

After examining upwards of 20 crystals from several different samples, only one was found to be of sufficiently high quality for data collection; all others showed evidence of twinning. Crystals from  $\text{CH}_2\text{Cl}_2$  did not diffract at all. The crystal was mounted in a glass capillary under dinitrogen with the  $b$  axis nearly coincident with the diffractometer  $\phi$  axis. Cell dimensions were based upon a Delaunay reduction of a cell obtained from the centering of 25 reflections on the diffractometer.

Intensity data (294 K) were measured by the  $\theta$ - $2\theta$  step scan technique with Mo  $K\alpha$  radiation from a graphite monochromator. A total of 1811 Bragg reflections were measured before excessive decomposition of the crystal in the X-ray beam halted data collection. The intensities of three standard reflections were measured after each 7200 s exposure to the X-rays and were used to correct for the approximately 40% intensity decay which occurred during the experiment. The correction ranged from 1 to 1.42. Empirical absorption corrections were made with the  $\omega$  scan technique ( $\mu = 61.4$ ). Averaging of equivalent reflection gave 1591 data points of which 1325 had  $F_o > \sigma(F_o^2/2F_o)$ ; these were used to refine the structure ( $\sigma^2(F_o^2) = \sigma^2 \text{ counting} + (0.05F_o^2)^2$  and  $\sigma(F_o) = \sigma(F_o^2)/2F_o$ ).

The structure was resolved by Patterson and Fourier methods. Least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$ , converged with  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.025$  and  $R_w = [\sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.032$ . Hydrogen atoms were placed in "ideal" X-ray positions<sup>29</sup> based on the location of at least one peak in a reasonable hydrogen atom position for each hydrogen bearing group. No extinction correction was applied. The

occupancy refinement and calculations followed the procedure reported in ref 2.

The maximum parameter shift on the last cycle was less than 0.01 times its esd, and the error in an observation of unit weight was 1.06. Atomic scattering factors were taken from ref 30. Final atomic positional parameters are included in Table II. Selected interatomic bond distances and angles are given in Table III.

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**Registry No.** 1a, 85798-76-1; 1b, 39049-86-0; 1c, 90245-62-8; 2a, 90245-65-1; 2b, 90245-66-2; 2c, 90245-67-3; 3, 90245-64-0; 4, 90245-69-5; 5, 90245-70-8; 7, 90245-72-0; 8, 90319-41-8;  $\text{WCl}_4$ -(Peme)<sub>3</sub>, 73133-10-5;  $\text{WCl}_2(\text{bpy})(\text{PMe}_3)_2$ , 90245-63-9;  $\text{WCl}_4(\text{bpy})$ , 12116-41-5;  $\text{WCl}_3(\text{PMe}_3)_3$ , 73133-11-6.

**Supplementary Material Available:** A listing of structure factor amplitudes, a table of calculated hydrogen atom positional parameters, and a table of thermal parameters (10 pages). Ordering information is given on any current masthead page.

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## Conversion of a (Methoxymethyl)iridium(I) Acetylene Complex to a Metallacyclobutene Iridium(III) Complex. Crystal and Molecular Structures of $\text{Ir}(\text{CH}_2\text{OCH}_3)(p\text{-tol-C}\equiv\text{C-}p\text{-tol})(\text{PMe}_3)_3$ and $\text{fac-Ir}[\text{CH}_2\text{C}(p\text{-tol})=\text{C}(p\text{-tol})]\text{Br}(\text{PMe}_3)_3$ <sup>†</sup>

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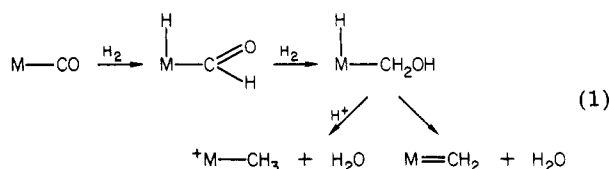
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The (methoxymethyl)iridium(I) acetylene complex  $\text{Ir}(\text{CH}_2\text{OCH}_3)(p\text{-tol-C}\equiv\text{C-}p\text{-tol})(\text{PMe}_3)_3$  (1) reacts with bromotrimethylsilane to form the iridium(III) metallacyclobutene complex  $\text{fac-Ir}[\text{CH}_2\text{C}(p\text{-tol})=\text{C}(p\text{-tol})]\text{Br}(\text{PMe}_3)_3$  (2). A methyleneiridium(I) complex is believed to be involved in the reaction. The kinetic product 2 thermally isomerizes to the *mer*-metallacyclobutene 3. Crystal structures of compounds 1 and 2 have been completed. Compound 1 (-100 °C): orthorhombic, space group *Pbca*,  $a = 18.310$  (2) Å,  $b = 17.696$  (3) Å,  $c = 18.408$  (2) Å,  $V = 5964$  (2) Å<sup>3</sup>,  $Z = 8$ . Compound 2 (-100 °C): monoclinic, space group *P2<sub>1</sub>/n*,  $a = 23.279$  (5) Å,  $b = 8.579$  (3) Å,  $c = 16.273$  (4) Å,  $\beta = 103.97$  (2)°,  $V = 3154$  (2) Å<sup>3</sup>,  $Z = 4$ . Final conventional and weighted agreement indices on  $F_o$  are 0.034 and 0.030 for compound 1 (3283 reflections with  $F_o > 3\sigma(F_o)$ ) and 0.031 and 0.038 for compound 2 (4827 reflections with  $F_o > 2\sigma(F_o)$ ). The important structural features of compound 1 are the  $\text{IrCH}_2\text{-O}$  distance (1.449 (9) Å) and the  $\text{C}\equiv\text{C}$  distance (1.30 (1) Å). The metallacyclobutene ring of compound 2 is planar with  $\text{Ir-C}$  distances of 2.134 (5) and 2.166 (6) Å and  $\text{C-C}$  distances of 1.344 (8) and 1.525 (7) Å.

### Introduction

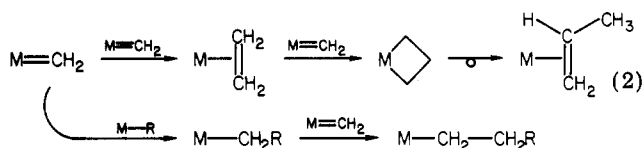
Transition-metal-bound carbene or alkylidene groups may participate in a number of important organometallic reactions, particularly olefin metathesis<sup>1</sup> and olefin polymerization.<sup>2</sup> Furthermore, methylene may play a key role in the Fischer-Tropsch process, both in CO reduction and the formation of multicarbon species (possibly by the reactions of eq 1 and 2).<sup>3</sup> To understand how the carbene



