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Carbon Dioxide Transformation in Imidazolium Salts: Hydroaminomethylation Catalyzed by Ru-Complexes

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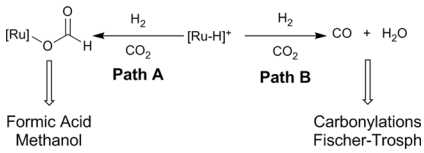
The catalytic species generated by dissolving $Ru_3(CO)_{12}$ in the ionic liquids 1-*n*-butyl-3-methyl-imidazolium chloride or 1-*n*-butyl-2,3-dimethyl-imidazolium chloride are efficient multifunctional catalysts for: (a) reverse water–gas shift, (b) hydroformylation of alkenes, and (c) reductive amination of aldehydes. Thus the reaction of alkenes with primary or secondary amines (alkene/amine, 1:1) under CO_2/H_2 (1:1) affords the hydroaminomethylations products in high alkene conversions (up to 99%) and selectivities (up to 96%). The reaction proceeds under relatively mild reaction conditions (120 °C, 60 bar = 6 MPa) and affords selectively secondary and tertiary amines. The presence of amine strongly reduces the alkene hydrogenation competitive pathway usually observed in the hydroformylation of terminal alkenes by Ru complexes. The catalytic system is also highly active for the reductive amination of aldehydes and ketones yielding amines in high yields (> 90%).

Introduction

The abundance of CO_2 and the impending shortage of fossil building blocks, has led to the proposal that CO_2 should be the C1 building block of the future.[1–3] However, CO_2 is very unreactive, residing in a thermodynamic minimum, and its activation requires large amounts of energy. One of the key solutions currently under intense investigation is the potential conversion of CO_2 into useful chemicals through the hydrogenation reaction.[4–6] For example, the conversion of CO_2 to syngas ($CO + H_2$), formic acid, methanol and dimethyl ether, hydrocarbons (via methane), and Fischer–Tropsch (FT) synthesis yields fuels and chemicals.[7,8] Other important applications of CO_2 as a C1 building block in organic synthesis include the direct synthesis of dimethylcarbonate, cyclic carbonates, urea and urethane derivatives, carboxylic acids, esters and lactones, and isocyanates.[9–13] The catalytic conversion of CO_2 to CO through the reverse water–gas shift (RWGS) reaction is the first step in the production of hydrocarbons via FT synthesis or for carbonylations using CO_2. The RWGS is a well-established reaction used to convert CO_2 into CO and water.[14,15] However, it is an equilibrium-limited endothermic reaction that is favored at high temperatures. In some cases, the products must be removed to shift the equilibrium toward the RWGS rather than the forward water–gas shift (WGS) reaction. In addition, CH_4 is often formed as an undesired side product, particularly at low temperatures (< 600 °C) when CH_4 is the thermodynamically-favored product.[16–22]

Recently, important breakthroughs in the activation and catalytic transformation of CO_2 have been reported using Ru and Rh complexes in many carbonylation reactions.[23] These include the Ru-catalyzed reductive methylation of imines,[24,25] amines,[26] and C–H bonds,[27] as well as the Ru-[28–30] or Rh-catalyzed carbonylation of alkenes, or even Au-promoted formation of methyl formate.[31] In the Ru-catalyzed carbonylations, it has been proposed that the first step of the reaction involves the presence of cationic Ru-hydrido ([Ru-H$^+$]) complexes and the addition of a proton source usually significantly improves the catalytic activity.[32] These [Ru-H]$^+$ species can generate reactive metal-formate intermediates (Scheme 1, path A) or CO (Scheme 1, RWGS, path B). Hence, by controlling the reactivity of [Ru-H]$^+$ species, the incorporation can either use the formate intermediate to produce, for example, formic acid or methanol, or the RWGS to generate carbonylation or FT products.

Generally, sophisticated ligands are required to control the reactivity of [Ru-H]$^+$ species and to improve both catalytic activity and selectivity.[24–26,29] However, it was reported that the RWGS/hydroformylation path may be favored in the absence of extra ligands if the reaction is performed in the presence of imidazolium salt-based ionic liquids (IL)[30] that can generate in situ abnormal Ru–carbene species (Scheme 2)[33] similar to



Scheme 1. Possible pathways involved in the hydrogenation of CO_2.

