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PREPARATION, REACTIONS AND CATALYTIC ACTIVITY OF COMPLEXES OF THE TYPE $[Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]A$ ($R = Cl$, F, H, CH_3 OR CH_3O; $A = ClO_4^-$ OR $B(C_6H_5)_4^-$)

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Summary

Complexes of the type $[Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]A$ ($R = Cl$, F, H, CH_3 or CH_3O; $A = ClO_4^-$ or $B(C_6H_5)_4^-$) have been prepared and their reactions with halogens, methyl iodide, chlorotrimethylsilane, carbon monoxide and hydrogen have been studied. The catalytic activity of the complexes in the hydrogenation of mono- and diolefins depends upon the basicity of the phosphine present.

Introduction

As has been shown by Shapley et al. [1], cationic species of the type $[Ir(COD)\{P(C_6H_5)_3\}_2]^+$ in acetone solution react with hydrogen to form complexes of type $[IrH_2\{P(C_6H_5)_3\}_2(Me_2CO)_2]ClO_4$, which act as homogeneous hydrogenation catalysts. Crabtree et al. [2] have observed that in the case of the homologous complexes $[Ir(COD)(PR_3)_2]PF_6$, use of non-coordinating solvents such as dichloromethane causes a significant increase in their catalytic activity, thus facilitating the rapid reduction of tri- or tetra-substituted olefins. They isolated several intermediates formed in these catalytic processes [3].

In the present paper we describe the synthesis of complexes of the type $[Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]A$ ($R = Cl$, F, H, CH_3 or CH_3O; $A = ClO_4^-$ or $B(C_6H_5)_4^-$) and a study of their reactions with halogens, methyl iodide, chlorotrimethylsilane, carbon monoxide and hydrogen. Furthermore, since variation of the substituent R in the $p\text{-}RC_6H_4$ group in the sequence Cl, F, H, CH_3 or CH_3O gives rise to a progressive increase in the basicity of the phosphine it has been possible to examine the influence of this factor on the catalytic activity of these complexes in the hydrogenation (at ordinary pressure) of 1-heptene, 1,4-cyclohexadiene and isoprene.

Results and discussion

Preparation and properties of the complexes

The addition of stoichiometric amounts of the phosphine $P(p\text{-}RC_6H_4)_3$ to methanol suspensions of $[IrCl(COD)]_2$ [4] gives red solutions, which after addition of the theoretical amount of $NaClO_4$ or $NaB(C_6H_5)_4$ and partial evaporation yield red microcrystalline solids, according to eq. 1.

$$1/2[IrCl(COD)]_2 + 2\ P(p\text{-}RC_6H_4)_3 + NaA \rightarrow [Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]A + NaCl \qquad (1)$$

$A = ClO_4$ or $B(C_6H_5)_4$

The IR spectra of the isolated complexes show bands which are characteristic of the coordinated ligands along with bands assignable to the anion viz. bands at ~1100sb and ~620m cm^{-1} for ClO_4^- (T_d) [5], and two intense bands in the 1600—1500 cm^{-1} region due to in-plane skeletal C—C stretching modes of the phenyl ring of uncomplexed $B(C_6H_5)_4^-$ [6].

Analytical and other data for the novel complexes are listed in Table 1. The complexes melt without decomposition at 110—160°C, and their conductivities are in the range 100—120 $ohm^{-1}\ cm^2\ mol^{-1}$ ($A = ClO_4^-$) or 70—90 $ohm^{-1}\ cm^2\ mol^{-1}$ ($A = B(C_6H_5)_4^-$), as expected for 1 : 1 electrolytes (taking into account the lower mobility of $B(C_6H_4)_4^-$ [7]).

Reactions

The oxidative addition of HX to cationic complexes of the type $[Ir(COD)L_2]A$ (L = monodentate phosphine ligand) was recently reported [8,9]. We have studied the oxidative addition reactions of $[Ir(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]A$ ($A = ClO_4^-$ (III) and $A = B(C_6H_5)_4^-$ (IV))!

Complex III reacts with a stoichiometric amount of chlorine in CH_2Cl_2 to give $[IrCl_2(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]ClO_4$ (XI), and IV reacts similarly with iodine to give $[IrI_2(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XII). The dichloro-com-

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, MELTING POINTS AND YIELDS OF THE COMPLEXES $[Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]A$

