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Acyclic amines as ancillary ligands in Ru-based catalysts for ring-opening metathesis polymerization
Probing the electronic and steric aspects of cyclic and acyclic amines

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Abstract

The present paper reports the ROMP of norbornene with $[RuCl_2(PPh_3)_2(L)_x]$, where L represents the acyclic amines diethanolamine, triethanolamine, triethylamine, phenylamine, diphenylamine or sec-butylamine. Previous representative results with cyclic amines are also cited to observe of the behavior of cyclic and acyclic amines as ancillary ligands. Three productive types of ligands were observed as a function of their electronic nature and steric hindrance: ligands with high cone angle and strong σ-donor character ($NH_2{}^sBu$, NEt_3 and piperidine), ligands with high cone angle and low σ-donor character (NH_2Ph and $NHPh_2$) and ligand with low cone angle and π-acceptor character (4-$H_2NC(O)$-pyridine). Ligands with low cone angle and strong σ-donor character can restrict the catalytic activity of the metal complex (imidazole, pyridine, 4-H_3C-pyridine and 4-H_2N-pyridine). Thus, latent complexes can be designed using different amines as ancillary ligands.

Keywords: Olefin metathesis; ROMP; Norbornene; Ancillary ligands; Amines; Ruthenium; Ligand electronic nature

1. Introduction

Ruthenium-based catalysts have been one of the most exciting developments in the area of olefin metathesis [1–4]. The greatest example is the second-generation Grubbs type catalysts $[RuCl_2(NHC)(L)(=CHR)]$, where NHC is an *N*-heterocyclic carbene and typically L = PCy_3 and R = Ph [1–4]. These catalysts can afford the syntheses of complex organic molecules *via* cross and ring-closing metathesis and make it possible to obtain polymers with low polydispersity indexes (M_w/M_n) *via* ring-opening metathesis polymerization (ROMP), controlling the initiation and propagation rates. Furthermore, the Ru-carbene complexes are usually functional-group-tolerant catalysts and active in different media.

Although it is reasonable to assume that Grubbs type complexes are powerful catalysts for olefin metathesis, new catalysts must be formulated when the design of new materials through catalysis is a continuous challenge [5,6]. In the interim, olefin metathesis is a reaction that can provide different materials and Grubbs type complexes are, of course, one of the catalyst models [1–4,7–16].

It is well known that an effective and versatile tool in the design of novel catalysts is the properties of the ancillary ligands that support the active metal centers [17–21]. Tuning the electronic and steric effects it is possible to drive the catalyst to achieve optimum activity and selectivity [6]. Many catalytic processes have been improved using transition metal complexes with different ligands [6,22], like in the case of the second-generation Grubbs type catalysts [1–4].

In tailoring transition metal complexes for catalysis, phosphines and phosphites were successfully introduced as ancillary ligands [23–25]. However, many trivalent phosphorus ligands may degrade under certain reaction conditions, as they are air- and moisture-sensitive, hazardous to manipulate and usually expensive. Therefore an option not very well explored in the development of homogeneous catalysts is to arrange phosphines and amines in the same metal center. Our particular interest and approach is in dealing with both σ-donor and steric hindrance aspects using ligands that are easy to manipulate and economically viable. Many amines can substitute phosphines in these aspects [26]. Amine-complexes are usually explored in catalysis as bidentate amines or hemilabile P–N ligands [6,27–33].

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Having in mind that a variety of phosphines and amine has individually promoted Ru(II) chemistry to applications in photochemistry, bioinorganic and catalytic processes, previous studies in our group have focused on the chemistry of complexes of type $[RuCl_2(PPh_3)_2(amine)_x]$ prepared from $[RuCl_2(PPh_3)_3]$ [34,35]. It was observed that piperidine and some 4-X-pyridines are effective as ancillary ligands for ROMP of norbornene and 2,5-norbornadiene. For example, quantitative polynorbornenes were obtained with piperidine ($x=1$) and isonicotinamide (4-$H_2NC(O)$-pyridine; $x=2$) derivative complexes for less than 1 min at room temperature and for 5 min at 50 °C, respectively. It is notorious to observe that these amines show different electronic and steric characteristics. Isonicotinamide does not behave as a typical σ-donor ligand (pK_a 3.61) as piperidine does (pK_a 11.2). Furthermore, piperidine is larger than isonicotinamide, where the cone angles (θ) are 121° and 100°, respectively [36,37]. In both cases there are evidences that the propagating metal species is coordinated to one PPh_3 molecule and to one amine [34,35]. Thus, the effects from each amine combined with the effects from the acid and sized PPh_3 molecule generated complexes that present very good activities with different induction periods. It is very important to observe the induction period since it involves the *in situ* formation of the catalyst itself and the initiation of the polymerization process [7]. Consequently, polymers with different characteristics can be obtained choosing certain complexes. In part, these different behaviors come from the fact that the illustrated complexes have different coordination numbers ($x=1$ or 2), but this cannot be generalized.

