# Molecular Solid–Gas Organometallic Chemistry. Catalytic and Stoichiometric Iridium-Assisted C–C Bond-Forming Reactions Involving Ethyne and Ethene

Claudio Bianchini,*[,1a] Mauro Graziani,[1b] Jan Kaspar,[1b] Andrea Meli,[1a] and Francesco Vizza[1a]

*Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 Firenze, Italy, and Dipartimento delle Scienze Chimiche, Università di Trieste, Via Valerio 38, 34127 Trieste, Italy*

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Treatment of crystals of the ($\eta^2$-ethene)dihydride complex [(triphos)Ir(H)$_2$(C$_2$H$_4$)]BPh$_4$ (**1**; triphos = MeC(CH$_2$PPh$_2$)$_3$) with ethyne (4 atm) at 70 °C for 3 h results in evolution of ethene and but-2-ene and formation of five different organometallic products, namely the $\eta^4$-benzene complex [(triphos)Ir($\eta^4$-C$_6$H$_6$)]BPh$_4$ (**2**), the $\eta^4$-buta-1,3-diene complex [(triphos)Ir($\eta^4$-C$_4$H$_6$)]BPh$_4$ (**3**), the $\eta^4$-cyclohexa-1,3-diene complex [(triphos)Ir($\eta^4$-C$_6$H$_8$)]BPh$_4$ (**4**), and the crotyl hydride isomers [(triphos)Ir(H)($\eta^3$-MeC$_3$H$_4$)]BPh$_4$ (**5**-*anti* and **5**-*syn*) in a kinetic product ratio of 35:5:23:28:9. At 100 °C, the solid–gas reaction produces catalytic amounts of benzene, the catalyst precursor being the $\eta^4$-benzene complex **2**. Temperature-programmed reactions carried out in a flow reactor and the use of isolated complexes in independent solid–gas reactions permit mechanistic conclusions which account for the varied organic and organometallic products. The ethene ligand in **1** is an essential ingredient for both cyclotrimerization and cooligomerization reactions of ethyne, which are traversed by $\eta^3$-crotyl complexes. Conversely, the ethene ligand is a competitive inhibitor for the reductive dimerization of ethyne to buta-1,3-diene, for which the two hydride ligands are mandatory. Comparison with fluid solution-phase systems provides evidence for the control exerted by the constraining environment of the crystal lattice on the solid–gas reactions.

## Introduction

Solid–gas reactions between transition-metal complexes and small molecules differ from reactions in solution essentially in the fact that solid-state reactions occur within the constraining environment of the reactant crystal lattice, which can control both the kinetics and the nature of the products.[2,3] Reaction products may not necessarily be those which are thermodynamically most stable but, rather, may result from reaction pathways exclusively accessible in the environment of the solid. For this reason, much of the present interest in molecular solid–gas organometallic reactions arises from the expectation of increasing the molecular level understanding of heterogeneous reactions, which is much less advanced than for homogeneous reactions. In fact, reactions between gaseous small molecules and solid transition-metal complexes may lead to formation of species not observable in analogous fluid-solution reactions and, consequently, to important mechanistic breakthroughs.[2] Solid-state kinetic control over the distribution and nature of products may yield new information on reaction mechanisms, particularly in the case of solid–gas reactions occurring at relatively low temperature, as they offer the advantage that structural elements can be preserved in the transformation from reactant to product. In this way, new structure types, including metastable species,[2m] may be arrived at through a series of mechanistically well-understood steps.

On the other hand, solid–gas reactions are *per se* worthy of attention due to the fact that environmental concerns currently have a profound influence on technical developments in the chemical industry. Particularly important is the application of catalytic technologies resulting in selective processes that preferentially eliminate hazardous solvents. Solid–gas reactions can address these problems through the elimination of solvent as well as increasing selectivity by increasing the shape and size control on both reagents and products.

Despite the constrained environment of such reactions, it is now apparent that in the solid state organometallic compounds can undergo a large variety of both intramolecular and intermolecular reactions. Such reactions include (i) migration of hydride ligands to coordinated olefins or other unsaturated ligands,[2a,d,e,g,o] (ii) reductive elimination and oxidative addition of C–H and H–H

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bonds,[2a,c-g] (iii) C–C bond-forming reactions,[2e] (iv) dimerization,[2d] (v) ligand displacement,[2a,d,e,k] (vi) hydrogen transport,[2c,f,i,p] and (vii) carbonylation reactions.[2b,d,e,k,m] Some catalytic reactions such as hydroformylation and hydrogenation of olefins[2d,g,j,4] and ethyne trimerization and $H_2/D_2$ equilibration[2e,i,p] have also been accomplished.

We are developing the solid-state chemistry of transition-metal complexes stabilized by tripodal polyphosphines such as $P(CH_2CH_2PPh_2)_3$ ($PP_3$), $N(CH_2CH_2PPh_2)_3$ ($NP_3$), and $MeC(CH_2PPh_2)_3$. Tripodal polyphosphine ligands are well suited to assist solid-state reactions for several reasons. These include the remarkable stability of tripodal polyphosphine–metal complexes against thermal decomposition and oxidation reactions, the thermal flexibility of the tripodal ligands, and the ease with which small organic molecules can penetrate crystals of the resulting metal complexes (particularly those stabilized by tetraphenylborate lattices), dissolving in the extensive hydrophobic region provided by the carbon backbones of the ligands (and counteranions). Indeed, it has been found that (i) the diffusion of small organic molecules into crystals of a solid reactant is favored when the reactant contains an extensive hydrophobic region and (ii) gaseous molecules better penetrate crystals of metal complexes comprised of bulky cations and anions due to the generally larger channels in the crystal lattice.

In spite of the participation of ethyne in numerous transformations of industrial relevance, detailed mechanistic information on its primary interaction with isolated metal sites is generally lacking.[5] Therefore, we decided to study the reaction of ethyne with crystals of the $\eta^2$-ethene dihydride complex $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$ (**1**; triphos = $MeC(CH_2PPh_2)_3$),[6] which is known to participate effectively in solid–gas organometallic transformations.[2d]

The results of our study are described in this paper together with comparisons with analogous fluid solution-phase systems in an attempt to provide unambiguous evidence of the control exerted by the reactant crystal lattice on the course of solid–gas reactions. A preliminary communication of part of this work has already appeared.[2]

## Experimental Section

**General Information.** Literature methods were used for the preparation of $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$ (**1**),[6] $[(triphos)Ir(\eta^4\text{-}C_6H_6)]BPh_4$ (**2**),[7] $[(triphos)Ir(\eta^4\text{-}C_4H_6)]BPh_4$ (**3**),[2l,8] $[(triphos)Ir(\eta^4\text{-}C_6H_8)]BPh_4$ (**4**),[9] $[(triphos)Ir(H)_2(THF)]BPh_4$ (**6**),[8] $[(triphos)Ir(C_2H_4)_2]BPh_4$ (**7**),[6] and $[(triphos)IrCl(C_4H_4)]$ (**8**).[10] 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 to the residual $^1H$ resonance of the deuterated solvent ($^1H$ NMR), to the deuterated solvent resonance ($^{13}C\{^1H\}$ NMR), or to 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. Computer simulations of NMR spectra were carried out with a locally developed package containing the programs LAOCN3[11] and DAVINS,[12] 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. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30-m (0.25-mm i.d., 0.25-$\mu$m film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 2000 apparatus equipped with a column identical with that used for GC analyses.

