Journal of Organometallic Chemistry, 220 (1981) 383—392
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

[Ir(3,4,7,8-Me_4phen) (CH_2=CH_2)$_2$Cl]: A VERY ACTIVE CATALYST PRECURSOR FOR HYDROGEN TRANSFER FROM ALCOHOLS TO UNSATURATED ORGANIC SUBSTRATES

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(Received May 29th, 1981)

Summary

Some new complexes of the type Ir^Ichel(CH_2=CH_2)$_2$Cl (chel = bipy; 4,4′-Me_2bipy; 4,4′-Ph_2bipy; phen; 5,6-Me_2phen; 4,7-Ph_2phen; 3,4,7,8-Me_4phen) behave as catalyst precursors for the hydrogen transfer from alcohols to ketones and Schiff bases. The most active of the complexes is the 3,4,7,8-Me_4phen derivative, which, at 83°C, gave turnovers of up to 2850 cycles/min with cyclohexanone, 2700 cycles/min with 4-tert-butylcyclohexanone and 5000 cycles/min with benzylidenaniline, at a catalyst concentration of 4×10^{-5} *M* and a KOH (cocatalyst) concentration of 8×10^{-4} *M*. Good catalytic activity was observed also at room temperature. Some catalytic activity was found at low substrate concentrations, even in the absence of KOH. The maximum stereoselectivity reached in the reduction of 4-tertbutylcyclohexanone was 97%, the *trans*-alcohol being formed.

Introduction

In a previous paper [1] we described the catalytic activity of Ir^IchelCODCl complexes (chel = bipy; 4,4′-Me_2bipy; phen; 4,7-Me_2phen; 4,7-Ph_2phen; 3,4,7,8-Me_4phen; COD = 1,5-cyclooctadiene) in the transfer of hydrogen from alcohols to ketones (eq. 1).

$$R_2CHOH + R'_2CO \overset{cat}{\rightleftharpoons} R_2CO + R'_2CHOH \qquad (1)$$

For this type of reaction the 3,4,7,8-Me_4phen derivative is the most active catalytic species and also the most stereoselective, giving predominantly the *trans* of the two epimeric alcohols. More recently we demonstrated the possibility of achieving enantioselective reduction of prochiral ketones by using chiral chelating ligands, namely some Schiff bases derived from pyridine-2-aldehyde and optically active primary amines [2].

0022-328X/81/0000—0000/$02.50

We present below results obtained using a new series of complexes $Ir^{I}chel(CH_2{=}CH_2)_2Cl$ (chel = bipy; 4,4′-Me_2bipy; 4,4′-Ph_2bipy; phen; 5,6-Me_2phen; 4,7-Me_2phen; 4,7-Ph_2phen; 3,4,7,8-Me_4phen) as catalyst precursors for the reduction of ketones and of Schiff bases.

Results and discussion

Synthesis of the catalyst precursors

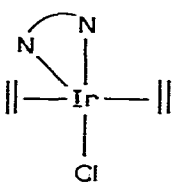
The $Ir^{I}chel(CH_2{=}CH_2)_2Cl$ complexes are orange crystalline compounds, insoluble in water. They were synthesized in high yield (≥90%), by the reaction sequence 2.

$$1/2\ Ir(COT)_2Cl_2 + 4\ CH_2{=}CH_2 \rightarrow Ir(CH_2{=}CH_2)_4Cl + COT\ [3] \qquad (2)$$

$$Ir(CH_2{=}CH_2)_4Cl + chel \rightarrow Irchel(CH_2{=}CH_2)_2Cl + 2\ CH_2{=}CH_2$$

Their characterization and reactivity will be described in a separate paper, and we confine ourselves here to considering some reactions of the 3,4,7,8-Me_4phen derivative (I) which confirm the presence of coordinated olefin. Thus, complex I reacts with molecular hydrogen in methanol at room temperature and atmospheric pressure to give ethane and an unidentified red solid, and when refluxed with propan-2-ol gives a mixture of ethylene and ethane, the latter probably formed by hydrogen transfer from solvent to ethylene. With molecular oxygen in propan-2-ol an orange solution is obtained, with probable formation of a peroxy intermediate, as recently reported for the pentacoordinated Irphen-CODI [4].