The present paper reports the ROMP of norbornene with $[RuCl_2(PPh_3)_2(L)_x]$ where L is an acyclic amine: diethanolamine ($NH(EtOH)_2$), triethanolamine ($N(EtOH)_3$), triethylamine (NEt_3), phenylamine (NH_2Ph), diphenylamine ($NHPh_2$) and sec-butylamine ($NH_2{}^sBu$). The aim is to collect more information about amines as ancillary ligands, as well as about amine–phosphine systems, to discuss the representative data from the studies with cyclic amines [34,35].

2. Experimental

2.1. General remarks

All manipulations were performed under argon atmosphere. All the solvents used were analytical grade and were distilled from the appropriate drying agents immediately prior to use. Other commercially available reagents were purified by standard procedures or used without further purification. $RuCl_3{\cdot}xH_2O$ from Stream, norbornene (NBE) from Across, $NH(EtOH)_2$, $N(EtOH)_3$, NH_2Ph, $NHPh_2$, NEt_3 and $NH_2{}^sBu$, 2,5-norbornadiene (NBdiene), ethyldiazoacetate (EDA) and PPh_3 from Aldrich were used as achieved. Room temperature (RT) was 24 ± 1 °C.

2.2. Instrumentation

Elemental analyses were performed using an EA 1110 CHNS-O Carlo Erba Instrument. EPR was carried out at RT using a Bruker ESP 300C apparatus (X-band) equipped with a TE102 cavity and HP 52152A frequency counter. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained in $CDCl_3$ solution at 25.0 ± 0.1 °C using a Bruker AC-200 spectrometer equipped with a probe operating at 200.13 and 81.015 MHz, respectively. The chemical shifts obtained are reported in ppm relative to the high frequency of tetramethylsilane or 85% H_3PO_4. Molecular weights (M_w, M_n) and molecular weight distribution (M_w/M_n) were obtained by gel permeation chromatography analyses obtained using a Shimadzu 77251 spectrometer system equipped with a PL gel column (5 μm MIXED-C: 30 cm, Ø = 7.5 mm). The retention time was calibrated with respect to standard monodispersed polystyrene using HPLC-grade $CHCl_3$ as eluent.

2.3. Synthesis and characterization of the complexes

The complexes of type $[RuCl_2(PPh_3)_2(L)_2]$, where $L = NH(EtOH)_2$, $N(EtOH)_3$, NH_2Ph or $(NH_2{}^sBu)$, were prepared adding 1.23 mmol of the amines to the solutions of $[RuCl_2(PPh_3)_3]$ (0.47 mmol; 450 mg) in acetone (50 mL). The mixtures were stirred at room temperature for 2 h under argon atmosphere. The complexes precipitated when the volumes of the solutions were reduced (∼5 mL) under vacuum. The solids were then filtered, washed with ethyl ether and dried in a vacuum. The absence of signals in the EPR spectra of the complexes suggests that the oxidation state of the ruthenium is +2 in each case. The six-coordinated nature of the isolated complexes is supported by the satisfactory analytical results. Anal. Calc. for $[RuCl_2(PPh_3)_2(NH(EtOH)_2)_2]$ (wine; 63% yield): C, 58.8; H, 5.8; N, 3.1; Found: C, 57.1; H, 5.6; N, 2.9. Anal. Calc. for $[RuCl_2(PPh_3)_2(N(EtOH)_3)_2]$ (wine; 65% yield): C, 57.9; H, 6.1; N, 2.8; Found: C, 58.1; H, 5.9; N, 2.9. Anal. Calc. for $[RuCl_2(PPh_3)_2(NH_2Ph)_2]$ (brown; 63% yield): C, 65.2; H, 5.0; N, 3.2; Found: C, 65.1; H, 5.3; N, 3.3. Anal. Calc. for $[RuCl_2(PPh_3)_2(NH_2{}^sBu)_2]$ (yellow pallid; 48% yield): C, 62.4; H, 6.2; N, 3.3; Found: C, 62.4; H, 6.5; N, 3.0.

