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HYDROGEN TRANSFER REACTIONS PROMOTED BY IRIDIUM COMPLEXES

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Summary

Iridium (I) complexes have been found to promote hydrogen transfer from ethanol to diphenylacetylene to give *trans*-stilbene. A mechanism is proposed.

Introduction

Several complexes of the platinum group metals will abstract hydrogen from organic substrates or coordinated ligands to give stable hydrido complexes. Thus, *trans*-$[Pt(PEt_3)_2Cl_2]$ dehydrogenates ethanol and *trans*-$[Pt(PEt_3)_2HCl]$ is formed [1,2]. The ability to abstract hydrogen from alcoholic sodium alkoxide displayed by Rh^I phosphine complexes is influenced by the nature of the coordinated phosphine, and hence depends on the electron density on the metal [3].

Hydrogen abstraction from coordinated phosphines has been found to take place via internal oxidative addition in the case of $[Ir(PPh_3)_3Cl]$; a hydrogen atom *ortho* to phosphorus is abstracted from the ligand and migrates to the metal giving a hydrido complex through internal metallation [4]; this accounts for insertion of the iridium atom into a C—H bond of a phenyl group of a coordinated triphenylphosphine. Complexes of the type $[ML_4H]$ (M = Co^I and Rh^I), $[RuL_nHCl]$ ($n = 3, 4$), $[RuL_3(N_2)H_2]$ and $[CoL_3(N_2)H]$ [L = PPh_3, $P(OPh)_3$] undergo similar ligand-metal hydrogen transfers [5].

A closely related subject is that of hydrogen transfer from organic substrates to an acceptor catalysed by transition metal complexes. Thus, complexes of type $[RhL_3(CO)H]$ (L = tertiary phosphine) promote the transfer of hydrogen from alcohols to n-octene at 130° [3]. Iridium(I) complexes of the type *trans*-$[Ir(PPh_3)_2(CO)X]$ catalyse the conversion of 1,4-cyclohexadiene to benzene and cyclohexene [6].

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A satisfactory interpretation of these catalytic processes assumes reversible oxidative addition of a C—H bond to a coordinatively unsaturated metal complex. A different mechanism has been proposed, however, for catalytic *cis* hydrogenation of an alkyne [7], transfer of hydrogen from 2-propanol to α,β-unsaturated ketones [8], and reduction of ketones to alcohols [9] catalysed by Ir^{III} complexes of the type $[IrCl_2(Me_2SO)_3H]$. In these cases the formation of a metal—alkyl or vinyl intermediate is assumed to occur by insertion of the double or triple bond into the Ir—H bond of the catalyst. *cis*-Stilbene is obtained consistently [7] with diphenylacetylene as the hydrogen acceptor. *cis*-Alkenes are also the main products from the homogeneous hydrogenation of alkynes catalyzed by Ru^{II} [10] and Rh^{I} [11] complexes. Abstraction of hydrogen from allyl alcohol is catalysed by Ru^{II} complexes, the catalysis involving both inter- and intra-molecular processes [12].

This paper describes the reactions of $[Ir(PPh_3)_2H_3]$ with diphenylacetylene in ethanol, and the same reaction in benzene in the presence of molecular hydrogen. The complex $[Ir(PPh_3)_2H_3]$ probably has a polymeric structure* and its properties are quite different from those of a PEt_2Ph analogue, which must be formulated as $[Ir(PEt_2Ph)_2H_5]$ in solution, as shown by its NMR spectra and reactions [13,14].

Results and discussion

Hydrogenation of PhC≡CPh in ethanol

The complex $[Ir(PPh_3)_2H_3]$ or $[Ir(PPh_3)_2H_5]$ enters into the equilibria (eqn. 1) in solution. The existence of an equilibrium involving penta-, tri- and mono-hydride complexes of iridium has been established by use of the soluble and well-characterized $[Ir(P\text{-}i\text{-}Pr_3)_2H_5]$ complex [15].

$$[Ir(PPh_3)_2H_5] \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} [Ir(PPh_3)_2H_3] + \text{Solvent} \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} [Ir(PPh_3)_2(\text{Solvent})H] \qquad (1)$$

(Solvent = CH_2Cl_2, THF)

