Mechanistic Study of $Ir(H)_2$-Assisted Transformations of Ethyne: Cyclotrimerization, Cooligomerization with Ethene, and Reductive Coupling

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The (ethene)dihydride complex $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$ (**1**) is capable of promoting a variety of transformations of ethyne, including cyclotrimerization to benzene, cooligomerization with ethene to hexa-1,3,5-triene, reductive coupling to buta-1,3-diene, and hydrogenation to ethene (triphos = $MeC(CH_2PPh_2)_3$). A detailed study under various experimental conditions, the detection of several intermediates along the various reaction paths, and the use of isolated complexes in independent reactions, taken together, permit mechanistic conclusions that account for the varied products. In particular, the cyclotrimerization and cooligomerization reactions are mediated by an iridacyclopentadiene species which is trapped by either ethyne or ethene. Consumption of the hydride ligands of **1** by C_2H_2 or C_2H_4 is an ingredient for both cyclotrimerization and cooligomerization reactions but is not necessary to accomplish the reductive dimerization of ethyne to buta-1,3-diene for which, conversely, the two hydride ligands are mandatory.

Introduction

The formation of carbon–carbon bonds mediated by transition-metal systems has emerged in the last decade as a major goal of experimental organometallic chemistry. Among the group of organic molecules most frequently studied in metal-assisted C–C bond-forming reactions, alkynes play a prominent role as is evident from their participation in numerous transformations of both fundamental and industrial relevance (cyclodimerization,[2] dimerization,[3] reductive dimerization,[4] cyclooligomerization,[5] polyoligomerization,[6] oxidative coupling,[5g-l,7] cooligomerization with alkenes and dienes,[5d,8] Reppe carbonylation,[9] etc.).

In this wide field of interest, understanding the primary interactions between the transition metal and the alkyne, particularly the mechanism of formation of the first C–C bond, is of key importance for developing selective processes. In this paper, we report a detailed study of the homogeneous reactions of the simplest alkyne, ethyne, with a number of iridium(I) and iridium(III) complexes stabilized by the tripodal triphosphine ligand $MeC(CH_2PPh_2)_3$ (triphos).

The major factor that distinguishes the system under study here from other metal-assisted transformations of ethyne so far investigated is the ability of the [(triphos)Ir] fragment to trap an unforeseen variety of intermediate species along the course of three relevant functionalization reactions of ethyne: cyclotrimerization to benzene, cooligomerization with ethene to hexa-1,3,5-triene, and reductive coupling to buta-1,3-diene.

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Experimental Section

General Procedures. All reactions and manipulations were routinely performed under nitrogen, except where otherwise stated, by using Schlenk-like techniques. Reagent grade chemicals were used in the preparation of the complexes. Tetrahydrofuran (THF) was purified by distillation from $LiAlH_4$ under nitrogen. All the other solvents were reagent grade and were used as received. Hexa-1,3,5-triene was purchased as a mixture of cis and trans isomers from Aldrich. Literature methods were used for the preparation of triphos,[10] $[Ir(COE)_2Cl]_2$ (COE = cyclooctene),[11] $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$ (**1**),[12] $[(triphos)Ir(C_2H_4)_2]BPh_4$ (**3**),[12] $[(triphos)Ir(H)_2(C_2H_5)]$,[12] and $[(triphos)IrCl(C_4H_4)]$ (**8**).[13] The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. $^{13}C_2H_4$ (99% enriched) was obtained from K&K-Greff Limited. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian VXR 300 (299.94, 121.42, and 75.43 MHz, respectively) or a Bruker ACP 200 (200.13, 81.01, and 50.32 MHz, respectively) spectrometer. Chemical shifts are relative either to residual ^1H resonances in the deuterated solvents (^1H NMR), the deuterated solvent resonance ($^{13}C\{^1H\}$ NMR), or the external 85% H_3PO_4, with downfield values reported as positive ($^{31}P\{^1H\}$ NMR). Broad-band and selective $^1H\{^{31}P\}$ NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. In general, the assignment of the proton and carbon chemical shifts was done on the basis of $^1H,^1H$ 2D-COSY, ^{13}C DEPT, and $^1H,^{13}C$ 2D-HETCOR NMR experiments; these experiments were conducted on the Bruker ACP 200 instrument. The computer simulation of NMR spectra was carried out with a locally developed package containing the programs LAOCN3[14] and DAVINS,[15] 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 experimental digitized spectra. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor R being less than 1% in all cases. 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.

Reaction of $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$ (1) with Ethyne. NMR Experiments. (A) Low temperature. A sample of **1** (ca. 0.03 mmol) was dissolved in CD_2Cl_2 (0.7 mL) in a 5-mm NMR tube under nitrogen. After two freeze/pump/thaw cycles at −196 °C, the solution was frozen and pumped on at −196 °C. After adding ethyne (ca. 2 equiv), the tube was sealed and then introduced into a NMR probe precooled at −70 °C. The reaction was then followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The reaction between **1** and ethyne already occurred at −50 °C. At the beginning, when the reagent ratio is approximately 1:2 (i.e., ethyne is the limiting reagent), the first intermediate detected shows an AM_2 $^{31}P\{^1H\}$ NMR pattern (δP_A −7.5, δP_M −23.2, $J(P_AP_M)$ = 16.2 Hz) and an AA′XX′Y ^1H NMR pattern in the hydride (A) region (δ −10.81, $|J(AX) + J(AX')|$ = 122.2 Hz, $J(AY)$ = 12.6 Hz). The phosphorus and hydride chemical shifts are within 1 ppm of those of **1**,[12] and we assign this product as $[(triphos)Ir(H)_2(C_2H_2)]BPh_4$ (**2**) (δ 3.02, π-C_2H_2). Thus, ethene substitution by ethyne is the first reaction. Free ethene is also detected (^1H NMR). Resonances for H_2 and C_2H_6 are absent. With time, free ethene is consumed and (under conditions of ethyne deficiency) **2** disappears. Formed in its place (^{31}P and ^1H NMR detection) are small amounts of $[(triphos)Ir(C_2H_4)_2]BPh_4$ (**3**),[12] $[(triphos)Ir(\pi\text{-}C_2H_2)]BPh_4$ (**4**), $[(triphos)Ir\{(1\text{-}\eta^1\text{:}4\text{-}6\text{-}\eta^3)\text{hexatriene}\}]BPh_4$ (**5**) (see below), and larger quantities of $[(triphos)Ir(\eta^4\text{-}C_6H_6)]BPh_4$ (**6**).[16] When additional ethyne is added to the solution at −50 °C, this same progression of production of **2**, then **3**, **4**, **5**, and **6** is observed. Finally, when excess ethyne is added and the solution allowed to stand at 25 °C, one observes essentially complete conversion to **5** and **6** in a 8:92 ratio; **2**, **3**, and **4** are completely consumed and ethene is liberated. The $^{31}P\{^1H\}$ NMR spectrum of intermediate **4** consists of an A_3 pattern (δ 6.2), while the ^1H NMR spectrum contains a quartet at 11.92 ppm ($J(HP)$ = 7.5 Hz) in the expected region of four-electron donor alkyne ligands. The $^{31}P\{^1H\}$ and ^1H NMR data of **4** are quite comparable with those of the known π-phenylacetylene complex $[(triphos)Ir(\pi\text{-}HC_2Ph)]BPh_4$.[17]

(B) Room temperature. CD_2Cl_2 (0.7 mL) was saturated with ethyne at 20 °C and then transferred into a screw cap 5-mm NMR tube containing a solid sample of **1** (0.03 mmol). $^{31}P\{^1H\}$ and ^1H NMR spectra, immediately recorded, showed the complete disappearance of the starting complex and formation of **4**, **5**, **6**, and $[(triphos)Ir(\eta^4\text{-}C_4H_6)][BPh_4$ (**7**) (see below). Free ethane and ethene were also detected (^1H NMR, singlets at 0.9 and 5.4 ppm, respectively). Within 15 min, **4** completely disappeared to give **5**, **6**, and **7** in a ratio of 30:67:3 and free ethane and ethene in a ca. 1:2 ratio. This product distribution did not change with time. An almost identical product distribution of this reaction was observed on a large scale (0.8 g of **1** in THF) for isolated compounds. When the isolated mixture was heated in THF-d_8 saturated with ethyne at 70 °C, we observed no apparent reaction involving **6**[18] or **7**, whereas **5** transformed into its *s-cis,s-cis*−*trans*-1-4-η^4-hexa-1,3,5-triene isomer **9** (see below).

Large-Scale Experiment under a Steady Stream of Ethyne. A sample of **1** (0.8 g, 0.64 mmol) was dissolved in THF (80 mL) under a steady stream of ethyne at room temperature. After 1 h, a ^{31}P NMR spectrum of a sample of the resulting orange solution showed the complete conversion of **1** to a mixture of **6** and **7** in ca. 95:5 ratio. No trace of **5** was observed. After ethyne was replaced by nitrogen, ethanol (40 mL) was added to the rest of the solution. Partial evaporation of the solvent resulted in the precipitation of yellow crystals which were filtered off and washed with *n*-pentane. Several recrystallizations from THF and ethanol gave pure samples of **6** in 80% yield. An almost identical product ratio was obtained when **1** was added to refluxing THF under a steady stream of ethyne.