Complex		Found (calcd.) (%)		Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)	Yield (%)
		C	H			
I	($R = CH_3O$, $A = ClO_4^-$)	54.47(54.36)	5.10(4.92)	111	120—122	60
II	($R = CH_3O$, $A = B(C_6H_5)_4^-$)	66.68(67.13)	5.73(5.59)	70	110	78
III	($R = CH_3$, $A = ClO_4^-$)	60.30(59.53)	5.43(5.39)	102	134—136	60
IV	($R = CH_3$, $A = B(C_6H_5)_4^-$)	73.36(72.35)	6.35(6.07)	76	112—114	65
V	($R = H$, $A = ClO_4^-$)	56.57(57.14)	4.71(4.57)	116	130—132	50
VI	($R = H$, $A = B(C_6H_5)_4^-$)	70.35(71.40)	5.41(5.42)	84	150	62
VII	($R = F$, $A = ClO_4^-$)	51.66(51.19)	3.37(3.51)	102	122—124	52
VIII	($R = F$, $A = B(C_6H_5)_4^-$)	64.13(65.23)	4.56(4.47)	82	158—160	29
IX	($R = Cl$, $A = ClO_4^-$)	46.86(47.21)	3.35(3.21)	120	145	49
X	($R = Cl$, $A = B(C_6H_5)_4^-$)	58.98(60.46)	4.22(4.14)	91	140	31

plex XI shows a band due to $\nu(\text{Ir—Cl})$ at ca. 315 cm^{-1} characteristic of two mutually *trans* Cl atoms [10]. The use of an excess of chlorine must be avoided in order to prevent further oxidation to Ir^{IV} [11].

The reaction of CH_3I with IV is slow and yields the complex $[IrCH_3I(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XIII). With $(CH_3)_3SiCl$ a yellow solution is immediately formed, from which $[Ir\{(CH_3)_3Si\}Cl(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]ClO_4$ (XIV) can be isolated ($\nu(\text{Ir—Cl})$ = 305 cm^{-1}).

Treatment of IV with CO or H_2 results in the displacement of the diolefin. Thus, bubbling of CO through a chloroform solution of IV leads to $[Ir(CO)_3\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_4)$ (XV), whose IR spectrum in chloroform exhibits a single band due to $\nu(C{\equiv}O)$ at 2010vs cm^{-1}, which is in accordance with a trigonal bipyramidal structure having the three CO groups in the equatorial plane [12,13]. Hydrogenation of XV results in the loss of one CO group and formation of $[IrH_2(CO)_2\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XVI) which does not absorb further hydrogen. Hydrogenation of acetone solutions of IV displaces the diolefin and yields $[IrH_2\{P(p\text{-}CH_3C_6H_4)_3\}_2(Me_2CO)_2]B(C_6H_5)_4$ (XVII), which can be carbonylated to yield XVI and then XV. Complex XVI shows absorptions due to $\nu(\text{Ir—H})$ and $\nu(C{\equiv}O)$ at 2155, 2140, 2070 and 2040 cm^{-1}, whilst those of XVII are located at 2240 and 2235 cm^{-1} ($\nu(\text{Ir—H})$) and 1655 cm^{-1} ($\nu(C{=}O)$).

Table 2 gives analytical and physical data for the novel complexes XI—XVII.

Catalytic activity

Dichloromethane solutions of $[Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]ClO_4$ containing mono- or diolefins (1 : 100 molar ratio) react with hydrogen at atmospheric pressure to form species [3] which catalyze the homogeneous hydrogenation of these unsaturated substrates.

Table 3 lists hydrogenation rates of 1-heptene along with the relative amount of C_7 hydrocarbons present after 1 min. It will be seen that rapid hydrogenation is generally accompanied by rapid isomerization of 1-heptene to *trans*-2-

TABLE 2

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, MELTING POINTS AND COLOUR OF COMPOUNDS XI—XVII

Complex		Found (calcd.) (%)		Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)	Colour
		C	H			
$[IrCl_2(COD)L_2]ClO_4$	(XI)	55.95(55.62)	5.23(5.64)	79	86	yellow
$[IrI_2(COD)L_2]B(C_6H_5)_4$	(XII)	58.96(59.97)	5.37(5.03)	70	68	brown-yellow
$[IrCH_3I(COD)L_2]B(C_6H_5)_4$	(XIII)	65.37(65.73)	5.84(5.66)	98	58	brown-yellow
$[Ir\{(CH_3)_3Si\}Cl(COD)L_2]ClO_4$	(XIV)	55.29(56.93)	5.29(5.64)	160	110	yellow
$[Ir(CO)_3L_2]B(C_6H_5)_4$	(XV)	68.83(68.85)	5.16(5.19)	78	114	white
$[IrH_2(CO)_2L_2]B(C_6H_5)_4$	(XVI)	69.85(69.35)	5.96(5.47)	83	98	white
$[IrH_2L_2(Me_2CO)_2]B(C_6H_5)_4$	(XVII)	70.29(69.82)	6.20(6.18)	83	128	white

[a] L = $P(p\text{-}CH_3C_6H_4)_3$.

