crystal was immersed in a lube-oil additive which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting-pin. Further details were described by Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization;* ACS Symp. Ser. No. 357; Wayda, A. L., Derensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987.

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[41] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974: (a) pp 99–101; (b) pp 149–150.

phine.[42] Fresh magnesium turnings (5.00 g, 0.206 mol) were slurried in anhydrous *n*-butyl ether (50 mL) in a 250 mL Schlenk flask under argon. With the Schlenk flask placed in a bath of room-temperature water, iodomethane-d_3 (20.0 g, 0.140 mol) was added dropwise over 1.0 h. The solution containing the Grignard reagent was cannula filtered away from the excess Mg turnings and cooled to 0 °C. Tri-*o*-tolyl phosphite (16.4 g, 0.047 mol) in *n*-butyl ether (25 mL) was then added dropwise to the Grignard solution over 1.5 h. When the addition was complete, a distillation head was attached to the top of a reflux condenser filled with water (the water was not circulated continuously). The reaction mixture was then heated until the *n*-butyl ether refluxed vigorously (ca. 178 °C). The product phosphine was slowly liberated from the mixture and collected in a storage flask equipped with a Kontes valve. The crude product was then vacuum transferred into another storage flask to remove excess *n*-butyl ether (2.1 g, 79% overall yield). ^{31}P NMR (C_6D_6): δ −65.9 (br s).

IrCl(CO)(P[CD$_3$]$_3$)$_2$(η^2-3,3-diphenylcyclopropene) (1–d_{18}). This compound was synthesized using the procedure described for **1**, but employing $P(CD_3)_3$ rather than $P(CH_3)_3$. ^{1}H NMR (C_6D_6): δ 3.32 (t, *HC*═*CH*, J_{HP} = 9.5 Hz). ^{31}P NMR (C_6D_6): δ 53.9 (br s).

Kinetics of Reaction of 1 with 3,3-Diphenylcyclopropene-*1,2*–d_2 in C_6D_6 and CD_2Cl_2. In the drybox, IrCl(CO)(PMe$_3$)$_2$(3,3-diphenylcylopropene) (10 mg, 1 equiv) was weighed in each of two NMR tubes. To one tube was added C_6D_6 (500 μL) and to the other tube was added CD_2Cl_2 (500 μL). 3,3-Diphenylcyclopropene-*1,2*–d_2 (6.4 mg, 2 equiv) was then added to each NMR tube. The disappearance of **1** and formation of new olefin complex **1–d_2** was observed by ^{1}H NMR using ferrocene as an internal standard. The kinetic runs were carried out at 21.6 °C and monitored until a dynamic equilibrium was obtained.

Observation of the Formation of 6. The η^2-cyclopropene complex **1** (5.0 mg) and IrCl(CO)(PMe$_3$)$_2$ (13.4 mg, 4 equiv) were dissolved in C_6D_6 (500 μL) in a 5 mm NMR tube. The mixture was allowed to rotate mechanically for 2 h and a ^{1}H NMR spectrum was acquired. ^{1}H NMR (C_6D_6): δ 1.01 (d, J_{HP} = 9.0 Hz) and 1.19 (d, J_{HP} = 10.5 Hz), 1.32 (d, J_{HP} = 9.6 Hz), 2.62 (pseudosextet), 4.22 (pseudoseptet). ^{31}P NMR (C_6D_6): δ −56.1 and −46.2 (d, J_{PP} = 17.5 Hz), 38.3 (br s), 14.5 (br s). ^{13}C NMR (C_6D_6): δ 14.1 (d of q, J_{CP} = 95.5 Hz, $J_{CP'}$ = 6.7 Hz, J_{CH} = 391.8 Hz), 14.9 (d, J_{CP} = 15.1 Hz), 15.2 (d, J_{CP} = 18.4 Hz), 17.6 (d, J_{CP} = 15.5 Hz), 17.8 (d, J_{CP} = 15.5 Hz), 66.0 (d of t, J_{CP} = 37.6 Hz, $J_{CP'}$ = 4.2 Hz, J_{CH} = 168.9 Hz), 146.6 (d, J_{CP} = 4.1 Hz), 147.7 (d, J_{CP} = 2.4 Hz), 166.3 (d of d, J_{CP} = 5.7 Hz, $J_{CP'}$ = 2.9 Hz), 174.3 (triplet, J_{CP} = 10.5 Hz).

Observation of the Formation of 6′-d_{18}. The η^2-cyclopropene complex **1** (5.0 mg) and IrCl(CO)(P[CD$_3$]$_3$)$_2$ (13.5 mg, 4 equiv) were dissolved in C_6D_6 (500 μL) in a 5 mm NMR tube. The mixture was allowed to rotate mechanically for 2 h and a ^{1}H NMR spectrum was acquired. ^{1}H NMR (C_6D_6): δ 1.01 (d, J_{HP} = 9.0 Hz) and 1.19 (d, J_{HP} = 10.5 Hz), 1.32 (d, J_{HP} = 9.6 Hz), 2.62 (pseudosextet), 4.22 (pseudoseptet).

Observation of the Formation of 6-d_{18}. The η^2-cyclopropene complex **1–d_{18}** (5 mg) and IrCl(CO)(PMe$_3$)$_2$ (13.2 mg, 4 equiv) were dissolved in C_6D_6 (0.5 ml) in a 5 mm NMR tube. The mixture was allowed to rotate mechanically for 2 h and a ^{1}H NMR spectrum was acquired. ^{1}H NMR (C_6D_6): δ 1.01 (d, J_{HP} = 9.0 Hz) and 1.19 (d, J_{HP} = 10.5 Hz), 1.32 (d, J_{HP} = 9.6 Hz), 2.62 (pseudosextet), 4.22 (pseudoseptet).

Kinetics of the Reaction of 1 with IrCl(CO)(PMe$_3$)$_2$ in C_6D_6 and CD_2Cl_2. In the drybox, a stock solution of IrCl(CO)(PMe$_3$)$_2$(η^2-3,3-diphenylcyclopropene) in C_6D_6 and CD_2Cl_2 was made by dissolving 25.0 mg of IrCl(CO)(PMe$_3$)$_2$(η^2-3,3–diphenylcyclopropene) in 1.25 mL of C_6D_6 or CD_2Cl_2. Approximately 250 μL of this stock solution was syringed into each of five different 5 mm NMR tubes. Next, a stock solution of IrCl(CO)(PMe$_3$)$_2$ was made by dissolving 36.4 mg of IrCl(CO)(PMe$_3$)$_2$ in 1.00 mL of C_6D_6 or CD_2Cl_2. Varying amounts of this second stock solution (65.9 μL, 0.7 mol equiv; 93.4 μL, 1.0 mol equiv; 186.8 μL, 2 mol equiv, 280.2 μL, 3 mol equiv, 373.6 μL, 4 mol equiv) were syringed into each of the five NMR tubes. Finally, additional C_6D_6 or CD_2Cl_2 was appropriately added to each of the NMR tubes to ensure equal concentrations. The kinetic runs were carried out at 21.6 °C and monitored by ^{1}H NMR for ca. 3 half-lives. Concentration of product **6** at time *t* was determined by NMR integration. Data manipulation was done using the KaleidaGraph curve-fitting module[43] to extract the second-order rate constants (k_2).

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Supplementary Material Available: A complete description of the X-ray diffraction experiment, the molecular drawings of **1**, and tables of crystal data, atomic coordinates, thermal parameters, distances and angles, and torsion angles (17 pages); a listing of structure factor amplitudes (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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