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Mechanism of Acetylene Cyclotrimerization Catalyzed by the fac-IrP3+ Fragment: Relationship between Fluxionality and Catalysis

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Reaction of $[(\text{triphos})\text{Ir}(C_2H_4)_2](BPh_4)$ with C_2H_2 at 25 °C gives $[(\text{triphos})\text{Ir}(\eta^4-C_6H_6)](BPh_4)$, 1. which was shown to have this Ir/benzene connectivity by single crystal X-ray diffraction. Crystal data (-155 °C): a = 16.471(6) Å, b = 17.126(6) Å, c = 12.030(4) Å, $\alpha = 101.22(2)$ °, $\beta = 10.030(4)$ Å, $\alpha = 101.22(2)$ °, $\beta = 10.030(4)$ Å, $\alpha = 101.22(2)$ °, $\alpha = 10.030(4)$ Å, $\alpha = 100.22(2)$ °, $\alpha = 10.030(4)$ Å, $\alpha = 10.030($ 93.61(2)°, and $\gamma = 75.46(1)$ ° with Z = 2 in space group $P\bar{1}$. This species reacts with C_2H_2 in the presence of Cl⁻ to give (triphos)IrCl(η^2 -C₄H₄), 2, which can be converted back to 1 with C₂H₂ in the presence of the chloride scavenger TlPF₆. Ethyne will displace C₆H₆ from 1 at 60 °C in THF, thus completing a catalytic cyclotrimerization of C₂H₂ to benzene. While the phosphorus nuclei in 1 form an AM₂ spin system, these undergo site exchange with activation parameters $\Delta H^* = 10.7(3)$ kcal/mol and $\Delta S^* = -9.5(6)$ kcal⁻¹ mol⁻¹. The benzene ring ¹H NMR spectra are also temperature-dependent, and the fluxionality can be accounted for by the same activation parameters appropriate to ³¹P site exchange; the same physical mechanism thus accomplishes both site exchanges. The structural study indicates that η^4 -C₆H₆, which is nonplanar, is a stronger π -acceptor than is butadiene itself. A multistep mechanism has been studied with extended Hückel calculations. It is shown that the C-C bond formation between the first two alkynes to give the unsaturated metallacyclopentadiene is permitted when the three spectator ligands are in a fac geometry but is forbidden when they are in a mer geometry, which explains the puzzling difference of reactivity between monodentate triphosphine and tripodal complexes. It is shown that this unsaturated metallacycle is highly reactive toward an incoming ligand since it is not strongly stabilized by conjugation within the π system. This explains why it can be isolated by trapping with a Lewis base. The addition of the third alkyne to the metallacyclopentadiene, leading to the η^4 -benzene complex, can be achieved in a concerted manner and leads directly to the product. The C-C bond lengths within the η^4 -benzene are shown to be due to the presence of a potent metal donor and to the nonplanarity of the benzene ring. The fluxionality of the n^4 -benzene, which makes all carbons of the ring and the three phosphine ligands equivalent on the NMR time scale, is suggested to be due to an easy displacement/ rotation of the IrP₃⁺ fragment around the ring. This displacement avoids η^6 -coordination (20electron species) but passes through unsaturated η^3 - and η^2 -benzene coordination modes. These unsaturated species (notably the η^2 one) have the proper low-lying LUMO to coordinate an additional alkyne. This leads back to the monoalkyne complex and benzene production. Fluxionality and reactivity of the η^4 -benzene ring are therefore interrelated. The efficiency of the catalysis is suggested to be due to the fact that all intermediates are reactive 16-electron species stabilized by additional donation from the conjugated π system of the organic ligand. The presence of an enforced fac arrangement of the three spectator ligands avoids the thermodynamic trap of the trigonal bipyramidal bis(alkyne) complex.

Introduction

The transition-metal catalyzed cyclotrimerization of alkynes is noteworthy as a process which forms three C-C bonds, yet it must stop there or run the risk of concurrently producing polyacetylene. It can be catalyzed by a wide variety of metals, oxidation states and d-electron configurations. It is undoubtedly the case that no single

mechanism governs cyclotrimerization at all of these varied catalytic centers. The evidence for various mechanisms has been thoroughly reviewed by Wigley, with particular reference to low-valent early (electropositive) transition metal centers.

We have reported² a series of studies where acetylene cyclotrimerization is effected at 25 °C by catalyst precursors containing the (triphos)Ir+ substructure (triphos = MeC(CH₂PPh₂)₃). At the same time, we have reported on

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the structure, bonding, and reactivity of the Ir(PMe₂Ph)₃+ moiety bound to alkynes, which shows no acetylene cyclotrimerization activity under the same conditions.3 We report here a study of the structures and fluxionality of species derived from $(triphos)M^{n+}$ with HC = CH, together with a molecular orbital study of the likely individual steps in a cyclotrimerization mechanism.4 This work shows the close relationship between those intramolecular migrations which lead to fluxionality and those which accomplish product (arene) release and return to the catalytic cycle by acetylene binding.

Experimental Section

General Information. All reactions and manipulations were routinely performed under nitrogen, unless otherwise stated, by using Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation from LiAlH₄ under nitrogen. All other solvents and reagents were reagent grade and were used as received. Bis-(triphenylphosphine)iminium chloride (PPNCl) was purchased from Aldrich. Literature methods were used for the preparation of [(triphos)Ir(C₂H₄)₂]BPh₄⁵ and [(triphos)IrCl(C₂H₄)].⁵ The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. ¹H and ³¹P{¹H} NMR were recorded on either a Varian VXR 300 (299.94- and 121.42-MHz) or a Bruker ACP 200 (200.13- and 81.01-MHz) spectrometer. ¹H NMR shifts were measured relative to the residual ${}^{\mbox{\tiny 1}}\mbox{H}$ NMR resonance in the deuterated solvent (CD₂Cl₂, δ 5.32; CDCl₃, δ 7.13). ³¹P NMR shifts are relative to external 85% H₃PO₄ with downfield values reported as positive. ¹³C{¹H} NMR spectra were recorded on the Bruker instrument operating at 50.32 MHz. Chemical shifts are relative to the deuterated solvent resonance (CD₂Cl₂, δ 53.1; CDCl₃, δ 77.7). Broad band and selective ³¹P{¹H} NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier. ¹³C-DEPT, 2D-HETCOR, and 2D-COSY NMR experiments were run on the Bruker ACP 200 spectrometer. The computer simulation of NMR spectra was carried out with a locallydeveloped package containing the programs LAOCN36 and DAVINS,7 running on a Compaq Deskpro 386/25 personal computer. The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using the experimental digitized spectrum. The line-shape analysis of the variable-temperature NMR spectra was accomplished by means of the DNMR3 program8 adapted for the Compaq computer. Errors in the calculated rate constants were estimated by varying the rate constant around the best-fit value, until an observable difference between simulated and experimental spectra, both displayed on the graphical terminal, could be detected. These errors proved to be 10% (only at the coalescence point) or less. Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10⁻³ M in nitroethane solutions at room temperature. GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and a 6-ft. 0.1% SP-1000 80/100 Carbopack C 1/8-in. stainless steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic correct area normalization method.

Synthesis of [(triphos)Ir(η^4 -C₆H₆)]BPh₄(1). A. [(triphos)- $Ir(C_2H_4)_2]BPh_4$ (0.41 g, 0.34 mmol) was dissolved in THF (30 mL) under ethyne (1 atm) at room temperature. After 1 h, ethyne was replaced with nitrogen and the resulting orange solution was treated with ethanol (40 mL). On partial evaporation of the solvent, yellow crystals of 1 precipitated. They were filtered off and washed with n-pentane; yield 95%. Anal. Calcd for C_{71} -H₆₅BIrP₃: C, 70.23; H, 5.40; Ir, 15.83. Found: C, 70.11; H, 5.36; Ir, 15.71. $\Lambda_{\rm M} = 48~{\rm cm}^2~\Omega^{-1}~{\rm mol}^{-1}$. Spectral data have been reported.4

B. An equimolar mixture of [(triphos)IrCl(C₂H₄)] (0.30 g, 0.34 mmol) and TlPF₆ (0.12 g, 0.34 mmol) in THF (30 mL) was stirred at room temperature under ethyne (1 atm) for 2 h. After replacing ethyne with nitrogen, TlCl was removed by filtration. Addition of NaBPh₄ (0.17 g, 0.5 mmol) and n-heptane (60 mL) to the orange solution led to the precipitation of a yellow solid. Two recrystallizations from THF/ethanol/n-heptane gave pure samples of 1 in 65% yield.

Reaction of [(triphos)Ir(n4-C6H6)]BPh4 (1) with Ethyne. A THF (10 mL) solution of 1 (0.06 g, 0.05 mmol) was stirred under a 1-atm pressure of ethyne at 60 °C for 24 h. At regular intervals (ca. every 30 min), the reaction mixture was sampled and monitored by GC analysis, showing formation of benzene (0.5 mol of benzene/mol of catalyst/h). ³¹P{¹H} NMR showed 1 to be the only phosphorus-containing compound present in solution during and at the end of the catalytic reaction. Compound 1 was quantitatively recovered at the end of the reaction. When the reaction was carried out at room temperature, no benzene production was observed.