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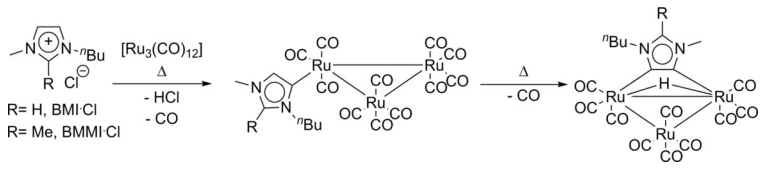


Scheme 2. Abnormal NHC carbenes possibly formed in the reaction of [BMI]Cl and [BMMI]Cl with $Ru_3(CO)_{12}$ under hydroformylation conditions using CO_2 as a CO source.[33]

those species observed in the reaction of 1,3-di-tert-butylimidazol-2-ylidene with $Ru_3(CO)_{12}$.[34] Note the formation of imidazolium-derived NHC carbenes in normal[35–38] and abnormal[39–41] positions are usually observed in reactions involving both 1,3- and 1,2,3-substituted imidazolium salts.

We also observed that the use of phosphines (i.e., PPh_3) and diphosphines [e.g., 1,1-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos)] as metal modifiers resulted in poor selectivities for the formation of carbonylation products with high selectivity for the hydrogenation of the alkenes. In contrast, phosphites [i.e., $P(OEt)_3$] provided an improvement in both the catalytic activity and oxo-product selectivity, as also observed by others.[28] However, ^{31}P NMR experiments revealed that this apparent ligand effect was caused by the formation of phosphoric acid (H_3PO_4) under our reaction conditions.[33] It is reasonable to assume, that even in the case of reactions involving CO_2/H_2 in imidazolium salt IL media, it will be possible to shift the selectivity towards the CO path by fine-tuning the reaction conditions. We report herein that the hydroaminomethylation can be easily performed with the simple catalytic system (i.e., imidazolium chloride IL/Ru_3CO_2/H_3PO_4).

Results and Discussion

Hydroaminomethylation of alkenes

The hydroaminomethylation of cyclohexene (**1**) with aniline (**2a**) was carried out using CO_2 as a CO source (entries 1–6, Table 1) using the same reaction conditions developed earlier for the hydroformylation of alkenes with CO_2.[33] Conversions of **1** up to 99% after 17 h and selectivity up to 98% for product (**3**) were achieved (Scheme 3). In all cases *N*-formylation (**5**) byproducts were also observed, indicating that both paths (A and B, Scheme 1) are operative under these reaction conditions. However, the RWGS pathway is predominant, as the system is selective to the hydroaminomethylation reaction rather than *N*-formylation.

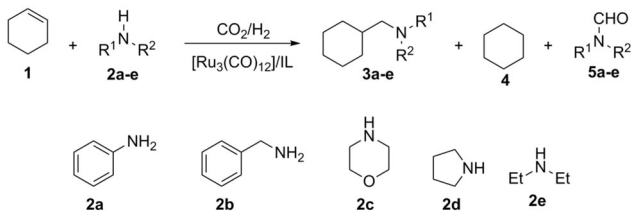
The use of the additive H_3PO_4 or $P(OEt)_3$ (that undergoes hydrolysis to yield acids under the reaction conditions used) produce an increase of the selectivity in the hydroaminoaminations products (**3**). This behavior is similar to that previously described in the Ru-catalyzed hydroformylation using CO_2 as a CO source, and it was attributed to the fact that the acid likely facilitates hydride transfer and protonolysis, which are key steps for the addition of hydrogen to carboxylate groups.[33] The beneficial effect of protic additives in the hydroaminomethylation results was also previously ascribed to an increase in the imine hydrogenation activity.[42] This is another indication that the reaction proceeds through RWGS, hydroformylation, imine-enamine formation, and reduction (see below). Other amines with distinct steric and electronic properties, such as benzylamine (**2b**), morpholine (**2c**), pyrrolidine (**2d**), and diethylamine (**2e**), were also evaluated in the hydroaminomethylation of **1** (entries 7–9, Table 1).

