benzene solution. After the mixture was thawed, the reaction was carried out at room temperature for 20 h, at which time the products were characterized by GC–mass spectrometry.

Observation of $Rh_2H_2(\mu\text{-SiR(NHR')})(CO)_2(dppm)_2$ (5b, R = Et, R' = Me; 5c, R = n-C_6H_{13}, R' = Me). Complex 5 was only observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and could not be isolated. The following general procedures were used for the preparation of NMR samples. A 0.5-mL portion of C_6D_6 was transferred into an NMR tube containing 10 mg of 3, followed by the addition of $MeNH_2$ (10 mL, 200 Torr). After the mixture was thawed, the reaction was followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Spectroscopic data for **5b**: ^1H NMR (C_6D_6) 7.62 (br s, 10 H), 7.33 (s, 2 H), 7.22 (s, 4 H), 6.85–6.63 (m, 24 H), 4.27 (m, 1 H), 3.80 (m, 1 H), 2.87 (m, 2 H), 2.72 (d, J = 6.5 Hz, 3 H), 1.72 (t, J = 8.0 Hz, 3 H), 1.65 (m, 2 H), –9.43 (t of m, J_t = 40 Hz, 2 H); $^{31}P\{^1H\}$ NMR 30.15 (dd, J_1 = 71 Hz, J_2 = 36 Hz), 29.33 (dd, J_1 = 68 Hz, J_2 = 39 Hz). Selective spectroscopic data for **5c**: ^1H NMR (C_6D_6) 7.66 (br s, 10 H), 7.36 (s, 2 H), 7.22 (s, 4 H), 6.9–6.6 (m, 24 H), 4.24 (m, 1 H), 3.77 (m, 1 H), 2.86 (m, 2 H), 2.79 (d, J = 6.5 Hz, 3 H), –9.36 (t of m, J_t = 45 Hz, 2 H); $^{31}P\{^1H\}$ NMR 30.43 (dd, J_1 = 71 Hz, J_2 = 36 Hz), 29.60 (dd, J_1 = 68 Hz, J_2 = 39 Hz). Selective spectroscopic data for **5d**: ^1H NMR (C_6D_6) 4.41 (m, 1 H), 3.80 (m, 1 H), 2.93 (m, 1 H), 2.79 (m, 1 H), 1.72 (m, 5 H), –9.40 (t of m, J_t = 57 Hz, 2 H); $^{31}P\{^1H\}$ NMR 30.94 (dd, J_1 = 72 Hz, J_2 = 34 Hz), 27.00 (dd, J_1 = 67 Hz, J_2 = 38 Hz). Selective spectroscopic data for **5e**: ^1H NMR (C_6D_6) 4.42 (m, 1 H), 3.83 (m, 1 H), 2.94 (m, 1 H), 2.81 (m, 1 H), –9.42 (t of m, J_t = 57 Hz, 2 H); $^{31}P\{^1H\}$ NMR 31.01 (dd, J_1 = 72 Hz, J_2 = 34 Hz), 27.11 (dd, J_1 = 67 Hz, J_2 = 38 Hz).

The intermediate $Rh_2H_2(\mu\text{-SiMe(NHMe)})(CO)_2(dppm)_2$, which was formed in the reaction of $Rh_2(\mu\text{-SiMeH})_2(CO)_2(dppm)_2$ with $MeNH_2$ in CD_2Cl_2, was identified by ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectroscopy with the following selective data: ^1H NMR (CD_2Cl_2) 4.17 (m, 1 H), 3.82 (m, 1 H), 2.70 (m, 2 H), 2.63 (d, J = 8 Hz, 3 H), 0.55 (s, 3 H), –9.92 (m, 2 H); $^{31}P\{^1H\}$ NMR 30.53 (dd, J_1 = 69 Hz, J_2 = 38 Hz), 27.74 (dd, J_1 = 71 Hz, J_2 = 35 Hz).

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Assembling Ethylene, Alkyl, Hydride, and CO Ligands at Iridium

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The iridacyclopropane complex [(triphos)Ir(Cl)(C_2H_4)] is the starting point to synthesize a number of stable iridium complexes containing various combinations of *participative* ligands such as hydride, ethylene, alkyls and heteroalkyls, alkynes, and carbon monoxide: Ir(H)(C_2H_4), Ir(H)$_2$(C_2H_4), Ir(C_2H_5)(C_2H_4), Ir(CO)$_2$, Ir(H)(C_2H_5)(CO), Ir(H)$_2$(CO), Ir(H)$_2$($CH_2CH_2PEt_2$), Ir(H)$_3$, Ir(H)$_2$(C_2H_5), Ir(H)$_2$(C_3H_7), Ir(C_2H_4)$_2$, Ir(RC≡CR), IrH(μ-H)$_2$HIr, and IrH(μ-Cl)$_2$HIr. Due to the tripodlike structure of the ligand MeC(CH_2PPh_2)$_3$ (triphos), all the complexes invariably exhibit a facial arrangement of the phosphorus and non-phosphorus ligands. The contemporaneous availability of so many related species has allowed a comparative experimental study on several important reactions. These include (i) reductive elimination of C–H and H–H bonds from dihydride alkyl complexes, (ii) reductive elimination of H–H bonds vs hydride migration in dihydride ethylene species, (iii) nucleophilic additions to coordinated double bonds, (iv) phosphine arm dissociation in triphos complexes, and β–H elimination vs C–H bond reductive elimination in hydride alkyl complexes. In most instances, such reactions are characterized by stereo- and chemoselectivity. Valuable information on the role played by the nature of the metal and of the phosphine ligands in determining the reactivity has been provided by a comparison among strictly related Rh and Ir complexes containing either triphos or three comparable monophosphines.

Introduction

Olefin-based reactions such as hydroformylation, hydrogenation, isomerization, polymerization, amination, and related nucleophilic additions contribute a large percentage of the whole body of metal-catalyzed homogeneous transformations of organic compounds. All of these reactions take place through multistep sequences involving (i) olefin or CO binding to the metal center, (ii) insertion of CO or olefins across M–H and M–C bonds, (iii) oxidative addition of H_2 or C–H bonds at the metal, and (iv) reductive elimination from the metal center to form C–H bonds. A good catalyst performs such reaction sequences very rapidly so that the observation of intermediates is generally difficult. This limitation can be overcome with the use of model complexes exhibiting high kinetic stability.

Due to the large radial extension of the dπ orbitals and the readily attainable π-d^6 electron configuration, third-row transition metals, particularly iridium, are being largely used to design model compounds for homogeneously catalyzed reactions.[1] A second, less common strategy to gain information about the structure of reaction intermediates involves the use of ancillary ligands that are capable of

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

complex	pattern	chem shift, ppm[b] $\delta(P_A)$	$\delta(P_M)$	$\delta(P_Q)$	coupling const, Hz $J(P_AP_M)$	$J(P_AP_Q)$	$J(P_MP_Q)$
1	AM_2	−6.14	−32.66		17.2		
2	AM_2	−21.25	−14.78		19.3		
3	AM_2	−28.75	−25.57		18.2		
cis-4	AM_2	−23.36	−8.44		10.0		
trans-4	AM_2	−22.40	−9.08		9.7		
5[c]	AM_2	−6.34	−22.54		22.6		
5[d]	AMQ	−5.20	−17.10	−26.45	13.0	10.8	16.3
6	A_3	−21.43					
7	AMQ	−12.77	−25.44	−34.16	25.1	24.9	18.1
9	AM_2Q[e]	−8.51	−11.47	38.93	16.9	36.0	≅0
11	AM_2	−12.98	−15.56		15.3		
12	AM_2	−11.49	−15.69		15.1		
13	A_3	−27.11					
14	A_3	−7.04					
15	A_3	−19.64					

[a] All spectra were recorded at room temperature (20 °C) in CD_2Cl_2 solutions unless otherwise stated. [b] The chemical shifts (δ's) are relative to 85% H_3PO_4 at 0.00 ppm with positive values being downfield from the standard. [c] At −20 °C. [d] In DMF-d_7 at room temperature. [e] In complex 9, Q refers to the phosphonium phosphorus atom.

conferring stability to their metal complexes, viz. polydentate ligands that may form chelate rings.[2a-o]

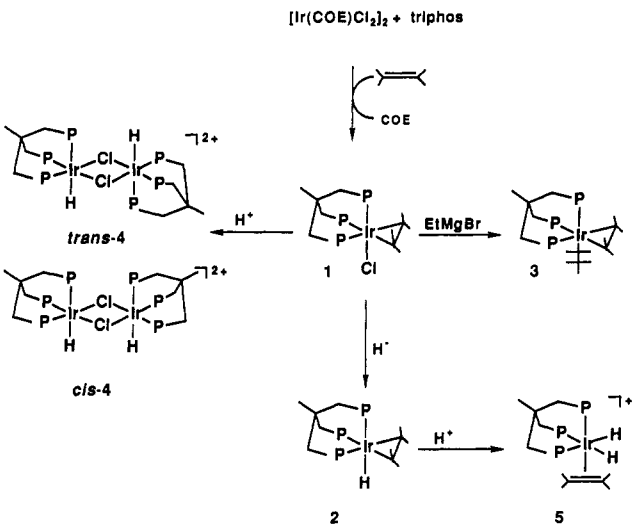
Our work is attempting to address the question of the structure and chemistry of reaction intermediates in olefin chemistry by examining the use of transition-metal catalysts stabilized by tripodal polyphosphines such as MeC-$(CH_2PPh_2)_3$ (triphos), $P(CH_2CH_2PPh_2)_3$ (PP_3), and N-$(CH_2CH_2PPh_2)_3$ (NP_3).[2b-i] Due to the tripodlike geometry these ligands combine the well-known *polyphosphine advantages*[2a] with a rigorous control on the stereochemistry of their complexes. As a result, tripodal polyphosphine metal complexes are invariably more stable than comparable complexes with monophosphine, while the reactivity of eventual *participative* coligands is generally preserved.

In the present paper, we report on the ability of the (triphos)Ir fragment to coordinate important reactive ligands such as ethylene, hydride, ethyl, and carbon monoxide in a stable manner and in an incredible variety of mutual combinations and bonding modes. As will be apparent in forthcoming pages, the (triphos)Ir moiety possesses the potential requisites to become an ideal model system to study the mechanisms of many organometallic reactions.

Results

The principal preparations and reactions of the complexes described in this paper are summarized in Schemes

Scheme I



I and II. Selected NMR data are collected in Tables I ($^{31}P\{^1H\}$ spectra) and II (^1H spectra). Significant IR absorptions and $^{13}C\{^1H\}$ NMR data are given either in the Experimental Section or elsewhere in the text.

Synthesis of [(triphos)IrCl(C_2H_4)]. When 2 equiv of triphos is reacted with $[Ir(COE)_2Cl]_2$ (COE = cyclooctene) under ethylene at −10 °C, an orange solution of [(triphos)IrCl(C_2H_4)] (1) is obtained. Lemon yellow crystals of 1 precipitate in ca. 85% yield by addition of ethanol. Compound 1 is air-stable in the solid state and in ambient-temperature deaerated solutions of common organic solvents in which it behaves as a nonelectrolyte.

