Interaction of Diphenylacetylene and other Acetylenes with Hydridonitrosyltris(triphenylphosphine)ruthenium, Carbonylhydridotris(triphenylphosphine)-rhodium and -iridium †

By **Roberto A. Sanchez-Delgado** and **Geoffrey Wilkinson,*** Imperial College of Science and Technology, London SW7 2AY

Hydridonitrosyltris(triphenylphosphine), RuH(NO)(PPh$_3$)$_3$, and an excess of diphenylacetylene react slowly in refluxing toluene to form the dimer, 1-benzylidene-2,3-diphenylindene, as the only organic product. No ruthenium complex intermediates could be isolated, but on the basis of n.m.r. studies a mechanism is proposed for the reaction.

The reactions of diphenylacetylene with the carbonyl complexes, MH(CO)(PPh$_3$)$_3$ (M = Rh and Ir) which are isoelectronic and isostructural with RuH(NO)(PPh$_3$)$_3$, have also been studied and in these cases the metal complex species can be characterised by analysis and i.r. and ^{1}H and ^{31}P n.m.r. spectroscopy.

A NUMBER of transition-metal complexes initiate the polymerisation of acetylenes to low molecular-weight linear and cyclic products; the nature of the organic products obtained in each case and the mechanism of their formation are very dependent on the reaction conditions and on the electronic and steric characteristics of both the acetylene and the transition-metal catalyst. It is now clear that π-bonded acetylenic,

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† No reprints available.

σ-bonded alkenylic, and metallocyclic intermediates are involved in these reactions.[1-8]

Although several stable complexes resulting from reactions of ruthenium complexes with disubstituted acetylenes have been characterised and the mechanism of their formation elucidated,[9-14] there has been only one detailed report on the oligomerisation of monosubstituted acetylenes with ruthenium complexes.[15] We now report a novel dimerisation of diphenylacetylene to 1-benzylidene-2,3-diphenylindene by use of hydridonitrosyltris(triphenylphosphine)ruthenium, and propose a mechanism for the reaction on the basis of ^{1}H n.m.r. evidence.

Since all attempts to isolate reaction intermediates have proved unsuccessful, diphenylacetylene was treated with the isoelectronic compounds $MH(CO)(PPh_3)_3$ (M = Rh or Ir) under similar conditions; the organic products of these reactions contain mixtures of low molecular-weight oligomers and stable intermediates have been isolated and characterised.

Monosubstituted acetylenes and hexafluorobut-2-yne are polymerised by $RuH(NO)(PPh_3)_3$ and under certain conditions a phenylacetylene trimer can be isolated.

RESULTS AND DISCUSSION

Reactions of $RuH(NO)(PPh_3)_3$.—*The dimerisation of diphenylacetylene.* Hydridonitrosyltris(triphenylphosphine)ruthenium[16] reacts with an excess of diphenylacetylene on prolonged refluxing in toluene to yield 1-benzylidene-2,3-diphenylindene[17] (I) as the only organic product, plus a complicated mixture of ruthenium compounds. Compound (I) was characterised by elemental analysis, molecular-weight determination (see Table 1), and *X*-ray diffraction.[18] Besides the molecular ion at *m/e* 356 the mass spectrum shows ions at *m/e* 279 and 202 corresponding to consecutive loss of two phenyl groups; the ^{13}C n.m.r. spectrum is very complicated and we have been unable to interpret it satisfactorily.

TABLE 1

Data for organic compounds

Compound	M.p. (θ_c/°C)	^{1}H n.m.r. (τ)	λ_{max}/nm^{-1} (ethanol)	C [a]	H [a]	*M* [b]
$C_{28}H_{20}$ (I)	197	2.96 (m)	303	94.4 (94.4)	5.6 (5.6)	356 (356)
$C_{24}H_{18}$ (II)	188—190	3.05 (m, 15 H) 4.05 (m, 3 H)	296	93.8 (94.1)	5.7 (5.9)	306 (306)

[a] Found (calcd.) %. [b] Mass spectrometrically.