Attempts to precipitate the complexes with either $NHPh_2$ or NEt_3 from the respective mother liquor have failed so far. Otherwise, these complexes are formed adding the amine (4.6 μmol) to a solution of $[RuCl_2(PPh_3)_3]$ (2 μmol) in $CHCl_3$ (2 mL). Following the reaction with NEt_3 by ^1H NMR in $CDCl_3$, the 5–8 ppm downshifts in the amine aliphatic signals indicate that NEt_3 coordinates to ruthenium for 8 h. In the case of $NHPh_2$, after 10 min the spectrum in the aromatic region shows the proton signals of both PPh_3 and $NHPh_2$ molecules bonded to Ru and those from the free phosphine, which was replaced by the amine; the N–H proton is observed at 5.85 ppm. In both cases, the ^{31}P NMR spectra confirmed the presence of free phosphine (−4.7 ppm) and the absence of signals from the dimeric specie $[Ru(\mu\text{-}Cl)Cl(PPh_3)_2]_2$ typical of the starting complex in solution [38–40]. It indicates that one molecule of PPh_3 is dissociated in the presence of amine and the coordination of the amine prevents the formation of binuclear complexes [38–40]. Thus, the NMR data suggest that the complexes with $NHPh_2$ and NEt_3 are formed in solution and exist as monomeric species.

2.4. Polymerization reactions

In a typical experiment using the isolated Ru(II) complexes with the amines $NH(EtOH)_2$, $N(EtOH)_3$, NH_2Ph or ($NH_2{}^sBu$), 1.0 μmol of complex is dissolved in 2 mL of $CHCl_3$ and 470 mg of monomer is added so that the molar ratio [monomer]/[Ru] is 5000:1, after which 5 μL of ethyldiazoacetate (EDA) are added. The solution is maintained at room temperature or at 50 ± 1 °C in silicone oil bath under magnetic stirring for the desired time. At room temperature, 5 mL of methanol are added and the precipitated polymer is filtered, washed with methanol and dried in a vacuum before being weighed.

Polymerization runs using the *in situ* generated complexes with the amines $NHPh_2$ or NEt_3 were performed using a solution of $[RuCl_2(PPh_3)_3]$ (1 μmol) in $CHCl_3$ (2 mL) previously stirred in presence of the amine (2.3 μmol) for 2 h at room temperature, then following the addition of monomer (470 mg) and EDA (5 μL) to the resulting solution. The polymerization procedure is the same as described above.

3. Results and discussion

All the studied complexes were effective to ROMP of norbornene at most for 5 min at 50 °C. The data of the isolated polynorbornenes obtained from the reactions are summarized in Table 1 (entries 3, 4, 6, 8, 10, 13, 14, 15, 18). The table also includes some previous results obtained with the complex without amine (1) and derivative complexes with the unsaturated cyclic amines (entries 2, 5, 7, 9, 11, 12, 16, 17) or piperidine (19,20) [34,35,41], to discuss the representative data.

Observing the results obtained with the *ex situ* generated complexes, the cases with $NH(EtOH)_2$ and $N(EtOH)_3$ showed the lowest catalytic activity among the acyclic amines (3, 4). The yield was roughly 20% better in relation to the precursor (L = PPh_3; 1) when the amine was NH_2Ph (10). An unusual catalytic activity was observed using the $NH_2{}^sBu$ derivative complex when 85% of polynorbornene had been obtained at RT for 5 min (13). This value was roughly the same at 50 °C for 5 min (92%; 15), considering 5–10% of experimental error and the fact that at elevated temperature the attached polymer catalyst becomes less crowed by the polymer chain allowing a better consumption of monomer.