The $^{31}P\{^1H\}$ NMR spectrum is invariant over the temperature range −90 to 30 °C and consists of an AM_2 spin system. The chemical shifts and coupling constants are typical of octahedral (OCT) Ir(III) complexes containing the triphos ligand.[2l,3] An OCT geometry for 1 can be inferred also from a perusal of the proton resonances due to the alkyl backbone of triphos. These appear as a broad pseudotriplet (4 H) and a doublet (2 H) and, in principle, should constitute and AA'BB'C_2 part of an AA'BB'C_2XX'Y spin system. This part of the ^1H NMR spectrum can be satisfactorily computed by using a simplified ABCX pattern with the following magnetic parameters: $\delta(H_a)$ 2.45, $\delta(H_b)$ 2.41, $\delta(H_c)$ 2.32; $J(H_aH_b)$ = 15.0 Hz, $J(H_aP_M)$ = 3.9

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

	$CH_2{=}CH_2$				hydride				alkyl			
compd	pattern[b]	chem shift[c]	J(HH)[c]	J(HP)[c]	pattern[b]	chem shift[c]	$J(HP_{trans})$[c]	$J(HP_{cis})$[c]	pattern[b]	chem shift[c]	J(HH)[c]	J(HP)[c]
1	AA′BB′-XX′Y[d]	1.23 (2 H) 2.37 (2 H)	1.7 (AA′) 7.1 (AB) 0.6 (AB′) 1.7 (BB′)	3.4 (AX) −1.8 (AX′) 2.1 (AY)								
2	AA′BB′-XX′Y[d]	1.06 (2 H) 2.58 (2 H)	2.4 (AA′) 6.8 (AB) 1.8 (AB′) 3.2 (BB′)	7.3 (AX) 0.6 (BX) 0.4 (AX′) 8.5 (BX′) 1.8 (AY) 2.8 (BY)	AX_2Y	−12.42 (1 H)	143.6	12.8				
3	AA′BB′-XX′Y[d]	1.40 (2 H) 1.79 (2 H)	2.0 (AA′) 6.8 (AB) 1.7 (AB′) 3.0 (BB′)	7.4 (AX) 0.6 (BX) 0.3 (AX′) 7.9 (BX′) 1.6 (AY) 2.5 (BY)					$A_3B_2X_2Y$	0.25 (2 H) 0.74 (3 H)	7.5	5.9 (BX) 6.8 (AY) 8.7 (BY)
cis-4					AX_2Y	−6.73 (2 H)	166.1	10.3				
trans-4					AX_2Y	−4.30 (2 H)	165.1	10.6				
5[e]	b s	2.98 (4 H)		2.0	AA′XX′Y[d]	−11.68 (2 H)	109.7 (AX)	11.4 (AY) −5.9 (AX′)				
5[f]					AXYZ	−8.20 (1 H)	157.3	10.8 (AX) 10.7 (AY)	A_3B_2XYZ	1.12 (2 H) 1.40 (3 H)	7.3	6.5 (BX) 6.5 (AY) 6.5 (BY) 6.5 (BZ)
7					AX_2Y	−10.20 (1 H)	110.2	12.6	b m b m	0.70 (2 H) 1.60 (3 H)[g]		
9[h]					AA′XX′Y-Z[d]	−9.54 (2 H)	132.8 (AX)	12.6 (AY) −11.2 (AX′) 7.1 (AZ)	A_2B_2XX'-YZ	0.72 (2 H) 2.50 (2 H)[g]	7.3	7 (AX) 7 (AX′) 7 (AY) 7 (AZ)
11					AA′XX′Y[d]	−9.45 (2 H)	129.8 (AX)	12.4 (AY) −5.5 (AX′)	$A_3B_2X_2Y$	0.87 (2 H) 1.73 (3 H)	7.4	7.1 (AY) 7.8 (BX) 5.6 (BY)
12[i]				AA′XX′Y[d]	−9.47 (2 H)	124.8 (AX)	11.7 (AY) −5.5 (AX′)	b m b m t		1.86 (2 H, H_α) 0.95 (2 H, H_β) 0.71 (3 H, H_γ)	5.8 ($H_\beta H_\gamma$)	
13	b s	2.18 (8 H)										
14				A_4X_6	−13.32 (4 H)		17.0 (AX)					

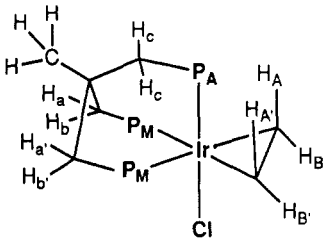
[a] All spectra were recorded at 299.945 MHz in CD_2Cl_2 solutions at room teperature (20 °C) unless otherwise stated. The resonances belonging to the triphos hydrogen atoms are not reported (see Experimenal Section). [b] The letters A and B denote hydrogen atoms. The letters X, Y, and Z refer to the triphos phosphorus atoms; in complex 9 Z indicates the phosphonium phosphorus atom. Key: s, singlet; t, triplet; m, multiplet; b, broad. [c] The chemical shift values (δ's) are in ppm and are relative to tetramethylsilane as external standard. J values are in Hz. [d] The spin simulation procedures (see Experimental Section) require the introduction of an additional coupling constant between the pair of phosphorus atoms P_X and $P_{X'}$. The computed values are as follows: 1, 9.0 Hz; 2, 0.2 Hz; 3, 0.2 Hz; 5, 6.4 Hz; 9, −9.4 Hz; 11, 11.0 Hz; 12, 11.0 Hz. [e] In CD_2Cl_2 at −40 °C. [f] In DMF-d_7 at 20 °C. [g] This resonance is partially masked by the aliphatic protons of triphos. [h] The alkyl resonance for complex 9 refers to the β-(triethylphosphonium)ethyl ligand. PEt_3: $\delta(CH_2CH_3)$ 1.00 ppm (6 H), J(HH) = 7.7 Hz, J(HP) = 12.1 Hz; $\delta(CH_2CH_3)$ 1.53 ppm (9 H), J(HP) = 17.1 Hz. [i] The letters α, β, and γ refer to the protons of the *n*-propyl ligand ($C_\alpha H_2C_\beta H_2C_\gamma H_3$).

Hz, $J(H_bP_M)$ = 2.5 Hz, $J(H_cP_A)$ = 9.9 Hz. Evidently, two methylene groups are equivalent but show inequivalent protons with a value of the geminal coupling of 15 Hz and almost comparable coupling to the phosphorus nuclei (3.9 and 2.5 Hz). As expected, the methyl group of triphos appears as a quartet (1.45 ppm), since it is equally coupled to the three phosphorus nuclei [J(HP) = 2.8 Hz]. While the IR spectrum is poorly informative, the ^1H NMR spectrum shows the presence of a static ethylene ligand. This originates two temperature-invariant multiplets of equal intensity (2 H) at 2.37 and 1.23 ppm, which have been properly simulated as an AA′BB′XX′Y spin system with the following parameters: $J(H_AH_{A'})$ = 1.7 Hz, $J(H_AH_B)$ = 7.1 Hz, $J(H_AH_{B'})$ = 0.6 Hz, $J(H_BH_{B'})$ = 1.7 Hz, $J(H_AP_X)$ = 3.4 Hz, $J(H_AP_{X'})$ = −1.8 Hz, $J(H_AP_Y)$ = 2.1 Hz, $J(P_XP_{X'})$ = 9.0 Hz. The geminal coupling of 7.1 Hz between H_A and H_B and the long-range coupling of H_A to the phosphorus nuclei are confirmed by selective decoupling experiments.

The $^{13}C\{^1H\}$ NMR spectrum of 1 is consistent with the proton spectrum. A single resonance (broad triplet) at δ 26.2 ppm for the ethylene carbons indicates they are chemically equivalent [$J(CP_M)$ = 15 Hz]. The two equivalent methylene groups of triphos exhibit a single resonance at 33.1 ppm as a pseudotriplet of doublets [$J(CP_M) = {}^3J(CP_{M'})$ = 12 Hz, $J(CP_A)$ = 4 Hz], while the carbon of the third CH_2 group resonates at 34.4 ppm and appears as a doublet [$J(CP_A)$ = 28 Hz] of triplets [$J(CP_M)$ = 4 Hz]. The splitting pattern of the two equivalent methylene groups may be explained in terms of a fortuitous concidence of the values of $^1J(CP_M)$ and $^3J(CP_{M'})$ (through-metal and through-backbone contributions).

Finally, it is worth mentioning that all of the spectroscopic data for 1 are qualitatively similar to those of the Rh analogue [(triphos)RhCl(C_2H_4)] recently authenticated by an X-ray analysis.[2b] In the OCT structure of the rhodium complex, triphos caps a triangular face of the octahedron, while the three remaining coordination sites are occupied by a chloride and by a dihapto-bonded ethylene ligand. The structural parameters associated with C_2H_4 ligation are consistent with a rhodacyclopropane structure. Reasonably, a structure of this type can be assigned also to 1.

Reactions of [(triphos)IrCl(C_2H_4)]. With Hydride-Containing Reagents. Stirring 1 in THF at room temperature under nitrogen with a slight excess of LiHBEt$_3$, NaBH$_4$, or PPNBH$_4$ produces a pale yellow solution from which off-white crystals of [(triphos)IrH(C_2H_4)] (2) can be obtained in almost quantitative yield by addition of ethanol.



1

Compound **2** is air-stable in both the solid state and solution even at high temperature or under a high pressure of C_2H_4 (up to 30 atm). A strong IR absorption at 2065 cm^{-1} [ν(Ir–H)] and a first-order proton resonance at −12.42 ppm diagnose that the chloride in **1** has been replaced by hydride. The ^1H NMR resonance for the hydride ligand appears as a doublet of triplets [$J(HP_{trans})$ = 143.6 Hz, $J(HP_{cis})$ = 12.8 Hz] as generally found for monohydrido OCT triphos complexes containing two chemically equivalent phosphorus nuclei [^{31}P NMR: temperature-invariant AM_2 pattern].[2b,3] The ^1H NMR spectrum in the 2.8/1.0 ppm region is particularly well resolved and is reported in Figure 1 together with the computed resonances of the ethylene hydrogens. Like in **1**, the C_2H_4 protons constitute the AA′BB′ part of an AA′BB′XX′Y spin system. The $^{13}C\{^1H\}$ resonance for the ethylene carbons is surprisingly high-field shifted (11.6 ppm)[2q] (^{13}C–^1H heteronuclear correlation 2D NMR) and appears as a triplet of doublets with $J(CP_M)$ = 12 Hz and $J(CP_A)$ = 3 Hz (Figure 2). A gated-decoupling experiment gave a J(CH) value of 151 Hz. The apparent td splitting pattern of the ethylene carbons may be due to the short bite of the ethylene ligand;[2b] i.e., the carbon atoms equally couple to the P_M phosphorus atoms because neither phosphorus lies perfectly trans to carbon.

