sions drawn by Jetz and Graham[16] concerning the nonuniqueness of group IVb trichlorides as ligands. Clearly the effect on the electronic environment around the iron atom in the (π-C_5H_5)Fe(CO)$_2$ moiety is the same for the $GeCl_2$ and $SnCl_2$ bridging groups in the neat solids. This observation can be exploited in the interpretation of data on analogous compounds in which the nature of the organic group bonded to the tin atom is systematically varied [*i.e.*, [(π-C_5H_5)Fe(CO)$_2$]$_2$SnR_2 and (π-C_5H_5)Fe(CO)$_2$SnR_3 in which R = CH_3, C_2H_5, C_6H_5, etc.]. Such experiments are currently under way in these laboratories.

IV. Summary and Conclusions

The preceding spectroscopic study suggests that the anomalous metal–metal and metal–halogen bond distances observed in [(π-C_5H_5)Fe(CO)$_2$]$_2$SnCl$_2$ and [(π-C_5H_5)Fe(CO)$_2$]$_2$GeCl$_2$ arise from the bonding interactions within the molecules rather than from intermolecular stacking forces between molecules in the solid. The ^{119}Sn resonance spectra of the –SnCl$_2$ compound—interpreted in conjunction with the ^{57}Fe resonance parameters and the infrared absorption data in the carbonyl region—show the existence of two different conformational entities in solution. These two forms are associated with the two rotational isomers which can be obtained by a rotation of the metal–metal bond and are analogous to those which have been suggested for related molecules in which the (π-C_5H_5)Fe(CO)$_2$ moiety is bonded to a fragment which lacks threefold or higher symmetry. It is obvious that Mössbauer spectroscopy can be used as a powerful spectroscopic tool in the study of organometallic compounds both as neat solids and in glassy matrices of appropriate solvents and thus provide a bridge between the structural information derived from X-ray diffraction data, on the one hand, and infrared and nuclear magnetic resonance data, on the other. In this way, the apparent discrepancy which has on a number of occasions been found to exist between the two sets of results may be resolved.

Acknowledgments.—This research was supported in part by the U. S. Atomic Energy Commission and constitutes Document NYO-2472-50. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Finally, the authors are indebted to Professor F. G. A. Stone and Drs. I. Paul and P. Woodward for a number of helpful discussions and for the samples generously provided.

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Metalocyclopentadiene Complexes of Iridium and Rhodium and Their Role in the Catalytic Cyclotrimerization of Disubstituted Acetylenes[1]

BY JAMES P. COLLMAN,[2] JUNG W. KANG, WILLIAM F. LITTLE, AND MICHAEL F. SULLIVAN[3]

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Metalocyclopentadiene complexes of iridium(III) and rhodium(III) have been prepared from acetylenes. Provisional structures have been assigned to these metalocycles on the basis of infrared and nmr spectra of five- and six-coordinate complexes. Cyclotrimerization of disubstituted acetylenes is catalyzed by the coordinatively unsaturated metalocycles. Using an isotopically labeled substrate, the sequential cyclotrimerization of acetylenes has been elucidated. A tentative mechanism is proposed for acetylene cyclization.

A wide variety of transition metal complexes, especially carbon monoxide derivatives, act as catalysts for the cyclotrimerization of acetylenes to benzene derivatives.[4–6] These reactions usually require heating, and induction periods are often observed.

An early suggestion[7] that cyclobutene complexes are intermediates in cyclotrimerization was later discarded when cyclobutene complexes[8] were found to be stable under the usual conditions for acetylene cyclization. Three other mechanisms have been advanced to account for the catalytic trimerization of acetylenes. Schrauzer[5] proposed coupling of three acetylenes which are coordinated to the metal at mutually *cis* positions. This mechanism has the advantage of explaining the cyclotetramerization of acetylene when a fourth coordination site is available. Meriwether[9] proposed a scheme based on the oxidative addition of

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(3) Abstracted from the Ph.D. Thesis of M. F. Sullivan, University of North Carolina, 1967.

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the acetylenic C–H bond to the metal so as to form a five-bonded acetylide–hydride complex. Meriwether's mechanism has the advantage that it can account for the linear polymers[9] which are often formed when terminal acetylenes are treated with metal carbonyl catalysts. However, this mechanism cannot explain the cyclotrimerization of disubstituted acetylenes.[9] Meriwether[9] and others[10,11] have proposed that metalocyclopentadiene complexes are intermediates in the cyclotrimerization of disubstituted acetylenes.

