

ACTIVATION OF THE C—H BOND. PENTAHYDRIDOBIS(TERTIARY-PHOSPHINE)IRIDIUM AND RELATED COMPLEXES AS HOMOGENEOUS CATALYSTS FOR HYDROGEN TRANSFER INVOLVING MONOOLEFINS

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(Received July 30th, 1974)

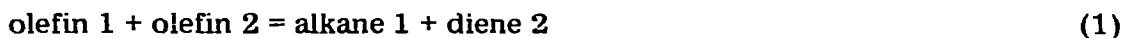
Summary

Iridium hydrido complexes IrH_5L_2 ($\text{L} = \text{PPh}_3, \text{P-}i\text{-Pr}_3, \text{PMe}_3$) and *mer*- IrH_3L_3 ($\text{L} = \text{PPh}_3$) have been found to catalyze hydrogen-transfer between monoolefins in homogeneous solution; equimolecular amounts of dienes and alkane being formed. A mechanism is proposed.

The new olefin complexes $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)\text{PPh}_2(\text{C}_6\text{H}_4^-) \cdot 1,5\text{-C}_7\text{H}_8$, $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P-}i\text{-Pr}_3)[\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6^-)]$, the π -allyl complexes $\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2$, $\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{P-}i\text{-Pr}_3)_2$, and a hydrido diene complex $\text{IrH}(\text{C}_4\text{H}_6)(\text{P-}i\text{-Pr}_3)_2$ of iridium(I), of relevance to the reaction, have been synthesized.

Hydrogen transfer reactions catalysed by Ir and Rh complexes in the homogeneous phase have previously been observed for cyclohexadienes, but these catalysts are not active for hydrogen transfer involving monoolefins [1–3]

We have found that the iridium hydrido complexes $\text{IrH}_5(\text{PPh}_3)_2^*$ and $\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ catalyse the reactions of carbon—hydrogen bonds of linear monoolefins in homogeneous phase under mild conditions. With olefins having $\text{C} \leq 4$ new olefins, π -allyl, or hydrido dieneiridium(I) complexes are obtained. With $\text{C} \geq 4$, a catalytic hydrogen transfer is observed:



Results

Reactions involving ethylene, propene and butene

Ethylene reacts readily with a suspension of $\text{IrH}_5(\text{PPh}_3)_2$ or a solution of

* This complex has been formulated as $\text{IrH}_3(\text{PPh}_3)_2$ [4]. We tentatively suggest the formula $\text{IrH}_5(\text{PPh}_3)_2$ by analogy with other iridium complexes, although its insolubility has prevented unambiguous characterization.