The solution of $[RuCl_2(PPh_3)_3]$ with amines $NHPh_2$ and NEt_3 showed reactivity at RT for 5 min with yields of 65% (6) and 67% (8), respectively. Runs at 50 °C for 5 min yielded 90% (14) and 98% (18) of polymers. These results support the formation of amine complexes since they are very different from that complex in the absence of amine, where the precursor complex is not active at RT for 5 min and yields ∼1/3 less polymers at 50 °C for 5 min (1). Furthermore, it is also considered that

Table 1
Data for the ROMP of norbornene with $[RuCl_2(PPh_3)_2(L)_x]$ in increasing order of the yield values

Entry	Ancillary ligand				Temperature (°C)	Time (min)	Yield (%)	M_n (10^4)	M_w/M_n
	L	pK_a[a]	θ[b] (°)	x					
1	PPh_3[c]	2.73	145	1	50	5	63	190	1.40
2	Imidazole[d]	6.95	82.9	2	50	5[e]	19	3.0	6.30
3	$NH(EtOH)_2$	8.96	125[f]	2	50	5	30	89	1.57
4	$N(EtOH)_3$	7.76	150[g]	2	50	5	36	23	2.43
5	4-H_2N-py[h]	9.17	91.9	2	50	5[e]	63	19	1.80
6	$NHPh_2$	0.78	136	NI	RT	5	65	54	2.10
7	Py[h,i]	5.23	91.9	2	50	5	67	4.2	1.32
8	NEt_3	10.8	150	NI	RT	5	67	64	2.00
9	4-H_3C-py[h,i]	5.98	91.9	2	50	5	70	4.3	1.46
10	NH_2Ph	4.60	111	2	50	5	78	9.4	1.62
11	Py[h,i]	5.23	91.9	2	50	120	82	74	1.75
12	4-H_3C-py[h,i]	5.98	91.9	2	50	120	83	80	1.72
13	$NH_2{}^sBu$	10.6	113	2	RT	5	85	73	1.46
14	$NHPh_2$	0.78	136	NI	50	5	90	62	1.90
15	$NH_2{}^sBu$	10.6	113	2	50	5	92	62	1.37
16	4-$H_2NC(O)$-py[h]	3.61	91.9	2	50	5	94	17	1.45
17	4-$H_2NC(O)$-py[h]	3.61	91.9	2	50	120	94	83	1.20
18	NEt_3	10.8	150	NI	50	5	98	69	1.70
19	Piperidine[c]	11.2	121	1	RT	<1	99	120	1.90
20	Piperidine[c,j]	11.2	121	1	RT	<1	99	220	1.14

[Ru] = 1 μmol, [monomer]/[Ru] = 5000, 5 μL EDA in $CHCl_3$. Py, pyridine; RT, room temperature; NI, complex was not isolated.

[a] Ref. [47].
[b] Ref. [36,37].
[c] Ref. [34].
[d] Ref. [41].
[e] Similar result for 120 min.
[f] $\theta \approx NEt_3$.
[g] $\theta \approx NHEt_2$.
[h] Ref. [35].
[i] [NBE]/[Ru] = 3000.
[j] [NBE]/[Ru] = 2000.

catalysis occurs with the amine–phosphine complexes since all the reactions were performed after the necessary times for the formation of the complexes, as accompanied by ^{1}H NMR (see Section 2). The *in situ* formation of highly active mononuclear ruthenium complexes was also observed with $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(PPh_3)_2$(triazol-5-ylidene)] in the presence of amine ligands when catalysis experiments were conducted for living radical polymerization of methyl methacrylate [42,43].

The catalytic activities at RT characterize fast initiation reactions in the cases with NEt_3 (8), $NHPh_2$ (6) and $NH_2{}^sBu$ (13), increasing the number of Ru species able to promote the propagation reaction, which could afford narrow polydispersity indexes. However, although the M_n values are in the same order of magnitude, the M_w/M_n values are relatively high, suggesting that a chain transfer occurred during the polymerization [44].

In general, the complexes with acyclic amines show better yields than those with cyclic amines, except in the case of 4-H_2NC(O)-py, which showed quantitative reaction at 50 °C for 5 min (16). Piperidine can be observed as a type of hybrid between acyclic and saturated cyclic ligands, which resembles $NHEt_2$ (pK_a 10.9; $\theta = 125°$), providing very good results when the run is carried out at RT (19, 20).

Observing all the cases, the high cone angle values seem to be the main beneficial effect since the largest amines afforded complexes to react under the lowest temperature for less reaction time.