**Solid-Gas Reactions (Static Reactor).** The reactions under controlled pressure of ethyne or ethene were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller and an Inconel safety rupture disk, by using the following general procedure. Crystalline samples (ca. 0.1 mmol, average crystal size 0.01 $mm^3$) were properly pressurized with the appropriate gaseous reactant at room temperature in a 100-mL bomb made of type 316 stainless steel and then heated at 70 °C (oil bath) for 3 h unless otherwise stated. After cooling, depressurizing, and venting under a nitrogen stream, the solid products were recovered and characterized by IR and multinuclear NMR spectroscopy. All compounds were verified by comparison with authentic specimens. Quantification of benzene produced in the catalytic reactions under ethyne was achieved by GC (*n*-nonane as internal standard) after the cold reactor was washed with three 3-mL portions of di-*n*-butyl ether. All reactions exhibit quantitative conversion, showing that all iridium centers are accessible to ethyne. The products appear opaque (cross-polarization microscope), and the single-crystal structure of the starting compound is lost, indicating that there is not coherence, at the molecular level, between the crystal lattices of the reactant and of products. *Caution!* Even though the solid–gas reactions under ethyne have been performed several times with no inconvenience, the use of a protective barrier is recommended, since ethyne can undergo explosive decomposition at elevated pressures.[13]

**Solid–Gas Reactions (Flow Reactor).** Temperature-programmed-reaction (TPR) measurements were carried out in a stainless-steel flow reactor under a flow of ethyne or ethyne/helium (total flow 10–20 mL $min^{-1}$, $C_2H_2$ pressure 4 atm) at heating rates of 2–5 °C $min^{-1}$. Analyses of the outcoming products were performed by either gas chromatography or use of an on-line VG200 quadrupole mass analyzer. Quantitative determination of $C_2H_2$, $C_2H_4$, and $C_2H_6$ was performed on a Hewlett-Packard 5890 II gas chromatograph equipped with a flame ionization detector.

**Fluid Solution-Phase Reactions.** All reactions and manipulations were routinely performed under nitrogen by standard

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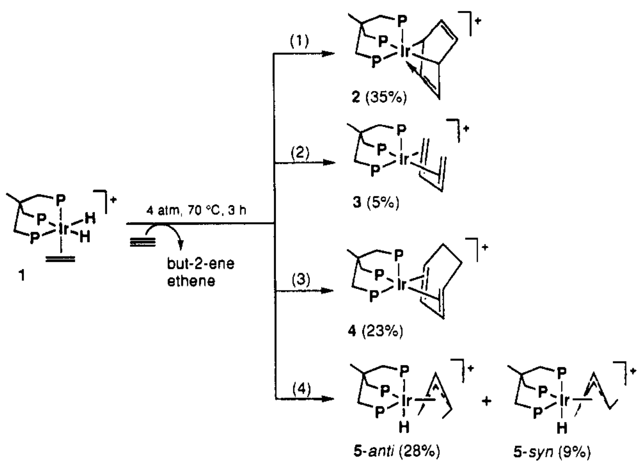
Schlenk or vacuum-line techniques, unless otherwise stated. Reagent grade chemicals were generally used. Tetrahydrofuran (THF) was purified by distillation from $LiAlH_4$ under nitrogen. Catalytic reactions in the homogeneous phase were carried out in the Parr 4565 reactor described above. A THF solution of 1 ($10^{-2}$ M) was pressurized with ethyne (4 atm) and then heated at 70 °C with stirring for 3 h.

**Reaction of [(triphos)Ir($\eta^4$-$C_6H_6$)]$BPh_4$ (2) with But-1-ene: Independent Synthesis of *anti*-[(triphos)Ir(H)($\eta^3$-$MeC_3H_4$)]$BPh_4$ (5-*anti*) and *syn*-[(triphos)Ir(H)($\eta^3$-$MeC_3H_4$)]$BPh_4$ (5-*syn*).** A solid sample of 2 (0.30 g, 0.25 mmol) was dissolved in THF (40 mL) saturated with but-1-ene at room temperature. The mixture was then transferred into the Parr reactor and heated at 70 °C for 3 h. After cooling and venting, the contents of the bomb were concentrated to dryness under reduced pressure. The residue was collected on a sintered-glass frit and washed with *n*-pentane before being dried under a stream of nitrogen. The product was characterized by IR and multinuclear NMR spectroscopy as a 72:28 mixture of the two $\eta^3$-crotyl isomers 5-*anti* and 5-*syn*. These complexes exhibit comparable solubility in most organic solvents and thus could not be separated from each other. A pale yellow crystalline sample of 5-*anti* and 5-*syn* was obtained by recrystallization from THF and ethanol. Anal. Calcd (found) for $C_{69}H_{67}BIrP_3$: C, 69.51 (69.32); H, 5.66 (5.60); Ir, 16.12 (16.00). $\Lambda_M = 54$ cm$^2$ $\Omega^{-1}$ mol$^{-1}$. IR: $\nu$(Ir–H) 2120 cm$^{-1}$. NMR data for 5-*anti* (abbreviations used to designate allyl ligand positions: c, central; s, syn; a, anti; s′, substituted syn; a′, substituted anti): $^{31}P\{^1H\}$ NMR (81.01 MHz, $CD_2Cl_2$, −50 °C, $\delta$): ABM pattern; −14.2 ($P_A$), −14.4 ($P_B$), −27.8 ($P_M$), $^2J(P_AP_B)$ = 7.9 Hz, $^2J(P_AP_M)$ = 23.0 Hz, $^2J(P_BP_M)$ = 22.6 Hz. $^1H$ NMR (200.13 MHz, $CD_2Cl_2$, 20 °C, $\delta$): 4.66 (dt, br, $^3J(H_cH_a)$ = 11.4 Hz, $^3J(H_cH_{s'})$ = 7.0 Hz, $^3J(H_cH_s)$ = 6.6 Hz, $H_c$), 3.90 (m, $^3J(H_{s'}Me)$ = 6.2 Hz, $^4J(H_{s'}H_s)$ < 2 Hz, $H_{s'}$), 3.81 (m, $^2J(H_aH_s)$ < 2 Hz, $H_a$), 2.89 (d br, $H_s$), 2.03 (m, *Me*), −12.52 (dt, $^2J(HP_M)$ = 139.3, $^2J(HP_A)$ = $^2J(HP_B)$ = 13.6 Hz, Ir–*H*). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CD_2Cl_2$, 20 °C, $\delta$): 92.1 (s, *CH*), 59.8 (d, $^2J(CP)$ = 24.8 Hz, *CHMe*), 29.9 (dd, $^2J(CP)$ = 37.5, 5.7 Hz, $CH_2$), 22.1 (dd, $^3J(CP)$ = 4.4, 1.9 Hz, *Me*). NMR data for 5-*syn*: $^{31}P\{^1H\}$ NMR (81.01 MHz, $CD_2Cl_2$, −50 °C, $\delta$): AMQ pattern; −14.0 ($P_A$), −15.3 ($P_M$), −27.0 ($P_Q$), $^2J(P_AP_M)$ = 0 Hz, $^2J(P_AP_Q)$ = 17.9 Hz, $^2J(P_MP_Q)$ = 15.1 Hz. $^1H$ NMR (200.13 MHz, $CD_2Cl_2$, 20 °C, $\delta$): 5.62 (td br, $^3J(H_cH_s)$ = 7.0 Hz, $^3J(H_cH_a)$ = $^3J(H_cH_{a'})$ = 10.3 Hz, $H_c$), 3.35 (m, $^2J(H_sH_a)$ < 2 Hz, $H_s$), 2.92 (m, $^3J(H_{a'}Me)$ = 6.2 Hz, $H_{a'}$), 1.99 (m, $H_a$), 1.51 (d br, *Me*), −13.42 (dt br, $^2J(HP_Q)$ = 127.9 Hz, $^2J(HP_A)$ = $^2J(HP_M)$ = 8.8 Hz, Ir–*H*). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CD_2Cl_2$, 20 °C, $\delta$): 94.3 (d, $^2J(CP)$ = 4.8 Hz, *CH*), 55.6 (d, $^2J(CP)$ = 23.5 Hz, *CHMe*), ca. 32 (partially masked by $CH_2$ carbon resonances of triphos, $CH_2$), 20.98 (s, *Me*).