Attempts to separate the ruthenium-containing mixtures by crystallisation or chromatography have proved unsuccessful. Stoicheiometric reactions were carried out in various solvents under similar conditions in the hope of isolating some reaction intermediates but again no complexes could be properly characterised. Thus we have attempted to elucidate the mechanism of dimerisation by n.m.r. techniques.

The proposed mechanism is shown in Scheme 1. The first step of the reaction is probably co-ordination of the acetylene to the ruthenium hydride with dissociation of a phosphine ligand to give complex (A), followed by a hydride transfer to form a σ-alkenyl intermediate (B); reaction with a second molecule of diphenylacetylene would then give the bis-insertion product (C) which after rotation about a C–C bond undergoes hydride transfer from the dienyl ligand to the metal with concomitant ring closure to yield the dimer (I) and regenerate $RuH(NO)(PPh_3)_3$.

Two different paths for the formation of (C) are possible: the vinyl complex (B) may add a second molecule of diphenylacetylene to form the acetylene complex (D); insertion of the π-bonded acetylene into the metal–carbon σ-bond then yields complex (C) (Scheme 2). Isolation of related rhodium and iridium complexes (see below) are in accord with this proposal. Alternatively, addition of the second acetylene molecule may occur *via* a dipolar intermediate (E) with retention of the metal–carbon σ-bond as in Scheme 3; the latter has been shown to be operative in reactions of cyclopentadienylruthenium hydrides with other disubstituted acetylenes,[11-13] but with the evidence available it is impossible to determine the precise mode of addition in this case.

It is, however, reasonable to assume that the stereochemistry of the σ-alkenyl ligand is retained on going from (B) to (C); in order to arrive at the correct stereochemistry for (I), the initial hydride transfer from the