Reaction of [(triphos)Ir(η⁴-C₆H₆)]BPh₄ (1) with Ethyne in the Presence of PPNCl. A solution of 1 (0.30 g, 0.25 mmol) and PPNCl (0.14 g, 0.25 mmol) in THF (40 mL) was heated at reflux temperature under ethyne (1 atm). After 2 h, the resulting colorless solution was concentrated under reduced pressure to ca. 10 mL and the precipitated PPNBPh eliminated by filtration. The filtrate, treated with n-heptane (30 mL), led to the precipitation of sandy crystals of [(triphos)IrCl(η^2 -C₄H₄)] (2) in 80% yield. Anal. Calcd for C₄₅H₄₃ClIrP₃: C, 59.76; H, 4.79; Ir, 21.25. Found: C, 59.74; H, 4.72; Ir, 21.09.

Reaction of [(triphos)IrCl(η^2 -C₄H₄)] (2) with Ethyne in the Presence of TIPF₆. A solid sample of 2 (0.30 g, 0.33 mmol) was added to a stirred THF (30-mL) solution of TlPF₆ (0.12 g, 0.34 mmol) under a steady stream of ethyne at room temperature. Within a few minutes, the solid dissolved to give an orange solution. After 1 h, TlCl was removed by filtration and then NaBPh₄ (0.17 g, 0.50 mmol) in ethanol (30 mL) was added. On partial evaporation of the solvent under a stream of nitrogen, yellow crystals of 1 precipitated in 80% yield.

Molecular Orbital Calculations. The extended Hückel calculations (EHT) were carried out by using the weighted H_{ii} formula.9 The atomic parameters for Ir are taken from the literature.3b The geometries for the several model species were taken from the experimental data on related complexes: P3Ir- $(\eta^4-C_6H_6)^+$, this work; $P_3Ir(C_2R_2)^+$, ref 3b, $P_3Ir(C_4R_4)^+$, ref 10; $P_3Ir(C_5H_5)$, ref 11 (with the following changes: Ir-P = 2.3 Å, C-C= 1.4 Å in the benzene complex, P-Ir-P = 90°). For the planar benzene complex, $Ir-(C_6H_6 plane) = 1.9 \text{ Å}$. The phosphines were modeled by PH₃.

X-ray Structure Determination of $[(triphos)Ir(C_6H_6)]$ -BPh₄·1/₂THF. A crystal of suitable size was mounted in a nitrogen atmosphere glovebag using silicone grease and was transferred to a goniostat where it was cooled to –155 °C for characterization

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Table 1. Crystallographic Data for [(triphos)IrC₆H₆]BPh₄·1/₂THF

chemical formula	C71H65BIrP3-1/2THF	space group	ΡĪ
a, Å	16.471(6)	T, °C	-155
b, Å	17.126(6)	λ, Å	0.710 69
c , $\mathbf{\mathring{A}}$	12.030(4)	$\rho_{\rm calcd}$, g cm ⁻³	1.252
α, deg	101.22(2)	$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	21.7
β , deg	93.61(2)	R	0.0845
γ, deg	75.46(1)	R_{w}	0.0819
V , \mathbb{A}^3	3221.68		
Z	2		
fw	1214.25		

(Table 1) and data collection (6° $< 2\theta < 45^{\circ}$). A systematic search of a limited hemisphere of reciprocal space revealed no symmetry among the observed intensities. An initial choice of space group $P\bar{1}$ was later proven correct by the fact that attempted refinement in space group P1 was unsatisfactory. Following complete intensity data collection and correction for absorption, data processing gave a residual of 0.047 for the averaging of 911 unique intensities which had been measured more than once. Four standards measured every 400 data showed no significant trends. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The Ir and P positions were determined from an initial E map and the remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and difference Fourier calculation. One group of residual peaks that formed a fivemembered ring was included as five half-weight carbons to model a partial-occupancy THF solvent molecule. The remaining residual peaks were rejected as being chemically unreasonable. The possibility of additional severely disordered solvent cannot be ruled out. Hydrogens were included in fixed calculated positions for all except the solvent atoms. The largest peak in the final difference map was 4.9 e/ų in a cage formed by Ir(1), P(2), P(15), P(28), and C(41)–C(44). A false peak this large is somewhat unusual; however, a second data set collected on a crystal of different shape from a different sample gave the same result. Results of the structure determination are shown in Tables 2 and 3. Additional details are available as supplementary material.

Results

[(triphos)Ir(η^4 -C₆H₆)]BPh₄ (1). When a steady stream of ethyne is passed at room temperature through a THF solution of either [(triphos)Ir(C₂H₄)₂]BPh₄ or [(triphos)IrCl(C₂H₄)] in the presence of TlPF₆ as chloride scavenger, orange crystals of [(triphos)Ir(η^4 -C₆H₆)]BPh₄ (1) are obtained in excellent yields by addition of ethanol/n-heptane, followed by slow evaporation of the solvent [triphos = MeC(CH₂PPh₂)₃]. Evolution of C₂H₄ was established by GC and ¹H NMR. Alternatively, 1 is synthesized in almost quantitative yield by treatment of the iridacyclopentadiene complex [(triphos)IrCl(η^2 -C₄H₄)] (2) (see below) in THF with a stoichiometric amount of TlPF₆ under a steady stream of ethyne at room temperature, followed by NaBPh₄ addition in ethanol.

Complex 1 is stable in the solid state and in deaerated solutions, in which it behaves as a 1:1 electrolyte. The IR spectrum is featureless in the 2500–1500-cm⁻¹ region where $\nu(\text{Ir}-H)$, $\nu(\text{Ir}-\sigma\text{-C}=\text{CH})$, $\nu(\text{C}=\text{C})$, and $\nu(\text{Ir}-\pi\text{-HC}=\text{CH})$ are generally observed. The only remarkable new band is a weak one at 1605 cm⁻¹ in the region of aromatic $\nu(\text{C}-\text{C})$.

The variable-temperature ³¹P{¹H} NMR spectra in CDCl₃ show 1 to be fluxional on the NMR time scale (Figure 1, left). In the fast exchange limit (>30 °C), the

spectrum consists of an A_3 spin system (δ -22.75 at 40 °C), which transforms into an AM2 pattern in the slow exchange limit (<0 °C) ($\delta(P_A)$ -27.13, $\delta(P_M)$ -19.56 at -60 °C) with an unusually small J(PP) (1.5 Hz). The mutual exchange mechanism that renders equivalent the three phosphorus atoms of triphos has been studied by spectral simulation, 13 assuming exchange between the three configurations $P_1P_2P_3 \Longrightarrow P_3P_1P_2 \Longrightarrow P_2P_3P_1$. A satisfactory simulation of the variable-temperature spectra (Figure 1, right) has been obtained by using $T_2 = 0.12$ s and the rate constants k shown in Figure 1. Plotting $\log k$ against 1/T results in a straight line (Figure 2). An Eyring plot yields the activation parameters ΔH^* (10.7 ± 0.2 kcal mol⁻¹), ΔS^* $(-9.5 \pm 0.6 \text{ cal K}^{-1} \text{ mol}^{-1})$, and $\Delta G^{*}_{298\text{K}}$ (13.5 ± 0.04 kcal mol⁻¹). The negative but near-zero value for ΔS^{\dagger} is consistent with the transition state for the fluxional process being intramolecular but ordered.

The variable-temperature ¹H NMR spectra of 1 in CDCl₃ are reported in Figure 3. The spectrum recorded at 50 °C shows a broad resonance at 5.18 ppm for the six hydrogens of the benzene ligand. At ca. 0 °C, this resonance decoalesces and, at lower temperature, emerges from the baseline to give three well-separated bands that at -40 °C fall at 6.49 ppm (partially masked by the resonances of the phenyl rings of triphos and BPh₄-), 5.86 ppm (2H), and 3.16 ppm (2H). Even at the lowest temperature attained (-100 °C in CD₂Cl₂), the three resonances show no well-resolved H-H couplings. However, from selective decoupling experiments as well as a H,H-COSY experiment, it is evident that the band at 3.16 ppm is correlated to the other two, which are not correlated with each other. This finding allows us to assign the highest field resonance to the central Ir—C—H hydrogens (H_B) and the lowest field resonance to the hydrogen atoms of the uncoordinated HC=CH moiety (H_A)

