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hexene hydrogenation reaction of
 $RuCl_2(DMSO)_2(NC_5H_4CO_2Na-3)_2$*

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Synthesis, characterization, and biphasic ionic liquid media 1-hexene hydrogenation reaction of $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$

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Abstract $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$ is very soluble in the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [(BMIM)BF₄]. The complex was prepared by reacting $\text{RuCl}_2(\text{DMSO})_4$ with $\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3}$, sodium nicotinate, in toluene, and was characterized by spectroscopic methods. The complex catalyzes the hydrogenation of 1-hexene (600 psi H₂, 100 °C) in a two-phase system consisting of cyclohexane/[(BMIM)BF₄] with 75% conversion in 24 h and modest substrate isomerization. The complex shows good stability and can be reused several times with little loss in activity.

Introduction

Recently, ionic liquids (ILs) have received worldwide academic and industrial attention as replacements for organic solvents in catalysis [1]. Some of the attractive features of ILs in catalysis include the versatility to act both as catalyst and solvent, the profound effect that may have on solvation, solvolysis, reaction rate, selectivity minimizing side reactions, and the opportunity of an easy recovery of the catalyst. Ionic liquids possess useful physical characteristics as solvents in biphasic catalytic reactions with organometallic complexes [2–9]. In general, transition metal-catalyzed hydrogenation reactions in ionic liquids are particularly promising owing in part to the large number of known ionic hydrogenation catalysts that are available [10]. The first successful hydrogenation reactions in ionic liquids were studied by the groups of

De Souza [11] and Chauvin [12] in 1995. De Souza et al. investigated the Rh-catalyzed hydrogenation of cyclohexene in 1-*n*-butyl-3-methylimidazolium [(BMI)BF₄] with 40% conversion in 120 h and turnover number (TON) = 6,000 and turnover frequency (TOF) = 50 h⁻¹. Chauvin et al. dissolved the cationic “Osborn complex” [Rh(nbd)(PPh₃)₂][PF₆] (nbd = norbornadiene, PPh₃ = triphenylphosphine) in ionic liquids with weakly coordinating anions (e.g., [PF₆]⁻, [BF₄]⁻, and [SbF₆]⁻) and used the obtained ionic catalyst solutions for the biphasic hydrogenation of 1-pentene. In our laboratory, we have performed a detailed study on the catalytic hydrogenation of 1-hexene using the $\text{RuCl}_2(\text{TPPMS})_3$ (DMSO), (TPPMS = triphenylphosphine monosulfonate) complex in the ionic liquid (BMI)PF₆ and have found that the system catalyzes 1-hexene hydrogenation (500 psi H₂, 100 °C) with 80% conversion in 24 h with TON = 480 and TOF = 20 h⁻¹ [13]. Campbell et al. [14] studied the hydrogenation of 1,3-cyclohexadiene with ruthenium nanoparticles (30 °C, 1.2 bar H₂, 90 min) in ionic liquid media with high selectivity toward cyclohexene and showed TON = 70 and TOF = 46 h⁻¹. Lee et al. [15] studied asymmetric catalytic hydrogenation reactions using a Rh complex stabilized in ionic liquid and found low catalytic activity loss during catalyst reuse. In this work, we report the synthesis, characterization, and catalytic hydrogenation reaction in ionic liquid media [(BMIM)BF₄] of the novel $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$ complex.