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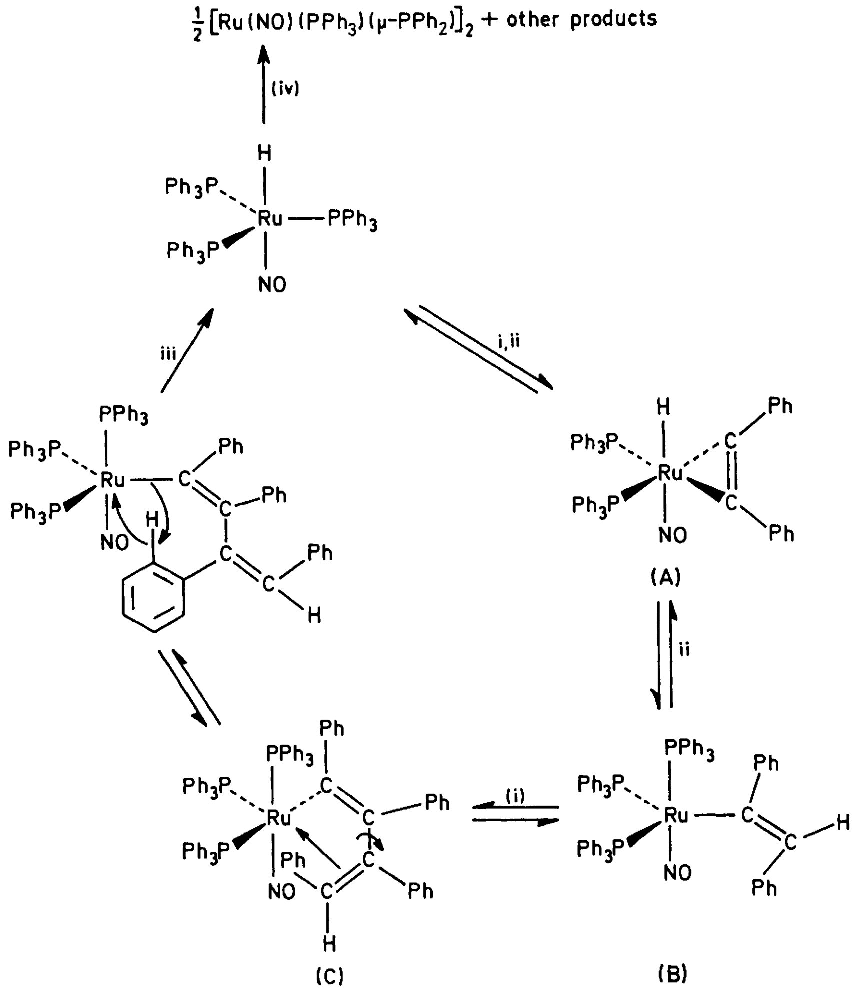
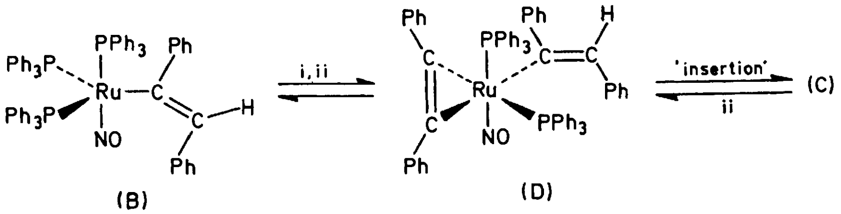
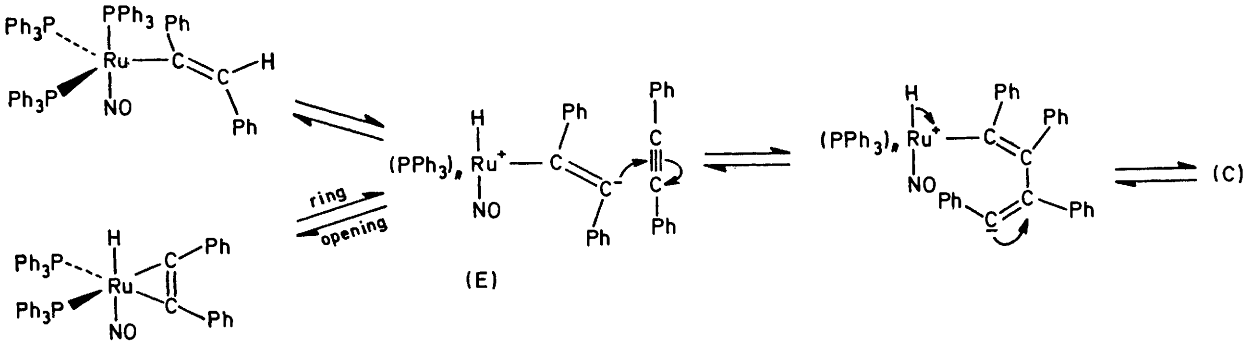


SCHEME 1 i, $+\mathrm{Ph_2C_2}$; ii, $-\mathrm{PPh_3}$; iii, −(I); iv, heat in solvent



SCHEME 2 i, $+\mathrm{Ph_2C_2}$; ii, $-\mathrm{PPh_3}$



SCHEME 3 $n = 2,3$

metal to the acetylene must be of the *trans*-type; it has been suggested that the stereochemical course of this type of transfer is governed by the steric bulk of the other ligands around the metal and of the substituents on the acetylene.[13]

N.m.r. experiments at room temperature support the proposed mechanism. In dideuteriodichloromethane the reaction can be followed by the decrease in intensity of the high-field line (τ 16.6) and the appearance of a signal at about τ 6.5 (corresponding to the vinylic proton in B) after *ca.* 40 h. With longer reaction times (*ca.* 5 days) the high-field line becomes undetectable, the signal at τ 6.5 decreases in intensity and a new signal is observed at about τ 8.5, assigned to the single proton of the dienyl ligand in (C). The spectrum of a sample of $RuH(NO)(PPh_3)_3$ in CD_2Cl_2 in absence of diphenylacetylene was unchanged after the same period of time thus showing that the disappearance of the high-field line is not due to H–D exchange with the solvent. In C_6D_6 the reaction is even slower and after 7 days at room temperature the high-field line is undetectable and signals at τ 6.2 and 8.8 are observed, the latter being the weakest.