A rough evaluation of the coupling interaction between the three different pairs of hydrogens can be obtained by selective homodecoupling experiments by measuring the decrease in line width $(w_{1/2})$ upon crossover irradiation of the three signals. In particular upon irradiation of the H_B signal, the $w_{1/2}$ values of the resonances due to H_A and H_C decrease by ca. 4 and 3 Hz, respectively. No variation of the peak width is observed when the resonances due to HA and H_C are selectively decoupled. An unambiguous computer simulation of the ¹H NMR spectra cannot be provided, as it is not possible to carry out a line-shape analysis. The spin system is, in fact, extremely complicated (AA'BB'CC'XX'Y). However, by using a simplified ABCX model and introducing the rate constants calculated from the activation parameters obtained from the temperaturedependent 31P NMR spectra, we have been able to reproduce the variable-temperature experimental spectra. The exchange mechanism is $ABC \Rightarrow BCA \Rightarrow CAB$ with the following coupling constants: J(AB) = 4 Hz, J(BC)

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Table 2. Fractional Coordinates and Isotropic Thermal Parameters* for [(triphos)IrC₆H₆]BPh₄·¹/₂THF

	Table 2.	Fractional Coordinates and isotropic Thermal Parameters for [(triphos)/iC6f16]DF 14.7/21 FF							
	10 ⁴ x	10 ⁴ y	10 ⁴ z	$10B_{\rm iso}~({\rm \AA}^2)$		10^4x	10 ⁴ y	$10^{4}z$	$10B_{\rm iso}~({\rm \AA}^2)$
Ir(1)	6176.9(4)	3223.0(4)	2389(1)	25	C(42)	8054(9)	2296(9)	3501(12)	28
P(2)	6166(2)	2840(2)	4128(3)	27	C(43)	6846(9)	1807(9)	4135(13)	30
C(3)	5148(9)	2823(8)	4671(11)	25	C(44)	7418(9)	1257(9)	2133(13)	31
C(4)	4981(10)	2118(10)	4951(13)	37	C(45)	8259(10)	873(9)	3830(14)	37
C(5)	4226(11)	2177(10)	5453(13)	37	C(46)	5831(13)	3759(12)	828(17)	57
C(6)	3638(11)	2911(11)	5683(13)	41	C(47)	5064(14)	3616(12)	1272(18)	62
C(7)	3801(9)	3595(10)	5415(13)	35	C(48)	4903(10)	3997(12)	2371(16)	52
C(8)	4549(9)	3553(9)	4927(13)	31	C(49)	5494(14)	4515(9)	2853(15)	54
C(9)	6499(9)	3482(8)	5391(11)	26	C(50)	5711(15)	4956(16)	2077(20)	76
C(10)	671 2 (9)	4213(8)	5322(12)	27	C(51)	5863(14)	4565(15)	983(21)	69
C(11)	6953(10)	4676(9)	6308(13)	37	B(52)	1340(10)	1690(9)	4445(13)	24
C(12)	6984(11)	4437(10)	7342(13)	39	C(53)	2210(8)	1188(7)	4970(11)	20
C(13)	6753(12)	3730(11)	7423(14)	45	C(54)	2375(9)	1245(8)	6149(12)	26
C(14)	6535(11)	3250(9)	6426(13)	37	C(55)	3122(10)	790(9)	6568(13)	34
P(15)	6462(2)	1845(2)	1553(3)	25	C(56)	3748(9)	271(8)	5839(13)	30
C(16)	6580(9)	1594(8)	19(12)	29	C(57)	3589(9)	224(9)	4671(12)	30
C(17)	7316(10)	1209(11)	-516(14)	29 44	C(58)	2857(9)	662(9)	4271(11)	28
C(18)	7387(13)	1036(13)	-1672(16)	56	C(59)	949(9)	1020(8)	3586(12)	25
C(19)	6695(13)	1298(9)	-2337(14)	44	C(60)	783(9)	342(8)	3937(12)	28
C(20)	5933(12)	1684(11)	-1849(12)	42	C(61)	486(10)	-280(9)	3217(14)	38
C(21)	5884(10)	1818(11)	-646(13)	39	C(62)	321(12)	-219(11)	2068(15)	47
C(22)	5666(8)	1289(8)	1689(11)	22	C(63)	479(12)	424 (11)	1675(14)	51
C(23)	5844(9)	440(9)	1339(11)	27	C(64)	771(12)	1041(11)	2415(14)	46
C(24)	5234(10)	7(9)	1396(12)	30	C(65)	656(8)	2201(8)	5428(11)	23
C(25)	4463(9)	388(10)	1781(12)	32	C(66)	-135(9)	2067(9)	5539(11)	27
C(26)	4272(9)	1230(10)	2156(14)	40	C(67)	-736(10)	2569(10)	6324(12)	34
C(27)	4887(10)	1671(9)	2097(13)	35	C(68)	-536(10)	3235(9)	7054(12)	33
P(28)	7616(2)	3082(2)	2633(3)	26	C(69)	253(10)	3367(9)	6992(12)	33
C(29)	8055(9)	3946(8)	3324(12)	27	C(70)	825(10)	2856(9)	6209(12)	30
C(30)	8576(10)	3926(9)	4271(13)	32	C(71)	1489(9)	2408(8)	3800(11)	26
C(31)	8884(10)	4615(9)	4717(13)	35	C(72)	2278(9)	2518(8)	3612(12)	27
C(32)	8714(10)	5283(8)	4253(13)	32	C(73)	2357(10)	3153(10)	3068(14)	37
C(33)	8222(10)	5303(9)	3291(14)	33	C(74)	1682(12)	3667(10)	2728(12)	39
C(34)	7875(10)	4641(9)	2789(13)	36	C(75)	871(10)	3604(10)	2924(14)	38
C(35)	8242(9)	2786(8)	1328(12)	25	C(76)	804(10)	2976(9)	3450(13)	34
C(36)	7932(12)	2909(15)	302(17)	63	C(77)	1579(20)	1140(19)	8912(33)	45
C(37)	8444(12)	2720(15)	-652(15)	60	C(78)	2102(26)	660(22)	9512(30)	53
C(38)	9255(11)	2428(10)	-568(13)	38	C(79)	2375(26)	1151(25)	10444(26)	58
C(39)	9597(13)	2284(20)	448(17)	98	C(80)	2336(42)	1852(30)	10114(48)	118
C(40)	9066(14)	2480(19)	1392(15)	92	C(81)	1776(28)	1970(22)	9213(32)	55
C(41)	7611(10)	1588(10)	3371(13)	38	` /	- (/	/	()	
- (/	()								

^a Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. Acta Crystallogr. 1959, 12, 609.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [(triphos)Ir(C₆H₆)]BPh₂·1/₂THF

[(triphos)lr(C ₆ H ₆)]BPh ₄ ·1/ ₂ THF						
Ir(1)-P(2)	2.313(4)	C(46)-C(47)	1.494(28)			
Ir(1)-P(15)	2.319(4)	C(46)-C(51)	1.372(28)			
Ir(1)-P(28)	2.327(4)	C(47)-C(48)	1.367(26)			
Ir(1)-C(46)	2.229(20)	C(48)-C(49)	1.493(27)			
Ir(1)-C(47)	2.245(22)	C(49)-C(50)	1.42(3)			
Ir(1)-C(48)	2.184(15)	C(50)-C(51)	1.36(3)			
Ir(1)-C(49)	2.196(16)					
P(2)-Ir(1)-P(15)	88.55(13)	C(47)-Ir(1)-C(48)	35.9(7)			
P(2)-Ir(1)-P(28)	88.25(14)	C(47)-Ir(1)- $C(49)$	65.2(7)			
P(2)-Ir(1)-C(46)	164.6(5)	C(48)-Ir(1)-C(49)	39.9(7)			
P(2)-Ir(1)-C(47)	127.0(6)	Ir(1)-C(46)-C(47)	71.1(12)			
P(2)-Ir(1)-C(48)	99.2(5)	Ir(1)-C(46)-C(51)	112.9(16)			
P(2)-Ir(1)-C(49)	98.7(5)	C(47)-C(46)-C(51)	115.2(18)			
P(15)-I(28)-P(28)	88.04(13)	Ir(1)-C(47)-C(46)	69.9(12)			
P(15)-Ir(1)-C(46)	98.5(5)	Ir(1)-C(47)-C(48)	69.6(11)			
P(15)-Ir(1)-C(47)	95.4(5)	C(46)-C(47)-C(48)	113.0(17)			
P(15)-Ir(1)-C(48)	120.6(6)	Ir(1)-C(48)-C(47)	74.5(12)			
P(15)-Ir(1)-C(49)	159.8(5)	Ir(1)-C(48)-C(49)	70.5(9)			
P(28)-Ir(1)-C(46)	105.6(5)	C(47)-C(48)-C(49)	113.5(17)			
P(28)-Ir(1)-C(47)	144.6(6)	Ir(1)-C(49)-C(48)	69.6(8)			
P(28)-Ir(1)-C(48)	150.4(6)	Ir(1)-C(49)-C(50)	108.2(15)			
P(28)-Ir(1)-C(49)	110.8(6)	C(48)-C(49)-C(50)	113.9(16)			
C(46)-Ir(1)-C(47)	39.0(7)	C(49)-C(50)-C(51)	118.2(21)			
C(46)-Ir(1)-C(48)	65.5(7)	C(46)-C(51)-C(50)	111.9(22)			
C(46)-Ir(1)-C(49)	70.3(7)					

= 2 Hz, J(BX) = 6 Hz. The second-order effects that broaden the resonances in the slow exchange region have been artifically reproduced by introducing a very low value

of T_2 (0.06 s). In contrast, in the fast exchange region where second-order effects are expected to disappear, a more realistic T_2 value (0.3 s) has been introduced. In the range 233-303 K, a reasonable agreement between experimental and computed spectra (Figure 4) has been found. Since a single set of activation parameters successfully accounts for the dynamic line shapes in both ^{31}P and ^{1}H NMR spectra, we conclude that a single mechanism accomplishes both site exchange processes.

