Selective Hydrogenation of PhCH=CHCOMe to the Unsaturated Alcohol catalysed by $[IrH_3(PR_3)_3]$ (R = alkyl or aryl) *

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Selective hydrogenation of benzylideneacetone (PhCH=CHCOMe) catalysed by iridium–phosphine systems prepared *in situ* is reported. Depending on the steric properties of the phosphine employed and the P:Ir ratio, different species are formed in solution, as evidenced by n.m.r. spectroscopy. $[IrH_5(PR_3)_2]$ (R = alkyl or aryl) is a catalyst for the hydrogenation of the carbon–carbon double bond, whereas $[IrH_3(PR_3)_3]$ catalyses the reduction of the carbonyl group with a selectivity up to 100%.

Reduction of the carbonyl group in α,β-unsaturated carbonyl compounds is often an important step in organic synthesis. Hydrogenation of the carbon–carbon double bond is readily accomplished under mild conditions with high selectivity, whereas catalytic reduction of the conjugated carbonyl group is still a challenging problem. In the presence of transition-metal catalysts, saturated carbonyl compounds and in some cases saturated alcohols are obtained.[1] Only a few examples are reported for the formation of unsaturated alcohols in high yield by reduction of α,β-unsaturated aldehydes in hydrogen transfer[2,3] or hydrogenation reactions.[4,5] Highly selective catalytic hydrogenation of α,β-unsaturated ketones is therefore an open problem and only in a preliminary account of this work[6] has it been reported that PhCH=CHCOMe is reduced to PhCH=CHCH(OH)Me with a selectivity close to 100% using iridium–phosphine systems as catalysts.

This paper reports a detailed study of this hydrogenation reaction; the various parameters influencing catalytic activity and selectivity have been investigated. Moreover, information about the nature of the catalytically active species have been obtained.

Results and Discussion

The hydrogenation of PhCH=CHCOMe catalysed by iridium–phosphine complexes can be represented by Scheme 1.

The catalytic system is prepared *in situ* from $[\{Ir(cod)(OMe)\}_2]$ (cod = cyclo-octa-1,5-diene) and the appropriate phosphine, using toluene or propan-2-ol as solvent. From the results summarized in Table 1, it can be seen that both the nature of the phosphine and the amount of phosphine employed play an important role in determining the activity and selectivity of the catalytic system. Runs 5—8 of Table 1 show the results obtained with $PMePh_2$ in the range of P:Ir ratio of 2—10. In the presence of a two-fold excess of phosphine the carbon–carbon double bond is hydrogenated, and the saturated ketone so formed can be further reduced to the corresponding saturated alcohol. Such a selectivity is generally the favoured one in the reduction of α,β-unsaturated ketones.[1] In the presence of a higher excess of phosphine, hydrogenation of the C=C bond [reaction (B)] is depressed and hydrogenation of the carbonyl group takes place [reaction (A)] with a drop in the overall catalytic activity. At P:Ir = 10 the selectivity in unsaturated alcohol reaches 100%.

When phosphines with a smaller cone angle[7] are used, as in the case of PMe_2Ph (cone angle θ = 122°), a rather different behaviour is observed. Addition of an excess of this phosphine depresses the catalytic activity, but formation of the unsaturated alcohol is not observed (Table 1, runs 1 and 2). Low selectivity in unsaturated alcohol is also obtained when phosphines with a large cone angle such as $P(C_6H_4Me\text{-}o)_3$ (θ = 194°) are used (Table 1, runs 20 and 21).

This behaviour is summarized in Figure 1, where the selectivity in unsaturated alcohol [reaction (A)] is plotted *vs.* the cone angle of the phosphines. Both in toluene and in propan-2-ol the same bell-shaped curve is obtained. Selectivity higher than 90% is found in the cone angle range 135—150°, but it drops to zero for cone angles out of this range.