Metalocyclopentadiene structures have been proposed for complexes of Ti,[12,13] Zr,[14] Fe,[15,16] Os,[17,18] and Co.[19] Several of these structures have been substantiated by X-ray diffraction studies[20] whereas others have been proposed on the basis of spectral evidence or the method of synthesis. Examples of metalocyclopentadiene complexes are illustrated in Figure 1. The binuclear iron complex (**1**) was formed by coupling two diphenylacetylene molecules.[15a] The mononuclear iron complex (**2**) was prepared by a metathetical reaction between $Fe(CO)_4{}^{2-}$ and a dichlorobutadiene.[16]

It should be noted that metalocyclopentadiene and cyclobutadiene complexes can be considered "valence tautomers" of one another. The formal oxidation state of the central metal is decreased by two units in going from the metalocyclopentadiene to the cyclobutadiene structure, but the coordination number remains constant. It is sometimes difficult to distinguish these two possible structures, as is the case with the titanium complex (**3a** or **4**) prepared from bis(π-cyclopentadienyl)titanium dicarbonyl and diphenylacetylene.[13] The analogous zirconium compound[14] was assigned the metalocyclopentadiene structure because of its synthesis from a butadiene substrate.

Conversion of one form into the other has been demonstrated by Yamazaki and Hagihara.[19] The cobaltocyclopentadiene (**5**) prepared from diphenylacetylene was converted into the known cobalt(I) cyclobutadiene **6** by heating **5** above it smelting point. Triphenylphosphine is lost as the six-coordinate cobalt(III) complex (**5**) is transformed into the coordinatively saturated five-coordinate cobalt(I) complex (**6**).

There is some evidence that metalocyclopentadiene complexes are involved in acetylene trimerization. Hübel[4] treated the binuclear iron complex (**1**) with di-(*p*-chlorophenyl)acetylene and obtained a 49% yield of hexa(*p*-chlorophenyl)benzene but only 4% of the mixed trimer, di(*p*-chlorophenyl)tetraphenylbenzene. He concluded that **1** was not a catalytic intermediate but decomposed to form the active catalyst. Similarly the cobalt complex **5** was found to react with diphenylacetylene in boiling toluene to form hexaphenylbenzene in only 8% yield.[19] It should be noted that both **1** and **5** are coordinatively saturated so that a ligand must be dissociated before an additional acetylene can enter the coordination sphere.

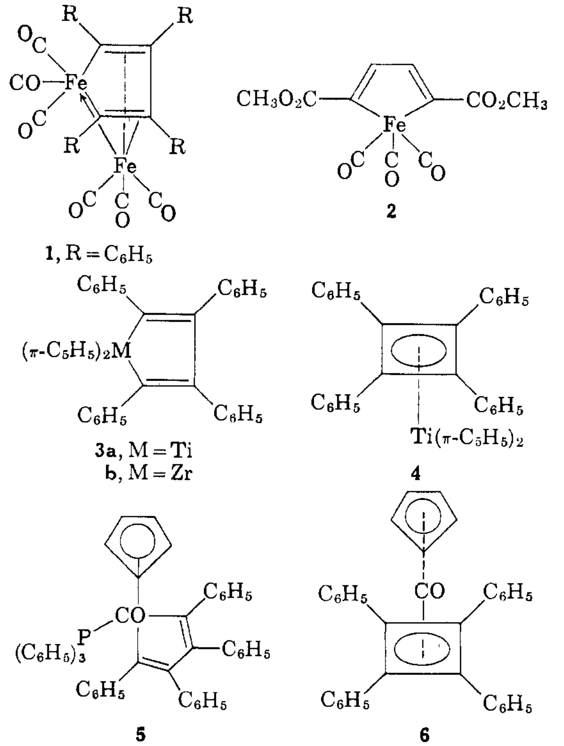

Figure 1.

In this paper we describe the synthesis and characterization of metalocyclopentadiene complexes containing iridium and rhodium and their role as catalysts in the cyclotrimerization of disubstituted acetylenes.

Earlier[11] we described acetylene complexes (**8**) formed by diplacing nitrogen from the iridium(I) complex **7** (Figure 2). When complex **8** derived from dimethyl or diethyl acetylenedicarboxylate was treated with another mole of the same acetylene, the iridocycle[21] **9** was formed in high yield. An experimentally more convenient preparation of **9** involves treatment of the iridium(I) carbonyl **11** with furoyl azide in the presence of the dialkyl acetylenedicarboxylate. The nitrogen complex **7** is formed *in situ* by this method.[22] A rhodium analog (**10**) was also prepared by the azide method from the triphenylarsine complex **12**.