The 13 C{ 1 H} NMR spectrum of 1 (CD₂Cl₂, -50 °C) exhibits three resonances at δ ca. 132 (masked by phenyl carbon atoms), δ 86.77 (brd, J(CP) = 6.7 Hz), and δ 55.31 (dd, J(CP) = 38.7, 6.2 Hz). When the temperature is raised, the resonances broaden and, at ca. 20 °C, merge into the baseline. On the basis of the C-P coupling constant values and, in particular, of a 13 C- 1 H heteronuclear 2D-NMR correlation study in CD₂Cl₂ at -50 °C (Figure 5), the three resonances were readily assigned to the C_C, C_A, and C_B carbon atoms, respectively.

Reaction of 1 with ethyne in THF at 60 °C shows (GC) production of benzene at a rate of 0.5 mol of benzene (mol of catalyst)⁻¹ h⁻¹, over a 24-h period. When the reaction was carried out in the presence of PPNCl, no catalytic process occurred, since the 16-electron intermediate [(triphos)Ir(η^2 -C₄H₄)] * is trapped by chloride to give [(triphos)IrCl(η^2 -C₄H₄)] (2) which is stable under catalytic

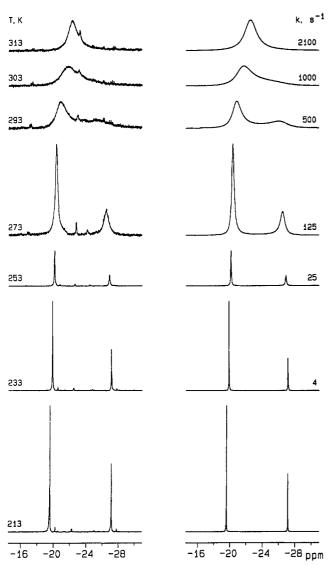


Figure 1. Experimental (left) and computed (right) variable-temperature ³¹P{¹H} NMR spectra of 1 (CDCl₃, 121.42 MHz). The intensities of the spectra at 273, 293, 303, and 313 K are purposefully increased by 10 times.

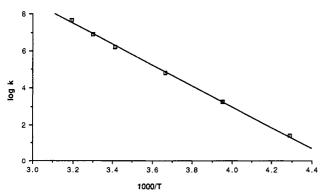


Figure 2. Arrhenius plot for the rate constants obtained from the computer simulation of the variable-temperature ³¹P{¹H} NMR spectra of 1.

conditions. However, addition of $TIPF_6$ and ethyne in THF regenerates the catalytically active 1.

[(triphos)IrCl(η^2 -C₄H₄)] (2). The complex behaves as a nonelectrolyte in CH₂Cl₂ and EtNO₂. The ³¹P{¹H} NMR spectrum in CD₂Cl₂ is temperature-invariant in the range +20 to -90 °C and consists of a first-order AM₂ spin system (20 °C: δ (P_A) -27.26, δ (P_M) -39.96, J(PP) = 15.9

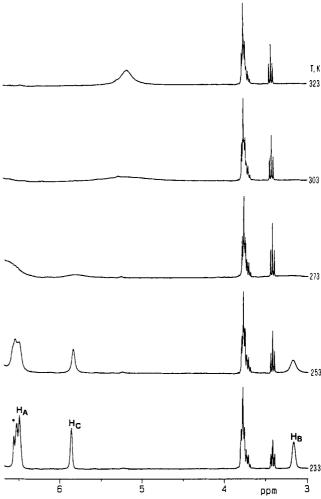


Figure 3. Experimental variable-temperature ¹H NMR spectra of 1 in the 7-3 ppm region (CDCl₃, 299.95 MHz). The asterisk refers to aromatic protons.

Hz). This pattern is typical of octahedral triphos metal complexes containing two chemically-equivalent phosphorus nuclei. The ¹H NMR spectrum (CD₂Cl₂, 20 °C) exhibits a multiplet at δ 6.45 (Figure 6b) readily attributable to the two β -hydrogens of a C₄H₄ diene ligand.² An H,H-COSY experiment shows this resonance to be correlated with a resonance at ca. 7.5 ppm (α -hydrogens) masked by the signals of the phenyl hydrogens. The higher field signal has been simulated (Figure 6a) as the AA' part of an AA'MM'XX'Y spin system with the following parameters (X, X', and Y denote the phosphorus atoms of triphos): $^3J(AA') = 4.5 \text{ Hz}, ^3J(AM) = 8.5 \text{ Hz}, ^4J(AM') = 1.0 \text{ Hz}, ^4J(AX) = 11.6 \text{ Hz}, ^4J(AX') = 1.2 \text{ Hz}, ^4J(AY) = -1.0 \text{ Hz}, ^4J(MM') = 6.8 \text{ Hz}, ^2J(XX') = 1.5 \text{ Hz}).$

The 13 C{\frac{1}H} NMR spectrum of 2 (CD₂Cl₂, 20 °C) exhibits a single resonance at 153.72 ppm for the α -carbons of the C₄H₄ moiety, showing they are chemically (but not magnetically) equivalent. This resonance consists of a ddd pattern and has been simulated as the AA' part of an AA'MM'Q spin system where M and M'denote the two phosphorus atoms trans to the C₄H₄ ligand and Q denotes the remaining phosphorus atom. The different values of $^2J(C_\alpha P)$ confirm the magnetic inequivalence of the phosphorus nuclei in 2 ($^2J(C_\alpha P_M) = 95.4$ Hz, $^2J(C_\alpha P_M) = 9.3$ Hz, $^2J(C_\alpha P_Q) = 7.4$ Hz). The resonance of the β -carbons of the C₄H₄ ligand falls at higher field, 142.36 ppm, and appears as a triplet ($^3J(C_\beta P) = 5.0$ Hz). From a comparison of the spectroscopic data of 2 with those of the rhodium

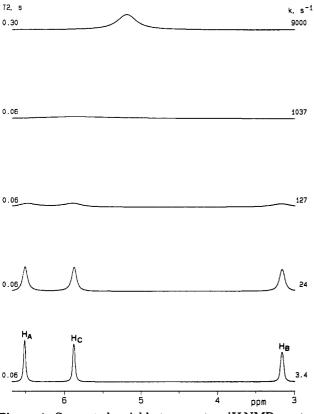
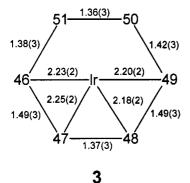


Figure 4. Computed variable-temperature ¹H NMR spectra of 1 in the 7-3 ppm region (CDCl₃, 299.95 MHz). The rate constants are calculated using the activation parameters obtained from the variable-temperature ³¹P NMR spectra.

derivative [(triphos)RhCl(η^2 -C₄H₄)] authenticated by an X-ray analysis,⁴ one may readily infer that the two compounds share the same primary geometry; i.e., the metal center is octahedrally coordinated by triphos, by the two terminal carbons of a C₄H₄ diene moiety, and by a chloride ligand.

Solid-State Structure of [(triphos)Ir(η^4 -C₆H₆)]-BPh₄·1/₂THF. This salt contains noninteracting BPh₄- and (triphos)Ir(η^4 -C₆H₆)⁺ ions, with THF filling holes in the lattice. The cation (Figure 7) has pseudomirror symmetry, with the mirror plane containing the Ir–P(28) bond and bisecting the C(47)–C(48) and C(50)–C(51) bonds. While the P–Ir–P angles are identical at 88°, the Ir–P(28) bond length (2.327(4) Å) is 3σ longer than the other two Ir–P distances (2.313(4) and 2.319(4) Å). This is consistent with a square-pyramidal structure with one of the Ir–P bonds as the apical group. While the four Ir–C bond lengths (3) show some distortions from mirror sym-



metry, these deviations do not exceed 2.5σ and are thus

not statistically significant. The pattern of C(46)–C(47), C(47)–C(48), and C(48)–C(49) bond lengths (while just significant at the 3σ level) is long–short–long, consistent with extensive back-bonding. In fact, they resemble the degree of back-bonding from low-valent early (i.e., electropositive) transition metals to butadiene much more than late transition metal butadiene compounds. However, this long–short–long pattern is generally observed for η^4 -arene compounds (which involve mainly late transition metals). The conclusion is that an η^4 -arene is a much stronger π -acceptor than is butadiene itself.

