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Regioselective reduction of quinolines catalyzed by rhodium and iridium complexes with mono-, di-, and tri-dentated phosphine ligands

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The systems prepared *in situ* by addition of the corresponding equivalents of the respective phosphine (mono-, di- and tri-dentated), called $M_2Cl_2(COE)_4/n$ phosphine (M = Rh, Ir; and COE = cyclooctene), are efficient and regioselective precatalysts for the hydrogenation of quinoline, isoquinoline, 5,6- and 7,8-benzoquinoline and acridine. The Rh systems were more active than the corresponding Ir ones, being the systems with 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) more active than those with 1,2-bis(diphenylphosphino)ethane (dppe), except for the case of acridine, where the inversed tendencies were observed (Ir > Rh and dppe > triphos). The systems with triphenylphosphine showed the lowest activities.

KEY WORDS: hydrogenation; rhodium and iridium precatalyst; phosphines; heteroaromatic nitrogen compounds.

1. Introduction

The hydrogenation of quinoline and related heteroaromatic nitrogen compounds is an area of considerable interest because it is related to the industrially important hydrodenitrogenation (HDN) process [1]. This process occurs by the selective hydrogenation of the nitrogen-containing ring, which takes place prior to any carbon–nitrogen bond cleavage [2]. Some Ru-, Os-, Rh- and Ir-complexes such as $[RuHCl(PPh_3)_3]$ [3], $[RhCl(PPh_3)_3]$ [4], $[Rh(\eta^5\text{-}Cp^*)(NCMe)_3]^{2+}$ [5], $[M(COD)(PPh_3)_2]^+$ [6], $[M(COD)(PPh_3)(NCPh)]^+$ and $[M(COD)(NCPh)_2]^+$ [7] (M = Rh or Ir and COD = 1,5-cyclooctadiene) and $[MH(CO)(NCMe)_2(PPh_3)_2]^+$ (M = Ru or Os) [8] have been found to catalyze the reduction of quinoline and related compounds. In all these cases only the reduction of the heterocyclic ring was observed. Recently, Borowski *et al*. [9] reported the regioselective hydrogenation of the non-heterocyclic rings of quinoline, isoquinoline and acridine by using $[RuH_2(\eta^2\text{–}H_2)_2(PCy_3)_2]$ (Cy = cyclohexyl) as the precatalyst. So far the used precatalysts are based on monodentade phosphines, although systems containing tris(pyrazolyl)borate ligands have been reported in the literature [10]. To the best of our knowledge, there are no examples of precatalysts for the homogeneous hydrogenation of heteroaromatic nitrogen compounds catalyzed by systems containing diphosphine ligands; however, there is only one report on the reduction of quinoline to 1,2,3,4-tetrahydroquinoline catalyzed by a complex containing the 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) ligand, namely [Rh(DMAD)(triphos)]PF_6 (DMAD = dimethylacetylendicarboxylate) [11].

Continuing our research studies on the hydrogenation of heteroaromatic nitrogen compounds, we are reporting in this work the results on the regioselective hydrogenation of heteroaromatic ring of quinoline (Q), isoquinoline (iQ), 5,6- and 7,8-benzoquinoline (BQ) and acridine (A) catalyzed by rhodium and iridium systems containing mono-, bi- and tri-dentated phosphines.

2. Experimental

All manipulations were conducted with rigorous exclusion of air. All the heteroaromatic nitrogen compounds and the solvents were purified by known procedures. Complexes $M_2(COE)_4Cl_2$(M = Rh, Ir) were prepared as described in the literature [12]. The IR spectra of the complexes (in KBr disk) were recorded on a Shimadzu 8300 FT-IR instrument. ^{1}H- and $^{31}P^1\{H\}$-NMR spectra were recorded on a Brucker AM-300 spectrometer; chemical shift are expressed in ppm upfield from Me_4Si and H_3PO_4, respectively.

The details regarding the apparatus used and the reaction procedure for the catalytic runs are similar to those reported earlier [8]. The catalytic reactions were carried out as following: a solution of the dimeric precatalyst (0.025 mmol), the corresponding equivalents of the respective phosphine, the substrate (5.0 mmol) and the solvent (50 mL total volume) were placed in the reactor. The solution was carefully deoxygenated, a preheated oil bath was placed around the reactor and

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the magnetic stirring started. When the reactor reached the thermal equilibrium, 4 atm of hydrogen was then admitted into the evacuated system. The reaction was followed by measuring the hydrogen pressure drop as a function of time and by using a 610 Series UNICAM gas chromatograph fitted with a thermal conductivity detector and a 3 m 10% SE-30 on Supelcoport glass column using helium as carrier gas, which was coupled to a UNICAM 4815 data system.

