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Catalytic hydrogen transfer activity of cationic iridium(I) complexes containing α-diimines

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Abstract

Cationic $[Ir(COD)(LL)]^+$ species (LL = α-diimines derived from biacetyl or glyoxal) in the presence of KOH are active catalysts in the homogeneous hydrogen transfer from isopropanol to acetophenone to give phenylethanol. The most active species is the cation containing biacetyloximehydrazone. α,β-unsaturated ketones are reduced to saturated ketones and alcohols. Cyclohexen-2-one is first selectively reduced at the olefinic double bond by the cation containing biacetyldianyl to give cyclohexanone that is subsequently hydrogenated to the saturated alcohol. This reaction goes through two intermediates in two parallel and finally concurrent pathways; the differential rate equations have been integrated and the simulation of the process agrees reasonably well with experimental measurements. Alcoholic KOH transforms 1-penten-3-one into the corresponding keto-alcohol, 1-pentanol-3-one, the presence of $[Ir(COD)(LL)]^+$ species leads to the subsequent formation of pentan-3-one or pentan-3-ol.

Keywords: Iridium; α-diimines; Hydrogen-transfer reduction; Acetophenone; α,β-unsaturated ketones; 'Steady-state approximation'

1. Introduction

Rhodium(I) and iridium(I) compounds are well known as catalyst precursors in hydrogen transfer reactions [1–4] and some iridium complexes are extraordinarily active [5,6]. Alkylcyclohexanones have being effectively reduced [7–9] and with some phenanthroline iridium complexes the trans alcohols have been selectively obtained [5,10,11] while analogous rhodium compounds show the opposite stereoselectivity [12]. Several iridium(I) complexes are active catalysts in the hydrogen-transfer reduction of α,β-unsaturated ketones [13–21], and benzylideneacetone or benzylideneacetophenone have been selectively reduced to the corresponding allylic alcohols by compounds with mixed-donor P–N ligands [13–16] or to the saturated ketones by compounds with phenanthroline type ligands [18,19] and by Ru–Ir heterobinuclear complexes containing 2,2′-biimidazolate bridges [20,21]. Cyclic enones have been hydrogen-transfer reduced to the corresponding saturated ketones and subsequently to the saturated alcohols by several ruthenium compounds [22–24] and in the case of hindered C=C bonds, preferential reduction to the unsaturated alcohols may take place [24]. Asymmetric transfer hydrogenation of prochiral ketones has been widely studied [1,25] and iridium compounds with terden-

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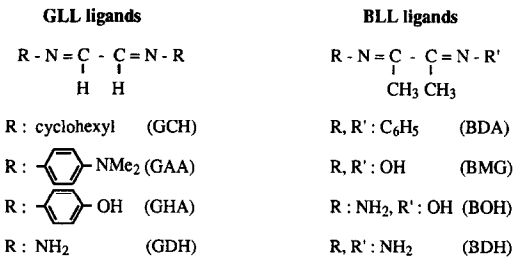


Scheme 1.

tate NNN or PNP donor ligands promote high chemio- and enantioselectivities in the reduction of α,β-unsaturated ketones to optically active allylic alcohols [26,27].

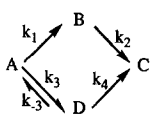
Recently, we have reported on the catalytic activity of iridium compounds containing α-diimines, depicted in Scheme 1, derived from glyoxal (GLL) or biacetyl (BLL) in the hydrogen-transfer reaction from isopropanol to cyclohexanone [28]. We report now on the catalytic activity of the corresponding [Ir(COD)(LL)]A (A = PF_6 or BF_4) species in the hydrogen transfer reactions from isopropanol to acetophenone and α,β-unsaturated ketones.

2. Experimental

The preparation of the metal complexes (catalysts precursors) was carried out at room temperature under nitrogen as previously reported [28]. The transfer hydrogenation reactions were carried out under nitrogen in refluxing isopropanol with magnetic stirring. The equipment consisted of a 100 ml round bottom flask, fitted with a condenser and provided with a serum cap. The catalysts were prepared by adding 0.2 mmol of potassium hydroxide in 10 ml of isopropanol to solutions (20 ml) of 0.02 mmol of [Ir(COD)(LL)]A. The resulting solutions were refluxed for 30 min and 4 mmol of the substrate in 10 ml of isopropanol were injected. The analysis of the catalytic reactions were carried out with a Shimadzu GC-14A chromatograph, connected to a Shimadzu C-R6A calculation integrator. The products of the hydrogen transfer reactions to acetophenone and 2-cyclohexen-1-one were separated with a Supelco 2.5%CW20M on GAW-DMCS 80/100 mesh column (2m × 1/8 in); those of 3-methyl-2-cyclohexen-1-one and 1-penten-3-one with a SGE BP20(polar) capillary column (25 m × 0.53 mm i.d.). NMR spectra were recorded with an XL-300 Varian spectrometer, ^1H (TMS internal standard) spectra were measured from CD_3OD solutions.