In order to avoid repulsion between filled C=C and metal orbitals, the benzene folds about the C(46)/C(49) line to a dihedral angle of 134.8°.¹⁶ Such bending must be considered as contributing to the π -acceptor capacity of η^4 -benzene. This folding moves C(50) and C(51) beyond 2.97 Å from iridium.

Summary of Experimental Conclusions. Our experimental results suggest that the catalytic cycle (Figure 8) which has long been suggested is operating in our Ir-(tripod) + system. The following points have been proven: (i) The η^4 -benzene complex produces benzene in a catalytic manner upon ethyne addition; the catalytic cycle is stopped by Cl-([PPN]Cl) and restarts if Cl- is removed by adding TlPF₆. (ii) A fluxional mechanism, which does not dissociate phosphines or benzene, makes all carbon and phosphorus atoms equivalent in 1. Fluxionality and the cyclotrimerization reactions occur at the same temperature. (iii) From previous studies, we have learned that $IrP_3(alkyne)^+$ (P = monodentate phosphine) is an isolable species, suggesting that the corresponding complex with tripodal phosphine is a viable intermediate. The complex with monodentate phosphine and tripodal phosphine differ by another important point. The complex with monodentate phosphine produces a cis-bis(alkyne) trigonal bipyramidal complex with additional alkyne, and the two coordinated alkynes do not couple to make a metallacyclopentadiene. This suggests that the dialkyne complex with a planar MP₃ unit is a thermodynamically-stable dead-end channel for the catalytic reaction.

In order to understand better the several aspects of this reaction, we have studied the reaction path with extended Hückel (EHT) calculations.

Molecular Orbital Study of the Alkyne Cyclotrimerization. The few relevant, previous theoretical studies are limited to only selected parts of the pathway. The coupling of two alkynes linked to a CpCo fragment was investigated via ab initio calculations and the orientation favoring the formation of the C–C bond was determined. 17a In the same study, the structure of the unsaturated species, CpCo(C₄H₄), was optimized and was shown to be pyramidal at the Co center, which is in agreement with a previous MO analysis of 6 CpML₂ complexes. 17b In a preliminary communication, 4 we demonstrated that the addition of an alkyne to a $P_{3}Ir(C_{4}H_{4})^{+}$ intermediate, facilitated by the match in symmetry between the frontier orbitals of

⁽¹⁴⁾ The long C(49)–C(50) bond length and the higher esd's associated with C(50) arise from the larger (by 30%) thermal parameter of C(50). Some disorder of this carbon is indicated, in spite of the low temperature of the data collection.

⁽¹⁵⁾ Erker, G.; Krüger, C.; Müller, G. Adv. Organomet. Chem. 1985, 24, 1. Yasuda, H.; Nakamura, A. Angew. Chem., Int. Ed. Engl. 1987, 26, 732

⁽¹⁶⁾ C(46)–C(49) are planar to within ± 0.02 Å, as are C(49), C(50), C(51), and C(46).

^{(17) (}a) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. J. Am. Chem. Soc. 1983, 105, 1907. (b) Hoffman, P. Angew. Chem., Int. Ed. Engl. 1977, 8, 536.



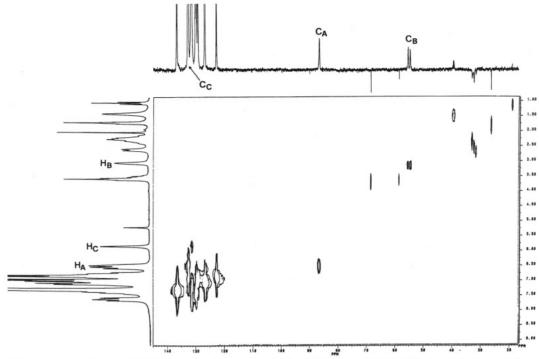


Figure 5. ¹³C-¹H heteronuclear 2D-NMR correlation study of 1 in CD₂Cl₂ at -50 °C. The trace at the right shows a DEPT experiment for separation of CH₂ (negative) from CH and CH₃ carbon atoms (positive).

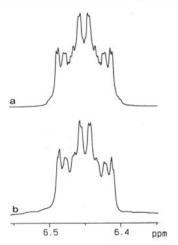


Figure 6. Experimental (b) and computed (a) ¹H NMR spectrum of the β -hydrogens of the β -C₄H₄ diene ligand in 2 (CD₂Cl₂, 200.13 MHz).

the two reactants leads, in a concerted manner, to the formation of $P_3Ir(\eta^4$ -benzene)⁺.

Formation of Metallacyclopentadiene. A. Reactivity of mer- and fac-P₃Ir(alkyne)^{+.18} The monoalkyne complex P₃Ir(alkyne)+ (P = PMe₂Ph) does not assume the classical planar structure expected for d8 ML₄ complexes, preferring instead a geometry which is intermediate between a tetrahedron and a square pyramid, (4).3 It has

been shown that this structure is due to the tendency of

the alkyne to donate more than 2 electrons to the metal which means that P₃Ir(alkyne)⁺ is intermediate between a 16- and an 18-electron system. The fact that the complex is not fully saturated is confirmed by its high reactivity toward any incoming nucleophile3 and supported by the presence of a low-lying LUMO pointing toward the vacant site, as shown in 5. In the specific case where the incoming nucleophile is an alkyne, two types of reactions are observed: (i) addition of the alkyne, leading to the formation of a bis(alkyne) complex, and (ii) coupling of the alkynes, leading to the unsaturated metallacycle.

The addition reaction (i) has been observed for monodentate phosphines and dicarbomethoxyalkyne.3b The two alkynes occupy the equatorial sites of the trigonal bipyramid, 6, and the three phosphines move from the fac

geometry in 4, to a mer arrangement, a reorganization which is only possible for monodentate phosphines. The coupling reaction (ii) occurs only for tripodal phosphines (where the fac arrangement is constrained), for Ir(I) or Rh(I), and leads to the formation of a metallacyclopentadiene. In the case of Rh, this intermediate has been trapped using Cl-. A similar reaction is believed to take place during the cyclotrimerization with CpCo (where the Cp group mimics three fac ligands). 19

This intriguing difference in product identity from the mer- and fac-P3Ir+ fragments (monodentate and tripodal

⁽¹⁸⁾ We use the term fac to indicate a pyramidal P₃M structure and mer to indicate a planar P3M structure.

Figure 7. Stereo ORTEP drawing of the non-hydrogen atoms of (triphos) $Ir(\eta^4-C_6H_6)^+$, showing selected atom labeling.

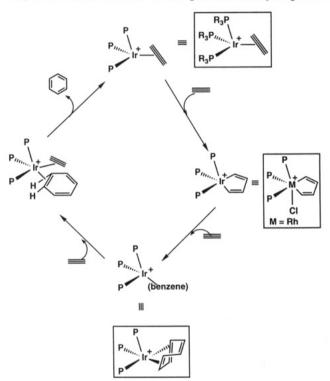


Figure 8. Representation of the catalytic reaction path for alkyne cyclotrimerization. The species which have been isolated and characterized by X-ray diffraction are indicated in boxes.

phosphines, respectively) needs to be explained. The most stable structure for a d⁸ ML₃L'₂ (L' = π -acceptor ligand) species is a trigonal bipyramid with the two L' ligands lying in the equatorial plane. There is a strong preference for this structure, especially with the heavy metal center and the absence of ancillary π -acceptor ligands. This strong structural preference is supported by the lack of fluxional behavior in P₃Ir(alkyne)₂+.²⁰ The complex adopts this structure if the three L ligands can adopt a *mer* arrangement, as is possible only for monodentate L.

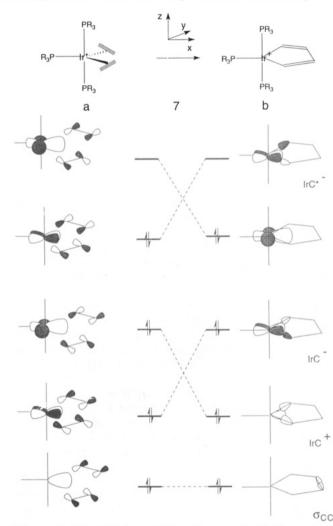


Figure 9. Simplified correlation diagram for C–C coupling in mer-(PH₃)₃Ir(C₂H₂)₂+, preserving C_{2v} symmetry.

We have constructed the correlation diagram (using the xz plane which bisects the incipient C-C bond as the symmetry element) for the coupling reaction, 7, transforming the trigonal bipyramid into the metallacyclobutadiene and have found that this transformation is symmetry-forbidden (Figure 9). The correlation diagram is similar to that published by Hoffmann $et\ al.$ for the coupling of two olefins in the same type of metallic system²¹ and the presence of the additional alkyne π orbitals (π_{\perp})

^{(19) (}a) McAllister, D. R.; Bercaw, J. E.; Bergman, R. G. J. Am. Chem.
Soc. 1977, 99, 1666. (b) Bönneman, H. Angew. Chem., Int. Ed. Engl.
1985, 24, 248. (c) Vollhardt, K. P. C. Angew. Chem., Int. Ed. Engl.
1984, 23, 539. (d) Gleiter, R.; Kratz, D. Angew. Chem., Int. Ed. Engl.
1990, 29, 276

⁽²⁰⁾ Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. J. Am. Chem. Soc. 1990, 112, 855.

