Hydrogenation of Indole by Phosphine-Modified Rhodium and Ruthenium Catalysts

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The selective hydrogenation of indole (IN) to indoline (INE) by rhodium and ruthenium catalysts modified with the tripodal polyphosphine ligand $MeC(CH_2PPh_2)_3$ (triphos) has been investigated in the homogeneous phase. Both $[Rh(DMAD)(triphos)]PF_6$ (DMAD = dimethyl acetylenedicarboxylate) and $[Ru(MeCN)_3(triphos)](SO_3CF_3)_2$ have been found to generate effective catalysts for the conversion of IN to INE in THF in the presence of triflic acid. The protic acid is required to generate the 3*H*-indolium cation, which contains a localized C=N bond. The rhodium precursor was more efficient than the ruthenium species and allowed for hydrogenation of the substrate even at 60 °C with turnover frequencies as high as 100. Catalytic experiments in autoclaves and in high-pressure sapphire NMR tubes have provided valuable information on the hydrogenation mechanism of IN.

Introduction

Nitrogen in petroleum and coal is contained in various organic compounds, which include polyaromatic heterocycles, aliphatic and aromatic amines, and nitriles. Both amines and nitriles are in low quantity, and their degradation via HDN (eq 1) is efficiently performed

$$C_aH_bN + cH_2 \rightarrow NH_3 + C_aH_d$$

hydrodenitrogenation (HDN) (1)

under hydrotreating conditions by applying commercial catalysts. In contrast, the aromatic heterocycles, e.g. quinolines, pyridines, pyrroles, and indoles, are more abundant and much more difficult to degrade.[1−3]

Since the reaction parameters in actual refinery reactors are optimized for the hydrodesulfurization (HDS) of sulfur-containing compounds (eq 2), the experimental conditions and the catalysts employed are not specifically optimized for HDN, which requires longer reaction times as well as higher temperature and H_2 pressure to occur as efficiently as the HDS of thiophenes.[1,3] The development of improved HDN catalysts is thus an actual priority in the petrochemical industry, nowadays made even more urgent by the increasing discovery of heavy-oil reservoirs worldwide, the growing use of coal and oil shale for the production of fuels, and the stringent environmental regulations concerning the amount of both sulfur and nitrogen permitted in gasoline and city diesel.[2]

$$C_aH_bS + cH_2 \rightarrow H_2S + C_aH_d$$

hydrodesulfurization (HDS) (2)

Homogeneous model studies have been very useful to elucidate the structure/reactivity relationships between molecular metal catalysts and N-heterocycles.[3−8] Most of the work done, however, has been focused on N-heterocycles containing a basic nitrogen donor such as pyridine and quinoline (Q) as they are more amenable than pyrrole or indole (IN) to form stable metal complexes.[3,4−7] Indeed, unlike Q ($pK_a = 4.9$), the nitrogen lone pair in IN ($pK_a = -3.6$) is delocalized over the five-membered ring and is not available for binding a metal center unless an intramolecular hydrogen transfer is induced to form 3*H*-indolenine (Scheme 1, **a**−**c**).[9−11]

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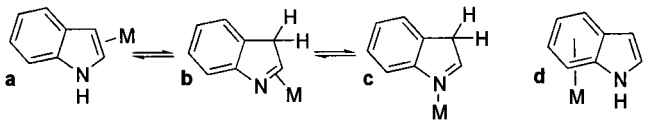
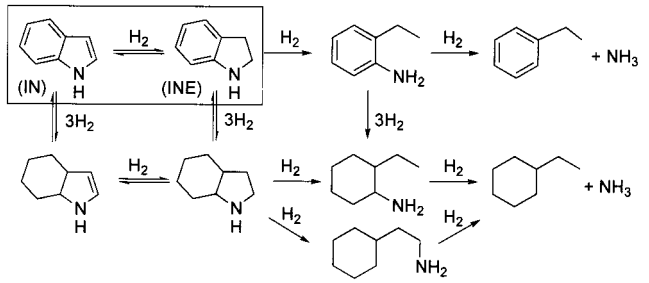
Scheme 1



Scheme 2



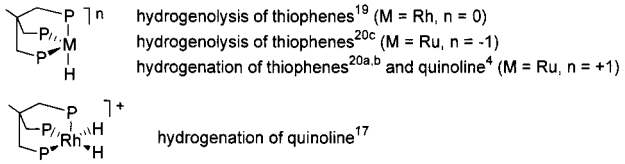
As a result, the most common bonding mode of IN to single metal sites is the η^6 mode through the carbocyclic ring (Scheme 1, **d**).[12]

No evidence has been ever provided for a stable *side-on* coordination (Scheme 1, either **a** or **b**) that would be crucial for the HDN of IN, as all the principal reaction pathways involve the preliminary hydrogenation of the heterocyclic ring prior to hydrogenolysis (Scheme 2).[1,3,4,13]

It is therefore apparent that a deep understanding of the elementary steps involved in the selective hydrogenation of IN to indoline (INE) is of utmost importance for designing improved HDN catalysts. Homogeneous catalysts that are capable of assisting the hydrogenation of IN to INE are virtually unknown,[4,14−16] however, and all the available mechanistic information on IN reduction has been provided by the heterogeneous studies.[1,3]

In the course of our studies of HDN and HDS catalysis by phosphine-modified late-transition-metal catalysts,[4,17−20] we have recently found that the tripodal tridentate ligand $MeC(CH_2PPh_2)_3$ (triphos) forms, in conjunction with rhodium[19] and ruthenium,[20] efficient

Chart 1



catalysts for the hydrogenation/hydrogenolysis of several S- and N-heterocycles, including the selective reduction of Q to 1,2,3,4-tetrahydroquinoline (THQ) (Chart 1).[4,17]

In this paper, we describe our successful attempts to hydrogenate IN to INE in the homogeneous phase with rhodium(III) and ruthenium(II) catalysts modified with the triphos ligand. It has been found that the presence of a strong protic acid in the reaction mixture is required to generate an effective catalyst system.