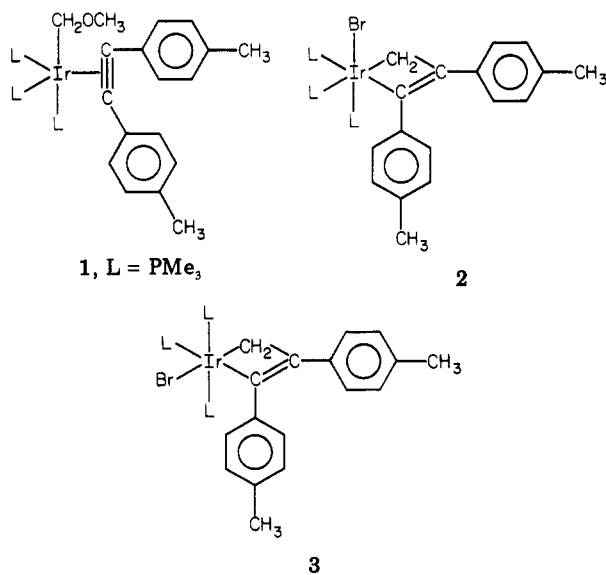
or alkylidene group may be involved in the formation of new carbon-hydrogen or carbon-carbon bonds, we have been studying electrophilic methylene complexes of iridium. Our interest in such compounds arises from our

<sup>†</sup>Contribution No. 3339.

earlier studies of formyl and hydroxymethyl complexes of iridium, where we observed several of the species and reactions of eq 1. Additionally, "incipient methylene" complexes, derived from well-characterized (methoxymethyl)- and (hydroxymethyl)iridium complexes, undergo some of the reactions of eq 2.<sup>4</sup>



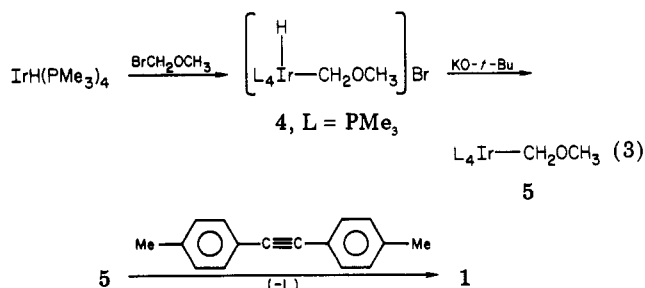
Use of the alkoxymethyl ligand (M-CH<sub>2</sub>OR) as a source of CH<sub>2</sub>, presumably via the formation of a highly reactive, electrophilic methylene complex upon protonation or silylation, is a well-established reaction;<sup>5</sup> related compounds are finding applications as cyclopropanation reagents.<sup>6</sup> The particular family of (methoxymethyl)iridium compounds we have been studying has the important feature that other reactive organic ligands, such as an olefin,<sup>4f</sup> a methyl group,<sup>4c</sup> or a hydrido hydrogen atom,<sup>4b</sup> may be coordinated adjacent to the methoxymethyl group. Protonation or silylation then causes the intramolecular reaction of the nascent methylene moiety with the bound organic ligand.



Recently we have explored the reactions of a (methoxymethyl)iridium(I) complex (and its methylene derivative) with di-*p*-tolylacetylene (tolyl = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-). The initial product is the (methoxymethyl)iridium(I) acetylene complex 1. While indefinitely stable under ambient conditions, complex 1 reacts readily with bromotrimethylsilane to form the metallacyclobutene complex 2. In this paper we describe the syntheses and the crystal and molecular structures of compounds 1 and 2 and the thermal rearrangement of the metallacyclobutene complex 2 to its more stable isomer 3.

## Results and Discussion

**Formation and Structure of the Acetylene Compound 1.** Compound 1 is synthesized from the hydrido-iridium(I) compound IrH(PMe<sub>3</sub>)<sub>4</sub> by the sequence of reactions outlined in eq 3. An analogous reaction sequence



was used previously in the preparation of a methoxymethyl ethylene complex of iridium(I).<sup>4f</sup> We chose di-*p*-tolylacetylene for these studies because the aromatic rings impart stability and crystallinity to the complexes and because the tolyl group has a simple <sup>1</sup>H NMR spectrum.

Preparation of compounds 4 and 5 (eq 3) deserves comment. The stable hydrido alkyl complex 4 is easily synthesized by addition of the alkyl halide BrCH<sub>2</sub>OCH<sub>3</sub> (Caution! This material is highly toxic and its chloro analogue is a suspected carcinogen!) to the iridium(I) hydrido complex IrH(PMe<sub>3</sub>)<sub>4</sub>. Other stable hydridoalkyl-iridium(III) complexes prepared by analogous alkylation of the hydrido-iridium(I) complex include [IrH-(CH<sub>2</sub>OCH<sub>3</sub>)(CO)(PMe<sub>3</sub>)<sub>3</sub>]Br, [IrH(CH<sub>3</sub>)(CO)(PMe<sub>3</sub>)<sub>3</sub>]I, [IrH(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>]I, and [IrH(CH<sub>2</sub>OSiMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>]I.<sup>4b,g</sup> Ordinarily, alkyl halides react with transition-metal hydrido compounds to form the alkane and the metal halide complex. Another example of hydrido alkyl formation by alkylation of a metal hydrido complex has been reported.<sup>7</sup> The remarkable stability of iridium(III) hydrido alkyl complexes certainly contributes to the successful formation of hydrido alkyl complexes by this route. However, even in the (trimethylphosphine)iridium system studied here the reaction is not general and hydrido alkyl complexes have been isolated only when the alkyl group is methyl, methoxymethyl, or siloxymethyl. Attempts to use other alkyl groups in this reaction result in formation of as yet uncharacterized products other than hydrido alkyl complexes.<sup>4g</sup> While we do not fully understand why iridium forms stable hydrido alkyl complexes, we have exploited this tendency in our syntheses of compound 5 (eq 3) and other iridium(I) alkyl complexes.

The methoxymethyl compounds 1 and 5 are unusual in that they contain the metal in its lowest common oxidation state. Most of the reported alkoxymethyl or (acyloxy)-methyl compounds have the metal in one of its higher common oxidation states. This is because the -oxymethyl

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Table I. Selected Bond Distances (Å) and Angles (deg) and Estimated Standard Deviations for Complex 1

