Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

Cyclopentadienyl-based Mg complexes in the Intramolecular Hydroamination of aminoalkenes: Mechanistic evidences for a cationic versus neutral magnesium derivatives.

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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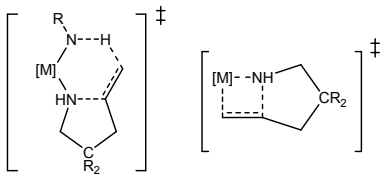
Carlos Gallegos,[a] Ruth Camacho,[a] Mercedes Valiente,[b] Tomás Cuenca,[a] Jesús Cano*,[a]

The neutral and cationic magnesium complexes stabilized by coordination of a cyclopentadienyl ligand with two different neutral hemilabile donor groups [Mg{η^5-C_5H_3-1,3-(CH_2CH_2N*i*Pr_2)($SiMe_2NPh_2$)}X(thf)] (X = Bz **2**; $N(SiMe_3)_2$ **3**) and [Mg{η^5-C_5H_3-1,3-($CH_2CH_2NiPr_2$)($SiMe_2NPh_2$)}][BPh_4] (**4**) have been prepared and characterized. ^{1}H-^{13}C HMBC and HSQC spectra for compounds **2** and **3** demonstrate the formation of 1,3 substituted cyclopentadienyl compounds and DOSY and ^{1}H-NMR experiments support the coordination-decoordination in solution of a THF molecule in complex **2**. No Schlenck-type ligand redistributions were observed in the chemical behaviour of these magnesium complexes. Compounds **2**-**4** are active catalysts in the hydroamination of aminoalkenes; stoichiometric reactions and kinetic measurements have been performed to gain an insight into their reaction mechanisms. A key contribution here is the catalytic reactivity of a cationic magnesium compound.

Introduction

Hydroamination of carbon-carbon multiple bonds is a convenient synthetic methodology to form new C–N bonds with high atom economy starting from simple and cheap precursors. New nitrogen-containing compounds can be obtained by reaction of amines with olefins or alkynes. This method is useful to prepare N-heterocycles if both functional groups (amine and unsaturated bond) are present in the same substrate molecule. This reaction requires the presence of a catalyst in order to achieve good reaction rate in soft conditions.[1] A wide variety of catalytic systems have been discovered to develop this transformation including derivatives based on lanthanides,[2] group 4 metals,[3] late transition metals[4] and more recently, main group elements.[5] The use of group 2 metal complexes in catalysis is an area that attracts widespread interest, with most of the studies focusing on the heavier alkaline-earth metal compounds.

Different mechanisms for the aminoalkene cyclization reaction have been reported, mainly dependent upon the nature of the metal complex.[6,7,8,9,10,11] Late transition metals operate through the activation of the C-C multiple bond, while early transition metals and group 2 metal complexes promote the N-H bond activation. However, in group 2 metal complexes, two different pathways with N-H activation have been described considering the transition states (Figure 1): a) a six-centre intermediate[5c] where the formation of the C-N bond with and a second ligand N-H activation in a concerted fashion is observed with a first order rate dependence on the catalyst and the substrate concentration and, b) a four-centre intermediate[5d] where the insertion of the alkene into the amide bond is rate determining with a zero-order rate dependence on the substrate concentration. However several examples of yttrium[12] and magnesium[5d] derivatives have been described that exhibit hydroamination reactivity with a second order dependence on the substrate concentration, no clear mechanistic pathway was assigned.



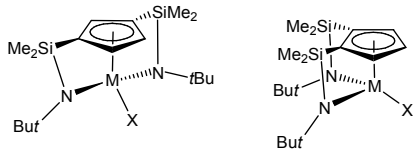
a) b)

Figure 1. Transition states in C-N formation proposed for group 2 hydroamination catalysts.

Heterocycles and nitrogen-containing molecules are important in the pharmaceutical industry. In this context, biocompatible metal-based catalysts are a good choice in order to reduce or minimize the purification steps and decrease the environmental impact of the general processes. Therefore, examples of magnesium, calcium or

[a] *Dpto de Química Inorgánica, Universidad de Alcalá, 28871 Alcalá de Henares. Spain. jesus.cano@uah.es*
[b] *Dpto de Química Física, Universidad de Alcalá, 28871 Alcalá de Henares. Spain..*
† Electronic Supplementary Information (ESI) available: [Text, tables, figures, and additional characterization data.]. See DOI: 10.1039/x0xx00000x