Figure 10. Simplified correlation diagram for C-C coupling in fac-(PH₃)₃Ir(C₂H₂)₂+, preserving C_s symmetry.

does not modify its general shape. The same transformation becomes allowed when the two alkynes are attached to the fac- P_3Ir^+ fragment, as in Figure 10, in agreement with Morokuma's calculations 17a which demonstrated that the reaction is also allowed for the isolobal CpCo fragment. 22

Figures 9 and 10 show a simplified version of the correlation diagrams for molecular orbitals which are lying in the horizontal xy plane. The other molecular orbitals, perpendicular to the xy plane, do not vary significantly in energy along the reaction path and correlate in an allowed manner.

In both geometries, 7a and 8a, the three lowest orbitals shown correlate with bonding orbitals of the metallacycle (σ_{cc} , IrC⁺, IrC⁻). The difference between the two geometries comes from the xy orbital, which correlates with the empty orbital IrC*- (the out-of-phase combination of the two Ir-C σ^* antibonding orbitals). The metal xy orbital is occupied in the trigonal bipyramid case, 7a, and the coupling reaction is thus forbidden. It is empty in the square-based pyramid 8a, and the reaction is allowed. In the latter structure, 8a, the HOMO is the lone pair at the metal, destabilized by the five surrounding ligands. It

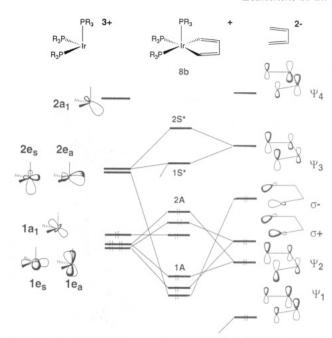


Figure 11. Orbital diagram for fac- $(PH_3)_3Ir(C_4H_4)^+$ as made from $(PH_3)_3Ir^{3+}$ and $C_4H_4^{2-}$.

correlates in an allowed way with $x^2 - y^2$ of the metallacycle. This coupling reaction, which oxidizes the metal from d^8 to d^6 and forms a C-C bond, is allowed if the metal can provide an extra orbital of the same symmetry as the σ_{cc} bond (i.e., symmetrical with respect to the xz plane). This is the case for 8a but not for 7a.

This analysis of the first step in the mechanism of Figure 8 suggests that the C-C coupling reaction is favored by preventing the bis(alkyne) complex from falling into the thermodynamic trap represented by a trigonal bipyramidal structure. Tripodal phosphines and Cp groups thus serve this function.

B. Structure of the Metallacyclopentadiene. The structure of the unsaturated metallacyclopentadiene, 8b, is unknown but may be inferred from the X-ray structure of the trapped product, $[(triphos)RhCl(\eta^4-C_4H_4)]$, 4 where the metallacyclopentadiene ring is planar. Test calculations on the unsaturated species show that the planar ring is also preferred. 23a This contrasts with the metallacyclopentadiene intermediates involved in the Dötz mechanism. 23b

The construction of the molecular orbitals of 8b from the [IrP₃]³⁺ and [C₄H₄]²⁻ fragments is given in Figure 11. The idealized P₃Ir³⁺ fragment has $C_{3\nu}$ symmetry, and this group's symmetry labels are used for the fragment orbitals although the metallacycle has C_s symmetry.²⁴ The two Ir–C σ bonds result from the two bonding interactions between the empty metal fragment orbitals, $2a_1$ and $2e_a$, and the two symmetry-adapted combinations, σ^+ and σ^- , respectively, of the carbon σ lone pairs. A π -type interaction between the metal and the ring results from the stabilization of the low-lying ψ_1 by the empty $2e_s$, but this interaction is very weak because $2e_s$ overlaps weakly with ψ_1 (0.06) and because there is a large energy gap. The back-bonding from $1e_a$ into ψ_4 is also negligible because

⁽²¹⁾ Stockis, A.; Hoffmann, R. J. Am. Chem. Soc. 1980, 102, 2952. McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. J. Am. Chem. Soc. 1981, 103, 2595.

⁽²²⁾ C–C coupling is also permitted when deviations from C_{2v} symmetry occur.^{17a}

^{(23) (}a) A small fold in the ring, as well as angular movement of the apical phosphine relative to the basal ligands does not alter the general bonding picture. (b) Hofmann, P.; Hämmerle, M.; Unfried, G. New J. Chem. 1991, 15, 769.

⁽²⁴⁾ Subscripts "s" and "a" are respectively symmetric and antisymmetric with respect to the xz plane.

of their small (δ) overlap (0.045) and large energy difference. The three occupied orbitals of the metal (1a₁, 1e_a, 1e_s) are mostly involved in four-electron destabilizing interactions with the occupied orbitals of the C₄H₄²-ligand and do not contribute to the stability of the complex. These orbitals will, however, play an important role in determining the reactivity of 8b.

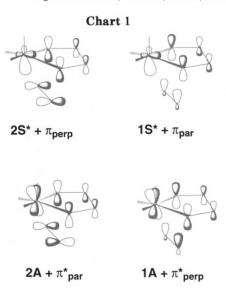
In consequence, although we cannot neglect the π character of the metallacycle, the small values of the Ir–C π bond indices (0.04) and the weak π -type electron transfer (0.14 electrons) between the two fragments suggest that it is not very pronounced. Thorn and Hoffmann commented on the weak π -conjugation in saturated Rh^{III}L₄-(C₄H₄),¹⁰ and the absence of one ligand L in our complex does not seem to cause a significant increase in π -conjugation.

It thus begins to appear that $P_3Ir(C_4H_4)^+$ has the orbital structure appropriate for an intermediate in the cyclotrimerization reaction. We have previously demonstrated that donation from the π_{\perp} orbital to the metal was central to the stability of the alkyne complex $P_3Ir(C_2H_2)^+$ (4); there is much less π donation (0.03 vs 0.14 electrons) in the metallacyclopentadiene. This should lead to noticeable differences in the reactivity toward an incoming ligand. It is also of interest to include the metallabenzene ring $P_3Ir(C_5R_5)^{11}$ in the comparison. The alkyne complex P₃Ir(C₂R₂)⁺ is reactive toward Lewis bases but may be isolated in the absence of such reagents; ${}^{3}P_{3}Ir(C_{4}R_{4})^{+}$ has not been isolated in the absence of a trapping ligand. In contrast, P₃Ir(C₅R₅) shows no marked reactivity toward Lewis bases. 11 A comparison of the energy of the LUMO is indicative in this case.

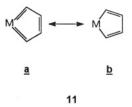
The LUMO energies for these three metallacycles are in the order $P_3Ir(C_4H_4)^+$ (-10.27 eV), $P_3Ir(C_2H_2)^+$ (-9.70 eV), $P_3Ir(C_5R_5)$ (-9.31 eV), which is in excellent agreement with the ordering of their reactivities toward Lewis bases. The LUMOs are derived predominantly from the interaction of the P_3Ir^{3+} 2e_s orbital with the closest π orbital of the carbon fragment which is symmetrical with respect to the xz plane. The low-lying LUMO of $P_3Ir(C_4H_4)^+$, 9, is



mainly the in-phase combination of 2es with the empty $C_4H_4^{2-}\psi_3$ (the occupied ψ_1 has a very weak influence), has bonding character, and is low-lying. The higher lying LUMO of $P_3Ir(C_2H_2)^+$, 5, is the out-of-phase combination of $2e_s$ and the acetylene π_{\perp} , which has a destabilizing effect on the LUMO. Finally, the highest LUMO, 10, of P₃Ir- (C_5R_5) is the out-of-phase combination of $2e_s$ with ψ_3 , the HOMO of $C_5H_5^{3-}$. The relationship between the energy of the LUMO and the degree of unsaturation of the metal can be derived from the above description. In $P_3Ir(C_4H_4)^+$, there is very little electron transfer from ψ_1 into $2e_s$ and the electron count at the metal is close to 16. In P₃Ir- $(C_2H_2)^+$, the electron transfer from π_{\perp} is larger and the electron count at the metal can be viewed as intermediate between 16 and 18. In P₃Ir(C₅H₅, the electron transfer from the HOMO of C₅H₅³- is large and the electron count at the metal is close to 18.



We have thus shown that the IrC_4 unit in the $P_3Ir(C_4H_4)^+$ intermediate has a planar ring structure. It is a 16-electron (Lewis-acidic) species, and the metal is only slightly stabilized by a small π donation from the conjugated carbon chain. Thus, the complex is better represented by 11b. Such small conjugation fails to permit isolation and characterization, yet it may be sufficient for the complex to serve as a reactive intermediate.