Bond Lengths			
Ir-P(1)	2.323 (2)	Ir-C(1)	2.136 (7)
Ir-P(2)	2.306 (2)	Ir-C(3)	2.128 (7)
Ir-P(3)	2.340 (2)	Ir-C(4)	2.103 (7)
C(1)-O	1.449 (9)	C(3)-C(4)	1.30 (1)
O-C(2)	1.39 (1)		
P(1)-C(11,2,3)	1.823 (9), 18 (9), 26 (9)		
P(2)-C(21,2,3)	1.837 (8), 29 (8), 41 (9)		
P(3)-C(31,2,3)	1.837 (8), 29 (9), 37 (8)		
C(3)-C(41)	1.46 (1)	C(4)-C(51)	1.46 (1)
C-C(ring 4)	1.38-42 (1)		
C-C(ring 5)	1.38-42 (1)		
C(44)-C(47)	1.51 (1)	C(54)-C(57)	1.54 (1)
Bond Angles			
P(1)-Ir-P(2)	102.78 (7)	P(2)-Ir-P(3)	93.39 (8)
P(1)-Ir-P(3)	100.50 (8)	P(2)-Ir-C(1)	89.7 (2)
P(1)-Ir-C(1)	87.8 (2)	P(2)-Ir-C(3)	149.0 (2)
P(1)-Ir-C(3)	107.5 (2)	P(2)-Ir-C(4)	113.2 (2)
P(1)-Ir-C(4)	142.4 (2)	P(3)-Ir-C(1)	170.3 (2)
C(1)-Ir-C(3)	84.7 (3)	P(3)-Ir-C(3)	87.9 (2)
C(1)-Ir-C(4)	82.0 (3)	P(3)-Ir-C(4)	88.3 (2)
C(3)-Ir-C(4)	35.8 (3)		
Ir-C(1)-O	116.4 (5)	Ir-C(3)-C(4)	71.0 (5)
C(1)-O-C(2)	112.3 (7)	Ir-C(4)-C(3)	73.1 (5)
Ir-C(3)-C(41)	146.5 (5)	C(4)-C(3)-C(41)	142.1 (7)
Ir-C(4)-C(51)	144.8 (6)	C(3)-C(4)-C(51)	142.0 (7)
Ir-P(1)-C(11,2,3)	121.9, 112.4, 120.0 (3)		
Ir-P(2)-C(21,2,3)	118.4, 120.6, 117.1 (3)		
Ir-P(3)-C(31,2,3)	119.7, 117.8, 114.9 (3)		
ring 4	116.4-122.6 (8)		
ring 5	117.0-121.8 (8)		

Table II. Non-Hydrogen Positional and Equivalent Isotropic Thermal Parameters of Complex 1<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
Ir	0.19877 (2)	0.02838 (2)	0.18650 (1)	1.387 (4)	C(32)	0.1730 (5)	0.1417 (5)	0.3455 (5)	2.9 (2)
P(1)	0.0860 (1)	0.0705 (1)	0.1452 (1)	1.91 (4)	C(33)	0.3190 (4)	0.1162 (5)	0.3105 (5)	3.0 (2)
P(2)	0.2774 (1)	0.0689 (1)	0.0967 (1)	1.98 (4)	C(41)	0.1257 (4)	-0.0698 (4)	0.3307 (4)	1.9 (2)
P(3)	0.2302 (1)	0.1269 (1)	0.2653 (1)	1.91 (4)	C(42)	0.0666 (4)	-0.0272 (5)	0.3554 (4)	2.0 (1)
O	0.1471 (3)	-0.0652 (3)	0.0559 (3)	2.9 (1)	C(43)	0.0171 (4)	-0.0550 (5)	0.4062 (4)	2.4 (2)
C(1)	0.1801 (4)	-0.0734 (4)	0.1270 (4)	1.9 (2)	C(44)	0.0232 (4)	-0.1290 (5)	0.4322 (4)	2.0 (2)
C(2)	0.1461 (5)	-0.1326 (6)	0.0175 (5)	3.9 (2)	C(45)	0.0802 (4)	-0.1726 (4)	0.4073 (4)	2.1 (2)
C(3)	0.1797 (4)	-0.0399 (4)	0.2798 (4)	1.6 (1)	C(46)	0.1307 (5)	-0.1452 (4)	0.3572 (4)	2.2 (2)
C(4)	0.2476 (4)	-0.0472 (4)	0.2600 (4)	1.8 (2)	C(47)	-0.0316 (5)	-0.1599 (5)	0.4858 (5)	3.3 (2)
C(11)	0.0721 (5)	0.1009 (6)	0.0517 (5)	4.2 (2)	C(51)	0.3143 (4)	-0.0880 (4)	0.2779 (4)	1.8 (2)
C(12)	0.0152 (5)	-0.0010 (5)	0.1540 (5)	3.0 (2)	C(52)	0.3680 (4)	-0.1023 (4)	0.2248 (4)	1.9 (2)
C(13)	0.0395 (5)	0.1476 (5)	0.1921 (6)	3.8 (2)	C(53)	0.4295 (4)	-0.1452 (4)	0.2417 (5)	2.2 (2)
C(21)	0.3012 (6)	0.0028 (5)	0.0235 (4)	3.3 (2)	C(54)	0.4402 (4)	-0.1748 (4)	0.3105 (5)	2.0 (1)
C(22)	0.2556 (5)	0.1521 (5)	0.0420 (4)	3.0 (2)	C(55)	0.3879 (5)	-0.1603 (5)	0.3631 (4)	2.4 (2)
C(23)	0.3702 (5)	0.0959 (5)	0.1250 (5)	2.8 (2)	C(56)	0.3266 (4)	-0.1183 (4)	0.3481 (4)	1.9 (2)
C(31)	0.2367 (5)	0.2240 (5)	0.2303 (4)	2.6 (2)	C(57)	0.5100 (4)	-0.2197 (5)	0.3290 (4)	2.5 (2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(\frac{1}{3})[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$ .

group is introduced in an oxidative reaction, either the oxidative addition of the appropriate halomethyl compound,<sup>4-6,8</sup> the alkylation (or acylation) of a bound formaldehyde ligand,<sup>9-11</sup> or alkoxide substitution in an oxidatively formed halomethyl compound.<sup>12</sup> Two other low oxidation state alkoxyethyl compounds, Co-

(CH<sub>2</sub>OCH<sub>3</sub>)(PMe<sub>3</sub>)<sub>3</sub>L (L = PMe<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>), are also prepared by an oxidation reaction but starting from the highly reduced compound KCo(PMe<sub>3</sub>)<sub>4</sub>.<sup>13</sup> Our synthetic scheme (eq 3) also introduces the methoxymethyl group in an oxidative step (cf. compound 4, containing Ir(III)), but a subsequent reduction forms the Ir(I) complex 5. Reduction by deprotonation of a "hydrido" complex has been utilized in the syntheses of other low-valent Os and Ir complexes.<sup>7,14,15</sup>

Replacement of a PMe<sub>3</sub> ligand of compound 5 with

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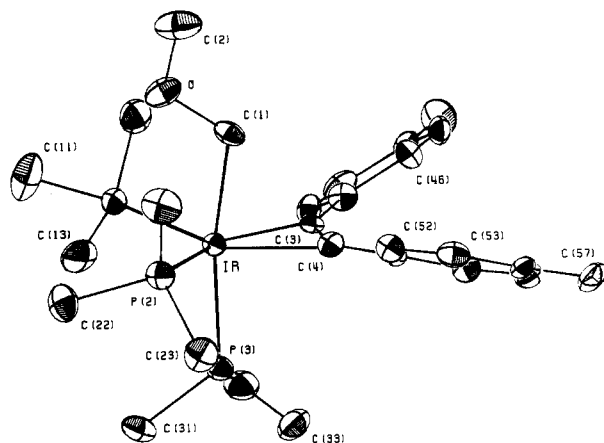
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**Figure 1.** A perspective view of  $\text{Ir}(\text{CH}_2\text{OCH}_3)(p\text{-tol-C}\equiv\text{C-p-tol})(\text{PMe}_3)_3$  (**1**). Vibrational ellipsoids are drawn at the 50% probability level. In both Figures hydrogen atoms have been omitted for clarity.

di-*p*-tolylacetylene (eq 3) occurs slowly at room temperature but rapidly at 75 °C. We have not studied the kinetics of this substitution reaction, but we suspect it proceeds by reversible loss of  $\text{PMe}_3$  from compound **5** to form a tris(phosphine)iridium(I) intermediate, followed by binding of the acetylene to form compound **1**. A slight excess of free  $\text{PMe}_3$  does not displace the bound diarylacetylene ligand of **1**. The room-temperature  $^1\text{H}$  NMR spectrum of compound **1** in benzene- $d_6$  is consistent with the structure found in the solid state.