The percentage of hydrogenation of the corresponding quinoline in the kinetic experiments was restricted to 5–10% in order to calculate the initial rate of the reaction [13]. The data for hydrogenation of the heteroaromatic nitrogen compounds were plotted as molar concentration of the corresponding product versus time yielding straight lines, which were fitted by conventional linear regression programs. Initial rates of the reaction were obtained from the corresponding slopes. Each reaction was repeated at least twice in order to ensure reproducibility of the results. Statistical analyses were carried out using analysis of variance (ANOVA) to test the difference between means. Significant differences were considered when $p < 0.05$.

The coordination chemistry experiments were carried out by the reaction of $[Ir_2(COE)_4Cl_2]$ (110 mg, 0.12 mmol) with one equivalent of dppe or triphos and the corresponding nitrogen compound (0.5 mL) in benzene solution (15 mL), at room temperature, in the presence and in the absent of hydrogen.

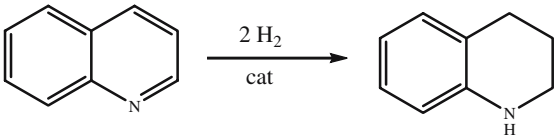
[IrCl(py)(dppe)]: ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm), 8.7–6.3 (series of m, 25H), 2.1 (m, 4H); $^{31}P^1$H-NMR ($CDCl_3$, 121 MHz, ppm), 18.9 (d, J_P–P = 4 Hz, 1P), 14.4 (d, J_P–P = 4 Hz, 1P).

[Ir(H)$_2$(Q)(triphos)]Cl: IR (KBr, cm^{-1}), 2060 (m,gν_{Ir}–H), 2047 (m, ν_{Ir}–H); ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm), 8.9–6.9 (series of m, 35H), 3.3 (m, 2H), 2.8 (m, 2H), 2.0 (m, 2H), 1.5 (s, 3H), −8.2 (part of an AA'XX'MZ spin system, 1H); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz, ppm), 3.2 (t, J_P–P = 12 Hz, 1P), −23.0 (d, J_P–P = 12 Hz, 2P).

3. Results and discussion

The catalytic systems used in the present work were prepared *in situ* by addition of the corresponding equivalents of triphenylphosphine (PPh_3), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to the dimeric complexes $M_2(COE)_4Cl_2$(M = Rh, Ir). All these systems were efficient and regioselective precatalysts for the homogeneous reduction of the heterocyclic ring of a series of heteroaromatic nitrogen compounds such as quinoline (Q), isoquinoline (iQ), acridine (A) and 5,6- and 7,8-benzoquinoline (BQ), under mild reaction condition (130 °C and 4 atm H_2). Although the values for initial rates are all rather similar, some significant differences are observed.

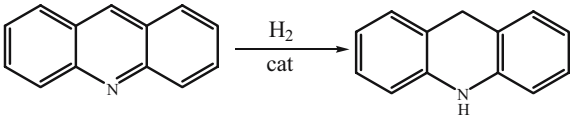
The results for the hydrogenation of Q to 1,2,3,4-tetrahydroquinoline (equation (1)) are showed in Table 1. The rhodium complexes showed to be more active precatalysts than the corresponding iridium ones. The reaction rate with the Rh_2/2 triphos system was



(1)

slightly higher than that of the Rh_2/2 dppe one and 6 times higher than those of the $Rh_2/nPPh_3$ ($n = 4$ and 6) systems; these latter systems showed similar rates and the lowest ones. With the iridium systems, a similar tendency was also observed.

The results for the hydrogenation of A to 9,10-dihydroacridine (equation 2) are showed in table 2. In this case, iridium systems were more active than the corresponding rhodium ones, being the systems with dppe more active than that of the triphos ones; again, the PPh_3 systems showed the lowes rates.