**Solid-Gas Reactions of a 1:1 Mixture of [(triphos)IrCl($C_4H_4$)] (8) and $TlPF_6$. (A) With Ethene.** The iridacyclopentadiene complex 8 (0.20 g, 0.22 mmol) and a stoichiometric amount of $TlPF_6$ (0.08 g, 0.23 mmol) were dissolved in THF (30 mL) at −10 °C (a temperature at which no reaction between the two compounds occurs). The solvent was then removed under reduced pressure at −10 °C to give a solid, which was dried in vacuo at room temperature until no change in weight was observed. The resulting amorphous solid (X-ray powder investigation; a 1:1 mixture of 8 and $TlPF_6$ as shown by $^{31}P$ NMR spectroscopy) was transferred into the Parr reactor and then heated at 70 °C under 4 atm of ethene. Quantitative conversion of the starting organometallic complex occurred after 3 h to give 4 as the $PF_6^-$ salt, [(triphos)Ir{(1-$\eta^1$:4–6-$\eta^3$)-hexatriene}]$PF_6$[8] (9) and [(triphos)Ir(*s-trans,s-cis-cis*-(1–4-$\eta^4$)-hexa-1,3,5-triene)]$PF_6$[8] (10) in a kinetic ratio of 20:5:75. TlCl was also formed. On further heating at 70 °C under either $C_2H_4$ or argon, all of the compound 9 disappeared. Formed in its place was 10, whereas 4 was found to be thermally stable. Independent thermal reactions carried out on authentic samples of solid 9 and 4 were fully consistent with these results; in particular, no conversion of 9 to 4 was observed even at 100 °C. Notably, compound 10 is thermally stable in the solid state up to 100 °C, which is the highest temperature investigated.

Scheme 1



**(B) With Ethyne.** When the amorphous mixture of 8 and $TlPF_6$ was reacted with ethyne (4 atm) at 70 °C for 3 h, clean conversion to the $\eta^4$-benzene complex 2 (as the $PF_6^-$ salt) was observed.

## Results

**Solid–Gas Reaction between [(triphos)Ir(H)$_2$($C_2H_4$)]$BPh_4$ (1) and Ethyne (Static Reactor).** Reaction of off-white crystals of 1 (*ca.* 0.1 mmol) with ethyne (4 atm) for 3 h at 70 °C yields five iridium complexes, namely the $\eta^4$-benzene complex [(triphos)Ir($\eta^4$-$C_6H_6$)]$BPh_4$ (2),[7] the $\eta^4$-buta-1,3-diene complex [(triphos)Ir($\eta^4$-$C_4H_6$)]$BPh_4$ (3),[2l,8] the $\eta^4$-cyclohexa-1,3-diene complex [(triphos)Ir($\eta^4$-$C_6H_8$)]$BPh_4$ (4),[9] and the crotyl hydride isomers *anti*-[(triphos)Ir(H)($\eta^3$-$MeC_3H_4$)]$BPh_4$ (5-*anti*) and *syn*-[(triphos)Ir(H)($\eta^3$-$MeC_3H_4$)]$BPh_4$ (5-*syn*) in a ratio of 35:5:23:28:9 (based on $^{31}P$ NMR integration) (Scheme 1). This product distribution does not appreciably change in the ethyne pressure range from 4 to 8 atm. Below 4 atm, the conversion of 1 to organometallic products is too slow to allow a reliable determination of the product distribution (at 1 atm of $C_2H_2$, almost no reaction occurs). No reaction between crystals of 1 and $C_2H_2$ is observed at room temperature, even at the highest $C_2H_2$ pressure investigated (8 atm).

More importantly, the organometallic product ratio is kinetic rather than thermodynamic, since for a longer reaction time (70 °C, 6 h) or at higher temperature (100 °C, 3 h) the product composition changes due to further reaction of the crotyl isomers with acetylene to give 2. In contrast, both the $\eta^4$-buta-1,3-diene complex 3 and the $\eta^4$-cyclohexadiene complex 4 do not apparently undergo further reaction with ethyne. In accord with this observation, we have found that pure samples of 3 and 4 do not react in the solid state with ethyne (4 atm) in the temperature range from 70 to 100 °C, whereas the *anti*- and *syn*-crotyl complexes, prepared by independent procedures (see below), have been found to react in the solid state with ethyne (4 atm, 70 °C, 3 h) to give the $\eta^4$-benzene complex 2 and but-2-ene (Scheme 2).[14]

At 100 °C under the solid–gas conditions, the reaction between 1 and ethyne (4 atm) produces catalytic amounts of benzene (0.7 mol of benzene (mol of catalyst)$^{-1}$ h$^{-1}$), the catalyst precursor being the $\eta^4$-benzene complex 2, as

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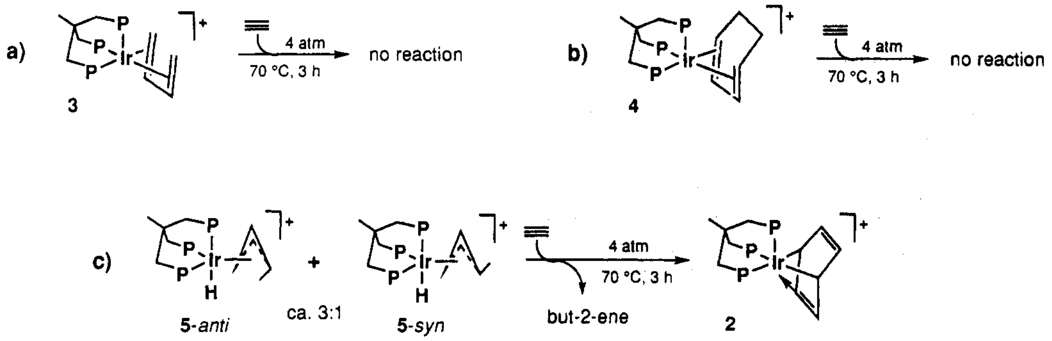
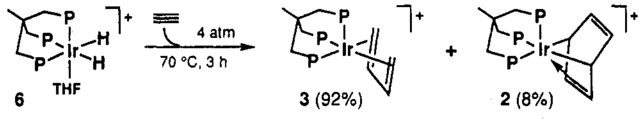
(14) We are unable to assign a stereochemistry to but-2-ene, as the *cis* and *trans* isomers exhibit identical mass fragmentation patterns.