TABLE 1. SPECTRAL DATA FOR THE NEW IRIIDIUM COMPLEXES

Complex	Structure	IR data		NMR data ^a			Solvent
		Frequencies (cm ⁻¹)	Assignment	Chem. shift (in τ)	Integrated intensities	Coupling constants (Hz)	
IrH ₅ (P-1-P ₃) ₂ ^b		1960 s	$\nu(\text{Ir-H})$	20.8 t	6	$J(\text{PH}) = 11$	C ₆ D ₆
		875 m	$\delta(\text{Ir-H})$	8.73 d 8.87 d 8.22 m (br)	18 18 6	$J(\text{CH-CH}_3) = 7$	
Ir(C ₂ H ₄) ₂ (PPh ₃)(PPh ₂ (C ₆ H ₄ -)) · 1.5C ₇ D ₈ ^c	Ref. 5	1550 w	$\nu(\text{C=C})$	7.5 br	8		C ₇ D ₈
		400 w 370 w	$\nu(\text{Ir-C}_2\text{H}_4)$	2.5 m 3.0 m	30		
Ir(C ₂ H ₄) ₂ (P-1-Pr ₃)(P-1-Pr ₂ (1-C ₃ H ₇ -)) ^d	Ref. 6	3055 w	$\nu(\text{C-H})$	9.0 m (br) ^e			C ₇ D ₈
		3045 w 2790 w					
Ir(π -C ₃ H ₅)(PPh ₃) ₂		1000 m	$\nu(\text{C=C})$	7.7 d (br)	2	$J = 12$	C ₆ D ₆
		550 m	$\delta(\text{C-C-C})$	6.9 d (br) 6.5 m 3.1 m; 2.5 m	2 1 ~35	$J = 7$	
Ir(π -C ₃ H ₅)(P-1-Pr ₃) ₂	Ref. 7	3045 w	$\nu(\text{C-H})$	8.9 d, 8.8 d	36	$J(\text{CH}_2\text{-CH}) = 7$	C ₇ D ₈
		3020 w 1000 m 512 m	$\nu(\text{C=C})$ $\delta(\text{C-C-C})$	8.5 d, 8.6 d 7.7 o 6.8 d (br) 6.1 m	2 6 2 1	$J = 11$ $J(\text{PH}) = J(\text{CH-CH}_3) = 7$ $J = 6$	
IrH(C ₄ H ₆)(P-1-Pr ₃) ₂	Ref. 7	3050 w	$\nu(\text{C-H})$	26.86 t		$J(\text{PH}) = 21$	C ₆ D ₆
		3050 w 3040 w 2070 vs 1965 vs 1925 vs	$\nu(\text{Ir-H})$ $\nu(\text{C=O})$	7.7-9.4 (br) 5.2 (br) 5.0 (br)			
Ir(CO) ₂ (PPh ₃)(PPh ₂ (C ₆ H ₄ -))	Ref. 5	2070 vs	$\nu(\text{Ir-H})$				C ₆ D ₆
		1965 vs 1925 vs	$\nu(\text{C=O})$				

^a TMS internal standard. *d* = doublet, *t* = triplet, *q* = quadruplet, *o* = octuplet, *m* = multiplet, *br* = broad. NMR data referred to 25°C. ^b After decoupling of P- and the C-bonded protons. ^c ¹H NMR shows a sextuplet 1/6/10/10/5/1, $J(\text{PH}) = 11$ Hz. ^c Recrystallized from C₇D₈. ^d $\nu(\text{C=C})$ is obscured by the phosphine absorption. ^e Only a broad unresolved absorption is observed. Some H-D exchange with the solvent is indicated by the formation of a peak at $\tau = 3.0$.

$\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ in benzene with evolution of ethane and formation of red solutions from which white (or pale yellow) complexes of general formula $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{L-C})\text{L}^*$ have been obtained. They are stable only in an inert atmosphere. Elemental analysis, IR and NMR data are in accord with the presence of two ethylene and two phosphine ligands. No evidence was found for hydride ligands (Table 1). X-ray crystallography definitely established the structure, showing that an isopropyl or a phenyl group of one of the phosphines is metallated by the iridium atom, giving rise to a four-membered ring [5]. The geometry around the iridium atom is a distorted trigonal bipyramid, a rather unusual coordination for iridium(I).

The coordinated ethylene does not exchange with the free ligand on the NMR time scale, as shown by the NMR spectrum of the complex in the presence of an excess of ethylene. On the other hand, the ethylene can be displaced by other ligands such as phosphines, propene, *cis*-2-butene, or carbon monoxide. Using CO, with $\text{L} = \text{PPh}_3$, the dicarbonyl complex $\text{Ir}(\text{CO})_2(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4^-) \cdot \text{THF}$ has been isolated, having a structure very similar to that of the ethylene complex [5]. Hydrogen reacts with $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{L-C})\text{L}$, with cleavage of the iridium-carbon bond, displacement of the ethylene, and formation of the original hydrido complexes.

Propene also reacts in mild conditions with $\text{IrH}_5(\text{PPh}_3)_2$ and $\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ yielding $\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)_2$ and $\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{P-}i\text{-Pr}_3)_2$. The same complex is also obtained by the reaction of propene with the metallated species $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P-}i\text{-Pr}_3)_2(\text{P-}i\text{-Pr}_3)[\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6^-)]$ under the same experimental conditions.

