

HOMOGENEOUS HYDROGENATION OF ALK-1-ENES AND ALKYNES CATALYZED BY THE 1-[Ir(CO)(PhCN)(PPh₃)]-7-C₆H₅-1,7-(σ-C₂B₁₀H₁₀) COMPLEX

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Summary

The complex [Ir(σ-carb)(CO)(PhCN)(PPh₃)], where carb = -7-C₆H₅-1,2-C₂B₁₀H₁₀, was found to be an effective catalyst for homogeneous hydrogenation of terminal olefins and acetylenes at room temperature and atmospheric or subatmospheric hydrogen pressure. Internal olefins are not hydrogenated, but simple alk-1-enes are readily converted into the corresponding alkanes. Isomerization of the double bond catalyzed by the metal complex occurs at very small extent. Catalytic hydrogenation of olefins having carboxylate substituents on the unsaturated carbon atoms is prevented by the formation of thermally stable chelate hydridoalkyl complexes of the type [Ir(H)(σ-CHR-CHR'C(OR'')(σ-carb)(CO)(PPh₃))]. Acetylenes are hydrogenated to alkenes. The alk-1-enes formed in the hydrogenation of the alkynes HC≡CR in turn undergo the more slow reactions either of hydrogenation to alkanes or isomerization to internal olefins which cannot be further hydrogenated. Hydrogenation of alkynes of the type RC≡CR' is stereospecifically *cis*, yielding *cis*-olefins. Catalyzed *cis* → *trans* isomerization reaction of these internal olefins occurs only to a negligible extent.

Introduction

In the course of our investigation on the synthesis and chemistry of transition metal complexes containing the -2-R-1,2-C₂B₁₀H₁₀ or -7-R-1,7-C₂B₁₀H₁₀ (R = H, CH₃, C₆H₅) ligands bonded to the metal atom through a metal-carbon σ bond, we have prepared and characterized neutral carboranyliridium (I) complexes of general formula [Ir(σ-carb)(CO)(RCN)(PPh₃)], where carb = -7-C₆H₅-

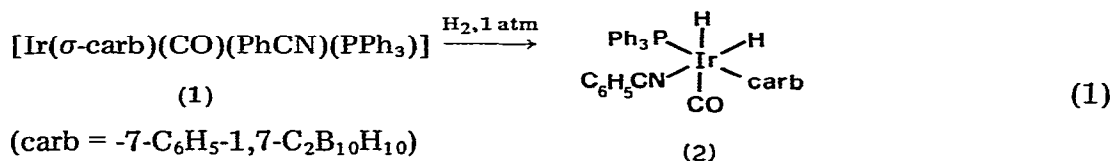
1,7- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ [1]. These complexes containing a weak donor nitrile ligand, appear to be effective catalysts for homogeneous hydrogenation of terminal olefins and acetylenes at 25–60°C under atmospheric or sub-atmospheric pressure of hydrogen. On the other hand, the corresponding bis-phosphino complexes, $[\text{Ir}(\sigma\text{-carb})(\text{CO})(\text{PPh}_3)_2]$, are scarcely active as hydrogenation catalysts under the same conditions. This is attributable to the fact that, unlike triphenylphosphine, the weak donor nitrile ligand can be easily displaced from the iridium atom by unsaturated substrates [2].

In the light of the general mechanistic features of catalyzed hydrogenation reactions, a transition metal complex should be able to act as catalyst when it can accommodate the reagents in its coordination sphere [3–7]. In agreement with this, the complexes $[\text{IrCl}(\text{CO})\text{PN}]$ and $[\text{IrCl}(\text{CO})\text{PCN}]$, where PN and PCN are the bidentate chelating ligands *o*-(diphenylphosphino)-*N,N*-dimethylaniline and *o*-(diphenylphosphino)-*N,N*-dimethylbenzylamine, respectively, are more effective than Vaska's compound, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, as hydrogenation catalysts [4]. The greater effectiveness of the complexes $[\text{IrCl}(\text{CO})\text{PN}]$ and $[\text{IrCl}(\text{CO})\text{PCN}]$ is in accord with the observation that the dissociation from iridium(I) of the coordinated dimethylamino group of the chelate ligands occurs quite readily.