Our reported procedure is more efficient in terms of activity and productivity than those reported earlier for Ru-catalyzed hydroaminomethylation of alkenes with secondary alkylic amines employing LiCl-benzyl triethyl ammonium chloride (BTAC) salts as additives, large amount of metal (6 mol% Ru) under harsh reaction conditions (160 °C, 80 bar = 8 MPa) and long reaction periods (5 days).[43] Furthermore, in general, the main drawback of the hydroaminomethylation reaction is that for primary amines the selectivity generally is low because of over-alkylation.[44] Our catalytic system provided the formation of secondary amines from primary amines (**2a** and **2b**) with no formation of over-alkylated amine. This selectivity is proba-

Table 1. Ru-catalyzed hydroaminomethylation of cyclohexene (**1**) using CO_2 as a CO source.[a]

Entry	Amine	IL	Additive[b]	Conv.[c] **1** [%]	Sel.[c] **3** [%]	Sel.[c] **4** [%]	Yield **5**[c,d] [%]
1	**2a**	[BMI]Cl	–	79	66	34	13
2	**2a**	[BMMI]Cl	–	68	49	51	2
3	**2a**	[BMI]Cl	$P(OEt)_3$	82	84	16	8
4	**2a**	[BMMI]Cl	$P(OEt)_3$	98	98	2	4
5	**2a**	[BMI]Cl	H_3PO_4	96	95	5	8
6	**2a**	[BMMI]Cl	H_3PO_4	99	98	2	3
7	**2b**	[BMMI]Cl	H_3PO_4	27	57	43	85
8	**2c**	[BMMI]Cl	H_3PO_4	57	65	35	32
9	**2d**	[BMMI]Cl	H_3PO_4	84	88	12	17
10	**2e**	[BMMI]Cl	H_3PO_4	36	64	36	16

[a] Reaction conditions: **1** (20.0 mmol), **2a–e** (20.0 mmol), imidazolium salt IL (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), 60 bar = 6 MPa CO_2/H_2 (1:1), 120 °C, 24 h. [b] Additive/Ru = 3.0. [c] Conversion of **1** (%), yield of **5** (%), and selectivity (%) determined by GC–MS and GC–FID. [d] Calculated from the conversion of **2**.



Scheme 3. Hydroaminomethylation of cyclohexene (**1**) with primary [aniline (**2a**) and benzylamine (**2b**)] and secondary amines [morpholine (**2c**), pyrrolidine (**2d**), and diethylamine (**2e**)] promoted by $Ru_3(CO)_{12}$ dissolved in [BMI]Cl or [BMMI]Cl. Reaction conditions: cyclohexene (20.0 mmol), amine (20.0 mmol), imidazolium salt IL (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), 60 bar = 6 MPa CO_2/H_2 (1:1), 120 °C, 24 h.

bly a result of removing the less soluble secondary amine from the catalyst-containing imidazolium salt IL phase.[45]

Under optimized reaction conditions, monosubstituted *n*-terminal alkenes, such as 1-hexene, gave full conversion, with the production of the corresponding amine (**6**) in high selectivity (up to 96%; see Table 2). Much lower selectivities for heptanols (up to 38%) were previously obtained in the Ru-catalyzed hydroformylation of 1-hexenes under similar reaction conditions.[33] This is a clear indication that the amines are probably acting also as modifiers, decreasing the C=C hydrogenation competitive pathway akin to that was observed in the hydroformylation employing Ru-N-containing ligands catalysts in molten salt media.[46]

Table 2. Conversion of alkene (%) and amine selectivity (%) obtained in the Ru-catalyzed hydroformylation of alkenes using CO_2 as a CO source.[a]

Entry	Alkene	Product	Conv.[b] [%]	Sel.[b] [%]
1	C_4H_9	C_4H_9 CH_2NHPh (**6**)	99	96
2	Ph	Ph CH_2NHPh (**7**)	99	15
3		NHPh (**8**)	97	72
4		NHPh (**8**)	97	96
5	Ph	Ph NHPh (**9**)	91	87
6		NHPh (**10**)	88	93
7[c]	O	PhHN NHPh (**11**)	99	60

[a] Reaction conditions: alkene (20.0 mmol), **2a** (21.5 mmol), [BMMI]Cl (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), H_3PO_4/Ru = 3.0, 60 bar = 6 MPa CO_2/H_2 (1:1), 120 °C, 36 h. [b] Conversion (%) and selectivity (%) determined by GC–MS and GC–FID. [c] **2a** (40.0 mmol).