With EtMgBr. Reaction with EtMgBr in THF at room temperature converts **1** into the metathesis product [(triphos)Ir(C_2H_5)(C_2H_4)] (**3**) isolable in 70% yield as off-white crystals. The product of this reaction may be contaminated by some **2** when the solvent is not completely dried.

The chemico–physical properties of **3** are quite comparable with those of the OCT parent complexes **1** and **2**, including the thermal stability in refluxing THF. This is surprising for an ethyl complex for which the hydride derivative **2** is even more stable.

A detailed description of the spectroscopy of **3** is not in order, since it is quite similar to that of **1** and **2** with the exception of the ^1H NMR spectrum in the alkyl region, which contains a quartet (3 H) at 0.74 ppm and a pseudoseptet (2 H) at 0.25 ppm. These resonances are due to the ethyl ligand that has replaced chloride and can be computed as an $A_3B_2X_2Y$ spin system with $J(H_AH_B)$ = 7.5 Hz, $J(H_AP_Y)$ = 6.8 Hz, $J(H_BP_X)$ = 5.9 Hz, and $J(H_BP_Y)$ = 8.7 Hz.

With Strong Protic Acids. Protic acids such as $HOSO_2CF_3$ or HBF_4 readily decompose **1** in CH_2Cl_2 at room temperature. As a result, ethylene is evolved and a nonracemic mixture of two isomeric products analyzing as [(triphos)IrH(μ-Cl)$_2$HIr(triphos)](BPh_4)$_2$ (**4**) is invariably obtained by addition of $NaBPh_4$ in ethanol. Both products appear as off-white crystals, stable in the solid state and in deaerated solutions in which they behave as 1:2 electrolytes. The IR spectrum of the mixture exhibits a medium-intensity absorption at 2110 cm^{-1} that is attributable to an Ir–H(terminal) stretching vibration. The $^{31}P\{^1H\}$ NMR spectrum consists of two independent AM_2 patterns with almost concident coupling constants [J-

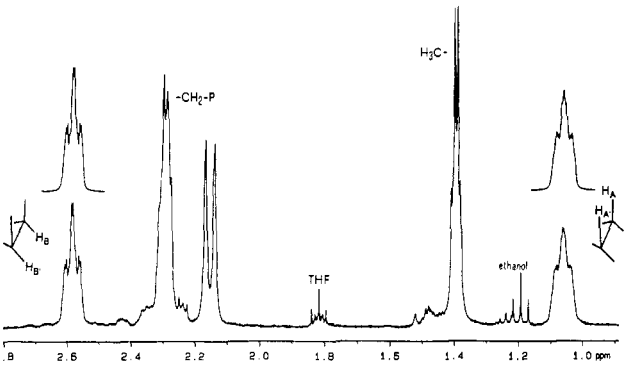


Figure 1. Experimental (bottom) ^1H NMR spectrum of **2** in the 2.8/1.0 ppm region (299.945 MHz, 20 °C, CD_2Cl_2, TMS reference) and computed (top) resonances of the η^2-C_2H_4 hydrogens.

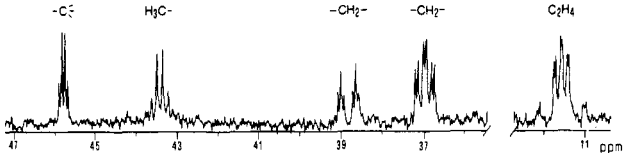


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of **2** showing the resonances of the carbon nuclei of triphos and of the ethylene ligand (75.429 MHz, 20 °C, THF-d_8, TMS reference).

(P_AP_M) = 10.0 and 9.7 Hz] but different chemical shifts (Table I). Analogously, the terminal hydride ligands originate for both metal species a dt pattern exhibiting quite similar $J(HP_{cis})$ and $J(HP_{trans})$ values but different chemical shifts. This allows a reliable determination of the percentage composition of each species by NMR integration. In CH_2Cl_2 the two compounds are in a ca. 7:3 ratio, which remains practically constant at room temperature over several days. Heating of a CD_3NO_2 solution up to 90 °C slowly and irreversibly converts one of the two isomers, namely the lower field one, into the other. After 40 min at 90 °C, only the thermodynamically favored product is found in the reaction mixture.

By analogy with the synthesis of [(triphos)RhH(μ-Cl)$_2$HRh(triphos)](BPh_4)$_2$ from [(triphos)RhCl(C_2H_4)] and $HOSO_2CF_3$, the two iridium isomers are assigned a dimeric structure where the metal centers are bridged by two chloride ligands.[4] The OCT geometry about each iridium is completed by the three phosphorus donors of triphos and by a terminal hydride. The two hydride ligands in each isomeric molecule may be mutually disposed either cis or trans, thus giving rise to *cis*-**4** and *trans*-**4** (Scheme I). However, in the absence of an X-ray analysis, it is not possible to correlate structures and NMR patterns. Intuitively, the more stable species would be *trans*-**4** because of the higher symmetry and the minor steric crowding.

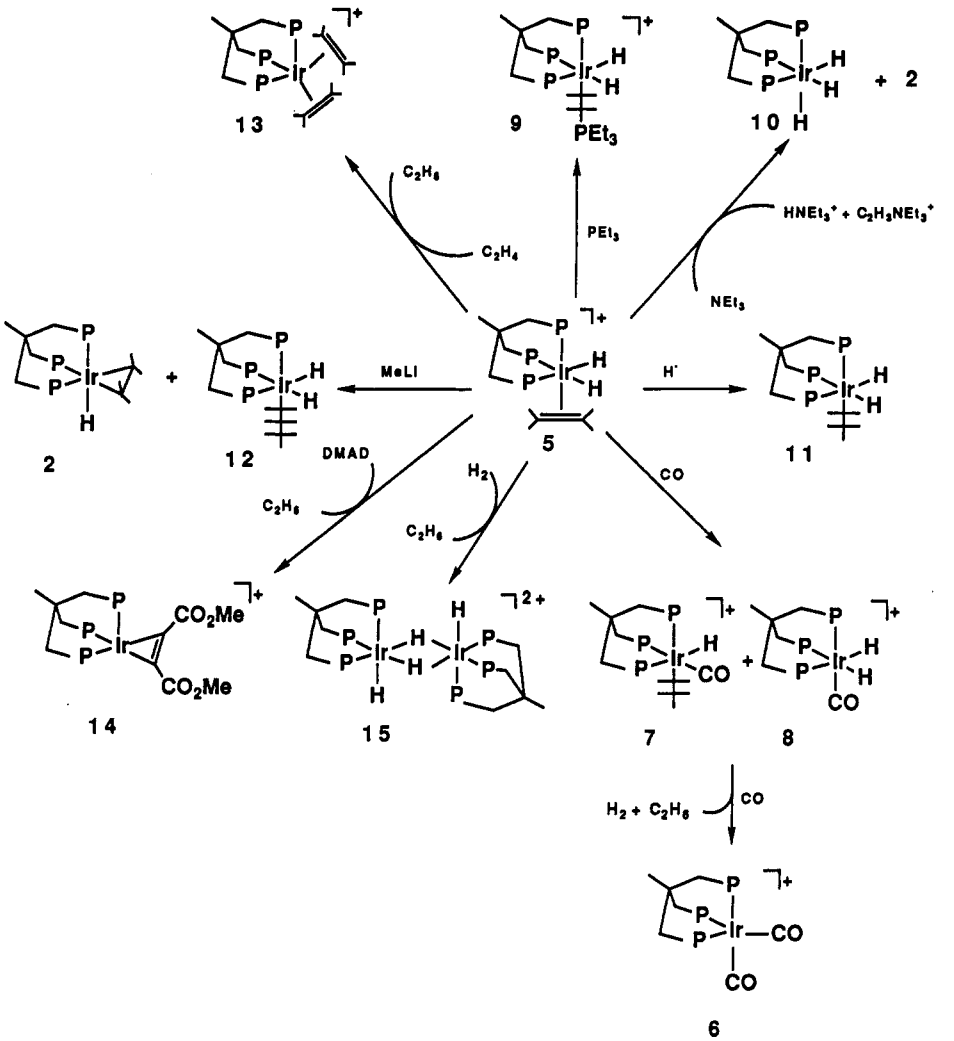
Synthesis of [(triphos)Ir(H)$_2$(C_2H_4)]BPh_4. Treatment of **2** in THF at room temperature with a slight excess of neat triflic acid produces a colorless solution from which crystals of [(triphos)Ir(H)$_2$(C_2H_4)]BPh_4 (**5**) precipitate in 90% yield by addition of $NaBPh_4$ in ethanol.

Compound **5** is air-stable in both the solid state and solution in which it behaves as a 1:1 electrolyte. The IR spectrum shows two medium-intensity absorptions at 2110 and 2062 cm^{-1} that are attributable to two terminal hydride ligands.

The complex is fluxional on the ^1H NMR time scale over the temperature range from −100 to 40 °C, above which temperature it decomposes evolving ethylene. In $CHCl_3$, we note appreciable conversion into **4** above 40 °C. In

(4) Bianchini, C.; Meli, A.; Laschi, F.; Ramirez, J. A.; Zanello, P.; Vacca, A. *Inorg. Chem.* **1988**, *27*, 4429.

Scheme II



halogenated solvents, THF, or acetone, the variable-temperature ^1H NMR spectra are consistent with two fluxional processes with different activation energies. The lower energy process (below −40 °C) essentially involves rotation of the C_2H_4 ligand about the metal–ligand axis. In fact, the four ethylene hydrogens show a single resonance at 2.98 ppm (4 H, CH_2Cl_2) [$J(HP_{trans}) = 2$ Hz, $w_{1/2} = 10.2$ Hz], which does not resolve down to −100 °C, while the two chemically but not magnetically equivalent hydride ligands give rise to a second-order doublet of multiplets. At −40 °C, this resonance has been computed as the AA′ part of an AA′XX′Y spin system with the following magnetic parameters: $\delta(H_A) = \delta(H_{A'}) = -11.68$; $J(H_AH_{A'}) = 3.2$ Hz, $J(H_AP_X) = 109.7$ Hz, $J(H_AP_X) = -5.9$ Hz, $J(H_AP_Y) = 11.4$ Hz, $J(P_XP_{X'}) = 6.4$ Hz (Figure 3). Above −40 °C, a second dynamic process involving both the ethylene hydrogens and the terminal hydride ligands begins to occur. We were not able to simulate this dynamic process; however, from a perusal of the sequence of experimental spectra shown in Figure 4, one may readily infer that the hydride ligands reversibly exchange with the ethylene hydrogens at a rate that increases with the temperature. In this respect, it is worth noticing that, as the temperature is increased, the resonance due to the C_2H_4 protons broadens ($w_{1/2}$ goes from 10.2 Hz at −45 °C to 162 Hz at 10 °C) and finally collapses into the baseline at ca. 20 °C. At this temperature the hydride resonance coalesces after analogous broadening. Unfortunately, the fast-exchange spectrum cannot be recorded due to the decomposition of **5** above 40 °C.