zinc complexes as active catalysts[5g, 13] in hydroamination reactions can be found in the literature. Nevertheless, the Schlenk-type ligand redistribution in solution is a significant inconvenience observed in the synthesis and/or the catalytic properties for heteroleptic alkaline-earth complexes.[14] Bulky multidentate ligands[15] have been used to design alkaline-earth complexes that can resist ligand redistribution reactions. Alkaline-earth heteroleptic derivatives, containing one ligand, which affords solubility to the metal complex and avoids the Schlenk-type ligand redistribution along with a second ligand (usually amido or alkyl) which acts as an initiator group in the catalytic processes, are good candidates for catalytic species in hydroamination reactions. In this context, the cyclopentadienyl group (Cp) is one of the most versatile ligands in organometallic chemistry. Cyclopentadienyl transition metal complexes have been massively used as catalysts in α-olefin polymerization, in the presence of the appropriate cocatalyst.[11] By tuning the steric and electronic properties of the Cp rings, the catalytic activity or selectivity of the corresponding complexes can be achieved. Well known examples of these modifications are *ansa*-metallocenes or constrained geometry catalysts (CGC).[16,17] In our research group we have introduced a modification of CGC by incorporating an additional amido group to the cyclopentadienyl ring (Figure 2). These compounds show high activity in ethylene polymerization and ethylene/1-hexene copolymerization.[18]



M = Ti, Zr; X = Cl, Bz, NMe_2.

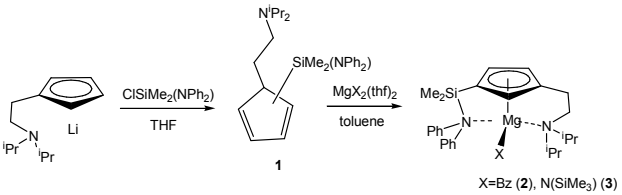
Figure 2. Doubly bridged di(silyl)amidocyclopentadienyl group 4 metal complexes.

With these results in mind, we decided to expand our studies to magnesium derivatives stabilized by coordination of ligands with two different neutral hemilabile donor groups attached to the cyclopentadienyl ring to test their activity as catalysts in the intramolecular hydroamination reactions. Some recent examples of cationic catalysts, particularly zinc cationic compounds,[8, 19] due to the low polarity of the Zn-C bond, and cationic group 4 metal complexes[20] have been reported. Nevertheless, no examples of cationic magnesium catalysts for this reaction have been described. Stoichiometric experiments and kinetic measurements were carried out in order to identify the catalytic mechanism of neutral and cationic magnesium species.

Results and discussion

Synthesis of double functionalized cyclopentadienyl complexes of magnesium.

The double functionalized cyclopentadienyl proligand $[C_5H_4(CH_2CH_2N\textit{i}Pr_2)(SiMe_2NPh_2)]$ was prepared as a yellow oil by reaction of the lithium salt $Li[C_5H_4(CH_2CH_2N\textit{i}Pr_2)]$[21] with $ClSiMe_2(NPh_2)$[22] in THF at –78 ºC (Scheme 1). The ^{1}H and ^{13}C-NMR spectra show the presence of a mixture of isomers due to sigmatropic rearrangements. Heteroleptic magnesium derivatives $[Mg\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CH_2CH_2N\textit{i}Pr_2)(SiMe_2NPh_2)\}X(thf)]$ (X = Bz **2**; $N(SiMe_3)_2$ **3**) were synthesized when compound **1** reacted with the corresponding magnesium starting reagent $MgX_2(thf)_2$ (X = Bz, or $N(SiMe_3)_2$), in toluene at 85 or 125 ºC respectively, after deprotonation of the most acidic cyclopentadienyl proton of **1** (Scheme 1). Complex **3** was also prepared by the reaction of **2** with $HN(SiMe_3)_2$ in toluene at 85 ºC.



Scheme 1. Synthesis of complexes **2** and **3**.

The elemental analysis of complexes **2** and **3** confirms the coordination of a THF molecule in the solid state. The ^{1}H-NMR spectra indicate the heteroleptic nature of these complexes with the signals of the benzyl protons at δ 1.43 and 1.26 in **2** and the amido group at δ 0.21 in **3**. The aromatization of the Cp ring is demonstrated by the three resonances observed at δ 6.75, 6.17 and 5.94 for **2** (see Table S1 and Figure S1 in the Supporting Information) and at δ 6.56, 6.43 and 5.30 for **3**. The diastereotopic nature of the Si*Me*$_2$ and the methylene protons of the ethylene side chain permits us to suggest that the amino moieties remain bound to the metal in the NMR time scale.[5d] The coordination of the $CH_2CH_2N(^i\text{Pr})_2$ moiety in **2** is also demonstrated by the highfield shifted resonances of the methylene protons connected to the N atom (C*H*$_2$N), observed in the range δ 2.02-1.95 (C*H*$_2$N). The methylene protons bound to the Cp ring (CpC*H*$_2$CH$_2$N) appear at δ 2.42-2.36.