The $[Ir(PPh_3)_2H_3]$ catalyses the homogeneous reaction of non-activated α-olefins with molecular hydrogen under normal conditions. The catalytic species is probably $[Ir(PPh_3)_2(\text{Solvent})H]$ [16]. Furthermore, the polymeric complex $[Ir(PPh_3)_2H_3]$, suspended in dichloromethane, hydrogenates α-olefins at room temperature according to eqn. 2.

$$\underset{\text{(white solid)}}{[Ir(PPh_3)_2H_3]} + RCH{=}CH_2 \xrightarrow[20°,\,10h]{(CH_2Cl_2)} \underset{\text{(green solution)}}{[Ir(PPh_3)_2(\text{Solvent})H]} + RCH_2CH_3 \qquad (2)$$

We have now found that when $[Ir(PPh_3)_2H_3]$ is treated with diphenylacetylene in refluxing oxygen-free ethanol under nitrogen for 24 h, *cis*-$[Ir(PPh_3)_3H_3]$, *trans*-stilbene, and acetaldehyde are obtained, together with a

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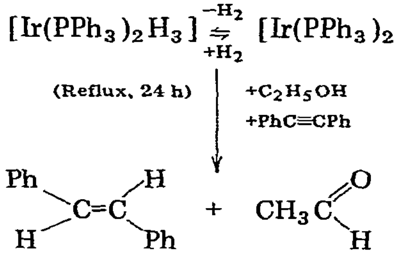
* Because of its insolubility the degree of association of this complex could not be determined. Although we formulate this complex as a trihydride, it could also be the corresponding pentahydride or a mixture of the two.

complex which is tentatively formulated as [Ir(PPh$_3$)(PhC≡CPh)H]. The reactions (*a*—*c*) occur in the overall process represented in eqn. 3.



(3)

(*a*) Hydrogen abstraction from ethanol by the iridium—hydride complex in the absence of diphenylacetylene may take place according to eqn. 4.

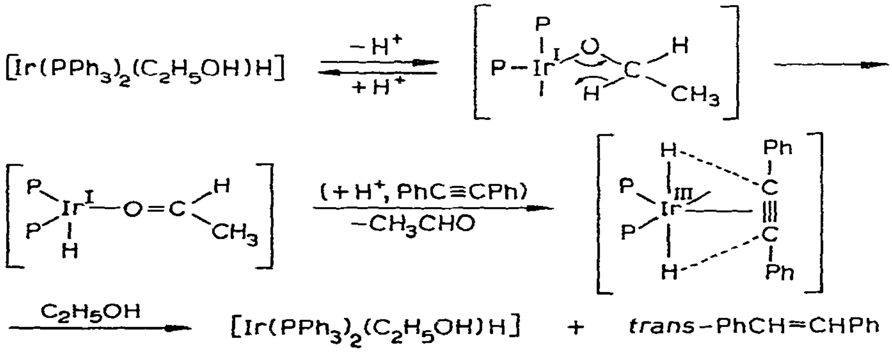
$$[Ir(PPh_3)_2H_3] + C_2H_5OH \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} [Ir(PPh_3)_2(C_2H_5OH)H] \xrightarrow{C_2H_5OH}$$

$$[Ir(PPh_3)_2(CO)H] + CH_4 + CH_3CHO + H_2 \qquad (4)$$

(*b*) In the presence of diphenylacetylene, no hydridocarbonyliridium complex is formed (see side reactions below).

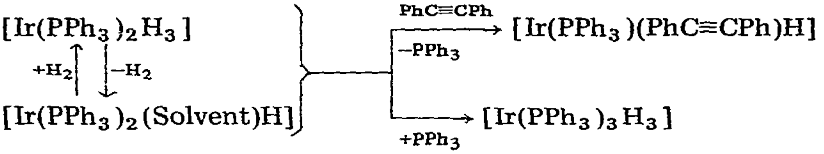
(c) The reaction of [Ir(PPh$_3$)$_2$H$_3$] with CO in CH$_2$Cl$_2$ gives [Ir(PPh$_3$)$_2$-(CO)H].

