Electron-rich iridium complexes: metal-basicity-controlled chemoselectivity in hydrogen transfer reductions

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Abstract

α,β-unsaturated ketones are selectively reduced to allylic alcohols by hydrogen transfer from propan-2-ol catalyzed by $[Ir(cod)X]_2$ (X = Cl or CH_3O) in the presence of aminophosphines or using $[H_2\overline{Ir(P-N(Me)CH_2(P-NMe_2)}]$. The results indicate that selectivity appears to be related to basicity of the metal.

Introduction

In the last few years we have been interested in the reduction of unsaturated carbonyl compounds catalyzed by iridium–phosphine complexes. Our attention has particularly focussed on the understanding of the factors which determine the chemoselectivity of the catalytic system. In hydrogenation conditions the steric properties of the ligands appear to play a key role on the selectivity of the catalyst: therefore complexes of the type H_3IrP_3 ($P = PEtPh_2$, PEt_2Ph, $PMePh_2$) promote the reduction of the carbonyl group in α,β-unsaturated aldehydes and ketones, whereas when H_5IrP_2 is employed ($P = PEt_2Ph$, $PCyPh_2$, PBu^tPh_2) only the C=C bond is hydrogenated [1, 2].

A completely different situation is expected to occur in hydrogen transfer reactions, where it has been proposed [3] that one of the crucial factors determining the chemoselectivity towards carbonyl group reduction is the nucleophilicity of the hydride ligand of the catalyst. The ability to stoichiometrically reduce ketones has actually been used as a test of hydridic character [4]. Electron-rich metal centers are good candidates as catalysts for selective reduction of α,β-unsaturated ketones, since they should form hydrides having good hydridic character. In fact, highly hydridic group IV metallocene complexes Cp_2MH_2 have been found to be good catalysts for hydrogen transfer reduction of α,β-unsaturated ketones to allylic alcohols [5].

We have previously reported [6] that selective reduction of α,β-unsaturated aldehydes to the unsaturated alcohols via hydrogen transfer in propan-2-ol can be performed using the catalytic system '$[Ir(cod)Cl]_2 + P(o\text{-}C_6H_4OMe)_3$' (P–O). Our results showed that selectivity in this reaction is strictly related to the presence of the *ortho*-anisyl group in the phosphine ligand. Chelation of the methoxide group in the *ortho* position was proposed to be responsible

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for the increased electron density on the metal, which is likely to have a crucial effect on the catalytic properties of the complex. Such chelation has also been suggested in the case of rhodium complexes [7] to account for the higher rate of oxidative addition of CH_3I when $P(o\text{-}C_6H_4OMe)_3$ with respect to PPh_3 is used as ligand [8].

The above iridium–tris(*o*-anisyl)phosphine system is effective in the reduction of the carbonyl group of α,β-unsaturated aldehydes, but when unsaturated ketones are used as substrates [9] the selectivity in allylic alcohol never exceeds 50%, owing to concurrent C=C bond reduction.

The presence of a nitrogen as donor atom in the *ortho* position as in $PPh_2(o\text{-}C_6H_4NH_2)$ (P—NH_2) or in $PPh_2(o\text{-}C_6H_4NMe_2)$(P–$NMe_2$) should give to this type of ligand a greater chelating ability than the P—O phosphine, with subsequent increase in the electron density on the metal center, hence promoting the selective reduction of unsaturated carbonylic substrates to allylic alcohols. In the present paper we report the selective catalytic reduction of enones to unsaturated alcohols via hydrogen transfer from propan-2-ol using iridium catalysts having a high metal basicity promoted by P—N chelation.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983 B spectrophotometer. The NMR spectrometers used for ^1H and ^{31}P NMR measurements were Bruker WP80 and Bruker WM250 instruments. ^{31}P chemical shifts are referred to 85% H_3PO_4 as external standard, with positive sign for downfield shift.

$IrCl_3 \cdot 3H_2O$ was purchased from Metalli Preziosi. The substrates were purified either by distillation or by recrystallization. The iridium complexes and the ligands were prepared under inert atmosphere. $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ were prepared as described elsewhere [1]. $P(o\text{-}C_6H_4OMe)_3$ was purchased from Strem Chemicals and used without further purification. $PPh_2(o\text{-}C_6H_4NH_2)$ [10] and $PPh_2(o\text{-}C_6H_4NMe_2)$ [11] were synthesized according to published procedures. The complexes $[H_2Ir\overline{(P-N(Me)CH_2)}\text{-}(P-NMe_2)]$ (**I**) and $[HIr\overline{Cl(P-N(Me)CH_2)}(P-NMe_2)]$ (**VI**) were prepared as described in [13].