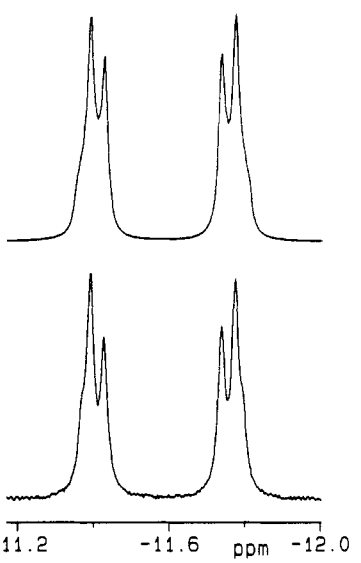


Figure 3. Experimental (bottom) and computed (top) ^1H NMR resonances of the hydride ligands in **5** (299.945 MHz, −40 °C, CD_2Cl_2, TMS reference).

The most straigthforward interpretation of the higher energy fluxional process is to think of a fast hydride migration/β-H elimination mechanism that, at room temperature, would equilibrate the six hydrogen atoms. In other words, the dihydride form of **5** and its hydride-migration product [(triphos)IrH(C_2H_5)]$^+$ seem to be in a rapid

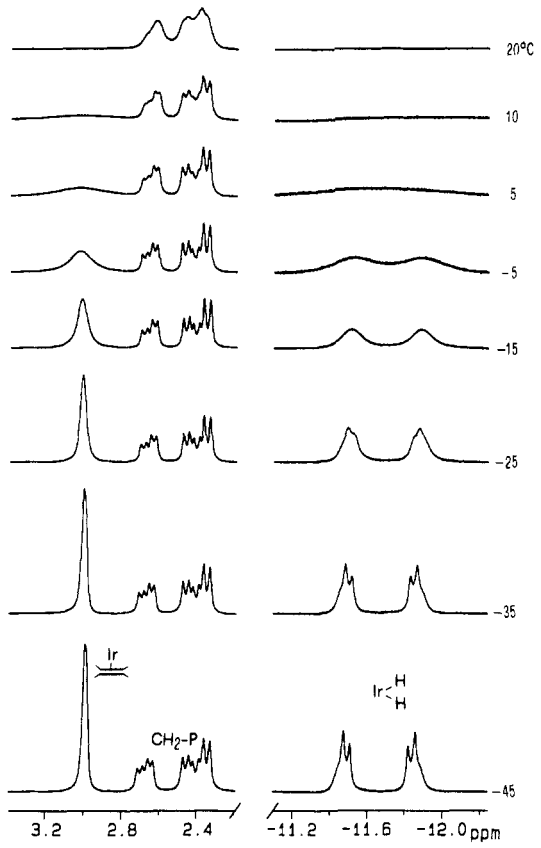
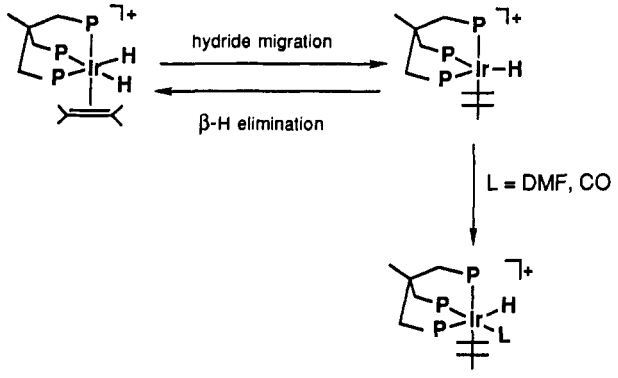


Figure 4. Variable-temperature ^1H NMR spectra of **5** in the 3.2/2.2 and −11.2/−12.0 ppm regions (299.945 MHz, CD_2Cl_2, TMS reference).

Scheme III



equilibrium in ambient-temperature solutions (Scheme III). In forthcoming pages, wide experimental evidence for such interconversion will be provided.

As expected, the lower energy dynamic process does not affect at all the triphos ligand, which remains practically rigid up to 20 °C. The bridgehead CH_3 group appears as a poorly resolved signal, while the CH_2 groups in the backbone of triphos give rise to a well-resolved set of resonances. As previously mentioned, the three methylene groups should constitute the AA'BB'C_2 part of an AA'BB'C_2XX'Y spin system; a satisfactory simulation of this part of the spectrum can be obtained by using the simplified ABCX spin model. As the higher energy fluxional process starts, extensive broadening of the methylene resonances occurs while the resonance of the bridgehead methyl assumes the typical quartet structure of fluxional triphos complexes exhibiting five-coordinate coordination.

The $^{31}P\{^1H\}$ NMR spectra of **5** are quite consistent with the proton spectra. Below −15 °C the spectrum consists of a well-resolved AM_2 spin system [$\delta(P_A)$ −6.34, $\delta(P_M)$ −22.56, $J(P_AP_M)$ = 22.6 Hz] typical for OCT triphos complexes containing two chemically equivalent ligands trans to the equatorial phosphorus nuclei. Although significantly broadened, the triplet and doublet structure of the spectrum is maintained up to 20 °C. Above this temperature both signals collapse to broad resonances with no discernible P/P couplings. The decomposition of the complex above 40 °C did not allow us to record the fast-exchange spectrum. However, there is little doubt that the spin system is approaching the A_3 pattern, i.e. that commonly observed for five-coordinate metal complexes of triphos such as the hydride-migration product [(triphos)IrH-(C_2H_5)]$^+$.[2b,n,o,3,5]

The occurrence of a rapid interconversion between the six-coordinate dihydride form of **5** and its five-coordinate hydride-migration product [(triphos)IrH(C_2H_5)]$^+$ in ambient temperature solutions is indirectly but unequivocally supported by ^1H and $^{31}P\{^1H\}$ NMR spectra in dimethylformamide-d_7 (DMF-d_7). In DMF the complex is rigid on the NMR time scale, exhibiting a first-order AMQ splitting pattern [$\delta(P_A)$ −5.20, $\delta(P_M)$ −17.10, $\delta(P_Q)$ −26.45, $J(P_AP_M)$ = 13.0 Hz, $J(P_AP_Q)$ = 10.8 Hz, $J(P_QP_M)$ = 16.3 Hz]. The spin system and the magnetic parameters are typical for OCT triphos complexes containing three different ligands trans to the phosphorus nuclei.[2f,6] Of these three ligands, two are certainly a hydride and an ethyl group, as shown by the appearance in the ^1H NMR spectrum of a first-order pseudotriplet (1 H) at −8.20 ppm [$J(HP_{trans})$ = 157.3 Hz, $J(HP_{cis})$ = 10.8, 10.7 Hz] and a characteristic A_3B_2XYZ pattern for the ethyl ligand [$\delta(H_A)$ 1.40, $\delta(H_B)$ 1.12, $J(H_AH_B)$ = 7.3 Hz]. It is therefore reasonable to conclude that the electronically unsaturated hydride-migration product has been stabilized by a coordinating DMF solvent molecule, which likely occupies the sixth coordination site around iridium(III).

Reactions of [(triphos)Ir(H)$_2$(C_2H_4)]BPh$_4$. With CO. Compound **5** in THF reacts with 1 atm of CO at room temperature to give different products depending on the reaction time. When carbon monoxide is reacted with **5** for more than 6 h, the known trigonal-bipyramidal dicarbonyl [(triphos)Ir(CO)$_2$]BPh$_4$ (**6**) quantitatively forms.[7] For shorter reaction times, mixtures of **5**, **6**, the novel complex [(triphos)IrH(CO)(C_2H_5)]BPh$_4$ (**7**), and the known carbonyl [(triphos)Ir(H)$_2$(CO)]BPh$_4$ (**8**)[3] are invariably obtained. Monitoring the reaction between **5** and CO in THF-d_8 by means of $^{31}P\{^1H\}$ NMR spectroscopy at different times shows CO to play a dual role. The favored pathway is the migration of hydride from iridium to coordinated ethylene to give **7**. Alternatively, CO simply displaces ethylene to form the dihydride **8**. After 30 min the product distribution is as follows: **5**, 48%; **7**, 43%; **8**, 5%; **6**, 4%. Ethylene evolution is observed by ^1H NMR spectroscopy together with traces of ethane and H_2. As the reaction is allowed to go on, the concentrations of **5** and **7** decrease and that of **6** increases, while the amount of **8** remains practically constant. After 2 h, the product distribution is as follows: **5**, traces; **7**, 25%; **8**, 5%; **6**, 70%. By ^1H NMR spectroscopy we note appreciable evolution of ethane.

In light of these results as well as those presented in the preceding section, a reasonable explanation for the reaction between **5** and CO is the following. Carbon monoxide may

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(6) Hommeltoft, S. I.; Cameron, A. D.; Shackleton, T. A.; Fraser, M.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 1380.
(7) Siegl, W. O.; Lapporte, S. J.; Collmann, J. P. *Inorg. Chem.* **1973**, *12*, 674.

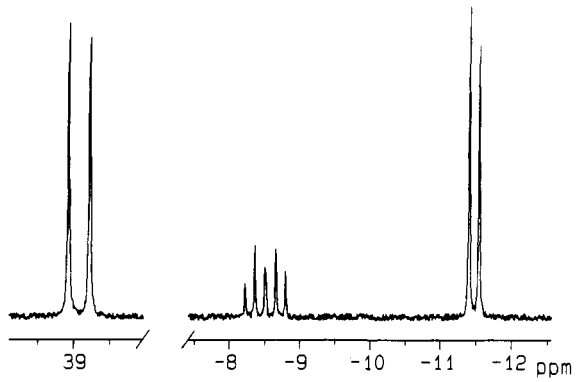

Figure 5. $^{31}P\{^1H\}$ NMR spectrum of **9** (121.42 MHz, 20 °C, CD_2Cl_2, 85% H_3PO_4 reference).

either stabilize the hydride-migration product of **5** via coordination to iridium or displace ethylene. The former pathway is most favored. Only at a later stage ethane is reductively eliminated from **7** and the dicarbonyl **6** forms. The latter complex can form also through the reaction of **8** with CO via H_2 reductive elimination. No trace of propionaldehyde was detected by GC, thus ruling out any eventual insertion of CO across the Ir–ethyl bond of **7** to account for the formation of **6**.

The structure of **7** as given in Scheme II was established by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum consists of a well-resolved AMQ spin system, while the presence of a single terminal hydride and of an ethyl ligand is readily shown by ^1H NMR spectroscopy (Tables I and II). A precise assignment of ν(Ir–H) in **7** cannot be made due to the presence of numerous terminal carbonyl ligands that obscure the 2060–1910-cm^{-1} region.

With Nucleophiles. PEt_3. Treatment of a THF solution of **5** with a slight excess of neat PEt_3 at room temperature results in a fast reaction that completely converts the starting ethylene complex into off-white crystals of the β-(triethylphosphonium)ethyl complex [(triphos)Ir-$(CH_2CH_2PEt_3)(H)_2$]BPh_4 (**9**).