We report below a study of the ability of the carboranyl nitrile iridium(I) complex 1- $[\text{Ir}(\text{CO})(\text{PhCN})(\text{PPh}_3)]$ -7- C_6H_5 -1,7-($\sigma\text{-C}_2\text{B}_{10}\text{H}_{10}$) (1) to catalyze the hydrogenation of simple and functionalized olefins and acetylenes under mild conditions.

Results and discussion

Catalyst precursor. On treatment with molecular hydrogen at room temperature the carboranyl iridium(I) complex $[\text{Ir}(\sigma\text{-carb})(\text{CO})(\text{PhCN})(\text{PPh}_3)]$, where carb = 7- C_6H_5 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (1), undergoes oxidative-addition to yield stereospecifically the six-coordinate iridium(III) dihydride 2, (eq. 1).



This reaction is fast in benzene or 1,2-dichloroethane. The dihydride 2 is a white solid, which was isolated as pure crystals and fully characterized by IR and ^1H NMR spectroscopy [1]. Ligand exchange reactions carried out on both the iridium(I) (1) and iridium(III) (2) derivatives testify to the lower stability of the Ir–NCR bond in the iridium(III) compared with the iridium(I) complexes [1,8].

To prepare a catalytically active mixture the solid complex 1 is added to a toluene solution of alkene or alkyne (0.6–2.0 M) at constant temperature (25 or 35°C) under molecular hydrogen maintaining a constant total pressure of 1 atm.

Hydrogenation of alkenes

The hydrogenation of terminal olefins, such as 1-pentene or 1-hexene, occurs quite readily in toluene containing catalytic amount of the complex **1** at room temperature and under hydrogen at atmospheric pressure. On the other hand, internal olefins, such as 2-butene, 2-pentene or cyclohexene, are not hydrogenated under the same conditions, and complex **1** is recovered as the dihydride **2**, oxidative-addition of hydrogen, reaction **1**, occurring. The failure of the complex **1** to catalyze the hydrogenation of the internal olefins is probably due to steric effects of the bulky carboranyl and triphenylphosphine ligands coordinated to the metal. Figure 1 shows the reaction profile for the hydrogenation of 1-hexene catalyzed by complex **1**. The results show that the hydrogenation is accompanied by a slower catalyzed isomerization of the olefinic double bond. Since the internal olefins so formed cannot be hydrogenated with this catalyst, hydrogen uptake data alone provide reliable information about the catalytic hydrogenation of 1-alkenes to the corresponding alkanes.

Figure 2 shows the conversion curves for the hydrogenation of 1-pentene and 1-hexene to the corresponding alkanes carried out in toluene at 25 and 35°C under a total constant pressure of 1 atm. The hydrogenation of 1-hexene at 35°C using different [olefin]/[cat] ratios was also investigated and the results