The metalocyclopentadiene structures are assigned on the basis of spectral evidence. The infrared spectra of the iridocycles **9**, **13**, and **14** and the analogous rhodium complex **10** exhibit two strong ester bands as well as

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Table I

Nuclear Magnetic Resonance Spectra in $CDCl_3$ with Tetramethylsilane as Internal Standard (τ)[a,b]

Compd	Phenyl	$-CO_2CH_3$	$-CO_2CH_2CH_3$	PCH_3
9a	2.2–2.6 m (31.5)	6.54 s (6) 6.74 s (6)		
9b	2.2–2.7 m (29.1)		CH_3 8.93 t (12) 9.13 t CH_2 6.50 q (8.8) 6.13 q	
13b	2.2–2.8 m (30)	6.75 s (5.2) 6.63 s (5.4)		
14a	2.2–3.2 m (30)	5.99 s (6.0) 6.08 s 6.62 s (4.0) 6.88 s (2.7)		7.78 m (8.7)
14b	2.15–3.40 m (30)		CH_3 8.49 t (12.4) 8.96 q CH_2 5.53 q (4.2) 6.27 sextet (4.7)	7.73 m (8.7)
13a	2.0–2.9 m (20)	6.44 s[c] (8.9) 6.48 s 6.75 s (2.5)		7.75 t (5.4) J = 6 cps
10	2.3–2.75 m (33)	6.58 s (12) 6.77 s		

[a] Integrated values in parentheses. [b] s, singlet; m, multiplet; q, quartet; t, triplet. [c] Resolved into two singlets at 100 Mc; τ 6.43 and 6.45.

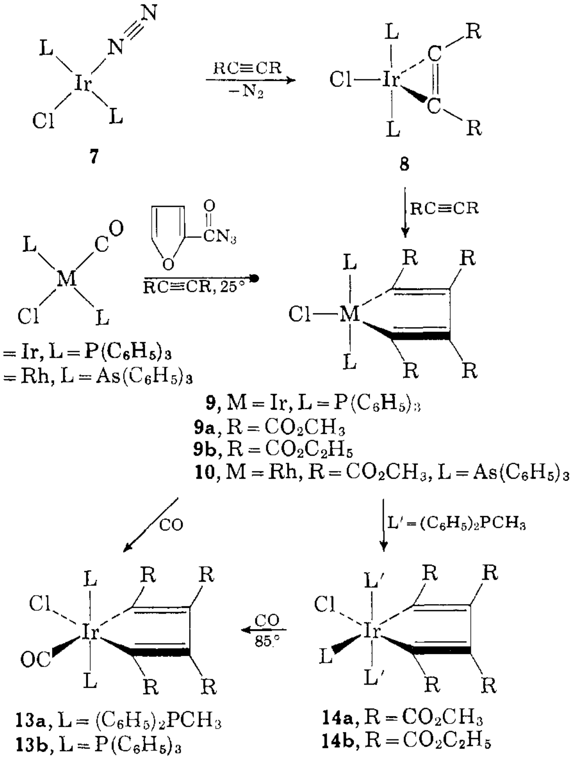

Figure 2.

two strong bands in the 1500-cm^{-1} region which seem to be characteristic of the metalocyclopentadiene rings (Table I). The iridocycles **9a** and **b** possess a latent site of unsaturation and take up 1 mol of CO to form the coordinatively saturated complex **13b**. The terminal carbonyl frequency (2050 cm^{-1}) exhibited by **13b** supports its formulation as a hexacoordinate iridium(III) complex. The unsaturated iridocycle also formed complexes with pyridine and acetonitrile, but these proved too labile for characterization. In each instance the intense red color of **9** changed to a lighter color upon coordinating with a sixth ligand.

The stereochemical disposition of the phosphine groups in these complexes was determined by taking advantage of virtual coupling whereby methyl groups attached to mutually *trans*-phosphine ligands exhibit a triplet in their nmr spectrum.[23] Earlier, we had employed this method to determine the configurations of iridium(III) oxidative addition adducts.[24] In the present case the method also provides evidence supporting the formulation of these complexes as metalocyclopentadienes. Treatment of the triphenylphosphine iridocycle **9** with diphenylmethylphosphine afforded a saturated complex (**14**) containing three phosphine groups. Although **14** gave acceptable elemental analyses, low experimental values for molecular weight suggested that a phosphine ligand reversibly dissociates from the coordination sphere. Thus it was not surprising to find that carbon monoxide readily replaces one diphenylmethylphosphine yielding **13a**. The nmr spectrum of **13a** (Table II) reveals a P–CH_3 triplet at τ 7.75 as well as four singlets for the CO_2CH_3 groups. Four CO_2CH_3 singlets are also found in the spectrum of the tris-phosphine complex **14**, but the P–CH_3 signal is not well resolved. In each instance the integrated intensities are consistent with the indicated structures. The nmr spectra of the CO_2CH_3 groups in the unsaturated metalocycles **9** and **10** showed in each two sharp singlets, which is to be expected if the chlorine is in the trigonal plane, the different signals arising from the CO_2CH_3 groups in α and β positions on the iridocycle. Cyclobutadiene complexes would be expected to experience a single average chemical environment for sub-

