Thermal and Photochemical C–H Bond Activation Reactions at Iridium. π-Coordination vs C–H Cleavage of Ethene, Styrene, and Phenylacetylene

Claudio Bianchini,* Pierluigi Barbaro, Andrea Meli, Maurizio Peruzzini,
Alberto Vacca, and Francesco Vizza

*Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione,
ISSECC, CNR, Via J. Nardi 39, 50132 Florence, Italy*

Received January 14, 1993

Thermolysis of [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1) in various solvents (benzene, THF, MeCN, DMF) results in formation of the 16-electron fragment [(triphos)IrH] and ethane. The reactive intermediate is capable of insertion into the C–H bonds of either solvents or appropriate substrates (1-alkynes, ethene), generally affording σ-organyl dihydrides of the formula [(triphos)Ir(H)$_2$(σ-organyl)] (organyl = C$_6$H$_5$, CH$_2$CN, C≡CPh, C≡CCO$_2$Et, CH=CH$_2$). The hydride carbonyl [(triphos)IrH(CO)] and dimethylamine are produced by reaction with *N*,*N*-dimethylformamide. Thermolysis of 1 in THF at 66 °C in the presence of ethene (1–4 atm) gives the vinyl hydride [(triphos)Ir(H)$_2$(CH=CH$_2$)] (8) and the π-complex [(triphos)IrH(C$_2$H$_4$)] (7) in a kinetic product ratio showing that π-complexation is not a precursor for C–H insertion. Under the same reaction conditions, styrene gives selectively the π-complex [(triphos)IrH(CH$_2$=CHPh)] (9). UV irradiation of 7 and 9 in either benzene or THF at 20 °C promotes insertion of iridium into the C–H bonds to give 8 and a 1:1 mixture of the *E* and *Z* styryl complexes [(triphos)Ir(H)$_2$(CH=CHPh)] (11, 12), respectively. Secondary photolysis on either 8 or 11 and 12 results in photoejection of ethene and dihydrogen, respectively. In the case of the vinyl complex, the reactive intermediate is trapped by the solvent, whereas the styryl dihydrides are converted to the stable π-alkyne hydride [(triphos)IrH(HC≡CPh)]. The latter complex is also obtained by photolysis of [(triphos)Ir(H)$_2$(C≡CPh)] in THF at 20 °C. Both the vinyl dihydride and the styryl dihydrides are thermodynamically unstable and convert to the corresponding π-olefin complex in refluxing THF. Irradiation of 1 in either THF or benzene at 20 °C produces several metal products and gases (C$_2$H$_6$, C$_2$H$_4$, and H$_2$) due to the occurrence of both primary and secondary photolysis reactions. Irradiation of the trihydride [(triphos)Ir(H)$_3$] in benzene results in formation of the phenyl dihydride [(triphos)Ir(H)$_2$(Ph)] and evolution of H$_2$. Possible mechanisms for the thermal and photochemical reactions are discussed.

Introduction

An understanding of the primary interaction between metal complexes and saturated or unsaturated hydrocarbons is of both considerable practical and fundamental interest. Practical motivations arise from the fact that hydrocarbons constitute the backbone of the chemical industry. On the other hand, hydrocarbon activation is a relevant feature in many life processes.

The last two decades have witnessed the rise of unifying ideas emerging from basic research. It is now generally agreed that hydrocarbon C–H activation is performed by either early d-block, lanthanide or actinide elements in their highest oxidation states, or highly energetic low-valent metal fragments endowed with sufficient energy to lower the barrier to C–H insertion. In the latter case, the best candidates are either coordinatively unsaturated 16-electron metal systems, possibly disregarding the square-planar geometry, or 14-electron fragments of the nickel triad.

Most studies of C–H activation have focused on aromatic,[1] acetylene[2] and aliphatic hydrocarbons.[3] Only recently, essentially due to the pioneristic work of Bergman[4] and Field,[5] has it been made evident that also alkenes can react with coordinatively unsaturated metal complexes by oxidative addition to give vinyl hydrides.[6] In this case, a crucial role seems to be played by the steric crowding at the metal center.[7]

Our work in the field of C–H activation is attempting to address the question of the primary interaction between

---

(1) (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 7. (c) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 234. (d) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (g) Fryzuk, M. D.; Jones, T.; Einstein, F. W. *Organometallics* **1984**, *3*, 185. (h) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (i) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856. (j) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (k) Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266. (l) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411. (m) Ghosh, C. K.; Graham, W. A. *J. Am. Chem. Soc.* **1989**, *111*, 375. (n) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(2) (a) Ittell, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Marder, T. B.; Zargarian, D.; Calabrese, J. C.; Herskowitz, T. H.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1484. (c) Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *346*, C53. (d) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179. (e) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540. (f) Bianchini, C.; Innocenti, P.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 2514. (g) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146. (h) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. (i) Klein, H. F.; Beck, H.; Hammerschmitt, B.; Koch, U.; Koppert, S.; Cordier, G.; Paulus, H. *Z. Naturforsch.* **1990**, *46B*, 147. (j) Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 11. (k) Hills, A.; Hughes, D. L.; Kashef, N.; Lemos, M. A. N. D. A.; Pombeiro, A. J. L.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1775.

0276-7333/93/2312-2505$04.00/0 © 1993 American Chemical Society

metals and hydrocarbons by examining the use of transition metal complexes stabilized by tripodal polyphosphine ligands. Due to their particular geometry, these ligands combine the well-known *polyphosphine advantages*[8] with a rigorous control on the stereochemistry of their complexes. As a result, tripodal polyphosphine metal complexes are invariably very stable and, therefore, often allow the isolation and characterization of reactive intermediates not normally seen in comparable reactions with ligands of lesser hapticity or different geometry.[9]

In the present paper, we report on the ability of the 16-electron reactive intermediate [(triphos)IrH], easily generated by either thermal or photochemical decomposition of the ethyl dihydride [(triphos)Ir(H)$_2$(C$_2$H$_5$)],[10] to activate a variety of saturated and unsaturated hydrocarbons in inter- and intramolecular fashion [triphos = MeC(CH$_2$PPh$_2$)$_3$]. Of particular relevance are our results on the relative stability of Ir(H)(CH=CHR) vs Ir(π-CH$_2$=CHR) (R = H, Ph) and Ir(H)(C≡CR) vs Ir(π-HC≡CR) (R = Ph) moieties.

Experimental Section

General Procedure. All reactions and manipulations were routinely performed under an atmosphere of nitrogen by using Schlenk-type techniques. Photochemical reactions were performed by using a Helios Italquartz UV 13F apparatus. The photolysis source was a 135-W (principal emission wavelength 366 nm) high-pressure mercury vapor immersion lamp equipped with a water filter to remove excess heat. Photolysis NMR experiments were carried out in quartz tubes. No substantial change was observed by using Pyrex tubes. Reactions under controlled pressure of ethene were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature and pressure controller. Tetrahydrofuran (THF), MeCN, and *N,N*-dimethylformamide (DMF) were purified by distillation over LiAlH$_4$, CaH$_2$, and CaO, respectively; benzene, di-*n*-butyl ether, and *n*-heptane, from sodium. The solvents were stored over molecular sieves and purged with nitrogen prior to use. LiHBEt$_3$ (1.0 M solution in THF) was purchased from Aldrich Chemical Co. All other reagents and chemicals were reagent grade and were used as received by commercial suppliers. The starting materials [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1), [(triphos)IrH(C$_2$H$_4$)] (7), and [(triphos)Ir(C$_2$H$_4$)$_2$]BPh$_4$ were prepared as previously described.[10] The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. Deuterated solvents for NMR measurements were dried over molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either a Varian VXR 300 (299.94 and 75.43 MHz) or a Bruker ACP 200 (200.13 and 50.32 MHz) spectrometer. ^{1}H NMR shifts were measured relative to residual ^{1}H resonance in the deuterated solvent: CD$_2$Cl$_2$ (δ 5.33); benzene-d_6 (δ 7.27). ^{13}C{^{1}H} NMR spectra were measured relative to the deuterated solvent resonance (CD$_2$Cl$_2$, δ 53.6; THF-d_8, δ 67.9, 25.8; pyridine-d_5, δ 123.5, 135.5, 149.2). ^{31}P{^{1}H} NMR spectra were recorded on the same instruments operating at 121.42 and 81.01 MHz, respectively. Chemical shifts are relative to external 85% H$_3$PO$_4$ with downfield values reported as positive. Broadband and selective ^{1}H{^{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. ^{13}C-DEPT, 2D-HETCOR, and 2D-COSY NMR experiments were conducted on the Bruker ACP 200 spectrometer. The computer simulation of NMR spectra was 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 the experimental digitized spectrum. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor *R* being less than 2% 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-μm FT) 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.