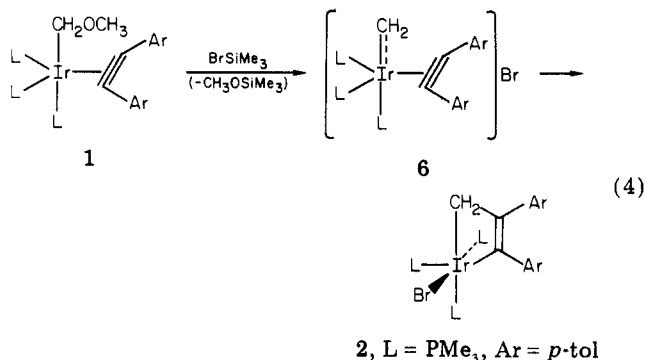
The molecular structure of compound **1**, as determined by X-ray diffraction, is shown in Figure 1; selected interatomic distances and angles are listed in Table I. Non-hydrogen atom positional and isotropic thermal parameters are listed in Table II. Anisotropic thermal parameters and hydrogen atom positions are available as supplementary material (Table III). The complex has the trigonal-bipyramidal structure expected for a pentacoordinate  $d^8$  complex, with the acetylene entity (counted as occupying a single coordination site) in the equatorial plane. This is one of the few structurally characterized mononuclear pentacoordinate  $d^8$  acetylene complexes.<sup>16</sup> The  $\text{C}(3)\equiv\text{C}(4)$  bond length (1.30 (1) Å) and  $\text{C}(\text{aryl})\text{C}\equiv\text{C}$  bond angles (average 142.0 (7)°) are consistent with a substantial amount of back bonding from the Ir(I) center.<sup>17</sup> Note that the acetylene ligand serves as a two-electron donor, based on electron counting considerations.<sup>16,17</sup> Important structural parameters of the methoxymethyl group are the Ir-C(1)-O angle (116.4 (5)°), slightly increased over the tetrahedral value, the C(1)-O-C(2) angle (112.3 (7)°), the C(1)-O and O-C(2) bond distances (1.449 (9) and 1.39 (1) Å, respectively), and the Ir-C(1) bond distance (2.136 (7) Å). The O-C(2) bond distance is considerably shorter than the value expected for an ether or alcohol (1.43 Å). This leads us to suspect that anisotropy associated with the oxygen and C(2) atoms may artificially shorten the C-O bond distances relative to their "true" values. If this is the case then the actual C(1)-O bond may be even longer—and, presumably, weaker—than derived from our structural data. Nonetheless, the C(1)-O bond length is slightly greater than the value expected for ordinary ethers,

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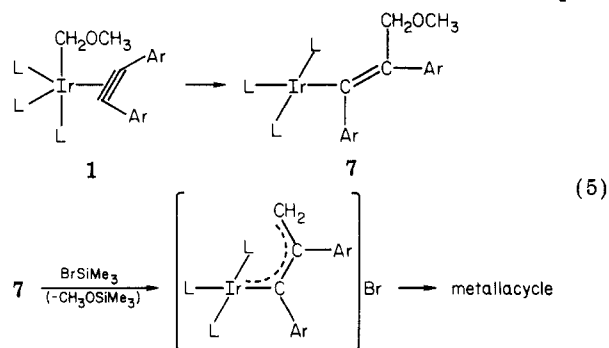
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consistent with some contribution from a "carbenoid" resonance structure. This feature was noted by Bau et al. in an iron alkoxymethyl complex<sup>18</sup> and also has been observed in an Ir(III) hydroxymethyl complex.<sup>4b</sup> However, the Ir-C(1) bond is not unusually short, implying that incipient multiple bonding between the iridium and carbon atoms is minimal.

**Conversion to the Metallacyclobutene Complex 2.** As in other -oxymethyl compounds, the C(1)-O bond of compound **1** is easily cleaved by electrophilic reagents. The silylating agent bromotrimethylsilane is the most convenient reagent for this purpose. While protonation of compound **1** in pyridine solution also appears to cause some C(1)-O bond cleavage, formation of hydrido-iridium(III) compounds is a competitive process, and we have not fully characterized the products. The sole kinetic product of the room-temperature reaction of compound **1** with  $\text{BrSiMe}_3$  is the metallacyclobutene complex **2**. The reaction probably proceeds by the mechanism of eq 4, although we have no direct evidence for the existence of the methylene acetylene complex **6**. The groups Ir- $\text{CH}_2\text{Br}$  and Ir- $\text{CH}_2\cdots\text{O}(\text{Me})(\text{SiMe}_3)$  are possible alternatives to a discrete methylene group.<sup>4b</sup>



An alternative mechanism (eq 5) involves acetylene insertion into the Ir- $\text{CH}_2\text{OMe}$  bond prior to C-O bond cleavage, forming the vinyl compound **7** as a reaction intermediate. We do not believe this mechanism is oper-



ating, for two reasons. First, compound **1** is indefinitely stable in the absence of electrophiles and we observe no evidence for compound **7**, which should be detectable if present. Second, if compound **7** were a reaction intermediate, the metallacyclobutene product would have the *mer* geometry. The kinetic formation of the *fac* isomer **2** (see below) is inconsistent with this mechanism.