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stituents on a freely rotating ring. The presence of four different R groups on the saturated iridocycles **13b** and **14** and the *trans* disposition of the phosphine ligands argue strongly for the structures depicted. The CO_2CH_3 groups in the simple acetylene complex **8** exhibit one signal. The nmr spectra of the complexes in which R is $CO_2C_2H_5$ are similar (Table II) and do not deserve further comment. The structures of the triphenylphosphine and triphenylarsine complexes are expected to be analogous to those of the diphenylmethylphosphine derivatives—a supposition that is further supported by the similarity of their infrared spectra.

TABLE II

INFRARED SPECTRA[c]

Compd	ν-(C—O), cm^{-1} [a]	ν(CO_2R), cm^{-1} [b]	ν(C=C), cm^{-1} [a,b]	Misc, cm^{-1}
9a		1715 vs, 1690 vs	1550 m, 1500 m	
9b		1710 vs, 1690 vs		
10		1725 vs, 1705 vs	1565 m, 1520 mw	
13b	2050 vs	1705 vs	1540 w, 1490 mw	
14a		1705 vs	1555 m, 1500 m	
14b		1705 vs	1550 m, 1495 m	
13a	2050 vs	1710 vs	1550 mw, 1500 mw	
18		1715 vs, 1690 vs	1550 m, 1500 m	ν (C—D) 2070 mw 2120 w 2180 mw 2250 mw

[a] Spectra recorded as KBr disks. [b] Spectra recorded as chloroform solutions. [c] Relative spectral intensities designated by: v, very strong; s, strong; m, medium; w, weak.

The facile exchange of phosphine ligands in the transformation from **9** to **14** is undoubtedly a result of the ability of the five-coordinate iridium(III) complex to take up a sixth ligand reversibly. Another peculiar example of this resulted from our early attempt to oxidize **9** with ceric ammonium nitrate. Oxidation does not take place, but a complex analogous to **9** in which nitrate has replaced chloride in the coordination sphere is formed. We plan to study the replacement of halide in **9** by other ligands. Rarely does one encounter such a stable, coordinatively unsaturated d^6 complex.

Earlier we suggested[11] that metalocycles such as **13** were intermediates in the trimerization of acetylenes by **11** and **12**. The unexpected synthesis of such complexes gave us an opportunity to test this hypothesis. The iridocycle **9** does catalyze the trimerization of dimethyl acetylenedicarboxylate. The reaction takes place at a reasonable rate in boiling toluene (110°) and is very slow in boiling benzene (80°). The closely related rhodocycle **10** is an effective trimerization catalyst in boiling benzene. A mechanism such as that shown in Figure 3 is proposed on the basis of our qualitative experiments. These results are summarized in Table III. Reversible coordination of an acetylene to the coordinatively unsaturated iridocycle **9** should form an intermediate such as **15**. The formation of **15** should take place with a much lower activation energy than its transformation into a hexasubstituted benzene and the iridium(I) fragment **16**. That a latent coordination site must be present is supported by the almost total inhibition of acetylene trimerization under 60 psi of CO (Table III). The fact that maleic anhydride does not react with **9**—even under forcing conditions—argues against a Diels–Alder mechanism. The fact that disubstituted acetylenes such as diphenylacetylene do not react suggests that the cyclization mechanism is sensitive to steric hindrance. Even diethyl acetylenedicarboxylate does not form appreciable amounts of trimer by reaction with **9b**. The steric difference between methyl and ethyl is apparently sufficient to retard the trimerization. The fragment **16** would be expected to capture rapidly an uncoordinated acetylene to form the mono adduct **8**. The formation of the iridocycle **9** from the acetylene complex **8** is relatively rapid even at ambient termperatures. Thus the rate-determining step in the trimerization should be closure of the aromatic ring (**15** to **16**). If the free acetylene concentration is low, the fragment **16** might form a dimer such as **17**, whose chemistry is at present a matter of speculation. As the trimerization reaction progresses, decreasing amounts of the catalytic complex **9** can be recovered. A more soluble, as yet unidentified, iridium complex has been isolated from the reaction medium. Its catalytic activity is presently unknown. Terminal acetylenes add a further complication—oxidative addition of the acetylene C–H bond to the iridium. For this reason, these substrates were not studied.