Synthesis of [(triphos)Ir(H)$_2$(Ph)] (2). A suspension of 1 (0.20 g, 0.23 mmol) in benzene (30 mL) was heated at reflux temperature. Within 2 h the solid dissolved to give a yellowish solution. On addition of a 1:3 mixture of ethanol and *n*-heptane (30 mL) and slow concentration under a stream of nitrogen, off-white crystals of 2 precipitated. They were collected by filtration and washed with *n*-pentane; yield 90%. Anal. Calcd for C$_{47}$H$_{46}$IrP$_3$: C, 63.00; H, 5.17; Ir, 21.45. Found: C, 62.89; H, 5.18; Ir, 21.36. IR: ν (Ir–H) 2063 (s) cm^{-1}; ν(C=C) phenyl vibration 1566 (m) cm^{-1}. Monitoring the reaction (benzene-d_6, 65 °C) in a sealed NMR tube by ^{1}H NMR spectroscopy revealed ethane evolution (singlet at ca. 0.8 ppm). Interestingly, (i) **2** converts to its perdeuterated isotopomer [(triphos)Ir(D)$_2$(C$_6$D$_5$)] (**2**-d_7) in benzene-d_6 at temperatures higher than 50 °C (^{31}P{^{1}H} NMR, 20° C: AM$_2$X$_2$ spin system, X = ^{2}D, δ(P$_A$) −8.5 (t), δ(P$_M$) −19.0 (q of intensity 1:2:2:1, J(P$_M$P$_A$) $\simeq$ J(P$_M$X) = 14.3 Hz)) and (ii) quantitative formation of **2** is observed also when a benzene solution of 1 is refluxed under a steady stream of CO for 2 h. At 10 atm of CO, thermolysis of 1 in benzene produces also the hydride carbonyl [(triphos)IrH(CO)] (4) in 18% yield.[13] Selective formation of **2** is found also when the thermolysis reaction was carried out in a 1:1 (v:v) mixture of benzene/MeCN.

Synthesis of [(triphos)Ir(H)$_2$(CH$_2$CN)] (3). A suspension of 1 (0.20 g, 0.23 mmol) in MeCN (15 mL) was heated at reflux temperature. After 8 h, addition of a 1:3 mixture of ethanol and *n*-heptane (30 mL) to the resulting pale yellow solution led to the

---

(3) (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel Publishing Co.: Dordrecht, The Netherlands, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Green, M. H. L.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (d) Bergman, R. G. *Science* **1984**, *223*, 902. (e) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (f) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825. (g) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1987**, *326*, C79. (h) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (i) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915. (j) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (k) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (l) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(4) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

(5) (a) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433. (b) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436.

(6) (a) Komiya, S.; Ito, K.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874. (b) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Sabat, M.; Zanobini, F. *Organometallics* **1986**, *5*, 2557. (c) Fernandez, M. J.; Rodriguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073. (d) Lehmkuhl, H. *Pure Appl. Chem.* **1990**, *62*, 731.

(7) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(8) (a) Meek, D. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 257. (b) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179.

(9) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226. (b) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (c) 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. (d) Barbaro, P.; Bianchini, C.; Mealli, C.; Meli, A. *J. Am. Chem. Soc.* **1991**, *113*, 3181. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Coord. Chem. Rev.* **1992**, *120*, 193. (f) Bianchini, C.; Caulton, K. G.; Folting, K.; Meli, A.; Peruzzini, M.; Polo, A.; Vizza, F. *J. Am. Chem. Soc.* **1992**, *114*, 7290.

(10) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227.

(11) (a) Bothner-By, A. A.; Castellano, S. *QCPE* **1967**, *11*, 111. (b) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

(12) Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1980**, *37*, 409.

precipitation of 3 as off-white crystals, which were collected by filtration and washed with *n*-pentane; yield 90%. Anal. Calcd for $C_{43}H_{43}IrNP_3$: C, 60.13; H, 5.05; Ir, 22.38; N, 1.63. Found: C, 60.03; H, 5.00; Ir, 22.04; N, 1.56. IR: ν(C≡N) 2194 (s) cm^{-1}; ν(Ir—H) 2041 (s) cm^{-1}.

Synthesis of [(triphos)IrH(CO)] (4).[13] A sample of 25 mg of 1 (0.03 mmol) was dissolved in 0.7 mL of DMF-d_7 under nitrogen. The resulting solution was transferred into an NMR tube which was flame-sealed and maintained at 100 °C for ca. 30 min. ^{1}H and ^{31}P{^{1}H} NMR spectra indicated the complete conversion of 1 to 4 (δ(P) – 11.0 (s); $\delta(H_{hydride})$ –10.05 (q), *J*(HP) = 20.5 Hz) and the evolution of ethane (singlet at ca. 0.9 ppm). In a separate experiment a 25-mL round-bottom flask was charged with a DMF (10 mL) solution of 1 (0.10 g, 0.12 mmol) and then placed in an oil bath at 100 °C. After ca. 1 h, the flask was cooled at –80 °C and opened and the solution sampled by a microsyringe. Almost quantitative production of $NHMe_2$ was determined by GC/MS. The precipitation of 4 as lemon-yellow crystals from the solution was obtained by addition of a 1:3 mixture of ethanol and *n*-heptane (50 mL); yield 95%. IR: ν(Ir—H) 2040 (s) cm^{-1}; ν(C≡O) 1886 (s) cm^{-1}. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ –12.9 (s). Compound 4 is thermally stable in refluxing THF and benzene.

Synthesis of [(triphos)Ir(H)$_2$(C≡CPh)] (5). To a suspension of 1 (0.30 g, 0.35 mmol) in either THF or benzene (40 mL) was added a 25-fold excess of phenylacetylene (0.98 mL, 8.8 mmol), and then the mixture was heated at reflux temperature. After ca. 3 h the resulting yellow solution was concentrated to ca. 20 mL and then diluted portionwise with *n*-heptane (20 mL). On standing, yellow crystals of 5 precipitated which were collected by filtration and washed with *n*-pentane; yield 85%. Anal. Calcd for $C_{49}H_{46}IrP_3$: C, 63.97; H, 5.04; Ir, 20.89. Found: C, 63.78; H, 5.09; Ir, 20.74. IR: ν(C≡C) 2100 (s) cm^{-1}; ν(Ir—H) 2053 (s) cm^{-1}; ν(C═C) phenyl vibration 1592 (m) cm^{-1}. Compound 5 was found to be completely stable in DMF at 100 °C.

Synthesis of [(triphos)Ir(H)$_2$(C≡CCO$_2$Et)] (6). To a suspension of 1 (0.30 g, 0.35 mmol) in THF (40 mL) was added a 25-fold excess of ethyl propiolate (0.89 mL, 8.8 mmol), and then the mixture was heated at reflux temperature. After ca. 3 h, the resulting bright orange solution was concentrated to ca. 20 mL. Addition of *n*-heptane (20 mL) precipitated yellow crystals of 6 which were collected by filtration and washed with *n*-pentane; yield 85%. Anal. Calcd for $C_{46}H_{46}IrO_2P_3$: C, 60.32; H, 5.06; Ir, 20.98. Found: C, 60.16; H, 4.98; Ir, 20.82. IR: ν(C≡C) 2073 (s) cm^{-1}; ν(Ir—H) 2036 (s) cm^{-1}; ν(C═O) 1659 (s) cm^{-1}; ν(C—O) 1198 cm^{-1} (partially masked by triphos absorptions).

Thermolysis of [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1) in the Presence of Ethene. A solution of 1 (0.06 g, 0.07 mmol) in THF (54 mL) was equally split into three portions. One portion was maintained under a steady stream of ethene at 66 °C for 1 h. After quenching the reaction by immersing the reaction vessel into an ice-water bath, the solvent was removed in vacuo to leave a white solid. Both the π-ethene complex [(triphos)IrH(C_2H_4)][10] (7) and the ethene C–H activation product [(triphos)Ir(H)$_2$(CH═CH$_2$)] (8) (see below) formed in a ratio of 79:21, as determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The total yield of the two products was 23%. The second portion, maintained in the above reaction conditions for 2 h, gave a 44% conversion with an 81:19 ratio. The third portion, heated at 66 °C under a 4 atm of ethene pressure for 1 h, gave a 28% total conversion of 1 to 7 and 8. The ethene hydride to vinyl dihydride ratio was 92:8. Remarkably, thermolysis of 1 in benzene at 80 °C under 1 atm of C_2H_4 selectively produces the phenyl dihydride 2.

Synthesis of [(triphos)IrH(π-H$_2$C═CHPh)] (9). Styrene (2.0 mL, 17.5 mmol) was added to a suspension of 1 (0.30 g, 0.35 mmol) in 80 mL of MeCN and the resulting mixture heated at reflux temperature. Within ca. 1.5 h, 1 completely dissolved to give a yellow solution. After 4 h, by concentrating the solution to ca. 10 mL, light yellow crystals of 9 began to precipitate; complete precipitation was achieved by adding ethanol (20 mL) to the mixture. They were filtered off and washed with ethanol and *n*-pentane; yield 85%. Anal. Calcd for $C_{49}H_{48}IrP_3$: C, 63.83; H, 5.25; Ir, 20.85. Found: C, 63.70; H, 5.16; Ir, 20.64. IR: ν(Ir—H) 2060 (s) cm^{-1}; ν(C═C) phenyl vibration 1596 (m) cm^{-1}. ^{13}C{^{1}H} NMR (pyridine-d_5, 20 °C): δ 33.6 (ddd, $^2J(CP_A)$ = 28.9 Hz, $^2J(CP_M)$ = 7.2 Hz, $^2J(CP_Q)$ = 2.3 Hz, CH_2═CHPh), 15.0 (ddd, $^2J(CP_M)$ = 38.3 Hz, $^2J(CP_A)$ = 7.8 Hz, $^2J(CP_Q)$ = 2.8 Hz, CH$_2$═*C*HPh).