**The Structure of Compound 2.** Structurally characterized examples of mononuclear metallacyclobutene complexes include the benzannulated compound  $\text{Ru}(\text{C}_6\text{H}_4\text{CH}_2)(\text{PMe}_3)_4$ <sup>19</sup> and the titanocene complexes de-

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Table IV. Selected Distances (Å) and Angles (deg) in Complex 2

Bond Lengths			
Ir-Br	2.6010 (8)	Ir-P(3)	2.340 (2)
Ir-P(1)	2.246 (2)	Ir-C(1)	2.134 (5)
Ir-P(2)	2.361 (2)	Ir-C(3)	2.166 (6)
C(1)-C(1A)	1.463 (8)	C(2)-C(1B)	1.485 (8)
C(1)-C(2)	1.344 (8)	C(2)-C(3)	1.525 (7)
P(1)-C(11,2,3)	1.833 (7), 21 (6), 34 (6)		
P(2)-C(21,2,3)	1.833 (7), 41 (6), 16 (6)		
P(3)-C(31,2,3)	1.826 (7), 26 (7), 39 (7)		
C-C (ring A)	1.376-1.405 (10)	C-C (ring B)	1.381-1.400 (9)
C(4A)-C(7A)	1.520 (9)	C(4B)-C(7B)	1.515 (9)
Bond Angles			
Br-Ir-P(1)	172.3 (1)	P(1)-Ir-C(1)	92.2 (2)
Br-Ir-P(2)	92.7 (1)	P(1)-Ir-C(3)	88.6 (2)
Br-Ir-P(3)	84.2 (1)	P(2)-Ir-C(1)	99.8 (2)
Br-Ir-C(1)	84.6 (2)	P(2)-Ir-C(3)	164.2 (2)
Br-Ir-C(3)	83.7 (2)	P(3)-Ir-C(1)	160.5 (2)
P(1)-Ir-P(2)	94.8 (1)	P(3)-Ir-C(3)	98.3 (2)
P(1)-Ir-P(3)	96.7 (1)	C(1)-Ir-C(3)	64.5 (2)
P(2)-Ir-P(3)	96.7 (1)		
Ir-C(1)-C(1A)	129.8 (4)	C(1)-C(2)-C(1B)	131.1 (5)
Ir-C(1)-C(2)	98.0 (4)	C(1)-C(2)-C(3)	106.1 (5)
Ir-C(3)-C(2)	91.2 (3)		
Ir-P(1)-C(11,2,3)	120.6, 114.8, 117.5 (2)		
Ir-P(2)-C(21,2,3)	115.7, 119.6, 117.6 (2)		
Ir-P(3)-C(31,2,3)	121.9, 112.0, 117.3 (2)		
ring A	117.2-121.9 (6)		
ring B	116.2-122.7 (6)		

Table V. Non-Hydrogen Positional and Equivalent Isotropic Thermal Parameters of Complex 2<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
Ir	0.06694 (1)	0.04141 (3)	0.27814 (1)	0.93 (1)	C(4A)	-0.1729 (3)	-0.1803 (8)	0.1188 (4)	2.5 (2)
Br	0.04672 (3)	0.23235 (7)	0.15017 (4)	1.86 (1)	C(4B)	-0.1564 (3)	0.5069 (7)	0.3680 (4)	2.0 (2)
Cl(1)	0.5939 (1)	0.0419 (2)	0.4949 (1)	3.23 (5)	C(5A)	-0.1596 (3)	-0.1935 (8)	0.2063 (4)	2.5 (2)
Cl(2)	0.6772 (1)	-0.1820 (3)	0.4550 (2)	4.7 (1)	C(5B)	-0.1717 (3)	0.3890 (8)	0.3081 (4)	2.3 (2)
P(1)	0.0816 (1)	-0.0961 (2)	0.3988 (1)	1.42 (4)	C(6A)	-0.1125 (2)	-0.1114 (8)	0.2567 (4)	2.0 (2)
P(2)	0.0635 (1)	-0.1792 (2)	0.1904 (1)	1.41 (4)	C(6B)	-0.1290 (3)	0.2894 (8)	0.2910 (4)	2.4 (2)
P(3)	0.1663 (1)	0.1037 (2)	0.2887 (1)	1.61 (4)	C(7A)	-0.2252 (3)	-0.2672 (10)	0.0639 (5)	3.8 (2)
C(1)	-0.0252 (2)	0.0686 (7)	0.2716 (4)	1.6 (1)	C(7B)	-0.2034 (3)	0.6101 (9)	0.3899 (5)	3.1 (2)
C(1A)	-0.0760 (2)	-0.0164 (7)	0.2210 (4)	1.6 (1)	C(11)	0.1214 (3)	-0.2821 (8)	0.4099 (4)	2.2 (2)
C(1B)	-0.0690 (2)	0.3076 (7)	0.3306 (4)	1.6 (1)	C(12)	0.0142 (3)	-0.1548 (8)	0.4286 (4)	2.2 (2)
C(1S)	0.6117 (3)	-0.0729 (10)	0.4139 (5)	3.4 (2)	C(13)	0.1224 (3)	-0.0013 (8)	0.4965 (4)	2.4 (2)
C(2)	-0.0219 (2)	0.2030 (7)	0.3149 (3)	1.5 (1)	C(21)	0.0105 (3)	-0.3310 (8)	0.2016 (4)	2.3 (2)
C(2A)	-0.0893 (3)	-0.0064 (7)	0.1322 (4)	1.9 (2)	C(22)	0.1309 (3)	-0.2960 (8)	0.1975 (4)	2.4 (2)
C(2B)	-0.0547 (3)	0.4310 (7)	0.3868 (4)	1.8 (2)	C(23)	0.0429 (3)	-0.1489 (8)	0.0766 (4)	2.4 (2)
C(3)	0.0438 (2)	0.2404 (7)	0.3456 (4)	1.6 (1)	C(31)	0.2266 (3)	-0.0131 (9)	0.3519 (4)	2.7 (2)
C(3A)	-0.1370 (3)	-0.0883 (8)	0.0831 (4)	2.5 (2)	C(32)	0.1852 (3)	0.2975 (9)	0.3336 (5)	3.1 (2)
C(3B)	-0.0972 (3)	0.5286 (8)	0.4063 (4)	2.1 (2)	C(33)	0.1908 (3)	0.1157 (10)	0.1896 (5)	3.0 (2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(\text{Å}^2/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + 2ab(\cos \gamma)\beta(1,2) + 2ac(\cos \beta)\beta(1,3) + 2bc(\cos \alpha)\beta(2,3)]$ .

scribed by Tebbe and co-workers.<sup>20</sup> Related three-carbon metallacyclic compounds of the earlier transition metals have arisen from studies of acetylene metathesis by Schrock and collaborators<sup>21</sup> and of (alkylidene)titanium reactions by the Grubbs research group.<sup>22</sup> Other related group 8 metallacyclic complexes are the iridacyclo-

butadiene complex reported some years ago by Tuggle and Weaver<sup>23</sup> and the rhodacyclobutadiene complex described by Frisch and Khare.<sup>24</sup> Closely related multinuclear compounds include the product of reacting a methylene-bridged iridium dimer with diphenylacetylene<sup>25</sup> and the reaction products of diazomethane with multinuclear acetylene complexes.<sup>26</sup> We note that one tautomer of the