Compound **9** is air-stable in both the solid state and solution in which it behaves as a 1:1 electrolyte. The IR spectrum contains two ν(Ir–H) absorptions at 2036 and 2017 cm^{-1}, thus showing that two terminal hydride ligands are still coordinated to the metal center. Also observed in the IR spectrum is a typical band at 1033 cm^{-1} due to $\nu(P-C_{alkyl})$. An OCT structure about iridium and the presence of chemically equivalent nuclei trans to two phosphorus atoms can be assigned to **9** on the basis of the ^{31}P AM_2Q splitting pattern (Figure 5), which is temperature-invariant in the range −90 to 90 °C, and of the values of the chemical shifts and coupling constants. The occurrence of chemoselective attack by PEt_3 at the ethylene ligand[8] to give a $CH_2CH_2PEt_3$ group can be readily inferred by ^{31}P and ^1H NMR spectroscopy. Like in **5**, the two terminal hydride ligands originate a second-order spectrum (Figure 6); however, due to the presence of the PEt_3 group the hydride resonance is now satisfactorily computed as the AA′ part of an AA′XX′YZ splitting pattern, Z being the phosphonium phosphorus nucleus [$J(H_AP_Z)$ = 7.1 Hz] and Y being the phosphorus trans to the ethylene-phosphonium ligand [$J(H_AP_Y)$ = 12.6 Hz]. The ^1H NMR signal of the CH_2 group of the phosphonium ligand closer to iridium (α-CH_2) at 0.72 ppm exhibits a septet multiplicity (A_2 part of an $A_2B_2XX'YZ$ system) due to the fortuitous coincidence of the coupling constants to the β-CH_2 hydrogens as well as the four phosphorus nuclei in the molecule [$J(H_AH_B) \cong J(H_AP_X) \cong$ etc. $\cong$ 7 Hz]. The β-CH_2 resonance is almost completely masked by the signal of the triphos CH_2 groups. In contrast, the three ethyl substituents on the phosphonium atom are well separated and give rise to a doublet of triplets at δ 1.00 [CH_2, J(HH) = 7.7 Hz, J(HP) = 12.1 Hz] and a doublet of quartets at δ 1.53 [CH_3, J(HP) = 17.1 Hz].

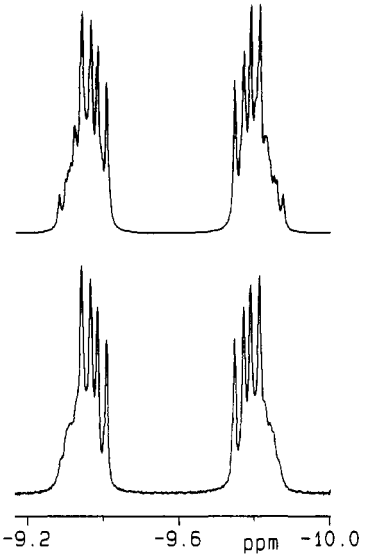

Figure 6. Experimental (bottom) and computed (top) ^1H NMR resonances of the hydride ligands in **9** (299.945 MHz, 20 °C, CD_2Cl_2, TMS reference).

NEt_3. In an effort to extend the reactions of **5** with nucleophiles, its reaction with NEt_3 was explored.[8b,9] Compound **5** was stirred in THF at room temperature with a 10-fold excess of neat NEt_3. Evaporation of the solvent under reduced pressure affords a white solid, whose $^{31}P\{^1H\}$ NMR spectrum shows it to be a 1:4 mixture of the hydride ethylene complex **2** and of the known trihydride [(triphos)IrH_3] (**10**).[3] The latter can be obtained in analytically pure form by recrystallization from THF/ethanol. The formation of **2** and **10** can be evidently detected also by ^1H NMR spectroscopy, which, however, reveals the massive presence of other hydrogen-containing compounds. These non-phosphorus-containing products, isolated by thin-layer chromatography (CH_2Cl_2 as eluent), have been authenticated as the triethylammonium salt [$HNEt_3$]BPh_4 and the vinyltriethylammonium salt [$(C_2H_3)NEt_3$]BPh_4 by comparison with authentic specimens prepared according to literature methods.[10] In light of these findings as well as the ascertained ability of **5** to undergo nucleophilic attack at the ethylene ligand (see the reaction with PEt_3 and those reported in forthcoming pages with MeLi and H^-), a plausible mechanism for the reaction with NEt_3 is the one shown in Scheme IV. This implies a dual role for NEt_3, which either deprotonates **5** to give **2** and [$HNEt_3$]BPh_4 or brings about a nucleophilic attack at ethylene to give an intermediate species containing a C-bonded β-(tri-

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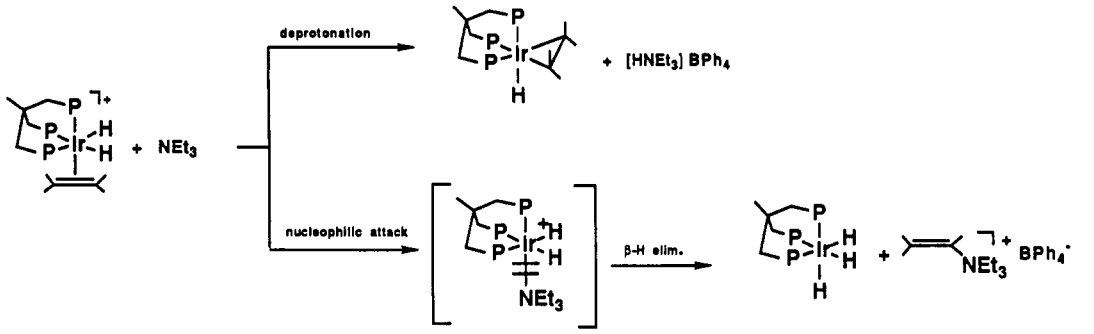
(9) (a) Gasc, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703. (b) Brunet, J.-J.; Neibecker, D.; Niedercorn, F. *J. Mol. Catal.* **1989**, *49*, 235. (c) Arnek, R.; Zettemberg, K. *Organometallics* **1987**, *6*, 1230. (d) Annibale, G.; Maresca, L.; Natile, G.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1587. (e) Al-Najjar, I. M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1651. (f) Benedetti, E.; De Renzi, A.; Paiaro, G.; Panunzi, A.; Pedone, C. *Gazz. Chim. Ital.* **1972**, *102*, 744.

(10) Reppe, W. *Liebigs Ann. Chem.* **1956**, *601*, 128.

Scheme IV



ethylammonium)ethyl ligand, e.g. [(triphos)Ir-$(CH_2CH_2NEt_3)(H)_2]^+$. For reasons that we are not able to address at this stage, this intermediate is not stable and converts via β-H elimination into the trihydride **10**, releasing the vinylammonium moiety. Complexes containing zwitterionic alkylammonium ligands are common intermediates in alkene amination reactions and, in some cases, can be isolated.[8b,9f] An X-ray structure determination is available for $[Pt(Cl)_2(NHEt_2)(CH_2CH_2NHEt_2)]$.[9f]

Hydride-Releasing Reagents. The ethyl dihydride [(triphos)Ir$(C_2H_5)(H)_2$] (**11**) has been obtained in almost quantitative yield by treatment of a THF solution of **5** with an excess of $LiHBEt_3$ or $NaBH_4$, followed by addition of ethanol. For short reaction times, compound **11** is air-stable even in ambient-temperature solutions in which it behaves as a nonelectrolyte. It is quite stable in the solid state and in deaerated solutions even in the presence of an excess of CO or C_2H_4 at room temperature. At reflux temperature in THF, benzene, or acetonitrile, the reductive elimination of ethane occurs with consequent formation of the extremely reactive [(triphos)IrH] moiety. In no case, however, was observed either the reductive elimination of H_2 to give **2** or a β-H elimination reaction leading to **10**.

An OCT geometry around the metal center in **11** can be assigned on the basis of the $^{31}P\{^1H\}$ NMR spectrum, which consists of a temperature-invariant AM_2 splitting pattern. The coordination polyhedron around iridium is completed by two terminal hydride ligands (IR: 2050, 2026 cm^{-1}. ^1H NMR: second-order doublet of multiplets at −9.45 ppm, AA′ part of an AA′XX′Y spin system) and by an ethyl ligand trans to P_Y, whose ^1H NMR signal has been properly computed as the A_3B_2 part of an $A_3B_2X_2Y$ spin system (Figure 7).

MeLi. The reaction of **5** with MeLi resembles that with NEt_3.[11] Under the same reaction conditions, except for the use of a stoichiometric amount of the alkali-metal reagent, one obtains the hydride ethylene complex **2** (deprotonation path; evolution of CH_4) as the major product (80%) and the C-bonded propyl complex [(triphos)Ir-$(CH_2CH_2CH_3)(H)_2$] (**12**) (nucleophilic attack by CH_3^- at ethylene). The major basicity of MeLi vs NEt_3 accounts for the largely predominant deprotonation pathway.

A detailed description of the spectroscopy of **12** is not in order, since it is quite similar to those of **11** with which the propyl complex shares most of the chemico-physical properties.

With Ethylene and Dimethyl Acetylenedicarboxylate. The bis(ethylene) complex [(triphos)Ir-$(C_2H_4)_2]BPh_4$ (**13**) is quantitatively obtained as off-white microcrystals by bubbling a steady stream of C_2H_4 through a THF solution of **5**.

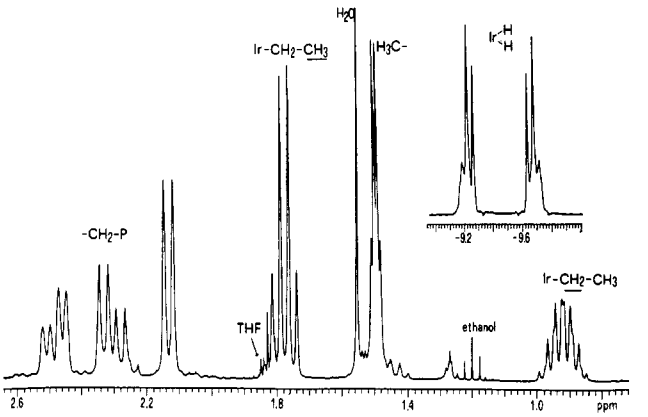


Figure 7. ^1H NMR spectrum of **11** in the 2.6/0.8 and -9.0/-9.8 ppm regions (299.945 MHz, 20 °C, CD_2Cl_2, TMS reference).

Compound **13** is rather air-stable in the solid state but rapidly decomposes in solution to give a double peroxo-bridge dimer. It is quite stable in C_2H_4-saturated solutions whereas it slowly loses ethylene at room temperature upon bubbling nitrogen or argon. Monitoring the reaction between **5** and C_2H_4 in a sealed tube by ^1H NMR spectroscopy reveals the selective elimination of ethane, thus suggesting a mechanism similar to the one shown in Scheme III for the reactions with DMF or CO. This implies the stabilization of the hydride-migration form of **5** by C_2H_4 to give an intermediate of the type [(triphos)-IrH$(C_2H_5)(C_2H_4)$], which eliminates ethane and then adds a second ethylene molecule to give the bis(ethylene) complex.