The structure we suggest for these complexes is of the type



Catalytic activity

Activation of the complexes

To obtain the catalytically active species from IrchelCODCl complexes it is necessary to oxidize them in propan-2-ol and to reflux the solutions under an inert atmosphere in the presence of KOH [1]. In the case of Irchel-$(CH_2{=}CH_2)_2Cl$ complexes it is sufficient to reflux them in propan-2-ol (displacement and reduction of the ethylene) and then to add the appropriate amount of KOH followed by the substrate. It is also possible to obtain the catalysts from the oxidized complexes, as shown in Scheme I (S = solvent).

SCHEME 1

$$\begin{array}{l} Irchel(CH_2{=}CH_2)_2Cl \xrightarrow[\text{iso-PrOH}]{\Delta} Irchel(S)_xCl + \begin{cases} CH_3CH_3 \\ CH_2{=}CH_2 \end{cases} \\ \quad \text{iso-PrOH} \downarrow \ O_2 \qquad\qquad\qquad\qquad \downarrow \ OH^- \\ complex(ox) \xrightarrow[\Delta]{OH^-} Irchel(S)_xOH \end{array} \qquad (3)$$

Reduction of ketones and Schiff bases

i) Influence of the chelating ligand. The catalytic activity of the methyl derivatives in the reductions of cyclohexanone (CH), 4-terbutyl cyclohexanone (4-TBCH) and benzylidenaniline (BA) increases linearly with the pK_a [5] of the chelating ligand (Fig. 1). For a given pK_a, higher activities are observed for the less delocalized bipy complexes. A similar effect was previously observed in the decarbonylation of dimethyloxalacetic acid catalyzed by Mn^{II} complexes containing the same ligands [6]. Since the methyl groups have low steric requirements their influence is mainly electronic. The phenyl derivatives, the least basic chelating ligands of the series, are sometimes more active than the complexes involving unsubstituted bipy or phen (Table 1).

Complex I is the most active of the series (from 20 to 200 times more active than that involving unsubstituted phen, dependent on the substrate), with initial rates in the range of 2000—5000 cycles/min. Its stability allows very good percentages of conversion to be obtained at high [S]/[cat] ratios (Table 2), the catalyst being unaffected by side-reactions even at very low concentration. Furthermore Table 3 shows that the catalytic activity of complex I is practically the same for the two possible modes of activation of the precursor (Scheme 1). The corresponding complex with COD shows a lower activity, probably owing to an incomplete reduction of the oxidized species. However, the activity of the latter is higher than previously reported [1], because of the more favourable experimental conditions.

ii) Influence of KOH concentration. In agreement with previous results [1], the catalytic activity at constant [S] decreases upon decreasing the [KOH]/[cat.] ratio. Tabe 4 shows that practically no activity is observed when [KOH]/[cat] = 5 and [S]/[cat] = 16 250. If [S] is lowered however, the catalytic activity is restored, clearly indicating its dependence on the [S]/[KOH] ratio.

By decreasing [S] the catalytic activity can be observed at lower and lower KOH concentrations. At suitably low concentration of S some catalytic activity was evident even in the absence of KOH (Table 5).

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TABLE 1

REDUCTION OF UNSATURATED SUBSTRATES WITH PROPAN-2-OL IN THE PRESENCE OF [Irchel(CH_2=CH_2)$_2$Cl] [a]

chel	pK_a [6]	CH [S]/[cat.] = 19.150 ITO (cycles/min)	4-TBCH		BA [S]/[cat.] = 4135 ITO (cycles/min)
			[S]/[cat.] = 16.200 ITO (cycles/min)	*trans*-alcohol (%)	
4.7-Ph_2phen	4.84	—	400	48.0	—
phen	4.93	95	70	57.9	20
5.6-Me_2phen	5.60	430	535	52.5	350
4.7-Me_2phen	5.95	1150	1475	54.5	1500
3.4.7.8-Me_4phen	6.31	2850	2700	77.6	5000
4.4-Ph_2bipy	4.35—4.40	450	590	34.2	430
bipy	4.44	450	400	46.2	510
4.4-Me_2bipy	5.32	1500	1150	45.6	3000

[a] [cat.] = 4×10^{-5} *M*; [KOH] = 8×10^{-4} *M*; H_2O = 0.6%.

