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Alkene Hydroformylation Catalyzed by Rhodium Complexes in Ionic Liquids: Detection of Transient Carbene Species

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D/H exchange reactions at the imidazolium cation of an ionic liquid were observed in hydroformylation reactions of 1-octene catalyzed by $[Rh(acac)(CO)_2]$(phosphine ligand) dissolved in 1-*n*-butyl-3-methylimidazolium-d_3 *N*-bis(trifluoromethanesulfonyl)imidate at 75 °C under 5 atm (constant pressure) of CO/H_2 (1:1). This D/H exchange occurs preferentially at the C2 position and occurs essentially in the presence of the phosphine ligand and the rhodium precursors, and it is more pronounced in the presence of bases, even a very weak one such as methanol. The presence of phosphine is also essential for the hydroformylation reaction. This result suggests the formation of *N*-heterocyclic carbenes (NHCs) in the biphasic hydroformylation reactions promoted by Rh complexes in imidazolium ionic liquids. These carbene species are easily displaced by the other species present in the ionic liquid, and they do not cause any significant changes in the catalytic activity or selectivity of the hydroformylation reaction.

Introduction

The hydroformylation reaction is one of the most investigated procedures in the field of catalysis.[1,2] Discovered by Roelen in 1938,[3] this reaction is an important industrial homogeneous catalytic process, as it is a powerful method to functionalize C═C bonds to provide aldehyde compounds.[4]

The common metal catalysts used in hydroformylation of general olefins are rhodium,[5−8] cobalt,[9,10] and platinum.[11] Supported metal catalysts also have been employed in an attempt to combine the practical advantages of a heterogeneous system with the efficiency of a homogeneous catalyst.[12,13] Also, different reaction media have been used for hydroformylation such as organic solvents,[14,15] aqueous media,[16] supercritical CO_2,[17] and ionic liquids,[18] in addition to solventless conditions.[19] In particular, ionic liquids (ILs) have demonstrated various advantages as immobilizing agents for catalytic biphasic hydroformylation reactions. Among the various advantages, it is worth mentioning catalyst stabilization and recycling, product separation (distillation, decantation, extraction with supercritical carbon dioxide, and continuous-flow processes, for example), selectivity controlled through ionic reaction pathways, and the possibility of using long-chain alkenes. [20−24]

However, as is well-known, the C2 deprotonation of 1,3-dialkylimidazolium ILs using relatively weak bases produces *N*-heterocyclic carbenes[25−27] derived from the imidazolium cation.[28] Moreover, imidazolium cations can oxidatively add to low-valent and electron-rich Ni(0), Pd(0), and Pt(0) complexes to form carbene complexes via C−H activation.[29−33] It

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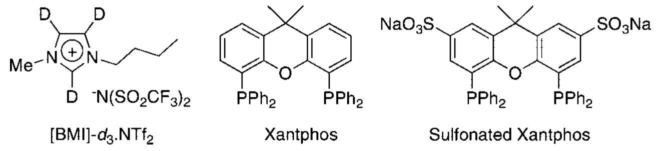

Figure 1. Structures of the deuterated ionic liquid and phosphines used.

is assumed that these processes are much likely to occur *in situ* when coordinatively unsaturated low-valent metal species (particularly ones bearing strong σ-donor ligands) are present or are formed during reactions in imidazolium ILs. It has been recently demonstrated, via labeling experiments, the involvement of carbenes in hydrogenation reactions catalyzed by iridium nanoparticles in imidazolium ionic liquids.[34] Interestingly, in these hydrogenations the D/H exchange occurs mainly at the least acidic positions (C4 and C5) on the imidazolium cation.[35] Herein we have demonstrated, via labeling experiments, that carbenes are also formed during the hydroformylation of 1-octene by [Rh(acac)(CO)$_2$] (phosphine) (acac = acetylacetonate) in [BMI]-d_3·NTf$_2$ (Figure 1) and, in particular, in the presence of weak bases such as methanol.