Complex **13** is highly fluxional on the NMR time scale over the temperature range −90 to 30 °C. The ^1H NMR spectrum shows a single resonance for either the eight ethylene hydrogens (2.18 ppm) or the three CH_2 groups of triphos [2.65 ppm, $J(HP)$ = 5.8 Hz]. At the same temperature range, the $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at −27.11 ppm for the three phosphorus atoms of triphos. The dynamic behavior of the complex seems to be favored by the tripodal ligand, which forces the two ethylene ligands to occupy cis positions. As a matter of fact, the related complex $[Ir(C_2H_4)_2(PMePh_2)_3]BF_4$ is stereochemically rigid in solution from −80 to 80 °C.[12]

Selective elimination of ethane occurs also when **5** is reacted with dimethyl acetylenedicarboxylate (DMAD). As a result, the π-alkyne complex [(triphos)Ir(π-DMAD)]BPh_4 (**14**) quantitatively forms as yellow orange crystals. No trace of either dimethyl maleate or dimethyl fumarate was detected by GC or ^1H NMR spectroscopy, thus indicating a reaction mechanism analogous to that suggested for the reaction with ethylene.

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(12) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165.

Complex **14** is quite stable in the solid state and in deoxygenated solutions in which it behaves as a 1:1 electrolyte. The IR spectrum contains a strong absorption at 1658 cm^{-1}, which is consistent with a four-electron-donor π-alkyne ligand (metallacyclopropane type structure).[2b] A broad band due to the ester ν(C=O) stretch is exhibited at 1727 cm^{-1}, while ν(C–O–C) is found at 1243 and 1213 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum consists of a single resonance at −7.04 ppm, which shows only a slight temperature dependence of the chemical shift down to −90 °C. This behavior is typical for five-coordinate complexes of triphos containing η^2-bonded coligands.[2b] The fluxionality is ascribed to a fast interconversion between trigonal-bipyramidal and square-pyramidal structures separated by a very low activation energy.[2b] It is worth reporting that, in some examples of this type authenticated by X-ray analyses, the solid-state structure is square pyramidal.[13] The fluxionality of the complex cation [(triphos)Ir(π-DMAD)]$^+$ is shown also by the ^1H NMR spectrum, which displays a unique resonance for the two OCH_3 groups of DMAD (3.98 ppm, 6 H) and for the six CH_2 hydrogens of triphos as well [2.63 ppm, J(HP) = 9.1 Hz].

With Dihydrogen. Complex **5** in THF reacts with 1 atm of H_2 at 60 °C to give a solution of the terminal-bridged tetrahydrido dimer **[(triphos)IrH(μ-H)$_2$HIr(triphos)](BPh$_4$)$_2$ (15). Ethane is evolved during the reaction** as determined by ^1H NMR spectroscopy.

Complex **15** is quite stable in the solid state and in deaerated solutions in which it behaves as a 1:2 electrolyte. The presence of terminal hydride ligands is evidenced by a strong IR absorption at 2127 cm^{-1} (this may have a shoulder at 2104 cm^{-1}). No band due to ν(Ir–H–Ir) can be safely assigned. This fact is not surprising as the stretching frequencies of bridging hydride ligands are generally very weak and difficult to recognize.[4] Compound **15** is stereochemically nonrigid in solution; the bridged–terminal interconversion of the four hydride ligands is rapid on the NMR time scale to −90 °C so that each hydride appears magnetically equivalent with all phosphorus atoms.[4] As a matter of fact, the ^1H NMR spectrum in the hydride region exhibits a well-resolved septet at −13.32 ppm [4 H; J(HP) = 17.0 Hz] also at the lowest temperature attained, and the $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at −19.64 ppm. In line with the observed fluxionality, the ^1H NMR spectrum shows a single resonance for the methylene protons in the backbone of the triphos ligand. The nonrigidity of **15** in solution cannot be explained uniquely by the terminal–bridge hydride exchange. Most likely, a cis–trans isomerization like that observed for **4** occurs. A combination of the two dynamic processes well accounts for the magnetic equivalence of both phosphorus and hydrogen atoms.

Discussion

Reductive Elimination of C–H and H–H Bonds from *cis*-Dihydride Alkyl and *cis*-Dihydride Ethylene Complexes. Due to the facile reductive elimination of either alkane or dihydrogen, relatively few alkyldihydridometal complexes have been isolated and properly characterized. An iridium complex, [Ir(H)$_2$(C$_2$H$_5$)(CO)(dppe)], has been recently prepared by Deutsch and Eisenberg and used to evaluate the relative tendency for H–H and C–H elimination.[14] Both reductive paths occur, but the elimination of H_2 was found to be thermodynamically favored over alkane elimination [$\Delta G^*(298)$ = 16.1 vs 23.4 kcal mol^{-1}]. Due to the facial disposition of the hydrides and alkyl ligands, complexes of the type [(triphos)Ir(H)$_2$R] [R = Et (**11**), Pr (**12**)] appear as appropriately designed to study the relative tendency for RH or H_2 elimination. In contrast to what observed by Deutsch and Eisenberg but in line with the literature data, we have found that alkane elimination is the prevailing reaction path for our complexes. As an example, **11** reacts with CO at 90 °C yielding the known hydride [(triphos)IrH(CO)] and ethane but not the carbonyl [(triphos)Ir(C$_2$H$_5$)(CO)], which is expected to be quite stable.[2b,p,5] However, as an anticipation of a future communication, we wish to report that ethane but not dihydrogen can be eliminated from **11** also by thermolysis in appropriate solvents. As a result, the unsaturated [(triphos)IrH] moiety forms, which can oxidatively cleave C–H bonds of any type [sp^3, sp^2(olefinic), sp^2(aromatic), sp] to give stable *cis*-dihydride σ-organyl derivatives.[15]

At a first glance, the different behavior of the related complexes [Ir(H)$_2$(C$_2$H$_5$)(CO)(dppe)] and [(triphos)Ir(H)$_2$(C$_2$H$_5$)] (**11**) may appear puzzling. But it is not. Eisenberg's compound differs from **11** in having a carbonyl in place of phosphorus and, therefore, is expected to have a minor electron density at the metal center. When the two complexes are forced to undergo a reductive elimination, they will reasonably get rid of the couple of ligands whose departure less destabilizes the residual Ir(I) fragment. According to this interpretation, it makes sense to have found that the dppe complex, less electron-rich than the triphos one, preferentially eliminates H_2 (maintaining the more donating ethyl ligand) whereas **11** selectively eliminates ethane.

The very low tendency for H_2 elimination shown by the present family of *cis*-dihydride metal complexes is confirmed by the reaction of **5** with CO, C_2H_4, or DMAD. All of these reagents selectively promote hydride migration from metal to ethylene and then alkane elimination. Only when no competitive reductive elimination reaction is available as in the carbonyl **8** can H_2 be eliminated.

The alternative displacement of ethylene from **5** may occur but is just a secondary process (see the two-step reaction with CO).

The easy hydride-migration path observed for the reaction of **5** with mono- or dihapto ligands is certainly favored by the electrophilic character of the ethylene ligand that can easily add nucleophiles (see next paragraph).

Nucleophilic Additions to the Ethylene Ligand in [(triphos)Ir(H)$_2$(C$_2$H$_4$)]BPh$_4$. The results presented in this paper on nucleophilic addition to the ethylene ligand in **5** provide an empirical correlation of reactivity with some readily obtainable experimental observables.

Four η^2-C_2H_4 complexes have been investigated; three of them, namely **1–3**, are neutral and quite rigid in solution on the NMR time scale. The coordinated double bond does not add either neutral or negatively charged nucleophiles such as PEt_3, NEt_3, H^-, CH_3^-, CN^-, and OR^-. The fourth complex, **5**, bears a positive charge and undergoes in solution two fluxional processes with different activation energies. Complex **5** readily reacts with nucleophiles to give either the corresponding σ-alkyl complexes (nucleophile = PEt_3, CH_3^-, H^-) or products derived from the addition of the nucleophile to ethylene (NEt_3). Depending on the nucleophile, the simple deprotonation reaction of **5** to give **2** competes and, in some cases (e.g. with CN^- and OMe^-), prevails over nucleophile addition.

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(14) Deutsch, P. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 714.

(15) Bianchini, C.; Meli, A. Manuscript in preparation.

The charge of the metal complex is certainly a driving force for a nucleophilic addition but is not the only one, as a decisive role is played also by the nature of the metal–olefin bond.[16] In particular, since π-back-bonding from metal to C_2H_4 makes the olefin less electrophilic, it is reasonable to have found that the neutral Ir(I) complexes **1–3** do not undergo nucleophilic attack.

Iridium–Triphos Complexes as Model Compounds for Mechanistic Studies of Homogeneous Hydrogenation and Hydroformylation Reactions. Comparison with Rhodium–Triphos Complexes. One of the major advantages of the use of tripodal polyphosphine ligands in organometallic reactions is the higher selectivity as compared to related reactions with monodentate phosphines. The selectivity provided by tripodal polyphosphine metal complexes is essentially due to the rigid control that such ligands exert on the stereochemistry and stoichiometry of the resulting complexes.[2] Within this context, a particular role is being played by triphos, whose complexes exhibiting as many as three free facial coordination sites can be used to promote a variety of catalytic reactions including hydrogenation and hydroformylation of alkenes. Rhodium is much better than iridium to accomplish such reactions, and actually, the complexes [(triphos)RhH-(C_2H_4)] and [(triphos)Rh(DMAD)]BPh_4 are good catalysts precursors for homogeneous hydrogenation and hydroformylation reactions of alkenes and alkynes.[2b] The use of triphos in place of three comparable monophosphine ligands allowed us to intercept some reaction intermediates such as the alkyl carbonyl [(triphos)Rh(CO)(R)], the carbonyl acyl [(triphos)Rh(CO)(COR)] (R = Me, Et, Ph) or the dihydride carbonyl [(triphos)Rh$(H)_2$(CO)]BPh_4. By replacing rhodium with iridium, we now provide direct experimental evidence for the existence of other species that were hypothesized to participate to rhodium-assisted catalysis cycles. These are the dihydride alkyl **11**, the ethylene dihydride **5**, and the hydride alkyl carbonyl **7**.

From a perusal of Scheme II, one could readily infer that, unlike the rhodium analogues, neither **2** nor **5** are able to function as catalyst precursors for hydroformylation reactions of alkenes, and indeed, they are not. In fact, CO does not react at all with **2** whereas the reaction with **5** gives carbonyl complexes but not σ-acyl compounds via CO insertion across Ir–C(alkyl) bonds.