From these results it appears that for obtaining an iridium–phosphine system highly selective toward reduction of the carbonyl group in α,β-unsaturated ketones two conditions should be met: (*i*) suitable steric hindrance of the ligands and (*ii*) high values of P:Ir. Figure 2 reports the selectivity in unsaturated alcohol as a function of P:Ir ratio, for those phosphines of intermediate bulk which meet condition (*i*). The excess of phosphine required to obtain a selective catalyst increases on increasing the bulk of the ligand. These results suggest that depending on the experimental conditions used, namely the bulk of the phosphine and the P:Ir ratio, different catalytic species with different selectivity will be formed. The species obtained at P:Ir = 2, which is responsible for the C=C bond reduction, is likely to have two co-ordinated phosphines. When phosphines of intermediate bulk are employed, using a greater excess of phosphine a different species is formed, which is a selective catalyst for the hydrogenation of the carbonyl group: such a species could be tentatively formulated as a complex with three or four phosphines in the co-ordination sphere of the iridium atom.

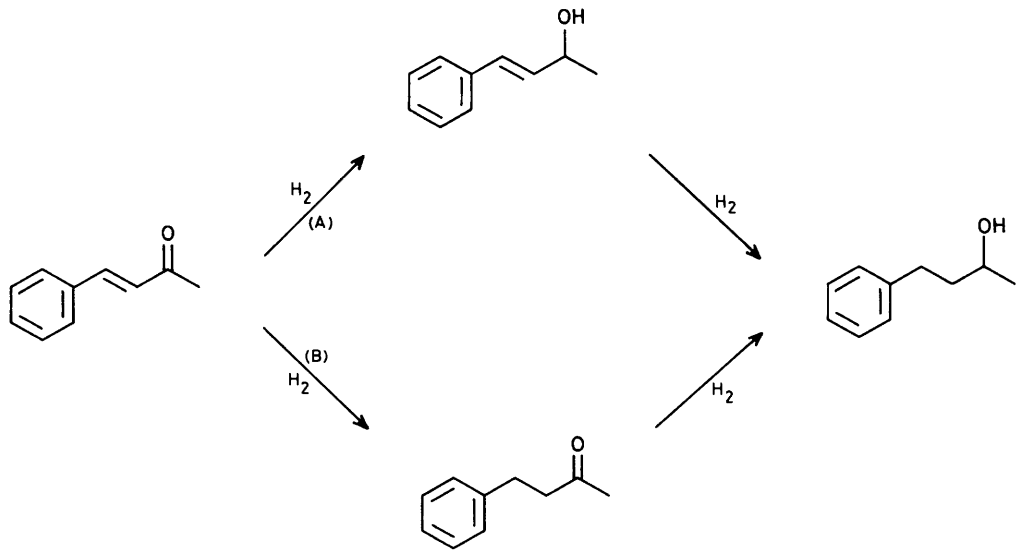
In order to obtain more information on the catalytic species formed *in situ* and involved in the reaction, we used some iridium–phosphine compounds as catalyst precursors. Under our experimental conditions $[Ir(cod)(PR_3)_2]^+$ (PR_3 = $PEtPh_2$ or $PMePh_2$)[8] have catalytic activity and selectivity very similar to those observed with the system prepared *in situ* from $[\{Ir(cod)(OMe)\}_2]$ + $PEtPh_2$ or $PMePh_2$ at P:Ir = 2. The results obtained using this species (Table 2, runs 1 and 10) are consistent with the previously reported reduction of olefins catalysed by $[M(diene)(PR_3)_2]^+$ (M = Rh or Ir; PR_3 = $PMePh_2$ or PPh_3).[9] Complexes with four co-ordinated phosphines $[Ir(PR_3)_4]^+$ (PR_3 = PEt_2Ph or $PMePh_2$),[10] compared with the system prepared *in situ* at P:Ir > 4, show the same high selectivity in unsaturated alcohol, but a lower catalytic activity (Table 2, runs 3 and 12). Such cationic species in the presence of H_2 give the dihydro complexes *cis*-$[IrH_2(PR_3)_4]^+$, as evidenced by ^1H n.m.r. (PR_3 = PEt_2Ph: triplet of doublets centred at δ −14.5 to high field of $SiMe_4$) and ^{31}P n.m.r. [two

* *Non-S.I. unit employed:* atm = 101 325 Pa.