(2)

Similarly, the rhodium and iridium systems containing dppe and triphos (the most active ones) proved to be efficient catalyst precursors for the homogeneous hydrogenation of the other heteroaromatic nitrogen compounds, such as iQ, 5,6-BQ and 7,8-BQ, under the same mild reaction conditions (see table 3); these substrates were hydrogenated to their corresponding 1,2,3,4-tetrahydroderivatives, similar to the Q substrate (equation 1).

As may be observed in table 3, the order of individual initial rate was A > Q > 5,6-BQ > 7,8-BQ > iQ, which reflects both steric and electronic effect. Similar

Table 1
Hydrogenation of Q (0.1 M) with the rhodium and iridium systems $M_2(COE)_4$(0.5 mM)/n phosphine in xylene at 130 °C under 4 atm of hydrogen

Precatalyst	$10^6 r_i$ (Ms^{-1})
$Rh_2Cl_2(COE)_4$/4 PPh_3	2.17 ± 0.01
$Rh_2Cl_2(COE)_4$/6 PPh_3	2.32 ± 0.03
$Rh_2Cl_2(COE)_4$/2 dppe	8.54 ± 0.20
$Rh_2Cl_2(COE)_4$/2 triphos	11.60 ± 1.00
$Ir_2Cl_2(COE)_4$/4 PPh_3	0.21 ± 0.01
$Ir_2Cl_2(COE)_4$/6 PPh_3	0.20 ± 0.01
$Ir_2Cl_2(COE)_4$/2 dppe	0.33 ± 0.01
$Ir_2Cl_2(COE)_4$/2 triphos	0.54 ± 0.02

r_i: initial rate.

Table 2
Hydrogenation of A (0.1 M) with the rhodium and iridium systems $M_2(COE)_4$(0.5 mM)/*n* phosphine in xylene at 130 °C under 4 atm of hydrogen

Precatalyst	$10^5 r_i$ (Ms^{-1})
$Rh_2Cl_2(COE)_4$/4 PPh_3	1.01 ± 0.02
$Rh_2Cl_2(COE)_4$/6 PPh_3	1.43 ± 0.01
$Rh_2Cl_2(COE)_4$/2 dppe	2.50 ± 0.05
$Rh_2Cl_2(COE)_4$/2 triphos	1.87 ± 0.06
$Ir_2Cl_2(COE)_4$/4 PPh_3	1.67 ± 0.02
$Ir_2Cl_2(COE)_4$/6 PPh_3	1.04 ± 0.01
$Ir_2Cl_2(COE)_4$/2 dppe	3.78 ± 0.20
$Ir_2Cl_2(COE)_4$/2 triphos	3.09 ± 0.03

r_i: initial rate.

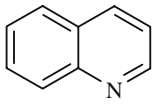
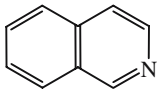
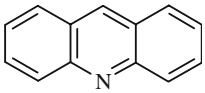
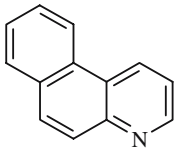
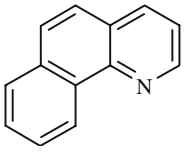
tendencies were observed and explained by Fish *et al.* [3–5], by Chin *et al.* [7] and by some of us [8], and therefore no additional comments will be made.

In order to gain further understanding of the mechanisms of the regioselective hydrogenation of heteroaromatic nitrogen substrates, the reaction of the dimeric iridium complex with each component of the catalytic mixture was carried out, with the aim of isolating or detecting some intermediates of the reaction; iridium dimer was chosen because of the higher stability of the species of this metal. The most important results are displayed in figure 1.

The reaction of dimeric iridium complex $[IrCl(COE)_2]_2$ with dppe in benzene at room temperature give a dark red solution from which red microcrystals could be isolated by addition of *n*-pentane; this complex is rather unstable and it was transformed to a yellow solid even at low temperature (−10 °C). However, we propose that this red species is IrCl(COE)(dppe), because the same reaction in the presence of py gave a yellow solid, which was characterized as IrCl(py)(dppe) by its ^{1}H-and $^{31}P^1$H-NMR spectra. The reaction of dimeric iridium complex with dppe and py in benzene solution at room temperature under 1 atm of H_2 produce unstable species which could not be identified. Similar reactions with acridine give a complex mixture of species which could not be characteized.