Reaction of $[(Triphos)Ir(C_2H_4)_2]BPh_4$ (3) with Ethyne. (A) Low Temperature. A solution of **3** and ethyne (ca. 2 equiv) in CD_2Cl_2 was prepared in a NMR tube as described above for the reaction at low temperature between **1** and ethyne. The progress of the reaction at −50 °C was then followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. A large part of **3** disappears and formed in its place are **4** and small amounts of **5** and **6**. Free ethene is also detected (^1H NMR, singlet at 5.4 ppm). When excess ethyne was added to the solution at −50 °C, the same progression of production of **4**,

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5, and **6** is observed. With time, **3** and **4** completely disappeared to give **5** and **6** in a ca. 10:90 ratio.

(B) Room Temperature. CD_2Cl_2 (0.7 mL) was saturated with ethyne at 20 °C and then transferred into a screw cap 5-mm NMR tube containing a solid sample of **3** (0.03 mmol). $^{31}P\{^1H\}$ and ^1H NMR spectra, immediately recorded, showed the complete disappearance of the starting complex and formation of **4** along with the larger amounts of **5** and **6**. Free ethene was also detected (^1H NMR, singlet at 5.4 ppm). Within 15 min, **4** completely disappeared to give **5** and **6** in ca. 10:90 ratio.

Independent Synthesis of [(Triphos)Ir(η^4-C_4H_6)]BPh_4 (7). Solid $[Ir(COE)_2Cl]_2$ (0.45 g, 0.5 mmol) was added to a solution of triphos (0.62 g, 1 mmol) in a buta-1,3-diene-saturated THF (40 mL) solution at room temperature. After 1 h, $NaBPh_4$ (0.32 g, 1 mmol) in ethanol (40 mL) was added to the resulting red solution, which immediately turned orange. On addition of ethanol (40 mL) and slow concentration, pale yellow crystals of **7** precipitated; yield 85%. Anal. Calcd (Found) for $C_{69}H_{65}BIrP_3$: C, 69.63 (69.51); H, 5.51 (5.46); Ir, 16.15 (16.02). $\lambda_M = 49$ cm^2 Ω^{-1} mol^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.42 MHz): 30 °C, A_3 pattern, δ −23.4 (br); −58 °C, AM_2 pattern, δP_A −25.0, δP_M −22.5, $J(P_AP_M) = 6.9$ Hz.

Reaction of [(Triphos)IrCl(η^2-C_4H_4)] (8) with Ethene in the Presence of $TlPF_6$. A solid sample of **8** (0.30 g, 0.33 mmol) was added to a stirred THF (30 mL) solution of $TlPF_6$ (0.12 g, 0.34 mmol) under a steady stream of ethene at 0 °C. Within a few minutes the solid dissolved to give a red-orange solution. After 2 h, TlCl was eliminated by filtration and then $NaBPh_4$ (0.17 g, 0.50 mmol) in ethanol (10 mL) was added, followed by *n*-heptane (50 mL). On partial evaporation of the solvents under a stream of nitrogen, rust red crystals of [(triphos)Ir{(1-η^1:4-6-η^3)-hexatriene}]BPh_4 (**5**) precipitated in 80% yield. Anal. Calcd (Found) for $C_{71}H_{67}BIrP_3$: C, 70.11 (70.00); H, 5.55 (5.63); Ir, 15.80 (15.69). $\lambda_M = 54$ cm^2 Ω^{-1} mol^{-1}. IR: ν(C=C) 1644 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 81.01 MHz): AMQ pattern, δP_A −17.4, δP_M −27.7, δP_Q −36.5, $J(P_AP_M) = 22.0$ Hz, $J(P_AP_Q) = 7.3$ Hz, $J(P_MP_Q) = 25.6$ Hz. **5** is rather unstable in ambient-temperature solutions, slowly converting to its η^4-hexa-1,3,5-triene isomer **9** (see below) (in THF at 20 °C, we observe ca. 50% conversion in 24 h). Solid samples of **5** are stable when stored under nitrogen at low temperature, whereas at room temperature, isomerization to **9** occurs also in the solid state (ca. 50% conversion in 3 weeks).

Reaction of [(Triphos)IrCl(η^2-C_4H_4)] (8) with $^{13}C_2H_4$ in the Presence of $TlPF_6$. The iridacyclopentadiene complex **8** (0.03 g, 0.03 mmol) and a stoichiometric amount of $TlPF_6$ (0.01 g, 0.03 mmol) were dissolved in THF-d_8 (0.7 mL) at −10 °C (a temperature at which no reaction between the two compounds occurs). The resulting solution was transferred to a 5-mm NMR tube maintained at −10 °C. This solution was then degassed (freeze/pump/thaw, three cycles) and the tube was charged with a 3-fold excess of $^{13}C_2H_4$ (99 atom %) and flame sealed. The tube was then shaken at room temperature for 3 h. $^{31}P\{^1H\}$ NMR (81.01 MHz): AMQXY pattern, δP_A −17.6, δP_M −27.8, δP_Q −36.5, $J(P_AP_M) = 22.0$ Hz, $J(P_AP_Q) = 7.4$ Hz, $J(P_MP_Q) = 25.6$ Hz, $J(P_MC_1) = 62.0$ Hz, $J(P_AC_1) = 3.4$ Hz, $J(P_QC_1) = 3.4$ Hz, $J(P_MC_2) = 10.4$ Hz. $^{13}C\{^1H\}$ NMR (50.32 MHz): enhanced intensity (i.e., enriched) at only δC_1 28.7, δC_2 146.0, $J(C_1C_2) = 58.2$ Hz.

Thermal Isomerization Reaction of [(Triphos)Ir{(1-η^1:4-6-η^3)-hexatriene}]BPh_4 (5). (A) A THF (30 mL) solution of **5** (0.30 g, 0.25 mmol) was heated at 70 °C. After 4 h, the solution was concentrated to dryness under vacuum to give [(triphos)Ir(*s-trans,s-cis−cis*-1-4-η^4-hexa-1,3,5-triene)]BPh_4 (**9**) as a pale yellow solid. Recrystallization from CH_2Cl_2 and *n*-heptane gave pale yellow microcrystals which were washed with *n*-pentane and collected by filtration; yield 85%. Anal. Calcd (Found) for $C_{71}H_{67}BIrP_3$: C, 70.11 (69.89); H, 5.55 (5.48); Ir, 15.80 (15.63). $\lambda_M = 53$ cm^2 Ω^{-1} mol^{-1}. IR: ν(C=C) 1616 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C, 81.01 MHz): AMQ pattern, δP_A −22.8, δP_M −24.6, δP_Q −25.8, $J(P_AP_M) = 9.6$ Hz, $J(P_AP_Q) = 18.4$ Hz, $J(P_MP_Q) = 8.8$ Hz.

(B) When a THF solution of **5** was heated at 90 °C for 4 h, the recovered solid was characterized as a 58:42 mixture of **9** and [(triphos)Ir(*s-trans,s-cis−trans*-1-4-η^4-hexa-1,3,5-triene)]BPh_4 (**10**) (see below).

Thermal Isomerization Reaction of [(Triphos)Ir(*s-trans,s-cis−cis*-1-4-η^4-hexa-1,3,5-triene)]BPh_4 (9). A THF (30 mL) solution of **9** (0.20 g, 0.16 mmol) was heated at 90 °C. After 6 h, the solution was concentrated to dryness under vacuum to give [(triphos)Ir(*s-trans,s-cis−trans*-1-4-η^4-hexa-1,3,5-triene)]BPh_4 (**10**) as a pale yellow solid. Recrystallization from CH_2Cl_2 and *n*-heptane gave pale yellow microcrystals which were washed with *n*-pentane and collected by filtration; yield 80%. Anal. Calcd (Found) for $C_{71}H_{67}BIrP_3$: C, 70.11 (70.23); H, 5.55 (5.47); Ir, 15.80 (15.70). $\lambda_M = 49$ cm^2 Ω^{-1} mol^{-1}. IR: ν(C=C) 1616 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C, 81.01 MHz): AMQ patten, δP_A −13.3, δP_M −27.7, δP_Q −31.7, $J(P_AP_M) = 4.6$ Hz, $J(P_AP_Q) = 21.1$ Hz, $J(P_MP_Q) = 6.5$ Hz.

Independent Synthesis of *s-trans,s-cis−cis* 9 and *s-trans,s-cis−trans* 10. [(Triphos)Ir(*trans*-1-4-η^4-hexa-1,3,5-triene)]BPh_4 Isomers. A solid sample of [(triphos)Ir-(C_2H_4)$_2$]BPh_4 (0.41 g, 0.34 mmol) was dissolved into a THF (40 mL) solution of hexa-1,3,5-triene (mixture of isomers, 0.38 mL, 3.4 mmol) at room temperature. After 2 h, ethanol (10 mL) and *n*-heptane (60 mL) were added to the resulting pale yellow solution. On standing, an approximately 40:60 mixture of **9** and **10** precipitated as pale yellow crystals. They were filtered off and washed with *n*-pentane; yield 95%.