Table 1. Effect of phosphorus:iridium ratio in the hydrogenation of PhCH=CHCOMe[a]

Run	Phosphine	Cone angle (θ)/°	P:Ir	% Conversion (hours)	% Saturated ketone	% Saturated alcohol	% Unsaturated alcohol	Selectivity[b]
1	PMe_2Ph	122	3	100 (24)	60	40	0	0
2			10	9 (21)	9	0	0	0
3	PBu^n_3	132	2	99 (5)	97	2	0	0
4			10	61 (23)	15	6	40	66
5	$PMePh_2$	136	2	98 (4)	92	5	1	1
6			3	98 (7)	26	26	46	47
7			5	94 (22)	11	1	82	87
8			10	51 (46)	0	0	51	100
9	PEt_2Ph	136	4	70 (5)	10	6	54	77
10			10	96 (28)	5	1	90	94
11	$PEtPh_2$	140	2	97 (5)	86	10	1	1
12			5	92 (7)	7	1	84	90
13			10	99 (10)	2	1	96	97
14	PPh_2Pr^i	150	2	99 (4)	92	7	0	0
15			5	88 (22)	36	17	35	39
16			10	93 (24)	6	2	85	92
17	PBu^tPh_2	157	10	26 (1)	9	0	17	65
				89 (4)	25	13	51	58
				98 (7)	20	31	47	48
				100 (24)	6	77	17	17
18	PBu^t_2Ph	170	2	100 (21)	77	23	0	0
19			10	84 (7)	23	10	51	60
				98 (24)	16	30	52	53
				100 (48)	13	44	43	43
20	$P(C_6H_4Me\text{-}o)_3$	194	10	97 (4)	80	16	1	1
21	$P(C_6H_4OMe\text{-}o)_3$	194	10	92 (5)	72	18	2	2

[a] Reaction conditions: catalyst prepared *in situ*, $[\{Ir(cod)(OMe)\}_2]$ + phosphine; [Ir] = 4 × 10^{-4} mol dm^{-3}, substrate:catalyst = 500, $P(H_2)$ = 30 atm, temperature = 100 °C, toluene solvent. [b] Selectivity in unsaturated alcohol (% unsaturated alcohol:% conversion).



Scheme 1.

triplets centred at δ −22.0 and −22.5 (free PEt_2Ph δ −17.0) to high field of 85% H_3PO_4]. This reaction has already been reported by Crabtree *et al.*[11] for $[Ir(PMe_2Ph)_4]^+$. $[IrH_2(PR_3)_4]^+$ also show a lower catalytic activity than the systems prepared *in situ* at P:Ir = 10 (Table 2, runs 6—9), ruling out the possibility that a tetraphosphine complex is the catalytically active species for the hydrogenation of the carbonyl group.

All the data so far discussed could be interpreted in terms of a possible equilibrium such as that shown below.

$$[IrH_a(PR_3)_2] \overset{+PR_3}{\rightleftharpoons} [IrH_b(PR_3)_3] \overset{+PR_3}{\rightleftharpoons} [IrH_c(PR_3)_4]$$

(1) (2) (3)

Table 2. Hydrogenation of PhCH=CHCOMe catalysed by iridium–phosphine complexes[a]