The cyclic amines present small cone angles (<100°) and seem to act as a function of the electronic balance in the Ru center. The strongest σ-donor amines poison the catalyst as they strongly bind the metal center throughout a phosphine ← Ru ← amine synergism effect, providing inert starting complexes. This is the case with imidazole (2) and 4-H_2N-py (5), which showed similar results for 120 min. A moderate σ-donor with a possibility to make some degree of amine ← Ru(II) π-back-bonding, such as pyridine (7) and 4-H_3C-py (9), can afford more polymer as a function of time when the yields increased for 120 min, where there exists a π-electron competition between PPh_3 and amine molecules. Thus, the different results among these cyclic amines can be attributed to the dissociation of the ligands, which are difficult to occur in the cases with imidazole (2) and 4-H_2N-py (5). It can be rationalized that π-acceptors improve the yields since π-electron competition will tune the dissociation of ligands to generate complexes with lower coordination numbers. This is the case with the weak σ-donor and moderate π-acceptor 4-H_2NC(O)-py (16), which produces quite quantitative polynorbornene under typical conditions. Thus, decreasing the σ-donor character and increasing the π-acceptor ability of the ligands, the complexes become more effective and the following order can be written characterizing different latent complexes: imidazole < 4-H_2N-py ≪ pyridine ∼ 4-H_3C-py ≪ 4-H_2NC(O)-py. This order is also an ancillary ligand order considering that the yields, molecular weights and polydispersity indexes are, in general, different; that is, the results suggest that the propagating species are electronically different. For example, the cases with pyridine and 4-H_3C-py show similar results for 120 min (11, 12), but they differ from that result with 4-H_2NC(O)-py (17) that produces polymer with low M_w/M_n for 120 min. Besides, the case with imidazole shows monomodal weight distribution with a high M_w/M_n value. Thus, it can be concluded that the large dispersion in the molecular weight is due to the electronic effects that generate complexes affording different initiation and propagation ROMP processes, since these type of ligands show similar and small cone angles.

The simple fact that the results are different from each other and from that obtained with L = PPh_3 suggests that the intermediate complexes are bonded to the respective amines and shows that these amines are capable of acting as ancillary ligands. The presence of the amines avoids forming binuclear complexes in solution, which is the behavior of the parent $[RuCl_2(PPh_3)_3]$ complex, as previously discussed in the case with piperidine [34]. Therefore, the high activity of the catalysts is attributed to the retention of the mononuclear character.

Acyclic amines with very low σ-donor and large θ (such as $NHPh_2$) can afford good metal complex reactivity, as well as good σ-donor with large θ amines (such as piperidine, $NH_2{}^sBu$ and NEt_3). These ligands provide high reactivity at RT, therefore one can conclude that the steric hindrance is really a very important factor independently of the σ-donor character of the ligand.

Good catalytic behaviors could be expected from the complexes with $NH(EtOH)_2$ and $N(EtOH)_3$ (3, 4), since they are σ-donors and the cone angles are probable ∼125° and ∼150°, which are the values of the ligands $NHEt_2$ and NEt_3 [36], respectively. However, these results can be attributed to the presence of the OH group in the ligands. Such group which can coordinate to the metal center competing with either the formation of the carbene active species or the incoming olefin substrate for the vacant coordination site; this will be like a hemilabile ligand. A poisoning of the active species by the OH group was observed when complexes $[RuCl_2(PPh_3)_2$(piperidine)] and $[RuCl_2(PPh_3)_2(imidazole)_2]$ were in the presence of 2-propanol used as additive [41]. A similar case could explain the behavior of the $[RuHCl(CO)(P^iPr_3)_2]$ complex, which is ∼4 times more active in the ROMP of norbornene in presence of toluene instead of 2-propanol [45].

Similarly what occurs with the complex with piperidine [34], the activity of the complex with $NH_2{}^sBu$ was sensitive to the amount of the monomer in the medium (Fig. 1). When a fresh feed of monomer was added to the reaction mixture up to a point where nearly all monomer of the previous batch had been consumed (5 min), the values of the M_n increased up to 5000. After 25 min (five batches), the isolated polymer presented monomodal weight distribution with low polydispersity index ($M_w/M_n = 1.47$), therefore it is possible to say that this complex shows living nature in the catalytic process.