These compounds are stable in an inert atmosphere in the solid state, but the triphenylphosphino complex is rather unstable in solution even under nitrogen or argon. The NMR spectra are typical of π -allyl complexes (Table 1). The absorption lines are mostly rather broad, but the *anti*-protons of the allylic group in $\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{P-}i\text{-Pr}_3)_2$ give rise to a well resolved four line signal, which is probably due to a coupling of the *anti* protons with the *trans* phosphorus nucleus [6]. X-ray crystallographic studies confirm the structure, revealing an almost planar geometry around the iridium atom [7] with two coordination sites occupied by the π -allyl ligand, and the other two by two phosphorus atoms.

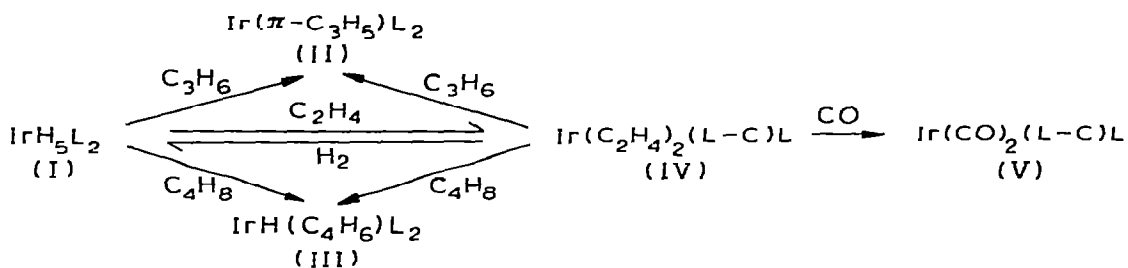
We are unable to separate any crystalline compound from the reaction between *cis*-2-butene and the same hydrides under mild conditions. However with the olefin as solvent and higher temperatures and pressures the diene complex $\text{IrH}(\text{C}_4\text{H}_6)(\text{P-}i\text{-Pr}_3)_2$ was isolated. The same complex can be obtained from the reaction of *cis*-2-butene with the metallated species $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P-}i\text{-Pr}_3)_2(\text{P-}i\text{-Pr})_2[\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6^-)]$ under similar conditions.

Analytical data are in accord with the formula $\text{IrH}(\text{C}_4\text{H}_6)\text{L}_2$. The presence of the hydride ligand is shown by IR and NMR data (Table 1). The presence of butadiene is also shown by GLC and mass spectrometric analysis of the gas evolved after addition of bis(diphenylphosphino)ethane to a solution of the complex. The structure has been fully elucidated by X-ray crystallographic studies [7].

The reactions are summarized in Scheme 1.

* (L-C) is $\text{PPh}_2(\text{C}_6\text{H}_4^-)$ or $\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6^-)$.

SCHEME 1



I, II, IV L = PPh₃, P-*i*-Pr₃; III L = P-*i*-Pr₃; V L = PPh₃

Reactions involving higher olefins

We have not been able to separate crystalline complexes from the reaction of IrH₅(PPh₃)₂ or IrH₅(P-*i*-Pr₃)₂ with longer chain olefins such as 1-pentene, 1-hexene and 2-hexene. The amorphous powders obtained from these reactions were shown by IR, NMR, mass spectra and elemental analysis to contain only iridium and phosphine in the same ratio as in the starting hydrido complexes. No hydrido or olefinic ligand could be detected in these materials.

On the other hand, with these larger olefins, a catalytic intermolecular hydrogen transfer reaction is observed*. This reaction gives rise to equimolecular amounts of dienes and saturated hydrocarbons, even at room temperature in the most favourable case (Table 2, exp. 1)**. The dienes formed are linear, conjugated and predominantly in the *trans, trans* configuration (Table 2, notes *b* and *c*).

Although the same olefin generally acts as both hydrogen acceptor and hydrogen donor, we have found that ethylene can also be used as acceptor, i.e. the hydrogen transfer reaction does not necessarily take place between identical olefins.

The reaction is clearly catalytic though the catalysts are not very efficient. The reaction rate decreases with time, and stops before completion (Fig. 1). The final product concentration is markedly influenced by the temperature (Table 2, exp. 1-3). It is also proportional to the catalyst concentration (Table 2, exp. 3 and 4) which indicates that the olefin/dienes/alkane system is not at thermodynamic equilibrium at the end of the reaction.