Results and Discussion

The hydroformylation of 1-octene was performed in the presence of the precursor [Rh(acac)(CO)$_2$](phosphine ligand) (substrate/Rh = 250) in [BMI]-d_3·NTf$_2$ at 75 °C and 5 atm (constant pressure) of a CO/H$_2$ (1/1) gas mixture (Scheme 1). Table 1 summarizes the obtained results for the hydroformylation of 1-octene as well as the control experiments performed.

The hydroformylation in the presence of the phosphine sulfonated Xantphos (molar ratio L/Rh = 4) gives 73% conversion after 21 h with a selectivity of 69% in aldehydes (l/b = 20), 23% octene isomers, and 8% octane (entry 1, Table 1). Most importantly, there was 80% of D/H exchange at the C2 position of the imidazolium cation and only 4% at the least acidic positions (C4 + C5), suggesting the formation of NHC species in the reaction medium. The reaction performed using Xantphos as ligand (molar ratio L/Rh = 1) in the hydroformylation of 1-octene gave similar results: 90% conversion after 1.5 h with a selectivity of 70% in aldehydes (l/b = 21), 28% octene isomers, and 2% octane (entry 3, Table 1). A high percentage of D/H exchange was verified at the C2 position (86%), but none at C4 and C5. The 1-octene hydroformylation performed without the addition of phosphine ligands, i.e. using only the precursor [Rh(acac)(CO)$_2$], gave almost complete olefin conversion after 21 h of reaction (entry 5, Table 1). However, in this case the products are constituted mainly of olefin isomers, octane, and traces of aldehydes. More interestingly, there was *no* detectable D/H exchange in any of the three imidazolium positions. The same result, i.e. no D/H exchange, was observed in the control experiment of [Rh(acac)(CO)$_2$] in [BMI]-d_3·NTf$_2$ at 75 °C and under 5 atm (constant pressure) of CO/H$_2$ without 1-octene after 21 h (entry 7, Table 1). This result indicates that the phosphine-free organometallic precursor is not responsible for the isotopic exchange (see Figure 2). It is also important to note that no significant D/H exchange reaction is attained in the reaction performed in the presence of the phosphine Xantphos without the metal catalyst precursor after 21 h under the same reaction conditions. Notably, in the experiment using [Rh(acac)(CO)$_2$] dispersed in [BMI]-d_3·NTf$_2$ at 75 °C and 5 atm (constant pressure) of CO/H$_2$ in the presence of Xantphos ligand (molar ratio L/Rh = 1), 85% of D/H exchange at the C2 position and just 1% at the least acidic positions (C4 + C5) were observed (entry 8, Table 1) (Figure 2). However, it is important to note that these D/H exchange reactions are more pronounced when the catalyst precursor and phosphine ligands were immobilized in the IL using methanol than when dichloromethane was used (compare entries 1 and 3 with entries 2 and 4, respectively). This result clearly indicates that even the presence of trace amounts of weak bases, such as methanol, increases the D/H exchange via dedeuteration/protonation reactions. Indeed, a relatively fast H/D exchange process was observed at C2 by the simple dissolution of BMI·NTf$_2$ (0.018 g) in CD$_3$OD (0.5 mL) (66% after 1.5 h at 25 °C) but no reaction was observed in CDCl$_3$. Therefore, carbenes are quite probably formed when the reactions are performed in imidazolium ionic liquids, even in the presence of weak bases.