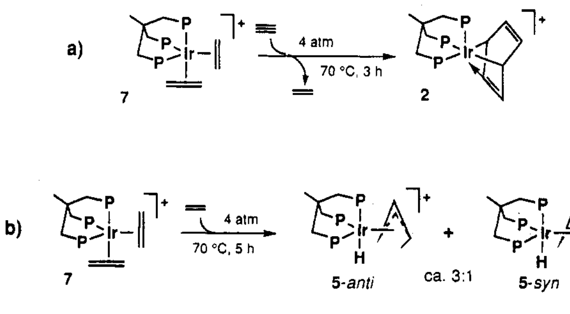
**Scheme 2. Related Solid–Gas Reactions**



**Scheme 3. Related Solid–Gas Reactions**



**Scheme 4. Related Solid–Gas Reactions**



shown by an independent catalytic reaction. Steady-state conditions were maintained for 48 h.

From a formal viewpoint, the reactions shown in Scheme 1 may be described as C–C bond-forming reactions between ethyne and/or ethene, in particular cyclotrimerization of ethyne to benzene (1), reductive dimerization of ethyne to buta-1,3-diene (2), cocyclization of ethyne with ethene to cyclohexa-1,3-diene (3), and dimerization of ethene to butene (4). In view of their fundamental and practical relevance, a mechanistic study has been carried out by using temperature-programmed-reaction (TPR) measurements as well as a variety of independent reactions performed, where possible, under solid–gas conditions, or else under fluid solution-phase conditions.

**Related Solid–Gas Reactions. Reaction of [(triphos)Ir(H)$_2$(THF)]BPh$_4$ (6) with Ethyne.** Substitution of crystals of the THF adduct[8] 6 for those of 1 in the solid–gas reaction with ethyne (4 atm, 70 °C, 3 h) results in quantitative conversion of 6 to a mixture of the $\eta^4$-butadiene complex 3 and of the $\eta^4$-benzene complex 2 in a ratio of 92:8 (Scheme 3).

**Reaction of [(triphos)Ir(C$_2$H$_4$)$_2$]BPh$_4$ (7) with Ethyne.** Reaction of crystals of the bis(ethene) complex 7 with ethyne (4 atm) at 70 °C for 3 h results in selective transformation of the starting organometallic complex into the $\eta^4$-benzene complex 2 and evolution of ethene (Scheme 4a).

**Thermal Rearrangement of 7.** When crystals of 7 are heated at 70 °C under a stabilizing ethene atmosphere (4 atm), their conversion to 5-*anti* and 5-*syn* in an approximate ratio of 3:1 occurs within 5 h (Scheme 4b). Once formed, the product ratio changes neither with time nor with temperature (up to 100 °C).

**Reaction of a 1:1 Mixture of [(triphos)IrCl(C$_4$H$_4$)] (8) and TlPF$_6$ with Ethene or Ethyne.** Heating a solid 1:1 mixture of the iridacyclopentadiene complex 8 and of TlPF$_6$, prepared as described in the Experimental Section, at 70 °C under 4 atm of ethene results in transformation of the starting organometallic complex into a mixture of 4 as the PF$_6^-$ salt, [(triphos)Ir{(1-$\eta^1$:4–6-$\eta^3$)-hexatriene}]PF$_6$ (9), and [(triphos)Ir(*s-trans,s-cis-cis*-(1–4-$\eta^4$)-hexa-1,3,5-triene)]PF$_6$ (10) in a kinetic ratio of 20:5:75 (Scheme 5a). When the reaction mixture is heated further at 70 °C under either C$_2$H$_4$ or argon, all compound 9 disappears. Formed in its place is 10, whereas 4 is thermally stable. Independent thermal reactions carried out on authentic samples of solid 9 and 4 are fully consistent with these results; in particular, no conversion of 9 to 4 is observed even at 100 °C. It is therefore reasonable to consider that the primary interaction of ethene with the metallacycle gives 4 and 9 through independent reaction paths, and only later does 9 thermally rearrange to 10. Notably, the latter compound is thermally stable in the solid state up to 100 °C, which is the highest temperature investigated, whereas in THF solution at 80 °C is rearranges to its *s-trans,s-cis-trans*-(1–4-$\eta^4$)-hexa-1,3,5-triene isomer 11 (see below).[8]

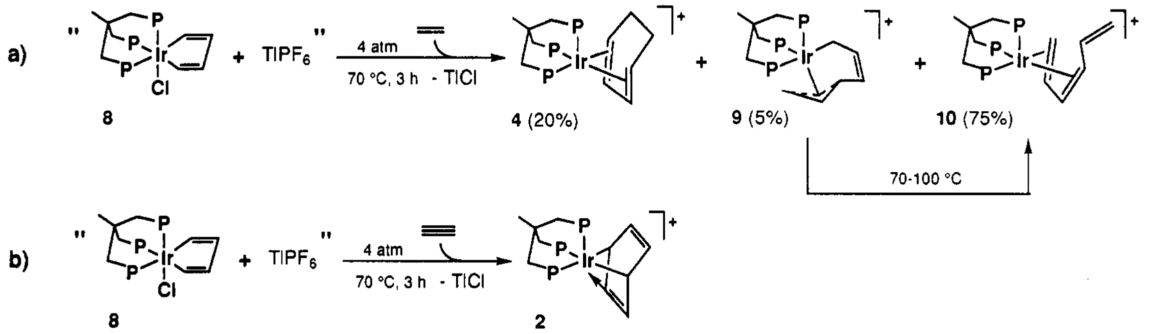
Substitution of ethyne for ethene in the reaction with solid "8 + TlPF$_6$" results in clean formation of 2 (Scheme 5b).

**Related Solution Reactions. Reaction of 2 with But-1-ene.** The $\eta^4$-benzene complex 2 in THF solution reacts with an excess of but-1-ene at 70 °C, resulting in a 72:28 mixture of the 5-*anti* and 5-*syn* isomers (Scheme 6). Under the solid–gas conditions, no reaction occurs between 2 and but-1-ene, a result that is not unexpected in view of the stability of 2 toward ethene (4–8 atm, 70 °C).