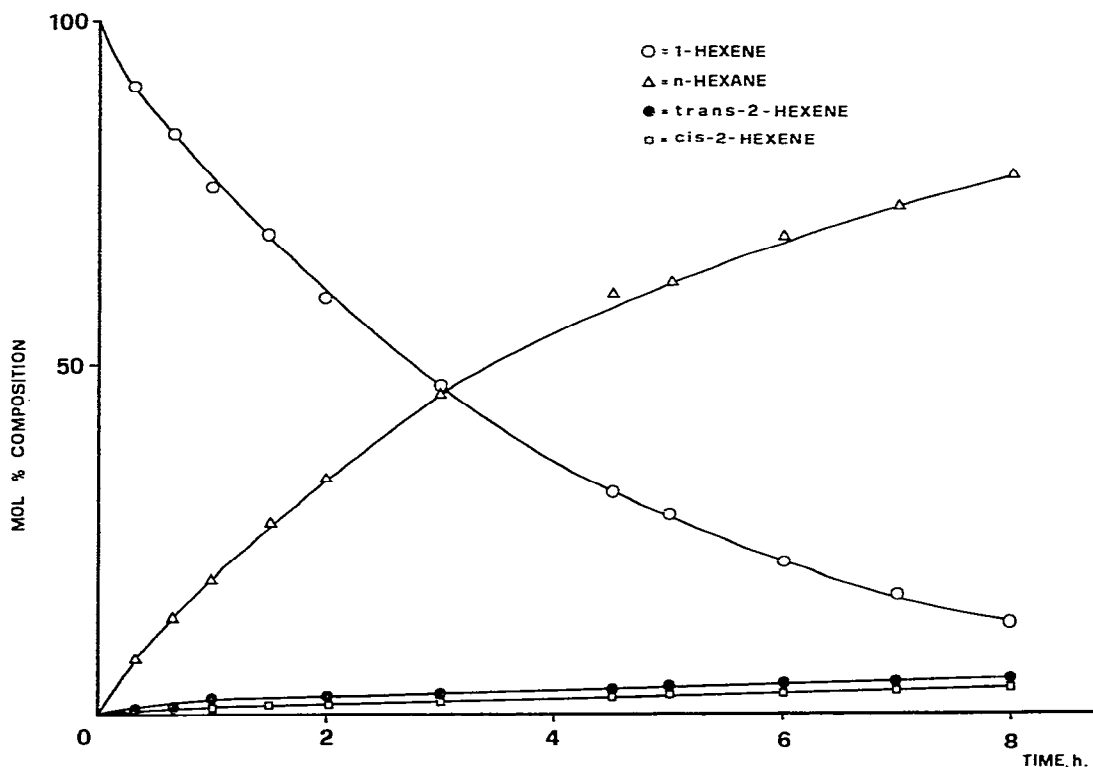


Fig. 1. Reaction profile for the catalytic hydrogenation of 1-hexene (2 M) with $[\text{Ir}(\sigma\text{-carb})(\text{CO})(\text{C}_6\text{H}_5\text{CN})\text{-(P(C}_6\text{H}_5)_3)_3]$ (**1**) (5.3 mM) in toluene; T 35°C; P_{H_2} 1 atm.