PR_3	Run	Procatalyst[b]	P_{total}: Ir	% Conversion (hours)	% Saturated ketone	% Saturated alcohol	% Unsaturated alcohol	Selectivity[c]
$PEtPh_2$	1	$[Ir(cod)(PR_3)_2]^+$			84	9		0
	2	$[Ir] + PR_3$	2	93 (5)	86	10	0	1
			2	97 (5)			1	
PEt_2Ph	3	$[Ir(PR_3)_4]^+$	4	36 (3)	6	0	30	84
	4	$[Ir] + PR_3$	4	70 (5)	10	6	54	77
	5	$[Ir(PR_3)_4]^+ + PR_3$	6	30 (5)	5	0	25	83
				96 (70)	4	1	91	95
	6	$[IrH_2(PR_3)_4]^+ + PR_3$	4	92 (28)	6	3	83	90
	7	$[IrH_2(PR_3)_4]^+ + PR_3$	6	71 (120)	6	2	63	89
	8	$[IrH_2(PR_3)_4]^+ + PR_3$	8	86 (144)	4	2	80	93
	9	$[Ir] + PR_3$	10	95 (28)	5	1	89	94
$PMePh_2$	10	$[Ir(cod)(PR_3)_2]^+$	2	99 (4)	94	5	0	0
	11	$[Ir] + PR_3$	2	98 (4)	92	5	1	1
	12	$[Ir(PR_3)_4]^+$	4	43 (92)	1	0	42	98
	13	$[Ir] + PR_3$	10	51 (46)	0	0	51	100
PBu^n_3	14	$[IrH_2(PR_3)_4]^+$	4	30 (25)	6	1	23	77
	15	$[Ir] + PR_3$	10	61 (23)	15	6	40	66
PMe_2Ph	16	$[Ir] + PR_3$	3	100 (24)	60	40	0	0
	17	$[IrH_2(PR_3)_4]^+$	4	3 (23)	3	0	0	0
	18	$[Ir] + PR_3$	10	9 (21)	9	0	0	0

[a] Reaction conditions as reported in Table 1. [b] [Ir] = $[\{Ir(cod)(OMe)\}_2]$. [c] Selectivity in unsaturated alcohol.

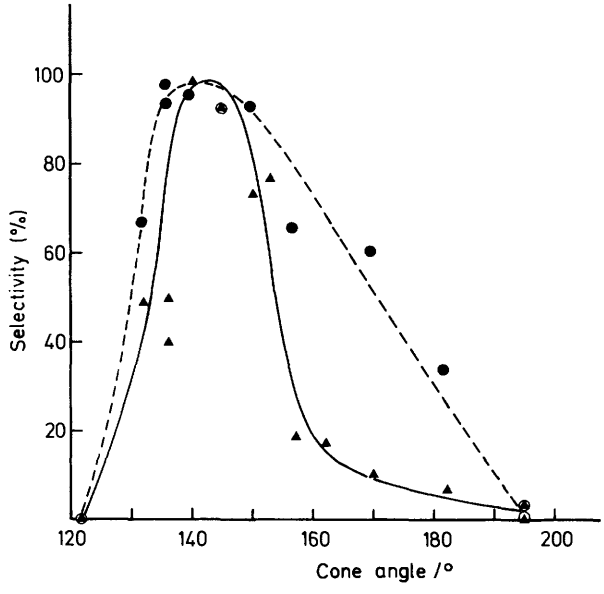


Figure 1. Selectivity in unsaturated alcohol *vs.* cone angle of the phosphines. Solvent: toluene (– – ● – –) or propan-2-ol (—▲—). Reaction conditions are reported in Table 1, P:Ir = 10