Experimental Section

General Methods. All reactions and manipulations, except as stated otherwise, were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Reactions under a controlled pressure of hydrogen were performed with a stainless steel Parr 4565 reactor (100 mL) equipped with a Parr 4842 temperature and pressure controller. The reactor was connected to a gas reservoir to maintain a constant pressure all over the catalytic reactions. IN (98%), trifluoromethanesulfonic acid (TfOH, 98%), and *p*-toluenesulfonic acid hydrate (TsOH, 98%) were purchased from Aldrich and used without further purification. The complexes [Rh(DMAD)(triphos)]PF_6[21a] (DMAD = dimethyl acetylenedicarboxylate), $[RhH(OTf)_2(triphos)]$,[17] and $[Ru(MeCN)_3(triphos)](OTf)_2$[20d] were prepared as previously described. The indole oligomers 2-(2-aminophenyl)-1,1-bis(3-indolyl)ethane[22,23a] and 2-(3-indolyl)-indoline[23a] were prepared according to the literature. THF and THF-d_8 were purified by distillation from $LiAlH_4$ under nitrogen. Deuterated solvents for NMR measurements were dried over molecular sieves. All of the other reagents and chemicals were reagent grade and were used as received from commercial suppliers. Routine and high-pressure ^1H (200.13 MHz) and $^{31}P\{^1H\}$ NMR (81.01 MHz) spectra were determined with a Bruker ACP 200 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR

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spectra of the protonated indole oligomers were recorded on a Bruker Avance DRX-500 spectrometer at 500.13 and 125.76 MHz, respectively. The assignments of the signals resulted from 1D spectra and 2D ^{1}H-COSY, ^{1}H-TOCSY, and ^{1}H−^{13}C correlation experiments using nonspinning samples. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the chemical shifts of residual solvent resonances (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P), with downfield values reported as positive. The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Firenze, Italy).[24] *Caution*! Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes. GC analyses were performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analyses.

Catalytic Hydrogenation of IN with the Catalyst Precursor [Rh(DMAD)(triphos)]PF_6 (1) in the Presence of TfOH. HPNMR Experiment. The reaction was followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. A 10 mm sapphire tube was charged with a THF-d_8 (2 mL) solution of **1** (11 mg, 0.011 mmol), TfOH (10 μl, 0.11 mmol), and a 20-fold excess of IN (26 mg, 0.22 mmol) under nitrogen at room temperature. The ^{1}H NMR spectrum of this sample showed the almost complete conversion of IN into a 3:1 mixture of the protonated forms of both the dimer 2-(3-indolyl)-indoline[23a] (**6H**$^+$) and the trimer 2-(2-aminophenyl)-1,1-bis(3-indolyl)ethane[22,23a] (**7H**$^+$) (see below), which are known to be in equilibrium with the 3*H*-indolium cation in protic acid media.[25,26] The tube was then pressurized with hydrogen to 30 bar. The reduction of the substrate started at ca. 60 °C with formation of the protonated form of INE (INEH$^+$). As the concentration of INEH$^+$ increased, the concentration of both oligomers decreased until IN and INEH$^+$ (at ca. 50% conversion) were the only organic compounds in the reaction mixture. Along with the hydrogenation of IN, **1** disappeared, while the catalytically inactive binuclear complex [(triphos)RhH(μ-H)$_2$HRh(triphos)](OTf)$_2$ (**5**) became visible at ca. 50% conversion. No intermediate metal species containing coordinated indole-derived ligands was detected in the course of the catalysis.

An identical NMR picture was obtained when the monohydride [RhH(OTf)$_2$(triphos)] (**3**; 11.3 mg, 0.011 mmol) was employed as the catalysis precursor in place of **1**: the hydrogenation of IN into INEH$^+$ occurred at ca. 60 °C, while no triphos−rhodium species was seen, except for the tetrahydride **5** at a late stage of the reaction.

Catalytic Hydrogenation of IN with the Catalyst Precursor [Ru(MeCN)$_3$(triphos)](OTf)$_2$ (2) in the Presence of TfOH. HPNMR Experiment. The reaction was followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. A 10 mm sapphire tube was charged with a THF-d_8 (2 mL) solution of **2** (13 mg, 0.011 mmol), TfOH (10 μl, 0.11 mmol), and a 20-fold excess of IN (26 mg, 0.22 mmol) under nitrogen at room temperature. The immediate conversion of IN into its oligomers **6H**$^+$ and **7H**$^+$ was observed by ^{1}H NMR spectroscopy. The tube was then pressurized with hydrogen to 30 bar. The reduction of the substrate occurred at ca. 60 °C. Details of this experiment are discussed in a following section.