2.1. Integration of differential equations for sequence I

For a reaction sequence (see discussion) such as



(sequence I)

the differential rate equations are:

$$-\frac{d[A]}{dt} = k_1[A] + k_3[A] - k_{-3}[D] \quad (1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (2)$$

$$\frac{d[D]}{dt} = k_3[A] - k_{-3}[D] - k_4[D] \quad (3)$$

$$\frac{d[C]}{dt} = k_2[B] + k_4[D] \quad (4)$$

If D is so reactive that it does not accumulate to an appreciable extent, compared to B and C, its concentration may be considered small and constant ('steady-state approximation'): $d[D]/dt = 0 = k_3[A]\text{-}k_{-3}[D]\text{-}k_4[D]$ and from there:

$$[D]_{ss} = \frac{k_3[A]}{k_{-3} + k_4} \quad (5)$$

taking Eq. (5) into Eq. (1):

$$-\frac{d[A]}{dt} = k_1[A] + k_3[A] - k_{-3}\frac{k_3[A]}{k_{-3} + k_4} \quad (6)$$

Integrating Eq. (6) between the time limits 0 and t and between the concentration limits $[A]_0$ (time 0) and [A] (time t) Eq. (7) or Eq. (8) are obtained:

$$\ln[A] = \ln[A]_0 - k't \tag{7}$$

or

$$[A] = [A]_0 e^{-k't} \tag{8}$$

being

$$k' = k_1 + k_3 - \frac{k_3 k_{-3}}{k_{-3} + k_4} \tag{9}$$

Consequently and according to Eq. (7) a plot of ln[A] versus t gives a slope of $-k'$.

Substitution of Eq. (8) into Eq. (2) yields:

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k't} - k_2[B] \tag{10}$$

To integrate Eq. (10) it must be taken into account that the differential equation

$$\frac{dy}{dx} = f(x) + g(x)y \tag{11}$$

has the following solution [29]:

$$y = e^{w(x)}\left[\int e^{-w(x)} f(x)\,dx + \text{constant}\right] \tag{12}$$

where

$$w(x) = \int g(x)\,dx \tag{13}$$

so that the solution for differential Eq. (10) is:

$$[B] = e^{-k_2 t}\int_0^t e^{k_2 t} k_1 [A] e^{-k't}\,dt \tag{14}$$

and finally:

$$[B] = \frac{k_1[A]_0}{k_2 - k'}(e^{-k't} - e^{-k_2 t}) \tag{15}$$

According to Eq. (15) [B] is the difference of two exponentials and so it will go through a maximum. A plot of ln[B] versus t goes through a maximum and has a linear portion for longer times where $e^{-k_2 t} \gg e^{-k't}$. From that linear portion k_2 can be calculated from the slope and k_1 from the intercept (provided that k' and k_2 are known). Substitution of Eq. (15) into Eq. (4) yields:

$$\frac{d[C]}{dt} = k_2 \frac{k_1[A]_0}{k_2 - k'}(e^{-k't} - e^{-k_2 t}) + k_4[D] \tag{16}$$

Eq. (5) and the value of [A] from Eq. (8) are then taken into Eq. (16) to yield:

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A]_0}{k_2 - k'}(e^{-k't} - e^{-k_2 t}) + \frac{k_3 k_4}{k_{-3} + k_4}[A]_0 e^{-k't} \tag{17}$$