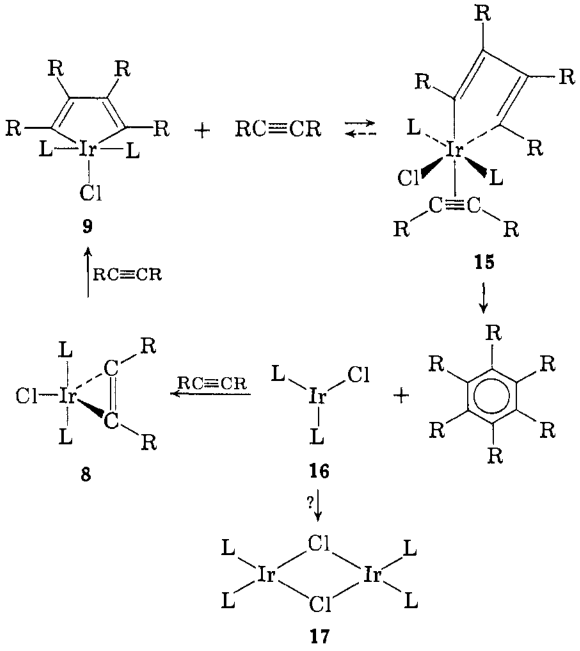

Figure 3.

The transformation of the complex **15** into aromatic product is undoubtedly complex and probably involves more than one step. The stereochemistry depicted for complex **15** would not allow a synchronous one-step ring closure. It is possible that prior to a concerted ring closure, this form is transformed into an isomer in which the iridocycle and the acetylene occupy a common face on the octahedron. On the other hand, ring closure

TABLE III

CATALYTIC TRIMERIZATION OF DIMETHYL ACETYLENEDICARBOXYLATE

Catalyst,[a] mmol	Dimethyl acetylenedicarboxylate, mmol	Reaction time, hr	Reaction temp,[b] °C	Yield of hexacarbomethoxybenzene, %	Recovered catalyst,[c] %
9a 0.513	7.05	16	110	80	25
9a 0.483	7.05	55	110	78	12
9a 0.024	7.05	18	110	6	...
9a 0.096	7.05	18	110	25	...
9a 0.290	7.05	18	110	35	...
13b 0.38[d]	7.05	21	110	8	28
9a 0.193	3.52	18	80	4	85
9a 0.145	3.52	14	110	48	33
9a 0.145	3.52	24	110	63	20
10 0.145	3.52	18	80	50	...
10 0.10	7.05	12	110	60	...

[a] Thirty milliliters of solvent was used in each run. [b] Toluene or benzene were used at their boiling points. [c] In several experiments no attempt was made to recover the catalyst. [d] This experiment was run under 60 psi of carbon monoxide.

may be stepwise going through a metalocycloheptatriene form.

The fate of the individual acetylene molecules during the course of trimerization has been followed by the experiments outlined in Figure 4. Hexadeuteriodimethyl acetylenedicarboxylate was used to prepare the deuterated iridocycle **18**. Treatment of the deuterioiridocycle **18** with dimethyl acetylenedicarboxylate afforded hexacarbomethoxybenzene (**19**) and dodecadeuteriohexacarbomethoxybenzene (**20**) as well as the tetracarbomethoxy iridocycle **9**. Careful mass spectral analysis of the aromatic product failed to detect the presence of any other isotopic species. Crude product isolation studies (*cf.* the Experimental Section) demonstrated the formation of larger quantities of the dodecadeuterio aromatic product **20** during the early stages of the reaction as well as the gradual demise of the deuterio iridocycle **18** and the consequent formation of the protio iridocycle **9**. These semiquantitative studies are insufficient to determine whether another catalytically reactive complex is being formed during the course of the reaction. Nevertheless, these experiments clearly demonstrate the stepwise fate of acetylene fragments in the catalytic trimerization reaction by the pathway indicated in Figure 3. We hope to clarify further this mechanism by making a kinetic analysis of this system.

Experimental Section

Iridium and rhodium salts were purchased from Engelhard Industries, Newark, N. J. All reactions except those under CO pressure were carried out under an atmosphere of purified nitrogen. Molecular weight measurements were performed in $CHCl_3$ using a Mechrolab vapor pressure osmometer. Infrared spectra were determined as KBr disks using Perkin-Elmer 307 and 421 grating spectrophotometers. Nmr spectra were recorded with Varian Associates Model A-60 or HR-100 spectrometers in $DCCl_3$ using tetramethylsilane (τ 10) as an internal standard. Mass spectra were determined using a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer.