Control NMR Study of the Reaction between IN and TfOH. A 5 mm NMR tube was charged with a THF-d_8 (1 mL) solution of IN (50 mg, 0.43 mmol) and TfOH (20 μl, 0.22 mmol) under nitrogen at room temperature. The preparation of the solution under an oxygen-free atmosphere was required, as the protonated indoles are rapidly oxidized by atmospheric oxygen.[25,26] The ^{1}H NMR spectrum of the sample showed the presence of **6H**$^+$ and **7H**$^+$ in a 3:1 ratio. Complete characterization of the products was achieved on the basis of ^{13}C{^{1}H} NMR spectra and 2D ^{1}H-COSY, ^{1}H-TOCSY, and ^{1}H−^{13}C-HETCOR experiments. Data for **6H**$^+$ are as follows. ^{1}H NMR (THF-d_8, 23 °C): δ 11.20 (br s, 1H, H_{1A}), 10.86 (br s, 1H, $H_{1'}$), 10.27 (br s, 1H, H_{1B}), 7.83 (dq, 1H, J_{HH} = 8.0, 0.9 Hz, $H_{7'}$), 7.78 (d, 1H, J_{HH} = 2.7 Hz, $H_{2'}$), 7.76 (ddt, 1H, J_{HH} = 7.6, 1.9, 1.1 Hz, H_7), 7.74 (dd, 1H, J_{HH} = 7.9, 0.7 Hz, H_4), 7.69 (td, 1H, J_{HH} = 7.5, 1.1 Hz, H_5), 7.65 (dt, 1H, J_{HH} = 8.2, 1.0 Hz, $H_{4'}$), 7.61 (tdt, 1H, J_{HH} = 7.6, 1.4, 0.8 Hz, H_6), 7.36 (ddd, 1H, J_{HH} = 8.2, 7.1, 1.0 Hz, $H_{5'}$), 7.26 (ddd, 1H, J_{HH} = 8.1, 7.1, 1.0 Hz, $H_{6'}$), 6.06 (tt, 1H, J_{HH} = 7.9, 6.5, 1.0 Hz, H_2), 3.98 (m, ABM spin system, 2H, $J_{H_{3A}H_{3B}}$ = 16.5 Hz, $J_{H_{3A}H_2}$ = 7.6 Hz, $J_{H_{3B}H_2}$ = 8.2 Hz, H_{3A-3B}). ^{13}C{^{1}H} NMR: δ 137.02 ($C_{7'a}$), 136.45 (C_{7a}), 130.82 (C_5), 129.33 (C_6), 127.79 ($C_{3'a}$), 126.82 (C_7), 126.61 (C_{3a}), 126.39 ($C_{2'}$), 123.12 ($C_{5'}$), 120.76 (C_4), 120.71 ($C_{6'}$), 119.3 ($C_{7'}$), 112.73 ($C_{4'}$), 110.21 ($C_{3'}$), 58.85 (C_2), 35.85 (C_3). Data for **7H**$^+$ are as follows. ^{1}H NMR (THF-d_8, 23 °C): δ 11.66 (br s, 2H, $H_{1'}$), 9.49 (br s, 1H, H_1), 7.64 (dd, 2H, J_{HH} = 8.0, 1.0 Hz, $H_{7'}$), 7.55 (dd, 1H, J_{HH} = 7.9, 1.9 Hz, H_6), 7.49 (dt, 2H, J_{HH} = 8.1, 0.9 Hz, $H_{4'}$), 7.47 (dd, 1H, J_{HH} = 7.0, 2.0 Hz, H_3), 7.40 (td, 1H, J_{HH} = 7.6, 2.1 Hz, H_4), 7.40 (d, 2H, J_{HH} = 0.7 Hz, $H_{2'}$), 7.39 (td, 1H, J_{HH} = 7.6, 1.5 Hz, H_5), 7.19 (ddd, 2H, J_{HH} = 8.1, 7.0, 1.0 Hz, $H_{5'}$), 7.04 (ddd, 2H, J_{HH} = 8.0, 7.1, 1.0 Hz, $H_{6'}$), 5.19 (tt, 1H, J_{HH} = 7.8, 0.9 Hz, H_9), 3.90 (d, 2H, J_{HH} = 7.6 Hz, H_8). ^{13}C{^{1}H} NMR δ 138.15 (C_2), 137.98 ($C_{7'a}$), 135.99 (C_7), 131.6 (C_3), 130.35 ($C_{3'a}$), 129.63 (C_5), 128.01 (C_4), 124.05 (C_6), 123.51 ($C_{2'}$), 121.77 ($C_{5'}$),119.59 ($C_{7'}$), 119.08 ($C_{6'}$), 118.92 ($C_{3'}$), 111.97 ($C_{4'}$), 37.08 (C_8), 34.24 (C_9).

Catalytic Hydrogenation of IN by either 1 or 2. Autoclave Experiments. The reaction conditions and the results of these experiments have been collected in Tables 1−3. In a typical experiment, a 30 mL solution of THF containing 0.022 mmol of catalyst precursor, 2.2 mmol of substrate, and the required amount of TfOH was introduced by suction into an autoclave. After the mixture was brought to the desired pressure of hydrogen at room temperature, it was heated to the appropriate temperature and then immediately stirred (750 rpm). During the reaction the pressure level was kept constant by continuous feeding of hydrogen from a high-pressure gas reservoir. After the desired time, the reaction was stopped by cooling the autoclave to room temperature. The pressure was then released. The product composition was determined by GC analysis of the crude reaction mixture. In the runs performed in the presence of acid coreagents, the added amounts of acid were neutralized with THF/water solutions of NaOH before carrying out the GC analysis.

Selected experiments were carried out in the presence of a large excess of elemental mercury (2000 equiv) in an attempt to evaluate the homogeneity of the catalytic reactions. In no case was an appreciable decay of the conversions observed.[19b]

Results and Discussion

In Situ NMR Studies. The catalyst precursors that have been employed in this study were the rhodium(I) complex [Rh(DMAD)(triphos)]PF_6[21] (**1**) and the ruthenium(II) tris(acetonitrile) complex [Ru(MeCN)$_3$(triphos)](OTf)$_2$[20] (**2**) (Chart 2).