We suggest that the catalytic hydrogen transfer process involves coordination of diphenylacetylene to [Ir(PPh$_3$)$_2$(Solvent)H] with formation of a hydridoacetylene irridium(III) intermediate complex. This promotes the transfer of hydrogen from ethanol to the coordinated diphenylacetylene. The reaction scheme (Scheme 1) for the hydrogen transfer process would require the formation of an ethoxide—hydridoiridium(I) complex, followed by hydride transfer to give an aldehyde complex [17]. This would react with protons and diphenylacetylene with elimination of acetaldehyde to afford a hydridoacetylene iridium(III) complex via oxidative addition. This then collapses to the initial iridium(I) complex, with concomitant liberation of stilbene. The formation of *trans*-stilbene may be attributed to *cis-trans* isomerization catalysed by the iridium hydrides which are always present in solution. The proposed reaction scheme is shown in eqn. 5 (charges on the complex are omitted). Therefore, the catalytically-active species for the hydrogen transfer must be the intermediate [Ir(PPh$_3$)$_2$(Solvent)H].



(5)

Side reactions. In the transfer of hydrogen from ethanol to diphenylacetylene, the latter reacts with the initial iridium system according to eqn. (6).

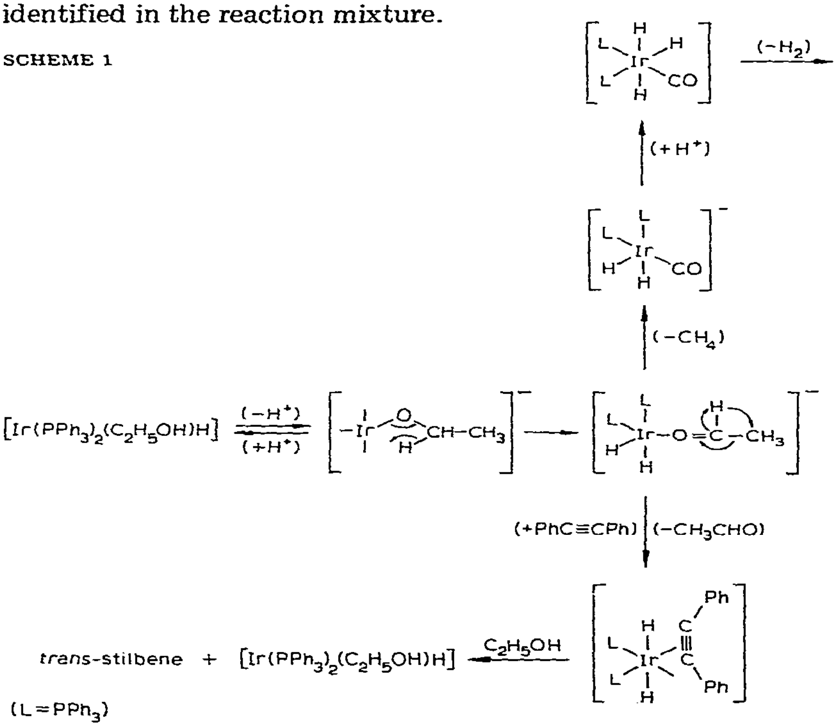


(6)

The complex $[Ir(PPh_3)(PhC\equiv CPh)H]$ was tentatively identified from its infrared spectrum [ν(Ir—H) 2000 cm^{-1}, ν(C≡C) 1960 cm^{-1}] [18], and from the elemental analysis of the unstable yellow complex isolated by chromatography on alumina.

The presence of this complex in solution suggests that the displacement of one molecule of phosphine from the original system by diphenylacetylene takes place. The displaced triphenylphosphine then reacts with the dehydrogenated complex $[Ir(PPh_3)_2(Solvent)H]$ (or with its precursor, $[Ir(PPh_3)_2H_3]$), to form the inert, coordinatively-saturated $[Ir(PPh_3)_3H_3]$, which has been identified in the reaction mixture.

SCHEME 1



Catalytic hydrogenation of diphenylacetylene with H_2 in benzene

When molecular hydrogen is bubbled through a suspension of $[Ir(PPh_3)_2H_3]$ in refluxing benzene containing diphenylacetylene, the latter is converted into *trans*-stilbene. In this case, also, side reactions occur, and the coordinatively-saturated complex $[Ir(PPh_3)_3H_3]$ was identified in appreciable amounts in the reaction mixture.