The limiting values of product concentration also depend on the type and number of phosphines coordinated to the metal. This is clearly revealed by the following results (the diene concentrations given are those observed after 40 h, at 130°, with 0.05 M catalyst): IrH₅(P-*i*-Pr₃)₂ (1.25 M dienes) is much more reactive than IrH₅(PPh₃)₂ (0.22 M dienes); *mer*-IrH₃(PPh₃)₃ is still less reactive (0.13 M dienes); IrH₅(PMe₃)₂ gives 0.12 M dienes, while IrH₅(PCy₃)₂*** is practically inactive (0.02 M dienes).

* The hydrogen-transfer also occurs with *cis*-2-butene, but this reaction has not been studied in detail.

** The alkane actually exceeds the dienes by a constant amount, which is accounted for by the initial hydrogenation of the olefin by the hydrogens of the complex (Fig. 1, Table 2).

*** PMe₃ = trimethylphosphine, PCy₃ = tricyclohexylphosphine.

TABLE 2
EXPERIMENTAL CONDITIONS AND PRODUCTS FORMED IN THE REACTION OF OLEFINS WITH VARIOUS COMPLEXES^a

No.	Complex	Conc. (M)	Olefin	Solvent ^b	T (°C)	Time (h)	Alkane (M)	Diene (M)
1	$\text{IrH}_5(\text{P}-i\text{-Pr}_3)_2$	0.050	1-hexene	1-hexene	25	3	0.25	0.10
2	$\text{IrH}_5(\text{P}-i\text{-Pr}_3)_2$	0.050	1-hexene	1-hexene	65	40	0.506	0.38
3	$\text{IrH}_5(\text{P}-i\text{-Pr}_3)_2$	0.050	1-hexene	1-hexene	130	40	1.45	1.25 ^c
4	$\text{IrH}_5(\text{P}-i\text{-Pr}_3)_2$	0.100	1-hexene	1-hexene	65	40	0.84	0.72
5	$\text{IrH}_5(\text{PPh}_3)_2$	0.023	1-hexene	benzene + 1-hexene	50	0.25	0.048	—
6	$\text{IrH}_5(\text{PPh}_3)_2$	0.050	1-hexene	benzene + 1-hexene	130	20	0.310	0.22 ^d
7	$\text{IrH}_5(\text{PPh}_3)_2$	0.023	1-pentene	benzene + 1-pentene	130	20	0.160	0.112
8	$\text{mer-IrH}_3(\text{PPh}_3)_3$	0.047	1-hexene	benzene + 1-hexene	130	40	...	0.13
9	$\text{IrH}_5(\text{PMe}_3)_2$	0.050	1-hexene	benzene + 1-hexene	130	40	0.24	0.12 ^c
10	$\text{IrH}_5(\text{PCy}_3)_2$	0.033	1-hexene	benzene + 1-hexene	130	40	0.075	0.020

^a The reactivity of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{L}-\text{C})\text{L}$, $\text{Ir}(\eta\text{-C}_3\text{H}_5)_2\text{L}_2$ and $\text{IrH}(\text{C}_4\text{H}_6)_2\text{L}_2$ has been checked by experiments similar to those reported in this Table for IrH_5L_2 (L = PPh_3 , $\text{P}-i\text{-Pr}_3$). The data are essentially the same for complexes having the same L. ^b The solvents are neat olefin or 1/1 by volume mixtures of olefin and benzene. ^c Diene composition, 2-*trans*, 4-*trans*, 2-*trans*, 4-*cis* = 28%; 1,3 = 7%; unidentified hexadienes = 2%. ^d Diene composition: 2-*trans*, 4-*trans*, 4-*cis* = 28%; 1,3 = 6%; unidentified hexadienes = 9%. The effects of the complex concentration and of temperature have been confirmed also with $\text{IrH}_5(\text{PPh}_3)_2$; the results are analogous to those with $\text{IrH}_5(\text{P}-i\text{-Pr}_3)_2$. ^e The reaction proceeds further, but is extremely slow.