The catalytic reactions were performed using the following procedure. The iridium dimer $[Ir(cod)X]_2$ (X = Cl, OMe) was dissolved in propan-2-ol, and to the resulting solution the appropriate ligand was added. Hydrogen was bubbled through the solution for 15 min, then the solution was again set under nitrogen flow, and heated to 83 °C. After 10 min at reflux, a concentrated solution of the substrate in propan-2-ol was added. When complex (**I**) (see Scheme 1) was used as catalyst precursor, the procedure simply consists of heating its propan-2-ol solution at 83 °C, and adding the substrate.

The catalytic reactions were monitored by GLC on a Perkin-Elmer Sigma 3B instrument, using a Supelcowax 10 wide-bore capillary column (30 m × 0.75 mm i.d.).

Results and discussion

Catalytic experiments

Reduction of benzylideneacetone ($PhCH{=}CHCOCH_3$) to the corresponding allylic alcohol ($PhCH{=}CHCH(OH)CH_3$) via hydrogen transfer from propan-2-ol was performed in the presence of a catalytic system prepared *in situ* from $[Ir(cod)X]_2$ (X = Cl, OMe) and an excess of the P–O or P–N ligand. The expected improvement in the chemoselectivity of the system by changing from the P–O to the P–N ligands was actually observed. When the chloro-bridged precursor is used, a basic cocatalyst is required, independently of the choice of the ligand (see Table 1, runs A.1 to B.3). Hydrogen transfer reactions from propan-2-ol are actually reported to occur only in the presence of added base [12].

An interestingly different situation is observed when employing the precursor $[Ir(cod)(OMe)]_2$. If P–O is used as a ligand, again addition of base appears necessary to transform the precursor into an active catalyst (Table 1, runs C.1 and C.2). However, in the presence of the ligand $P{-}NH_2$ or $P{-}NMe_2$, highly active and chemoselective catalysts are obtained without any added base. These differences are related to the particular type of chemistry developed by the methoxo derivative of iridium in comparison to the chloro dimer, as will be discussed in the following paragraph.

As was reported in a preliminary communication [13], we were able to identify the compound formed under catalytic conditions. This complex has been isolated and characterized as $[H_2\overline{Ir(P{-}N(Me)CH_2)}(P{-}NMe_2)]$ (**I**), formed via intramolecular oxidative addition of a *N*-methyl C–H bond . This species is indeed a close catalyst precursor, as can be noted by comparison of the results reported in Table 2 with those of the system *in situ* (see for instance run 1 in Table 2 and run E.1 in Table 1). The chemoselectivity of compound (**I**) appears to be strongly dependent on the nature of the substrate employed. The extent of carbonyl group reduction decreases with decreasing degree of substitution on the C=C bond, and at the same time a loss in catalytic activity is observed (Table 2, runs 3–5). In the case of a carbon–carbon triple bond, as for 4-phenyl-3-butyn-2-one, the system is completely inactive, suggesting irreversible coordination to iridium. Esters are not reduced by this catalytic system.

*Formation and reactivity of $[H_2\overline{Ir(P{-}N(Me)CH_2)}(P{-}NMe_2)]$ (**I**).*

The cyclometallated complex (**I**) can be formed either in propan-2-ol or in benzene solution, under hydrogen atmosphere. The steps involved in this reaction have been followed in solution by ^1H and ^{31}P NMR. Reaction of $[Ir(cod)(OMe)]_2$ with 2 equivalents of the ligand $P{-}NMe_2$ initially leads (reaction A in Scheme 1) to cleavage of the methoxo bridge, with formation of $[Ir(cod)(OMe)(P{-}NMe_2)]$ (**II**) [^1H NMR (C_6D_6): δ 8.0–6.8 (m, 14H, Ar), δ 4.1 (m, 4H, CH=CH), δ 3.29 (s, 3H, OMe), δ 2.72 (s, 6H, NMe_2), δ 2.4–1.7 (m, 8H, CH_2); ^{31}P NMR (C_6D_6): δ + 10.5 s (free $P{-}NMe_2$ δ − 13.6)].