It is worth nothing that in both cases (hydroformylation[33] and hydroaminomethylation) the isomerization of the terminal alkene to internal ones allowed the formation of mixtures of products with similar amount of the linear and branched isomer (i.e., linear/branched ratio of 0.9–1.2).

Mono-substituted alkenes conjugated with aromatic groups (i.e., styrene) gave full conversions with high-hydrogenated product selectivity and low selectivity of the hydroaminomethylation product (**7**; Table 2). This behavior was ascribed to the relatively faster hydrogenation rate of the C=C bond of these types of substrates (terminal alkyl-substituted alkenes and substrates with alkenes conjugated to aromatic groups) when compared to the other two processes (RWGS and hydroformylation).

Cyclic di-substituted dienes (1,5-cyclooctadiene), cyclic di-substituted conjugated dienes (1,3-cyclooctadiene), and 2,2-di-substituted alkenes (methylsytrene, (*R*)-(+)-limonene and carvone) were easily hydroaminomethylated, thus leading to the amines **8**–**11** with moderate-to-high conversions (88 to >99%) and selectivities (60 to 96%), as shown in Table 2.

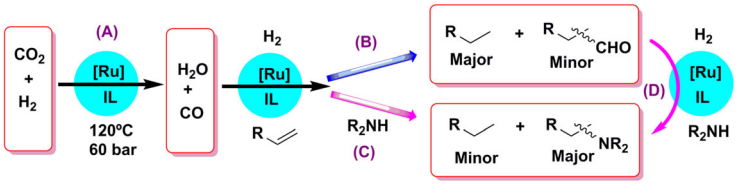
It should be noted that in both cases (hydroformylation[33] and hydroaminomethylation) the transformation of the 2,2-di-substituted alkenes allowed the exclusive formation of linear products.

In the case of carvone (Table 2, entry 7), the corresponding di-amine **11** was obtained through a reductive amination step of the carbonyl function of its cyclohexanone skeleton. For this reason, the hydroaminomethylation of carvone was conducted using a carvone/aniline (**2a**) ratio of 1:2. This is further evidence that under the catalytic condition used, the carbonyl groups present in the medium react with the amines to generate imines (from primary amines) and enamine salts (from secondary amines) that are further reduced to secondary and tertiary amines, respectively.

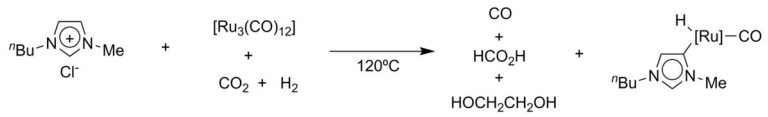
Mechanistic insights

The main reactions paths involved in the hydroaminomethylation of alkenes by the $Ru_3(CO)_{12}$/imidazolium salt IL catalytic system is presented in Scheme 4. The first step is the RWGS reaction (Path A, Scheme 4) that is well known to occur in many processes that involve the use of CO_2 and H_2 mixtures and it is the main step during the activation of CO_2 for many carbonylation reactions.[47] However, the RWGS reaction is an endothermic reaction ($\Delta H_{298K} = 41.2\ kJ\,mol^{-1}$), and thus conventional catalysts require high temperatures[48] to promote the formation of CO. Note that some noble metal catalysts (e.g., Pt, Ru, and Rh) and promoters based in ionic additives (e.g., Li salts) were revealed to be efficient catalysts for the RWGS at mild-to-low temperatures.[48]

We already reported that $Ru_3(CO)_{12}$/imidazolium salt IL catalytic system promote the RWGS at much lower temperatures (120 °C) than those observed using classical catalysts. Therefore, the reported catalytic system is one of the most active to allow the use of CO_2 as a CO source as for example in hydroformylation of alkenes.[33] In these hydroformylation reactions, preliminary spectroscopic (IR and NMR) investigations have revealed the involvement of Ru-hydride-carbonyl-carbene complexes as possible catalytic active species[33] akin to observed in the hydroformylation using CO.[49] ^1H and ^{13}C HP NMR experiments have been performed to investigate the nature and structure of the species formed by dissolving $Ru_3(CO)_{12}$ either in the 1-*n*-butyl-3-methyl-imidazolium chloride ([BMI]Cl) or 1-*n*-butyl-2,3-dimethyl-imidazolium chloride ([BMMI]Cl). The main results are summarized in Scheme 5 and a detailed discussion



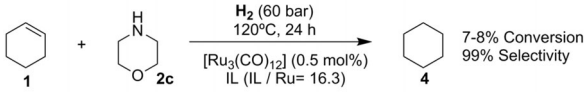
Scheme 4. Main steps involved in the hydroaminomethylation of alkenes by $Ru_3(CO)_{12}$/imidazolium salt IL catalytic system.