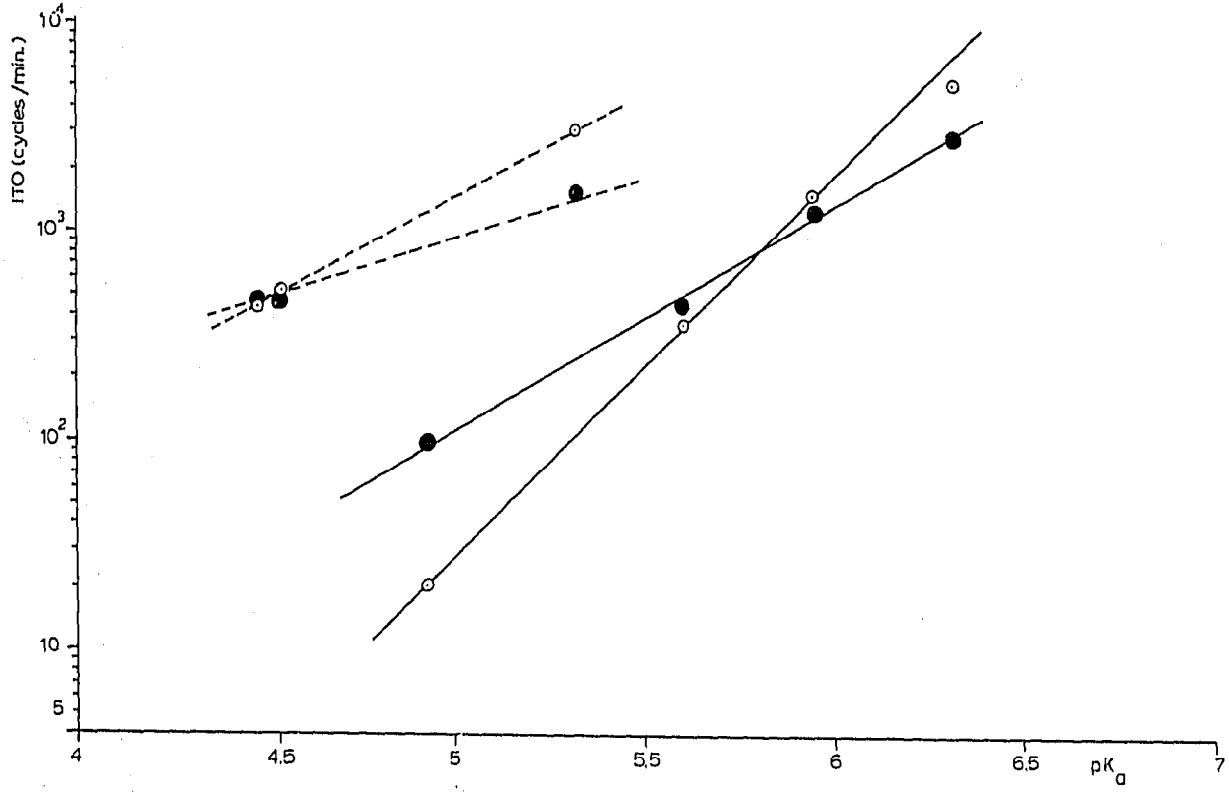


Fig. 1. Reduction of CH and BA with propan-2-ol in the presence of [Irchel(CH_2=CH_2)$_2$Cl]: influence of the nature of chel on the initial reduction rate. [cat] = 4×10^{-5} *M*; [KOH]/[cat.] = 20.0; • CH, [S]/[cat.] = 19150; ○ BA, [S]/[cat.] = 4135.

TABLE 2

REDUCTION OF 4-TBCH WITH PROPAN-2-OL IN THE PRESENCE OF [Ir(3,4,7,8-Me_4phen)(CH_2=CH_2)$_2$Cl] [a]

[S]/[cat.]	Conversion (%)	Time (min)
16.200	99.3	30
40.580	98.8	40
121.750	97.7	120

[a] [KOH] = 8×10^{-4} *M*; H_2O = 0.6%.

