Molecular Solid–Gas Organometallic Chemistry. Catalytic and Stoichiometric Transformations of Ethyne at Iridium

Claudio Bianchini,*,† Piero Frediani,‡ Mauro Graziani,§ Jan Kaspar,§ Andrea Meli,†
Maurizio Peruzzini,† and Francesco Vizza†

*Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR,
Via J. Nardi 39, 50132 Firenze, Italy, Dipartimento di Chimica Organica, Università di
Firenze, 50121 Firenze, Italy, and Dipartimento delle Scienze Chimiche, Università di Trieste,
Via Valerio 38, 34127 Trieste, Italy*

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Summary: The η^2-ethene dihydride $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$ (1; triphos = $MeC(CH_2PPh_2)_3$) reacts in the solid state with ethyne (4 atm) at 70 °C to give five different organometallic products, namely $[(triphos)Ir(\eta^4\text{-}C_6H_6)]BPh_4$ (2), $[(triphos)Ir(\eta^4\text{-}C_6H_8)]BPh_4$ (3), $[(triphos)Ir(\eta^4\text{-}C_4H_6)]BPh_4$ (4), $[(triphos)Ir(H)(\eta^3\text{-}MeC_3H_4)]BPh_4$ (5-anti), and $[(triphos)Ir(H)(\eta^3\text{-}MeC_3H_4)]BPh_4$ (5-syn), and but-2-ene. At 100 °C, the solid–gas reaction produces catalytic amounts of benzene, the real catalyst being the η^4-benzene complex 2. Comparison with fluid solution systems provides evidence for the control exerted by the constraining environment of the crystal lattice of the organometallic complex on the reaction.

The field of molecular solid–gas organometallic chemistry has made considerable progress since its inception.[1]

In reactions between solid metal complexes and gaseous organic molecules, the constraining environment of the reactant crystal lattice can control both the kinetics and the nature of the products. As a result, the product of a solid–gas reaction may not necessarily be the one obtainable in solution but may rather be the one dictated by the reaction pathways accessible in the contraining environment of the solid reactant.

As a remarkable example of the control exerted by the reactant crystal lattice, we report in this paper that ethyne (4 atm) reacts at 70 °C for 3 h with off-white crystals of the η^2-ethene dihydride $[(triphos)Ir(H)_2(C_2H_4)]BPh_4$[2] (1; triphos = $MeC(CH_2PPh_2)_3$) to give different organic and organometallic products according to whether the reaction is performed in either heterogeneous (solid–gas) or homogeneous fashion.

In tetrahydrofuran (THF) solution (ca. 10^{-2} M), 1 reacts with ethyne to give a 92:8 mixture of the η^4-benzene complex $[(triphos)Ir(\eta^4\text{-}C_6H_6)]BPh_4$[3] (**2**) and of the η^4-buta-1,3-diene complex $[(triphos)Ir(\eta^4\text{-}C_4H_6)]BPh_4$[4] (**4**) together with free benzene at a rate of 4 mol (mol of catalyst)$^{-1}$ h^{-1}.[5] Under analogous reaction conditions but in the solid state, five iridium complexes, namely **2**, $[(triphos)Ir(\eta^4\text{-}C_6H_8)]BPh_4$[6] (**3**), **4**, $[(triphos)Ir(H)(\eta^3\text{-}MeC_3H_4)]BPh_4$[7] (**5**-*anti*), and $[(triphos)Ir(H)(\eta^3\text{-}MeC_3H_4)]BPh_4$[7] (**5**-*syn*), are obtained in a ratio of 35:23:5:28:9 (Scheme I).[8] This 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 the η^4-benzene complex **2**. In contrast, both the η^4-cyclohexadiene complex **3** and the η^4-buta-1,3-diene 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 an independent procedure, have been found to react in the solid state with

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† CNR, Firenze.

‡ Università di Firenze.

§ Università di Trieste.

[1] (a) Bianchini, C.; Peruzzini, M.; Zanobini, F. *Organometallics* **1991**, *10*, 3415. (b) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1992**, *114*, 3698. (c) Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993**, *115*, 1753. (d) Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 2058. (e) Siedle, A. R.; Newmark, R. A. *Organometallics* **1989**, *8*, 1442. (f) Aubart, M. A.; Pignolet, L. H. *J. Am. Chem. Soc.* **1992**, *114*, 7901.

[2] Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227. Complex 1 is stable in the solid state under an inert atmosphere (N_2 or He) or under reduced pressure (0.1 Torr) at 110 °C.