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Table 1. Hydrogenation of IN to INE Catalyzed by 1 and 2[a]

entry	precursor	amt of TfOH (equiv)	time (h)	*T* (°C)	yield (%)
1	**1**	0	1	60	<1
2	**1**	0	1	100	1
3	**1**	0	5	100	11
4	**1**	20	1	60	16
5	**1**	20	1	100	21
6	**1**	20	5	100	51
7	**1**	40	1	60	25
8	**1**	40	1	100	34
9	**1**	40	5	100	70
10	**1**	100	1	60	96
11	**2**	0	1	100	<1
12	**2**	0	5	100	4
13	**2**	20	1	100	17
14	**2**	20	5	100	45
15	**2**	40	1	100	17
16	**2**	40	5	100	47
17	**2**	100	1	100	13
18[b]	**1**	40	1	100	32
19[c]	**1**	40	1	100	34
20[b]	**2**	40	1	100	14
21[c]	**2**	40	1	100	16

[a] Experimental conditions: precursor **1** (or **2**), 0.022 mmol; IN, 2.2 mmol; THF, 30 mL; $p(H_2)$, 30 bar. [b] Precursor **7**, 0.011 mmol. [c] Precursor **6**, 0.007 mmol.

Table 2. Dependence of the Hydrogenation of IN to INE Catalyzed by 1 and 2 on Hydrogen Pressure[a]

entry	precursor	amt of TfOH (equiv)	$p(H_2)$ (bar)	*T* (°C)	yield (%)
1	**1**	100	30	60	96
2	**1**	100	15	60	94
3	**1**	100	10	60	92
4	**1**	100	5	60	89
5	**2**	40	30	100	17
6	**2**	40	15	100	10
7	**2**	40	10	100	7
8	**2**	40	5	100	5

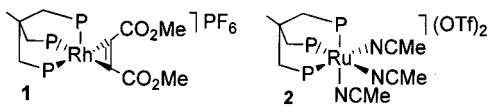
[a] Experimental conditions: precursor, 0.022 mmol; IN, 2.2 mmol; THF, 30 mL; time, 1 h.

Table 3. Hydrogenation of Equimolar Q/IN Mixtures Catalyzed by 1 and 2[a]

entry	precursor	THQ yield (%)	INE yield (%)
1	**1**	96 [98][b]	9 [21][c]
2	**2**	97 [98][b]	12 [17][c]

[a] Experimental conditions: precursor, 0.022 mmol; precursor/Q/IN ratio, 1:100:100; TfOH, 0.44 mmol; THF, 30 mL; $p(H_2)$, 30 bar; *T*, 100 °C; time, 1 h. [b] In the absence of IN.[4,17] [c] In the absence of Q; see Table 1.

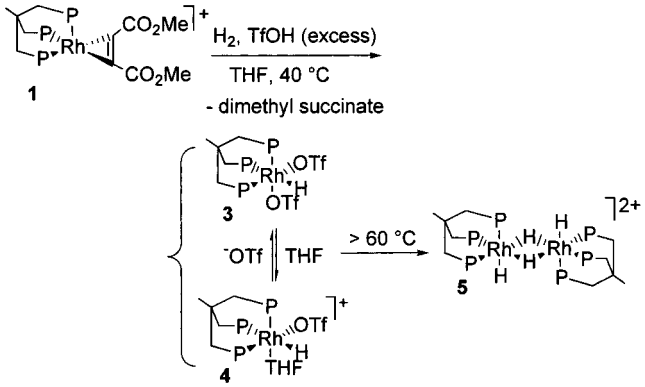
Chart 2



1 2

The hydrogenation of **1** in THF in the presence of triflic acid has been reported previously.[17] To reiterate, the rhodium precursor reacts with H_2 (30 bar) in the presence of an excess of TfOH to give the mononuclear rhodium(III) complexes [RhH$(OTf)_2$(triphos)] (**3**) and [RhH(THF)(OTf)(triphos)]OTf (**4**), which interconvert into each other even at room temperature (Scheme 3). Above 60 °C, both **3** and **4** transform slowly but irreversibly into the binuclear complex [(triphos)RhH-(μ-H)$_2$HRh(triphos)]$(OTf)_2$ (**5**). The substitution of TsOH for TfOH gave [RhH$(OTs)_2$(triphos)], analogous to the case for **3**, while the use of HBF_4·OEt_2 led to the formation of the tetrahydride [(triphos)RhH(μ-H)$_2$HRh-(triphos)]$(BF_4)_2$ at any temperature.[17]