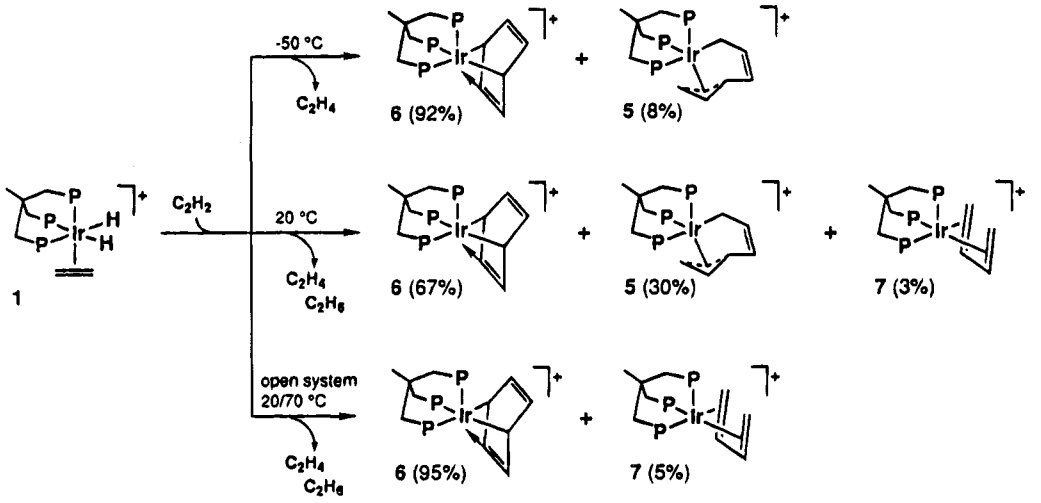
Synthesis of [(Triphos)Ir(H)$_2$(THF)]BPh_4 (11). Neat $HOSO_2CF_3$ (42 μL, 0.47 mmol) was syringed into a stirred suspension of [(triphos)Ir(H)$_2$(C_2H_5)] (0.40 g, 0.47 mmol) in THF (50 mL). Within a few minutes the solid dissolved to give a colorless solution. After 1 h, $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (10 mL) was added to the resulting solution, followed by *n*-heptane (30 mL). On standing overnight, under a steady stream of nitrogen, **11** precipitated as an off-white solid, which was collected by filtration and washed with a 1:1 mixture of ethanol and *n*-pentane and then *n*-pentane; yield 75%. Anal. Calcd (Found) for $C_{69}H_{69}BIrOP_3$: C, 68.48 (68.37); H, 5.75 (5.81); Ir, 15.88 (15.69). $\lambda_M = 53$ cm^2 Ω^{-1} mol^{-1}. IR: ν(Ir−H) 2050 cm^{-1}. $^{31}P\{^1H\}$ NMR (THF-d_8, 20 °C, 81.01 MHz): AM_2 pattern; $\delta(P_A)$ −1.6, $\delta(P_M)$ −6.3, $J(P_AP_M) = 11.7$ Hz. ^1H NMR (THF-d_8, 20 °C, 200.13 MHz): δ −6.70 (second-order doublet of multiplets computable as the AA′ part of an AA′XX′Y spin system, where X and Y denote the triphos phosphorus atoms, $|J(AX) + J(AX')| = 127.2$ Hz, $J(AY) = 14.7$ Hz, Ir*H*).

Occasionally, NMR spectra of the samples also showed variable amounts of one or two other products exhibiting quite similar AM_2 $^{31}P\{^1H\}$ NMR patterns and AA′XX′Y ^1H NMR patterns in the hydride region. The phosphorus and the hydride chemical shifts were very close to those of **11**. These products were recognized as the solvento complexes [(triphos)-Ir(H)$_2$(solv)]BPh_4 (solv = ethanol, **12**; H_2O, **13**) obtained by displacement of coordinated THF by either ethanol or adventitious water in the reaction mixture. Addition of excess of either ethanol or H_2O to THF-d_8 solutions of **11** resulted in quantitative formation of **12** and **13**, respectively. The THF complex **11** is unstable in CH_2Cl_2; precipitation of a yellow-orange crystalline solid occurs within a few minutes after dissolution. The nature of this product is currently under investigation.

[(Triphos)Ir(H)$_2$(EtOH)]BPh_4 (12). $^{31}P\{^1H\}$ NMR (THF-d_8, 20 °C, 81.01 MHz): AM_2 pattern; $\delta(P_A)$ −1.4, $\delta(P_M)$ −8.0, $J(P_AP_M) = 12.8$ Hz. ^1H NMR (THF-d_8, 20 °C, 200.13 MHz): δ(hydrides) −6.91 (second-order doublet of multiplets computable as the AA′ part of an AA′XX′Y spin system, where X and Y denote the triphos phosphorus atoms), $|J(AX) + J(AX')| = 127.6$ Hz, $J(AY) = 14.1$ Hz.

[(Triphos)Ir(H)$_2$(OH$_2$)]BPh_4 (13). $^{31}P\{^1H\}$ NMR (THF-d_8, 20 °C, 81.01 MHz): AM_2 pattern; $\delta(P_A)$ −0.8, $\delta(P_M)$ −10.0, $J(P_AP_M) = 13.5$ Hz. ^1H NMR (THF-d_8, 20 °C, 200.13 MHz):

Scheme 1



δ(hydrides) −6.97 (second-order doublet of multiplets computable as the AA′ part of an AA′XX′Y spin system, where X and Y denote the triphos phosphorus atoms), $|J(AX) + J(AX')| = 129.7$ Hz, $J(AY) = 13.6$ Hz.

Reaction of [(Triphos)Ir(H)$_2$(THF)]BPh$_4$ (11) with Ethyne. (A) Reflux Temperature. A solid sample of **11** (0.18 g, 0.15 mmol) was dissolved into refluxing THF (30 mL) under an ethyne atmosphere. After 30 min, the solution was concentrated to dryness in vacuo and the residue washed with *n*-pentane. Multinuclear NMR spectroscopy indicated the complete conversion of **11** to a 93:7 mixture of [(triphos)Ir(η^4-C_4H_6)]BPh$_4$ (**7**) and [(triphos)Ir(η^4-C_6H_6)]BPh$_4$ (**6**).

(B) Room Temperature. A THF (30 mL) solution of **11** (0.18 g, 0.15 mmol) was stirred under an ethyne atmosphere at room temperature for 2 h. A ^{31}P NMR spectrum (THF/THF-d_8, 1:1 v/v) of a sample of the resulting yellow solution showed the selective conversion of **11** to **7**. Addition of ethanol (30 mL) to the rest of the solution and partial evaporation of the solvent under a steady stream of nitrogen led to the precipitation of a pure sample of **7** as pale yellow crystals. They were collected by filtration and washed with ethanol and *n*-pentane; yield 90%.

(C) Low Temperature. A sample of **11** (ca. 0.02 mmol) was dissolved in THF-d_8 (0.7 mL) in a 5-mm NMR tube under nitrogen. After two freeze/pump/thaw cycles at −196 °C, the solution was frozen and pumped on at −196 °C. After adding ethyne (ca. 3 equiv), the tube was sealed and then introduced into a NMR probe precooled at −50 °C. The reaction was then followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The reaction between **11** and ethyne occurred at ca. −10 °C. On following the progress of the reaction, only the signals due to **11** and **7** were observed; no intermediates were detected. The reaction was complete in ca. 1 h. Analogous evidence was obtained by using an excess of ethyne. When the experiment was performed in CD_2Cl_2, the reaction already occurred at −40 °C. However, in this case also, only clean conversion of **11** to **7** was observed. A small amount of the unknown orange product that forms by dissolving **11** in CH_2Cl_2 (see synthesis of **11**) precipitated in the NMR tube during the experiment.

Results

Reaction of [(Triphos)Ir(H)$_2$(C_2H_4)]BPh$_4$ with Ethyne under Different Experimental Conditions. Reaction of the (ethene)dihydride **1** with an excess of ethyne in THF (or CH_2Cl_2) at 20 °C in a closed system results in evolution of ethane and ethene in an approximate ratio of 1:2 and formation of [(triphos)Ir(η^4-C_6H_6)]BPh$_4$ (**6**), [(triphos)Ir{(1-η^1:4-6-η^3)hexatriene}]-BPh$_4$ (**5**), and [(triphos)Ir(η^4-C_4H_6)]BPh$_4$ (**7**) in a ratio of 67:30:3 (Scheme 1). Initially, one may observe the formation of some π-ethyne complex [(triphos)Ir(π-C_2H_2)]BPh$_4$ (**4**), which rapidly disappears. The observed product ratio does not change with reaction temperature up to 70 °C, although slow intramolecular rearrangement of **5** to its 1,4-η^4-hexatriene isomer [(triphos)Ir(*s-trans,s-cis*−*cis*-1-4-η^4-hexa-1,3,5-triene)]BPh$_4$ (**9**) occurs (vide infra).

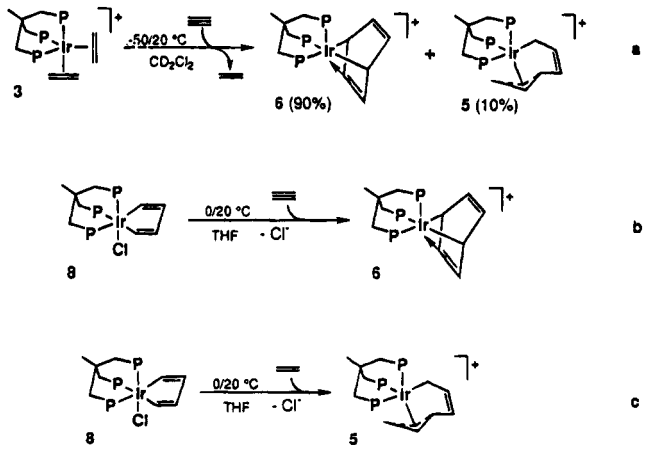
At −50 °C, the course of the reaction between **1** and ethyne is quite different. Ethane is not evolved, the η^4-butadiene complex is not formed, and the η^4-benzene complex becomes the predominant product (the ratio of **6** to **5** is 92:8). As shown by an in situ NMR study, displacement of ethene from **1** by ethyne to give the (π-ethyne)dihydride [(triphos)Ir(H)$_2$(C_2H_2)]BPh$_4$ (**2**) is the first step of the reaction. Later, ethene reenters the metal coordination sphere to form the bis(ethene) complex [(triphos)Ir(C_2H_4)$_2$]BPh$_4$ (**3**), which in turn undergoes displacement of ethene by ethyne to give the π-ethyne complex **4**. From this intermediate, both the η^4-benzene and the 1-η^1:4-6-η^3-hexatriene complex are formed through the common intermediacy of an iridacyclopentadiene derivative of the formula [(triphos)Ir-(η^2-C_4H_4)]$^+$ (vide infra), which can add ethene and ethyne, respectively. The necessary presence of ethene in the reaction mixture for the formation of **5** is clearly demonstrated by the fact that no trace of the hexatriene complex is observed when the reaction is performed in an open system where evolved ethene is carried outside the reactor by the steady stream of ethyne (Scheme 1).