No trace of products arising from C–H activation of either MeCN or styrene was observed.

Photolysis of [(triphos)IrH(C$_2$H$_4$)] (7) To Give [(triphos)Ir(H)$_2$(CH═CH$_2$)] (8). (A) Benzene. A solution of 7 (0.20 g, 0.24 mmol) in benzene (100 mL) was irradiated with UV light at 20 °C. After 20 min, the resulting light yellow solution was concentrated to dryness in vacuo to give a white solid whose ^{1}H and ^{31}P{^{1}H} NMR spectra showed a 95% conversion of 7 to 2 (5%) and 8 (90%). Recrystallization from THF/ethanol gave a pure sample of 8 as off-white crystals; yield 80%. Anal. Calcd for $C_{43}H_{44}IrP_3$: C, 61.05; H, 5.24; Ir, 22.72. Found: C, 60.82; H, 5.21; Ir, 22.31. IR: ν(Ir—H) 2053 (s) cm^{-1}; ν(C═C) 1546 (m) cm^{-1}. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 138.1 (dt, $^2J(CP_A)$ = 78.7 Hz, $^2J(CP_M)$ = 8.3 Hz, *C*H═CH$_2$), 126.6 (td, ^3J(CP) = 7.0 Hz, ^3J(CP) = 1.6 Hz, CH═*C*H$_2$).

Exposing solutions of 7 to UV radiations for a longer time (3 h) selectively transforms 8 into 2. In line with these results, irradiation of a pure sample of 8 in benzene selectively produces 2. Monitoring the latter reaction by ^{1}H NMR spectroscopy (sealed quartz tube) showed that the formation of the phenyl dihydride complex is accompanied by C_2H_4 evolution. Occasionally, the formation of 2 is accompanied by that of some unidentified species, probably due to further secondary photolysis.

(B) THF. A solution of 7 (0.20 g, 0.24 mmol) in THF (100 mL) was irradiated with UV light at 20 °C. After 30 min, the resulting light yellow solution was concentrated to 10 mL in vacuo. On addition of a 1:3 mixture of ethanol and *n*-heptane (25 mL), an off-white crystalline product precipitated which was filtered off and washed with *n*-pentane. Traces (less than 5%) of products arising from the activation of the solvent were observed, indicating that, also in this case, some elimination of ethene takes place. Pure samples of 8 were obtained by repeated recrystallizations from THF/ethanol; yield 80%.

Thermal Isomerization of [(triphos)Ir(H)$_2$(CH═CH$_2$)] (8) to [(triphos)IrH(C$_2$H$_4$)] (7). A solution of pure 8 (0.025 g, 0.030 mmol) in THF (20 mL) was heated at 66 °C under nitrogen. After 1 h, the reaction was quenched by immersing the reaction vessel into an ice-water bath and then the solvent was removed in vacuo. A white solid was obtained which was shown to contain 11% 7. Almost identical conversions (±1%) were obtained for reactions carried out under either a steady stream of ethene or a 4 atm ethene pressure. Analogous results were observed when the isomerization reactions were performed in benzene.

Kinetic Measurements on the Isomerization of 8 to 7. In a typical experiment a sample of 8 (0.020 g, 0.024 mmol) in benzene-d_6 (3 mL) was sealed under vacuum in a 10-mm NMR tube and then introduced into the probe of the NMR spectrometer preheated at a fixed temperature. The kinetics of the reactions was followed by determining the concentration of 8 as a function of time (^{31}P NMR integration); spectra were recorded every 10 min for 4 h. Experiments were carried out at 70, 75, 80, 90, and 100 °C. For the last three temperatures spectra were recorded every 4 min.

Photolysis of [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1). (A) Benzene. A solution of 1 (0.10 g, 0.12 mmol) in benzene (90 mL) was irradiated at 20 °C. After 3 h, the solution was concentrated to dryness under vacuum to give a white solid. Its ^{31}P NMR spectrum displayed a 66% conversion with the following product distribution: 2 (59%), 7 (2%), 8 (27%), and [(triphos)Ir(H)$_3$][13] (10) (12%).

(B) THF. By working up as above, a 69% conversion was observed. Compounds 7 (7%), 8 (37%), and 10 (16%) were detected in solution along with 40% unidentified compounds.

---

(13) Janser, P.; Venanzi, L. M.; Bachechi, F. J. *J. Organomet. Chem.* **1985**, *296*, 229.

All of these compounds usually form when THF solutions of 1 are subjected to prolonged heating at temperatures higher than 70 °C.

In parallel experiments performed by irradiating a sealed quartz NMR tube containing benzene-d_6 (or THF-d_8) solutions of 1, evolution of H_2, C_2H_4, and C_2H_6 was detected by ^{1}H NMR spectroscopy.

Photolysis of [(triphos)Ir(H)$_3$] (10). By working up as in the above method A, 10 converted selectively to 2 (37%).

Photolysis of [(triphos)IrH(π-H$_2$C=CHPh)] (9). A suspension of 9 (0.20 g, 0.22 mmol) in THF (30 mL) was irradiated at 20 °C for 5 h, during which time the complex dissolved to give a yellow solution. This was concentrated to dryness in vacuo, and the residue washed with *n*-pentane (5 × 10 mL). The product was characterized by IR and NMR spectroscopy as a mixture of two σ-styryl isomers of formula [(triphos)Ir(H)$_2$(CH=CHPh)] (11, 12) and of [(triphos)IrH(π-HC≡CPh)] (13) (see below) in a 5:5:2 ratio. On the basis of their thermal stability (see below), 11 and 12 were assigned *E* and *Z* configurations, respectively. When the photochemical reaction was prolonged up to 7 h, the products were identified in a 1:1:2 ratio. Monitoring the secondary photolysis reaction by ^{1}H NMR spectroscopy (sealed quartz tube) showed the conversion of 11 and 12 to 13 to proceed *via* H_2 elimination. Due to their comparable solubility in most organic solvents, compounds 11–13 could not be separated from each other. IR (11, 12): ν(Ir—H) 2050 (s) cm^{-1}; ν(C=C) 1546 (m) cm^{-1}.

Synthesis of [(triphos)Ir(π-HC≡CPh)]BPh$_4$ (14). Into a THF (20 mL) solution of [(triphos)Ir(C$_2$H$_4$)$_2$]BPh$_4$ (0.30 g, 0.24 mmol) at room temperature was syringed a 10-fold excess of neat phenylacetylene (0.26 mL, 2.40 mmol). After 30 min, addition of di-*n*-butyl ether (30 mL) to the resulting red solution led to the precipitation of 14 as red crystals. They were collected by filtration and washed with ethanol and *n*-pentane; yield 80%. Anal. Calcd for $C_{73}H_{65}BIrP_3$: C, 70.81; H, 5.29; Ir, 15.52. Found: C, 70.54; H, 5.21; Ir, 15.42. IR: ν(C=C) phenyl vibration 1598 (m) cm^{-1}. Λ_M = 50 cm^2 Ω^{-1} mol^{-1}.

Independent Synthesis of [(triphos)IrH(π-HC≡CPh)] (13). To a red orange solution of 14 (0.24 g, 0.19 mmol) in THF (20 mL) at room temperature was added a 2-fold excess of LiHBEt$_3$ (0.38 mL, 0.38 mmol) with stirring. After 2 h, addition of *n*-heptane (30 mL) led to the precipitation of a crystalline pinky precipitate of 13. This was filtered off and washed with water (2 × 3 mL), ethanol (3 × 2 mL), and *n*-pentane; yield 85%. Anal. Calcd for $C_{49}H_{46}IrP_3$: C, 63.97; H, 5.04; Ir, 20.89. Found: C, 63.81; H, 4.87; Ir, 20.64. IR: ν(Ir—H) 2064 (s) cm^{-1}; ν(C≡C) 1613 (s) cm^{-1}. ^{13}C{^{1}H} NMR (THF-d_8, 20 °C): δ 155.0 (ddd, ^2J(CP$_{trans}$) = 80.2 Hz, ^2J(CP$_{cis}$) = 9.6, 6.3 Hz, PhC≡*C*H, assigned by DEPT experiment), δ 153.3 (dt, ^2J(CP$_{trans}$) = 82.7 Hz, ^2J(CP$_{cis}$) = 6.3 Hz, Ph*C*≡CH). Compound 13 is thermally (THF, 100 °C) and photochemically stable for a long time (12 h).