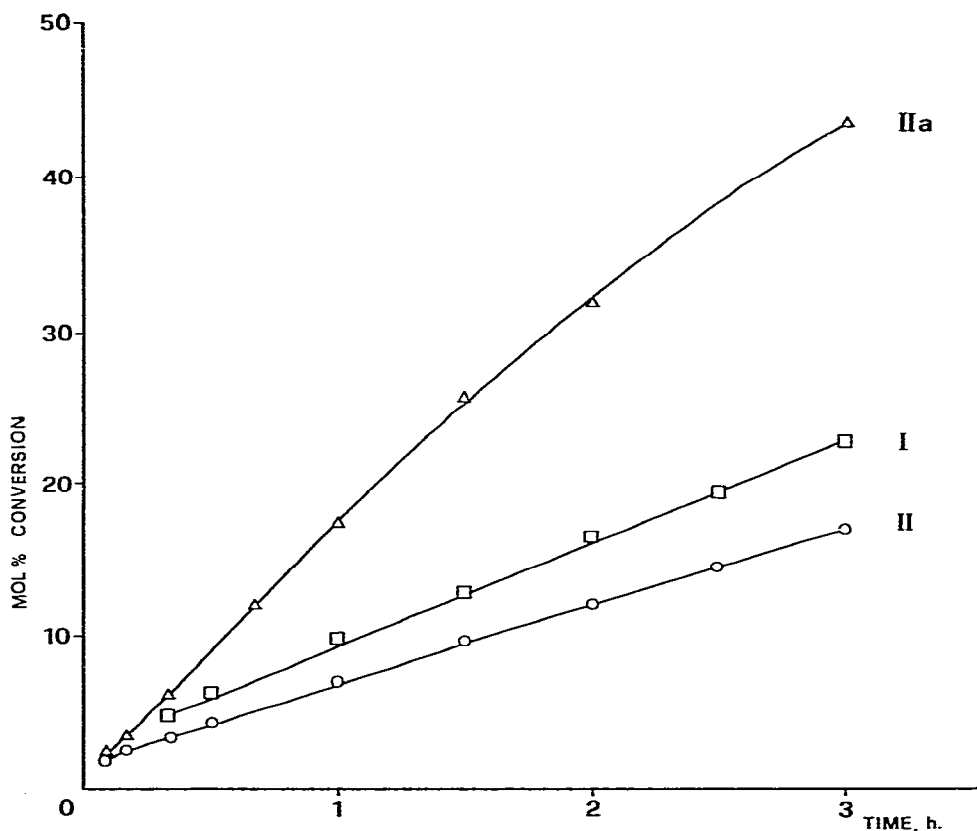


Fig. 2. The hydrogenation of 1-pentene (I) and 1-hexene (II, IIa) catalyzed by 1 (5.3 mM) in toluene at 25°C (I, II) and 35°C (IIa); [olefin] = 2 M; P_{H_2} 1 atm.

are shown in Fig. 3. Addition of an equimolecular amount of the free PhCN or PPh_3 ligand to the catalyst 1 causes a dramatic decrease in the hydrogen uptake; thus, the 1-hexene $\rightarrow$ hexane conversion at 35°C was reduced to ca. 0.6 mol% and 1.0 mol%/h upon addition of PhCN and PPh_3 , respectively. This behaviour can be explained by assuming that the effective catalyst is a five-coordinate dihydride species produced by dissociation of the weakly donor ligand PhCN from the dihydride 2 formed initially by fast hydrogen oxidative-addition to 1 (eq. 1). Thus, addition of free PhCN reduces the concentration of the five coordinate intermediate species and lowers the nitrile ligand dissociation. On the other hand the addition of PPh_3 gives the bisphosphinoiridium(III) derivative $[Ir(H)_2(\sigma\text{-carb})(CO)(PPh_3)_2]$ by ligand exchange; an authentic sample of the latter complex [1,9] exhibited the same catalytic activity as the mixture obtained by addition of PPh_3 to 2 (conversion of 1-hexene = 1.0 mol%/h). The results, may be explained by assuming that one bulky carboranyl group and two triphenylphosphine ligands coordinated to the metal atom in the bisphosphinoiridium(III) derivative give rise to steric strain which induces a small PPh_3 dissociation, thus generating a coordinatively unsaturated active species.

Hydrogenation of olefins "activated" with electron-withdrawing groups

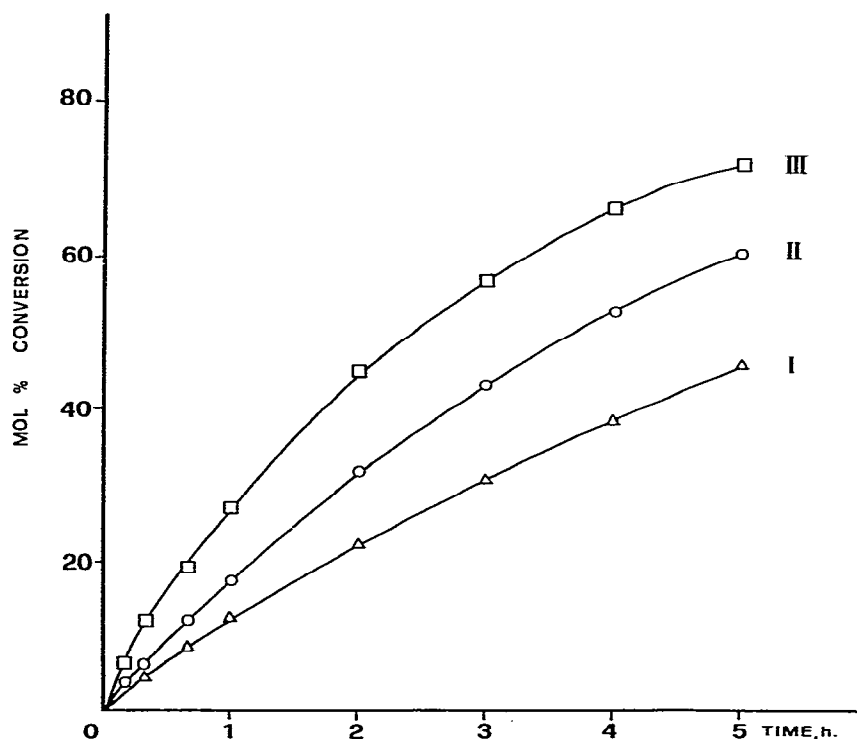
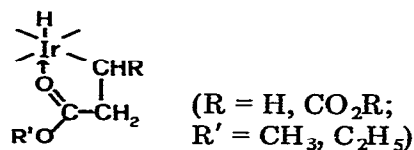