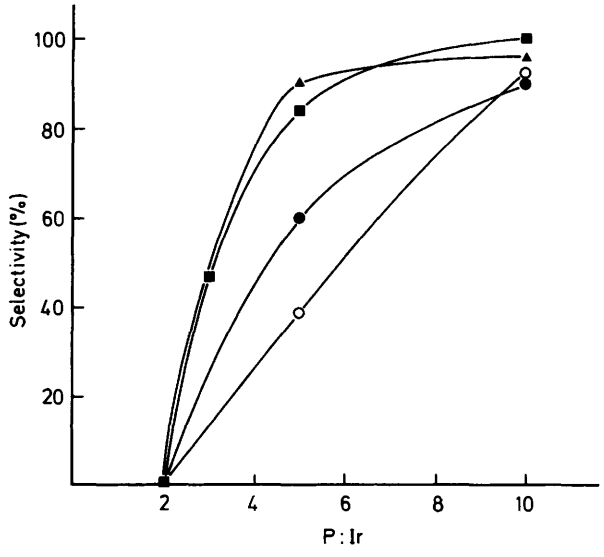


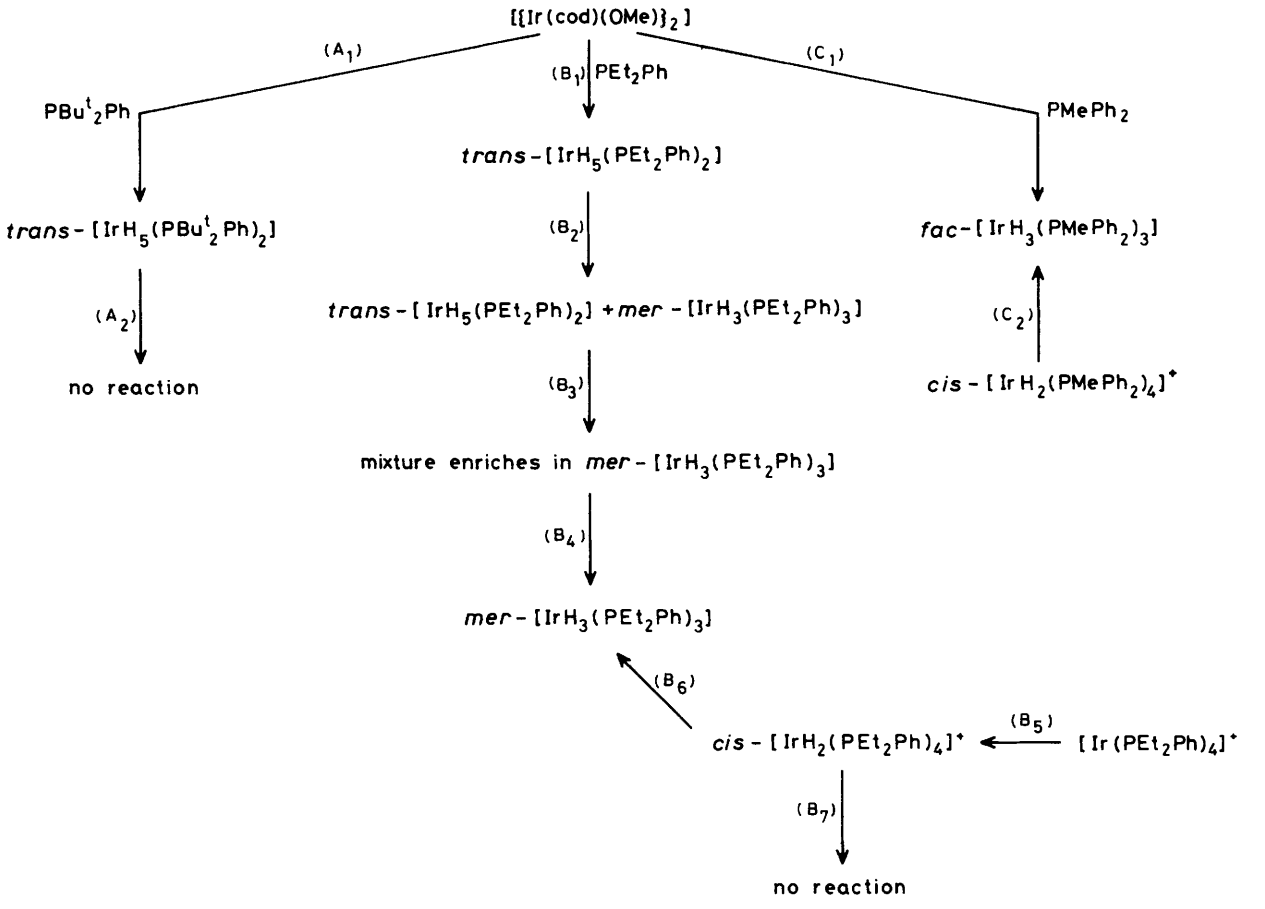
Figure 2. Selectivity in unsaturated alcohol *vs.* P:Ir ratio. PR_3 = $PMePh_2$ (θ = 136°) (■), $PEtPh_2$ (θ = 140°) (▲), $P[CH_2CH(Me)Et]Ph_2$ (θ = 145°) (●), or PPh_2Pr^i (θ = 150°) (○)