While thermodynamic constraints, notably those associated with the strength of the Ir–C bond, are certainly important in limiting the reactivity of iridium complexes,[17,18] we think that a more important role to account for the major kinetic inertness of iridium compounds versus rhodium analogues is played by the lower tendency of iridium to decoordinate a phosphine arm of triphos. As recently shown by Caulton[2p,q] and us,[18] the chelate effect due to the polydentate structure of triphos enhances the thermodynamic stability of metal–phosphorus bonds. Nevertheless such bonds may be kinetically labile on the preparative time scale, thus providing free coordination sites at the metal. This process, known as "arm dissociation mechanism" or "arm-off" mechanism, frequently occurs in organometallic reactions assisted by Rh–triphos complexes but has never been observed for iridium. An enlightening example of the major kinetic stability of iridium complexes is provided by the reactions of [(PP_3)RhMe] and [(PP_3)IrMe] with 1 atm of CO [PP_3 = $P(CH_2CH_2PPh_2)_3$].[18] The Rh complex readily undergoes the insertion of CO across the metal–carbon bond to give the σ-aryl [(PP_3)Rh(COMe)] whereas the iridium complex remains quite stable. Monitoring the reaction between CO and the rhodium complex by IR and ^{31}P NMR spectroscopy allows one to detect the formation of a kinetic σ-methyl carbonyl intermediate with a free phosphine arm, namely [{$Ph_2PCH_2CH_2P(CH_2CH_2PPh_2)_2$}Rh(CO)(Me)].

Comparison with Iridium–Monophosphine Complexes. The dihydride η^2-ethylene complex [Ir$(H)_2$-(C_2H_4)(PMe_2Ph)$_3$]BF_4 has been recently found to be a catalyst precursor for an interesting case of ethylene hydrogenation.[12] The catalysis cycle proposed by Caulton et al. implies the intermediacy of two species, namely the hydride alkyl complex [Ir(H)(C_2H_5)(PMe_2Ph)$_3$]$^+$ and its ethylene adduct [Ir(H)(C_2H_5)(C_2H_4)(PMe_2Ph)$_3$]$^+$, of which no direct experimental evidence was provided. Our results with triphos complexes not only are nicely consistent with those of PMe_2Ph compounds (in particular we have been able to confirm that the reduction of ethylene is "ethylene promoted") but also include the interception and the spectroscopic characterization of unforeseen species such as the hydride alkyl complex in DMF and its adduct with CO.

Miscellaneous Considerations. In light of our experimental evidence, the intramolecular chemistry of the dihydride alkyl compound **9**, **11**, and **12**, of the ethylene ethyl complex **3**, and of the hydride ethyl carbonyl complex **7** has been exclusively discussed in terms of a competition between reductive elimination of C–H and H–H bonds. However, in principle, all of these compounds might undergo a third intramolecular reaction of the "dissociative" type: a β-H elimination that converts an alkyl ligand into hydride and alkene moieties. It is therefore reasonable to wonder why no alkyl complex of the many described in this paper undergoes such a reaction, particularly as one recalls that the rhodium complex [(triphos)Rh(C_2H_5)(C_2H_4)] is not stable in solution where it rapidly and reversibly converts into the hydride [(triphos)RhH(C_2H_4)].[2b] In our opinion, the reasons for the stability of the present alkyl complexes must be sought again in the unusual strength of the iridium–phosphorus(triphos) bond. Such strong bonds virtually blocks one of the major downhill paths for a β-H elimination, namely the availability of a free coordination site at the metal. In this respect, it is worth mentioning that the only β-H elimination reaction occurring at the (triphos)Ir fragment involves a coordinatively unsaturated species, namely the iridium(III) hydride migration of **5** [(triphos)Ir(H)(C_2H_5)]$^+$ (Scheme III).

As a final comment, we wish to draw the reader's attention to the ^1H NMR spectra of the complexes containing σ-alkyl ligands (**3**, **9**, and **11**). For all of these compounds, selective decoupling experiments and computer simulation of the resonances of the alkyl hydrogens show appreciable ^4J(HP) long-range coupling of the methyl (or β-CH_2) hydrogens to the trans phosphorus nucleus.[14] The particular cleanliness of the spectra has allowed us to accurately evaluate such couplings for **3** ($^4J(H_AP)$ = 6.8 Hz, $^3J(H_BP)$ = 8.7 Hz) and **11** ($^4J(H_AP)$ = 7.1 Hz, $^3J(H_BP)$ = 5.6 Hz). From a perusal of these data, one is struck by the higher value of ^4J(HP) in **11** as compared to ^3J(HP).

Concluding Remarks

With the combination of a tripodal polyphosphine ligand such as triphos and of a third-row transition metal such as iridium, we have synthesized an unforeseen family of organometallic compounds, most of which cannot be isolated by using either conventional ligands or first- and second-row metals.

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The variety of mutual arrangements and bonding modes of the *participative* coligands (hydride, ethylene, alkyls and heteroalkyls, alkynes, and carbon monoxide) and the selective *fac* disposition of the phosphorus donors around iridium have made available a number of unusually stable model compounds to study organometallic reactions. These include either fundamental processes such as C–H and H–H reductive elimination/oxidative addition and β-H elimination or olefin-based homogeneous reactions such as hydroformylation, hydrogenation, isomerization, amination, and related nucleophilic additions.

Surveying the results presented in the paper, one may draw, inter alia, the following conclusions. (i) The reductive elimination of alkane from iridium dihydride alkyl complexes can be made prevailing over dihydrogen elimination by increasing the electron density at the metal. (ii) The charge of the complex is an experimental observable for predicting a nucleophilic addition to the double bond. (iii) Creation of a free coordination site at the metal is a necessary requisite for the occurrence of a β-H elimination step. (iv) Tripodal polyphosphine ligands have great potential in homogeneous catalysis due to their control on the stereochemistry of the complexes and the possibility of providing free coordination sites by unfastening a phosphine arm. The latter property much depends on the nature of the metal center.

Experimental Section

General Information. All reactions and manipulations were routinely performed under nitrogen, except where otherwise stated, by using Schlenk-line techniques. Reagent grade chemicals were used in the preparations of the complexes. THF and CH_2Cl_2 were purified by distillation from $LiAlH_4$ and P_2O_5 under nitrogen, respectively. All the other solvents were reagent grade and were used as received. Literature methods were used for the preparation of triphos[19] and $[Ir(COE)_2Cl]_2$.[20] The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 299.945, 121.421, and 75.429 MHz, respectively, on a Varian VXR 300 spectrometer. Peak positions are relative to tetramethylsilane as an external reference (proton spectra) or to external 85% H_3PO_4, with downfield values reported as positive (phosphorus spectra) or are calibrated against the solvent (carbon spectra). Simulation of NMR spectra was achieved by using an updated version of the DAVINS program.[21] The initial choices of shifts and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions of better than 0.3 Hz. Conductivities were measured with a 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.

[(triphos)IrCl(C_2H_4)] (1). Solid $[Ir(COE)_2Cl]_2$ (0.90 g, 1 mmol) was added to a solution of triphos (1.25 g, 2 mmol) in THF (100 mL) under ethylene at −10 °C. After 1 h the resulting orange solution was allowed to reach room temperature and eluted with ethanol (100 mL) under nitrogen. On slow concentration lemon yellow crystals precipitated, which were collected by filtration and washed with ethanol and *n*-pentane; yield 85%. Anal. Calcd for $C_{43}H_{43}ClIrP_3$: C, 58.66; H, 4.92; Ir, 21.83. Found: C, 58.43; H, 4.88; Ir, 21.49. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 26.2 (br t, $^2J(CP_M)$ = 15 Hz, C_2H_4), 33.1 (pseudo-td, $^1J(CP_M) = {}^3J(CP_{M'})$ = 12 Hz, $^3J(CP_A)$ = 4 Hz, 2 CH_2P), 34.4 (dt, $^1J(CP_A)$ = 28 Hz, $^3J(CP_M)$ = 4 Hz, CH_2P), 39.8 (m, Me and quaternary C).

[(triphos)IrH(C_2H_4)] (2). $LiHBEt_3$ (1 M THF, 5 mL, 5 mmol) was syringed into a stirred suspension of **1** (1 g, 1.14 mmol) in THF (60 mL) under nitrogen at room temperature. After the starting solid dissolved (ca. 1 h) ethanol (50 mL) was added to the resulting pale yellow solution. On concentration under a stream of nitrogen off-white crystals precipitated in ca. 90% yield. They were filtered off and washed with ethanol and *n*-pentane. Alternatively, **2** was obtained by using $NaBH_4$ or $PPNBH_4$ instead of $LiHBEt_3$. Anal. Calcd for $C_{43}H_{44}IrP_3$: C, 61.05; H, 5.24; Ir, 22.72. Found: C, 61.83; H, 5.18; Ir, 22.58. IR: 2065 cm^{-1}, ν(Ir–H). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.39 (q, J(HP) = 2.7 Hz, 3 H, Me), 2.16 (d, $J(HP_A)$ = 8.3 Hz, 2 H, CH_2P), 2.30 (m, 4 H, CH_2P). $^{13}C\{^1H\}$ NMR (THF-d_8, 20 °C): δ 11.6 (td, $^2J(CP_M)$ = 12 Hz, $^2J(CP_A)$ = 3 Hz, ^1J(CH) = 151 Hz (gate-decoupling experiment), C_2H_4), 37.1 (pseudo-td, $^1J(CP_M) = {}^3J(CP_{M'})$ = 14 Hz, $^3J(CP_A)$ = 5 Hz, 2 CH_2P), 38.8 (dt, $^1J(CP_A)$ = 26 Hz, $^3J(CP_M)$ = 5 Hz, CH_2P), 43.3 (q, ^3J(CP) = 10 Hz, Me), 45.6 (q, ^2J(CP) = 6 Hz, quaternary C) (assigned by a ^{13}C NMR DEPT experiment).

[(triphos)Ir(C_2H_5)(C_2H_4)] (3). A stirred suspension of **1** (0.30 g, 0.34 mmol) in THF (30 mL) under nitrogen at room temperature was treated with EtMgBr (2 M THF, 1.5 mL, 3 mmol). Within 30 min the starting product dissolved, producing a yellow solution. Elution with ethanol and partial evaporation of the solvent gave off-white crystals, which were filtered off and washed with ethanol and *n*-pentane. The crude product may contain from 5 to 10% of **2** depending on the care used to dry THF. Repeated crystallizations from THF/ethanol gave analytically pure **3** in 70% yield. Anal. Calcd for $C_{45}H_{48}IrP_3$: C, 61.84; H, 5.54; Ir, 21.99. Found: C, 61.63; H, 5.48; Ir, 21.78. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.47 (q, J(HP) = 2.6 Hz, 3 H, Me), 2.18 (d $J(HP_A)$ = 8.8 Hz, 2 H, CH_2P), 2.28 (m, 2 H, CH_2P), 2.72 (m, J(HH) = 15.3 Hz, 2 H, CH_2P).