TABLE 3

REDUCTION OF 4-BTCH AND BA WITH PROPAN-2-OL IN THE PRESENCE OF [Ir(3,4,7,8-Me_4phen)-L_2Cl]

L_2	4-TBCH [a]		BA [b]	
	Conv. (%)	Time (min)	Conv. (%)	Time (min)
(CH_2=CH_2)$_2$ [c]	98.7	30	95.0	3
(CH_2=CH_2)$_2$ [d]	98.9	30	95.6	4
COD [d]	95.4	60	87.9	20

[a] [cat.]: 4×10^{-5} *M*; [KOH]/[cat.]: 10; [S]/[cat.]: 16200; H_2O = 0.6%. [b] [cat.]: 2×10^{-5} *M*; [KOH]/[cat.]: 40; [S]/[cat.]: 8270; H_2O = 0.6%. [c] Added as solid. [d] Added as oxidized solution (see Experimental).

TABLE 4

REDUCTION OF 4-TBCH WITH PROPAN-2-OL IN THE PRESENCE OF [Ir(3,4,7,8-Me_4phen)(CH_2=CH_2)$_2$Cl] [a]. INFLUENCE OF [S] AND [KOH].

[KOH] (*M*)	[S] (*M*)	Conversion (%) (after 30 min)	*trans*-Alcohol (%)
8×10^{-4}	6.5×10^{-1}	99.3	77.8
4×10^{-4}	6.5×10^{-1}	98.7	78.9
2×10^{-4}	6.5×10^{-1}	5.0	—
2×10^{-4}	2.6×10^{-1}	98.4	78.1

[a] [cat.] = 4×10^{-5} *M*; H_2O = 0.6%.

TABLE 5

REDUCTION OF CH AND 4-TBCH WITH PROPAN-2-OL IN THE PRESENCE OF [Ir(3,4,7,8-Me_4phen)-(CH_2=CH_2)$_2$Cl] [a]

S	[S]/[cat.]	Conversion (%)	Time (h)
4-TBCH	810	52.7	52
CH	950	21.6	24

[a] [cat.] = 4×10^{-5} *M*.

TABLE 6

REDUCTION OF CH AND 4-TBCH WITH PROPAN-2-OL AT DIFFERENT TEMPERATURES [a]

Temperature (°C)	CH ([S]/[cat.] = 1000)			4-TBCH ([S]/[cat.] = 640)		
	Conv. (%)	Time (min)	r [b] (Cycles/min)	Conv. (%)	Time (min)	r (cycles/min)
83	99.2	10	307.5	99.8	5	352
60	99.9	15	129	100.0	10	84
40	99.4	40	45.5	100.0	30	28.5
25	99.0	75	24.5	96.2	90	10.5

[a] Cat. = [Ir(3,4,7,8-Me_4phen(CH_2=CH_2)$_2$Cl]; [cat.] = 1.33×10^{-4} *M*; [KOH]/[cat.] = 4; H_2O = 0.6%. [b] *r* = average rate, measured at conversions between 20 and 30%.

iii) Influence of temperature. Data related to the dependence of catalytic activity on temperature in the range 83—25°C are shown in Table 6. It can be seen that lowering the temperature by 58°C lowers the initial rate only 12 times for CH and almost 33 times for 4-TBCH and so the 3,4,7,8-Me_4phen derivative shows a good catalytic activity even at room temperature. Above 60—70°C 4-TBCH is reduced more rapidly than CH, while the opposite behaviour is observed at lower temperatures.

iiii) Stereoselectivity. The stereoselectivity of the above complexes was examined by using 4-TBCH as a substrate. Complex I is the most suitable species (giving the highest percentage of *trans* alcohol, Table 1). The stereoselectivity is substantially increased by decreasing the [KOH]/[cat.] ratio, but at the expenses of the catalytic activity. A maximum value of 96.5% is reached at 83°C. Upon lowering the temperature in the range 60—25°C there is a small decrease in stereoselectivity at a [KOH]/[cat.] ratio of 4, but this effect is negligible at [KOH]/[cat] $\geq$ 1 (Table 7). The stereoselectivity increases with increasing conversion, and this is more evident at the lowest temperatures. The selectivity depends on the substrate concentration. By operating at low substrate concentrations a selectivity $\geq$ 90% was observed at [KOH]/[cat.] > 1,