Analysis of the time evolution of NMR spectra of the reaction at −50 °C clearly shows that, under the experimental conditions, the displacement of ethene from **1** by ethyne is faster than its subsequent return to the metal. The latter step is slower than those leading to formation of **3** and **4** (and following), which accounts for the very small concentrations of **3** and **4** detected. A function of ethyne is thus to consume the two hydride ligands of **1** and be converted to ethene, but this reaction only occurs in the presence of dissolved ethene by its action as an incoming ligand (vide infra).

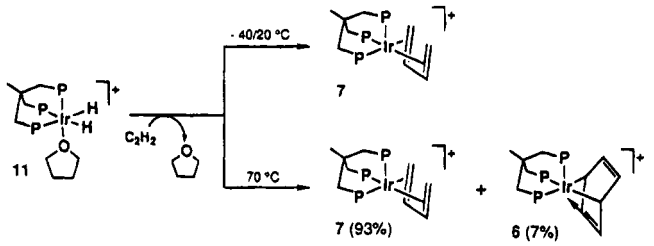
A number of independent reactions have been performed, which provide additional experimental evidence supporting the reaction sequence observed in the low-temperature reaction:

(i) The bis(ethene) complex **3** has been shown to react

Scheme 2



Scheme 3



with ethyne below 20 °C to give free ethene and the π-ethyne intermediate **4**, which rapidly disappears. Formed in its place are the 1-η^1:4-6-η^3-hexatriene complex **5** and a larger amount of the η^4-benzene **6** (10:90 ratio) (Scheme 2a).

(ii) The known iridacyclopentadiene complex [(triphos)IrCl(η^2-C_4H_4)] (**8**) reacts with ethyne below 20 °C in the presence of a chloride scavenger such as $TlPF_6$ to give quantitatively the η^4-C_6H_6 complex **6** (Scheme 2b).[13]

(iii) The iridacyclopentadiene complex **8** reacts with ethene in THF below 20 °C in the presence of $TlPF_6$ to give selectively the 1-η^1:4-6-η^3-hexatriene complex **5** (Scheme 2c).

An explanation for the formation of some η^4-butadiene complex **7** only when **1** is reacted with ethyne at room or higher temperatures will be given in a forthcoming section.

Reaction of [(Triphos)Ir(H)₂(THF)]BPh₄ with Ethyne under Different Experimental Conditions. To contrast the situation when the initial ligand L in [(triphos)Ir(H)$_2$(L)]$^+$ is not ethene (thus altering the second step of the reaction between **1** and ethyne by virtue of the absence of free C_2H_4), we have studied the analogous reaction of ethyne with the solvento complex [(triphos)Ir(H)$_2$(THF)]BPh_4 (**11**).

In the temperature range from −40 to 20 °C, the reaction selectively gives the η^4-C_4H_6 complex **7**. No intermediate species was detected by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (Scheme 3). At 70 °C, **7** is still the predominant product, but appreciable formation (7%) of the η^4-C_6H_6 complex **6** is observed, suggesting the concomitant occurrence of an alternative process at higher energy than the one leading to formation of the η^4-butadiene complex.

Chemical and Spectroscopic Characterization of the New Complexes. [(Triphos)Ir{(1-η^1:4-6-η^3)-hexatriene}]BPh_4 (5) and its η^4-Hexatriene Isomers (9, 10). Formally **5** is the product of a metal-assisted condensation of two ethyne molecules with one ethene molecule. The resulting cooligomerized ligand (linear C_6H_8) uses a terminal CH_2 group and the allyl portion constituted by the C_6, C_5, and C_4 carbon atoms to bind the iridium center (see sketch in Table 1). To the best of our knowledge, this bonding mode of hexatriene has no precedent, whereas a few examples of hexatriene ligands bonded via two η^3-allyl moieties to different metal centers in polynuclear complexes have been reported.[19a,b] In particular, an X-ray structure is available for [$(CpCo)_2(\mu$-η^3:η^3-Ph$(CH)_6$Ph)].

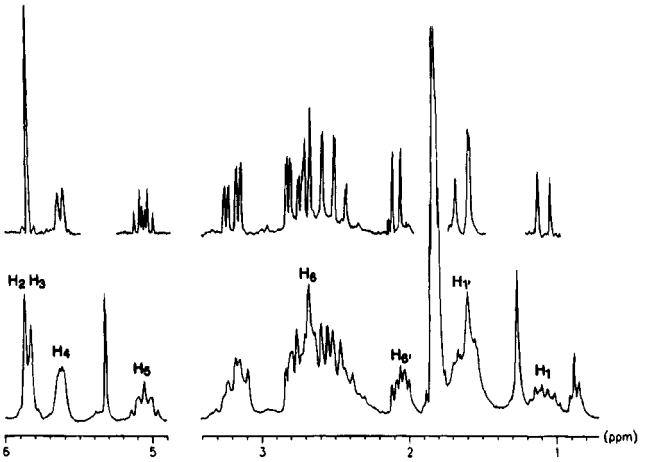


Figure 1. Broad-band $^1H\{^{31}P\}$ (inset, above) and ^1H NMR spectra of **5** in the 6.0−4.9 and 3.4−0.7 ppm regions (CD_2Cl_2, 20 °C). Unlabeled resonances are due to triphos ligand.

The structural assignment for **5** has been corroborated by a number of both spectroscopic (^1H,^1H 2D-COSY, ^{13}C DEPT, and ^1H,^{13}C 2D-HETCOR NMR) and chemical experiments. The ^1H and $^1H\{^{31}P\}$ NMR spectra of **5** are shown in Figure 1. It may be useful to point out some relevant spectroscopic features. The $J(H_5H_4)$ and $J(H_5H_6)$ values (ca. 7 Hz) indicate that H_4 and H_6 occupy syn positions in the η^3-allyl moiety; the $J(H_5H_{6'})$ value of 10.8 Hz is in accord with previous findings for central and anti hydrogens of η^3-allyl ligands.[20,21] Also, it is worth mentioning that both the hydrogen and carbon chemical shifts relative to the C_2H=C_3H fragment are typical of *free* olefins, which is consistent with the presence of a ν(C=C) band at 1644 cm^{-1} in the IR spectrum (Nujol mulls). Finally, $^{13}C\{^1H\}$ NMR chemical shift and coupling to phosphorus of C_1 show that the CH_2 group is σ-bonded to the metal.

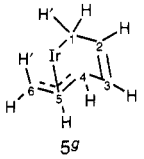
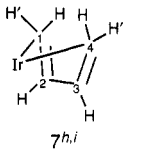
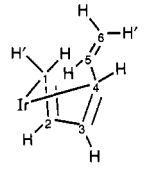
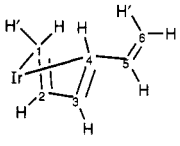
5 is slightly unstable in both the solid state and ambient-temperature solutions and slowly rearranges to its *s-trans,s-cis*−*cis*-1-4-η^4-hexa-1,3,5-triene isomer **9**. At 70 °C in THF solution, the isomerization is complete in 4 h. Above 80 °C, a second isomerization process occurs that converts **9** to the isomer [(triphos)Ir(*s-trans,s-cis*−*trans*-1-4-η^4-hexa-1,3,5-triene)]BPh_4 (**10**) (Scheme 4). The **9** to **10** conversion is quantitative after

(19) (a) Wadepohl, H.; Büchner, K.; Pritzkow, H. *Organometallics* **1989**, *8*, 2745. (b) King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4846. (c) Powell, P. *J. Organomet. Chem.* **1983**, *244*, 393. (d) McArdle, P.; Sherlock, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1678.

(20) (a) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164. (b) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516. (c) Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129.