The complex with $NH_2{}^sBu$ showed activity for ROMP of 2,5-norbornadiene with yield of 80% at 50 °C for 5 min (Table 2). This result is much better than those obtained with $[RuCl_2(PPh_3)_3]$ and complex with piperidine, where both are five-coordinated. Unfortunately, the obtained polynorbornadiene was insoluble in $CHCl_3$ and was not characterized at this time.

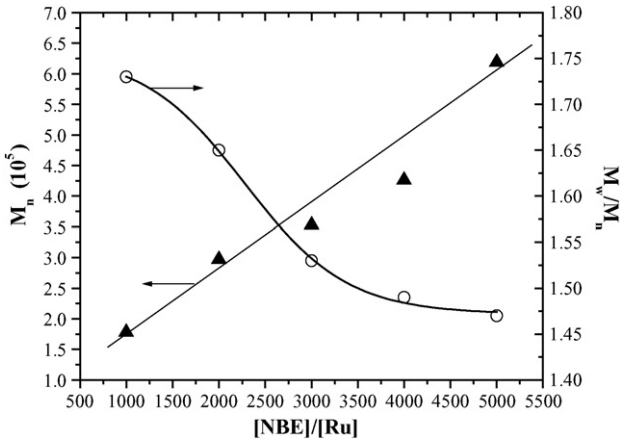

Fig. 1. Values of M_n and M_w/M_n recorded by GPC during the ROMP of norbornene as a function of [NBE]/[Ru] molar ratio using $[RuCl_2(PPh_3)_2(NH_2{}^sBu)_2]$ in $CHCl_3$ at RT; [Ru] = 1 μmol, 5 μL of EDA.

Table 2
Data for the ROMP of 2,5-norbornadiene with $[RuCl_2(PPh_3)_2(L)_x]$

L	x	Temperature (°C)	Time (min)	Yield (%)	M_n (10^4)	M_w/M_n
PPh_3[a]	1	50	5	6	0.34	3.53
Piperidine[a]	1	RT	5	48	0.53	3.40
$NH_2{}^sBu$	2	50	5	80	[b]	[b]

[Ru] = 1 μmol, [monomer]/[Ru] = 5000, 5 μL EDA in $CHCl_3$.
[a] Ref. [34].
[b] Polymer was insoluble.

^{1}H NMR made it possible to observe the formation of a copolymer with norbornene and 2,5-norbornadiene using the $NH_2{}^sBu$ derivative at 50 °C for 5 min with 52% of isolated polymer.

Although the carbene complexes were generated *in situ*, all the isolated polymers showed monomodal weight distribution.

4. Conclusions

Large amines provide good reactivity independently of the basic character. For example, although the increased basic strength of the primary amine NH_2Ph over $NHPh_2$ can be attributed to the electron-accepting effect of the phenyl group, it is obvious that such an effect is insufficient to explain the relationship of the yields. However, the σ-donor effect improves the performance of the complex when comparing the better results obtained in the case with $NH_2{}^sBu$ (13, 15) with those from the case with NH_2Ph (10), which show the cone angles are similar. The π-electron competition seems to be a very important factor, since π-acceptor with low θ, such as 4-$H_2NC(O)$-py, is better than amine with high θ and very weak σ-donor, such as $NHPh_2$ or NH_2Ph, which are not π-acceptors. It is interesting to highlight that six-coordinated complexes are capable of promptly starting the reaction for 5 min at either RT or 50 °C, which is the reaction condition necessary to activate most of the complexes. The increase in the yield with an increase in the temperature is a typical kinetic effect of a dissociation of coordinated ligand. Therefore, this can be used to control the lability of complexes. Five-coordinated complexes can obviously provide faster reactions as in the case with piperidine.

It can be concluded that amines as ancillary ligands can be a valuable contribution to fundamental and practical catalyst research and can constitute a promising approach towards achieving certain goals in molecular catalytic chemistry. They can be used to design latent catalysts that can be switchable on by a certain event. Thus, a very interesting perspective could be predicted using cyclic and acyclic amines substituted with carbene function, instead of substituted pyridine, as used by different authors [46].

Research with this type of catalytic system can combine the advantage of a satisfactory steric control of the coordination mode of the substrate with a good electronic catalytical activity.

Tests with σ-donor phosphines replacing PPh_3 in $[RuCl_2(PPh_3)_2(amine)_2]$ are currently ongoing in our laboratory and will be soon reported.

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