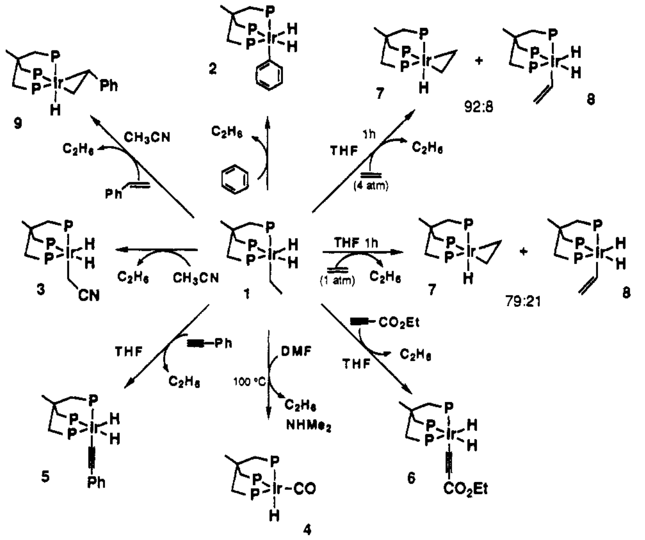
Photolysis of [(triphos)Ir(H)$_2$(C≡CPh)] (5). A solution of 5 (0.10 g, 0.11 mmol) in THF (30 mL) was irradiated with UV light for 2 h at 20 °C. The resulting solution was concentrated to dryness in vacuo and the residue recrystallized twice from THF and ethanol. The product was characterized by IR and NMR spectroscopy as 13 (yield 60%).

Thermal Isomerization of a 1:1 Mixture of 11 and 12 to 9. A 10-mm NMR tube was charged with a benzene-d_6 (3 mL) solution of a 5:5:2 mixture (30 mg) of 11–13 under nitrogen and placed for 2 h into the probe of the NMR spectrometer preheated at 80 °C. ^{31}P{^{1}H} NMR spectra were recorded every 15 min showing the progressive transformation of both isomers 11 and 12 into 9. The conversion of 12 to 9 is 4 times faster than that of isomer 11. Compounds 13 and 9 are quite stable under the experimental conditions.

Results

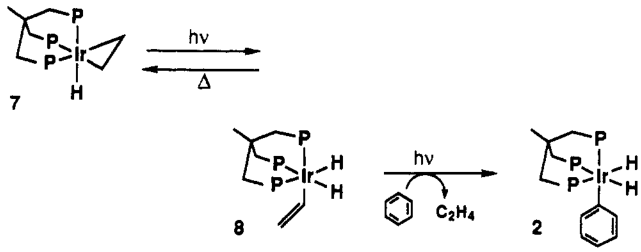
The preparations and the principal reactions of the complexes described in this paper are illustrated in Schemes I–V. Selected NMR spectral data are collected in Table I [^{31}P{^{1}H} NMR] and Table II [^{1}H NMR].

Scheme I. Thermal Reactions of [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1)^a



^{a} All reactions were carried out at reflux temperature unless otherwise stated.

Scheme II



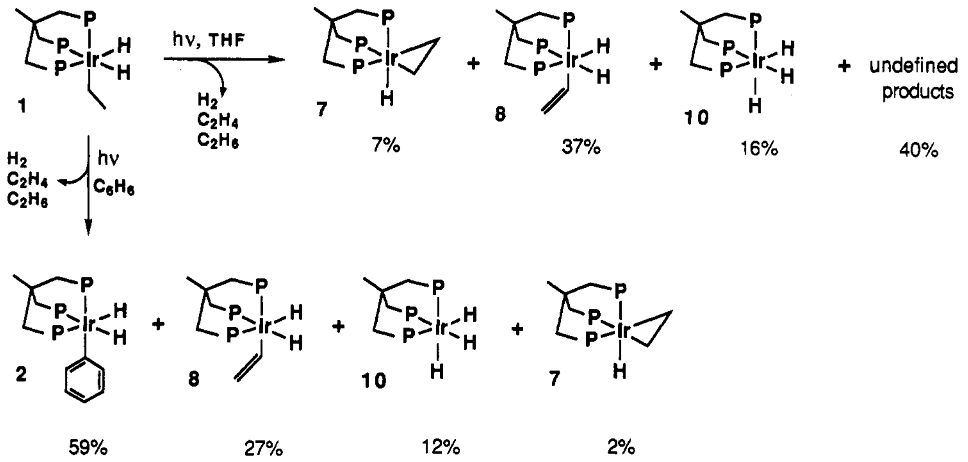
Thermolysis Reactions of [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1). Thermolysis of the ethyl dihydride 1 in benzene and acetonitrile at the corresponding reflux temperatures results in the irreversible, selective formation of the σ-organyl dihydrides [(triphos)Ir(H)$_2$(Ph)] (2) and [(triphos)Ir(H)$_2$(CH$_2$CN)] (3), respectively, and ethane.

Complexes 2 and 3 maintain the primary geometry of the precursor; *i.e.* the iridium center is octahedrally coordinated by the triphos ligand (^{31}P{^{1}H} NMR AM$_2$ spin system), by σ-bonded phenyl or cyanomethyl groups and by two terminal hydride ligands (2, AA′XX′Y pattern; 3, AA′C$_2$XX′Y pattern). The more complicated spin system of the hydride ligands of 3 is originated by coupling of the hydrides to the methylene hydrogens of the cyanomethyl group [^3J(HH) = 1.1 Hz]. As generally observed for triphos metal dihydrides,[10,13] the two terminal hydride ligands are chemically but not magnetically equivalent and give rise to a second-order spectrum (Figure 1a). This has satisfactorily been simulated as the AA′ part of an AA′C$_2$XX′Y spin system, C$_2$ being the CH$_2$CN hydrogens and X, X′, Y being the phosphorus atoms of triphos (Figure 1b).

Noteworthy, selective formation of 2 occurs also when the thermolysis reaction is carried out at 100 °C in either a 1:1 (v:v) mixture of benzene and MeCN. Compound 2 converts to its perdeuterated isotopomer 2-d_7 in benzene-d_6 at temperatures higher than 50 °C. Such isotope H/D exchanges are known to occur *via* sequences of reductive elimination–oxidative additions steps of benzene/benzene-d_6.

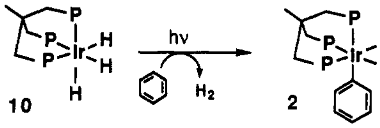
Thermolysis in DMF at temperatures >60 °C slowly and selectively converts 1 to the known trigonal-bipyramidal hydride carbonyl [(triphos)IrH(CO)][13] (4) and

Scheme III. Photolysis of [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (1), in THF and Benzene Solutions at 20 °C for 3 h[a]



[a] Percentages are given with respect to the observed conversion.

Scheme IV



Scheme V

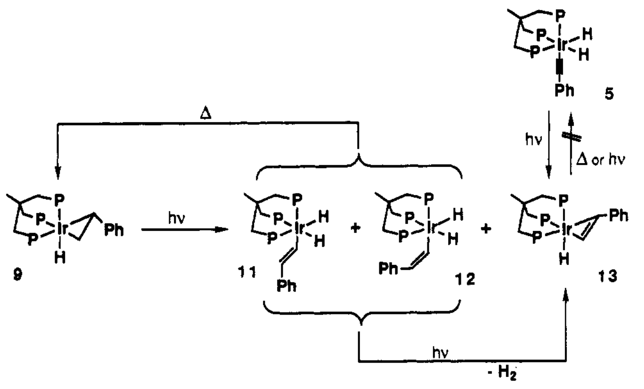


Table I. $^{31}P\{^1H\}$ NMR Spectral Data for the Complexes[a]

		chem shift, ppm[b]			coupling const, Hz		
complex	pattern	δ(P_A)	δ(P_M)	δ(P_Q)	$J(P_AP_M)$	$J(P_AP_Q)$	$J(P_MP_Q)$
2	AM_2	–9.6	–19.3		14.5		
3	AM_2	–7.7	–16.0		16.7		
5	AM_2	–6.7	–25.9		17.4		
6	AM_2	–7.5	–25.1		18.5		
8	AM_2	–10.9	–19.7		16.3		
9	AMQ	–11.7	–16.8	–18.2	32.0	17.3	20.0
11	AM_2	–11.1	–18.6		16.8		
12	AM_2	–10.6	–18.7		15.7		
13	AMQ	–11.3	–22.4	–46.3	14.6	15.6	20.3
14	A_3	3.3					

[a] All spectra were recorded at 20 °C in CD_2Cl_2 solutions. [b] The chemical shifts (δ's) are relative to 85% H_3PO_4; downfield values are assumed as positive.

produces dimethylamine and ethane. At 100 °C, the reaction is complete in 1 h. The hydride carbonyl **4** is also obtained by thermolysis of **1** in benzene under a high CO pressure. At 10 atm of CO, the reaction gives **2** and **4** in an 82:18 ratio. No appreciable formation of **4** is observed when **1** is heated in benzene under a steady stream of CO.