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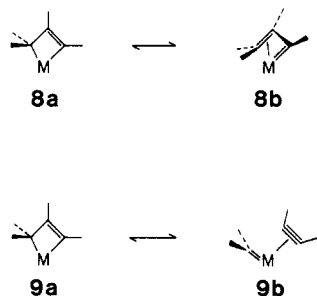
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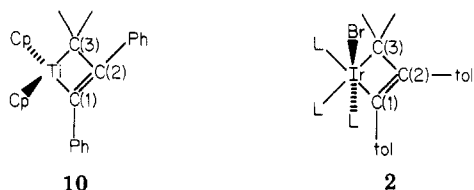
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metallacyclobutene moiety **8a–9a** is a carbene–olefin complex, **8b**, at least one example of which has been structurally characterized.<sup>27</sup> Another valence tautomer is a methylene acetylene complex, **9b**. A carbene acetylene complex of tungsten has very recently been reported,<sup>28</sup> and related chromium complexes are likely intermediates in acetylene–carbene coupling reactions.<sup>29</sup>



The structure of compound **2** is shown in Figure 2, with selected interatomic distances and angles listed in Table IV. Table V lists non-hydrogen atom positions and isotropic thermal parameters. Table VI (supplementary material) lists hydrogen atom positions and non-hydrogen atom anisotropic thermal parameters. The most interesting aspect of compound **2** is the iridacyclobutene ring, which is planar with a maximum deviation from the mean plane of 0.032 Å. Bond distances within the ring compare remarkably well with values for the diphenyltitanacyclobutene complex **10** (see Table VII). Compound **2** thus



represents the “metallacyclobutene extreme” of the possible continuum of structures suggested by the tautomerism **9a–9b**.<sup>20</sup> Remarkably, the alignments of the aryl rings of compounds **2** and **10** coincide, with the ring at C(2) approximately parallel to the metallacyclobutene plane and the ring at C(1) orthogonal to this plane. Both aryl rings of compound **2** (and of compound **3**) rotate freely in solution at room temperature.

**Isomerization of Compound 2 to Compound 3.** Treatment of a solution of compound **1** in benzene with  $\text{BrSiMe}_3$  causes the metallacyclobutene complex to precipitate from solution. When redissolved in  $\text{CD}_2\text{Cl}_2$ , the initial product is at least 85% compound **2** by  $^1\text{H}$  NMR analysis. Similarly, the reaction of compound **1** with  $\text{BrSiMe}_3$  in  $\text{CD}_2\text{Cl}_2$  provides compound **2** in excellent yield and purity. Upon standing in  $\text{CD}_2\text{Cl}_2$  solution compound **2** undergoes a slow rearrangement to compound **3**, with  $35 \pm 5\%$  isomerization after 4 days at room temperature and  $80 \pm 5\%$  conversion after 12 h at 40 °C. Since an acetonitrile solution of compound **2** rapidly precipitates  $\text{AgBr}$  when treated with  $\text{AgPF}_6$ , the bromide ligand of complex **2** must be relatively labile. The isomerization reaction probably proceeds by bromide loss from **2**, rearrangement of the resulting coordinatively unsaturated cationic com-

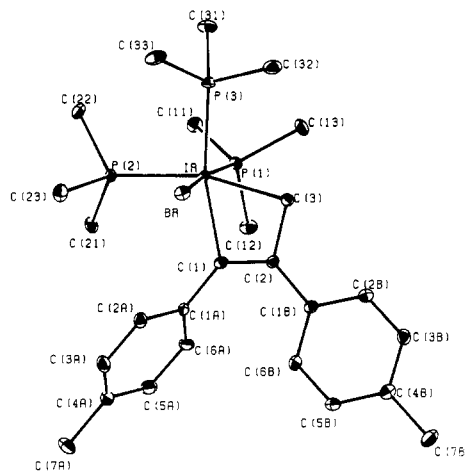


Figure 2. A perspective view of *fac*- $\text{IrBr}[\text{CH}_2\text{C}(p\text{-tol})=\text{C}(p\text{-tol})](\text{PMe}_3)_3$  (**2**). Vibrational ellipsoids are drawn at the 25% probability level.

Table VII. Structural Comparison of **2** and **10**<sup>a</sup>

	<b>10</b>	<b>2</b>
M–C(1)	2.104 (4)	2.134 (5)
M–C(3)	2.122 (5)	2.166 (6)
C(1)–C(2)	1.344 (6)	1.344 (8)
C(2)–C(3)	1.537 (6)	1.525 (7)

<sup>a</sup> Bond lengths in Å.

plex, and readdition of bromide to form compound **3**. The structure of compound **3** is uniquely established from its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (see Experimental Section).

The existence of two isomeric forms of the metallacyclobutene complex is an intriguing aspect of this chemistry. We believe the product isomer distribution provides us with some information about the details of the transformation **1** → **2**. In particular, pentacoordinate  $d^8$  complexes are often prone to facile rearrangements at the metal center,<sup>30</sup> yet we know any rearrangement (before or during the C–C bond-forming reaction) that would lead to the thermodynamically preferred isomer **3** does not occur. With this restriction in mind and continuing the assumption that the metallacyclobutene unit is formed according to the mechanism outlined in eq 4, we examine the fate of the initial methylene acetylene complex **6** (eq 6).

We consider two mechanisms likely. One possibility (path A, eq 6) is the direct formation of the C–C bond, leading to a nonplanar  $\text{IrC}_3$  unit;<sup>31</sup> subsequent formation of the Ir–Br bond leads directly to the kinetic product **2**. An attractive aspect of this path is that the nonplanar  $\text{IrC}_3$  unit might be stabilized by an olefin–carbene resonance structure, **11** (cf. **8a** ↔ **8b**).

A second possibility (path B, eq 6) is sequential acetylene rotation and formation of the C–C bond, to form a planar  $\text{IrC}_3$  unit (**12**). One complication is that rotation of an olefinic or acetylenic moiety in pentacoordinate structures is usually difficult unless accompanied by a pseudorotation at the metal center.<sup>32</sup> Yet, any permissible rearrangement at the metal center cannot lead to formation of the trans isomer **3**. Consequently we can exclude structures such as **14**, but structure **13** remains feasible.

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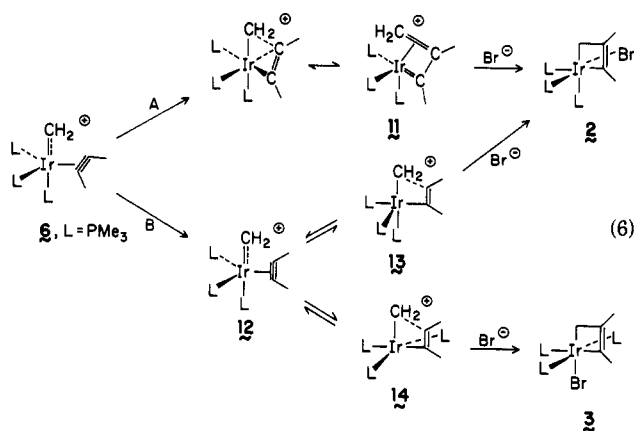
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Table VIII. Summary of X-ray Diffraction Data