TABLE 7

REDUCTION OF 4-TBCH WITH PROPAN-2-OL [a]. STEREOSELECTIVITIY AS FUNCTION OF TEMPERATURE

Temperature (°C)	[KOH]/[cat.] = 4 [b]				[KOH]/[cat.] = 0.75 [c]		
	trans-Alcohol (%) (conv. (%))		*trans*/*cis*	*trans*-Alcohol (%) (conv. = 100%)	*trans*/*cis*	*trans*-Alcohol (%) (conv. = 100%) [d]	*trans*/*cis*
25	62.5	(10)	1.7	80	4.0	97	32.3
40	68.0	(10)	2.1	82.5	4.7	97 [e]	32.3
60	76	(14)	3.2	85	5.6	96.5	27.5

[a] Cat. = [Ir(3,4,7,8-Me_4phen)(CH_2=CH_2)Cl]; [cat.] = 1.33×10^{-4} *M*; H_2O = 0.3%. [b] [S]/[cat.] = 640; [c] [S]/[cat.] = 80. [d] The stereoselectivity is not significantly changed by prolonging the reaction for 1 h. [e] The same value is obtained at [KOH]/[cat.] = 1; 97.5% with 0.6% H_2O.

TABLE 8

REDUCTION OF 4-TBCH WITH PROPAN-2-OL [a]. STEREOSELECTIVITY AS FUNCTION OF [S]

[S]/[cat.]	*trans*-Alcohol (%)	Conversion (%)	*trans*/*cis*
640	82.5	100	4.7
160	90	100	9.0
80	91	100	10.1

[a] Cat. = [Ir(3,4,7,8-Me_4phen)(CH_2=CH_2)Cl]; [cat.] = 1.33×10^{-4} *M*; [KOH]/[cat.] = 4; H_2O = 0.6%; 40°C.

TABLE 9

REDUCTION OF 4-TBCH WITH PROPAN-2-OL IN THE PRESENCE OF [Ir(3,4,7,8-Me_4phen)L_2Cl] [a]

L_2	[KOH]/[cat.]	Conversion (%)	Time (min)	*trans*-Alcohol (%)
(CH_2=CH_2)$_2$ [b]	5.0	98.0	15	76.0
(CH_2=CH_2)$_2$ [b]	2.5	98.0	30	80.3
(CH_2=CH_2)$_2$ [b]	1.1	95.0	120	94.7
(CH_2=CH_2)$_2$ [c]	1.1	91.0	180	95.7
COD [c]	1.1	98.2	300	96.4

[a] [cat.] = 4×10^{-5} *M*; [S]/[cat.] = 1.620; H_2O = 0.6%. [b] Added as solid. [c] Added as oxidized solution (see experimental).

while values $\geq$97% were reached at [KOH]/[cat.] ratio $\leq$1 (Table 8). On the other hand, the stereoselectivity does not depend significantly on the nature of the precursor or on the mode of activation (Table 9), which suggests that only one catalytic species is formed, and that this is the same for all the precursors.