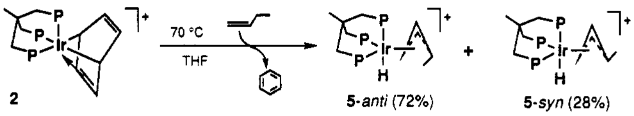
**Reactions of the Iridacyclopentadiene Complex 8 with Ethyne or Ethene.** It has recently been reported that treatment of 8 in THF at room temperature with a chloride scavenger such as TlPF$_6$ in the presence of ethyne results in quantitative formation of 2 (Scheme 7a).[8,10] According to a theoretical analysis, the addition of ethyne to the metallacycle is believed to proceed as a metal-assisted Diels–Alder addition.[10]

Substitution of ethene for ethyne under comparable reaction conditions selectively yields the (1-$\eta^1$:4–6-$\eta^3$)-hexatriene complex 9 *via* a ring-expansion mechanism.[8] Compound 9 is stable in THF solution at room temperature but rapidly rearranges to the *s-trans,s-cis-cis*-(1–4-$\eta^4$)-hexa-1,3,5-triene isomer 10 as the temperature is increased to 70 °C. At higher temperature (>80 °C), conversion of 10 to the *s-trans,s-cis-trans*-(1–4-$\eta^4$)-hexa-1,3,5-triene isomer 11 was selectively observed (Scheme 7b).[8]

**Scheme 5. Related Solid–Gas Reactions**



**Scheme 6. Related Solution Reactions**



**Solid–Gas Reaction between 1 and Ethyne (Flow Reactor).** The solid-state transformation of 1 in the presence of ethyne was also investigated by means of TPR experiments carried out in a flow reactor.

When a sample of 1 is treated with a flow of ethyne (4 atm, 10 mL min$^{-1}$) for 3 h at 70 °C, compounds 2–5 are formed in a ratio essentially identical with that found in the analogous static reaction. Under these experimental conditions, no significant information on the nature and formation of eventual gaseous products was obtained. Conversely, valuable information on the gaseous products was obtained from TPR experiments performed at a heating rate of 5 °C min$^{-1}$, starting from room temperature. In this case, evolution of but-2-ene[14] and benzene is observed, starting approximately from 110 °C, as is shown in Figure 1A. Notably, a separate experiment, analyzed gas chromatographically, showed that ethene is evolved, starting from 110 °C, and that *ca.* 0.1 mol of ethene/mol of 1 is evolved in the temperature range from 110 to 150 °C, while simultaneously ca. 6 mol of ethyne/mol of 1 is adsorbed. No trace of ethane was detected. The organometallic product distribution as determined by $^{31}$P NMR integration is again in good correlation with that observed in the static reaction.

Under analogous experimental conditions, the TPR of a 3:1 mixture of 5-*anti* and 5-*syn* (Figure 1B) showed but-2-ene evolution starting at ca. 80 °C, while benzene evolution was observed above 100 °C. The drop of temperature in the evolution of both but-2-ene and benzene from the crotyl dihydrides as compared to 1 is consistent with the observation that at 70 °C the overall solid-state reaction of 1 is kinetically driven. In particular, the lower reaction temperature may be taken as an indication that the rate of formation of 2 from 5-*anti*/5-*syn* is faster than the rate of formation of 5-*anti*/5-*syn* from 1. Also, it is consistent with the observation that the crotyl hydrides are precursors to 2, which in turn is the catalyst precursor for the cyclotrimerization of ethyne.

**Characterization of the Organometallic Complexes.** All iridium complexes were authenticated by comparing their IR (Nujol mulls) and $^{31}$P, $^{1}$H, and $^{13}$C NMR spectra ($CD_2Cl_2$ solutions) with those of pure samples prepared by independent procedures in either the solid state or solution (vide infra).

The only new compounds are the crotyl hydrides 5-*anti* and 5-*syn*. In accord with the proposed stereochemistries, the $^{31}$P NMR spectra of both compounds show the phosphorus nuclei to be magnetically inequivalent (ABM and AMQ patterns, respectively) and the terminal hydride ligands to be located trans to the high-field-shifted phosphorus atom. The experimental and computed second-order $^{31}$P{$^{1}$H} NMR spectra of 5-*anti* are shown in Figure 2. While the presence of crotyl ligands in both compounds is strongly suggested by their thermal behavior (but-2-ene elimination), unambiguous evidence of *anti*- and *syn*-$\eta^3$-$MeC_3H_4$ ligands was provided by the $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra and in particular by $^{1}$H,$^{1}$H 2D-COSY, $^{13}$C DEPT, $^{1}$H,$^{13}$C 2D-HETCOR, and selective decoupling experiments. In particular, discrimination between the *anti* and *syn* structures of the allyl ligand can readily be made on the basis of the *J*(HH) coupling constants of the central hydrogen to the terminal ones (5-*anti* $\delta(H_c)$ 4.66, $^3J(H_cH_a) = 11.4$ Hz, $^3J(H_cH_s) = 6.6$ Hz, $J(H_cH_{s'}) = 7.0$ Hz; 5-*syn* $\delta(H_c)$ 5.62, $^3J(H_cH_a) = {}^3J(H_cH_{a'}) = 10.3$ Hz, $^3J(H_cH_s) = 7.0$ Hz).[15] Conversely, the spectroscopic data do not discriminate between *cisoid* and *transoid* orientations of the crotyl ligands. A *transoid* orientation may be suggested in light of the X-ray structure of [(triphos)Co($\eta^3$-*i*-$C_4H_7$)]$BPh_4$.[16]

## Discussion

For a better understanding of the chemistry described in this paper, it is useful to summarize some characteristics of the starting complex 1. The compound is stable in the solid state under an inert atmosphere up to 110 °C. Above this temperature, thermal decomposition occurs, following two distinct reaction paths.[2d] The predominant path is ethane elimination to give the unsaturated [(triphos)Ir]$^+$ fragment. In addition, the compound can lose ethene to form the unsaturated dihydride [(triphos)Ir(H)$_2$]$BPh_4$, which then dimerizes to the tetrahydride [(triphos)IrH($\mu$-H)$_2$HIr(triphos)]($BPh_4$)$_2$.

In the presence of added gaseous reagents such as CO and $H_2$, ethane elimination from solid 1 prevails over ethene elimination and, most importantly, the reactions occur at a temperature much lower (60–90 °C) than those performed under an inert atmosphere.[2d] Evidence has also been provided for the intermediacy of an ethyl hydride species, in equilibrium with the ethene dihydride form, in the reductive elimination of ethane from 1.[2d,6]

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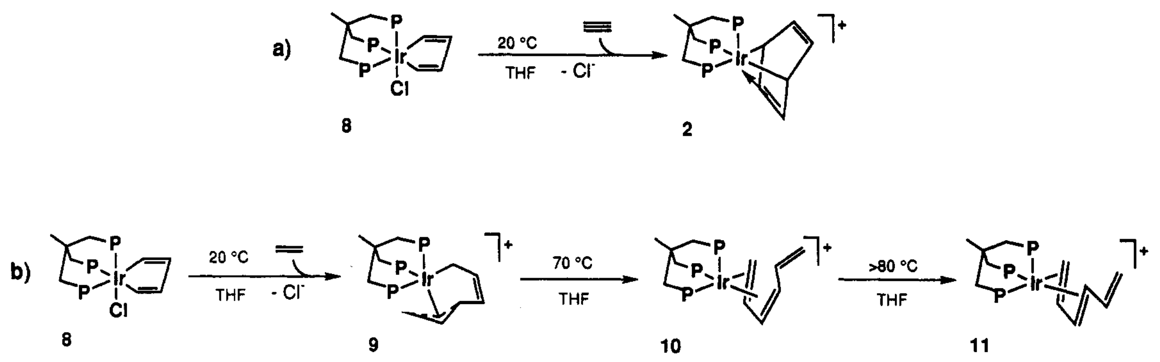
[15] (a) Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129. (b) Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16. (c) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394. (d) Merola, J. S. *Organometallics* **1989**, *8*, 2975. (e) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2555. (f) Nixon, J. F.; Wilkins, B.; Clement, D. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1993.