	1	2
complex	Ir(CH <sub>2</sub> OCH <sub>3</sub> )( <i>p</i> -tol) <sub>2</sub> C <sub>2</sub> (PMe <sub>3</sub> ) <sub>3</sub>	Ir(CH <sub>2</sub> C( <i>p</i> -tol)=C( <i>p</i> -tol))Br(PMe <sub>3</sub> ) <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
formula	C <sub>27</sub> H <sub>46</sub> IrOP <sub>3</sub>	C <sub>26</sub> H <sub>43</sub> IrBrP <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
fw	671.79	805.59
space group	<i>Pbca</i> (No. 61)	<i>P2<sub>1</sub>/n</i> (No. 14)
<i>a</i> , Å	18.310 (2)	23.279 (5)
<i>b</i> , Å	17.696 (3)	8.579 (3)
<i>c</i> , Å	18.408 (2)	16.273 (4)
β, deg	90	103.97 (2)
<i>V</i> , Å <sup>3</sup>	5964 (2)	3154 (2)
<i>Z</i>	8	4
ρ(calcd), g cm <sup>-3</sup>	1.496	1.696
cryst dimens, mm	0.20 × 0.22 × 0.25	0.21 × 0.25 × 0.34
temp, °C	-100	-100
radiatn	Mo Kα (0.710 69 Å from graphite monochromator)	
μ, cm <sup>-1</sup>	49.1	58.1
2θ limits, deg	4.0-53.0	4.0-55.0
total no. of unique observns	6794	6004
data, <i>F</i> <sub>o</sub> <sup>2</sup> > 3σ( <i>F</i> <sub>o</sub> <sup>2</sup> )	3283	
data, <i>F</i> <sub>o</sub> <sup>2</sup> > 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )		4827
final no. of variables	289	307
<i>R</i>	0.034	0.031
<i>R</i> <sub>w</sub>	0.030	0.038



In both these possibilities we assume the bromide ion does not coordinate until after the C-C bond is at least partly formed, as coordination prior to that time would result in a 20-electron complex. In our view the methylene-acetylene complex 6 is still an 18-electron complex of Ir(I) and the C-C bond formation results in a formal oxidation of the iridium center. We note again that compound 6 has not been detected and may not even be an observable species. However, a related osmium methylene compound has recently been reported, which lends support to the general accessibility of pentacoordinate d<sup>8</sup> methylene compounds.<sup>33</sup>

### Summary and Conclusions

The conversion, compound 1 → compound 2, provides an excellent example of the coupling of an unsaturated organic molecule with a methylene fragment. While the crystal structure determinations have revealed no surprising features, they have served to define the geometries of the reacting complex 1 and the kinetic product 2. The observation of the further isomerization of the kinetic product 2 to the thermodynamic product 3 provides some insight into the conversion 1 → 2; in particular it has allowed us to rule out the involvement of species 14 (eq 6) that would otherwise be an attractive possibility.

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### Experimental Section

General experimental procedures are described elsewhere.<sup>4a,b</sup> Bromotrimethylsilane, bromomethyl methyl ether, and potassium *tert*-butoxide were obtained from Aldrich Chemical Co. and were used as supplied. The compounds IrH(PMe<sub>3</sub>)<sub>4</sub><sup>4b</sup> and di-*p*-tolylacetylene<sup>34</sup> were synthesized according to literature methods. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts are reported in parts per million downfield from external Me<sub>4</sub>Si. All reactions were carried out in an atmosphere of dinitrogen, at room temperature unless otherwise noted.

**Hydrido(methoxymethyl)tetrakis(trimethylphosphine)iridium(III) Bromide, [IrH(CH<sub>2</sub>OCH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>]Br (4), and (Methoxymethyl)tetrakis(trimethylphosphine)iridium(I), Ir(CH<sub>2</sub>OCH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub> (5).** A solution of IrH(PMe<sub>3</sub>)<sub>4</sub> (from [IrH<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>]Cl,<sup>4b</sup> 0.79 g, 1.48 mmol) in 3 mL of THF (tetrahydrofuran) was added, dropwise, to a stirred solution of bromomethyl methyl ether (**Caution!**) (0.20 g) in 5 mL of THF. A white solid, [IrH(CH<sub>2</sub>OCH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>]Br (4), precipitated immediately (0.65 g, 1.04 mmol, 70% based on [IrH<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>]Cl): <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>) IrH, -13.4, d (126 Hz) of t (24 Hz) of d (14 Hz); P(CH<sub>3</sub>)<sub>3</sub>, 1.36, d (7 Hz) of d (1 Hz), 1.54, t (3.5 Hz), 1.60, d (7 Hz); IrCH<sub>2</sub>OCH<sub>3</sub>, 3.64, q (6.5 Hz) of d (2 Hz); CH<sub>2</sub>OCH<sub>3</sub>, 3.05, s. Anal. Calcd: C, 27.01; H, 6.80. Found: C, 26.28; H, 6.66. This material was suspended in 15 mL of THF, and 0.13 g of potassium *tert*-butoxide was added. The mixture was filtered after being stirred 1 h; the solution was set aside and the insoluble material was suspended in 10 mL of fresh THF, together with 0.10 g of potassium *tert*-butoxide. After being stirred 20 min, this mixture was filtered and the filtrate was combined with the previous solution and evaporated. The residue was extracted with pentane, and the pentane extract was evaporated, leaving a sticky yellow solid (compound 5, 0.45 g, 0.83 mmol, 79% from compound 4). Recrystallization from concentrated pentane solution provided analytically pure Ir(CH<sub>2</sub>OCH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>. Anal. Calcd: C, 31.05; H, 7.63. Found: C, 31.18; H, 7.61. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): P(CH<sub>3</sub>)<sub>3</sub>, 1.4, br s; IrCH<sub>2</sub>OCH<sub>3</sub>, 4.15, quintet (6.5 Hz); OCH<sub>3</sub>, 3.30, s.

**(Methoxymethyl)(di-*p*-tolylacetylene)tris(trimethylphosphine)iridium(I) (1).** Compound 5 (0.39 g) and di-*p*-tolylacetylene (0.15 g) dissolved in 1.5 mL of C<sub>6</sub>D<sub>6</sub>, and the solution, open to a N<sub>2</sub> atmosphere, was heated to 75 °C for 15 min. The resulting cloudy solution was filtered and found to consist almost entirely of compound 1 (<sup>1</sup>H NMR analysis). From the solution, 0.165 g of amber crystals was obtained by vapor diffusion of pentane. An additional crop of crystalline compound 1 (0.154 g) was obtained by evaporating the mother liquor, redissolving the residue in diethyl ether, and cooling to -30 °C. Combined yield: 0.319 g, 66%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): P(CH<sub>3</sub>)<sub>3</sub>, 1.00, d (8 Hz),

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1.51, t (4 Hz); ArCH<sub>3</sub>, 2.23, s; OCH<sub>3</sub>, 3.10, d (1 Hz); IrCH<sub>2</sub>, 3.58, t (7 Hz) of d (4 Hz); C<sub>6</sub>H<sub>4</sub>, 7.05, d, 7.78, d (8 Hz).