Mechanism

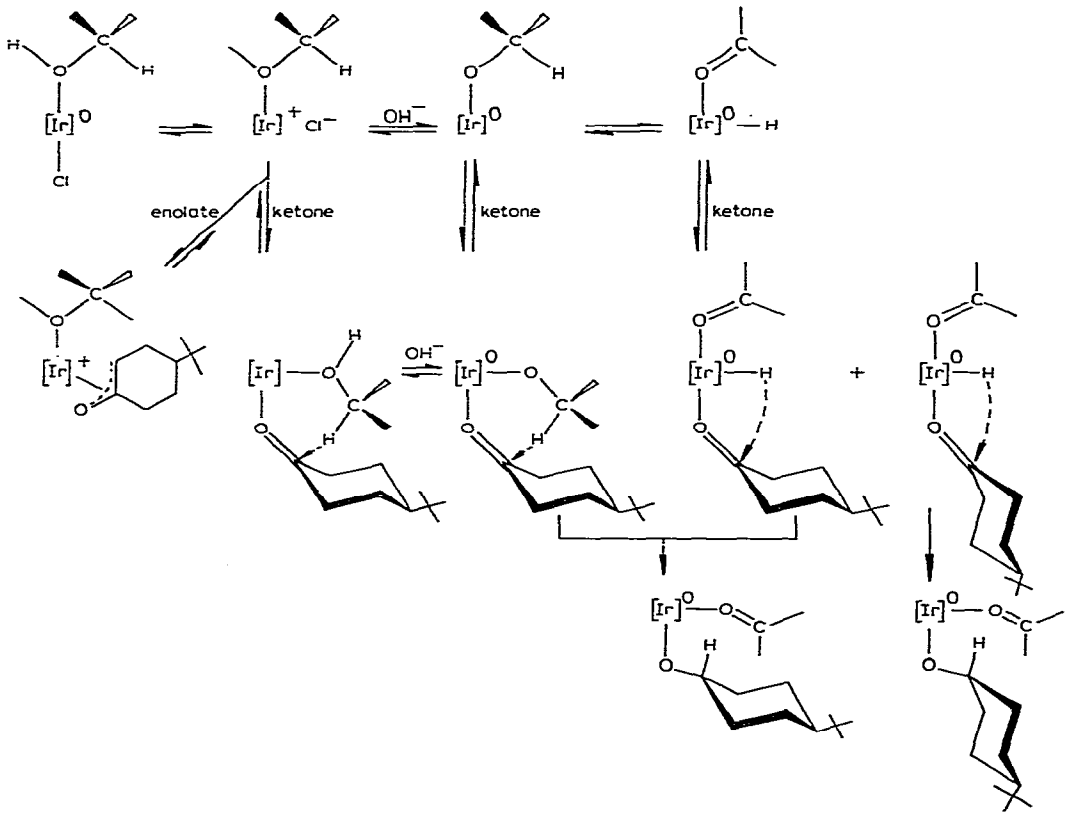
On the basis of the results it is possible to define in greater detail the mechanism previously suggested for the catalytic cycle [1] (Scheme 2). We still regard as the active species the cationic solvated Ir^I complex, which is in equilibrium with the neutral form with coordinated chloride after ethylene displacement from the precursor. The presence of KOH is very important for the reaction. The main rôle of the OH^- ion is to convert the propan-2-ol coordinated to the Ir^I ion in the neutral isopropoxy derivative. Furthermore, it favours the formation of enolate, which, when coordinated to the cationic derivative, would act as an inhibitor, which accounts for the loss of catalytic activity at high substrate concentrations.

The hydrogen of the isopropoxy group can be transferred to the coordinated ketone in two ways. The first, already discussed [1], involves the formation of an Ir^I hydride derivative through β-elimination followed by transfer of the hydride hydrogen to the ketone *. The second assumes direct transfer of hydrogen from isopropoxy to the coordinated ketone, through a six-centre transition state of the type proposed for the Meerwein-Ponndorf-Oppenauer

* In agreement with this hypothesis a slow evolution of hydrogen was observed in the absence of ketone [7].

SCHEME 2

Mechanism of reduction of ketones with propan-2-ol in the presence of Ir^I complexes of bipy, phen and derivatives (represented as [Ir])



reaction [8]. This route is followed when the coordination of the ketone precedes the formation of the hydride, and is favoured by a high ratio of isopropoxy to hydride derivative (that is by an increase in the ratio between the rates of hydride transfer and β-elimination). In agreement with the sharp increase in the reaction rate with the increase in the pK_a of the nitrogen-containing donor system [9], the second route must be responsible for the high stereoselectivity observed at low KOH and substrate concentrations, as found for aluminium alkoxides [8]. The loss of stereoselectivity upon increasing [KOH] and [S] must be due to an equilibration, and also implies a contribution by the hydride route, which seems to give the opposite stereoselectivity [10].

Conclusion

Ketones and Schiff bases are reduced with satisfactory results by hydrogen transfer from propan-2-ol in the presence of the above complexes. Complex I is a better precursor than the corresponding COD derivative because it is activated more easily and more completely and shows a high catalytic activity even at room temperature.

We have so far considered the factors which influence the rate and selectivity of the catalytic system only from a qualitative point of view. We intend to make a quantitative study of these factors in order to provide a more detailed description of the mechanism, on the basis of appropriate kinetic data.

Up to now high selectivity has been obtained only at the expenses of activity or by operating at very low [S]/[cat] ratios. The observed trends suggest, however, that high activity and selectivity could be reached at the same time by starting from IrchelL_2OR derivatives, which should be active even in the absence of KOH. The activity and stereoselectivity would probably also be improved by using more basic chelating ligands.