Scheme 3

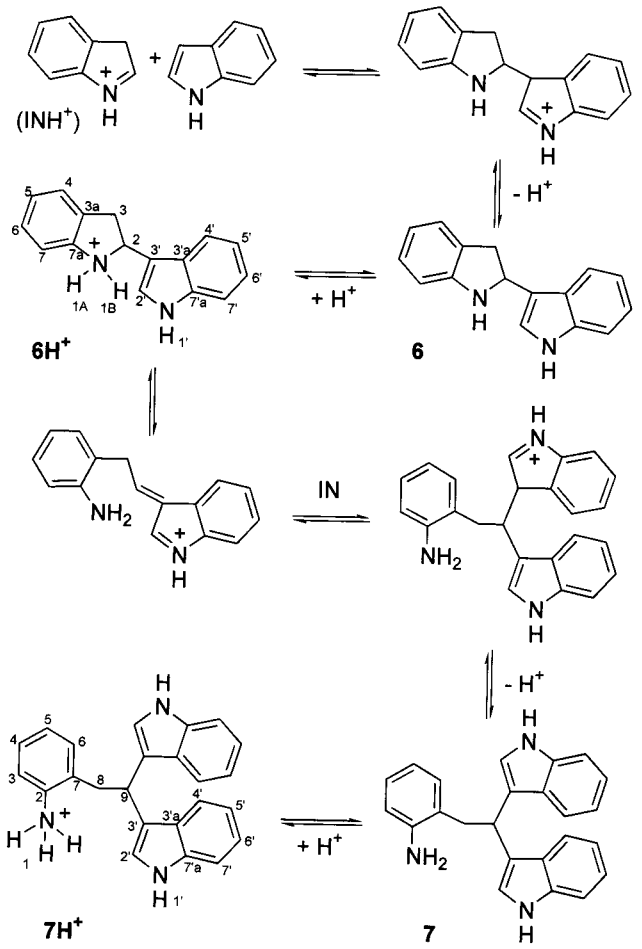


Since the reduction of IN to INE with **1** requires the presence of an excess of protic acid to occur effectively (vide infra), the hydrogenation of **1** by high-pressure NMR spectroscopy (HPNMR) has been studied in THF-d_8 in the presence of 20 equiv of substrate and 10 equiv of TfOH under the same pressure of the catalytic reactions (30 bar of H_2). No triphos complex containing indole-derived species was detected by $^{31}P\{^1H\}$ NMR spectroscopy in the course of the reaction in the temperature range from 20 to 60 °C, while ^1H NMR spectroscopy showed the conversion of IN into a 3:1 mixture of the protonated forms of the dimer 2-(3-indolyl)indoline[23a] (**6**) and the trimer 2-(2-aminophenyl)-1,1-bis(3-indolyl)ethane[22,23a] (**7**) even at room temperature. The reduction of the substrate started at ca. 60 °C with formation of protonated INE ($INEH^+$). The binuclear tetrahydride **5** became visible by NMR spectroscopy only when ca. 50% of the substrate was consumed. Before this stage, no triphos−rhodium complex was detected by NMR spectroscopy, which indicates the presence of species with a lifetime shorter than the NMR time scale. Independent experiments showed **5** to be catalytically inactive for the hydrogenation of IN in the presence of any acid coreagent even under harsh reaction conditions (160 °C, 40 bar of H_2).

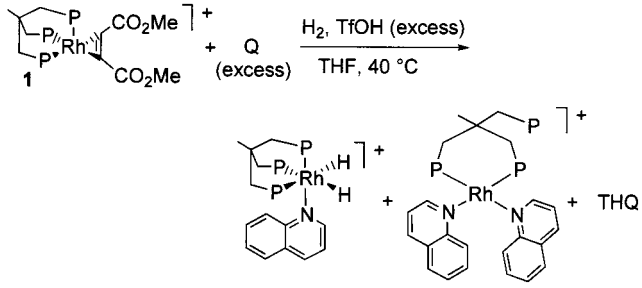
Complete protonation of IN has been reported to occur in strongly acidic media with formation of the 3*H*-indolium cation (INH^+),[26] while moderately strong acids (e.g. trifluoroacetic or triflic acid)[26c] give the oligomers **6** and **7**, which are in equilibrium with IN, INH^+, and their protonated forms $\mathbf{6H}^+$ and $\mathbf{7H}^+$ (Scheme 4).[25]

As shown in Scheme 4, the acid-catalyzed formation of the oligomers **6** and **7** from IN does involve a complex series of equilibria.[22,23,25,26] The protonation of IN gives INH^+, which reversibly reacts with IN to give **6** in two steps.[23] This dimer undergoes reversible ring opening by proton attack to give a product that, upon further nucleophilic attack by IN, yields **7**. On the basis of the equilibria shown in Scheme 4, the presence of $\mathbf{6H}^+$ and $\mathbf{7H}^+$ in the catalytic mixtures ensures the presence of an equilibrium concentration of INH^+.[25,26] Indeed, control experiments with either **1** or **2** as precatalyst and **6** or **7** as substrate in place of IN gave similar productions of INE in the autoclave experiments as well as identical NMR spectra (vide infra).

Scheme 4



Scheme 5



The fact that no rhodium complex with IN, INE, or INH^+ was detected in the catalytic mixture reflects the scarce ligating properties of these N-heterocycles.[3,4,7,9−12] Q, which is a fairly good nitrogen nucleophile, behaves differently: its hydrogenation to THQ in the presence of **1** and TfOH proceeds, in fact, via isolable Q adducts as either catalytically active species ($[Rh(H)_2(\eta^1\text{-}N\text{-}Q)(triphos)]^+$) or the resting state ($[Rh(\eta^1\text{-}N\text{-}Q)_2(\eta^2\text{-}triphos)]^+$) (Scheme 5).[17]

The formation of the monohydride complexes **3** and **4** by hydrogenation of **1** in the presence of TfOH does not necessarily imply the occurrence of a heterolytic splitting of H_2 at rhodium, which, however, has several precedents in homogeneous catalysis for triphos complexes with d^6 metal ions.[20a,27−30] In fact, following the hydrogenation of DMAD to dimethyl succinate, a rhodium(I) fragment is formed that may oxidatively add either TfOH or H_2 (Scheme 6). In the former case, an