[(triphos)IrH(μ-Cl)$_2$HIr(triphos)](BPh$_4$)$_2$ (4). A stoichiometric amount of HSO_3CF_3 (30 μL, 0.34 mmol) (or HBF_4) was syringed into a stirred solution of **1** (0.30 g, 0.34 mmol) in CH_2Cl_2 (30 mL) under nitrogen at room temperature. Immediately the solution turned from pale yellow to colorless. After addition of 20 mL of ethanol and concentration under a slow stream of nitrogen off-white crystals formed. They were filtered off and washed with ethanol and *n*-pentane; yield 85%. ^{31}P and ^1H NMR spectroscopy showed the product to be a 7:3 mixture of two isomers, namely, *trans*-**4** and *cis*-**4**. ^1H NMR in CD_2Cl_2 evidenced C_2H_4 evolution. Anal. Calcd for $C_{130}H_{120}B_2Cl_2Ir_2P_6$: C, 66.58; H, 5.16; Ir, 16.39. Found: C, 66.38; H, 5.11; Ir, 16.24. Λ_M = 106 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: 2110 cm^{-1}, ν(Ir–H).

[(triphos)Ir(H)$_2$(C_2H_4)]BPh$_4$ (5). To a stirred and deaerated suspension of **2** (0.85 g, 1 mmol) in THF (40 mL) at room temperature was added at 10% excess of HSO_3CF_3 (97 μL, 1.1 mmol). Within 30 min the starting solid dissolved, producing a colorless solution. After addition of $NaBPh_4$ (0.51 g, 1.5 mmol) in ethanol (30 mL) and concentration under a slow stream of nitrogen off-white crystals precipitated, which were collected by filtration and washed with ethanol and *n*-pentane; yield 90%. Anal. Calcd for $C_{67}H_{65}BIrP_3$: C, 69.01; H, 5.62; Ir, 16.48. Found: C, 68.98; H, 5.57; Ir, 16.33. Λ_M = 43 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: 2110–2062 cm^{-1}, ν(Ir–H). ^1H NMR (CD_2Cl_2, −40 °C): δ 1.75 (s, 3 H, Me), δ_A 2.82, δ_B 2.57, δ_C 2.48 (6 H, CH_2P) (AA′BB′C_2 part of an AA′BB′C_2XX′Y spin system computed by using a simplified ABCX pattern with the following magnetic parameters: $J(H_AH_B)$ = 16.1 Hz, $J(H_AP_X)$ = 7.8 Hz, $J(H_BP_X)$ = 9.3 Hz, $J(H_CP_Y)$ = 10.2 Hz). At 20 °C the methyl hydrogens appear as a quartet with ^4J(HP) = 3.0 Hz.

Reaction of 5 with CO. A steady stream of carbon monoxide was bubbled through a solution of **5** (0.20 g, 0.17 mmol) in THF (20 mL) at room temperature. Depending on the reaction time different products were obtained. For more than 6 h, the product obtained was the known dicarbonyl [(triphos)Ir(CO)$_2$]BPh$_4$ (**6**); yield 90%. Λ_M = 47 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: 2053–1954 cm^{-1}, ν(CO). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.59 (q, J(HP) = 3.3 Hz, 3 H, Me), 2.52 (m, 6 H, CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −21.43. When CO was bubbled for times ranging from 2 to 5 h, the solid obtained was shown to be a mixture of **6**, [(triphos)IrH(CO)(C_2H_5)]BPh$_4$ (**7**), and the known [(triphos)Ir(H)$_2$(CO)]BPh$_4$ (**8**). For reaction times shorter than 2 h, some unreacted **5** was found. After 30 min ca. 50% of **5** was transformed essentially into **7**. Following the reaction between **5** and CO at room tem-

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perature in a sealed NMR tube (saturated with CO at −20 °C) allowed us to detect the predominant evolution of ethane together with minor amounts of ethylene and hydrogen. Ethylene evolves first and then remains practically constant, while the concentration of ethane progressively increases up to a concentration that roughly correspond to that of **6**.

[(triphos)Ir(H)$_2$(CH$_2$CH$_2$PEt$_3$)]BPh$_4$ (9). A mixture of **5** (0.20 g, 0.17 mmol) and PEt_3 (30 μL, 0.20 mmol) in THF (20 mL) was stirred at room temperature for 1 h. On addition of ethanol off-white crystals precipitated in 70% yield. Anal. Calcd for $C_{73}H_{80}BIrP_4$: C, 68.27; H, 6.28; Ir, 14.96; P, 9.65. Found: C, 68.03; H, 6.13; Ir, 14.78; P, 9.51. Λ_M = 43 cm^2 Ω^{-1} mol^{-1}. IR: 2036–2017 cm^{-1}, ν(Ir–H). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.58 (q, J(HP) = 2.8 Hz, 3 H, Me), 2.22 (d, $J(HP_A)$ = 8.9 Hz, 2 H, CH_2P), 2.43 (J(HH) = 15.6 Hz, $J(HP_M)$ = 9.0 Hz, 2 H, CH_2P), 2.56 ($J(HP_M)$ = 7.5 Hz, 2 H, CH_2P).

Reaction of 5 with NEt$_3$. A solution of **5** (0.20 g, 0.17 mmol) was treated with a 10-fold excess of freshly distilled NEt_3 at room temperature. After 1 h the solution was concentrated to dryness under reduced pressure and washed with *n*-pentane. ^{31}P NMR spectra showed the solid product to be a 1:4 mixture of **2** and [(triphos)Ir(H)$_3$] (**10**). Repeated recrystallizations from THF/ethanol gave **10** in analytically pure form. Thin-layer chromatograph (CH_2Cl_2 as eluent) was used to separate two non-phosphorus-containing products, namely, $[HNEt_3]BPh_4$ and $[C_2H_3NEt_3]BPh_4$, which were authenticated by comparison with authentic specimens.

Reaction of 5 with CN$^-$ or OMe$^-$. When solutions of **5** in THF were treated with KCN or NaOMe in methanol, only the deprotonation product **2** was quantitatively obtained.

[(triphos)Ir(C$_2$H$_5$)(H)$_2$] (11). To a stirred suspension of **5** (1.17 g, 1 mmol) in THF (60 mL) at room temperature was added $LiHBEt_3$ (1 M THF, 10 mL, 10 mmol). After the solid dissolved (ca. 30 min) ethanol (30 mL) was added. On concentration, off-white crystals precipitated in 85–95% yield. Alternatively **11** was obtained by using $NaBH_4$ instead of $LiHBEt_3$. Anal. Calcd for $C_{43}H_{46}IrP_3$: C, 60.91; H, 5.47; Ir, 22.67. Found: C, 60.88; H, 5.43; Ir, 22.38. IR: 2050–2026 cm^{-1}, ν(Ir–H). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.48 (q, J(HP) = 2.8 Hz, 3 H, Me), 2.14 (d, $J(HP_A)$ = 8.2 Hz, 2 H, CH_2P), 2.30 (J(HH) = 15.4 Hz, $J(HP_M)$ = 7.9 Hz, 2 H, CH_2P), 2.48 ($J(HP_M)$ = 7.2 Hz, 2 H, CH_2P).

[(triphos)Ir(C$_3$H$_7$)(H)$_2$] (12). A 1:1 mixture of **5** (0.2 g, 0.17 mmol) and MeLi (1.6 M diethyl ether) in THF (60 mL) was stirred at room temperature for 1 h. Elution with ethanol (30 mL) and concentration gave a crystalline precipitate, which on the basis of NMR spectroscopy was characterized as a mixture of **2** and **12** in ca. 4:1 ratio. Compound **12** was obtained analytically pure by repeated recrystallizations from THF/ethanol. Anal. Calcd for $C_{44}H_{48}IrP_3$: C, 61.31; H, 5.61; Ir, 22.30. Found: C, 61.28; H, 5.53; Ir, 22.15. IR: 2053–2029 cm^{-1}, ν(Ir–H). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.52 (q, J(HP) = 2.8 Hz, 3 H, Me), 2.18 (d, $J(HP_A)$ = 8.1 Hz, 2 H, CH_2P), 2.36 (J(HH) = 15.4 Hz, $J(HP_M)$ = 7.8 Hz, 2 H, CH_2P), 2.49 ($J(HP_M)$ = 7.2 Hz, 2 H, CH_2P).

[(triphos)Ir(C$_2$H$_4$)$_2$]BPh$_4$ (13). Compound **5** (0.2 g, 0.17 mmol) was dissolved into a C_2H_4-saturated THF solution (30 mL) at room temperature. After 1 h, addition of *n*-heptane (100 mL) led to the precipitation of a white solid, which was collected by filtration and washed with *n*-pentane under ethylene. Anal. Calcd for $C_{69}H_{67}BIrP_3$: C, 69.51; H, 5.66; Ir, 16.12. Found: C, 69.38; H, 5.63; Ir, 16.00. Λ_M = 46 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.63 (q, J(HP) = 3.1 Hz, 3 H, Me), 2.18 (s, 8 H, C_2H_4), 2.65 (m, J(HP) = 5.8 Hz, 6 H, CH_2P).

[(triphos)Ir(π-DMAD)]BPh$_4$ (14). A solution of **5** (0.20 g, 0.17 mmol) and dimethyl acetylenedicarboxylate (0.05 g, 0.34 mmol) in CH_2Cl_2 (20 mL) was stirred under nitrogen at room temperature for 1 h. On addition of ethanol (30 mL) and partial evaporation of the solvent orange crystals precipitated in 90% yield. Anal. Calcd for $C_{71}H_{65}BIrO_4P_3$: C, 66.71; H, 5.13; Ir, 15.04. Found: C, 66.73; H, 5.09; Ir, 14.98. Λ_M = 46 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.75 (q, J(HP) = 3.2 Hz, 3 H, Me), 2.63 (m, J(HP) = 9.1 Hz, 6 H, CH_2P), 3.98 (s, 6 H, OMe). In a separate experiment a sample of **5** (0.05 g, 0.04 mmmol) and a 2-fold excess of DMAD (ca. 12 μL) were dissolved at −30 °C in a minimum amount of CD_2Cl_2 and the solutions were transferred under nitrogen to an NMR tube, which was flame-sealed and then allowed to stand for 1 h at room temperature. ^{1}H NMR showed evolution of C_2H_6 (δ 0.86) and quantitative conversion of **5** into **14**.

[(triphos)IrH(μ-H)$_2$HIr(triphos)](BPh$_4$)$_2$ (15). A solution of **5** (0.20 g, 0.17 mmol) in THF (40 mL) was heated at 60 °C under hydrogen for 2 h. On addition of ethanol (30 mL) and partial evaporation of the solvent off-white crystals precipitated in 70% yield. Anal. Calcd for $C_{130}H_{122}B_2Ir_2P_6$: C, 68.54; H, 5.40; Ir, 16.87. Found: C, 68.47; H, 5.39; Ir, 16.68. Λ_M = 110 cm^2 Ω^{-1} mol^{-1}. IR: 2127–2104, ν(Ir–H). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.57 (q, J(HP) = 2.9 Hz, 6 H, Me), 2.45 (m, J(HP) = 6.2 Hz, 12 H, CH_2P).

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