It is quite plausible to assume that this D/H exchange process occurs through the oxidative addition of the imidazolium ring to the metal center, generating Rh-containing carbene species, similar to those recently isolated from the mixture of Rh(I) dimeric species dissolved in imidazolium ionic liquids.[36] The presence of the phosphine is apparently necessary to increase the complex electron density, thus favoring the C−D addition process and/or acting as a base. Moreover, the formation of the carbene is also observed from the simple deprotonation of the C2 of the imidazolium ring by methanol. Therefore, the basicity of the methanol increased when dissolved in the ionic liquid akin to the basicity of water when dissolved in ILs.[37] No deuterated alkene, alkane, or aldehydes were detected by NMR, IR, or MS analysis of the organic phase isolated after the catalytic reactions. Therefore, the deuterium is much probably incorporated in the acid−base reaction and/or by exchange of the Rh−D intermediate with molecular hydrogen. It is also clear that the catalytic species contains the phosphine ligands, since the selectivity (l/b = 20) is typical of complexes containing Xantphos type ligands.[8,38]

The formation of NHC carbenes during the hydroformylation reaction in ILs is also evident, but these species are easily displaced by the other compounds present in the media and/or are transient species, since they do not inhibit the reaction rates or significantly change the selectivity (l/b). Indeed, no hydroformylation, hydrogenation, or isomerization products were detected in the reaction performed in the presence of a base (t-BuOK) and in the absence of a phosphine ligand (entry 6, Table 1). Moreover, the D/H exchange occurred in modest yield at the C2 position (19%), indicating that both the hydroformylation and the D/H exchange reactions are catalyzed essentially by the Rh−phosphine complex in the IL.

Interestingly, the system employing Xantphos as ligand shows a higher catalytic activity in 1-octene hydroformylation as compared to that of the sulfonated Xantphos phosphine (Figure 3).

The same behavior was observed in the hydroformylation of heavy olefins by Rh−phosphines in 1-*n*-butyl-3-methylimida-

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Scheme 1. Biphasic Hydroformylation of 1-Octene Catalyzed by [Rh(acac)(CO)$_2$](phosphine) Complexes in [BMI]-d_3·NTf$_2$

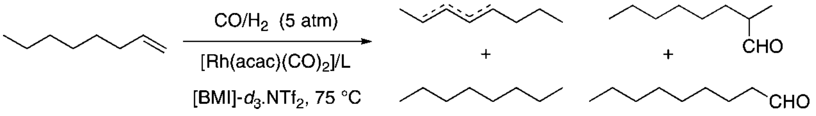

Table 1. Hydroformylation of 1-Octene in [BMI]-d_3·NTf$_2$[a] at 75 °C and 5 atm (Constant Pressure) of CO/H$_2$ (1/1) with the Precursor [Rh(acac)(CO)$_2$] (1-Octene/Rh = 250) and Control Experiments

entry	system	time (h)	alkene conversn (%)	D/H exchange at C2 (%)	D/H exchange at C4 + C5 (%)
1	1-octene + [Rh(acac)(CO)$_2$](sulfonated Xantphos) (L/Rh = 4)[g]	21.0	73[b]	80	4
2	1-octene + [Rh(acac)(CO)$_2$](sulfonated Xantphos) (L/Rh = 1)[h]	21.0	30[c]	1	9
3	1-octene + [Rh(acac)(CO)$_2$](Xantphos) (L/Rh = 1)[g]	1.5	90[d]	86	
4	1-octene + [Rh(acac)(CO)$_2$](Xantphos (L/Rh = 1)[h]	1.5	62[e]	6	7
5	1-octene + [Rh(acac)(CO)$_2$][g]	21.0	99[f]		
6	1-octene + [Rh(acac)(CO)$_2$](*t*-BuOK) (base/Rh = 2)[g]	21.0		19	2
7	[Rh(acac)(CO)$_2$][g]	21.0			
8	[Rh(acac)(CO)$_2$](Xantphos) (L/Rh = 1)[g]	20.0		85	1
9	[Rh(acac)(CO)$_2$](Xantphos) (L/Rh = 1)[h]	21.0		6 (100)[i]	8 (16)[i]

[a] 93% D at C2 and 90% at C4 + C5 (88% C4, 92% C5). [b] 69% aldehydes (l/b = 20), 23% octene isomers, 8% octane. [c] 43% aldehydes (l/b = 7), 54% octene isomers, 3% octane. [d] 70% aldehydes (l/b = 21), 28% octene isomers, 2% octane. [e] 67% aldehydes (l/b = 20), 29% octene isomers, 4% octane. [f] traces of aldehydes, 83% octene isomers, 17% octane. [g] IL and catalyst previously dissolved in MeOH. [h] IL and catalyst previously dissolved in CH$_2$Cl$_2$. [i] The values in parentheses were obtained after the addition of MeOH (0.5 mL) and the reaction was conduced for 2 h at 25 °C.