Chloro(1,2,3,4-tetracarbomethoxybutadiene-1,4-di-σ)bis(triphenylphosphine)iridium(III) (9a). Method A.—A mixture of the iridium(I) nitrogen complex **7** (500 mg, 0.064 mmol) and dimethyl acetylenedicarboxylate (300 mg, 0.211 mmol) was added to 10 ml of thiophene-free benzene, and the mixture was stirred at 40–45° for 5 hr. The mixture was cooled to ambient temperature and the red crystalline product was removed by filtration. Partial evaporation of the filtrate afforded additional product; combined yield 620 mg (93%). Recrystallization from chloroform–methanol gave an analytical sample, mp 250–251° dec. *Anal.* Calcd for $C_{48}H_{42}O_8ClP_2Ir$: C, 55.62; H, 4.09; Cl, 3.42; P, 5.98; mol wt, 1036. Found: C, 55.38; H, 4.13; Cl, 4.00; P, 5.81; mol wt, 1048.

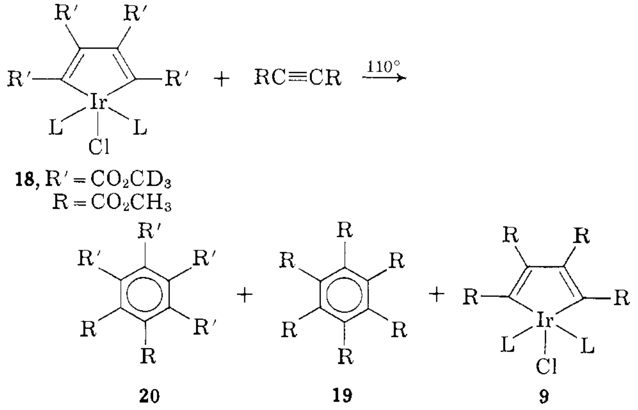

Figure 4.

Method B.—To a suspension of chlorocarbonylbis(triphenylphosphine)iridium(I)[25] (1.00 g, 1.28 mmol) in 30 ml of $CHCl_3$ was added dimethyl acetylenedicarboxylate (1.00 g, 7.05 mmol). After 5 min, furoyl azide (250 mg, 1.82 mmol) was added to the pale yellow solution. After stirring overnight, solvent was removed under vacuum to leave a dark red, oily residue which was washed with ether, and the resulting crude red crystalline product **9a** was collected on a filter; yield 1.27 g (96%). Recrystallization afforded an analytical sample identical with that described above.

Chloro(1,2,3,4-tetracarboethoxybutadiene-1,4-di-σ)bis(triphenylphosphine)iridium(III) (9b).—Method B afforded an 80% yield of the pure product isolated as red plates, mp 222–228° dec. *Anal.* Calcd for $C_{52}H_{50}O_8ClP_2Ir$: C, 57.16; H, 4.61; Cl, 3.25; P, 5.67; mol wt, 1093. Found: C, 56.36; H, 4.60; Cl, 3.68; P, 5.62; mol wt, 1112.

Chloro(1,2,3,4-tetracarbomethoxybutadiene-1,4-di-σ)bis(triphenylarsine)rhodium(III) (10).—To a suspension of chlorocarbonylbis(triphenylarsine)rhodium(I) (1.00 g, 1.28 mmol) in 30 ml of toluene was added furoyl azide (250 mg, 1.82 mmol) with stirring at −5°. After stirring at −5° for 30 min, dimethyl acetylenedicarboxylate (500 mg, 3.52 mmol) was added. The mixture was warmed to 35–40° and stirred for 10 hr. Filtration of the cooled reaction mixture afforded 800 mg of **10**, and an additional 180 mg was obtained from the filtrate. The crude complex (980 mg, 74%) was recrystallized from chloroform–methanol to yield the pure product **10** as orange crystals, mp 238–240° dec. *Anal.* Calcd for $C_{48}H_{42}O_8ClAs_2Rh$: C, 55.87; H, 4.06; Cl, 3.48; As, 14.49; mol wt, 1035. Found: C, 55.76; H, 4.26; Cl, 3.71; As, 14.19; mol wt, 1010.