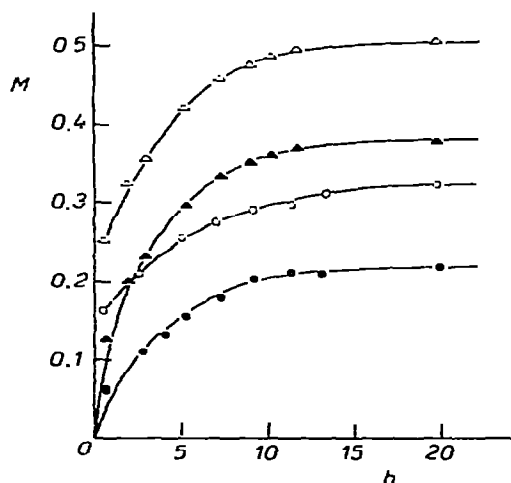


Fig. 1. Products formed in the reaction of 0.05 M $\text{IrH}_5(\text{PR}_3)_2$ with 1-hexene, vs. time: ●, dienes, R = Ph, T = 130°; ○, hexane, R = Ph, T = 130°; ▲, dienes, R = *i*-Pr, T = 65°; △, hexane, R = *i*-Pr, T = 65°.

On the other hand, the ethylene, allyl and butadiene complexes described above are just as efficient catalysts for the same reactions as the corresponding hydrides from which they are prepared (Table 2, note *a*).

Further experiments were carried out in an attempt to establish the reasons for the fall-off in the reaction rate.

At the end of the reaction under the conditions of Table 2, expts. 3 and 6, all the volatile material was distilled off at room temperature, and IrH_5L_2 was added to the distillate and the solution obtained was subjected to the same reaction conditions as before. No further hydrogen transfer was observed.

Furthermore, the addition of the appropriate diene (i.e. 2-*cis*,4-*trans*, or 2-*trans*,4-*trans*) does not inhibit the reaction. Thus it seems that the inhibition must be ascribed to some product other than dienes.

It should also be noted that benzene has been detected in the products of the reactions involving IrH_5L_2 , *mer*- IrH_3L_3 , $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{L}-\text{C})\text{L}$, (L = PPh_3) and with pure 1-hexene or 1-pentene. This indicates a partial destruction of the PPh_3 ligand.

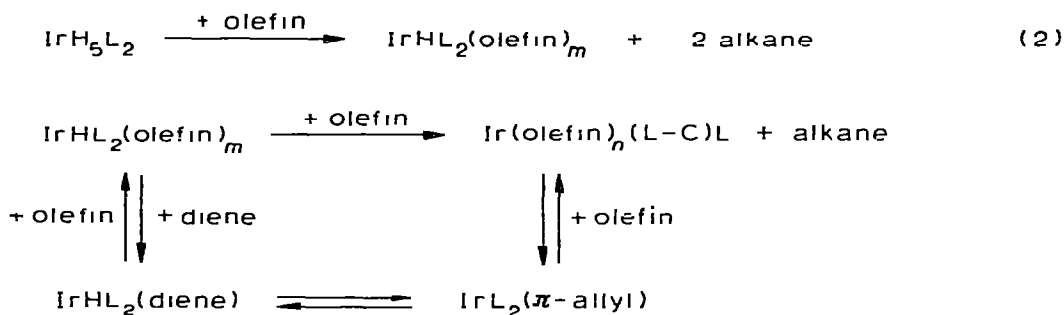
Discussion

The mode of formation and the catalytic activity of the ethylene, allyl and butadiene complexes described above suggest a general scheme for the hydrogen transfer reaction with higher olefins (Scheme 2).

The numerical values of *m* and *n* have not been determined, but they are unlikely to be greater than two because of steric hindrance. The only species of the type $\text{Ir}(\text{olefin})_n(\text{L}-\text{C})\text{L}$ isolated is the pentacoordinated ethylene complex (*n* = 2), but higher olefins could also form tetracoordinated complexes. We have not isolated any species of the type $\text{IrHL}_2(\text{olefin})_m$, but they could be formed in solution either by reaction of IrH_5L_2 with the olefin (reaction 2), or from displacement of a diene ligand by a monoolefin in IrHL_2 (diene).