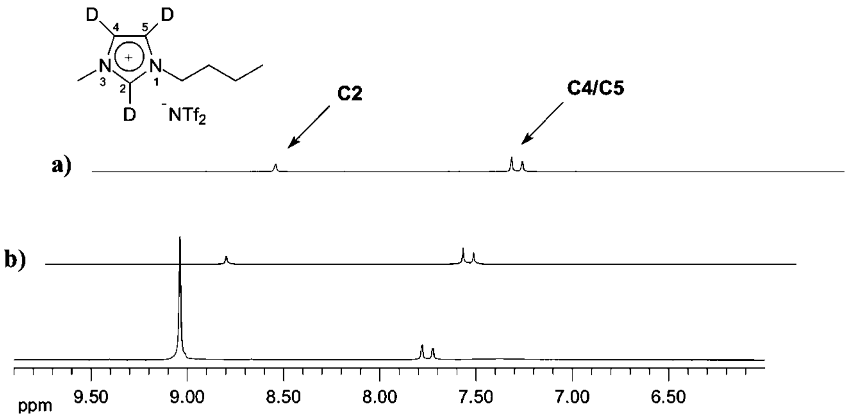

Figure 2. Parts of the ^{1}H NMR spectra (a) of the pure [BMI]-d_3·NTf$_2$ ionic liquid containing 93% D at C2, 88% D at C4, and 92% D at the C5 position of the imidazolium ring, (b) after the control experiment using [Rh(acac)(CO)$_2$] in [BMI]-d_3·NTf$_2$ without 1-octene (entry 7 in Table 1), and (c) after the control experiment using the same catalytic system but with the presence of Xantphos (entry 8 in Table 1).

zolium hexafluorophosphate ionic liquid.[24] The considerable difference in the catalytic activity observed for both hydroformylation systems is probably related to the different kinds of interactions between the phosphine ligand in the modified catalyst and the IL. Indeed, it was recently reported that the sulfonated phosphine TPPMS (TPPMS = triphenylphosphine-monosulfonated) interacts with the IL mainly through C−H···X$^-$ hydrogen bonding with the sulfonate group (where the IL is an anion receptor), while for the neutral phosphine TPP (TPP = triphenylphosphine), supramolecular structures[39,40] are formed by π-stacking interactions.[41] It is quite possible that the reactions performed with the nonionic phosphines[42] occurs in both phases (organic and in the ionic liquid), whereas those performed with the sulfonated ligands occur preferentially in the ionic phase (typical under multiphase conditions).

Conclusions

There is almost no doubt that there is involvement of NHC species during the hydroformylation of 1-octene by the complex [Rh(acac)(CO)$_2$] in the presence of phosphine ligands dispersed in a deuterated imidazolium-based ionic liquid. Most importantly, the phosphine ligands in the presence of methanol play an essential role in the occurrence of D/H exchange reactions. Therefore, *N*-heterocyclic carbenes derived from imidazolium cations are probably present, even in typical hydroformylation reactions in ionic liquids promoted by metal complexes without strong σ-donor ligands. Also of great importance, the probability for the formation of these carbene species is increased in the presence of weak bases such as an IL dissolved in methanol.