Attempted Synthesis of an Unsymmetrically Substituted Iridocycle.—A solution of the dimethyl acetylenedicarboxylate complex **8** (110 mg, 0.123 mmol) and diethyl acetylenedicarboxylate (40 mg, 0.24 mmol) in 10 ml of benzene was heated at reflux for 2 hr. The solution was analyzed by thin layer chromatography on silica gel with 10% methylene chloride–ether as an eluent using pure samples of the tetracarbomethoxy and tetracarboethoxy iridocycles **9a** and **9b** as markers. The reaction mixture contained three components, two of which had the same R_f values as **9a** and **9b**. The third component exhibited an R_f intermediate between those for **9a** and **9b** and is presumably an unsymmetri-

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(25) J. P. Collman, C. T. Sears, Jr., and M. Kubota, *Inorg. Syn.*, **11**, in press.

cally substituted iridocycle. An attempt to isolate this pure complex by preparative thin layer chromatography was unsuccessful.

Chloro(1,2,3,4-tetracarbomethoxy- and -tetracarboethoxybutadiene-1,4-di-σ)tris(diphenylmethylphosphine)iridium(III) (14).—A solution of the iridocycle **9a** (400 mg, 0.368 mmol) and 1 ml of diphenylmethylphosphine in 40 ml of benzene was heated at reflux for 15 min. Removal of solvent under vacuum yielded a bright orange oil. A mixture of the oil and 75 ml of hexane was heated under reflux for 30 min, and after cooling, the pale orange crystalline product was collected on a filter and washed several times with ether; yield 400 mg (93%). An analytical sample was prepared by crystallization from methylene chloride–methanol. *Anal.* Calcd for $C_{51}H_{51}O_8ClP_3Ir$: C, 55.06; H, 4.62; Cl, 3.19; P, 8.35; mol wt, 1113. Found: C, 54.91; H, 4.52; Cl, 2.95; P, 8.15; mol wt, 755.

The carboethoxy analog was prepared in the same way. *Anal.* Calcd for $C_{55}H_{59}O_8ClP_3Ir$: C, 56.52; H, 5.09; Cl, 3.03; P, 7.95; mol wt, 1169. Found: C, 56.23; H, 4.91; Cl, 3.06; P, 8.04; mol wt, 710.

Chlorocarbonyl(1,2,3,4-tetracarbomethoxybutadiene-1,4-di-σ)bis(diphenylmethylphosphine)iridium(III) (13a).—The trisphosphine complex **14** (500 mg, 0.45 mmol) in 30 ml of benzene was heated for 1 hr at 85° under 60 psi of carbon monoxide. The carbon monoxide was vented, and the solvent was removed under vacuum yielding a pale orange oil which was crystallized from ether–pentane at −78° to give a light pink solid (330 mg, 78%). An analytical product was obtained by an additional crystallization. *Anal.* Calcd for $C_{39}H_{38}O_9ClP_2Ir$: C, 49.81; H, 4.07; Cl, 3.77; P, 6.59; mol wt, 940. Found: C, 49.80; H, 4.57; Cl, 4.10; P, 6.15; mol wt, 984 (benzene).

Chlorocarbonyl(1,2,3,4-tetracarbomethoxy- and -tetracarboethoxybutadiene-1,4-di-σ)bis(triphenylphosphine)iridium(III) (13b).—A solution of the unsaturated iridocycle **9a** (400 mg, 0.368 mmol) in 30 ml of chloroform was treated with 30 psi of carbon monoxide. The red solution immediately changed to a pale yellow. The reaction can also be performed at atmospheric pressure. Removal of the solvent and recrystallization of the cream-colored product afforded the pure carbonyl **13b** (350 mg 85%). *Anal.* Calcd for $C_{49}H_{42}O_9ClP_2Ir$: C, 55.29; H, 3.98; Cl, 3.33; P, 5.82; mol wt, 1064. Found: C, 55.30; H, 4.02; Cl, 3.33; P, 6.00; mol wt, 1117.

The analogous light tan crystalline tetracarboethoxy complex was prepared in the same manner in 86% yield. *Anal.* Calcd for $C_{53}H_{50}O_9ClP_2Ir$: C, 56.81; H, 4.50; Cl, 3.16; P, 5.53; mol wt, 1121. Found: C, 56.88; H, 4.58; Cl, 3.38; P, 5.95; mol wt, 1115.