[16] Sernau, V.; Huttner, G.; Fritz, M.; Zsolnai, L.; Walter, O. *J. Organomet. Chem.* **1993**, *453*, C23.

**Scheme 7. Related Solution Reactions**



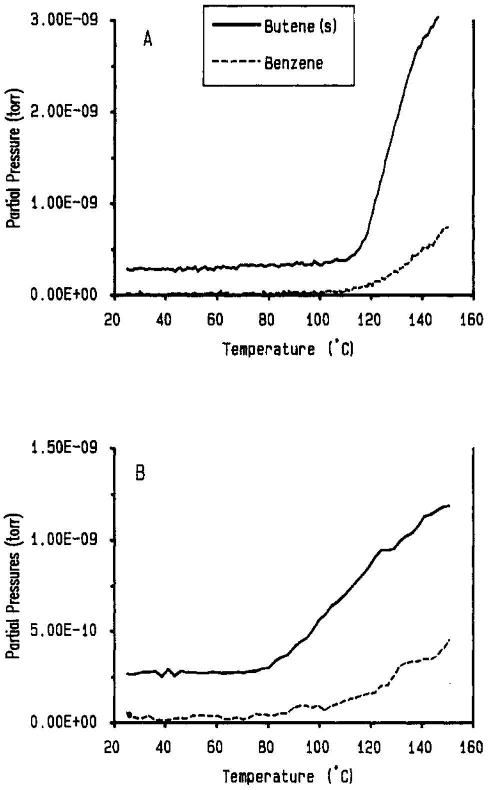


**Figure 1.** Temperature-programmed reactions of 1 (A) and 5-*anti*/5-*syn* (B) with ethyne.

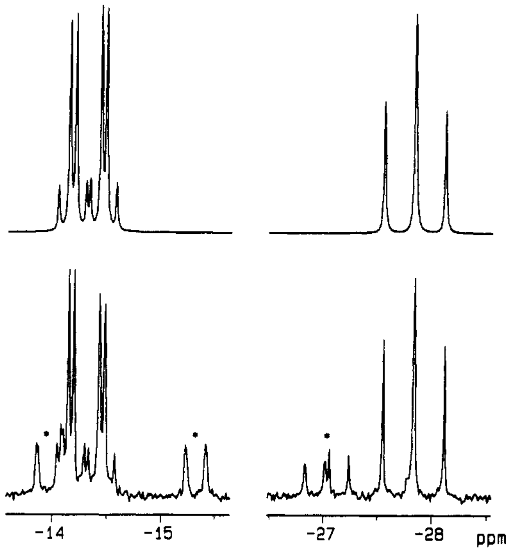


**Figure 2.** Experimental (below) and computed (above) $^{31}P\{^1H\}$ NMR spectra of 5-*anti* ($CD_2Cl_2$, -50 °C, 81.01 MHz). Asterisks denote the resonances of 5-*syn*.

In light of the results of the TPR experiments reported above, it is therefore apparent that, under the present experimental solid–gas conditions, ethyne can displace ethene from 1 to form the $\pi$-ethyne dihydride $[(triphos)Ir(H)_2(C_2H_2)]^+$, which has recently been detected as a transient species in the low-temperature (-50 °C) reaction between 1 and ethyne in dichloromethane solution.[8]

**Cyclotrimerization of Ethyne, Its Reductive Dimerization to Buta-1,3-diene, and Formal Dimerization of Ethene to Butene.** Incorporation of all of the above experimental evidence leads to the mechanism shown in Scheme 8 for the solid–gas reaction between 1 and ethyne, yielding the $\eta^4$-benzene complex 2, the $\eta^4$-buta-1,3-diene complex 3, and the crotyl hydrides 5-*anti* and 5-*syn*. This scheme shows only the C–H and C–C bond-forming events.

Initially, the ethene ligand in 1 is displaced by ethyne (step a). The resulting $\pi$-ethyne dihydride is appropriate to undergo hydride migration from metal to coordinated alkyne to give a vinyl hydride intermediate (step b). Analogous solid–gas hydride-migration processes have already been observed;[2a,d,e,g,o] see for example the heterogeneous reaction of $[(PPh_3)_2Ir(H)_2]_3(PW_{12}O_{40})$ with $C_2H_4$ reported by Siedle and Newmark.[2e]

Reasonably, step b is reactant-promoted and thus the formation of the subsequent $\pi$-ethyne vinyl hydride (step c) may proceed straightforwardly. From this intermediate, a bis(vinyl) complex is formed (*via* a second hydride-migration step), which ultimately converts to the $\eta^4$-buta-1,3-diene complex 3 (step e). Indeed, bis(vinyl)metal complexes, which typically exhibit a low barrier to reductive coupling, are considered key intermediates for the synthesis of buta-1,3-diene derivatives *via* C–C bond formation reactions.[17]

Route a–e incorporates the hydride ligands of 1 in the diene ligand of 3 and liberates ethene. Thus, the ethene ligand in 1 is not necessary for the formation of 3, as is independently demonstrated by the solid–gas reaction of the THF adduct 6 with ethyne, which almost exclusively gives 3 (Scheme 3). On the other hand, the latter reaction also produces an appreciable amount (8%) of the $\eta^4$-benzene complex 2. This means that only a small fraction of the vinyl hydride intermediate produced in step b undergoes the reductive-elimination step f to give compound 2 *via* route g–j (such a reaction sequence has been unambiguously established in solution;[8] see also Schemes 4a, 5b, and 7a).

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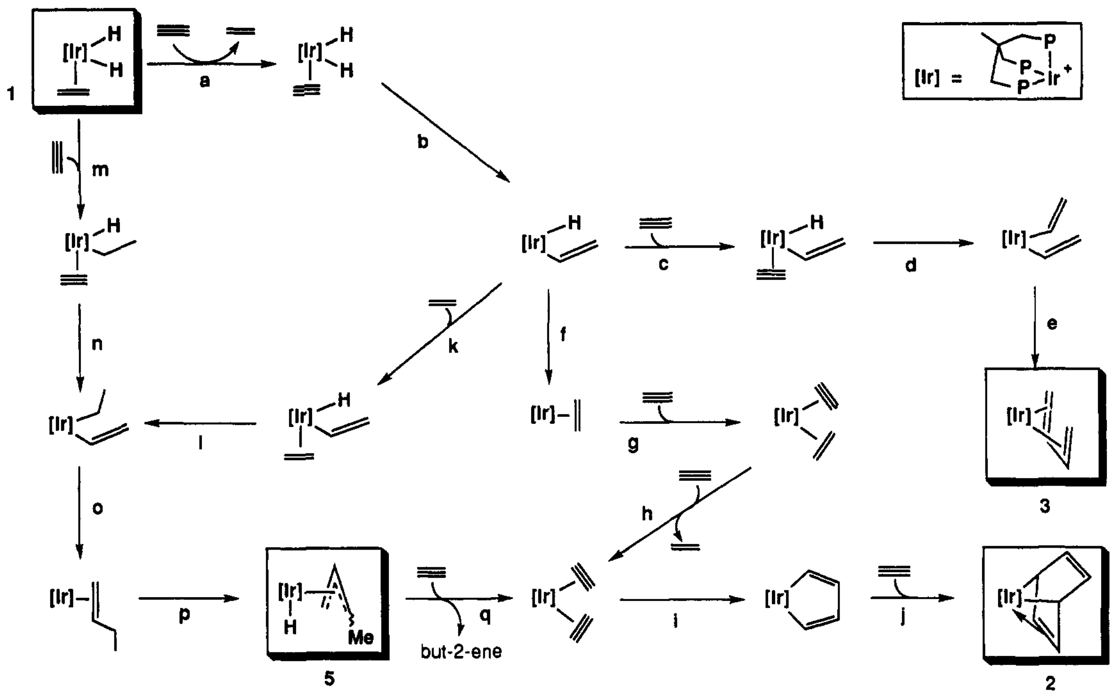
[17] (a) Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945. (b) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298. (c) Lehmkuhl, H.; Keil, T. *J. Organomet. Chem.* **1988**, *342*, C38.