Fig. 3. The effect of the catalyst 1 concentration on the hydrogenation of 1-hexene (2 M) in toluene at 35°C and P_{H_2} 1 atm. [catalyst] = 2.7 mM (I); 5.3 mM (II) and 10.6 mM (III).

occurs at higher temperatures. Thus, for example, maleic anhydride is catalytically hydrogenated to succinic anhydride by 1 when the reaction is carried out at $T > 50^\circ\text{C}$. At lower temperatures a hydrido derivative of iridium(III) $[\text{Ir}(\text{H})-(\sigma\text{-carb})(\sigma\text{-CHCH}_2\text{C}(\text{O})\text{OC}(\text{O}))(\text{CO})(\text{PhCN})(\text{PPh}_3)]$, is formed. This complex, stable at room temperature, was isolated and characterized by IR and ^1H NMR spectroscopy. On raising the temperature above 50°C , this intermediate species undergoes reductive elimination of succinic anhydride, regenerating the catalyst 1.

On the other hand, olefins containing carboxylate groups as substituents on the unsaturated carbon atoms, such as $\text{CH}_2=\text{CHCO}_2\text{R}$, on treatment with 1 under molecular hydrogen give chelate organometallic derivatives of iridium(III) stable towards the alkane reductive-elimination reaction, and these have been identified as complexes of type 3 by IR and ^1H NMR spectroscopy [8]. Thus,



(3)

catalytic hydrogenation of olefins having carboxylate substituents on the β

carbon atom is prevented by the formation of thermally stable chelate hydrido-alkyliridium(III) complexes.

Hydrogenation of alkynes

Bulkily substituted acetylenes, such as di-*t*-butylacetylene are not catalytically hydrogenated by the complex 1, likely owing to steric effects. On the other hand, $\text{CH}_3\text{C}\equiv\text{CH}$, $t\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$, $\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CH}$, $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$, $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$, $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$, readily undergo hydrogenation to the corresponding alkenes under very mild conditions. The terminal acetylenes are converted into 1-alkenes, which in turn undergo both slow further hydrogenation to alkanes and a slower double bond isomerization. The internal olefins formed by isomerizations are not further hydrogenated with the catalysts used (see above).

For the hydrogenation of 1-pentyne at T 35°C, gas-chromatographic analysis led to the reaction profile shown in Fig. 4. The data indicate that the isomerization is negligible for reaction times less than four hours. Complex 1 catalyzes the hydrogenation of internal acetylenes specifically to *cis* olefins. Thus, for example, diphenylacetylene is selectively reduced at 30°C in benzene to give *cis*-stilbene as the primary product. *cis*-Stilbene in turn undergoes a slow isomerization to *trans*-stilbene. As shown in Fig. 5 the ratio *cis*/*trans*-stilbene decreases on increasing the reaction time, as a consequence of *cis* $\rightarrow$ *trans* isomerization catalyzed by the iridium(I) derivative. This was confirmed by heating to 50°C a benzene mixture containing an authentic sample of *cis*-stilbene and catalytic amount of 1.

Alkynes activated with electron-withdrawing groups such as CO_2R are catalytically hydrogenated to alkenes at higher temperature; when the hydrogen-