Depending on the nature of the phosphine employed and the P:Ir ratio, one of these hydrido-iridium complexes could be the prevalent species in the reaction mixture. In the presence of an excess of a very bulky phosphine (cone angle θ > 155°) the main species is likely to be the bis(phosphine) complex (**1**), as the mutual steric interactions would prevent the co-ordination of a third phosphine.[12] Such a species can co-ordinate the substrate either *via* the carbonyl group or *via* the C=C bond, but the latter co-ordination is the favoured one, therefore selective hydrogenation of the olefinic function is observed (Table 1, runs 20 and 21). When phosphines of intermediate bulk (θ = 135–155°) are used, the predominant species in solution could be that with three co-ordinated phosphines (**2**), resulting in a rather crowded situation in the co-ordination sphere of the iridium atom. Co-ordination of the substrate to such species through the carbon–carbon double bond would be sterically unfavoured,

Table 3. Asymmetric hydrogenation of PhCH=CHCOMe catalysed by the iridium–*S*(+)-P[$CH_2CH(Me)Et$]Ph_2 system[a]

Run	P:Ir	% Conversion (hours)	% Saturated ketone	% Saturated alcohol	% Unsaturated alcohol	Selectivity[b]	E.e.[c]
1	2	100 (4)	86	14	0	0	0
2	5	86 (23)	27	7	52	60	7
3	10	98 (24)	6	3	89	90	6
4	20	96 (22)	3	3	90	94	4

[a] Reaction conditions as reported in Table 1. [b] Selectivity in unsaturated alcohol. [c] % Enantiomeric excess (e.e.) in *S*(−) isomer.



Scheme 2. All the reactions were carried out in toluene. (A_1) P:Ir = 5, $P(H_2)$ = 1 atm, 25 °C; (A_2) $P(H_2)$ = 20 atm, 100 °C; (B_1) P:Ir = 2, $P(H_2)$ = 1 atm, 25 °C; (B_2) P:Ir = 5, $P(H_2)$ = 1 atm, 25 °C; (B_3) P:Ir = 10, $P(H_2)$ = 1 atm, 25 °C; (B_4) P:Ir = 10, $P(H_2)$ = 1 atm, 80 °C; (B_5) $P(H_2)$ = 1 atm, 25 °C; (B_6) $P(H_2)$ = 20 atm, 100 °C; (B_7) $P(H_2)$ = 1 atm, 80 °C; (C_1) P:Ir = 5, $P(H_2)$ = 1 atm, 25 °C; (C_2) $P(H_2)$ = 20 atm, 100 °C

therefore co-ordination *via* the less sterically demanding carbonyl group probably occurs, with consequent selective hydrogenation of this function (Table 1, runs 8, 10, 13, and 16). If the reaction is performed in the presence of an excess of a small phosphine ($\theta < 135°$), type (**3**) complexes could be formed in high concentration. Such a species has four phosphines in the co-ordination sphere of the iridium atom, and is therefore unable to co-ordinate the substrate, with consequent low catalytic activity (Table 1, run 2). Consistently in the hydrogenation of the saturated ketone PhCOMe with $[IrH_2(PR_3)_4]^+$ as catalyst precursor, the catalytic activity decreases in the order PR_3 = PEt_2Ph, PBu^n_3, PMe_2Ph, the last phosphine giving a totally inactive system.