**Scheme 8. Suggested Mechanism for the Formation of 2, 3, and 5 from the Solid–Gas Reaction between 1 and Ethyne (70 °C, 4 atm)**



In conclusion, even though some $\eta^4$-benzene complex may be directly formed from the vinyl hydride species without cooperation of ethene, *most of 2 is necessarily produced in the reaction of 1 with ethyne, which, thus, is an ethene-assisted reaction.* This suggests that not all the ethene ligand liberated in step a comes out of the metal reactant crystal lattice. In fact, the major part might remain trapped in the crystal lattice and be actually responsible for the formation of compounds 2, 4, and 5. This hypothesis is indirectly supported by the solid–gas reaction performed in the flow reactor, which gives an organometallic product distribution essentially identical with that found in the static reactor. Thus, ethene may reenter the metal coordination sphere at the stage of the vinyl hydride intermediate to give a $\pi$-ethene vinyl hydride complex (step k), which is a suitable precursor to the crotyl hydride complexes *via* thermal rearrangement as reported by Carmona et al.[18] (see also Scheme 4b). These authors have more recently shown that Tp*Ir($C_2H_4$)(H)($C_2H_3$) (Tp* = hydridotris(3,5-dimethyl-1-pyrazolyl)borate) undergoes insertion of ethene into the Ir–H bond to give an ethyl vinyl complex in coordinating solvents such as MeCN or by addition of a monodentate ligand such as $PMe_3$.[19] Accordingly, it is reasonable to propose that also in the solid state the $\pi$-ethene vinyl hydride intermediate converts to the ethyl vinyl species (step l).[20] As is shown in Scheme 8 (upper left), there is an alternative mechanism which may account for the formation of the ethyl vinyl intermediate. This involves formation of a $\pi$-ethyne ethyl hydride (step m) through the stabilization of the ethyl hydride form of 1 with ethyne as occurs in the solid–gas reactions between 1 and CO or $H_2$.[2d] The following conversion to the ethyl vinyl intermediate then proceeds *via* ethyne insertion into the Ir–H bond (step n).

Unfortunately, the concidence of the temperatures at which ethene and but-2-ene are evolved in the TPR of 1 does not allow us to discriminate between the two reaction paths for the formation of the ethyl vinyl intermediate. It may also be possible that the two processes take place independently. Whatever the mechanism of its formation, it is certain that the ethyl vinyl complex is a key intermediate for the formation of the crotyl hydrides and thus of the $\eta^4$-benzene complex 2 (and of the $\eta^4$-cyclohexa-1,3-diene complex 4 as well; see next section). The formation of the crotyl hydride complexes from the ethyl vinyl intermediate is rather ordinary, as it involves reductive elimination to give a $\pi$-bonded but-1-ene complex (step o), followed by oxidative addition of a C–H bond from the methylene group (step p). This mechanism has several precedents in the literature,[21] including examples in solid–gas reactions[2e] (see also the reaction of 2 with but-1-ene; Scheme 6).

Once the crotyl hydride complexes are formed, their conversion to 2 is easily rationalized on the basis of the experimental results described in Schemes 2c, 5b, and 7a; in particular, a key role is played by the iridacyclopentadiene fragment, which can add ethyne *via* a Diels–Alder mechanism.[10]

As previously mentioned, the solid–gas reaction of 2 with ethyne (4 atm) at 100 °C produces catalytic amounts of benzene. In this reaction, 2 is the only termination metal product. The experimental evidence reported in Scheme 5b suggests a mechanism involving the intermediacy of a metallacyclopentadiene complex, as occurs in the homogeneous phase for the cyclotrimerization of ethyne catalyzed by 2 and, generally, for metal-assisted

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[18] Pérez, P. J.; Poveda, M. L.; Carmona, E. *J. Chem. Soc., Chem. Commun.* **1992**, 8.

[19] Carmona, E. Private Communication. See also: Carmona, E.; Hudson, S.; Nicasio, M. C.; Pérez, P. J.; Poveda, M.; Rey, L. Latin-American Inorganic Chemistry Meeting, Santiago de Compostela, Spain, Sept 13–17, 1993; Book of Abstracts, p 248.

[20] The conversion of the $\pi$-ethene vinyl hydride to the bis(ethene) complex 7 *via* reductive elimination of hydride and vinyl ligands is ruled out by us in light of the results shown in Scheme 4b.

[21] (a) Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428. (b) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (c) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516. (d) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

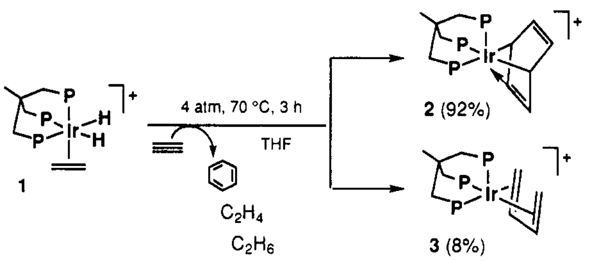
cyclotrimerization reactions of alkynes.[22] Catalytic formation of benzene from ethyne in solid–gas systems has previously been reported by Siedle and Newmark.[2e] In their case, the catalyst precursor was the 14-electron fragment $[(PPh_3)_2Ir(H)_2]^+$, stabilized in the $PW_{12}O_{40}^{3-}$ lattice, and therefore the resulting iridium complex contains an $\eta^6$-benzene ligand.

**Formal Cocyclization of Ethyne with Ethene to Cyclohexa-1,3-diene.** The formation of the $\eta^4$-cyclohexa-1,3-diene complex **4**, as illustrated in Scheme 1, is discussed separately from those of **2**, **3**, and **5** since we have not been able to either unambiguously perform the synthesis of **4** *via* independent solid–gas reactions or show any correlation with the other organometallic products obtained from the reaction between **1** and ethyne.