Because of the generally weak and poorly resolved nature of the spectra no further evidence on the stereochemistry of the intermediates could be derived from these experiments; the chemical shifts, however, are in the same regions as those of related well-characterised complexes.[11-13]

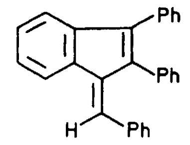
The yields of the organic dimer (I) do not suggest a catalytic reaction. The low yield is due, at least partly, to the formation of $\{Ru(NO)(PPh_3)(\mu\text{-}PPh_2)\}_2$ under the reaction conditions. This compound has been previously synthesised by thermolysis of $RuH(NO)(PPh_3)_3$ in decalin;[19] we have also identified this phosphido-bridged dimer as one of the products of thermolysis of $RuH(NO)(PPh_3)_3$ in toluene (in absence of diphenylacetylene), but other ruthenium nitrosyl-phosphine complexes which we have been unable to characterise are also produced in the reaction.

Reactions of $RuH(NO)(PPh_3)_3$ *with other acetylenes.* Phenylacetylene reacts with hydridonitrosyltris(triphenylphosphine)ruthenium in toluene at room temperature to yield a non-crystalline trimer (III); the mechanism of trimerisation probably involves formation of metal-acetylide complexes as in other well known systems,[20,21] but attempts to isolate reaction intermediates failed also in this case. Under reflux, orange gums are produced, presumably corresponding to higher polymers; hex-1-yne, prop-2-ynyl alcohol, propiolic acid, and hexafluorobut-2-yne all polymerise immediately upon contact with toluene solutions of $RuH(NO)(PPh_3)_3$ at and below room temperature to yield intractable oils and tars.

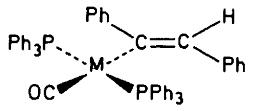
Reactions of $MH(CO)(PPh_3)_3$ $(M = Rh$ *or* $Ir)$ *with Diphenylacetylene.*—In order to obtain further evidence in support of the proposed mechanism of dimerisation of diphenylacetylene we have investigated its reactions with the complexes $MH(CO)(PPh_3)_3$ (M = Rh or Ir), which are isoelectronic with $RuH(NO)(PPh_3)_3$.

When stoicheiometric amounts of the metal hydride and the acetylene are refluxed in toluene for 2—4 h the solutions become darker and crystalline complexes (III) and (IV) can be isolated in high yield; analytical and spectroscopic data for these and other complexes are collected in Tables 2 and 3.

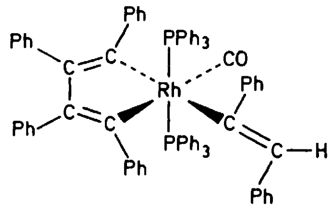
The rhodium compound (III) has been previously synthesised[22] by a slow (7 days) reaction in diethyl ether and characterised by C, H analysis, i.r. and ^1H n.m.r. spectroscopy, and cleavage with HCl to yield *trans*-stilbene; we have recorded the ^{31}P n.m.r. spectrum of this compound which consists of a doublet (J_{Rh-P} 160 Hz) in accord with the proposed structure having *trans*-phosphine ligands. The absence of coupling between the vinylic proton and the phosphorus nuclei (Table 3) may be taken as further evidence for a *trans*-configuration of the σ-alkenyl ligand.[12]



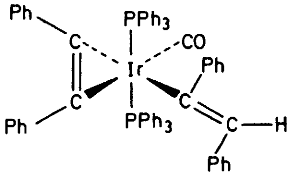
(I)



(III) M = Rh
(IV) M = Ir



(V)



(VI)

The iridium complex (IV) shows a single line in its ^{31}P n.m.r. spectrum; the i.r. spectrum is essentially identical to that of the rhodium analogue and on cleavage with dry HCl in benzene *trans*-stilbene is obtained in almost quantitative yield, along with a mixture of Vaska's compound, $IrCl(CO)(PPh_3)_2$, its dioxygen adduct $IrCl(CO)(O_2)(PPh_3)_2$, and $IrHCl_2(CO)_2(PPh_3)_2$, as identified by i.r. spectroscopy. In tetrahydrofuran with careful exclusion of air, cleavage with