C. Reactivity of Metallacyclopentadiene. The reactivity of 8b with respect to an incoming ligand can be analyzed using a frontier orbital approach. The presence of a low-lying metal-centered LUMO, 9, accounts for the addition of a monodentate ligand (e.g., Cl-) at the metal. If the incoming ligand is an acetylene, the addition reaction is facilitated provided that there is a proper symmetry match between the frontier orbitals of the two reactants. The four frontier orbitals of 8b are the two occupied inphase orbitals (1A) and out-of-phase (2A, HOMO of π character) combinations of ψ_2 and $1e_a$ and the two vacant in-phase (1S*, LUMO, already shown as 9) and out-ofphase (2S*) combinations of $2e_s$ and ψ_3 . These four frontier orbitals are delocalized on both the metal and the ligand. The four alkyne orbitals $(\pi_{\parallel}, \pi^*_{\parallel}, \pi_{\perp}, \pi^*_{\perp})$ are ideally adapted to overlap with the four frontier orbitals of 8b in such a way that Ir-C and C-C bonds form in a concerted manner (Chart 1). Thus, the orbital π_{\parallel} interacts with 1S*, π_{\perp} with 2S*, π^*_{\perp} with 2A, and π^*_{\parallel} with 1A. These interactions lead to a product where the third alkyne makes up the central two carbons of an η^4 -benzene ligand.

How does the presence of an additional ligand (such as Cl) prevent the addition reaction of the alkyne? This aspect of the reaction was also remarked upon in an earlier experimental study. ^{19a} The rhodium metallacycle becomes active in the catalytic cycle only after removal of the halide ligand. In the presence of the halide, a Diels-Alder type reaction could have been envisaged with a direct interaction between the diene (the C₄H₄ moiety) and the dienophile, followed by the displacement of Cl⁻ by the

alkyne. This is not as suitable, firstly because of the obvious steric problem of getting the two reactants to a bonding distance. Secondly, the orbitals are no longer well adapted to interact with an alkyne. For example, the 1S* orbital is used by the chlorine and is no longer available for an incoming reagent.

We conclude that the addition of an alkyne to the metallacycle proceeds in a concerted manner to give an η^4 -benzene complex. This is the second step in the reaction mechanism in Figure 8. The reaction may be viewed as a metal-assisted Diels-Alder addition, where the metal plays an important role as a reactive center. This contrasts with the classical acid catalyzed Diels-Alder addition where the only role of the electrophile is to activate the diene, but not to form bonds to the dienophile.

 η^4 -Benzene Complex. A. Structure of the η^4 -Benzene Complex. In the complex $P_3Ir(C_6H_6)^+$, schematically shown in 12, the benzene ligand is η^4 -coordinated and thus resembles, in many aspects, a diene

complex. The terminal C(1)–C(2) and C(3)–C(4) bonds are elongated, and the central C(2)–C(3) bond is shortened. The conformation of the IrP_3^+ is also typical of diene complexes with one Ir–P bond below the mouth of the diene. In fact, the changes in bond lengths are considerably larger than those found in η^4 -diene complexes, 13, where an equalization of the three carbon–carbon bond lengths is generally observed. In the experimental η^4 -benzene complex, these changes are accentuated, as the central C–C bond (1.37 Å) is considerably shorter than the terminal C–C bonds (1.49 Å). Similar features have been observed in other η^4 -benzene complexes.²⁵

Two factors are responsible for the unusual C–C bond lengths in a bound η^4 -arene. First, fac- P_3 Ir $^+$ is a potent electron donor 3b and the empty orbitals of the conjugated ligand accept considerable electron density. In the diene complex, 13, the back-donation from the metal populates the diene LUMO (ψ_3) which is antibonding between the terminal carbons (C(1)–C(2) and C(3)–C(4)) and bonding between the two central (C(2)–C(3)) carbons.

The second factor controlling the C–C bond lengths in η^4 -arene complexes is related to the fact that the coordinated arene is no longer planar. The folding at C(1) and C(4) diminishes the π overlap between C(1) (C(4)) and C(2) (C(3)). We have simulated this effect by calculating the C–C bond orders in the free and coordinated butadiene using both planar and distorted structures (Table 4). In Table 4, these results are compared to the free and coordinated η^4 -benzene. It appears that the folding of the butadiene also weakens C(1)–C(2) and strengthens C(2)–C(3). Coordination to the metal fragment augments this effect until the C(1)–C(2) (C(3)–C(4)) bond orders are larger than that of C(2)–C(3). The observed C–C bond lengths in (tripod)Ir(η^4 -C₆H₆)⁺ are thus due to the

Table 4. Mulliken Overlap Population for the C-C Bonds in Butadiene and Benzene^a

dien	e	bond	planar C ₄ H ₆	dist C ₄ H ₆ ^b	η^{4} -C ₆ H ₆
free		C(1)-C(2)	1.18	1.15	1.01
		C(2)-C(3)	0.95	0.97	1.11
comple	exa	C(1)-C(2)	1.00	0.97	0.95
		C(2)-C(3)	1.04	1.06	1.10

^a All C-C bond lengths are equal to 1.4 Å to permit direct comparison. ^b The two endo H of the terminal C(1) and C(4) of butadiene are out of the plane of butadiene and are positioned along the C(1)-C(6) and C(4)-C(5) directions, as in the experimental η^4 -benzene complex. ^c Coordinated to Ir(PH₃)₃⁺.

combined effect of the potent electron-donating capacity of the Ir(I) center and the distortion of the benzene, which changes the hybridization at the C(1) and C(4) carbons. These features make the benzene a stronger electron acceptor than butadiene itself.

B. Fluxionality of the η^4 -Benzene Complex. How do all six benzene hydrogens, all six benzene carbons, and all three phosphines become time-average equivalent? We showed above that this process occurs without Ir-P bond cleavage and that a single activation energy governs both P and ring hydrogen fluxionality. We therefore now explore all plausible structures for the coordination of benzene to an intact [IrP₃]⁺ fragment. We shall see how what begins as a study of fluxionality will also explain the benzene-release step in the cyclotrimerization reaction.

Our approach to this problem is to analyze the different binding modes of $[IrP_3]^+$ to benzene. We have chosen to dissect the problem into two parts: (i) the flattening of the bent η^4 -coordinated benzene and (ii) the torsional and migrational motion of $[IrP_3]^+$ over a planar benzene. We assume that no dissociation of a phosphine occurs during this process. This dissection of the problem limits the degrees of freedom to a manageable number. However, this approach is chemically reasonable because there is a thermodynamic preference for a planar benzene and because it maintains a maximum use of metal d orbitals (i.e., number of Ir/C contacts).

(a) The Unlikelihood of $(\eta^6$ -benzene) IrP₃⁺. The $[(\eta^6$ -benzene) IrP₃]⁺, 14, is a 20-electron complex and is therefore highly unstable. The orbital pattern of an $(\eta^6$ -



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benzene) ML_3 is well-known.²⁶ The HOMO of 14 is one component of the degenerate pair arising from the antibonding combination of the 2e'' benzene orbitals with the 1e set of the IrP_3^+ fragment. The system should therefore be a spin triplet, but there is no evidence of paramagnetic species during the catalytic cycle, which suggests that a more stable diamagnetic intermediate exists. Jahn-Teller distortion of 14 provides some reasonable alternative structures which retain a planar benzene ring and are now evaluated as a mechanism for fluxionality.

(b) Site Exchange between the Planar Benzene Carbons. The energy variation for the movement of the $[IrP_3]^+$ fragment over a planar benzene ring at a fixed

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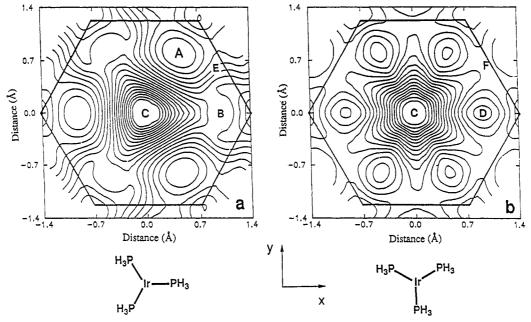


Figure 12. Potential energy surfaces for movement of (PH₃)₃Ir⁺ below the plane of the benzene surface. The distance between Ir and the benzene plane is equal to 1.9 Å. Energy levels are separated by 2 kcal/mol. For surface a, one Ir-P bond is kept parallel to the x axis. For surface b, one Ir-P bond is kept parallel to the y axis.

Ir/plane distance is represented by the two potential energy surfaces a and b (Figure 12). Each energy surface was calculated by allowing the metal to move over the ring without any rotation of the phosphines.