The only firm point is that the ethene ligand in **1** is of mandatory importance to obtain the cyclohexa-1,3-diene ligand. Also, we have found that the $\eta^4$-buta-1,3-diene complex **3** does not react with ethyne under either solid–gas conditions (4–8 atm, 70–100 °C) or in the homogeneous phase (THF, 4 atm of $C_2H_2$, 70 °C). The lack of reactivity of **3** toward ethyne apparently rules out the occurrence of a mechanism involving metal-assisted coupling between buta-1,3-diene and alkyne ligands, of which there are several examples in the literature. See for example the reaction of hexafluorobut-2-yne with $Fe(CO)_3(C_4H_6)$ reported by Green, Woodward, et al.[23a] and the reaction of ethyne with $Cp^*RuCl(C_4H_6)$ reported by Itoh et al.[23b]

The alternative reaction in which alkynes cooligomerize with alkenes at metal centers to give cyclohexa-1,3-diene is the one between metallacyclopentadiene metal complexes and alkenes *via* either Diels–Alder addition or ring expansion, followed by reductive elimination.[24] As suggested in a previous section, an iridacyclopentadiene species most likely traverses the solid–gas formation of the $\eta^4$-benzene complex **2** (the intermediacy of this metalla ring has been unambiguously shown in solution). Accordingly, one may reasonably suggest that the iridacyclopentadiene fragment $[(triphos)Ir(C_4H_4)]^+$ also traverses the formation of the cyclohexa-1,3-diene complex **4**. Experimental support for this hypothesis is provided by the solid–gas reaction of "**8** and $TlPF_6$" with ethene, even though caution must be adopted to evaluate this experiment, which was carried out on an amorphous solid. As shown in Scheme 5a, after the chloride ligand in **8** has been removed by $TlPF_6$ (such solid–solid thermal reactions are well-known),[3] the resulting amorphous solid, containing an unsaturated iridacyclopentadiene system, reacts with ethene to give **4** and the *s-trans,s-cis-cis*-(1–4-$\eta^4$)-hexa-1,3,5-triene complex **10** (the precursor to **10** is the (1-$\eta^1$:4–6-$\eta^3$)-hexatriene isomer **9**) in a ratio of 1:4. This result markedly contrasts with the result observed under comparable conditions in the homogeneous phase (Scheme 7b), where **10** is selectively produced *via* **9**. The result of the reaction of amorphous $[(triphos)Ir(C_4H_4)]^+$ with ethene thus lies in between what occurs in solution and what we expect to occur within a crystalline sample of the iridametallacycle, where the internal pressure in the solid[2f] would favor the formation of the less sterically demanding cyclohexa-1,3-diene ligand. This effect is clearly shown by the fact that crystalline **10** thermally converts to its bulkier *s-trans,s-cis-trans*-(1–4-$\eta^4$)-hexa-1,3,5-triene isomer **11** in solution, whereas it does not in the solid state (compare Schemes 5a and 7b).

**Scheme 9**



The anomalous behavior of amorphous iridacyclopentadiene may tentatively be explained in terms of a higher number of surface metal species as well as larger channels in the solid (due to the lack of crystalline organization) as compared to ideal crystalline $[(triphos)Ir(C_4H_4)]BPh_4$.

In conclusion, we suggest that the formation of the cyclohexa-1,3-diene ligand may involve the intermediacy of an unsaturated iridacyclopentadiene fragment. Whether the coupling reaction with ethene (liberated in steps a and h of Scheme 8) occurs *via* Diels–Alder addition or ring expansion is a question that cannot be addressed experimentally.

**Comparison with Fluid Solution-Phase Systems.** Under analogous experimental conditions but in THF solution (Scheme 9), the reaction between **1** and ethyne gives a 92:8 mixture of **2** and **3** together with free benzene at a rate of 4 mol (mol of catalyst)$^{-1}$ h$^{-1}$. Ethene and ethane are also produced. The homogeneous reaction thus significantly differs from the heterogeneous one shown in Scheme 1. In particular, the evolution of ethane (not formed in the solid-state reaction) indicates that, in solution, ethyne can promote the reductive coupling of hydride and ethyl ligands at iridium. In contrast, ethene displacement from **1** by ethyne occurs in both the solid state and solution. However, under our observational experimental conditions in THF solution (4 atm of $C_2H_2$, 70 °C), the liberated ethene in solution apparently does not reenter the metal coordination sphere, as neither the $\eta^4$-cyclohexa-1,3-diene complex **4** nor the crotyl hydrides **5**-*anti*/**5**-*syn* are formed.

## Conclusions

A variety of oligomerization and cooligomerization products (eqs 1–4) are formed by reaction of ethyne with solid $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$.

With the use of isolated complexes in independent solid–gas reactions and of TPR experiments, one may draw several mechanistic conclusions which account for the

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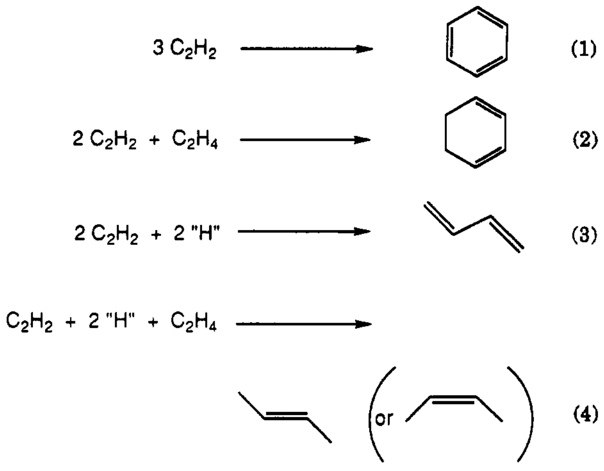
[22] (a) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666. (b) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (c) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067. (d) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L.; Chiang, M. Y. *Organometallics* **1989**, *8*, 2696. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 645. (f) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.

[23] (a) Bottrill, M.; Davies, R.; Goddard, R.; Green, M.; Hughes, R. P.; Lewis, B.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1252. (b) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, *12*, 2221.

[24] (a) Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494. (b) Brown, L. D.; Itoh, K.; Suzuki, H.; Hirai, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 8232. (c) Zhou, Z.; Battaglia, L. P.; Chiusoli, G. P.; Costa, M.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1632. (d) Zhou, Z.; Battaglia, L. P.; Chiusoli, G. P.; Costa, M.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Organomet. Chem.* **1991**, *417*, 51. (e) Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581. (f) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (g) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081.



varied organometallic and organic products. *Inter alia*, the following points deserve comment.

(i) The cyclotrimerization reaction is traversed by a number of intermediates, among which are π-ethene vinyl hydride, ethyl vinyl, $\eta^3$-crotyl hydride, and iridacyclopentadiene species. The last compound is a likely intermediate also for the cooligomerization of ethyne with ethene to cyclohexa-1,3-diene.

(ii) The reductive coupling of ethyne to buta-1,3-diene occurs at iridium *via* subsequent insertion of two ethyne molecules into Ir–H bonds, followed by reductive elimination from a bis(vinyl) intermediate. A competitive inhibitor for this reaction is the ethene ligand in **1**, as it may either disfavor the insertion of a second ethyne molecule into an Ir–H bond by forming a π-ethene vinyl hydride complex or insert into an Ir–H bond to give an ethyl vinyl species.

(iii) A π-ethene vinyl hydride intermediate, formed by intramolecular C–H bond activation of π-ethene, traverses the thermal conversion of the bis(ethene) complex **7** to the $\eta^3$-crotyl hydride complexes.

(iv) Comparisons with analogous fluid solution-phase systems or with amorphous systems show that the reactions between gaseous molecules and crystalline metal complexes invariably lead to the formation of the least sterically demanding products.

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