Experimental

Preparation of the Irchel(CH_2=CH_2)$_2$Cl complexes

0.25 g (0.28 mmol) of Ir(COT)$_2$Cl is dissolved in deaerated benzene(25 ml) under inert argon or nitrogen. The filtered orange solution is saturated with ethylene for 10 min, turning light yellow. A small excess (0.6 mmol) of recrystallized chel is then added under an ethylene stream: gas is immediately evolved and orange-red solids are formed. Some very soluble complexes (chel = 4,7-Phen$_2$phen; 4,4'-Me$_2$bipy; 4,4'-Ph$_2$bipy) are precipitated by addition of 10—15 ml of n-heptane, saturated with ethylene. After 20—30 min the products are filtered off and dried briefly in vacuo at room temperature. Some complexes contain benzene of crystallization, as can be seen from the analytical data listed in Table 10. Low values for C and H analyses are due to the fact that the complexes lose ethylene more or less easily, depending on the chelating ligand.

Hydrogen transfer reactions

Chemicals. All the reagents for the catalytic reactions were redistilled and 4-TBCH (Fluka) was recrystallized twice from hot propan-2-ol. The propan-2-ol

TABLE 10

ELEMENTAL ANALYSES OF THE [Irchel(CH_2=CH_2)$_2$Cl] · *n* BENZENE COMPLEXES

Chel	*n*	Found (calcd.) (%)		
		C	H	N
phen	0	41.4	3.45	5.80
		(41.4)	(4.10)	(5.69)
5,6-Me$_2$phen	0	42.8	3.88	5.40
		(43.9)	(4.10)	(5.69)
4,7-Me$_2$phen	0	41.3	3.96	5.45
		(43.9)	(4.10)	(5.69)
4,7-Ph$_2$phen	0	53.1	3.96	4.31
		(56.4)	(3.93)	(4.55)
3,4,7,8-Me$_4$phen	1/2	48.6	4.86	5.04
		(49.4)	(4.87)	(5.01)
bipy	1/2	42.7	4.05	5.98
		(42.6)	(4.00)	(5.85)
4,4'-Me$_2$bipy	0	39.9	4.23	5.71
		(41.4)	(4.31)	(6.00)
4,4'-Ph$_2$bipy	0	52.1	4.25	4.71
		(52.7)	(4.09)	(4.73)

used as the hydrogen donor was a Baker commercial product (No. 8067) and was redistilled over CaO. The aqueous solution of KOH was freshly prepared each time and deaerated before use. BA was prepared by condensation of benzaldehyde and aniline in anhydrous ethanol at 60°C and recrystallized twice from hot ethanol.

Procedure. The reaction was carried out in a three-necked flask of 100 ml which was placed in an electrical mantle intended for 50 ml containers in order to ensure only partial contact of the reaction flask with the heater, so avoiding deposition of catalyst at the edge of the solution. The flask was connected to an argon source and equipped with a reflux condenser and a dropping funnel thermostatted at 60—61°C with a water jacket. A slow stream of inert gas was maintained over the solution during the reaction to exclude air. Magnetic stirring was provided. The complex was used as the solid or as an oxidized solution, prepared by suspending the solid in stirred propan-2-ol overnight (e.g. 11.4 mg in 100 ml of solvent) in contact with air. The clear yellow-orange solution formed can be stored unchanged for months.

When the solid was used, it was added to 50 ml of boiling propan-2-ol and refluxed for 10—15 min before addition of the KOH solution. The hot solution of the substrate was added dropwise after a further 30 min.

In the case of the oxidized solution, the required amount was pipetted from the mother solution, diluted to 50 ml and refluxed for 10—15 min; KOH was then added, followed after 45—50 min by the substrate. The time of reaction was reckoned from completion of the substrate addition.

The reactions at lower temperatures were performed in a thermostatted three-necked flask. Activation of the catalyst was achieved by heating the precursor in deaerated isopropanol at 60°C for 30 min and then in the presence of KOH for one hour more. Afterwards the solution was brought to the reaction temperature before addition of the substrate.

Analyses. The reactions were monitored by GLC. Samples were drawn at appropriate intervals from the reaction flask and analyzed (2 m columns, filled with Cromosorb W 80—100 mesh; active phases: 10% Carbowax 20M (4-TBCH 130°C, CH 120°C) OS 200 (BA, 175°C)).

Acknowledgements

This work was carried out with the financial support of Donegani, (Montedison S.p.A.) and of the University of Trieste. Dr. E. Cebulec performed the elemental analyses.

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