Scheme 5. Main species detected by in situ ^{1}H, ^{13}C, and $^{13}C\{^{1}H\}$ NMR spectroscopy of the reaction of a solution of $Ru_3(CO)_{12}$ in [BMI]Cl and [BMMI]Cl.

and the NMR spectra are available in the Supporting Information (Figure SI1–SI6). These new data corroborate the formation of Ru-hydride-carbonyl-carbene complexes by heating $Ru_3(CO)_{12}$ in presence of [BMI]Cl under CO_2/H_2 or inert atmosphere, whereas the decomposition of the $Ru_3(CO)_{12}$ under H_2 atmosphere that generates Ru nanoparticles akin to previously reports in the literature.[50,51] In particular, the appearance of a singlet at 160 ppm in the ^{13}C NMR spectra (Figure SI2, SI4, and SI6) of either [BMI]Cl or [BMMI]Cl indicate the formation of "abnormal" type carbenes as usually observed under similar conditions.[34] Most important, ^{13}CO, formic acid ($H^{13}COOH$), and ethylene glycol ($^{13}CH_2OH^{13}CH_2OH$) have been observed in the reaction employing $^{13}CO_2$ (Figure SI2). Therefore, both paths proposed in Scheme 1 are operative in these reaction conditions, but the RWGS is the main path. The reaction kinetics for the formation of the Ru-hydride-carbonyl-carbene complexes under inert atmosphere was also monitored, and thus, the initially formed main hydride species ($\delta = 19.3$ ppm in the ^{1}H NMR) evolved to generate a second hydride specie ($\delta =$ 17.6 ppm and in the ^{1}H NMR spectra, Figure SI3 and SI5). Finally, by the addition of $P(OEt)_3$, the high-field hydride signal became predominant and no organometallic species associated with P-ligands were detected. Indeed, none of the signals coupled with ^{13}P by ^{1}H, ^{13}C, or ^{31}P NMR spectroscopy, thus reinforcing the decomposition path of $P(OEt)_3$ into H_3PO_4[52] (observed by ^{31}P NMR) that is an extra source of H^+ necessary in the protonation step.[32]

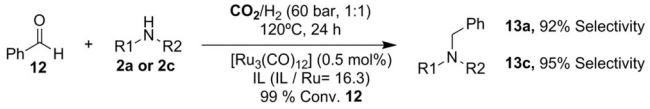
We have also observed CO and water in the gas phase (by GC) of the reaction of 60 bar = 6 MPa CO_2/H_2 (1:1) at 120 °C for 24 h, hence indicating the occurrence of RWGS reaction at this relative low temperature. Consequently, it can be assumed that the second step of the hydroaminomethylation reaction will follow the same paths observed for the hydroaminomethylation using CO (Scheme 4, paths B, C, and D).[53] The addition of alkenes (in absence of amine) under these reaction conditions affords alcohols resulting from the hydrogenation of the hydroformylation products (paths B and C, Scheme 4). Therefore, the amine is decreasing the rate of the simple hydrogenation of the alkene. Indeed, the $Ru_3(CO)_{12}$/imidazolium salt IL catalytic system displays very low cyclohexene hydrogenation activity in the absence of CO_2 (Scheme 6).



Scheme 6. Reaction of cyclohexene (**1**) with H_2 in the presence of morpholine (**2c**) and in the absence of CO_2. Reaction conditions: **1** (20.0 mmol), **2c** (20 mmol), [BMMI]Cl (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), 60 bar = 6 MPa H_2, 120 °C, 24 h.