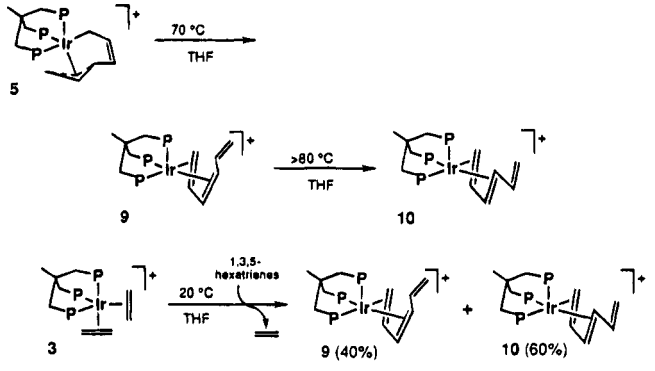
(21) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

Table 1. Selected NMR Spectral Data for the Complexes[a]

complex	^{1}H NMR assign	^{1}H NMR δ (multiplicity, J)[b,c]	^{13}C{^{1}H} NMR assign	^{13}C{^{1}H} NMR δ (multiplicity, J)[b]
 5[g]	H_2,H_3	5.84 (m)[d]	C_2	146.1 (d, ^3J(CP) = 10.4)
	H_4	5.61 (m, $^3J(H_4H_5)$ = 7.2)	C_3	136[e]
	H_5	5.05 (m, $^3J(H_5H_{6'})$ = 10.8, $^3J(H_5H_6)$ = 7.1)	C_5	97.5 (s)
	H_6	2.7[f]	C_4	87.6 (d, ^2J(CP) = 25.2)
	$H_{6'}$	2.05 (m)	C_6	47.1 (d, ^2J(CP) = 30.4)
	$H_{1'}$	1.65 (m, $^2J(H_1H_1)$ = 16.8)	C_1	28.6 (dt, $^2J(CP_{trans})$ =
	H_1	1.08 (m)		61.9, $^2J(CP_{cis})$ = 3.4)
 7[h,i]	H_2,H_3	5.39 (m)	C_2,C_3	87.6 (s)
	H_1,H_4	2.06 (m)	C_1,C_4	29.1 (d, ^2J(CP) = 32.6)
	H_1,H_4	1.48 (m)		
 9	H_5	6.17 (ddd, $^3J(H_5H_{6'})$ = 16.6, $^3J(H_5H_6)$ = 10.1, $^3J(H_5H_4)$ = 7.6)	C_5	135[e]
			C_6	115.4 (s)
	H_2	5.82 (td, $^3J(H_2H_3)$ = 4.9, $^3J(H_2H_1')$ = 8.1, $^3J(H_2H_1)$ = 7.3)	C_2	93.8 (s)
			C_3	85.5 (s)
	H_3	5.57 (t, $^3J(H_3H_4)$ = 6.0)	C_4	47.3 (d, ^2J(CP) = 32.6)
	H_6	5.26 (br d, $^2J(H_6H_{6'})$ = 2.2)	C_1	38.1 (d, ^2J(CP) = 26.4)
	$H_{6'}$	4.97 (br d)		
	H_4	4.05 (t)		
	$H_{1'}$	2.62 (m, $^2J(H_1H_1)$ = 2.8)		
	H_1	2.09 (dd)		
 10	H_3	5.87 (m, $^3J(H_3H_4)$ = 8.0, $^3J(H_3H_2)$ = 4.2)	C_5	143.7 (s)
	H_5	5.69 (m, $^3J(H_5H_{6'})$ = 16.6, $^3J(H_5H_6)$ = 9.7, $^3J(H_5H_4)$ = 10.3)	C_6	116.7 (s)
			C_3	89.0 (s)
	$H_{6'}$	5.45 (br d, $^2J(H_{6'}H_6)$ = 2.0)	C_2	81.4 (s)
	H_2	5.31 (m, $^3J(H_2H_{1'})$ = 5.8, $^3J(H_2H_1)$ = 6.3)	C_4	54.1 (d, ^2J(CP) = 28.5)
	H_6	4.89 (br d)	C_1	36.8 (d, ^2J(CP) = 30.5)
	H_4	3.15 (m)		
	$H_{1'}$	1.6[j]		
	H_1	1.10 (m, $^2J(H_1H_{1'})$ = 2.5)		

[a] All spectra were recorded at room temperature in THF-d_8 solutions unless otherwise stated. [b] Chemical shifts are given in ppm and are relative to either the residual ^{1}H resonances in the deuterated solvents (^{1}H NMR) or the deuterated solvent resonance (^{13}C{^{1}H} NMR). Key: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Coupling constants (J) are in hertz. [c] The J(HH) values were determined on the basis of ^{1}H{^{31}P} NMR experiments. [d] J(HH) values between the olefinic hydrogens H_2 and H_3 and the proximal hydrogens H_1, $H_{1'}$ and $H_{4'}$ although shown by ^{1}H, ^{1}H 2D-COSY NMR experiment, could not be precisely estimated <2 Hz). [e] Masked by the phenyl carbon resonances; the chemical shift was determined from ^{13}C, ^{1}H heteronuclear 2D-NMR correlation studies. [f] Masked by CH_2 hydrogen resonances of triphos; the chemical shift was determined from ^{1}H, ^{1}H 2D-COSY NMR experiment. [g] The ^{1}H NMR spectrum was recorded at room temperature in CD_2Cl_2. [h] The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded in CD_2Cl_2 at 30 and −40 °C, respectively. [i] The butadiene hydrogens constitute an AA'MM'XX' spin system. The ^{1}H{^{31}P} NMR spectrum (CD_2Cl_2, 30 °C) was properly computed with the following magnetic parameters: $^3J(H_2H_3)$ = −2.8 Hz, $^3J(H_2H_{1'})$ = 6.3 Hz, $^4J(H_2,H_{4'})$ = 1.1 Hz, $^3J(H_2H_1)$ = 7.4 Hz, $^4J(H_2H_4)$ = −1.0 Hz, $^4J(H_{1'}H_{4'})$ = 2.3 Hz, $^2J(H_{1'}H_1)$ = −3.5 Hz, $^4J(H_{1'}H_4)$ = 0.2 Hz, $^4J(H_1H_4)$ = 3.1 Hz. [j] Masked by the methyl hydrogen resonance of triphos; the chemical shift was determined from ^{1}H, ^{1}H 2D-COSY NMR experiment.

Scheme 4



a pure sample of the former compound is heated at 90 °C in THF for 6 h.

A 4:6 mixture of **9** and **10** can independently be prepared by treatment of the bis(ethene) complex **3** with an excess of hexa-1,3,5-triene (mixture of isomers) in THF at 20 °C (Scheme 4). This alternative synthetic procedure (under very mild conditions) indirectly supports the chemical nature of **5**; i.e., this complex, which is obtainable by either straightforward reaction of the iridacyclopentadiene complex **8** with ethene or treatment of **1** with ethyne, is indeed the result of a C−C bond formation reaction at iridium.

No intermediate species was observed in the course of the isomerization of **5** to **9**, which apparently involves a redistribution of electrons within the metal−organyl fragment (the formal oxidation state of the metal changes from +3 in **5** to +1 in **9**), as part of the making and breaking of Ir−C bonds.

9 and **10** are stable in both the solid state and nitroethane solution in which they behave as 1:1 electrolytes. The IR spectra of both complexes in the solid state contain a band at 1616 cm^{-1} which is attributable to ν(C=C) of a free olefin.

Unlike **5**, which is rigid on the ^{31}P NMR time scale, both **9** and **10** are fluxional in solution. Interestingly, the fluxionality involves only the phosphine ligands and not the hexatriene ligands which, in fact, show temperature-invariant resonances of their carbon and hydrogen atoms. This situation is quite common for d^8 ML$_3$(diene) complexes and will be discussed below, together with the analogous fluxionality of the η^4-butadiene complex **7**. At room temperature, the ^{31}P-

{^{1}H} NMR spectra of **9** and **10** in THF-d_8 consist of AMQ spin systems with poorly discernible J(PP) couplings. All J(PP) coupling constants become visible at −20 °C. As the temperature is increased, the phosphorus signals lose resolution at 30 °C, then broaden and, finally, at ca. 65 °C, coalesce. A single broad resonance centered at ca. −26 ppm emerges from the baseline at 80 °C (DMSO-d_6).

Valuable information on the structures of **9** and **10** is provided by the ^{1}H and ^{13}C NMR data. In particular, the presence in both compounds of an uncoordinated vinyl moiety is shown by both its hydrogen and carbon chemical shifts and J(HH) values (J(trans) ~ 17 Hz, J(cis) ~ 10 Hz, J(gem) ~ 2 Hz), while the larger value of $J(H_4H_5)$ found for **10** (8 vs 6 Hz) is suggestive of an *s-trans,s-cis−trans* structure of the hexa-1,3,5-triene ligand.[19] All the other ^{1}H and ^{13}C NMR data are in agreement with those reported for analogous transition-metal complexes containing η^4-hexa-1,3,5-triene ligands.[19] Illustrative examples of η^4-hexa-1,3,5-triene complexes are the mononuclear species [CpCo(η^4-CHPh=CH-CH=CHCH=CHPh)][19a] and [CpCo(η^4-CH_2=CH-CH=CHCH=CH_2)],[19b] and the clusters [$Ru_6(CO)_{14}$(μ_6-C)(μ-*s-cis,s-cis−trans*-1,2-η^2-3,6-η^4-CH_2CHCH-CHCHCH_2] and [$Ru_6(CO)_{14}$(μ_6-C)(μ-*s-trans,s-cis−trans*-1,2-η^2-3,6-η^4-CH_2CHCHCHCHCH_2].[22] The thermodynamically more stable Ru cluster was found to be the one with the *s-trans,s-cis−trans* conformation of hexatriene, which is consistent with the thermal rearrangement of **9** to **10** herein described.

As stated in the Experimental Section, commercially available hexa-1,3,5-triene is a mixture (ca. 50:50) of the two possible geometric isomers. The (triphos)Ir$^+$ system thus reacts with both isomers, and in particular it stabilizes the *s-trans,s-cis−cis* and *s-trans,s-cis−trans* conformations.