With the aim of finding evidence for such an equilibrium we carried out an investigation by n.m.r. spectroscopy of the species formed under our experimental conditions. The system prepared *in situ* from [{Ir(cod)(OMe)}$_2$] + PEt_2Ph at P:Ir = 2 (solvent C_6D_6) in the presence of H_2 forms *trans*-$[IrH_5(PEt_2Ph)_2]$ (^{1}H n.m.r. spectrum: triplet at δ −9.9, J_{PH} = 13.5 Hz).[13] Formation of this species probably occurs *via* an intermediate such as $[IrH(cod)(PEt_2Ph)_2]$.[14] As in these experimental conditions the C=C double bond of benzylideneacetone is hydrogenated, this pentahydrido complex is likely to be the catalyst responsible for this reaction. By increasing the P:Ir ratio, a new hydridic signal is detected together with the triplet at δ −9.9: the relative intensity of these

Table 4. Asymmetric hydrogenation of PhCH=CHCOMe in various solvents catalysed by the iridium–*S*(+)-P[$CH_2CH(Me)Et$]Ph_2 system[a]

Run	Solvent[b]	% Conversion (hours)	% Saturated ketone	% Saturated alcohol	% Unsaturated alcohol	Selectivity[c]	E.e.[d]
1	Pr^iOH	98 (24)	2	1	95	96	1
2	Bu^sOH	71 (46)	4	0	67	94	2
3	MeOH	20 (94)	4	0	16	80	*e*
4	EtOH	70 (46)	2	0	68	97	0
5	thf	97 (24)	3	1	93	96	4
6	1,4-Dioxane	96 (45)	3	1	92	96	3
7	MeCOOH	15 (20)	15	0	0	0	
8	dmf	50 (69)	2	0	48	96	5
9	$C_2H_4Cl_2$-1,2	2 (21)	2	0	0	0	
10	Cyclohexane	50 (24)	3	0	47	94	2
11	Toluene	96 (22)	3	3	90	94	4

[a] Reaction conditions as reported in Table 1; P:Ir = 20. [b] thf = Tetrahydrofuran, dmf = dimethylformamide. [c] Selectivity in unsaturated alcohol. [d] % Enantiomeric excess (e.e.) in *S*(−) isomer. [e] E.e. not measured.

absorptions is shifted in favour of the former if a further excess of phosphine is added. When the sample obtained at P:Ir = 10 is heated to 80 °C, the triplet at δ −9.9 disappears; the pattern of the signal at higher field, which is now the only absorption in the hydridic region, consists of a doublet of quartets centred at δ −11.8 together with a doublet of triplets of triplets centred at δ −13.5: the chemical shifts and the coupling constants correspond to those[15] of *mer*-[$IrH_3(PEt_2Ph)_3$] [see Scheme 2, routes (B_1—B_4)]. This complex, which forms in the experimental conditions used for the selective hydrogenation of the carbonyl group, could be active species for this reaction, or at least a close catalyst precursor. [$IrH_3(PPh_3)_3$] has been reported to be an active catalyst for the hydrogenation of saturated[16] or unsaturated aldehydes,[17] but only if acetic acid is present, which actually reacts with the catalyst to give a mixture of products.

The formation of *mer*-[$IrH_3(PEt_2Ph)_3$] is also observed *via* n.m.r. starting from [$Ir(PEt_2Ph)_4$]$^+$ or [$IrH_2(PEt_2Ph)_4$]$^+$; however this reaction requires more severe experimental conditions [see Scheme 2, routes (B_5), (B_6), (B_7), or (C_2)], accounting for the lower catalytic activity obtained with these cationic complexes.

A similar behaviour is observed when $PMePh_2$ is used. The species obtained with this phosphine, at P:Ir = 5 in a hydrogen atmosphere, is identified[18] as *fac*-[$IrH_3(PMePh_2)_3$] (second-order multiplet centred at δ −11.5), whereas formation of the pentahydrido bis(phosphine) species is not observed (Scheme 2, route C_1). The system with $PEtPh_2$ gives rise under the same experimental conditions to a mixture of *fac*- and *mer*-[$IrH_3(PEtPh_2)_3$] in approximately equal amounts. When bulkier phosphines are used (*e.g.* $PBu^t{}_2Ph$, Scheme 2, route A), at P:Ir ratios in the range 5—20 the stable species is *trans*-[$IrH_5(PBu^t{}_2Ph)_2$] (triplet at δ −9.8, J_{PH} = 12.0 Hz),[19] and formation of [$IrH_3(PBu^t{}_2Ph)_3$] is not observed.