Integration of Eq. (17) with [C] = 0 at $t = 0$ and rearrangement yield:

$$[C] = \frac{k_1 k_2 [A]_0}{k_2 - k'}\left(\frac{1 - e^{-k't}}{k'} + \frac{e^{-k_2 t} - 1}{k_2}\right) + \frac{k''[A]_0}{k'}(1 - e^{-k't}) \tag{18}$$

where

$$k'' = \frac{k_3 k_4}{k_{-3} + k_4} = k' - k_1 \tag{19}$$

3. Results and discussion

Cationic [Ir(COD)(LL)]A complexes show good catalytic activity in the homogeneous hydrogen transfer from isopropanol to acetophenone and the obtained results are collected in Table 1. In all cases hydrogenation of the ketone occurs and phenylethanol is obtained. As in the hydrogenation of cyclohexanone [28], the catalysts derived from biacetyl (**1–4**) are more active than those derived from glyoxal (**5–8**). Comparison of BDH (**3**) and GDH (**6**) compounds indicates that the presence of methyl groups in the biacetyl ligands enhances the catalytic activity. Methyl substituted phenanthrolines are also more active than phenanthroline [11]. Complexes with biacetyl derivatives con-

Table 1
Hydrogen-transfer reduction of acetophenone to phenylethanol and cyclohexanone by $[Ir(COD)(LL)]^+$ [a]

Complex [b]	Substrate	
	acetophenone % conv. (time, min)	cyclohexanone [c] % conv. (time, min)
(1) $[Ir(COD)(BOH)]PF_6$	90 (8)	90 (14)
(2) $[Ir(COD)(BMG)]PF_6$	90 (57)	90 (55)
(3) $[Ir(COD)(BDH)]PF_6$	90 (73)	90 (36)
(4) $[Ir(COD)(BDA)]PF_6$	77 (240)	90 (156)
(5) $[Ir(COD)(GHA)]BF_4$	60 (240)	90 (210)
(6) $[Ir(COD)(GDH)]PF_6$	37 (240)	—
(7) $[Ir(COD)(GCH)]PF_6$	46 (240)	90 (85)
(8) $[Ir(COD)(GAA)]PF_6$	10 (240)	90 (90)

[a] Reaction conditions: $[Ir] = 5 \times 10^{-4}$ M; [substrate]/[Ir] = 200; [KOH]/[Ir] = 10; solvent Pr^iOH (40 cm^3); $T = 83°C$; activation time = 30 min.
[b] (1–4) are derivatives of biacetyl; (5–8) are derivatives of glyoxal.
[c] From ref. 28 for comparison purposes.

taining hydroxy or amino substituents in the imino nitrogens, i.e. BOH (**1**), BMG (**2**) or BDH (**3**) are efficient compounds and the most active species is the BOH complex, containing one OH and one NH_2 substituent. Usually acetophenone is less readily reduced than cyclohexanone [5,22–24,30]. This is also the behavior of most of our compounds (see Table 1) except with the BOH (**1**) and BMG (**2**) species where acetophenone is reduced at similar rate than cyclohexanone and this appears to be related to the presence of OH groups in the donor atom of the ligand.

The cationic [Ir(COD)(LL)]A species are also active in the hydrogen transfer reaction from isopropanol to cyclic enones such as cyclohexen-2-one. In all cases the olefinic bond is first reduced and the saturated ketone formed is subsequently hydrogenated to the saturated alcohol. The obtained results are collected in Table 2 and show that the most active catalysts for ketone reduction, BOH (**1**), BMG (**2**) or BDH (**3**) compounds, are poorly selective and give the saturated alcohol, along with small amounts of unsaturated alcohol that never exceeds 9%. The most selective catalyst is the BDA (**4**) complex, that was the less active biacetyl derivative in ketones reduction (see Table 1) and reaches 81% selectivity on saturated ketone at 88% conversion. The complexes **5** and **6** containing glyoxal derivatives are also less active than the biacetyl derivatives in the reduction of the olefinic double bond and their selectivity is low. The complexes containing GCH (**7**) or GAA (**8**) are almost inactive.

Table 2
Hydrogen-transfer reduction of  by $[Ir(COD)(LL)]^+$ [a]

Complex	LL	% conv. (time, min)	% sat. ketone	% sat. alcohol	% unsat. alcohol
(1)	BOH	54 (4) [b]	30	24	0
		100 (22)	1	90	9
(2)	BMG	66 (31) [b]	39	21	6
		100 (255)	8	87	5
(3)	BDH	61 (23) [b]	37	24	0
		100 (125)	3	91	6
(4)	BDA	88 (18) [b]	71	11	0
		98 (255)	12	86	0
(5)	GHA	74 (62) [b]	49	19	6
		93 (255)	47	40	6
(6)	GDH	70 (61) [b]	44	21	5
		87 (255)	41	40	6
(7)	GCH	13 (170)	7	6	0
(8)	GAA	6 (170)	5	1	0

[a] Reaction conditions: $[Ir] = 5 \times 10^{-4}$ M; [substrate]/[Ir] = 200; [KOH]/[Ir] = 10; solvent Pr^iOH (40 cm^3); $T = 83°C$; activation time = 30 min.
[b] Maximum amount of saturated ketone.