TABLE 3

THE HYDROGENATION OF SOME UNSATURATED SUBSTRATES WITH $[Ir(COD)\{P(p\text{-}RC_6H_4)_3\}_2]ClO_4$

Catalyst precursor		Reduction of 1-heptene					Reduction of 1,4-cyclohexadiene	
		Rate of formation [a] of heptane	Products after one minute				Rate of formation [a] of cyclohexene	Max. % of cyclohexene
			heptane	1-heptene [b]	*trans*-2-heptene	*cis*-2-heptene		
I	(R = CH_3O)	64	64	15	17	4	20	93
III	(R = CH_3)	54	54	19	22	5	17	90
V	(R = H)	42	42	25	27	6	13	92
VII	(R = F)	13	13	42	45	0	10	88
IX	(R = Cl)	6	6	45	49	0	8	94

[a] mol (mol Ir)$^{-1}$ min^{-1}. [b] 3-heptene can be integrated in this peak (GLC).

heptene and small amounts (<7%) of *cis*-2-heptene.

Whereas Schrock and Osborn [14] observed, that in the case of the rhodium species [Rh(diolefin)PR$_3$)$_2$]$^+$ the *cis*- and *trans*-2-hexene formed during the reduction of 1-hexene are not reduced until the concentration of 1-hexene is very low, we have found with our cationic iridium complexes that 1-heptene and *trans*-2-heptene are reduced at approximately the same rate. The data for the hydrogenation of 1,4-cyclohexadiene (see Table 3) show a 88—94% selectivity for cyclohexene. Figure 1 represents a typical hydrogenation with [Ir(COD)$\{$P(p-CH$_3$OC$_6$H$_4$)$_3\}_2$]ClO$_4$ as catalyst precursor.

The catalytic hydrogenations of 1-heptene and 1,4-cyclohexadiene clearly reveal the dependence of the rate on both the substrate and the basicity of the phosphine. Thus, electron-releasing *p*-substituents on the aromatic ring enhance the activity and it appears that a more basic phosphine increases the electron density at the iridium atom and favours the formation of intermediate dihydrides and coordination of the diolefin. Nevertheless, it is likely that the insertion of the coordinated olefin into the Ir—H bond is the rate-limiting step in the hydrogenation [3].

Table 4 shows the results for the catalytic hydrogenation of isoprene and the rate is again seen to increase with the basicity of the triarylphosphine. The hydrogenation results with this diolefin are similar to those obtained for homologous cationic rhodium complexes with bidentate ligands [15], i.e. the diolefin undergoes 1,2- and 1,4-addition of hydrogen and preferential formation of terminal and internal monoolefins. Although some 2-methylbutane can be

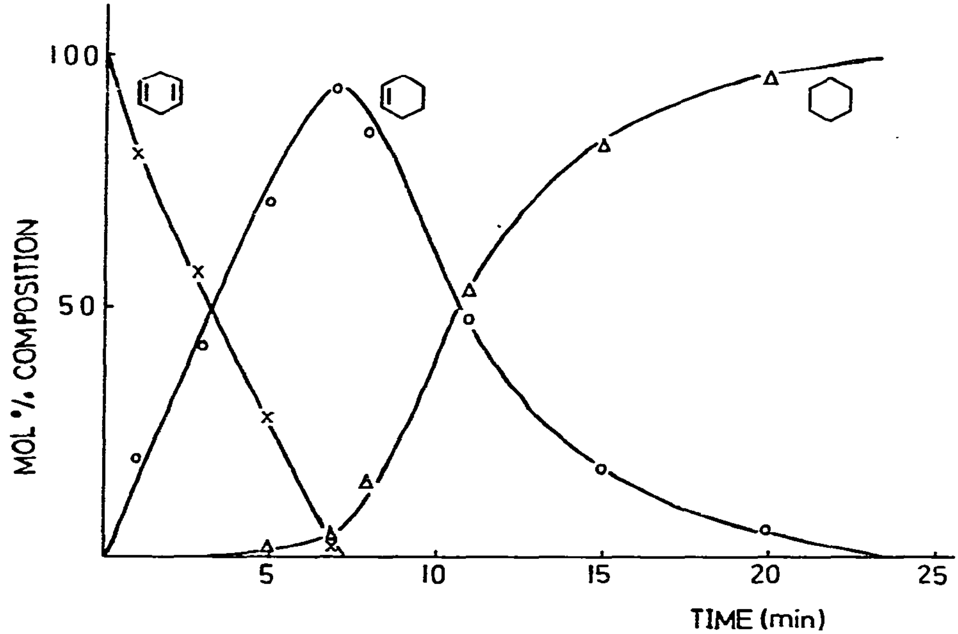

Fig. 1. The catalytic hydrogenation of 1,4-cyclohexadiene in dichloromethane with [Ir(COD)$\{$P(p-CH$_3$OC$_6$H$_4$)$_3\}_2$]ClO$_4$.