Trimerization of Dimethyl Acetylenedicarboxylate with the Iridocycle 9a.—A solution of dimethyl acetylenedicarboxylate (500 mg, 3.52 mmol) and the iridocycle **9a** (150 mg, 0.145 mmol) in 15 ml toluene was heated under reflux for 14 hr. After cooling, 35 ml of hexane was added and the mixture was filtered to remove a reddish solid which was extracted with hexane in a Soxhlet apparatus for 24 hr. The oil obtained by removing the solvent from the filtrate was extracted with several portions of hot hexane. The combined hexane extracts afforded 240 mg (48% conversion based on starting acetylene) of crude hexacarbomethoxybenzene. Recrystallization from methanol gave the pure product, mp 186–187.5°, identical in all respects with an authentic sample.

The residue from the Soxhlet extraction was recrystallized from methylene chloride–methanol, resulting in 50 mg (33% recovery) of the pure iridocycle **9a**.

The cyclotrimerization experiments summarized in Table III were carried out by the same general procedure.

Preparation of Perdeuteriodimethyl Acetylenedicarboxylate.—A modification of the published procedure[26] for the *protio* compound was used. Acetylenedicarboxylic acid (2.0 g, 17.5 mmol) was added to a cooled solution of 2.5 ml of methanol-d_4 and 2.1 ml of concentrated sulfuric acid. The mixture was carefully warmed on a steam bath until dissolution was complete and then allowed to remain at room temperature for 4 days. Water (10 ml) was added and the mixture was extracted five times with 25-ml portions of ether. The combined ether extracts were washed successively with 100 ml of water, 7 ml of saturated sodium bicarbonate, and 100 ml of water. After drying over calcium chloride, the solvent was removed under vacuum and the residual yellow oil was distilled to give perdeuteriodimethyl acetylenedicarboxylate (1.26 g, 50.5%), bp 73–75° (6 mm). Vapor-phase chromatography revealed only one component having the same retention time as dimethyl acetylenedicarboxylate. The mass spectrum revealed a molecular ion at *m/e* 148 (148 calcd). The d_5 and d_4 isomers were present to the extent of 1.18 and 0.80% of the total product.

Chloro(1,2,3,4-tetracarbomethoxy-d_{12}-butadiene-1,4-di-σ)bis(triphenylphosphine)iridium(III) (18).—This complex was prepared in the same manner as described earlier for **9a** from 500 mg (3.38 mmol) of perdeuteriodimethyl acetylenedicarboxylate and the iridium carbonyl **11** (1.00 g, 1.28 mmol). The nmr spectrum of the deuterated iridocycle **18** exhibited a phenyl multiplet at τ 2.2–2.75 but no methyl signals in the τ 6–7 region.

Trimerization Using the Deuterated Iridocycle 18.—The trimerization experiments were run under the same conditions described above. The isotopic composition of the hexacarbomethoxybenzene was determined by mass spectral analysis. The iridocycle catalyst (a mixture of **9a** and **18**) was analyzed by nmr by comparing the integrated intensities of the phenyl and methyl signals.

In the first experiment 0.478 mmol of **18** and 1.45 mmol of dimethyl acetylenedicarboxylate in 30 ml of toluene were heated at reflux for 18 hr. The aromatic product (83% conversion) consisted of 58% d_{12} and 42% d_0. The iridocycle (54% recovered) consisted of 42% d_0 complex **9a** and 58% d_{12} complex **18**.

In the second experiment the ratio of **18** to acetylene was 0.478:0.74 (1:1.5) and the aromatic product (86% yield) consisted of 63% d_{12} and 37% d_0 compounds, whereas, the iridocycle (58% recovered) consisted of 17% d_0 (**9a**) and 83% d_{12} (**18**).

In the third experiment the ratio of **18** to acetylene was 0.239:1.44 (1:6), and the aromatic product consisted of 32% d_{12} and 68% d_0. The recovered iridocycle (20% of the starting material) consisted of 43% d_0 and 57% d_{12}, but these values are less reliable because of the small quantity available for analysis.

Attempted Oxidation of the Iridocycle 9a.—To a suspension of the complex **9a** (500 mg, 0.048 mmol) in 15 ml of chloroform and 10 ml of methanol was added ceric ammonium hexanitrate (500 mg, 0.091 mmol). The mixture was stirred for 1 hr, and the solvent was evaporated under vacuum. The residue was extracted with chloroform to give 500 mg of crude pale yellow solid. Recrystallization from methanol–chloroform afforded 430 mg of an analytical sample as yellow crystals. Elemental analyses were consistent with nitrato(1,2,3,4-tetracarbomethoxybutadiene-1,4-di-σ)bis(triphenylphosphine)iridium(III). *Anal.* Calcd for $C_{43}H_{42}O_{16}NP_2Ir$: C, 54.24; H, 3.95; P, 5.84; mol wt, 1060. Found: C, 54.00; H, 3.74; P, 5.73; mol wt, 1070.

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