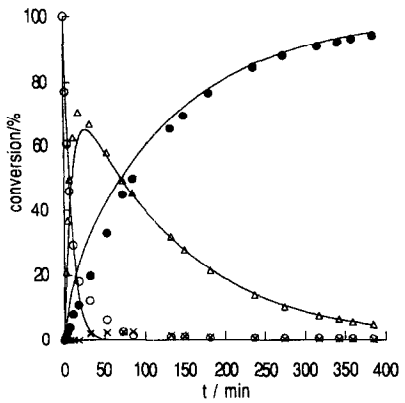


Fig. 1. Hydrogen-transfer reduction of 2-cyclohexen-1-one (○) to cyclohexanone (△), 2-cyclohexenol (×) and cyclohexanol (●) by $[Ir(COD)(BDA)]^+$. Solid line curves (—), simulated concentration profiles.

It is well known (see sequence I) that the catalytic hydrogen transfer reduction of unsaturated ketones (A) to saturated alcohols (C), with transition metal complexes as catalysts, may proceed via the intermediate formation of the saturated ketone (B) and/or the unsaturated alcohol (D) [14,17,19,20,24]. In our case both intermediates are formed as indicated by the course of 2-cyclohexen-1-one reduction by $[Ir(COD)(BDA)]^+$ (Fig. 1). Taking into account that the reaction proceeds practically to completion (100% conversion from A to C), that the intermediate B reaches a high concentration and that D does not accumulate, the reaction sequence I can be proposed (see Section 2). The reversible formation of intermediate D is chemically acceptable (the unsaturated alcohol can also behave as a source of hydrogen) but a similar behavior is unlikely in the case of intermediate B (saturated ketone); the reversible formation of product C seems to be kinetically precluded as the conversion reaches practically 100%.

The reaction sequence I consists of two parallel and finally concurrent pathways: one of them with two steps occurring in series (A → B → C) and the other one via a reversible step (A ⇄ D → C). To confirm that sequence I agrees with the experimental data the differential rate equations must be integrated, the experimental data are then used to calculate the rate constants and the process can then be simulated to check the model. Each of the two paths of sequence I is well known in chemical kinetics but the whole sequence does not seem to be so frequent; a similar sequence has been reported [19] but the differential equations were not integrated, so we accomplished this integration (see Section 2). Eq. (7) was valid for longer than two half-lives and the linear portion of Eq. (15) extended from 32 min on. From such plots the calculated values for the rate constants under these conditions were found to be:

$k_1 = 1.4 \times 10^{-3}\ s^{-1}$

$k_2 = 1.2 \times 10^{-4}\ s^{-1}$

$k' = 1.8 \times 10^{-3}\ s^{-1}$

$k'' = 4 \times 10^{-4}\ s^{-1}$

Taking the rate constant values into Eqs. (8), (15) and (18), the kinetic profiles were simulated and they are represented by the solid line curves in Fig. 1. The results obtained can be considered satisfactory even if sometimes the simulated curves do not perfectly fit the experimental data points. This can be due, at least in part, to the 'steady-state approximation' applied to intermediate D, though some extra complexity in the reaction kinetics can not be ruled out. The reaction profiles for the other species studied look quite alike to those of Fig. 1, but only in the case of the BDA complex (**4**) the reaction sequence I gave satisfactory results. The main reason could well be that the unsaturated alcohol (intermediate D) should always be at very low concentrations to allow the 'steady-state approximation' to be applied; this can be considered approximately true for the BDA case but not for the other species (see Table 2).