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TABLE 2

Analytical data for rhodium and iridium complexes. Found (calcd.) %

Compound	Colour	M.p. (θ_c/°C)	C	H	P	*M* [a]
$Rh(CO)\{C(Ph){:}CHPh\}(PPh_3)_2$	Yellow-orange	138—141	73.2 (73.4)	5.8 (4.9)	7.5 (7.4)	762 (834)
$Ir(CO)\{C(Ph){:}CHPh\}(PPh_3)_2$	Yellow	166—171	66.3 (66.2)	4.4 (4.5)	6.7 (7.2)	962 (923)
$Rh(CO)\{C(Ph){:}CHPh\}\{C(Ph){:}C(Ph)\cdot C(Ph){:}C(Ph)\}(PPh_3)_2$	Brick-red	130—134	79.6 (79.7)	5.2 (5.1)	5.1 (5.2)	562 [b] (1 190)
$Ir(CO)\{C(Ph){:}CHPh\}\{C(Ph){:}C(Ph)\}(PPh_3)_2\cdot(PhCH_3)$ [c]	Yellow	174—178	72.5 (72.4)	5.3 (4.9)	5.6 (5.2)	— [c]

[a] Cryoscopically in benzene. [b] Low value due to dissociation of a phosphine ligand as shown by ^{31}P n.m.r. [c] Compound too insoluble for determination.

TABLE 3

Spectroscopic data for rhodium and iridium complexes

Complex	I.r. (cm^{-1})	^1H n.m.r. τ [a]	^{31}P n.m.r. [b]
$Rh(CO)\{C(Ph){:}CHPh\}(PPh_3)_2$	ν_{CO} 1 940 (s) $\nu_{C=C}$ 1 585 (w)	2.3 (m, 10 H) 3.1 (m, 30 H) 5.82 (s, 1 H)	+34.21 (d) J_{Rh-P} 160 Hz
$Ir(CO)\{C(Ph){:}CHPh\}(PPh_3)_2$	ν_{CO} 1 926 (s) $\nu_{C=C}$ 1 570 (w)	2.5 (m)	+24.51 (s)
$Rh(CO)\{C(Ph){:}CHPh\}\{C(Ph){:}C(Ph)\cdot C(Ph){:}C(Ph)\}(PPh_3)_2$	ν_{CO} 1 945 (s) $\nu_{C=C}$ 1 595 (m)	3.0 (m, 50 H) 5.81 (s, 1 H)	+46.10 (d) J_{Rh-P} 195 Hz
$Ir(CO)\{C(Ph){:}CHPh\}\{C(Ph){:}C(Ph)\}(PPh_3)_2$	ν_{CO} 1 949 (s) $\nu_{C=C}$ 1 580 (w)	2.8 (m)	+24.14 (s)

[a] In C_6D_6. [b] Spectra proton noise decoupled, measured in C_6D_6 at 25 °C. Shifts in p.p.m. to high frequencies of external 85% H_3PO_4.

HCl yields $IrHCl_2(CO)(PPh_3)_2$ quantitatively, but isolation of *trans*-stilbene is difficult due to the presence of high boiling, oily materials resulting from cleavage of the solvent.

Although this evidence confirms the structure of (IV) as proposed, the expected signal for the vinylic proton in the ^1H n.m.r. spectrum cannot be detected, presumably due to its being hidden beneath the phenyl pattern. The reaction of $IrH(CO)(PPh_3)_3$ with diphenylacetylene has been briefly mentioned [23] but only a dioxygen adduct of complex (IV) was isolated.

When the reactions are carried out in presence of an excess of diphenylacetylene, mixtures of organic compounds are obtained which are difficult to separate; the highest peak in the mass spectra of these mixtures corresponds to a diphenylacetylene trimer.