Unlike the thermal reactions of **1** in benzene, CH_3CN and DMF, thermolysis of **1** in refluxing THF produces a plethora of unidentified products likely arising from the activation of the solvent. In contrast, in the presence of hydrocarbon substrates containing sp and sp^2(olefin) C–H bonds, thermolysis of **1** in refluxing THF results in the formation of well-defined C–H bond cleavage products.

In the presence of an excess of either phenylacetylene or ethyl propiolate, facile insertion of iridium into the C–H bond occurs to give the σ-alkynyl dihydrides [(triphos)Ir(H)$_2$(C≡CPh)] (**5**) and [(triphos)Ir(H)$_2$(C≡C-CO$_2$Et)] (**6**). Both compounds retain the octahedral geometry of the precursor, the only difference being the substitution of σ-alkynyl groups for ethyl. The high values of ν(C≡C) in both complexes (2100 and 2073 cm^{-1}) are consistent with the absence of $d\pi$(metal) → π^*(alkynyl) interaction, as expected for a d^6 configuration of the metal center in octahedral geometry.[14] No trace of products arising from the activation of either THF or the phenyl substituent of phenylacetylene is detected by NMR spectroscopy. In accord with this finding, thermolysis of **1** in benzene solution containing an excess of phenylacetylene selectively gives **5**.

A quite interesting result is observed when **1** is heated at 66 °C in THF under a steady stream of ethene. After 1 h, the starting compound is partially (23%) converted to a mixture of the known π-ethene hydride [(triphos)IrH(C$_2$H$_4$)][10] (**7**) and of the new vinyl dihydride [(triphos)Ir(H)$_2$(CH=CH$_2$)] (**8**) in a 79:21 ratio. Doubling the reaction time increases the overall conversion to 44%, while the product ratio appears to be little affected (81:19). In contrast, the η^2-ethene:vinyl ratio significantly increases by increasing the pressure of ethene: at 4 atm of C_2H_4 for 1 h, the thermolysis reaction of **1** results in formation of **7** and **8** in a ratio of 92:8, while the overall conversion slightly increases (28%). The use of benzene in place of THF totally quenches the activation of ethene, the phenyl dihydride **2** being the only product formed.

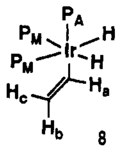
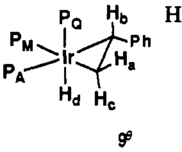
The vinyl derivative **8** exhibits spectroscopic features which are in line with those observed for all σ-organyl dihydrides described in this paper. The presence of a σ-vinyl ligand to complete the octahedral geometry around the metal center is unambiguously shown by IR and ^{1}H and ^{13}C NMR data which are in excellent agreement with the literature data.[4,5,15]

---

[14] Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, F. M. *Organometallics* **1990**, *9*, 360.

[15] (a) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444. (b) McCamley, A.; Perutz, R. N.; Stahl, S.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1690. (c) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212. (d) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790. (e) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425.

Table II. Selected ^{1}H NMR Spectral Data for the Complexes[a]

	π-hydrocarbon				hydride			σ-organyl			
compd	assignt	δ	J(HH)	J(HP)	δ	J(HP$_{trans}$)	J(HP$_{cis}$)	assignt	δ	J(HH)	J(HP)
2					−8.94[b]	124.1	13.7				
3					−9.43[c]	136.6	12.9	CH_2CN	0.98 (qt)	1.1	7.3
							−11.0				
5					−9.76[b]	123.1	12.9				
6					−9.93[b]	118.5	12.7	$\mathrm{OC}H_2\mathrm{CH}_3$	4.04 (q)	7.1	
								$\mathrm{OCH_2C}H_3$	1.24 (t)		
 **8**					−9.32[b]	121.6	12.7	H_a	7.25[d]	11.3 (ab)	12.0 (bA)
								H_b	6.30 (m)	18.4 (ac)	1.0 (bM)
								H_c	5.87 (dddt)	5.4 (bc)	7.3 (cA)
											1.7 (cM)
 **9**[e]	H_a	3.11 (m)	6.9 (ab)	4.6 (aA)	−11.52 (dt)	144.8 (dQ)	14.2 (dA)				
	H_b	2.89 (m)	3.5 (ac)	8.8 (aM)			10.8 (dM)				
	H_c	1.77 (m)	2.8 (ad)	2.0 (aQ)							
			7.4 (bc)	9.4 (bA)							
			1.8 (bd)	6.3 (bM)							
			1.8 (cd)	1.1 (bQ)							
				5.6 (cA)							
				8.5 (cM)							
				4.3 (cQ)							
11[f]					−9.26[b]	120.5	12.6				
12[f]					−9.05[b]	121.0	12.5				
13					−9.97 (dt)	124.4	11.2				
							11.2				
14	HC≡CPh	12.18 (q)		7.2							

[a] All spectra were recorded in CD_2Cl_2 solutions at 20 °C. Chemical shifts (δ's) are given in ppm and are relative to the residual ^{1}H resonance in the deuterated solvent (δ 5.32). Coupling constants (J) are in hertz. [b] Second-order doublet of multiplets computable as the AA′ part of an AA′XX′Y spin system. The J(HP$_{trans}$) and J(HP$_{cis}$) values refer to |J(AX) + J(AX′)| and J(AY), respectively. [c] Second-order doublet of multiplets properly computed as the AA′ part of an AA′C$_2$XX′Y spin system. The letter C denotes the cyanomethyl hydrogen atoms, while X and Y refer to the triphos phosphorus atoms. The spin simulation procedures (see Experimental Section) request the introduction of the following additional coupling constants: J(AA′) = 3.6 Hz, J(XX′) = 5.9 Hz. [d] Masked by the phenyl protons of triphos; the chemical shift was determined by a H,H 2D-COSY experiment. [e] The hydride and styrene hydrogen atoms have been computed as an ACEGXYZ spin system where the letters refer to H_d, H_a, H_b, H_c, P_A, P_M, and P_Q, respectively. [f] Styryl resonances are masked by the phenyl protons of triphos.

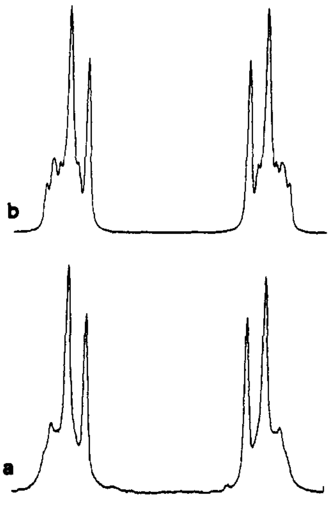


Figure 1. Experimental (a) and computed (b) ^{1}H NMR resonances for the hydride ligands in **3** (299.94 MHz, 20 °C, CD_2Cl_2).

A π-alkene monohydrido complex of the formula [(triphos)IrH(CH$_2$=CHPh)] (**9**) and ethane are quantitatively and selectively obtained by heating at reflux temperature a MeCN solution of **1** in the presence of an excess of styrene. No formation of products arising from the activation of either styrene or MeCN is observed. The use of MeCN in place of THF is necessary because the latter solvent competes with styrene in reacting with the metal center.

Compound **9** exhibits spectroscopic features quite similar to those of several π-alkene hydrido metal complexes of triphos, i.e. [(triphos)RhH(CH$_2$=CHPh)],[16] [(triphos)IrH(C_2H_4)] (**7**),[10] and [(triphos)IrH(C_6H_{10})],[9f] for which a metallacyclopropane structure has unambiguously been established. The ^{31}P{^{1}H} and ^{1}H NMR spectra of **9** deserve some comment. As expected, the three phosphorus atoms of triphos give rise to an AMQ pattern because of the presence of three different ligating groups trans to each phosphorus. Interestingly, the terminal hydride ligand and the three olefin hydrogens in **9** are appreciably coupled to each other and to the three phosphorus atoms. As a result, the spin system for the four hydrogen nuclei is of the type ACEGXYZ, where the alkene hydrogens constitute the CGE portion and the hydride ligand is the A part. In light of homo- and heteronuclear selective decoupling, H,H 2D-COSY, and ^{13}C,^{1}H 2D-HETCOR experiments, the assignments of the hydrogen and phosphorus resonances are as reported in the drawing of Figure 2, which also shows a computer simulation of the olefin and hydride resonances. Even though the spectroscopic data do not allow one to distinguish between two stereoisomers differing in the orientation of the phenyl substituent, a preference for the endo position is supported by steric arguments.

In refluxing THF, ethene is preferentially activated over styrene, whereas both alkenes do not react with [(triphos)-IrH] in benzene, the latter solvent being able to trap all the reactive Ir(I) intermediate.

Photolysis of [(triphos)IrH(C_2H_4)] in Benzene and THF. Irradiation of the ethene hydride **7** in benzene solution for 20 min gives the vinyl dihydrido complex **8** as the largely major product (*ca.* 95%) (Scheme II). Some

---

[16] Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Albinati, A. *Organometallics* **1990**, *9*, 2283.