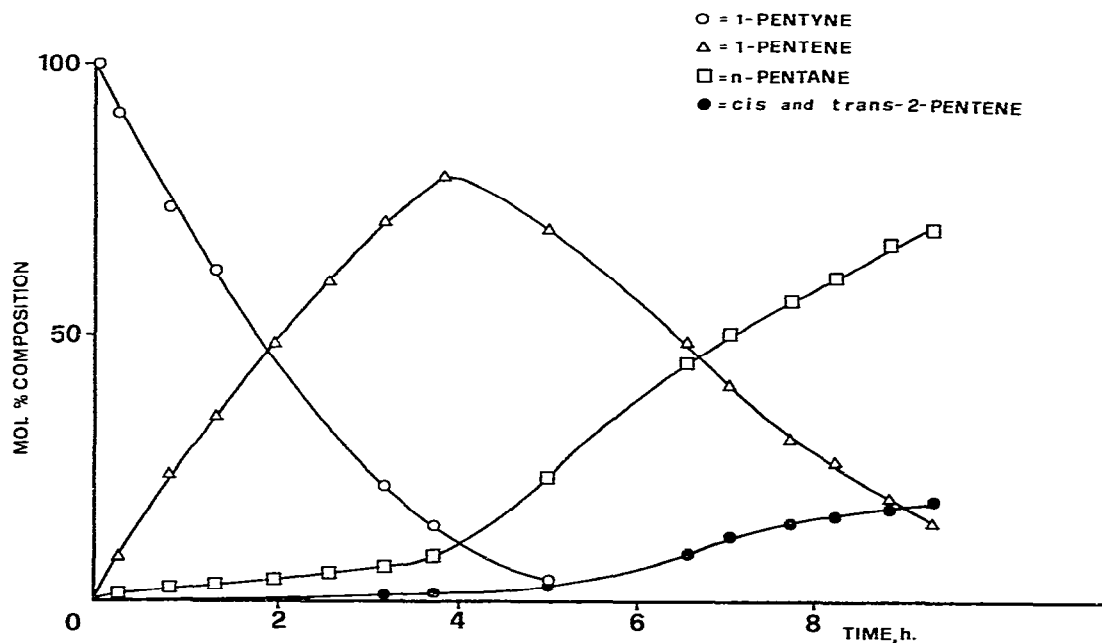


Fig. 4. Reaction profile for the catalytic hydrogenation of 1-pentyne (1 M) with complex 1 (0.02 M) in benzene. T 40°C; P_{H_2} 1 atm.

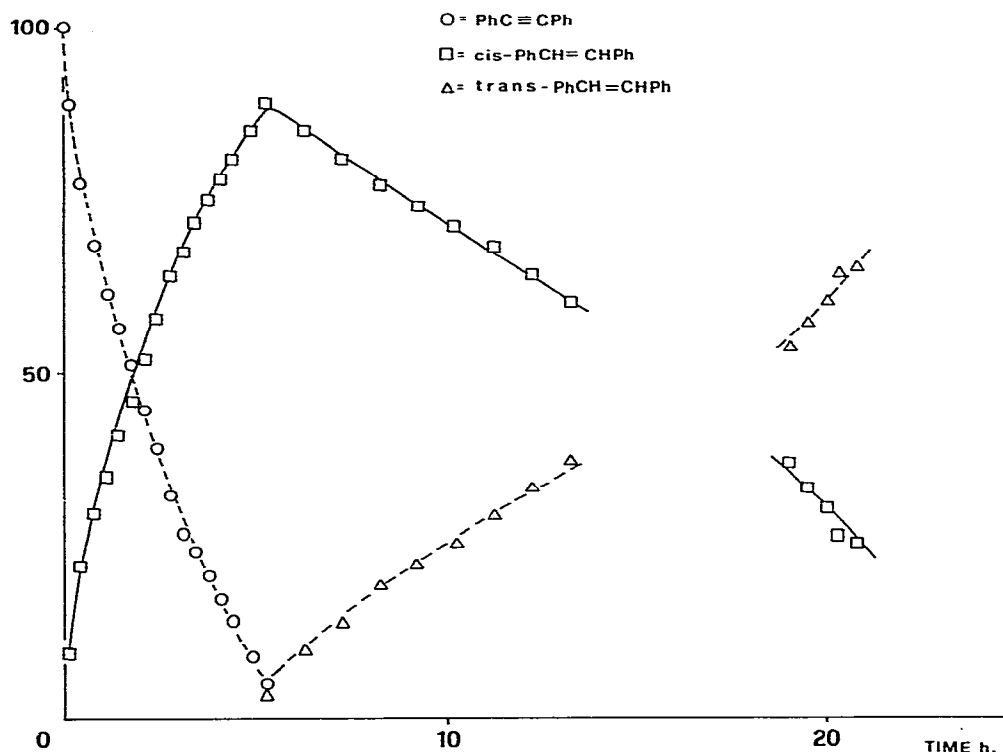
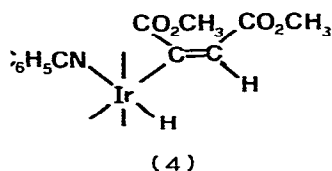