Therefore, it is reasonable to assume that the presence of amine increases the RWGS path by increasing the solubility of CO_2 in the ionic phase and/or promoting the metal-formate intermediate reduction to CO. Note that no C–N bond forming reaction between cyclohexene (**1**) and morpholine (**2c**), and thus the involvement of reductive amination of alkenes in the reaction mechanism, can be excluded.[54]

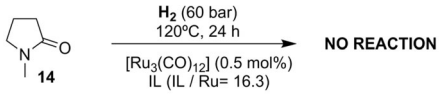
The reaction of the formed carbonyl compounds with primary and secondary amines affords the imines and enamines, respectively, that subsequently are reduced the amines. Indeed, minor amounts of imines or enamines, derived from aniline (**2a**) were detected by GC and GC–MS analysis of the hydroaminomethylation reaction mixtures. This reaction pathway is also supported by the observed reductive amination of carvone (Table 2, entry 7). Furthermore, the reaction of benzaldehyde and amines under the same reaction conditions affords the expected hydroaminomethylation product (Scheme 7) similar to other complexes reported in the literature.[44] Hence the reductive amination of aldehydes and ketones probably occurs under hydroaminomethylation conditions.



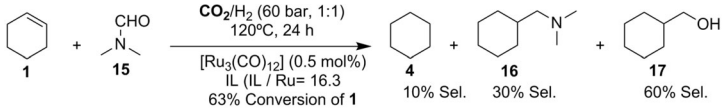
Scheme 7. Reductive amination of benzaldehyde (**12**) with aniline (**2a**) or morpholine (**2c**) in the presence of CO_2. Reaction conditions: **12** (20.0 mmol), **2a** or **2c** (20 mmol), [BMMI]Cl (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), 60 bar = 6 MPa CO_2/H_2 (1:1), 120 °C, 24 h.

The possible involvement of amides in the reaction mechanism can be in principle discarded as no catalytic activity for the reduction of amide (**14** was used as a model amide, Scheme 8) was observed.

Moreover, the high selectivity for the alcohol (**17**), which is formed by a hydroformylation–hydrogenation sequence, and only moderate selectivity for the amine in the hydroformylation–hydroaminomethylation of alkenes using dimethylformamides (**15**) as a CO source (Scheme 9), shows that the involvement of *N*-formamides in the reaction mechanism as main pathway can be also discarded.



Scheme 8. Attempt to hydrogenate amide by $Ru_3(CO)_{12}$/imidazolium salt IL. Reaction conditions: **14** (20 mmol), [BMMI]Cl (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), 60 bar = 6 MPa H_2, 120 °C, 24 h.



Scheme 9. Reaction of cyclohexene (**1**) with dimethyl formamide (**15**) under the same reaction conditions used for the hydroaminomethylation protocol. Reaction conditions: **1** (20.0 mmol), **15** (20 mmol), [BMMI]Cl (5.1 mmol), 0.5 mol% $Ru_3(CO)_{12}$ (1.5 mol% Ru), 60 bar = 6 MPa CO_2/H_2 (1:1), 120 °C, 24 h.

Therefore, all the supporting studies indicated that the hydroaminomethylation reaction involves the sequential RWGS, hydroformylation, and reductive amination pathways (Scheme 4).

Conclusions

$Ru_3(CO)_{12}$/imidazolium salt ionic liquid (IL) is an efficient catalytic system for the hydroaminomethylation of both primary and secondary amines using CO_2 under mild reaction conditions (120 °C, 60 bar = 6 MPa). This catalytic system provided the formation of secondary amines from primary amines with no formation of over-alkylated amine usually observed with other catalytic systems. This procedure is much more efficient in terms of activity and productivity than those reported earlier for Ru-catalyzed hydroaminomethylation of alkenes with secondary alkylic amines using CO_2 as a CO source that employs higher Ru concentration and operates at 160 °C. The reaction proceeds through sequential RWGS and hydroformylation followed by imines/enamines reduction. The $Ru_3(CO)_{12}$/imidazolium salt IL is one of the most active systems to promote the endothermic RWGS at temperature as lower as 120 °C. We have also demonstrated that the presence of amine dramatically decreases the competitive alkene hydrogenation pathway usually observed with terminal alkenes in hydroformylation reactions promoted by Ru precursors.

Research details described herein are expected to contribute to the development of new processes involving the use of CO_2 as an abundant, cheap, easily accessible and green source of CO for important industrial carbonylation processes under relative mild reactions conditions and the need of the use of sophisticated ligands.