Under these conditions molecular hydrogen competes successfully with diphenylacetylene for the species [$Ir(PPh_3)_2$(Solvent)H] and hence a large proportion of diphenylacetylene is hydrogenated. In ethanol, the side reactions are favoured and the catalytic efficiency is reduced.

An interesting feature is that the presence of triphenylphosphine inhibits the catalysed process. For the catalytic efficiency of this process to be high it is necessary that the hydrogen acceptor (in our case diphenylacetylene) does not have strong coordinating properties towards the metal complex, otherwise side reactions will occur. At the same time, the neutral ligand (PPh_3 in our case) displaced by the hydrogen acceptor must be trapped chemically. This might possibly be achieved if the reaction were carried out in the presence of acids.

Experimental

[$Ir(PPh_3)_2H_3$] was prepared as previously described [19].

Reaction of [Ir(PPh₃)₂H₃] with ethanol

The complex (0.3 g, 0.416 mmoles) was heated at 70° for 24 h in 50 ml of anhydrous oxygen-free ethanol under nitrogen with stirring. The suspension turned green after 4 h and gave a yellow product after 10 h. Filtration of the solution gave some unreacted [$Ir(PPh_3)_2H_3$] as a white precipitate. The filtrate was concentrated and treated with n-hexane to give a pale yellow precipitate, which was characterized as [$Ir(PPh_3)_2(CO)H$] [19] (m.p. 128°, IR (Nujol) 2037, 1975, 1913 cm^{-1}; satisfactory analytical data). Acetaldehyde was detected in the solution by isolation of its dinitrophenylhydrazone derivative and by gas-chromatography.

Reactions of [Ir(PPh₃)₂H₃] with carbon monoxide in dichloromethane

The suspension of the complex (0.1 g) in 50 ml of dichloromethane under nitrogen with stirring gave a green solution after ca. 4h. Bubbling of carbon monoxide slowly through this solution for 5 h turned it yellow. On concentration and addition of n-hexane a pale yellow precipitate separated and was characterized as [$Ir(PPh_3)_2(CO)H$] [19].

Hydrogenation of diphenylacetylene in ethanol

Diphenylacetylene (0.35 g, 2 mmoles) was added to a suspension of [$Ir(PPh_3)_2H_3$] (0.72 g, 1 mmole) in refluxing anhydrous oxygen-free ethanol under nitrogen with stirring. After 24 h the red-brown mixture gave a pale yellow precipitate, identified as *cis*-[$Ir(PPh_3)_3H_3$] [20] (m.p. 230°, IR(CH_2Cl_2) 2085 cm^{-1}s satisfactory elemental analysis).

The concentrated filtrate was chromatographed on neutral Al_2O_3 with benzene as the eluant to give two bands. The first, a brown product, gave an off-white iridium-free precipitate on addition of n-hexane, and this was recrystallised from ethanol and identified as *trans*-stilbene. The second, a yellow band, on treatment with n-hexane gave a pale-yellow iridium-containing precipitate which was recrystallized from ethanol and identified as [$Ir(PPh_3)(PhC{\equiv}CPh)H$]. (M.p. 109° IR 2000 m, 1963 s cm^{-1}. Analysis found C, 59.1, H, 4.2. $C_{32}H_{26}IrP$ calcd.: C, 60.5, H, 4.26%.)

Catalytic hydrogenation of diphenylacetylene by molecular hydrogen in benzene

$[Ir(PPh_3)_2H_3]$ (0.3 g, 0.416 mmole) was heated with diphenylacetylene (0.45 g, 2.6 mmoles) in 60 ml of anhydrous oxygen-free benzene under hydrogen at reflux for 2 h with stirring. Hydrogen was introduced at 1 atm into the cooled, evacuated reaction mixture. After 6 h the red-brown solution was concentrated, treated with *n*-hexane, and the pale yellow precipitate was filtered off and identified as *cis*-$[Ir(PPh_3)_3H_3]$. The filtrate was taken to dryness and recrystallised from ethanol to give a white solid identified as *trans*-stilbene.

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