Fig. 5. Reaction profile for the hydrogenation of diphenylacetylene (0.6 *M*) catalyzed by complex 1 (0.013 *M*) in benzene. *T* 30°C; *P*_{H₂} 1 atm.

tion of such substrates is carried out at room temperature, hydridoalkenyliridium(III) derivatives are formed, and these have been isolated and characterized [8]. These compounds undergo alkene reductive-elimination reaction upon heating to an appropriate temperature. Thus, dimethyl acetylenedicarboxylate is specifically hydrogenated to dimethyl maleate in toluene at *T* > 80°C. At lower temperatures a hydridoalkenyliridium(III) intermediate of type 4 is formed, and this undergoes reductive elimination of dimethylmaleate, with regeneration of the iridium(I) catalyst 1, upon heating to 80°C.



Conclusion

The results obtained, considered together with those for the stoichiometric reaction between the iridium(III) dihydride 2 and "activated" unsaturated hydrocarbons [8], indicate that the hydrogenation reaction catalyzed by the carbonylnitrileiridium(I) complex 1 takes place by a "hydride route". Thus the

dihydrido derivative of iridium(III) **2** is initially formed by fast oxidative-addition reaction of molecular hydrogen to the carboranyl nitrile iridium(I) complex **1**. Upon dissociation of the weak donor nitrile ligand, the dihydrido formed yield coordinatively unsaturated species which are able to accommodate a molecule of unsaturated substrate derivatives in the coordination spheres. A fast insertion of the coordinated C=C or C≡C groups into one Ir—H bond gives hydridoalkyl- or hydridoalkenyl-iridium(III) intermediates, which in turn undergo reductive-elimination of alkane or alkene to regenerate the Ir^I catalyst **1**.

Experimental

Reagents. The catalyst complexes [Ir(σ -carb)(CO)(PhCN)(PPh₃)], carb = -7-C₆H₅-1,7-C₂B₁₀H₁₀ (**1**) was prepared as previously described [1] by treating the bis(phosphino)iridium(I) complex *trans*-[Ir(σ -carb)(CO)(PPh₃)₂] with benzonitrile at room temperature. The compound **1**, a pale yellow crystalline solid, has a square planar structure with the nitrile molecule end-on coordinated to iridium(I).

The alkenes and alkynes used were commercial samples, dried and vacuum distilled prior to use. Reagent grade solvents were purified by standard methods and were dried and degassed before use.

Hydrogenation reactions

The hydrogenations were carried out in a 100 ml four-necked water-jacketed flat bottom flask equipped with magnetic stirrer. The flask was fitted with a T-shaped three way stopcock connected to vacuum or N₂ and to a hydrogen manifold via a water-jacketed gas buret equipped with a mercury leveling manometer. The weighed unsaturated substrate and with a measured volume of freshly distilled and degassed solvent were introduced through a side arm in the flask previously evacuated and refilled with H₂. The hydrogen pressure was then equilibrated with the mercury leveling manometer and the catalyst, weighed to ± 0.1 mg in a Teflon-capsule, was added to the solution through a solid injector device. The total pressure was maintained at 1 atm with the leveling manometer and by periodic addition of H₂. The temperature was held constant continuously by circulating water ($\pm 0.5^\circ\text{C}$) through the jackets. Gas chromatographic analyses were performed on a Perkin—Elmer Sigma 3B Gas Chromatograph fitted with 4 m column with dimethylsulpholane on Chromosorb W/HP. The flame ionization detector was interfaced to a Perkin—Elmer Sigma 10B chromatography Data Station. The ¹H NMR spectra were recorded on a Bruker WP-60 FTNMR instrument at 60 MHz in C₆D₆ solution.

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