On surface a, one of the Ir-P bonds points away from the benzene ring center when θ (the rotation angle of one Ir-P bond projection with respect to the x axis) = 0.120. and -120° and toward the center of the ring when $\theta = 60$, 180, and -60°. On surface b, one of the Ir-P bonds bisects a benzene edge either away from or toward the center when $\theta = (30^{\circ} + n60^{\circ})$. The two surfaces, plotted using a common reference energy, permit a complete analysis of the haptotropic shift of the metal fragment which includes the rotation of the phosphines about the metal-

There are a number of important positions on each surface which require discussion. On both surfaces, the η^6 structure, 14, is calculated to be a maximum (point C) which means that the migration of the [IrP₃]⁺ fragment must occur without ever passing over the benzene ring center (a Jahn-Teller unstable structure). The absolute minimum on surface a is found at A ($\theta = 60^{\circ}$) and all the energies are quoted relative to this point. There is a secondary minimum at B ($\theta = 0^{\circ}$) at 12 kcal/mol. The minimum on surface b is at D (5 kcal/mol). The point F on surface b (just outside the ring) will also be important (10 kcal/mol). This region of space on surface a which has almost the same energy as F is called E.

The difference between A, D, and B corresponds to rotation by 30 or 60° of the IrP3 group around its C3 axis. At these points, the metal is close to three carbon centers and can be viewed as containing the η^3 -coordinated benzene complex. At E and F, which differ by a 30° rotation of IrP₃, the complex can be recognized as containing η^2 coordinated benzene. Rotation of the olefin is clearly a low-energy process for this latter structure.

The fluxional process requires movement of the metal over the ring (change in θ) combined with a rotation of the IrP₃ group with respect to the edges of the ring. Our energy surfaces lead to a description of the fluxional process as

a "waltz". Starting at the minimum A, the complex moves to E. At E, the rotation of the IrP₃ group is a low-energy process and it may rotate by 60°, via F (thus surface a \rightarrow surface b). The complex may then continue on surface b to a point which is B in terms of θ , but now the IrP₃ group has rotated by 60° and B has become an A point. This waltz continues, alternating between an A structure, where the metal is close to one apex of the hexagon, and an F structure, where the metal is close to the middle of an edge. The waltz is accompanied by rotation of IrP3 such that at each A point, an Ir-P bond points toward the center of the ring. In this process, all six carbons and all three phosphorus atoms become equivalent, without ever passing through the central (η^6) structure, C. The calculated energy cost of this migration is 12 kcal/mol.

This potential energy surface shows two structures which are low in energy and are best described as η^3 - and η^2 coordinated benzene. It is remarkable that the η^4 structure is not a minimum. The reason is that it could only exist with a strong distortion away from planarity of the benzene ring. Similar distortions are actually required to stabilize the η^2 structure (15). It should also be pointed out that although the site exchange process requires the sixmembered ring to be more planar than in the η^4 structure, total planarity need not be achieved. Our conclusions would not be affected by some folding of the ring during the metal migration. It appears that the carbon and phosphine exchange is a facile reaction. Unfortunately, EHT calculations do not readily permit more quantitative analysis of the exchange process.

Despite the planar ring constraint, these η^3 and η^2 structures have clear relationship with isolable related species. However, their molecular orbital scheme shows the presence of small HOMO-LUMO gaps. These species will not be isolated and are at best short-lived species.

(c) The Allyl Structure (η^3 -Benzene)IrP₃⁺. In the $(\eta^3$ -benzene)IrP₃+ species, the bonding of the three carbons to iridium resembles that of an allylic species. An η^3 coordination mode would polarize the benzene π orbitals in a (C_3^+, C_3^-) manner, with the negatively charged part bonded to the metal. Although this polarization is unlikely in free substituted benzene, such a structure may be still a reactive intermediate, provided that it is stabilized by the metal fragment. The preferred orientation of the three phosphines with one Ir-P bond below the open mouth of the allyl fragment (A) is also that observed in a d8 ML₃-(allyl) complex.27

(d) The η^2 -Benzene Complex. The (η^2 -benzene) Ir P_3 ⁺ species (with nonhybridized coordinated carbons or hybridized carbon like in 15) is very reactive because the

 η^2 -benzene gives only the two electrons of the coordinated double bond. The low-lying LUMO 16 is ideally suited for interacting with an incoming ligand. Therefore, unlike the d⁸ P₃Ir(alkyne) + complex in which the alkyne is acting as a 4-electron donor, the 16-electron η^2 -benzene complex can only be isolated with an additional ligand to the metal like in CpML(η^2 -benzene).²⁸ The rotation of the benzene ligand is energetically easy for the same reasons that rotation of alkyne is easy in the P₃Ir(alkyne)⁺ complexes.^{3b}

In conclusion, the energetically easy waltz of the metal fragment under the benzene ring as well as its rotation around its own C3 axis is the suggested route for the observed fluxional process.

(e) Alternative Mechanisms for Fluxionality. An alternative approach might be to consider the rearrangement to an η^2 -metallanorbornadiene form, 17. Passage

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through this structure does not exchange all carbons,29 and other structural reorganizations would be required if this intermediate were on the reaction path. Reaching the metallanorbornadiene structure implies an oxidation process at the metal. EHT calculations disfavor this intermediate by 70 kcal/mol, and although such a value should be treated with caution, it suggests that the metallanorbornadiene is an unlikely intermediate.

(29) It generates only a time-averaged mirror plane perpendicular to

the ring, but not a Ce axis.

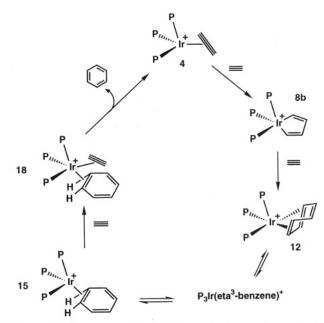


Figure 13. Representation of the catalytic reaction path for alkyne cyclotrimerization showing the relationship between the fluxionality of the η^4 -benzene ligand and the catalytic reaction.

(f) Reactivity of the η^4 -Benzene Complex. The benzene ring of the n^4 -benzene complex, 1, reacts with hydride to form a C-H bond and a σ -allyl complex. ³⁰ Since butadiene complexes do not react under similar conditions, we can assume that this addition does not occur in the ground state of the complex. The experiment was performed at a temperature where fluxionality is rapid, and from our interpretation of this process, we can propose two intermediates on the potential energy surface that may favor such an addition reaction. One of these is the η^3 -benzene complex, which has a polarization of the benzene π cloud such that some of the benzene carbons are electrophilic. This favors direct addition to the ring anti to the metal. The second is the η^2 complex, which has a vacant site at the metal, making it very reactive $toward\ nucleophilic\ attack\ and\ addition\ syn\ to\ the\ metal.$ While the experimental results do not allow us to distinguish between the two processes, the proposed exchange mechanism is clearly in full agreement with the reactivity of the complex.

(g) Relationship between the Site Exchange and Catalytic Processes. A scheme showing both the exchange and catalytic processes is given in Figure 13. Flattening the benzene ring from its ground state η^4 coordination, 12, results in a displacement of the metal away from its center toward an η^3 -coordination mode. Rotation of the IrP₃ fragment about its local C₃ axis is achieved via an η^2 -coordination mode. In the absence of an external reagent, the η^2 complex will convert into a different η^3 complex, which may return to the η^4 ground state structure or may continue to move over the benzene

In the presence of a new reagent, the very low-lying LUMO of the η^2 complex, 15, facilitates coordination of the reagent to give 18. If this reagent is an alkyne (which can serve as a 4-electron donor), the metal becomes too rich in electrons and one of the two ligands is forced to

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leave. The departure of the benzene is thermodynamically favorable because an uncoordinated benzene will recover its aromaticity and $IrP_3(alkyne)^+$ complexes, 4, are detectable species. The catalytic cycle can thus continue. Thus, since the fluxionality involves a decrease in hapticity of the C_6H_6 ligand, it naturally furnishes a path for displacement of the benzene product by the incoming monomer (alkyne).

Why is the catalytic cycle efficient? None of the intermediates species are "pure" 16-electron species, being more or less enriched by donation from the π systems of the carbon chains. However, they all have a low-lying LUMO and are reactive toward an incoming reagent. It is important that the metallic fragment has a fac (pyramidal) ML₃ geometry because this prevents the system from falling in the stable trigonal bipyramidal bis(alkyne) well, which is a dead end for the C-C coupling reaction. Similarly, the coordinated benzene complex should not be highly stable; otherwise the reaction would be stoichiometric and not catalytic. This aspect of the reaction has been examined by Chaudret et al., 31 who treated

[CpRu(OMe)]₂ in the presence of acetylene and CF₃SO₃H in CH₂Cl₂. This yields a stoichiometric amount of stable CpRu(η^6 -benzene)⁺. Since CpRu(η^6 -benzene)⁺ is a stable 18-electron species, it has no driving force to partially decoordinate the benzene ligand. This reduces the chances of a new acetylene molecule to coordinate and stops the catalytic cycle. The (tripod)Ir^I or (tripod)Rh^I fragments, with two additional electrons relative to CpRu⁺, have all the requirements to be efficient catalysts for alkyne cyclotrimerization.

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Supplementary Material Available: Tables of full crystal-lographic details and anisotropic thermal parameters for [(triphos)Ir(C₆H₆)](BPh₄) (3 pages). See any current masthead page for ordering information.

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