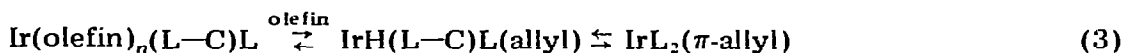
Few complexes containing both coordinated hydrido and olefinic ligands

SCHEME 2



have been isolated [8–10], although they have been postulated as intermediates in several hydrogenation mechanisms. Their lability has been taken as a clear indication of their tendency to undergo olefin insertion into the M–H bond, with formation of a metal- σ -alkyl complex [11]. Therefore a complex of the type $\text{IrHL}_2(\text{olefin})_m$ is expected to be very reactive, and give the metallated species $\text{Ir}(\text{olefin})_n(\text{L-C})\text{L}$ via a number of steps involving iridium alkyls.

As for abstraction of an allylic hydrogen with formation of $\text{IrL}_2(\pi\text{-allyl})$, some examples in the literature support this possibility [12, 13]. Such abstraction should be favoured in our case by the release of strain on opening of the metallated ring:



The abstraction of the second hydrogen, with formation of diene, is known only in a few special cases, e.g. in molecules having C–H bonds activated by electron-withdrawing groups [14], or under drastic pyrolytic conditions [15], or when the driving force of the overall reaction is the aromatization of a cyclic olefin [1, 2, 16]. Our results show that the reaction is more general.

The hydrogen-transfer reaction described is clearly a rather complex process in which a considerable number of more or less labile species are involved. The reaction is even more complicated by the deactivation and inhibition effects which cause a fall-off in the reaction rate. Moreover, the PR_3 ligand is not only involved in the reaction but also undergoes some decomposition which converts part of the catalyst into a new species which is not active for the catalysis.

Although Scheme 2 probably depicts the most important reaction paths, it is a rather rough simplification. A fuller study of the inhibition effect is under study at present in this laboratory.

Experimental

All operations were carried out under dry nitrogen. The reagent grade solvents and the olefins were purified and dried by standard methods, and stored under nitrogen.

Infrared spectra were recorded on a Perkin–Elmer 225 grating spectrophotometer, NMR spectra on Varian HA 100 and XL 100 spectrometers, and mass spectra on the Atlas Werke CH4, and LKB 9000 instruments. GLC was recorded on a Perkin–Elmer F11 gas chromatograph.

The GLC analyses were performed using two types of columns. The first, 3 m long and packed with 30% Carbowax 400 on 60/80 mesh firebrick, was used for the hexadienes (column temp. 60°, vaporizer 150°, carrier gas 100 ml/min) and the pentadienes (column temp. 40°, vaporizer 100°, carrier gas 25 ml/min); quantitative analyses were made with cyclohexane as internal standard. The second 4 m long, and packed with 30% 2,4-dimethyl sulfolane on 80/100 mesh Chromosorb P, was used for the analysis of the lower olefins, (column temp. 30°, vaporizer 75°, carrier gas 10 ml/min).

In a typical hydrogen-transfer experiment, $\text{IrH}_5(\text{PPh}_3)_2$ (0.2 mmole) was transferred under N_2 , together with 1-hexene (2.0 ml), benzene (2.0 ml) and cyclohexane (25 mg), into a 20 ml pressure vessel fitted with a neoprene syringe cap. The apparatus was then carefully closed and placed in an oil bath at 130°. At appropriate time intervals the reaction mixture was analysed by the following procedure: the vessel was cooled to room temperature, and a small volume (0.4 μl) of solution was drawn by a microsyringe through the neoprene cap, and injected into the gas-chromatograph. The dienes were identified by GLC by comparison with authentic samples, and were confirmed by GLC-mass spectrometry. The quantitative analysis of the products was carried out by comparison with the cyclohexane standard.