[3] Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127.

[4] Selected NMR data are as follows. $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, δ): AM_2 pattern; 20 °C, −23.9 (br, P_A), −23.1 (br, P_M); −58 °C, −25.0 (t, $J(P_AP_M)$ = 6.9 Hz, P_A), −22.5 (d, P_M). ^1H NMR (200.13 MHz, CD_2Cl_2, 28 °C, δ): 5.39 (m, 2 H, C*H*), 2.06 (m, 2 H, CH*H*), 1.48 (m, 2H, C*H*H). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, −40 °C, δ): 87.6 (s, *C*H), 29.1 (d, br, $J(CP)$ = 32.6 Hz, *C*H_2). A pure sample of **4** was obtained by the following procedure: Solid $[Ir(COE)_2Cl]_2$ (COE = cyclooctene) (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) was added to the resulting solution, the color of which immediately changed from red to orange. On addition of ethanol (40 mL) and slow concentration, pale yellow crystals of **4** were obtained in 85% yield.

[5] The organometallic product distribution does not appreciably change in the temperature and ethyne pressure ranges from 20 to 70 °C and from 1 to 4 atm, respectively. At room temperature, no catalytic production of benzene is observed.

[6] Bianchini, C.; Caulton, K. G.; Folting, G.; Meli, A.; Peruzzini, M.; Polo, A.; Vizza, F. *J. Am. Chem. Soc.* **1992**, *114*, 7290.

[7] Selected NMR data for **5**-*anti* are as follows. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2, −50 °C, δ): ABM pattern; −14.2 (P_A), −14.4 (P_B), −27.8 (P_M), $J(P_AP_B)$ = 7.9 Hz, $J(P_AP_M)$ = 23.0 Hz, $J(P_BP_M)$ = 22.6 Hz. ^1H NMR (200.13 MHz, CD_2Cl_2, 20 °C, δ): 4.66 (dt br, $J(H_cH_a)$ = 11.4 Hz, $J(H_cH_{s'})$ = 7.0 Hz, $J(H_cH_s)$ = 6.6 Hz, H_c), 3.90 (quintet br, $J(H_{s'}Me)$ = 6.2 Hz, $J(H_{s'}H_s)$ < 2 Hz, $H_{s'}$), 3.81 (m, $J(H_aH_s)$ < 2 Hz, H_a), 2.89 (d br, H_s), 2.03 (m, Me), −12.52 (dt, $J(HP_M)$ = 139.3, $J(HP_A)$ = $J(HP_B)$ = 13.6 Hz, Ir–H). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 20 °C, δ): 92.1 (s, *C*H), 59.8 (d, $J(CP)$ = 24.8 Hz, *C*HMe), 29.9 (dd, $J(CP)$ = 37.5, 5.7 Hz, *C*H_2), 22.1 (dd, $J(CP)$ = 4.4, 1.9 Hz, Me). Selected NMR data for **5**-*syn* are as follows. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2, −50 °C, δ): ABM pattern; −14.0 (P_A), −15.3 (P_B), −27.0 (P_M), $J(P_AP_b) \cong 0$ Hz, $J(P_AP_M)$ = 17.9 Hz, $J(P_BP_M)$ = 15.1 Hz. ^1H NMR (200.13 MHz, CD_2Cl_2, 20 °C, δ): 5.62 (td br, $J(H_cH_s)$ = 7.0 Hz, $J(H_cH_a)$ = $J(H_cH_{a'})$ = 10.3 Hz, H_c), 3.35 (m, $J(H_sH_a)$ < 2 Hz, H_s), 2.92 (m, $J(H_{a'}Me)$ = 6.2 Hz, $H_{a'}$), 1.99 (m, H_a), 1.51 (d br, Me), −13.42 (dt br, $J(HP_M)$ = 127.9, $J(HP_A)$ = $J(HP_B)$ = 8.8 Hz, Ir–*H*). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 20 °C, δ): 94.3 (d, $J(CP)$ = 4.8 Hz, *C*H), 55.6 (d, $J(CP)$ = 23.5 Hz, *C*HMe), ca. 32 (partially masked by CH_2 carbon resonances of triphos, *C*H_2), 20.98 (s, Me). Independent synthesis of **5**-*anti* and **5**-*syn*: A solid sample of **2** (0.30 g, 0.25 mmol) was dissolved in THF (40 mL) saturated with 1-butene at room temperature. The mixture was then transferred into an autoclave and heated at 78 °C for 3 h. After cooling and venting, the contents of the bomb were concentrated to dryness under reduced pressure and the residue washed with *n*-pentane. The product was characterized by IR (Nujol: ν (cm^{-1}) 2120, Ir–H) and multinuclear NMR spectroscopy as a 72:28 mixture of the two η^3-crotyl isomers **5**-*anti* and **5**-*syn*.