TABLE 4

THE CATALYTIC HYDROGENATION OF ISOPRENE

Catalyst precursor		Rate of disappearance [a]	Rate of formation [a] (Max. %)				% of mono-olefins when the isoprene has disappeared
			Terminal	mono-olefins	Internal	mono-olefin	
I	(R = CH_3O)	19	9	(49)	7	(77)	82
III	(R = CH_3)	12	6	(46)	4	(84)	88
V	(R = H)	11	5	(42)	3	(81)	85
VII	(R = F)	3.5	1.2	(41)	1.3	(65)	81
IX	(R = Cl)	1.6	0.4	(20)	0.7	(60)	61

[a] mol (mol Ir)$^{-1}$ min^{-1}.

detected initially, appreciable isomerization of the terminal to the internal olefin only takes place when isoprene is almost completely reduced.

The precursor catalyst [Ir(COD){P(p-RC_6H_4)$_3$}$_2$]ClO_4 generally become inactive as soon as the reduction of the corresponding unsaturated substrate is complete.

The hydrogenation of acrylonitrile and 1-hexyne with [Ir(COD){P(p-CH_3-C_6H_4)$_3$}$_2$]ClO_4 proved unsuccessful, probably because of the strong coordination of these substrates. The IR spectra of the recovered compounds showed absorptions at 2225 (ν(C≡N)) and 2040 cm^{-1} (ν(C≡C)).

Experimental

The C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. Conductivities were measured in ca. 5 × 10^{-4} M acetone solutions with a Philips 9501/01 conductimeter. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the 4000—200 cm^{-1} range).

Catalytic activity experiments were performed in a conventional hydrogenation apparatus. The order of introduction of reactants into the hydrogenation flask was: 0.03 mmol of the catalyst precursor, 3 mmol of the substrate in 15 ml of dichloromethane, and hydrogen. A rapid colour-change was observed as soon as the mixture was stirred in a thermostat bath at 20°C. The hydrogenation rate were determined by analyzing the products with a Perkin-Elmer 3920B chromatograph. The peak areas were obtained with a Minigrator Computing Integrator.

Preparation of the complexes

All the syntheses were carried our at room temperature.

Complexes of the type [Ir(COD){P(p-RC_6H_4)$_3$}$_2$]A (A = ClO_4 or B(C_6H_5)$_4$ (I—X). A methanol suspension of the dimeric complex [IrCl(COD)]$_2$ [4] and a stoichiometric amount of the corresponding phosphine was stirred for 30 min and the calculated amount of $NaClO_4$ or $NaB(C_6H_5)_4$ was then added. The solution was concentrated until a red precipitate was formed, and this was filtered off on kieselguhr, washed with cold methanol and ether, and dissolved in dichloromethane. Evaporation of the solvent yielded the required complexes.

[$IrCl_2(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2ClO_4$ (XI). Chlorine was bubbled through a dichloromethane solution of complex III until the red solution turned yellow, whereupon the chlorine stream was immediately stopped. Complex XI was isolated by evaporating the solvent.

[$IrI_2(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XII). The addition of a stoichiometric amount of iodine to a dichloromethane solution of IV caused a slow colour change to yellow. XII was isolated by evaporating the solvent.

[$IrCH_3I(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XIII). An excess of methyl iodide was added to a dichloromethane solution of IV and stirred for 16 h. The yellow complex XIII was isolated by evaporation.

[$Ir\{(CH_3)_3Si\}Cl(COD)\{P(p\text{-}CH_3C_6H_4)_3\}_2]ClO_4$ (XIV). The addition of chlorotrimethylsilane to a dichloromethane solution of III caused an instantaneous change of colour (red to yellow) whereupon complex XIV was precipitated with ether.

[$Ir(CO)_3\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XV). Carbon monoxide was bubbled for 30 min at room temperature and atmospheric pressure through a chloroform solution of IV. Complex XV was isolated by precipitation with ether.

[$IrH_2(CO)_2\{P(p\text{-}CH_3C_6H_4)_3\}_2]B(C_6H_5)_4$ (XVI). Hydrogen was bubbled for 1 h at room temperature and atmospheric pressure through a chloroform solution of XV, and complex XVI was isolated by addition of ether.

[$IrH_2\{P(p\text{-}CH_3C_6H_4)_3\}_2(Me_2CO)_2]B(C_6H_5)_4$ (XVII). Bubbling of molecular hydrogen for 1 h through an acetone solution of IV gave complex XVII, which was precipitated with ether.

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