The procedure was the same for all cases, except the complex concentration and the temperature were varied. With the isopropylphosphine complexes, 4.0 ml 1-hexene was used instead 2.0 ml 1-hexene + 2.0 ml benzene.

$\text{IrH}_5(\text{PPh}_3)_2$ [4], $\text{IrH}_5(\text{PMe}_3)_2$ [17] and *mer*- $\text{IrH}_3(\text{PPh}_3)_3$ [18] were synthesized by published methods.

$[\text{PH-i-Pr}_3]^+ [\text{IrCl}_4(\text{P-i-Pr}_3)_2]^-$

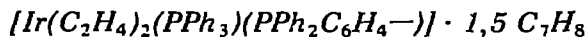
$\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (17.4 g) was dissolved in ethanol (160 ml) containing concentrated HCl (20 ml). This solution was heated under reflux for two hours, until the brown colour turned to green. After removal of the heat source, P-i-Pr₃ (18 ml) in degassed ethanol (70 ml) was added slowly, with vigorous stirring. The suspension was heated under reflux for 4 h and then left overnight at 0°.

The purple crystals were filtered off, washed with cold ethanol, and dried under vacuum. Yield 16 g (58%). The complex was shown to be $[\text{PH-i-Pr}_3]^+ [\text{IrCl}_4(\text{P-i-Pr}_3)_2]^-$. Analysis found: C, 39.5; H, 7.8; Cl, 17.2. $\text{IrC}_{27}\text{H}_{64}\text{Cl}_4\text{P}_3$ calcd.: C, 39.8; H, 7.9; Cl, 17.4%.

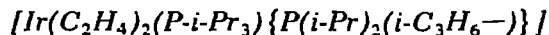
$\text{IrH}_5(\text{P-i-Pr}_3)_2$

To a THF solution (110 ml) containing $[(\text{PH-i-Pr}_3)]^+ [\text{IrCl}_4(\text{P-i-Pr}_3)_2]^-$ (3.15 g) LiAlH_4 was added in small portions with vigorous stirring, until the violet solution became a grey suspension. After stirring for half an hour, the residual LiAlH_4 was hydrolyzed with THF (15 ml) containing water (5 ml). The solvent was removed under reduced pressure, and the residue extracted with petroleum ether (100 ml) and filtered. The yellow solution was concentrated to small volume and then treated with methanol (50 ml). The solution was again concentrated to small volume. The precipitate was filtered, washed twice with cold methanol, and dried under vacuum.

After recrystallization from petroleum ether and methanol, white $\text{IrH}_5(\text{P-i-Pr}_3)_2$ was obtained. Yield 1.8 g (90%). Analysis found: C, 42.3; H, 9.1. $\text{IrC}_{18}\text{H}_{47}\text{P}_2$ calcd.: C, 41.9; H, 8.8%.



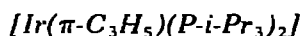
Ethylene was bubbled through a suspension of $\text{IrH}_5(\text{PPh}_3)_2$ (2.10 g) in benzene (200 ml) at 45° . After 45 min the suspension changed to a reddish solution. The solvent was removed under reduced pressure, the residue was dissolved in toluene (15 ml) and the solution was concentrated to 10 ml. (At this stage a supersaturated solution is sometimes obtained). The orange crystals were filtered, washed with cold toluene and dried under vacuum. After recrystallization from toluene, white crystals were obtained. Yield 1.4 g (53%). Analysis found: C, 65.3; H, 5.2. $\text{IrC}_{50.5}\text{H}_{50}\text{P}_2$ calcd.: C, 66.6; H, 5.5%.



Ethylene was bubbled through a solution of $\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ (1.0 g) in benzene (10 ml) at 45° for 3 h. The colour turned to red. The solvent was removed under reduced pressure and the residue was dissolved in n-pentane (5 ml). This solution was cooled to -70° and left overnight. The crystals were filtered off, washed with cold n-pentane, and dried under vacuum. Recrystallization gave pale yellow crystals. Yield 0.51 g (47%). Analysis found: C, 45.7; H, 9.1. $\text{IrC}_{22}\text{H}_{49}\text{P}_2$ calcd.: C, 46.8; H, 8.9%.