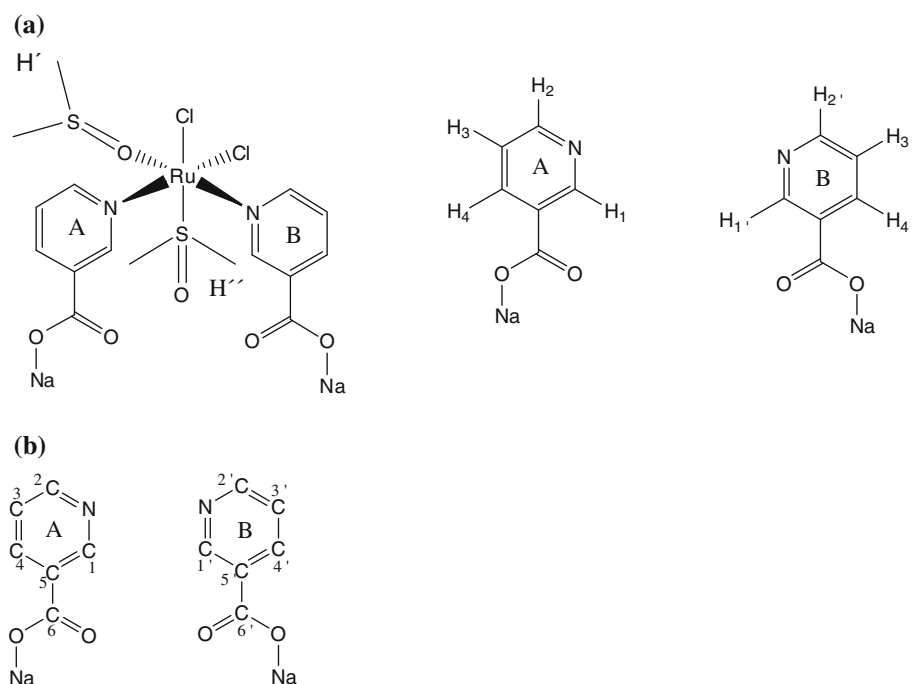
Experimental

Materials and methods

All manipulations were carried out under argon atmosphere, using standard Schlenk techniques. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

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Fig. 1 Proposed structure for complex, $\text{RuCl}_2(\text{DMSO})_2(\text{C}_6\text{H}_4\text{O}_2\text{Na})_2$ according to a (a) ^1H NMR and (b) ^{13}C NMR



(Strem) and NaBF_4 (Aldrich) were used without further purification. DMSO (Analar), 1-methylimidazol, *n*-butyl chloride, 1-hexene, and cyclohexane (Aldrich) were purified by distillation prior to use. H_2 and Ar (Gases Industriales de Venezuela) were obtained commercially and used as received. $[(\text{BMIM})\text{BF}_4]$ and $\text{RuCl}_2(\text{DMSO})_4$ were synthesized and characterized according to the literature [16–18].

Physical measurements

Vibrational spectra ($5,000\text{--}400\text{ cm}^{-1}$, KBr pellets) were taken with a Fourier Transform Perkin-Elmer 1725X spectrophotometer. Room temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ nuclear magnetic resonance NMR spectra were recorded as *DMSO- d_6* solutions using a Bruker Avance DRX 400-MHz spectrometer. Chemical shifts are expressed in ppm downfield from external TMS. Mass spectra (EI) were obtained on a Hewlett-Packard 5988 GC/MS spectrometer.

Synthesis of $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$

A solution of $\text{RuCl}_2(\text{DMSO})_4$ (1.00 g, 2.07 mmol) in toluene (10 mL) was mixed with a solution of sodium nicotinate (0.60 g, 4.13 mmol) in toluene (10 mL). The resultant solution was refluxed for 3 h, yielding an air-stable dark orange solid. This solid was recrystallized from methanol, and dried under vacuum. Yield 1.02 g (80%), decomposes $>300\text{ }^\circ\text{C}$, soluble in water, methanol. FTIR $\nu(\text{cm}^{-1})$ (s = strong, m = medium, w = weak), DMSO: $\nu\text{C-H}$ 3008w, 2921w; $\nu\text{S-O}$ 1,088 m, 922 m; $\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3}$: $\nu\text{C=N}$ 1,615 s, 1,564 $\nu\text{C=C}$ and νCOO^- 1,384 s. ^1H NMR data and assignments