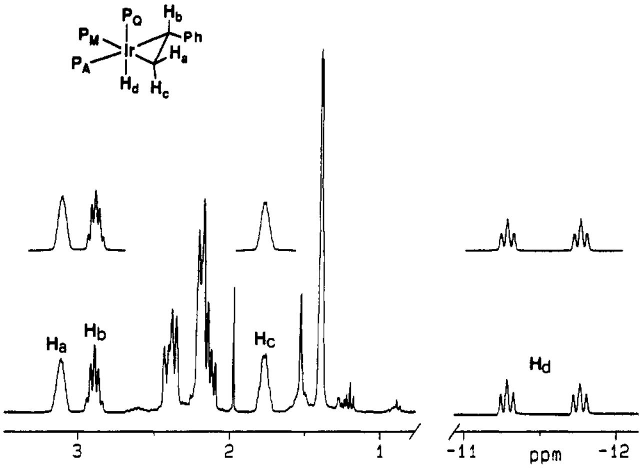


Figure 2. Experimental (lower) and computed (upper), ^{1}H NMR spectra of **9** in the 3.5/0.8 and −10.9/−12.1 ppm regions (299.94 MHz, 20 °C, CD_2Cl_2).

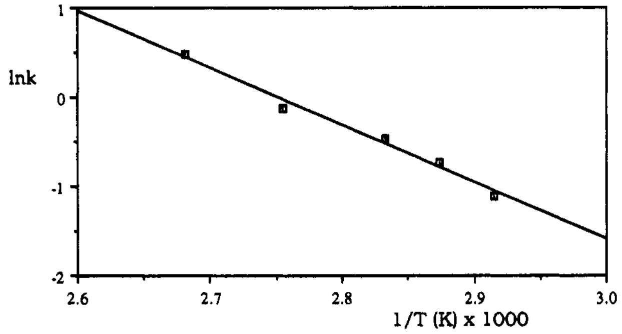


Figure 3. Plot of ln k vs $1/T$ for the thermolysis of the vinyl complex **8** in benzene-d_6 at five temperatures between 70 and 100 °C.

phenyl dihydride **2** is also formed. The latter compound originates by secondary photolysis on **8**, as shown by an independent experiment in benzene. The formation of **2** is accompanied by C_2H_4 evolution (^{1}H NMR).

Quite similar results are obtained upon irradiation of **7** in THF, the only difference being that secondary photolysis on **8** provides the THF-activation products alreay mentioned.

Thermolysis of [(triphos)Ir(H)$_2$(CH═CH$_2$)] in THF and Benzene. Heating THF or benzene solutions of **8** at temperatures higher than 60 °C results in clean isomerization to the ethene hydride **7** (Scheme II). No trace of products arising from the activation of the solvent was detected. It is noteworthy that identical conversions have been obtained for isomerization reactions carried out under C_2H_4 pressures ranging from 1 to 4 atm.

$^{31}P\{^1H\}$ NMR spectroscopy in benzene solution provides a reliable method for evaluating the kinetic and thermodynamic parameters associated with the vinyl dihydride to ethene hydride isomerization. In fact, **7** and **8** show well-separated resonances of the triphos phosphorus nuclei. The first-order rate law has been determined at a fixed temperature by varying the starting concentration of **8**. Values of the rate constants as a function of temperature in the range from 70 to 100 °C are reported in Figure 3. From the Arrhenius plot, we have determined the activation parameters, which are as follows: $\Delta H^\ddagger = 12 \pm 1$ kcal mol^{-1}, $\Delta S^\ddagger = -25 \pm 3$ cal K^{-1} mol^{-1}, $\Delta G^\ddagger = 20 \pm 2$ kcal mol^{-1}, and $E_a = 13 \pm 1$ kcal mol^{-1}.

Photolysis of [(triphos)Ir(H)$_2$(C$_2$H$_5$)]. UV irradiation of **1** in THF for 3 h at 20 °C gives rise to several products (Scheme III). Three of them, namely **7**, **8**, and the trihydride [(triphos)Ir(H)$_3$] (**10**),[13] have been identified by comparison with authentic specimens prepared by independent synthetic procedures. The remaining products, although not identified, are, however, those obtainable by thermolysis of **1** in THF. The scarce selectivity of the photolysis reaction is shown also by the fact that three gaseous products, ethane, ethene, and dihydrogen, are evolved (^{1}H NMR experiments in quartz tubes). The same gaseous products are detected also in the course of the photolysis of **1** in benzene at 20 °C. In this case, however, the reaction produces only well-defined metal complexes, namely **2**, **7**, **8**, and **10**.

Secondary photolysis experiments in benzene at 20 °C show that the trihydride **10** is highly sensitive to UV light which selectively promotes H_2 elimination and transforms the trihydride into the phenyl dihydride **2** (Scheme IV). In a similar way, photolysis of **10** in THF leads to formation of the products arising from the activation of the solvent.

Photolysis of [(triphos)IrH(CH$_2$═CHPh)]. Irradiation of a suspension of **9** in THF at 20 °C for 5 h produces a yellow solution from which a 5:5:2 mixture of three metal complexes is obtained after removal of the solvent (Scheme V). The two major products exhibit almost concident $^{31}P\{^1H\}$ and ^{1}H NMR spectra. In particular, their phosphorus spectra consist of AM_2 patterns, while the proton spectra in the hydride region contain second-order resonances which are typical of two chemically but not magnetically equivalent hydride ligands. The IR spectrum shows ν(Ir—H) (2050 cm^{-1}) and ν(C═C) (1546 cm^{-1}) absorptions for the two compounds.

On the basis of all of these data as well as their thermal behavior, we suggest that the two compounds are *Z* and *E* stereoisomers of the formula [(triphos)Ir(H)$_2$(CH═CHPh)] (**11** and **12**). Since the vinyl hydrogen resonances are totally masked by the phenyl hydrogen resonances, it is not possible to precisely correlate the spectroscopic data with either of the two configurations. In light of thermal stability arguments (*vide infra*), however, there is a good probability that the styryl dihydride **11** is the *E* isomer.

In contrast, there is little doubt that the third product generated by photolysis of **9** is the π-alkyne hydride [(triphos)IrH(HC≡CPh)] (**13**). In fact, the latter complex can be prepared in analytically pure form by an independent procedure which involves hydride addition to the cationic π-phenylacetylene complex [(triphos)Ir(HC≡CPh)]BPh$_4$ (**14**).

The π-alkyne hydride **13** exhibits spectroscopic properties which are comparable with those of the π-styrene hydride **9**. The only remarkable difference between **13** and **9** is the presence of a two-electron donor alkyne ligand in place of alkyne [ν(C≡C) 1613 cm^{-1}; $^{13}C\{^1H\}$ NMR δ (*C*H≡CPh) 155.0, δ(CH≡*C*Ph) 153.3 ppm]. As for **14**, the compound belongs to a well-known family of metal complexes of the formula [(triphos)M(alkyne)]$^+$ [M = Co and alkyne = HC≡CPh, PhC≡CPh; M = Rh, Ir and alkyne = MeO$_2$CC≡CCO$_2$Me].[9a,10,17] Like **14**, all these complexes are highly fluxional in solution due to a fast interconversion between trigonal-bipyramidal and square-pyramidal structures separated by a very low activation energy. The square-pyramidal structure is generally found in the solid state.

Interestingly, secondary photolysis experiments (THF, 20 °C) carried out on the 5:5:2 mixture of **11**–**13** promotes

---

[17] Bianchini, C.; Dapporto, P.; Meli, A.; Sacconi, L. *J. Organomet. Chem.* **1980**, *193*, 117.

the evolution of H_2 (^1H NMR) and converts the styryl derivatives to the π-alkyne hydride complex. After 2 h, a product ratio of 1:1:2 is observed. Since **13** is quite stable under UV light even for long exposures (12 h), dihydrogen is certainly eliminated from the styryl complexes.

Thermal Isomerization of the Styryl Dihydrides 11 and 12 to the π-Styrene Hydride 9. Heating a 1:1 mixture of **11** and **12** in benzene solution at 66 °C for 2 h selectively converts the couple of styryl dihydride stereoisomers to the π-styrene hydride **9**, which is quite stable under the experimental conditions. It is worth noticing that (i) the transformation of **12** into **9** is faster than that of isomer **11**; (ii) no product originated by benzene activation is observed.

Photolysis of [(triphos)Ir(H)$_2$(C≡CPh)]. Irradiation of a THF solution of **5** at 20 °C for 2 h quantitatively transforms the starting complex into the π-alkyne hydride **13**. The latter compound is thermally stable in THF solution up to 100 °C.