Experimental Section

General Considerations. The synthesis of deuterated ionic liquids was performed under an argon atmosphere using Schlenk tubes. The hydroformylation reactions were performed on a modified Fischer−Porter bottle immersed in a silicon oil bath and connected to a gas reservoir. The system temperature was kept at 75 °C with constant stirring (400 rpm). The fall in the gas pressure

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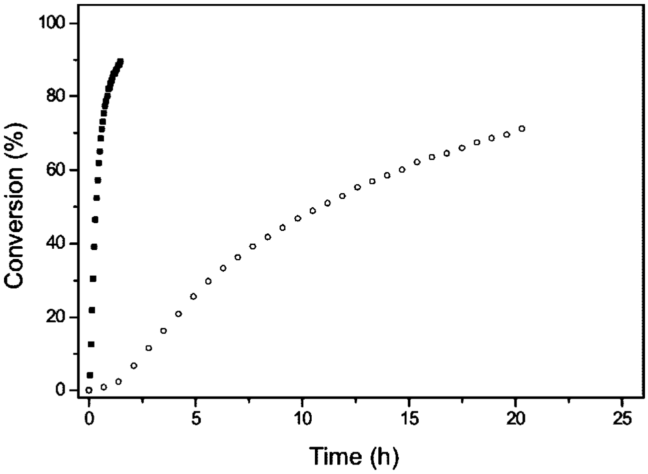

Figure 3. Biphasic hydroformylation of 1-octene in [BMI]-d_3·NTf$_2$ at 75 °C and 5 atm of CO/H$_2$ (constant pressure) with the precursor [Rh(acac)(CO)$_2$] (substrate/Rh = 250) in the presence of (■) Xantphos and (○) sulfonated Xantphos.

in the reservoir was monitored with a pressure transducer interfaced through a Novus converter to a PC, and the data were worked up via Microcal Origin 7.0. The total pressure of gas (~5 atm) in hydroformylation reactions was estimated by considering that before the catalytic reaction the Fischer−Porter bottle was placed under vacuum (3.0−5.0 mmHg) for 5 s in order to remove the argon atmosphere and then 4 atm of the gas mixture was added to the reactor. NMR spectra were recorded on a Varian VNMRS 300 MHz instrument. For ^{1}H NMR studies the following spectral parameters were used: pulse, 45°; acquisition time, 2.049 s; relaxation delay, 10.0 s; scan repetitions, 128; total acquisition time, 26 min 7 s. Mass spectra were obtained using a GC-MS Shimadzu QP-5050 spectrometer (EI, 70 eV). Gas chromatography analyses were performed with a Hewlett-Packard 5890 gas chromatograph with a FID and 30 m capillary column with a polyphenylmethylsiloxane stationary phase. Reagents were purchased from commercial sources (Strem Chemicals, Acros, Aldrich) and used without further purification. The deuterated ionic liquid [BMI]-d_3·NTf$_2$ was synthesized as previously reported[35] from the methanesulfonate imidazolium salt.[43] Analysis of ^{1}H NMR indicates a deuterium content of 93% at C2, 88% at C4, and 92% at the C5 position of the imidazolium ring.

Procedure for 1-Octene Hydroformylation. In a Fischer−Porter bottle reactor, [Rh(acac)(CO)$_2$] (0.0134 g; 0.052 mmol) and sulfonated Xantphos (0.163 g, 0.208 mmol) or Xantphos (0.0301 g, 0.052 mmol) was dissolved in methanol (2.0 mL) or dichloromethane (2.0 mL) and then the d_3 ionic liquid (1.0 mL) was added with stirring at room temperature. The volatiles were evaporated under reduced pressure at 50 °C (methanol) or 25 °C (CH$_2$Cl$_2$) for 1 h. In sequence, 1-octene (1.46 g, 13.0 mmol, substrate/catalyst adjusted for a molar ratio of 250) was added, CO/H$_2$ (1/1 mixture; 5 atm of constant pressure) was admitted to the reactor, and the mixture was heated to 75 °C. The products were analyzed by GC-MS.

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Supporting Information Available: Figures giving ^{1}H and ^{13}C NMR spectra of the ILs before and after hydroformylation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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