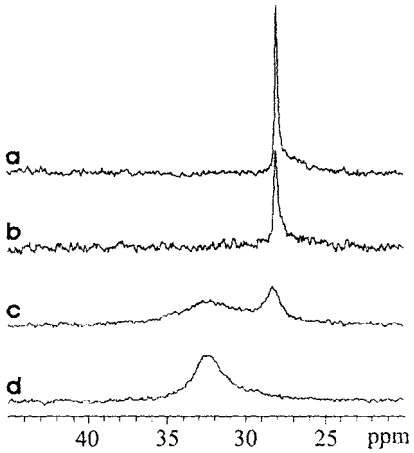
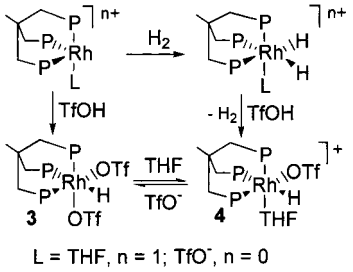


Figure 1. $^{31}P\{^1H\}$ HP NMR study (sapphire tube, THF-d_8, 81.01 MHz) of the catalytic hydrogenation of IN in the presence of **2** and TfOH (30 bar of H_2, IN:TfOH:**1** = 20:10:1): (**a**) at room temperature; (**b**) at 40 °C; (**c**) at 60 °C; (**d**) at 80 °C.

Scheme 6



equilibrium mixture of **3** or **4** will be straightforwardly obtained, while the oxidative addition of H_2 will give a dihydride complex containing either THF or triflate ligands, e.g. $[Rh(H)_2(THF)(triphos)]^+$ or $[Rh(H)_2(OTf)(triphos)]$.[17] Both of these products have been previously isolated and observed to transform into a mixture of **3** and **4** by reaction with TfOH in THF.[17]

HPNMR spectroscopy was employed also to study the hydrogenation of IN with the ruthenium precursor **2** under experimental conditions comparable to those employed in catalysis. Like rhodium, no catalytically relevant species was seen on the NMR time scale. A sequence of $^{31}P\{^1H\}$ HPNMR spectra is shown in Figure 1 for a reaction in which **2** was used in conjunction with TfOH (10 equiv) to catalyze the hydrogenation of IN (20 equiv) in THF-d_8. At room temperature (trace **a**), the tris(acetonitrile) complex reacted with neither H_2 (30 bar) nor TfOH. Only above 40 °C did the $^{31}P\{^1H\}$ NMR resonance of the ruthenium precursor decrease in intensity with concomitant formation of a much broader signal at lower field (ca. 32 ppm) (traces **b** and **c**). The formation of $INEH^+$ started to occur at ca. 60 °C, while the signal of **2** disappeared at ca. 80 °C (trace **d**). Decreasing the temperature regenerated the initial signal of **2** with no apparent decrease in intensity. No product derived from the possible hydrogenation of acetonitrile was observed by GC/MS.[20a,c] Since heating a THF-d_8 solution of **2** in the presence of TfOH under N_2 gave an identical $^{31}P\{^1H\}$ NMR picture, it was concluded that the broad signal at 32 ppm is due to a fluxional ruthenium(II) complex in which MeCN, triflate, and solvent molecules are in fast exchange.

Nevertheless, the hydrogenation of the substrate took place, which means that either IN or INH^+ is able to interact with ruthenium and then accept hydrogen atoms from activated H_2. Our preference is for INH^+ that can use the localized C═N bond for coordination. Substrate binding to ruthenium and the following hydrogen transfer are apparently much faster than the NMR time scale, as neither hydride nor coordinated INH^+ has been detected.

The activation of H_2 by the "Ru^{II}(triphos)" fragment has been the subject of several studies: either a nonclassical ruthenium(II) η^2-H_2 adduct or a classical ruthenium(IV) may be formed, depending on the experimental conditions as well as the nature of the coligands.[20,27,28,31] In the absence of detected hydride-containing intermediates, neither activation path of H_2 can be ruled out in the present catalytic reactions.

Catalytic Experiments in the Autoclave. In homogeneous phase, IN is much more difficult to reduce than Q.[1,3,4] Only $[RuHCl(PPh_3)_3]$[14] and $[RuH(CO)(MeCN)(PPh_3)_2]BF_4$[15] have been reported to hydrogenate IN to INE, but the catalytic activity was very low (TOF ≤ 1). The η^1(N) coordination, which is critical for selective nitrogen ring reduction in Q, is virtually unknown for IN, which prefers to bind metal centers using the carbocyclic ring.[9−12]

To the best of our knowledge, the only catalyst systems that are able to regioselectively hydrogenate IN to INE with acceptable turnover frequencies are those generated by the catalyst precursors **1** and **2**.

As shown in Table 1, both the rhodium and ruthenium precursor generates effective and selective catalysts for the homogeneous hydrogenation of IN to INE in the presence of a protic acid coreagent. Other Brønsted acids whose conjugated bases behave as weak but effective ligands toward rhodium(III) and ruthenium(II) ions (e.g. TsOH) could be equally used. In contrast, acids with very weak conjugated bases (e.g. HBF_4) did not generate any efficient catalyst due to either formation of inactive species[17] (e.g. the rhodium tetrahydride **5**) or extensive decomposition of the metal precursor (ruthenium).

Irrespective of the metal, almost no hydrogenation occurred in the absence of acid within 1 h at 100 °C (entries 2 and 11), while both **1** and **2** led to 21% (entry 5) and 17% (entry 13) production of INE, respectively, when 20 equiv of TfOH was added to the catalytic mixture.