TABLE 1

Hydrogen transfer reduction of benzylideneacetone ($PhCH{=}CHCOCH_3$) catalyzed by *in situ* iridium–phosphine systems[a]

Run	Precursor	Phosphine	P/Ir	KOH/Ir	% Conversion (min)	Saturated ketone (%)	Saturated alcohol (%)	Unsaturated alcohol (%)	Selectivity[b] (%)
A.1	$[Ir(cod)Cl]_2$	$P(o\text{-}MeOPh)_3$	10	4	81(60)	34	16	31	38
2	$[Ir(cod)Cl]_2$	$P(o\text{-}MeOPh)_3$	5	4	36(60)	20	2	14	39
B.1	$[Ir(cod)Cl]_2$	$P{-}NH_2$	5	4	94(30)	1	5	88	94
2	$[Ir(cod)Cl]_2$	$P{-}NH_2$	2	4	94(30)	1	6	87	93
3	$[Ir(cod)Cl]_2$	$P{-}NH_2$	1	4	47(30)	12	1	35	74
C.1	$[Ir(cod)(OMe)]_2$	$P(o\text{-}MeOPh)_3$	2	2	24(60)	10	1	13	54
2	$[Ir(cod)(OMe)]_2$	$P(o\text{-}MeOPh)_3$	2	–	0(60)	0	0	0	0
D.1	$[Ir(cod)(OMe)]_2$	$P{-}NH_2$	2	–	95(30)	1	6	88	93
2	$[Ir(cod)(OMe)]_2$	$P{-}NH_2$	1	–	95(480)	25	15	55	58
E.1	$[Ir(cod)(OMe)]_2$	$P{-}NMe_2$	2	–	95(60)	2	3	90	95
2	$[Ir(cod)(OMe)]_2$	$P{-}NMe_2$	1	–	75(240)	7	2	66	88

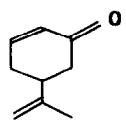
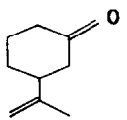
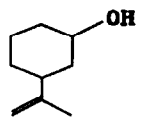
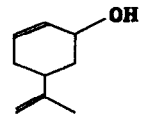
[a]Reaction conditions: $[Ir] = 4 \times 10^{-4}$ M; [substrate]/[Ir] = 500; solvent = propan-2-ol; reaction temperature 83 °C.
[b]Selectivity = (% unsaturated alcohol) (% conversion)$^{-1}$.

TABLE 2

Hydrogen transfer reduction of unsaturated ketones and esters catalyzed by the $[H_2\overline{Ir(P-N(Me)CH_2)}(P-NMe_2)]$ catalyst[a]

Run	Substrate	% Conversion (h)	Saturated ketone (%)	Saturated alcohol (%)	Unsaturated alcohol (%)	Selectivity[b] (%)
1	$PhCH=CHCOCH_3$	99(1)	1	6	92	93
2	$PhCH=CHCOPh$	94(1)	13	14	67	71
3	$(CH_3)_2C=CHCOCH_3$	65(7)	2	1	62	95
4	$CH_3CH=CHCOC_2H_5$	35(7)	23	0	12	34
5	$CH_2=CHCOC_2H_5$	9(7)	8	0	1	13
6	$PhC\equiv CCOCH_3$	0(7)	0	0	0	0
7	carvone[c]	43(48)	0	21	22	51
8	$CH_3(CH_2)_3COOCH_3$	0(8)	0	0	0	0
9	$PhCH=CHCOOCH_3$	1(6)	0	0	0	0

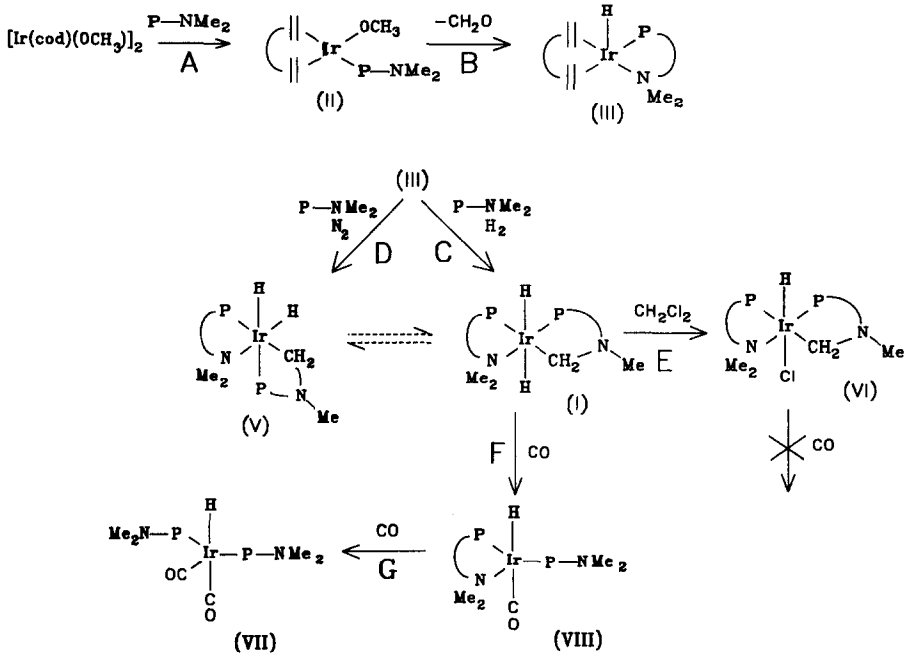
[a]Reaction conditions: $[Ir]=4\times10^{-4}$ M; [substrate]/[Ir] = 500; solvent = propan-2-ol; reaction temperature 83 °C.
[b]Selectivity = (% Unsaturated alcohol) (% Conversion)$^{-1}$.