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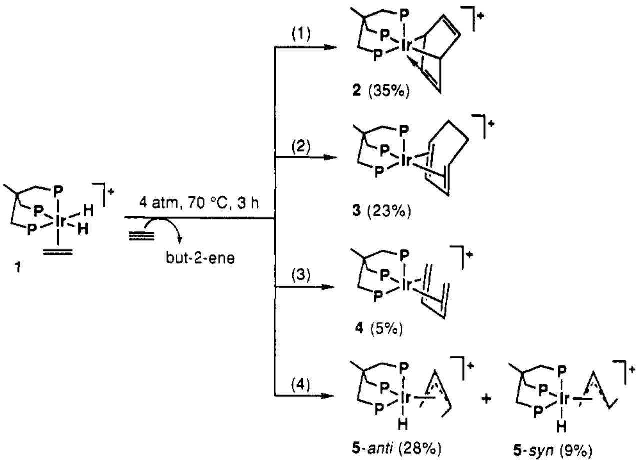
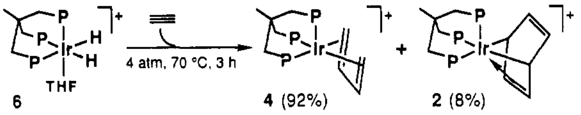
Scheme I



Scheme II



ethyne (4 atm, 70 °C, 3 h) to give the η^4-benzene complex 2 and a stoichiometric amount of but-2-ene.

The kinetic control of the solid–gas reaction is further confirmed by a temperature-programmed reaction (TPR)[9] of 1 with ethyne which shows evolution of but-2-ene[10] starting at about 70 °C, followed by that of benzene at 100 °C. As a matter of fact, 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 real catalyst being the η^4-benzene complex 2 as shown by an independent catalytic reaction.[11]

From a formal viewpoint, the reactions shown in Scheme I may be described as unprecedented solid–gas examples of cyclotrimerization of ethyne to benzene (1), of cocyclization of ethyne with ethene to cyclohexa-1,3-diene (2), of reductive dimerization of ethyne to buta-1,3-diene (3), and of dimerization of ethene to butene (4).

Studies are in progress in order to gain insight into the overall mechanism of the solid–gas reaction shown in Scheme I as well as the factors that may tip the balance in favor of the formation of each product. It may be anticipated here that the presence of the ethene ligand in 1 is of mandatory importance for the formation of the η^4-cyclohexadiene and η^3-crotyl complexes. In fact, substitution of the solvento complex [(triphos)Ir(H)$_2$(THF)]BPh$_4$ (6)[12] for 1 in the solid–gas reaction with ethyne (4 atm, 70 °C, 3 h) results in selective formation of the η^4-butadiene complex plus some η^4-benzene complex (Scheme II). A crotyl hydride complex of the formula Tp*Ir(H)(η^3-C$_4$H$_7$) (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) has recently been synthesized from a bis(ethene) complex *via* an ethene vinyl hydride intermediate.[13] A reaction sequence of this type may account for the formation of the η^3-crotyl complexes 5-*anti* and 5-*syn* once ethyne is reduced to either ethene or vinyl by the hydride ligands of 1.

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(8) The reactions under controlled pressure of ethyne 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) were pressurized with ethyne to 4 atm at room temperature in a 100-mL bomb made of type 316 stainless steel and then heated at 70 °C 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 authenticated by comparison with authentic specimens. 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 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.

(9) TPR measurements were carried out in a flow reactor under a flow of ethyne (10 mL min^{-1}, total pressure 4 atm) at a heating rate of 5 °C min^{-1}. Analyses of the outcoming products were performed on an on-line quadrupole VG200 analyzer.

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

(11) Quantification of benzene produced in the catalytic reaction 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.

(12) The synthesis and spectroscopic properties of 6 will be published elsewhere: Bianchini, C.; Caulton, K. G.; Johnson, T. J.; Meli, A., submitted for publication.

(13) Pérez, P. J.; Poveda, M. L.; Carmona, E. *J. Chem. Soc., Chem. Commun.* 1992, 8.