Under comparable conditions, the rhodium precursor was more efficient than the ruthenium species and allowed for almost complete hydrogenation of the substrate even at 60 °C when the acid was added in an amount comparable to that of IN (entry 10). In contrast, the activity of the ruthenium precursor did not increase using acid-to-catalyst ratios higher than 20 (entries 13−17). Eventually, a decrease was observed, which may be due to competitive binding of triflate ion vs substrate or H_2 (entry 17).

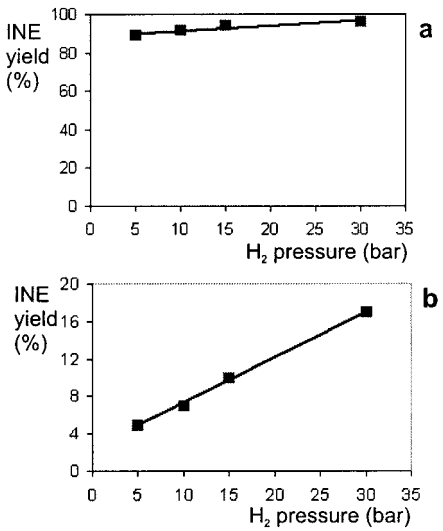


Figure 2. Plots of conversion vs H_2 pressure for the hydrogenation of IN to INE by **1** (**a**) and **2** (**b**).

In situ NMR experiments showed that the acid generates the indole oligomers $\mathbf{6H}^+$ and $\mathbf{7H}^+$ in equilibrium with the 3*H*-indolium cation. The latter possesses a localized C═N double bond, which is much easier to reduce than the pseudoaromatic C═C bond of IN.

The beneficial effect of the protic acid on the hydrogenation rate is not surprising, as also the heterogeneous hydrogenation of IN with either Raney nickel or copper chromate requires the presence of strong acids to occur.[32]

Irrespective of the catalyst precursor, the substitution of the oligomers **6** and **7** for IN in reactions with 40 equiv of acids gave similar conversions (entries 18−21), while no activity was observed when syngas (30 bar of 1:1 CO/H_2) was employed in the place of H_2. The final solutions of these reactions were concentrated to dryness in vacuo, and the residues, dissolved in CD_2Cl_2, were analyzed by NMR spectroscopy. The known dicarbonyl complexes $[Rh(CO)_2(triphos)]^+$ and $[RuH(CO)_2(triphos)]^+$ were unambiguously recognized.[33,34] These dicarbonyl complexes were independently employed as catalyst precursors for the hydrogenation of IN (THF, 30 bar of H_2, 40 equiv of TfOH, 100 °C), but no substrate conversion was observed. The reactions with syngas and with the isolated dicarbonyl complexes showed that IN binding is important for its reduction and therefore ruled out the occurrence of free radical mechanisms such as that reported for the hydrogenation of anthracene by $Co_2(CO)_8$.[35]

Selected catalytic reactions were carried out varying the H_2 pressure from 5 to 30 bar. In the case of rhodium (Table 2, entries 1−4), the rate was independent of the H_2 pressure (Figure 2**a**). In contrast, the conversions obtained with the ruthenium catalyst increased linearly by increasing the H_2 pressure (Table 2, entries 5−8),

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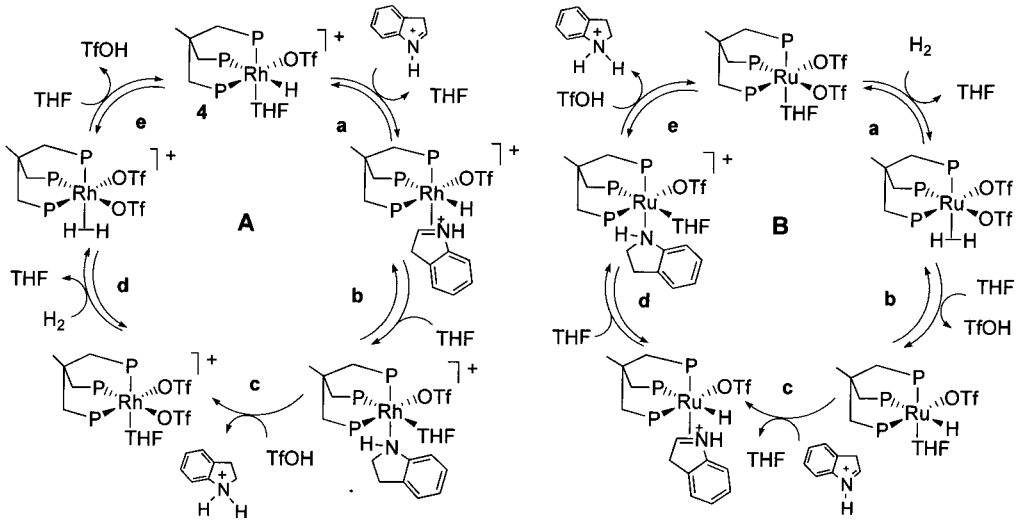
Scheme 7



which suggests a first-order dependence on H_2 concentration (Figure 2**b**).

No hydrogenation of IN was observed in the absence of H_2, while the presence of a large excess of elemental mercury did not inhibit the catalytic activity, which is consistent with truly homogeneous processes.[19b] Moreover, no dehydrogenation[3a,25] occurred when INE was employed in the place of IN under identical catalytic conditions.