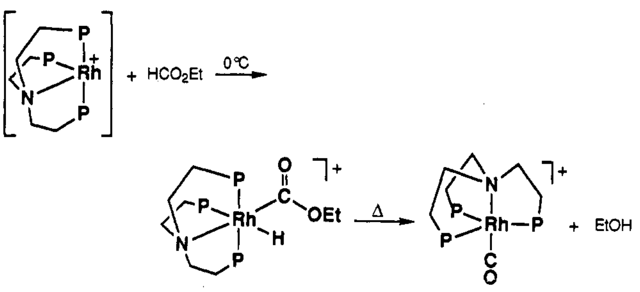
Discussion

Thermal Reactions. From the results reported in the previous sections, one may readily infer that thermolysis of **1** in various solvents (benzene, THF, MeCN, DMF) results in formation of the 16-electron fragment [(triphos)IrH][18] and ethane. The reactive intermediate, which can be trapped by CO, is capable of insertion into the C–H bonds of either solvents or appropriate substrates (1-alkynes, ethene) dissolved in excess. No cyclometalated products are observed.

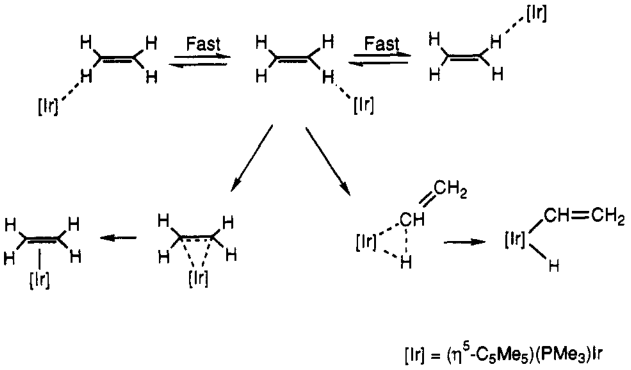
Solvents bearing chemically equivalent C–H bonds (benzene, MeCN) give rise to formation of insertion products, *i.e.* phenyl or cyanomethyl dihydrides. In contrast, THF forms several products, a results that is not completely unexpected since THF possesses two chemically inequivalent CH_2 groups, one of which, namely the α group, is potentially susceptible to undergoing a double C–H activation by metal centers.[19] A case apart is represented by DMF which contains both sp^3 and sp^2 C–H bonds. Even though there is little doubt that the metal preferentially cleaves the formyl C–H bond, no mechanistic conclusion for the formation of the hydrido carbonyl complex **4** can be given in the absence of detected intermediates (recall that the reaction is carried out at 100 °C). It is likely, however, that the reaction proceeds through a stepwise mechanism similar to that established for the decarbonylation of ethyl formate by the 16-electron fragment [(NP$_3$)Rh]$^+$[NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$] (Scheme VI);[20] *i.e.* the metal initially inserts into the formyl C–H bond to give an Ir(III) octahedral (η^1-C(O)NMe$_2$) dihydride, which then converts to the Ir(I) hydrido carbonyl *via* reductive elimination of dimethylamine.[21]

Thermolysis of **1** in THF at 66 °C in the presence of ethene gives two products, namely the π-olefin complex **7** and the vinyl dihydride **8**. Also, at this temperature, the vinyl dihydride isomerizes to the π-complex. Accordingly, one may think that the vinyl dihydride is the sole kinetic product of the reaction. We have been able to probe that this is not true. In fact, the isomerization rate of **8** in THF at 66 °C is much slower than the rate of formation of **7**, so slow that the ratio between **7** and **8** is almost invariant (79:21 after 1 h, 81:19 after 2 h) during the thermolysis reaction of **1**. Most importantly, increasing the C_2H_4 pressure up to 4 atm favors the formation of the π-complex, while the isomerization rate of the vinyl dihydride is not influenced at all. All these findings indicate that the product ratio observed after 2 h is kinetic rather than thermodynamic, although the π-olefin complex is thermodynamically more stable than the vinyl dihydride. Accordingly, the two products would form in parallel reactions *via* two different transition states within an overall mechanism of the type reported previously by Stoutland and Bergman for the interaction of the isoelectronic (η^5-Me$_5$C$_5$)Ir(PMe$_3$) fragment with ethene (Scheme VII).[7]

Scheme VI



Scheme VII



Intermolecular C–H activation reactions of ethene have been observed for mononuclear iron,[5] rhenium,[11] and iridium[7] complexes. It is generally agreed that highly energetic, unsaturated metal fragments are excellent candidates for cleaving the C–H bonds of unactivated olefins due to their capability of lowering the energy barrier to C–H insertion. Thus, systems that cannot exist in the square-pyramidal geometry are the best candidates. However, it is also important to consider the role played by steric factors, as they can affect the thermodynamic stability of π-olefin complexes.[22] Within this context, it is reasonable to have found that [(triphos)IrH], which is among the least sterically demanding systems, gives rise to the largest amount of olefin complex formation (recall that the triphos ligand invariably exhibits *fac* coordination, while the 16-electron configuration is attained by using the smallest available coligand, *i.e.* the hydride).

With a few exceptions,[23] the majority of (vinyl)hydridometal complexes are thermodynamically unstable

---

(18) We cannot distinguish between intervention of free [(triphos)IrH] and the corresponding solvated complex, which may in fact be the intermediate in the C–H activation reactions. Throughout this paper we will utilize the former notation for simplicity.

(19) Boutry, O.; Gutierrez, E.; Monge, A.; Nicasio, M. C.; Perez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288.

(20) Bianchini, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *348*, C9.

(21) Vrieze, K.; Collman, J. P.; Sears, C. T. Jr.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

(22) (a) Herberhold, M. *Metal π-Complexes*; Elsevier: New York, 1974; Vol. 2. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.

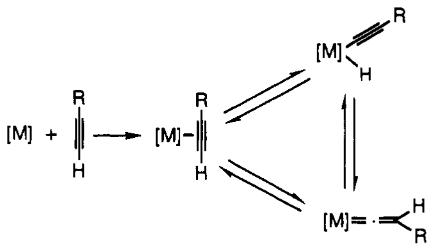
with respect to the corresponding ethene complexes.[5,7,15c,d] Our vinyl dihydride follows the general trend converting to the π-ethene isomer at temperatures higher than 60 °C. In principle, the vinyl hydride to π-ethene conversion might proceed *via* either intramolecular or dissociative mechanisms. The latter process, which would require complete dissociation of ethene from **8** and then reformation of the π-complex, can be ruled out for several reasons. First of all, thermolysis of **8** selectively gives **7** even when the reaction is performed in benzene. If the unsaturated system [(triphos)IrH] was an intermediate in the π-olefin complex formation, one would expect to see the formation of the phenyl diydride **2**, which is stable under the thermolysis conditions. Second, the isomerization process is not influenced by an increase in the ethene pressure up to 4 atm. Finally, the occurrence of an intramolecular mechanism is strongly supported by the activation parameters, particularly by the negative entropy of activation ($\Delta S^{\ddagger} = -25 \pm 3$ cal K^{-1} mol^{-1}), which excludes a dissociative transition state.

Substitution of styrene for ethene has a dramatic influence on the thermolysis of **1**. Indeed, it was surprising to observe no formation of C–H activation products, even in THF. In fact, the styryl dihydrides **11** and **12** are isolable compounds, which slowly convert to the π-olefin complex in benzene at 80 °C. From the observation that the rate of isomerization of **11** is faster than that of **12**, the former compound is assigned the more sterically demanding *E* structure.

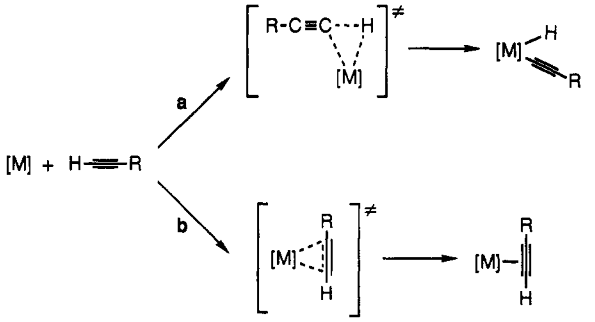
Several examples are known in which mononuclear transition metal complexes insert into the C–H bonds of either activated or unactivated alkenes. Baker and Field described the reactions of the square-planar Fe(0) systems [Fe(depe)$_2$] and [Fe(dmpe)$_2$] with several unactivated alkenes, demonstrating that the C–H insertion products are kinetically favored although the π-olefin isomers are thermodynamically more stable [depe = 1,2-bis(diethylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane].[5] In the reactions with alkenes, these iron systems give rise to the vinyl hydride as the major product, whereas our iridium fragment produces the largest amount of π-olefin complex. As previously suggested, the preference of iridium for π-olefin coordination may be due to its less sterically demanding environment. On the other hand, it is worth mentioning that, provided Bergman's mechanism shown in Scheme VII is valid,[7] the formation of a σ (or agostic) complex prior to insertion would be disfavored for a substituted olefin such as styrene.

Of particular interest are the thermal reactions of **1** in solutions containing 1-alkynes. We note that (i) activation of phenylacetylene and ethyl propiolate is favored over activation of either any solvent (THF, benzene, MeCN) or substrate (ethene, styrene); (ii) the reactions selectively give σ-alkynyl dihydrides, which are quite thermally stable up to 100 °C. The latter result and the observation that the π-phenylacetylene hydride **13** is an isolable and thermally stable compound deserve some comment.