Finally, it is worth pointing out that the NMR data for the hexatriene ligand in both **9** and **10** are consistent with the absence of any movement of the (triphos)Ir fragment along the face of the triene as this would average the hydrogen and carbon resonances, which, in fact, is not observed. Interconversion in solution of shift isomers of hexatriene complexes has been reported for disubstituted η^4-hexa-1,3,5-triene-iron tricarbonyls.[23]

[(Triphos)Ir(η^4-C_4H_6)]BPh$_4$, 7 is formally the product of a reductive dimerization of ethyne at a metal center (i.e., hydrogenation with C−C coupling). A square-pyramidal structure is proposed for **7** on the basis of the following multinuclear NMR data as well as by analogy with other known M(η^4-diene)L_3 complexes.[24] The ^{1}H NMR spectrum of the butadiene hydrogens in THF-d_8 is invariant from 50 to −50 °C. The portion of the ^{1}H{^{31}P} NMR spectrum (CD_2Cl_2) of

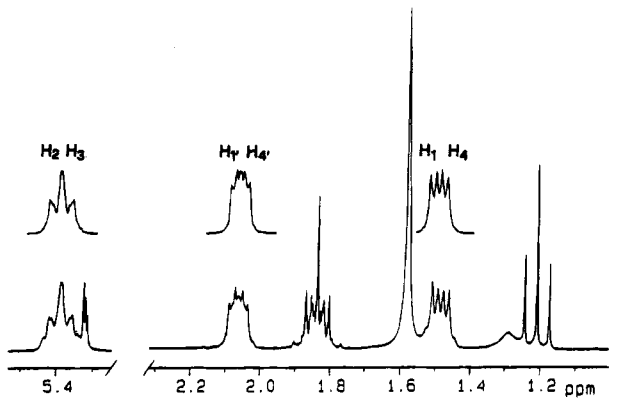


Figure 2. Experimental and computed (inset, above) broad-band ^{1}H{^{31}P} NMR spectra of the buta-1,3-diene hydrogens in **7** (CD_2Cl_2, 30 °C).

the C_4H_6 hydrogens is reported in Figure 2 together with the computed spectrum. The butadiene hydrogens give rise to an AA'MM'XX' spin system (Table 1). The ^{1}H NMR spectrum shows a very small coupling of H_1 and H_4 to the phosphorus atoms. Both the chemical shifts and coupling constants fall in the proper range for square-pyramidal η^4-C_4H_6 complexes such as [Co(η^4-C_4H_6)(PMe_3)$_3$]BPh$_4$,[24c,d] [Fe(η^4-C_4H_6)(PMe_3)$_3$],[24e] [Ir(η^4-C_4H_6)(PMe_2Ph)$_3$]BF_4,[24g] and [(triphos)M(η^4-C_4H_6)]BPh$_4$ (M = Co, Rh).[24a,f]

The ^{13}C{^{1}H} NMR spectrum in CD_2Cl_2 at −40 °C is consistent with the proposed structure for **7** as it shows the carbons of the diene ligand to constitute two equivalent pairs (CH, δ 87.6 (s); CH_2, δ 29.1 (d), J(CP) = 32.6 Hz). Thus, both nuclei of the CH_2 groups couple to P more strongly than do those of the CH group.

As anticipated in a previous section, the ^{31}P{^{1}H} NMR spectrum shows **7** to be fluxional on the NMR time scale. The room-temperature spectrum in THF-d_8 consists of a broad signal at ca. −23 ppm, which appears as a sharp singlet at +50 °C. The complex becomes stereochemically rigid at ca. −10 °C, showing an AM_2 spin system. Interestingly, the complex exhibits a significant temperature dependence of the phosphorus chemical shifts (Figure 3). This phenomenon prevents a reliable computer simulation of the dynamic process by DNMR spectroscopy in the temperature range for which a variation in the line shape is observed. Accordingly, no calculated activation parameter can be given. On the other hand, the nature of the fluxional process operating for **7**-like compounds is rather clear and has been widely investigated in recent years. It is generally agreed that no motion other than rotation of the diene can make the three phosphorus ligands equivalent.[24g] This is certainly reasonable for **7** itself, where the three phosphorus donors are constrained to be part of a tridentate phosphine. A similar type of fluxionality is exhibited by the triene complexes **9** and **10**, the only difference being a higher barrier to fluxionality as compared to the diene analog. This finding confirms that fluxionality is not an intrinsic property of pentacoordination but is highly dependent on the nature of the ligands and the metal.[24g]

The activation barriers to fluxionality in the molecules reported here are systematically larger for Ir(III) than for Ir(I). This correlates well with the idea that an octahedron (Ir(III)) is more stereochemically rigid than any five-coordinate shape (Ir(I)).

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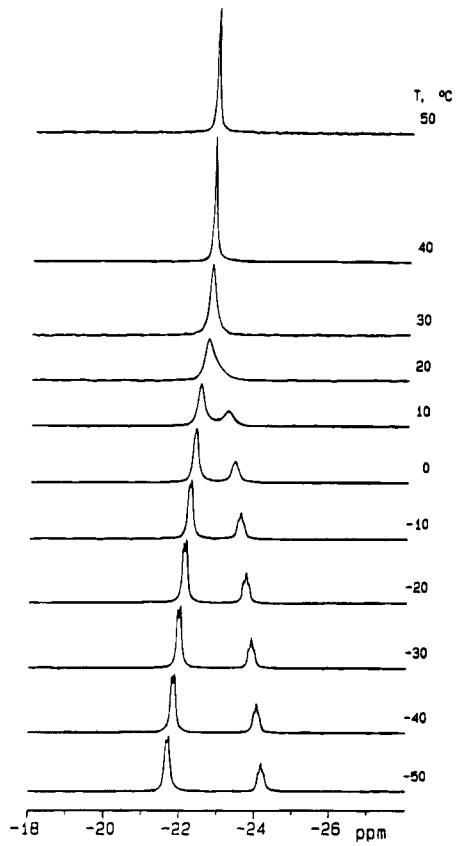


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **7** (THF-d_8).

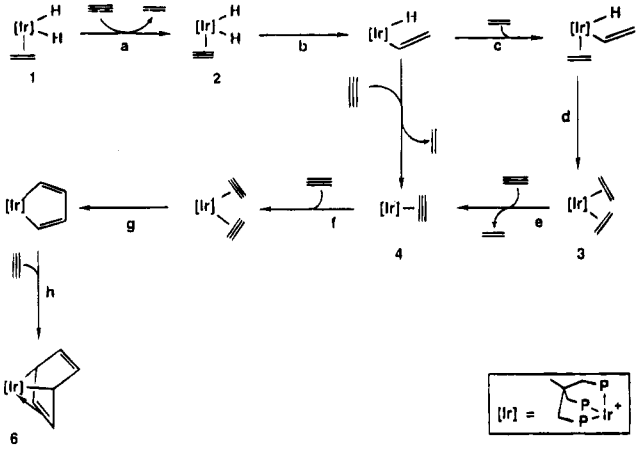
[(Triphos)Ir(H)$_2$(THF)]BPh$_4$. The solvento complex **11** is prepared by adding a stoichiometric amount of triflic acid to a stirred suspension of [(triphos)Ir(H)$_2$-(C_2H_5)] in THF, followed by precipitation with $NaBPh_4$. In the course of the reaction, ethane is evolved. The complex is stable in both the solid state and room-temperature THF solution. The THF ligand in **11** is very labile and can readily be displaced by weak ligands, including other solvents (EtOH, acetone) and the water occasionally present in THF, to give the corresponding solvento complexes. Halogenated solvents must be avoided as they react with **11** to give a yellow-orange crystalline product whose chemical nature is presently being studied.

In **11**, the metal center is octahedrally coordinated by the three phosphorus atoms of triphos ($^{31}P\{^1H\}$ NMR AM_2 pattern), by two terminal hydride ligands (ν(Ir–H) = 2050 cm^{-1})), and by a THF molecule. As commonly observed for stereochemically rigid dihydrido metal complexes of the formula [(triphos)Ir(H)$_2$L], the two hydride ligands are chemically but not magnetically equivalent and thus give rise to a second-order doublet of multiplets (AA'XX'Y spin system, A = H, X, Y = P).[12,17]

Discussion

For a better understanding of the chemistry described in this paper, it is useful to summarize some characteristics of the starting complex, **1**.[1,12] In poorly coordinating solvents (CH_2Cl_2, THF) at room temperature, the (ethene)dihydride complex is in a rapid equilibrium with its hydride migration product [(triphos)Ir(H)-(C_2H_5)]$^+$, which can be stabilized by several ligands including CO, Cl$^-$, and dimethylformamide to give octahedral adducts of the formula [(triphos)Ir(H)-(C_2H_5)L]$^{n+}$ (n = 0, 1).[12] In the absence of added ligands, the complex decomposes evolving ethane, slowly at room temperature and rather rapidly above 40 °C. Below −40 °C, the migration of hydride to ethene is slowed and the complex adopts an octahedral coordination geometry, although the ethene ligand continues to rotate about the metal–ligand axis even at −100 °C.

Scheme 5. Suggested Mechanism for the Cyclotrimerization of Ethyne at −50 °C (Closed System)



Cyclotrimerization of Ethyne and its Cooligomerization with Ethene. Incorporation of all of the above experimental evidence leads to the mechanism shown in Scheme 5 for the low-temperature reaction between **1** and ethyne to give the η^4-benzene complex **6**. This scheme shows only the C–H and C–C bond-forming events.