**cis-1,1,1-Tris(trimethylphosphine)-1-bromo-2,3-di-*p*-tolyl-1-iridacyclobut-2-ene (2).** Method A. Compound 1 (0.32 g) in C<sub>6</sub>D<sub>6</sub> (1 mL) was treated with 0.076 g of BrSiMe<sub>3</sub> and allowed to stand. After 6 h the yellow-white precipitate was collected; yield 0.20 g (58%). When redissolved in CD<sub>2</sub>Cl<sub>2</sub> and analyzed by <sup>1</sup>H NMR, this material was found to consist primarily of compound 2 (85%) with a small amount (ca. 15%) of compound 3. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): P(CH<sub>3</sub>)<sub>3</sub>, 1.35, d (8 Hz), 1.63, d (8 Hz), 1.72, d (10 Hz); ArCH<sub>3</sub>, 2.27, s; 2.39, s; C<sub>6</sub>H<sub>4</sub>, 7.31, d, 7.03, d (8 Hz); 6.96, d, 6.86, d (8 Hz). Signals for the IrCH<sub>2</sub>C hydrogen nuclei were obscured by the PMe<sub>3</sub> resonances. <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): IrCH<sub>2</sub>, -8.76, d (74 Hz) of pseudo t (3 Hz); P(CH<sub>3</sub>)<sub>3</sub>, 17.71, d (29 Hz), 19.34, d (40 Hz), 19.67, d (22 Hz); ArCH<sub>3</sub>, 21.10; 21.36; C<sub>6</sub>H<sub>4</sub>, 124.86, 126.48, 128.13, 129.01, 133.26, 133.74.

**Method B.** Compound 1 (0.02 g) in 1 mL of CD<sub>2</sub>Cl<sub>2</sub> was treated with 0.007 g of BrSiMe<sub>3</sub>. The yellow color of compound 1 bleached immediately, and the <sup>1</sup>H NMR spectrum of the solution (taken within 15 min) revealed the quantitative conversion of compound 1 to the metallacyclobutene compound 2. None of the isomeric compound 3 could be detected, nor could any other species except the expected MeOSiMe<sub>3</sub> and unreacted BrSiMe<sub>3</sub>.

**trans-1,1,1-Tris(trimethylphosphine)-1-bromo-2,3-di-*p*-tolyl-1-iridacyclobut-2-ene (3).** A methylene chloride solution of compound 2 (prepared from 0.05 g of compound 1 and 0.015 g of BrSiMe<sub>3</sub>) was refluxed for 5 h. The solution was evaporated and the residue redissolved in CD<sub>2</sub>Cl<sub>2</sub>. Analysis of the solution (<sup>1</sup>H NMR) revealed an approximately equimolar mixture of compounds 2 and 3. A second sample of compound 2 was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution was refluxed 12.5 h, after which the <sup>1</sup>H NMR spectrum of the material revealed 80 ± 5% isomerized metallacyclobutene 3. A spectroscopically pure sample of compound 3 was obtained from this solution by the addition of hexane followed by slow evaporation. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): IrCH<sub>2</sub>, 1.16, quartet (3 Hz); P(CH<sub>3</sub>)<sub>3</sub>, 1.50, t (3.5 Hz), 1.60, d (8 Hz); ArCH<sub>3</sub>, 2.35, 2.33; C<sub>6</sub>H<sub>4</sub>, 6.95, d, 7.64, d (8.5 Hz), 7.07, d, 7.20, d (8 Hz). <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): IrCH<sub>2</sub>, -17.96, t (7 Hz); P(CH<sub>3</sub>)<sub>3</sub>, 15.1, t (20 Hz), 17.8, d (27 Hz); ArCH<sub>3</sub>, 21.4, 30.3; C<sub>6</sub>H<sub>4</sub>, 126.1, 128.0, 128.9, 130.7, 134.1, 134.8.

**X-ray Data Collection and Structure Solutions and Refinements.** Crystals of compound 1 were grown from diethyl ether by cooling to -30 °C. A suitable crystal was encapsulated in a glass capillary under an atmosphere of N<sub>2</sub>. The crystal was then placed on a Syntex P3 diffractometer and cooled to -100 °C. After the cell and space group had been determined (see Table VIII) the unit cell parameters were refined on the basis of 50 computer-centered reflections.

The ω-scan technique was used for collecting the intensity data (variable scan rate, 4.0–10.0° min<sup>-1</sup>, 1.0° range). Four standard reflections were chosen, and their intensities were remeasured every 200 reflections; no significant deviations in these standard intensities were observed. Empirical corrections for absorption were derived from the intensities of several reflections measured

every 10° about the diffractor vector. The data were processed by using counting statistics and a *p* value of 0.02 to derive standard deviations.<sup>35</sup>

The solution and refinement of the structure were carried out by using local modifications of programs supplied by the Enraf-Nonius Corp.<sup>36</sup> The structure was solved and refined by the usual combination of Patterson and Fourier syntheses and full matrix least-squares refinements. In the least-squares refinements the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are, respectively, the observed and calculated structure amplitudes and where  $w = 1/\sigma^2(F_o)$ . The atomic scattering factors and anomalous dispersion terms were taken from the standard compilations.<sup>37</sup> Hydrogen atoms were located, placed in idealized positions, and included as fixed contributions in the final cycles of refinement. The positional and isotropic thermal parameters for the atoms are listed in Table II, with tables of anisotropic thermal parameters and hydrogen atom positions (Table III) available as supplementary material, as are observed and calculated structure factor amplitudes (Table IX). Final values for the agreement indices are in Table VIII.

Crystals of the metallacyclobutene complex 2 were grown by slow evaporation of a cold solution of the compound in a methylene chloride–hexamethyldisiloxane solvent mixture. Data collection and processing and structure solution and refinement were carried out in a manner analogous to that above, except that a *p* value of 0.03 was used to derive standard deviations.<sup>35</sup> Crystallographic data are included in Table VIII. Positional and isotropic thermal parameters of the atoms of compound 2 are listed in Table V. Anisotropic thermal parameters and hydrogen atom positions (Table VI) are available as supplementary material as is a listing of observed and calculated structure factor amplitudes (Table X). A methylene chloride solvent molecule was located and satisfactorily refined; coordinates for these atoms are included in Table V. The agreement indices are listed in Table VIII.

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**Registry No.** 1, 89922-28-1; 2, 89922-29-2; 3, 89955-99-7; 4, 89956-00-3; 4b, 83380-23-8; 5, 89922-30-5; IrH(PMe<sub>3</sub>)<sub>4</sub>, 83380-16-9; BrCH<sub>2</sub>OCH<sub>3</sub>, 13057-17-5; BrSiMe<sub>3</sub>, 2857-97-8.

**Supplementary Material Available:** Tables III and VI, anisotropic thermal parameters and hydrogen atom coordinates for compounds 1 and 2, and Tables IX and X, observed and calculated structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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