Scheme VIII



Scheme IX



Three species can be isolated upon stoichiometric reaction between low-valent unsaturated metal fragments and 1-alkynes, π-alkyne, σ-alkynyl hydride, and vinylidene complexes (Scheme VIII), and evidence has been provided for either reversible or irreversible interconversion of the three isomers. However, it is generally agreed that the initial interaction between the metal system and the alkyne is of the π-type and that only at a later stage does the π-intermediate eventually convert to either isomer.[2d,h,24] Our results, as well as similar observations by Hackett and Whitesides[3h] for the reactions of [bis(dicyclohexylphosphine)ethane]Pt(0) with 1-alkynes, re-open the question. In fact, even though it may be possible that both the iridium and the platinum alkynyl hydride transforms into the π-alkyne isomer at temperatures higher than those examined, the π-alkyne and alkynyl hydride compounds apparently form in parallel reactions *via* different transition states (Scheme IX), as occurs for the reaction with ethene. In the case of our iridium system, only path a seems to be accessible, which is consistent with a much higher barrier to π-alkyne complex formation with respect to insertion of the metal into the C–H bond.

In light of the results of the several experiments described in this paper, one may reasonably conclude that the thermodynamic preference for the insertion of [(triphos)IrH] into hydrocarbon C–H bond follows the order sp > sp^2 (aromatic) > sp^2 (olefinic) > sp^3, which has been previously reported and discussed in detail.[1d,i,3h]

The fact that metal-mediated C–H activation reactions are observed more frequently with alkynes, alkenes, and arenes than with saturated hydrocarbons has been related to the ability of the unsaturated substrates to form intermediate π-complexes.[1] At least in two cases, namely in the reactions with ethene and phenylacetylene, our evidence contrasts this general belief since the π-complexes appear as dead ends for the thermal insertion of the metal into the C–H bonds.

Photochemical Reactions. A number of photoisomerizations of transition metal π-ethene complexes to the corresponding vinyl hydrides have been reported in recent years.[5,7,15c–e]

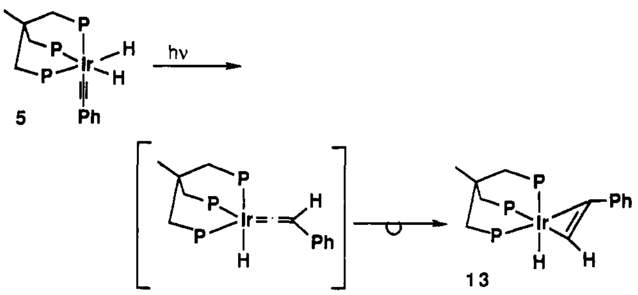
Valuable mechanistic information has been provided by Perutz *et al.* in 1990 for the isomerization of [CpM-

---

(23) (a) Werner, H.; Dirnberger, T.; Schulz, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 948. (b) Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480. (c) Carmona, E.; Perez, P. J.; Poveda, M. *J. Chem. Soc., Chem. Commun.* **1992**, 8.

(24) (a) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852. (b) Werner, H.; Dirnberger, T.; Höhn, A. *Chem. Ber.* **1991**, *124*, 1957. (c) Werner, H.; Höhn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777. (d) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Retting, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979. (e) Lomprey, J. R.; Seleque, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (f) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

Scheme X



(PMe_3)(C_2H_4)] [M = Rh, Ir] in argon matrices at 12–20 K.[15c] Of the various mechanisms proposed by Perutz, only the one involving a three-centered intermediate or transition state appears reasonable by our iridium system. Indeed, we have accumulated enough experimental evidence which excludes any dissociative mechanism. Actually, in benzene or THF, photoejection of ethene from **7** does occur after and not prior to formation of the vinyl dihydride **8** (Scheme II). Analogous formal photoejections of alkenes have been observed by Perutz,[15c] Bergman,[7] Scanner,[25] and Field.[5] The last author also discovered that irradiation of the π-1-pentene complex [Fe(π-C_5H_{10})(dmpe)$_2$] at −80 °C gives equal amounts of *Z* and *E cis*-vinyl hydride isomers, which at room temperature convert to the more thermodynamically stable π-olefin complex.[5a] Our π-styrene complex **9** undergoes quite similar photochemistry with the difference that the formation of the *E* and *Z* styryl dihydrides **11** and **12** does not represent a photostationary state. Indeed, secondary photolysis experiments show that the styryl dihydrides lose H_2 and quantitatively transform into the π-phenylacetylene hydride **13** (Scheme V). To the best of our knowledge, this reaction is unprecedented and thus worthy of accurate studies. At this stage, in the absence of labeling studies, it is not possible to discriminate between H_2 formation from either coupling of the two terminal hydride ligands or coupling of one terminal hydride with a hydrogen atom coming from the styryl ligand. Perutz has reported that photolysis of [CpIr(C_2H_4)(CH=CH_2)H] causes ethene loss and formation of the vinylidene complex [CpIr(C=CH_2)(H)$_2$].[15c] Accordingly, one may tentatively suggest that **13** forms *via* an Ir(I) vinylidene intermediate, [(triphos)IrH(C=CHPh)], which then isomerizes to the corresponding π-alkyne derivative. With more confidence, an identical vinylidene intermediate can reasonably be proposed for the photochemical isomerization of the alkynyl dihydride **5** to **13** (Scheme X). In fact, although occurring as thermal steps, intramolecular migrations of hydrogen atoms from metal to the β-carbon of alkynyl ligands are well-known reactions for which kinetic and thermodynamic data are also available.[2d,h,24a–c]

It remains to be ascertained why an Ir(I) vinylidene of the formula [(triphos)IrH(C=CHPh)] would be less thermodynamically stable than the π-alkyne isomer **13**. Indeed, a theoretical analysis would probably help in understanding this point. In its absence, it is worth mentioning that stable Ir(I) vinylidenes, *i.e.* [Ir(C=CH_2){N($SiMe_2CH_2PPh_2$)$_2$}][24d] and [IrCl(C=CHR)(P-*i*-Pr_3)$_2$] (R = H, C_7H_9, $SiMe_3$, CO_2Me),[24a–c] are invariably 16-electron square-planar species. A five-coordinate Ir(I) vinylidene of the formula [(triphos)IrH(C=CHPh)] might be too electron rich and, thus, appropriate to rapidly undergo oxidative isomerization to the alkyne, as occurs for the isomerization of [Cr(CO)$_2${C=C($SiMe_3$)$_2$}(η-C_6Me_6)] to the [Cr(CO)$_2$($Me_3SiC{\equiv}CSiMe_3$)(η-C_6Me_6)] isomer recently reported by Connelly *et al.*[26]

Consideration of the results of both thermal and photochemical studies provides an interesting overall view of the interactions of HC≡CPh with the reactive intermediate [(triphos)IrH]. The thermal interaction shows a neat preference for C–H cleavage *via* a three-centered transition state. In contrast, the intramolecular conversion of the C–H activation product to the π-alkyne isomer requires photon energy to overcome the thermodynamic barrier and most likely proceeds *via* a vinylidene transition state or intermediate.

Irradiation of **1** in either benzene or THF at 20 °C is a complicated reaction in that several metal complexes are obtained, most of which are due to secondary photolysis. Photoejection of ethane and consequent formation of products arising from C–H ativation of the solvent show that the reactive intermediate [(triphos)IrH] is one of the products of primary photolysis. Nevertheless, part of the solvent C–H activation products is certainly originated by secondary photolysis of either the vinyl dihydride **8** or the trihydride **10**, as shown by independent experiments on pure samples of both compounds (Schemes II and IV). The formation of the trihydride can reasonably be interpreted in terms of a β-H elimination step from the ethyl ligand, followed by C_2H_4 expulsion. This reaction sequence has a few precedents in the literature. Baker and Field reported the photoconversion of [Fe(dmpe)$_2$(σ-C_5H_{11})H] to [Fe(dmpe)$_2H_2$] and 1-pentene,[3f] while Bergman showed that irradiation of [Cp(PMe_3)$_2$Re(σ-C_3H_5)H] in cyclopropane gives the dihydride [Cp(PMe_3)$_2ReH_2$] as the main product.[1i]

The third gaseous product which is evolved during photolysis of **1** is dihydrogen. Part of it is undoubtedly generated upon secondary photolysis of **10**. The major part, however, should form by direct H–H coupling of the terminal hydride ligands. In fact, only through such an initial step, followed by β-H elimination from the remaining ethyl ligand, is the formation of the π-ethene hydride complex **7** accounted for. Ultimately, the latter complex photoisomerizes to the vinyl dihydride **8**.

Low-temperature photochemical studies, possibly with the use of laser flash-photolysis techniques, are presently scheduled in our laboratory in order to establish more accurately the photodecomposition pathways of **1**.

Acknowledgment. Thanks are due to "Progetto Finalizzato-Chimica Fine II", CNR, Rome for financial support.

OM930026H

---

(25) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818.

(26) Connelly, N. G.; Orpen, A. G.; Rieger, A. L.; Rieger, P. H.; Scott, C. J.; Rosair, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1293.