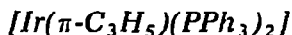


Carbon monoxide was bubbled for 1/2 h, through a solution of $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4-)] \cdot 1,5 \text{ C}_7\text{H}_8$ (0.5 g) in benzene (10 ml). The benzene was removed under vacuum and the residue was dissolved in THF (3 ml). The solution was kept at 0° for four days until precipitation was complete. The yellow crystals were filtered off, washed with THF, and dried under vacuum. Yield 0.24 g (51%). Analysis found: C, 59.6; H, 4.6. $\text{IrC}_4\text{H}_3\text{O}_3\text{P}_2$ calcd.: C, 59.7; H, 4.53%.



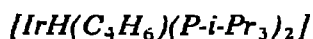
(a) Propene was bubbled through a solution of $\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ (1.7 g) in benzene (25 ml) at 45° for 6 h, during which the solution became red. The solvent was removed under vacuum and the residue dissolved in n-pentane (4 ml) and cooled to 0° . The precipitate was filtered, washed with n-pentane and dried under vacuum. Recrystallization from n-pentane afforded red crystals, 0.52 g (28%). Analysis found: C, 45.3; H, 8.6. $\text{IrC}_{21}\text{H}_{47}\text{P}_2$ calcd.: C, 45.6; H, 8.6%.

(b) The same allyl compound was similarly obtained from $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P-}i\text{-Pr}_3)-[\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6)]$ (0.77 g). Yield 0.34 g (45%).



(a) The preparation has been carried out by the procedure used for the isopropylphosphine analogue. The pale yellow product was recrystallized from benzene.

(b) The allyl complex was similarly obtained from the ethylene complex (0.6 g). Yield 0.33 g (60%). Analysis found: C, 61.9; H, 4.5. $\text{IrC}_{39}\text{H}_{35}\text{P}_2$ calcd.: C, 61.8; H, 4.7%.



(a) A pressure vessel containing $\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ (1.6 g) was cooled to -35° ,

and *cis*-2-butene (6 ml) was condensed in. The vessel was closed and then heated for 8 h at 60°. The reaction mixture was cooled to 4°, and unreacted butene was allowed to evaporate slowly. The orange residue was dissolved in *n*-pentane (10 ml), concentrated to 3 ml, and cooled in a refrigerator. The precipitate was filtered, washed with *n*-pentane and dried. After recrystallization, orange crystals were obtained. Yield 0.65 g (37%). Analysis found: C, 46.5; H, 8.7. $\text{IrC}_{22}\text{H}_{49}\text{P}_2$ calcd.: C, 46.5; H, 8.7%.

(b) Starting from $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)] \cdot 1,5\text{-C}_7\text{H}_8$ (0.50 g) and following the same procedure, 0.20 g of product were obtained (40%).

Hydrogenation of $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P-}i\text{-Pr}_3)\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6-)]$ with molecular hydrogen.

$[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{P-}i\text{-Pr}_3)\text{P}(i\text{-Pr})_2(i\text{-C}_3\text{H}_6-)]$ (1.0 g) was dissolved in benzene (5 ml) and allowed to react with a stream of hydrogen, at room temperature. The solution was stirred for 8 h. The NMR spectrum of the solution showed the presence of the hydride $\text{IrH}_5(\text{P-}i\text{-Pr}_3)_2$ ($\tau = 20.8$).

Hydrogenation of $[\text{Ir}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)] \cdot 1,5\text{-C}_7\text{H}_8$ with molecular hydrogen

The complex (1.2 g) was dissolved in benzene (15 ml) and allowed to react with hydrogen at 1 atm. and room temperature. The solution slowly became turbid and a precipitate began to form. After 16 h the reaction was stopped and the solid filtered, washed with benzene and dried under vacuum. $\text{IrH}_5(\text{PPh}_3)_2$ was identified by elemental analysis and IR spectroscopy.

Acknowledgements

We are indebted to Prof. P. Chini for helpful discussion in the course of this work, and to the Direction of Snam Progetti/DIRIS for permission to publish.

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