[c]Carvone  ; saturated ketone  ; saturated alcohol  ; unsaturated alcohol. 

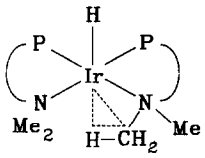
Subsequent β-abstraction from the methoxo ligand is then suggested to occur, in agreement with the results reported by Fernandez *et al.* [14], with formation of species (**III**), in which the $P-NMe_2$ ligand is proposed to be coordinated in a bidentate fashion on the basis of the ^{31}P NMR chemical shift ($\delta+25.3$ s) which is in the range expected for the formation of a five-membered chelate ring [15] [^1H NMR (C_6D_6) δ -9.59 d, $J(P-H)+21.5$ Hz; IR (RbI) $\nu(Ir-H)=2023$ cm^{-1}, no bands at 2785 cm^{-1} attributable to uncoordinated $-NMe_2$].

If the resulting solution is then heated at 80 °C, coordination of a second phosphine takes place, and formation of $[H_2\overline{Ir(P-N(Me)CH_2)}(P-NMe_2)]$ (**I**) is observed [^1H NMR (C_6D_6) $\delta-7.73$ (pseudotriplet, $J(P-H)=14.2$ Hz); ^{31}P NMR (C_6D_6) $\delta+33.4$ d and $\delta+12.5$ d, $J(P-P)=5$ Hz]; for more detailed spectroscopic data see [13]. this reaction is likely to proceed via the intermediate hydride $[HIr(P-NMe_2)_2]$ (**IV**) shown in Fig. 1, where both the phosphines are coordinated in a bidentate fashion. Such a situation creates a rather electron-rich metal center, which will insert into the C–H bond of the *N*-methyl group [13] through a three-centered transition state [16] of the type shown in the figure.

When the synthesis of $[H_2\overline{Ir(P-N(Me)CH_2)}(P-NMe_2)]$ is performed in C_6H_6, together with compound (**I**) another product is formed, which is likely to be the *cis* isomer (**V**) of the cyclometallated complex, as proposed on the basis of NMR data [^1H NMR (C_6D_6): δ -7.53 (ddd, $J(P-H)=141.4$ and 22.9 Hz), δ -22.76 (td, $J(P-H)=15.0$ Hz, $J(H-H)=3.5$ Hz); ^{31}P NMR



Scheme 1.



(IV)

Fig. 1. Intermediate hydride [HIr(P–NMe_2)$_2$] (IV).

(C_6D_6) δ +24.9 d, and δ +15.9, J(P–P) = 5 Hz]. If the reaction is performed in benzene under inert atmosphere, the hydrogen flow being maintained only for 15 min at r.t., then the main product obtained is compound (V), together with less than 10% of the *trans* isomer. These results can be rationalized by suggesting that the presence of molecular hydrogen favors the formation of the *trans* isomer, perhaps by inhibiting the isomerization (I) → (V).