After chromatographing the reaction mixtures crystalline complexes (V) and (VI) are obtained in high yields; the metallocyclic structure (V) depicted for the rhodium complex is supported by analytical and spectroscopic data (Table 2 and 3); the i.r. spectrum shows, in addition to the metal carbonyl band at 1 945 cm^{-1}, a medium to strong band at 1 595 cm^{-1} assigned to a C=C stretch associated with the metallocycle; the ^1H n.m.r. spectrum consists of a complex multiplet centred at τ 3.0 (50 H) and a sharp singlet at τ 5.81 (1 H). The ^{31}P n.m.r. spectrum shows a doublet (J_{Rh-P} 195 Hz) in accord with a *trans*-arrangement of the phosphine ligands. A structure analogous to (V) has been proposed for an iridium complex with hexafluorobut-2-yne.[23]

For the iridium complex (VI) analytical data indicate the presence of only two acetylene molecules per iridium atom; the medium to strong band assigned to the C=C stretch of the metallocycle in (V) is absent and the ^1H n.m.r. spectrum shows only the complex multiplet at τ 2.8. A sharp singlet is observed in the ^{31}P n.m.r. spectrum and thus structure (VI) seems the most reasonable to accommodate the evidence. Similar iridium complexes with other disubstituted acetylenes have been previously characterised.[23,24]

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College and The Butterworth Microanalytical Consultancy Limited.

Apparatus.—^1H N.m.r. spectra were recorded on Perkin-Elmer R12A (60 MHz) and Varian HA100 (100 MHz) spectrometers and ^{31}P n.m.r. spectra on a Varian XL-100-12 spectrometer operating in the pulse and Fourier transform mode at 40.505 MHz. Perkin-Elmer model 257 and 457 spectrometers were used to record i.r. spectra. M.p.s were determined using an Electrothermal melting point apparatus in open capillary tubes.

Materials.—Ruthenium trichloride trihydrate, rhodium trichloride trihydrate, and iridium trichloride trihydrate were from Johnson Matthey; triphenylphosphine (Albright and Wilson Limited), diphenylacetylene (Emmanuel Ltd.), phenylacetylene (B.D.H.), prop-2-ynyl alcohol (B.D.H.), hex-1-yne (Koch–Light), and propiolic acid (Farcham Research Labs.) were used as obtained. $RuH(NO)(PPh_3)_3$,[16] $RhH(CO)(PPh_3)$,[25] and $IrH(CO)(PPh_3)_3$ [26] were prepared by published methods.

Procedure.—All manipulations were normally carried out in an atmosphere of oxygen-free nitrogen or argon using standard techniques.

All solvents were dried and degassed before use.

Reaction of $RuH(NO)(PPh_3)_3$ *with Diphenylacetylene.*—A mixture of $RuH(NO)(PPh_3)_3$ (0.9 g, 1 mmol) and diphenylacetylene (1.8 g, 10 mmol) in toluene (30 ml) was refluxed for 24 h with rapid stirring. The solvent was then evaporated to *ca.* 5 ml and the mixture chromatographed in a column (50 × 3 cm) packed with alumina using toluene as the eluant. The first yellow band was concentrated to low volume to yield orange crystals of 1-benzylidene-2,3-diphenylindene, which was recrystallised from a benzene–light petroleum mixture (50—60% yield based on Ru).

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The second, brown band was eluted with dichloromethane or methanol but no separation was achieved.

Reaction of RuH(NO)(PPh$_3$)$_3$ *with Phenylacetylene.*—The procedure was essentially the same as for diphenylacetylene except that the reaction was carried out at room temperature. After chromatography and recrystallisation from benzene–light petroleum mixtures, an orange powder of the phenylacetylene trimer (II) was obtained (60% yield based on Ru).

Reactions of RuH(NO)(PPh$_3$)$_3$ *with other Acetylenes.*—An excess of the acetylene was added to a vigorously stirred solution of RuH(NO)(PPh$_3$)$_3$ at room temperature or at -20 °C; polymerisation took place immediately giving dark oils, gums, or tars. Reactions with hexafluorobut-2-yne were carried out in sealed Carius tubes.