Initially, the ethene ligand in **1** is displaced by ethyne to give **2**. Later, ethene reenters the metal coordination sphere to form the bis(ethene) complex, although *both* ethene ligands are subsequently dissociated and are among the products of the reaction (eq 1).

$$Ir(H)_2(^*C_2H_4)^+ + 4C_2H_2 \rightarrow Ir(C_6H_6)^+ + C_2H_4 + {}^*C_2H_4 \quad (1)$$

One ethyne is sacrificed to consume the two hydride ligands. Reasonable intermediates in this transformation are an unsaturated ethyne migration product (step b), which may be stabilized by ethene to form an (ethene)(hydride)vinyl complex (step c). This species has not been detected, but its possible formation along the reaction path is indirectly substantiated by the recent isolation of the related iridium complex [Tp*Ir-(H)(CH=CH_2)(C_2H_4)] [Tp* = hydridotris(3,5-dimethyl-1-pyrazolyl)borate].[25]

The bis(ethene) complex **3** is not stable in the presence of ethyne, which, in fact, readily displaces both olefins and forms the π-ethyne complex **4** (Scheme 5). The latter species has been detected spectroscopically, and some related examples are known[12] (e.g., [(triphos)Ir-(HCCPh)]BPh_4),[17] in which the ethyne ligand behaves as a four-electron donor. Complex **4** reacts with a second ethyne molecule, most likely via a bis(ethyne)

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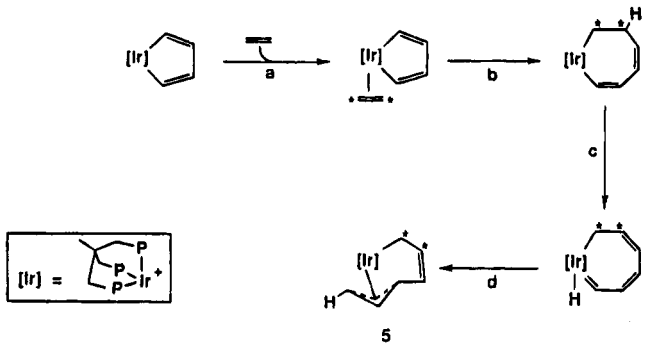
Scheme 6. Suggested Mechanism for the Co-oligomerization of Ethyne with Ethene

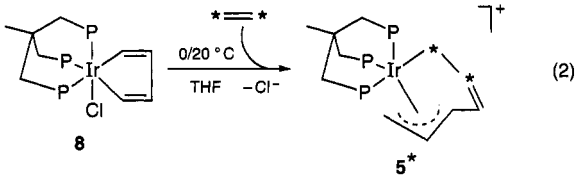


5

(two-electron donor) intermediate (step f), to form an iridacyclopentadiene species,[5g-l,6e,7f,24f] which has independently been shown to react with ethyne (step h) producing the cyclotrimerization η^4-C_6H_6 complex. Both the coupling reaction of two ethynes at the [(triphos)-Ir]$^+$ fragment to give an iridacyclopentadiene complex and the subsequent reaction of this metallacycle with ethyne have recently been studied by means of EHMO calculations.[13] According to the theoretical analysis, the addition of ethyne to the metallacycle proceeds in a concerted manner; i.e., the reaction may be viewed as a metal-assisted Diels–Alder addition, where the metal plays an important role as a reactive center (in contrast to acid-catalyzed Diels–Alder additions, where the only role of the metal is to activate the diene).

The addition of ethyne is not the only reaction path accessible to the metallacycle under the present experimental conditions, since 2 equiv of ethene is dissolved in the reaction mixture. As shown by an independent reaction, ethene can react with the iridacyclopentadiene fragment to form the 1-η^1:4-6-η^3-hexatriene complex **5**. On the basis of the observed product ratio of **6** to **5** (92:8), one may conclude that, at −50 °C, ethyne uptake by the metallacycle is kinetically favored over ethene uptake.

From a mechanistic viewpoint, the formation of **5**, necessarily occurring via a multistep reaction sequence, is still rather obscure since no intermediate achieves detectable concentrations. It has been possible to establish (eq 2) which carbons of the C_6 ligand are



8 5* (2)

formed from the entering ethyne. The $^{13}C\{^1H\}$ NMR spectrum of **5*** shows selective incorporation of ^{13}C at the C_1 and C_2 positions of the C_6H_8 ligand. The $J(C_1C_2)$ value of 58.2 Hz is typical of one-bond C–C coupling constants between sp^3 and sp^2 carbon nuclei.[26] Therefore, in Scheme 6, we suggest a mechanism involving ring expansion at iridium (step b), followed by β-H elimination from the alkyl portion of the seven-membered metallaring. Redistribution of the double bonds within the metallacycle would then produce a carbene hydride, which is appropriate to undergo migration of hydride from the metal to the carbene carbon atom,[27] thus leading to **5**. Even though not proved experimentally, steps b and c of Scheme 6 have several precedents in the literature. In particular, ring expansions involving metallacyclopentadiene complexes and alkenes have precedent in a number of cycloaddition reactions.[8,28] Of relevance to the case at hand are the reactions of [Ru(CO)(η^4-C_4Ph_4)(η-C_5H_5)]BF_4 with alkenes to give η^4-cyclohexadiene derivatives[27b] as well as the reactions of [(triphos)RhCl(η^4-C_4H_4)] with CO, CH_3CN, and CS_2 to give coordinated cyclopentadienone and free 2-methylpyridine and dithiopyrone, respectively.[24f] The latter reactions have been suggested to proceed via insertion of the incoming organic reagent into a M–C bond, followed by reductive elimination.

The fact that the reaction of the iridacyclopentadiene fragment with ethene does not produce the η^4-cyclohexadiene complex [(triphos)Ir(η^4-C_6H_8)]BPh_4, which is a stable and isolable compound,[29] suggests that (Scheme 6, step c) the β-H elimination step from the seven-membered metallaring is faster than its reductive elimination to 1,3-cyclohexadiene.

Most but not all of the above mechanistic considerations can be extended to the reaction between **1** and ethyne performed at room temperature in either open or closed systems. In fact, irrespective of the type of reactor, significant amounts of ethane and of the η^4-butadiene complex **7** (Scheme 1) are produced. Furthermore, under a steady stream of ethyne, **5** is never formed. While the latter result is quite reasonable, since the liberated ethene is transported out of the reactor by the continuous flow of ethyne, the formation of ethane and of the η^4-butadiene complex is less obvious. Both products evidently come from processes with higher activation energy than those shown in Scheme 5. To progress further, we now consider whether the formation of ethane is correlated with formation of **7** or whether these two products are formed by independent reaction paths.

Reductive Dimerization of Ethyne. Before illustrating our mechanistic interpretation for the reductive dimerization of ethyne at iridium, it may be useful to recall that the η^4-butadiene complex **7** is the predominant product (up to 100%) when the (THF)dihydride **11** is substituted for the (ethene)dihydride **1** in the reaction with ethyne. From this observation, one may readily infer that (i) ethene is of importance for the formation of the η^4-C_6H_6 and 1-η^1:4-6-η^3-hexatriene complexes from dihydride **1**, whereas its presence in the reaction system as either a ligand or a free reactant disfavors the reductive dimerization of ethyne and (ii) ethane and **7** are not produced in a single process, but instead the two products form in *independent* reactions.

In light of the solution chemistry of **1**, it is reasonable that ethane is eliminated from the hydride migration product, which, in fact, at room temperature is in equilibrium with the (ethene)dihydride form (see Scheme 7, which illustrates a proposed mechanism for the

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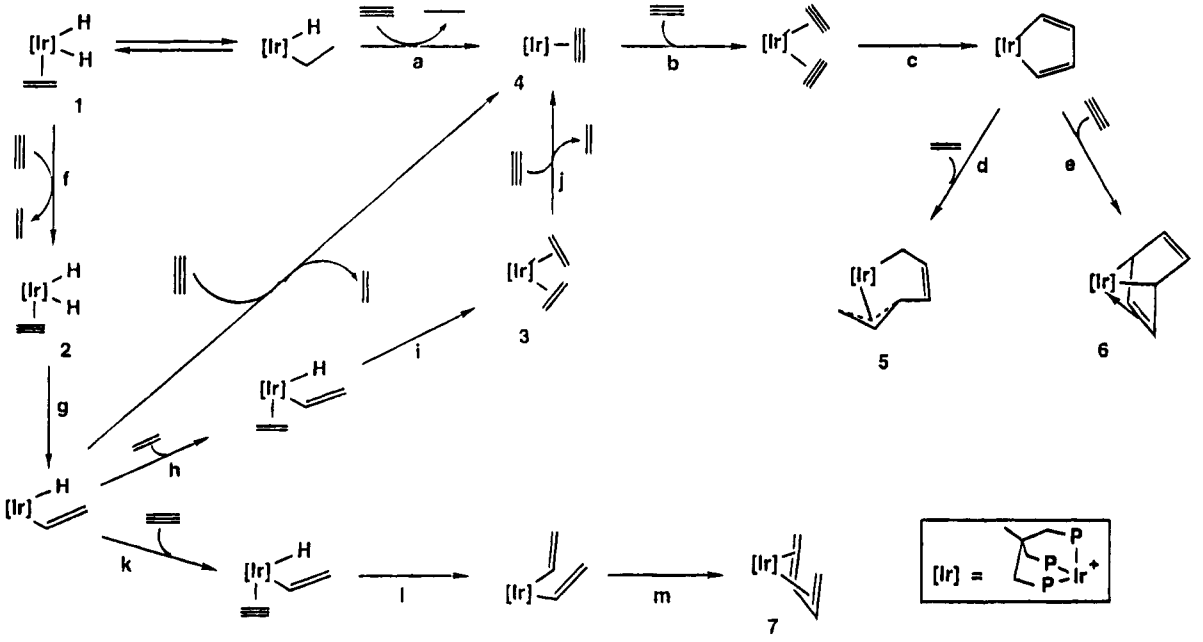
Scheme 7. Suggested Mechanism for the Reaction between 1 and Ethyne at 20 °C (Closed System)