Using the chiral phosphine *S*(+)-P[$CH_2CH(Me)Et$]Ph_2 (θ = 145°) the system [{Ir(cod)(OMe)}$_2$] + chiral phosphine catalyses the hydrogenation of PhCH=CHCOMe to *S*(−)-PhCH=CHCH(OH)Me, as reported in Table 3. The enantiomeric excess (e.e.) is however rather poor and it never reaches 10%, even when regioselectivity is greater than 90%; the optical yield is only slightly dependent on the excess of phosphine employed. Various solvents have been tested in order to find the experimental conditions which could give a better e.e.; the results are reported in Table 4. In MeCOOH the reaction is slow and only the C=C bond is reduced to form the saturated ketone, which is consistent with the result previously found that [$IrH_3(PPh_3)_3$] in MeCOOH does not catalyse ketone hydrogenation whereas it is a good catalyst for aldehyde reduction.[16]

The low values of e.e. obtained could probably be increased by using more rigid ligands such as chiral diphosphines.

From the results reported in this paper a major conclusion can be drawn. Iridium–phosphine systems behave as flexible catalysts for the hydrogenation of benzylideneacetone. Employing a suitable phosphine of intermediate steric hindrance and by choosing the correct P:Ir ratio the selectivity of the reaction can be controlled, so that either the carbon–carbon double bond or the carbonyl group can be reduced in high yield.

Experimental

The ^1H and ^{31}P n.m.r. spectra were recorded on a Bruker WP80 instrument. Infrared spectra were measured on a Perkin-Elmer 983 B spectrophotometer interfaced to a Perkin-Elmer 3600 Data Station.

$IrCl_3 \cdot 3H_2O$ was purchased from Metalli Preziosi; tertiary phosphines were purchased from Strem Chemicals and used without further purification. Benzylideneacetone (Fluka) was recrystallized three times from propan-2-ol before use. Propan-2-ol was distilled over CaO and stored under nitrogen; toluene was distilled before use.

All preparations were carried out under an inert atmosphere. [{Ir(cod)Cl}$_2$] was prepared according to the literature.[20] [{Ir(cod)(OMe)}$_2$] was prepared by a slight modification of the literature[21] method: [{Ir(cod)Cl}$_2$] was added to a warm solution of Na_2CO_3 in methanol and the reaction mixture was refluxed for 2 h.

[Ir(cod)(PR_3)$_2$]BPh_4 (PR_3 = $PEtPh_2$, PEt_2Ph, or $PMePh_2$),[8] [Ir(PR_3)$_4$]BPh_4 and [IrH_2(PR_3)$_4$]BPh_4 (PR_3 = $PBu^n{}_3$, PEt_2Ph, $PMePh_2$, or PMe_2Ph)[10] were prepared according to the literature.

Catalytic reactions were performed using a stainless steel autoclave. A typical procedure was as follows. [{Ir(cod)-(OMe)}$_2$] (9.95 mg, 1.5 × 10^{-5} mol) in toluene (75 cm^3) was treated with an excess of phosphine under an inert atmosphere. Hydrogen was bubbled through the solution for 15 min at room temperature, and then the substrate added. The reaction mixture was transferred into the autoclave, which was charged with H_2 (30 atm) and heated to 100 °C. The reaction was monitored by g.l.c. on a Perkin-Elmer Sigma 3B, using a Supelcowax 10 wide-bore capillary column (30 m × 0.75 mm internal diameter).

Optical yields were determined by optical rotation

measurements on a Perkin-Elmer 141 polarimeter, using α (589.3 nm, 20 °C, 5 g in 95 g of $CHCl_3$) = +27.4° for *R*(+)-PhCH=CHCH(OH)Me.[22]

Acknowledgements

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