Thermolysis of RuH(NO)(PPh$_3$)$_3$.—Hydridonitrosyltris-(triphenylphosphine)ruthenium (1.0 g, 1 mmol) was refluxed in toluene (50 ml) for 3 days. The solvent was evaporated to dryness and the solid recrystallised from tetrahydrofuran–light petroleum mixtures to yield dark-brown microcrystals of {Ru(NO)(PPh$_3$)(μ-PPh$_2$)}$_2$ (10—15% yield). The product could not be obtained in an analytically pure form but it was identified by i.r. spectroscopy.[19] Other dark-brown solids were crystallised in an impure state; their i.r. spectra showed broad absorption between 1 600—1 800 cm^{-1} apart from triphenylphosphine bands.

Carbonyl(trans-1,2-*diphenylethenyl*)*bis*(*triphenylphosphine*)*rhodium*, Rh(CO){C(Ph):CHPh}(PPh$_3$)$_2$.—RhH(CO)-(PPh$_3$)$_3$ (1.8 g, 2 mmol) and diphenylacetylene (0.4 g, 2 mmol) were refluxed in toluene (40 ml) for 2—3 h after which the solution turned dark orange. Upon concentration of the solution and addition of light petroleum, yellow-orange crystals of the *complex* precipitated; these were collected under nitrogen, washed with light petroleum, and dried *in vacuo*. Further purification could be achieved by recrystallisation from dichloromethane–light petroleum mixtures (yield 75%).

Carbonyl(trans-1,2-*diphenylethenyl*)*bis*(*triphenylphosphine*)*iridium*, Ir(CO){C(Ph):CHPh}(PPh$_3$)$_2$.—Stoicheiometric amounts of IrH(CO)(PPh$_3$)$_3$ and diphenylacetylene were refluxed in toluene for 3—4 h after which the yellow solution had become orange. The solvent was removed under vacuum to yield an orange oil; addition of diethyl ether and rapid stirring caused precipitation of yellow crystals of the *complex* (yield 82%).

Reaction of RhH(CO)(PPh$_3$)$_3$ *with an Excess of Diphenylacetylene.*—A mixture of RhH(CO)(PPh$_3$)$_3$ and a ten-fold excess of diphenylacetylene was refluxed in toluene for 12 h to yield a brown-red solution. The mixture was chromatographed on alumina using toluene to elute first a red band and tetrahydrofuran to elute a second, brown band. The red solution was reduced to a dark-red oil which was dissolved in the minimum amount of diethyl ether; addition of light petroleum caused precipitation of brick-red microcrystals of complex (V) (80% yield). The brown solution contained mixtures of organic compounds the separation of which proved to be difficult.

Reaction of IrH(CO)(PPh$_3$)$_3$ *with an Excess of Diphenylacetylene.*—The procedure was identical as for the rhodium complex. Chromatography yielded a yellow toluene solution from which yellow crystals of complex (VI) were obtained on recrystallisation from toluene–light petroleum mixtures (yield 73%), and a brown solution eluted with tetrahydrofuran containing a mixture of organic compounds.

Cleavage of Ir(CO){C(Ph):CHPh}(PPh$_3$)$_2$ *with Hydrogen Chloride.*—Ir(CO){C(Ph):CHPh}(PPh$_3$)$_2$ (2.5 g, 2.5 mmol) was dissolved in benzene (200 ml) and dry gaseous HCl was bubbled through the solution for 12 h at room temperature; the solution at this stage was very pale yellow. The volume was reduced to *ca.* 5 ml, the resulting yellow solid was filtered off, and the solution evaporated to dryness to yield a yellow oily solid. Extraction and repeated recrystallisation from light petroleum yielded white needles of *trans*-stilbene (95% yield) identified by its m.p. and i.r. and ^{1}H n.m.r. spectra. IrCl(CO)(PPh$_3$)$_2$, IrHCl$_2$(CO)-(PPh$_3$)$_2$, and IrCl(CO)(O$_2$)(PPh$_3$)$_2$ were separated by fractional crystallisation and identified by i.r. spectroscopy.

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