Complex (I) when dissolved in CH_2Cl_2 reacts with the solvent to give the partially chlorinated product (VI); this reaction has been followed by NMR and is complete within 24 h at r.t. The product (VI) has been characterized by X-ray diffraction, and the hydride ligand has been located according to the NMR data [^{1}H NMR (C_6D_6) δ 7.8–6.9 (m, 28H, Ar), δ 3.57s and 3.45s (3H each, NMe_2), δ 3.03 (s, 3H, $NCH_2\underline{Me}$), δ 3.3–2.5 (partially overlapped signals for AB spin system, 2H, $N\underline{CH_2}Me$), δ −21.44 (dd, 1H, Ir–H, J(P–H) = 12.8 and 21.5 Hz); ^{31}P NMR (C_6D_6) δ +17.9d and δ +4.3d (J(P–P) = 4 Hz)] [13].

In order to determine the ease of possible reductive elimination, we investigated the reactivity of both complexes (I) and (VI) with CO. When a benzene solution of (I) is treated with CO at 80 °C, an iridium carbonyl compound is formed, which is formulated as (VII) on the basis of spectroscopic data [^{1}H NMR (C_6D_6): δ 8.2–6.8 (m, 28H, Ar), δ 3.11 (s, 12H, $-NMe_2$), δ −9.10 (t, 1H, Ir–H, J(P–H) = 19.3 Hz); ^{31}P NMR (C_6D_6) δ −8.0s; IR (RbI) ν(Ir–H) and ν(Ir–CO) = 2074, 2000, 1962 and 1945 cm^{-1}]. Such a compound is probably formed via reductive elimination from the hydrido-alkyl iridium compound (I) to reform the *N*-methyl group, giving compound (VIII), followed by displacement of the $-NMe_2$ end of the aminophosphine ligand (reactions F and G in Scheme 1). Accordingly, [Rh(P–NMe_2)$_2$]$^+$ was found to react with CO to give the bis-carbonylated species [Rh(CO)$_2$(P–NMe_2)$_2$]$^+$, in which the phosphines are both coordinated in a monodentate fashion [17]. Carbonylation of compound (VI), in the same experimental conditions used in the case of (I), leads to no reaction product, leaving the starting species unaffected. This result supports the hypothesis that the easy reductive elimination in compound (I) is probably related to the presence of the two *trans* hydrides, which labilize each other.

Conclusions

In the hydrogenation of α,β-unsaturated ketones to allylic alcohols we have proposed [1] that selectivity is mainly associated with the steric crowding around iridium metal center rather than with the hydridic character of the coordinated hydride. It was also shown that $[RuH_4(PPh_3)_3]$ is a more active catalyst than $[RuH_3(PPh_3)_3]^-$ in the hydrogenation of cyclohexanone [18], supporting the idea that carbonyl group hydrogenation is not necessarily related to the extent of negative charge on the metal. However, the factors determining the selectivity in the reduction of enones via hydrogen transfer appear to be totally different from those acting in hydrogenation. The selectivity of catalyst (I), which is rather effective in promoting the formation of allylic alcohols via hydrogen transfer, does not exceed 50% if the same reaction is performed in hydrogenation. On the other hand, catalysts of the type H_3IrP_3 having high selectivity in hydrogenation are not selective catalysts in hydrogen transfer reduction.

The compound (I) could react with propan-2-ol present in excess, or alternatively with the substrate, following a pathway similar to that outlined by reaction F giving $[HIr(P{-}NMe_2)_2(L)]$ (L = propan-2-ol or substrate) as first step of the catalytic cycle. The coordination of substrate or propan-2-ol respectively will follow. The high basicity of the metal center will promote the transfer of the hydride from the donor molecule to the carbonyl group of the substrate. We already reported that the presence of hybrid amino-phosphine $P{-}NMe_2$ ligand in the coordination sphere of iridium creates an electron-rich metal center, capable of intramolecular C–H activation (reactions C and D in Scheme 1) [13]. Moreover, it has been found that by reaction of $[Ir(cot)_2Cl]_2$ with $PPh_2(o\text{-}C_6H_4NMe_2)$ in the presence of NH_4PF_6 the product was not the anticipated rhodium analog iridium complex $[Ir(P{-}NMe_2)_2]^+$, but instead $[IrHCl(P{-}NMe_2)_2]^+$, in which the hydrogen has come from the ammonium ion. The former iridium complex is probably formed during the reaction, but it is sufficiently basic to deprotonate the ammonium ion [19]. Transfer of hydrogen from alcohol to the substrate has been proposed by some authors [20] to proceed without formation of metal hydride; this is probably the case in the selective reduction of carbonyl group in α,β-unsaturated aldehydes catalyzed by $[Ru_4H_4(CO)_8L_4]$ in propan-2-ol, in which no ruthenium deuteride was detected using fully deuterated propan-2-ol as the source of hydrogen [21].

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