(see Fig. 1a) $\delta(\text{ppm})$: $\text{H}_{1'}$ = 9.24(s,1H); H_1 = 9.07(s,1H); $\text{H}_2, \text{H}_2', \text{H}_4$ = 8.78 (d,3H, J = 6.0 Hz); $\text{H}_{4'}$ = 8.29 (d, 1H, J = 6.0 Hz); H_3 = 7.98 (t,1H, J = 6.5 Hz); $\text{H}_{3'}$ = 7.41 (t,1H, J = 6.5 Hz); DMSO: H' = 3.3 (s,6H), H'' = 2.68 (s,6H). ^{13}C NMR data and assignments (see Fig. 1b) $\delta(\text{ppm})$: C_1 = 156.3; C_2 = 145.4; C_3 = 127.2; C_4 = 144.8; C_5 = 136.2; C_6 = 171.8; $\text{C}_{1'}$ = 155.4; $\text{C}_{2'}$ = 143.8; $\text{C}_{3'}$ = 125.6; $\text{C}_{4'}$ = 139.6; $\text{C}_{5'}$ = 133.8; $\text{C}_{6'}$ = 171.8. Mass spectrum: $[\text{M}^+]$, m/e = 621; m/e = 540 (DMSO loss); m/e = 462 (two DMSO loss); $[\text{Ru}(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})]^+$ m/e = 246.

Catalytic runs

Catalytic trials were performed in a 10 mL Parr reactor with internal glass liner, heating unit, temperature and stirring control, and sampling valve. Conditions for a typical trial were as follows: cyclohexane (3.0 mL), $[(\text{BMIM})\text{BF}_4]$ (3.0 mL), 1-hexene (0.22 g, 2.6 mmol), $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$ (4.0 mg, 6.5×10^{-3} mmol), substrate/catalyst = ca. 400:1, H_2 pressure (200–1,000 psi), temperature (25–125 $^\circ\text{C}$), 1,600 rpm, 24 h reaction time. Reaction products were analyzed on a Perkin-Elmer Autosystem 900 GC, using 50 m column (0.52 μm diameter) quadrex of methyl silicone with H_2 carrying gas and a TC detector.

Results and discussion

Comparing the FTIR spectra of the complex and the free ligand $\text{NC}_5\text{H}_4\text{CO}_2\text{Na}$, it was observed that the assigned

COO⁻ group vibrations remain unaltered upon coordination, therefore suggesting that bonding does not occur through the carboxylate groups, but instead through the pyridyl nitrogen [19]. The ¹H, ¹³C NMR spectra show two series of signals that corresponds to a pair of nicotinate sodium rings and two molecules of DMSO in different chemical environments. The mass spectrum shows, in the range *m/z* 625–612, a series of peaks that are consistent with the isotopic pattern of Ru calculated with the Sheffield Chemputer program [20]. Exploration of the area up to *m/z* 2,000 shows no evidence of the presence of metal clusters. Finally, the analysis of the spectroscopic evidence and the proposed structure are both consistent with the minimum energy structure for this complex obtained by calculations performed with PC Spartan Plus software [21].

Hydrogenation reactions

The results of varying hydrogen pressure on the 1-hexene hydrogenation reaction are given in Fig. 2. Hydrogenation of 1-hexene increases when hydrogen pressure increases to 600 psi (64% conversion); however, at pressures greater than 600 psi, there is a significant decrease in the production of hexane, this is probably due to a hydrogen diffusion problem or the formation of catalytically inactive species. The isomerization reaction at 1,000 psi has high activity (35% total isomerization conversion) while at low pressures the rate of isomerization is lower.

The effects of temperature are shown in Fig. 3. There is a gradual increase in n-hexane hydrogenation product with a temperature increase from 25 to 125 °C. An increase in temperature decreases the ionic liquid viscosity, probably allowing better contact between the substrate and the

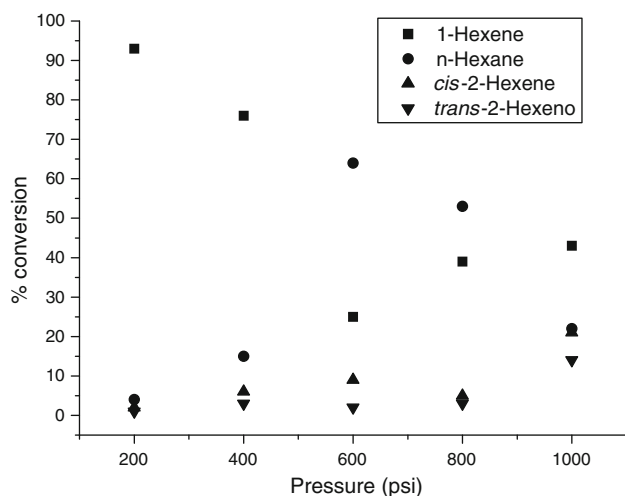


Fig. 2 H₂ pressure effect on 1-hexene hydrogenation. 100 °C, S/C: 400:1, cyclohexane (3.0 mL), 3.0 mL (BMIM)BF₄, 24 h