reaction between **1** and ethyne at room temperature). The reductive elimination of ethane, which appreciably occurs at higher temperature (40 °C), would be facilitated by interaction with incoming ethyne (step a). Once the π-ethyne complex **4** is formed, its subsequent conversion to either **5** or **6** follows the independently established route (b–e; see also Scheme 6). The ethylene ligand thus scavenges hydrogen in this route. However, at room temperature, intermediate **4**, which only leads to **5** and **6**, must be in competition with another reaction since we note also the evolution of considerable ethene (the ethene to ethane ratio is ca. 2:1). Accordingly, also at room temperature, displacement of ethene from **1** by ethyne takes place to give **2**, which transforms into a (hydride)vinyl species via ethyne insertion into an Ir–H bond. At room temperature, this highly unsaturated Ir(III) vinyl can be trapped in two ways: the uptake of ethene (h and i, wherein hydrogen is scavenged by ethyne) to give **3** (as it selectively does at −50 °C) and the uptake of ethyne (k) to give a (vinyl)(ethyne)hydride which ultimately converts to **7** (l and m) via a bis(vinyl) intermediate. This latter route incorporates the hydride ligands in the diene ligand of **7**. Indeed, bis(vinyl) metal complexes, which typically exhibit a low barrier to reductive coupling,[30] are considered key intermediates for the synthesis of buta-1,3-diene derivatives via C–C bond formation reactions; see, for example, the conversion of $[Cp_2Zr(CH{=}CHPh)_2]$ to $[Cp_2Zr(\eta^4\text{-}C_4H_4Ph_2)]$[4] and of $[(\eta^5\text{-}C_5Me_5)Ru(NO)(CH{=}CH_2)_2]$ to $[(\eta^5\text{-}C_5Me_5)Ru(NO)(\eta^2\text{-}C_4H_6)]$.[30]

In conclusion, an increase in the temperature from −50 to 20 °C of the reaction between **1** and ethyne has the effect of favoring both the reductive elimination of ethane from **1** and the uptake of ethyne by the (vinyl)hydride intermediate. Essential to the formation of **7**, this pathway forms two hydrogen-rich (C_2H_3) ligands on one metal center.

When the $[(triphos)Ir(H)_2]^+$ fragment is reacted with ethyne at room temperature (this is the case of the THF–solvento complex **11**), then selective formation of the η^4-butadiene complex **7** occurs (Scheme 8, reaction sequence a–e), which is consistent with the fact that both the cyclotrimerization of ethyne and its cooligomerization with ethene are ethene-assisted. In this case, in fact, there is no chance of formation of the bis(ethene) complex **3** and thus of the iridacyclopentadiene species, which is the mandatory intermediate for production of **5** and **6**.

Only at a much higher temperature (70 °C) does **11** lead to detectable quantities of the η^4-benzene complex **6** (7%). One explanation for this finding (Scheme 8, reaction sequence f–j) is to think that the (vinyl)hydride intermediate may undergo the reductive coupling to form ethene (step f) and that this process, unless assisted by ethene (see Scheme 5), requires the highest activation energy of any other step in Scheme 8. This is consistent with the relative bond strengths of the iridium–carbon bonds, which increase in the order $IrCH{=}CH_2 > IrCH_2CH_3$, and, therefore, with the observation that vinyl–hydride iridium complexes typically undergo reductive elimination more slowly than analogous alkyl–hydride complexes.[31] It is also true that the ethene complex will be a high-energy species because it is truly unsaturated (compare the product of step c).

Conclusions

The variety of reactions reported here (eqs 3–5) are controlled by a combination of material balance and (in some cases) kinetic competition between available reagents. Obviously, the C_6H_8 products require some source of hydrogen (hydride ligands or C_2H_4) to increase the H to C ratio above the 1:1 of acetylene. The same applies to producing butadiene. Clearly, acetylene cyclotrimerization would be inhibited by any reagent

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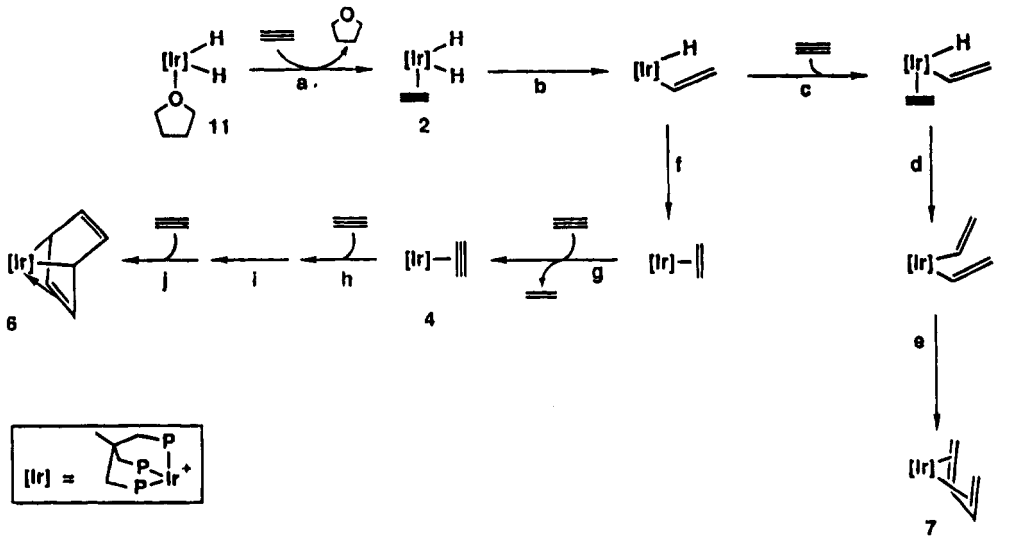
Scheme 8. Suggested Mechanism for the Reaction between 11 and Ethyne at 20 (Reaction Sequence a–e) and 70 °C (Reaction Sequence a–j)



$$3C_2H_2 \longrightarrow \bigcirc \qquad (3)$$

$$2C_2H_2 + C_2H_4 \longrightarrow C_6H_8 + C_6H_8 \qquad (4)$$

$$2C_2H_2 + 2\text{"H"} \longrightarrow \qquad (5)$$

other than C_2H_2. Ethene can thus be a competitive inhibitor, and hydride ligands might have been, except that they can be rendered impotent by transfer to C_2H_2 or especially to C_2H_4. The yield of isomeric cooligomerization ($2C_2H_2 + C_2H_4$) products depends on competition between the two unsaturated hydrocarbon reagents for coordination at iridium. Again, these products might have been suppressed by hydride ligands except that hydrides are rapidly removed from reactive roles by transfer to C/C unsaturation. From the point of view of product selectivity, the simplest iridium reagents are thus (triphos)Ir(π-alkyne)$^+$ and (triphos)Ir(η^2-C_4H_4)$^+$; no hydride transfer or ethene-derived products are possible. The high IrH to C_2H_4 ratio in (triphos)Ir(H)$_2$(THF)$^+$ leads selectively to the most hydrogen-rich product, butadiene. (triphos)Ir(H)$_2$(C_2H_4)$^+$ and (triphos)Ir(C_2H_4)$_2^+$ increase the complexity still further because the ethene is both more abundant and (being coordinated) more competitive with acetylene. Hydride ligands are never eliminated as H_2,[32] apparently because of the abundance of hydrogen acceptor substrates, together with the facile occurrence of β-H migration promoted by iridium. Pervading this chemistry is the efficient binding of substrates by highly electrophilic metal centers. This follows because the coordination sphere is devoid of halide or pseudo-halide ligands which have the ability to stabilize apparently unsaturated intermediates by X → Ir π-donation.[33]

With the combination of a polyphosphine ligand and of a kinetically sluggish third-row transition metal, we have been able to detect several species intermediate to various C–C bond-forming reactions of ethene and ethyne. Surveying the results herein presented, one may draw several mechanistic conclusions:

(i) The cyclotrimerization reaction is traversed by a number of intermediates among which are metal–π-alkyne, metal–bis(π-alkyne), and metallacyclopentadiene species.

(ii) Metallacyclopentadiene complexes can also be intermediates for the linear cooligomerization of alkynes with alkenes via ring-expansion reactions rather than via Diels–Alder addition (i.e., no cyclohexadiene is formed here).

(iii) The reductive coupling of alkynes to buta-1,3-dienes can proceed at one metal center via subsequent insertion of two alkyne molecules into two M–H bonds, followed by reductive elimination from a bis(vinyl) intermediate. This mechanism is alternative to reaction of metallacyclopentadiene complexes with H_2.[12]

(iv) Alkenes function as coreactants in the cyclotrimerization reaction of alkynes assisted by polyhydrido metal complexes either by preventing the insertion of a second alkyne molecule into an M–H bond (thus impeding the reductive dimerization reaction) or by consuming the hydride ligands (being reduced to alkanes).

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