It has been reported that cyclic enones with hindered C=C bonds may be preferentially reduced to the unsaturated alcohols [24]. 3-methyl-2-cyclohexen-1-one is reduced by $[Ir(COD)(BLL)]^+$ and the presence of the methyl group in the substrate slows down the catalytic reaction by making the reduction of the double bond more difficult. The obtained results are

Table 3
Hydrogen-transfer reduction of  by [Ir(COD)(LL)]$^+$ [a]

Complex	LL	% conv. (time, min)	% sat. ketone	% sat. alcohol	% unsat. alcohol
(1)	BOH	94 (150)	0	86	8
(2)	BMG	47 (260)	1	25	21
(3)	BDH	28 (260)	1	13	14
(4)	BDA	22 (260)	2	10	10

[a] Reaction conditions: [Ir] = 5×10^{-4} M; [substrate]/[Ir] = 200; [KOH]/[Ir] = 10; solvent Pr^{i}OH (40 cm^3); T = 83°C; activation time = 30 min.

collected in Table 3 and show that the BOH (**1**) compound gives unselective hydrogenation of the olefin and the ketone thus leading to the saturated alcohol. When using [Ir(COD)(BLL)]$^+$ (BLL = BDH, BMG or BDA) the hydrogen-transfer reactions are much slower and equimolar mixtures of saturated and unsaturated alcohols are obtained.

Acyclic unsaturated ketones with terminal olefinic bonds such as 1-penten-3-one have been hydrogen-transfer reduced to the saturated ketone by osmium, ruthenium or iron catalysts with no need of a basic cocatalyst. The ruthenium catalyst gives subsequently the saturated alcohol [24]. Under similar conditions iridium compounds containing mixed-donor P–N ligands are less active giving mainly the saturated ketone [13,14]. We have studied the catalytic reduction of $C_2H_5COCH{=}CH_2$ by isopropanol using [Ir(COD)(BLL)]$^+$ in the presence of a basic cocatalyst i.e. KOH. In this case GC of 1-penten-3-one/KOH mixtures in isopropanol indicates the immediate transformation, up to 98%, of the substrate into the corresponding keto-alcohol, $C_2H_5COCH_2CH_2OH$. This was confirmed by GC and ^{1}H-NMR of 1-penten-3-one/KOH mixtures in CD_3OD that show three triplets centered at 3.72, 2.77 and 1.01 ppm respectively and a quadruplet at 2.60 ppm. As expected [31] this transformation promoted by alcoholic KOH was not observed for the cyclic enones studied previously. In the presence of [Ir(COD)(BLL)]$^+$ and KOH the keto-alcohol is also immediately formed and further reaction occurs to give 3-pentanone, 1-penten-3-ol and 3-pentanol while the amount of 1-pentanol-3-one drops, indicating the occurrence of the intermediate retro-Michael reaction [31]. Table 4 collects the obtained results with iridium compounds containing biacetyl derivatives. BMG (**2**), BDH (**3**) or BDA (**4**) complexes promote the reduction to the saturated ketone while the BOH (**1**) compound catalyses its subsequent reduction to the saturated alcohol.

4. Conclusions

[Ir(COD)(α-diimine)]$^+$/KOH mixtures promote the homogeneous hydrogen transfer from

Table 4
Hydrogen-transfer reduction of 1-penten-3-one by [Ir(COD)(LL)]$^+$ [a]

Complex	LL	% conv. (time, min)	% sat. ketone	% sat. alcohol	% unsat. alcohol
(1)	BOH	87 (26)	64	15	8
		99 (260)	39	60	0
(2)	BMG	98 (180)	79	16	3
		98 (260)	77	18	3
(3)	BDH	70 (260)	62	4	4
(4)	BDA	89 (260)	81	5	3

[a] Reaction conditions: [Ir] = 5×10^{-4} M; [substrate]/[Ir] = 200; [KOH]/[Ir] = 10; solvent Pr^{i}OH (40 cm^3); T = 83°C; activation time = 30 min.

isopropanol to different ketones. Acetophenone is selectively reduced to phenylethanol. Cyclohexen-2-one is reduced to the saturated alcohol according to sequence I with formation of the saturated ketone and low amounts of the unsaturated alcohol as intermediates. When using the BDA complex this pattern can satisfactorily explain the kinetic results and allows to calculate some of the kinetic constants of the process. Alcoholic KOH promotes the transformation of 1-penten-3-one into the corresponding keto-alcohol. In the presence of $[Ir(COD)(\alpha\text{-diimine})]^+$ retro-Michael reaction occurs and subsequently pentan-3-one or pentan-3-ol are formed.

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