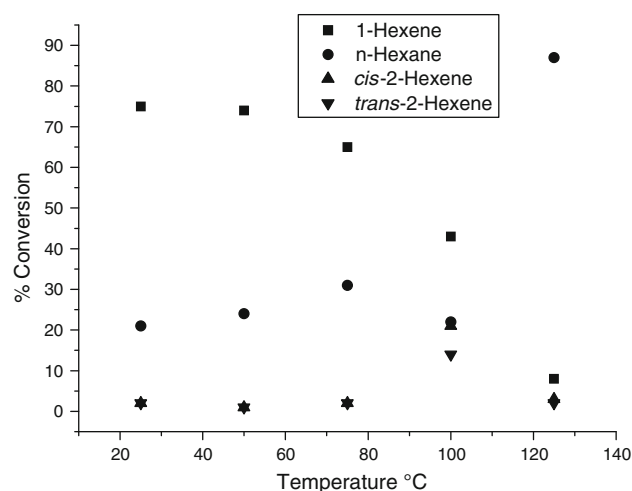


Fig. 3 Temperature effect on 1-hexene hydrogenation. 600 psi H₂ pressure, S/C: 400:1, cyclohexane (3.0 mL), 3.0 mL (BMIM)BF₄, 24 h

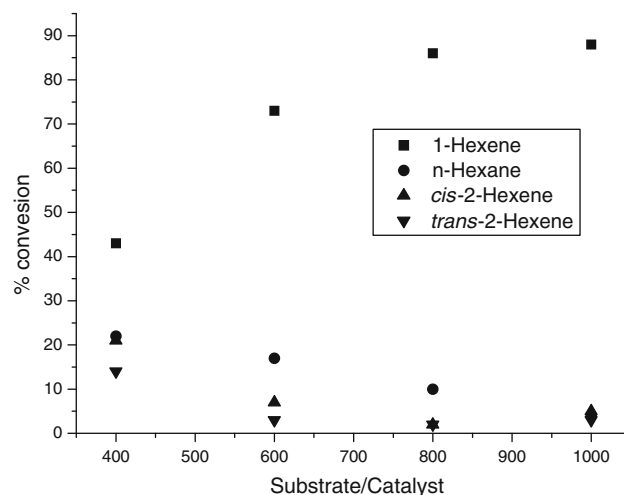


Fig. 4 Substrate/catalyst (S/C) effect on 1-hexene hydrogenation. 600 psi H₂ pressure, 100 °C, cyclohexane (3.0 mL), (BMIM)BF₄ (3.0 mL), 24 h

catalytic precursor improving total conversion, this behavior has also been observed in similar systems [13]. Isomerization products remain below 5%, but at 100 °C we observed an increase of isomers production (35%).

The results of varying the substrate/catalyst ratio (S/C) are shown in Fig. 4. For lower S/C values (greater relative amount of catalyst), there are higher rates of conversion, this is presumably due to a saturation of active sites in the catalytic precursor with the excess of substrate. The optimum condition for the catalytic tests studied was S/C = 400/1 because the highest substrate conversion was obtained under this condition; however, this also gave high isomerization products formation (35%).

The ionic liquid layer containing the Ru complex can be recycled at least five times without apparent catalytic activity loss. Test reactions performed in the presence of liquid mercury do not show any significant activity change, indicating that metallic ruthenium is not the catalytic phase.

The complex $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$ showed a TON = 296 and TOF = 12 h^{-1} , which was lower than another study done in our laboratory (TON = 480, TOF = 20 h^{-1}), in biphasic catalysis with ionic liquid [13].

Conclusions

The new ruthenium complex $\text{RuCl}_2(\text{DMSO})_2(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-3})_2$ was synthesized and characterized by spectroscopic techniques. Under moderate reaction conditions, this complex catalyses the 1-hexene hydrogenation in the biphasic system cyclohexane/[(BMIM)BF₄].

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