On the other hand, the reaction of $[IrCl(COE)_2]_2$ with triphos in benzene in presence of Q under the catalytic reaction conditions yielded a yellow solution, from which a yellow solid could be isolated. This species was

Table 3
Hydrogenation of heteroaromatic nitrogen compounds (0.1 M) with the rhodium and iridium systems $M_2(COE)_4$/2 dppe and $M_2(COE)_4$/2 triphos ($[M_2(COE)_4]$ = 0.5 mM, [phosphine] = 1.0 mM) in xylene at 130 °C under 4 atm of hydrogen

Substrate	$10^6 r_i$ (Ms^{-1})			
	Rh_2/2 dppe	Rh_2/2 triphos	Ir_2/2 dppe	Ir_2/2 triphos
	(8.54 ± 0.20)	(11.60 ± 0.10)	(0.33 ± 0.01)	(0.54 ± 0.02)
	(0.16 ± 0.01)	(0.80 ± 0.04)	(0.04 ± 0.01)	(0.58 ± 0.06)
	(25.0 ± 0.50)	(18.7 ± 0.60)	(37.8 ± 0.30)	(30.9 ± 0.30)
	(7.65 ± 0.20)	(5.13 ± 0.09)	(0.48 ± 0.02)	(0.20 ± 0.01)
	(0.37 ± 0.01)	(0.27 ± 0.01)	(0.03 ± 0.01)	(0.34 ± 0.01)

r_i: initial rate.

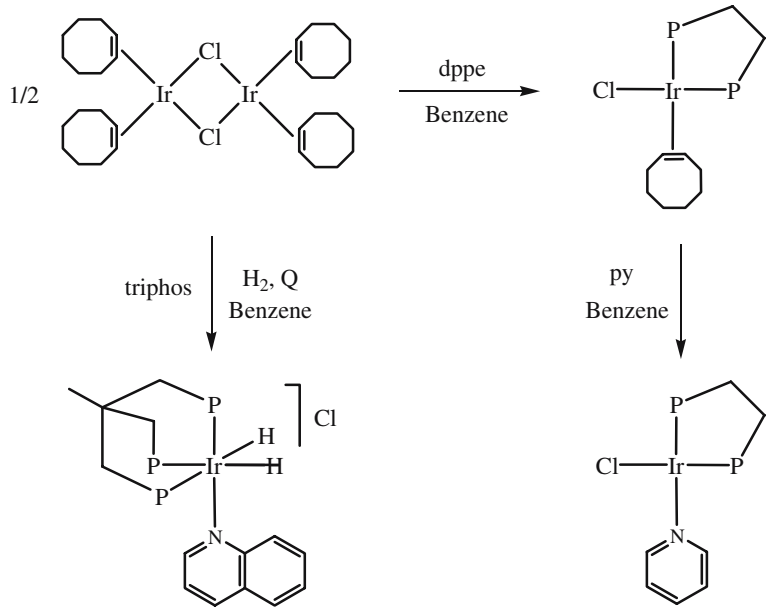


Figure 1. Coordination chemistry related with the hydrogenation of heteroaromatic nitrogen compounds catalyzed by the systems $M_2(COE)_4$ containing dppe and triphos ligands.

characterized by its IR, ^{1}H- and $^{31}P^1$H-NMR spectra as the chloride salt of a cationic species, which was formulated as $[Ir(H)_2(Q)(triphos)]^+$.

Complexes such as IrCl(py)(dppe) and $[Ir(H)_2(Q)(triphos)]^+$, which were isolated and characterized in the present work, and similar species may be involved in the catalytic cycle of the hydrogenation of heteroaromatic nitrogen compounds. Detailed kinetic analysis of these reactions and further coordination chemistry studies related with these reactions are in progress, in order to explain the differences between the A hydrogenation and the other substrates.

4. Conclusion

The Rh and Ir complexes containing mono-, di- and tridentated phosphine ligands showed to be efficient precatalysts for the hydrogenation of a series of quinolines. In general, Rh systems were most active than the corresponding Ir ones, being the systems with triphos more active than those with dppe, except for the case of A, where inversed tendencies were observed (Ir > Rh and diphos > triphos); the PPh_3 systems showed the lowest activities. The order of individual initial rate was A > Q > 5,6-BQ > 7,8-BQ > iQ, which suggests both steric and electronic effects.

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