Experimental Section

Experimental details. Reagents and solvents were purified when required by following standard procedures.[55] The imidazolium salt ILs were prepared following previously reported procedures.[56–58] The Ru precursor triruthenium dodecarbonyl $[Ru_3(CO)_{12}]$ was purchased from Johson & Mathey. H_2 (> 99.999%) and CO_2 (> 99.999%) were purchased from White-Martins Ltd. Brasil. Amines (morpholine, pyrrolidine, diethylamine, benzyl amine, and aniline), alkenes (cyclohexene, 1-hexene, 1,5-cyclooctadiene, 1,3-cyclooctadiene, α-methylstyrene, styrene, Limonene, and Carvone), amides (*N*-methylpyrrolidone and dimethylformamide), and aldehydes (benzaldehyde) were purchased from Sigma–Aldrich. GC–flame ionization detector (FID) analyses were run with an Agilent GC System 6820 (column DB-17; T injector = 250 °C; *P* = 103 kPa; T program = 10 min at 40 °C, 10 °C min^{-1} until 250 °C, then 10 min at 250 °C). GC–MS analyses were run with a Shimadzu GC System QP50 (column DB-17; T injector = 250 °C; *P* = 103 kPa; T program = 10 min at 40 °C, 10 °C min^{-1} until 250 °C, then 10 min at 250 °C; EI = 70 eV). ^{1}H, ^{13}C, COSY, and HSQC NMR analysis were performed on a Varian 400 MHz at the CNANO/UFRGS using $CDCl_3$ as a solvent. Chemical shifts (ppm) are given relative to trimethylsilane (TMS) in ^{1}H NMR and $CDCl_3$ in ^{13}C NMR. The ESI–MS mass spectra (Figure S17 and S18) were acquired using a Q-Tof (Micromass) mass spectrometer with an ESI capillary voltage of 3 kV and a cone voltage of 10 V. The sample (10 μL aliquots of reaction mixture added to 1 mL of methanol) injection was performed using a syringe pump set to 5 μL min^{-1}.

General procedure for the hydroaminomethylation of alkenes using CO_2 as a CO source. In a typical experiment, the corresponding substrate (20.0 mmol of alkenes) was mixed with the amine (20.0 mmol), and they were added to a 100 mL reactor vessel (Parr Micro-reactor 4590) containing 0.5 mol% $Ru_3(CO)_{12}$ (1.5% mol Ru) and the imidazolium salt IL (5.1 mmol). Then, the reactor was pressurized with CO_2/H_2 and warmed to the desired reaction temperature and reaction time. After that, the reactor was cooled and the reaction products were extracted with diethyl ether (3 × 15 mL). The reaction products were analyzed by NMR and GC–MS analysis (DB-17, T injector = 250 °C, *P* = 15 psi = 0.10 MPa, and T programme = 10 min at 40 °C, 10 °C min^{-1} until 250 °C, and 10 min at 250 °C). Conversion, selectivity, and yield were determined by GC–FID analysis using *n*-heptane as internal standard.

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Keywords: carbon dioxide · hydroaminomethylation · ionic liquid · reversed water–gas shift · ruthenium

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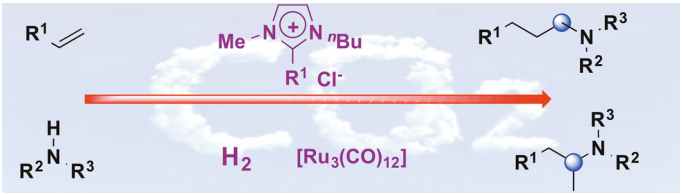

VersatILe catalysis: The catalytic species generated by dissolving $Ru_3(CO)_{12}$ in the ionic liquids 1-*n*-butyl-3-methyl-imidazolium chloride or 1-*n*-butyl-2,3-dimethyl-imidazolium chloride are efficient multifunctional catalysts for: (a) reverse water–gas shift, (b) hydroformylation of alkenes, and (c) reductive amination of aldehydes. The hydroaminomethylation using CO_2 as CO source proceeds under mild reaction conditions (120 °C, 60 bar = 6 MPa) and affords amines selectively.

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Carbon Dioxide Transformation in Imidazolium Salts: Hydroaminomethylation Catalyzed by Ru-Complexes

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