Hydrogenation reactions of equimolecular Q/IN mixtures catalyzed by either **1** or **2** have been studied under experimental conditions at which the conversion was quantitative for Q and partial for IN. A perusal of the results (Table 3) shows that Q slows down the hydrogenation rate of IN, which may be interpreted in terms of either competitive binding of Q to the metal center[3,14,36] or reduced acid concentration due to the greater basicity of Q and THQ as compared to IN.

Mechanistic Considerations. In addition to the formation and disappearance of the oligomers **6H**$^+$ and **7H**$^+$, the only species observed under catalytic conditions by in situ HP NMR spectroscopy was a ruthenium(II) resting state in which triflate ions exchange quite rapidly with solvent molecules. Apparently, both the coordination of the substrate and the following hydrogenation step are very fast and proceed via intermediates that cannot be seen by NMR spectroscopy. On the other hand, no intermediate containing either Q as η^2-(C,N) ligand or 1,2-dihydroquinoline (1,2-DHQ) as η^2-(C,C) ligand was similarly detected by NMR spectroscopy along the hydrogenation of Q with **1** in the presence of a protic acid coreagent.[17]

The failure in observing catalytically relevant intermediates and in obtaining detailed kinetic data due to the complexity of the catalytic mixtures does not allow one to propose unambiguous catalytic cycles for the acid-assisted hydrogenation of IN by either **1** or **2**. Nonetheless, an attempt to rationalize these reactions can be made on the basis of some sound experimental observations.

(i) The HP NMR studies of the hydrogenation of **1** in the presence of an excess of TfOH show the rhodium precursor to give an equilibrium mixture of the monohydrides **3** and **4**, which disappear upon addition of IN; this means that the INH$^+$ generated in situ does interact with the metal centers (Schemes 3 and 6). In the case of ruthenium, the only metal species visible on the NMR time scale contains neither hydride ligands nor indole-derived compounds. The same ruthenium species was seen with or without H_2 and IN, in fact. It is therefore reasonable to conclude that ruthenium resides during the catalysis in a sort of resting state, e.g. [Ru(OTf)$_2$(THF)(triphos)], where triflate ions and solvent molecules exchange rapidly. Consistent with a resting state of this type, it has been found that a overly high concentration of triflate ions lowers the activity of the ruthenium-based catalyst.

(ii) The reaction rate is zero order in H_2 concentration with rhodium, while it is first order with ruthenium.

(iii) The occurrence of substrate hydrogenation via a coordination mechanism and not by a free radical process is confirmed by the reactions with syngas, which inhibits the reduction of IN.[36a]

Incorporation of all these observations leads to the catalytic cycles illustrated in Scheme 7**A** for rhodium and in Scheme 7**B** for ruthenium.

The rhodium cycle is initiated by complex **4**, which undergoes displacement of a solvent molecule by INH$^+$ (step **a**). The following hydride migration from rhodium to the C_2 carbon atom of the coordinated INH$^+$ (step **b**) would produce INE, which may coordinate the metal and be removed from it by reaction with TfOH. The activation of H_2 to restore **4** (steps **d** and **e**) can be accomplished via either oxidative addition or heterolytic splitting of η^2-H_2.[27,28] Our preference for the latter hypothesis is absolutely arbitrary; however, a Rh(V) dihydride is quite unlikely for triphos. The zero-order dependence on H_2 pressure suggests that the rate-limiting step should be sought in either hydride migration from rhodium to coordinated INH$^+$ or INE elimination. The irreversibility of step **c** is consistent with the failure of INE dehydrogenation under catalytic conditions.

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The ruthenium cycle **B** is rather similar to the rhodium cycle, the major difference being the rate-limiting step that should be step **a**, as it involves the only species seen by NMR spectroscopy during the catalysis and is also consistent with the first-order rate dependence on H_2 concentration. Like rhodium, the formation of an η^2-H_2 transient species is arbitrary, as a Ru(IV) dihydride may be equally possible.

Conclusions

In this and several previous papers,[17−20] the hydrogenation of N- and S-heterocycles has been investigated with the use of homogeneous catalysts containing rhodium and ruthenium supported by the tripodal ligand triphos. To reiterate, rhodium(I) and ruthenium(0) fragments as in [RhH(triphos)] and [RuH(triphos)]$^-$ (Chart 1) insert into the C−S bond of thiophenes, leading ultimately to catalytic hydrogenolysis to thiols,[19−20b,c] while they are inactive for both hydrogenation and hydrogenolysis of N-heterocycles such as Q and IN. It is generally agreed that the much higher bond energy of C−N bonds as compared to C−S bonds (by 3−9 kcal mol^{-1}) makes C−N insertion much more difficult to accomplish than C−S insertion. However, the *soft* character of the metal centers in the electron-rich systems [RuH(triphos)]$^-$ and [RhH(triphos)] certainly contributes to disfavor the coordination of *hard* nitrogen donors, which is a propaedeutical condition to both hydrogenation and hydrogenolysis of most N-heterocycles.[3−8,13−17,36] Indeed, the rhodium(III) and ruthenium(II) fragments [Rh(H)$_2$(triphos)]$^+$ and [RuH(triphos)]$^+$ bind Q in an η^1(N) fashion and are efficient catalysts for its hydrogenation to THQ.[4,17]

It is shown in this paper that analogous rhodium(III) and ruthenium(II) systems are able to hydrogenate IN. Unlike Q, however, a protic acid coreagent is mandatory for the occurrence of catalytic reactions. It is proposed that the acid is important to allow for substrate coordination as a η^2(C,N)-3*H*-indolium cation as well as maintain rhodium and ruthenium in the +3 and +2 oxidation states, respectively, over all the catalytic reactions.

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