Disubstituted cyclopentadienylsilanes present a fluxional behaviour in solution due to sigmatropic rearrangements affording a mixture of different isomers with a molar ratio and subsequent interconversion rate dependent on the nature of the substituents.[23] Starting from disubstituted cyclopentadienylsilanes, several disubstituted cyclopentadienyl metal complexes have been synthesized as mixtures of the 1,2 and 1,3 isomers.[24,25,26,27] However, the formation of the 1,3 derivative in some cases is reported as the unique reaction product. [18a,28,29] ^{1}H-^{13}C HMBC and HSQC spectra for compounds **2** and **3** demonstrate the formation of 1,3 substituted cyclopentadienyl compounds as the pure derivative. This isomer is described to be more thermodynamically stable than the 1,2 counterparts[27] and since the synthesis reactions of **2** and **3** are carried out at 85 and 125 ºC the 1,3 isomer is formed selectively. In the ^{1}H-^{13}C HMBC NMR correlation spectra for compound **2**, the methylene protons (δ 2.42-2.36) of the ethylene moiety are coupled with the C-H carbons of the Cp ring observed at

110.2 and 105.9, which is consistent with the formation of the 1,3 isomer (Figure 3 and Table S2 and Figure S2 in the Supporting Information). The 1,2 isomer is not formed since coupling between the methylene protons and the two C_{ipso} of the ring was not observed.

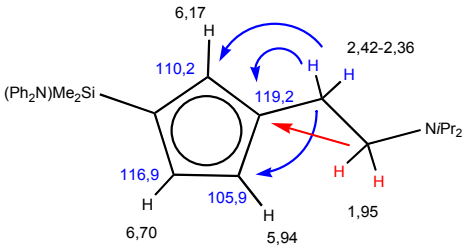
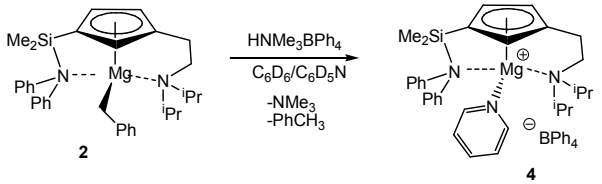


Figure 3. ^{1}H-^{13}C HMBC NMR correlation studies for **2**.

Diffusion-Ordered Spectroscopy (^{1}H-DOSY) is a powerful tool to understand molecular structure in solution, affording molecular parameters such as molecular weight (FW)[30] or hydrodynamic radii, and consequently to have knowledge about the nature of the active species in catalytic reactions.[31] To develop this method,[30b] internal references have been chosen to obtain a molecular weight value by the relative diffusion coefficient of compound **2**. A diffusion coefficient of 5.84×10^{-10} m^2 s^{-1} and a molecular weight of 478.25 (10% error) were obtained (Table S3 in the Supporting Information). However, in the DOSY spectrum, the THF resonances are observed at higher diffusion coefficients and therefore lower M_W than the cyclopentadienyl ligand (Figure S3 in the Supporting Information). This evidence implies that in solution the THF molecule in **2** is not permanently coordinated to the metal complex, suggesting a coordination-decoordination equilibrium.[32] Moreover, the ^{1}H-NMR spectrum in solution shows wide signals for the THF protons which are also consistent with this coordination-decoordination equilibria.[32] However, these results contrast with the behaviour observed for **2** in the solid state with the elemental analysis revealing the presence of one THF molecule per metal atom.

Compound **2** reacts with $HNMe_3BPh_4$ in C_6D_6/C_6D_5N to yield the cationic complex $[Mg\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CH_2CH_2NiPr_2)(SiMe_2NPh_2)\}][BPh_4]$ (**4**) (Scheme 2). Deuterated pyridine was added to the reaction mixture because the cationic species precipitated as a yellow solid when the reaction was carried out in C_6D_6. The ^{1}H-NMR spectrum in C_6D_6/C_6D_5N shows the formation of **4** together with NMe_3 and toluene, due to the protonolysis of the Mg-benzyl bond. All ^{1}H-NMR signals for the cationic compound **4** are down-field shifted with respect to the neutral benzyl complex. Bidimensional ^{15}N-^{1}H HMBC and ^{29}Si NMR experiments for compounds **1**-**4** allowed a full assignment of the nitrogen and silicon resonances displayed (see Experimental Part). ^{1}H DOSY experiment with C_6H_5N shows that **4** in pyridine is a solvent-separated ion pair in solution (see supporting information).



Scheme 2. Synthesis of complex **4**.

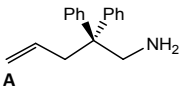
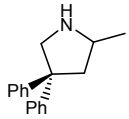
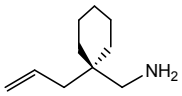
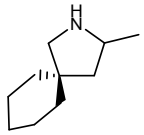
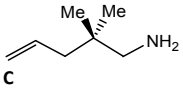
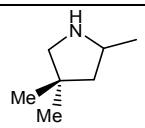
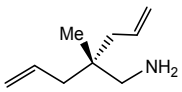
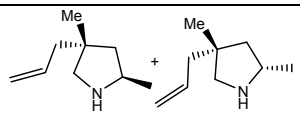
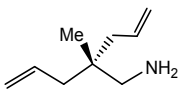
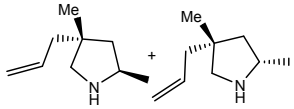
Intramolecular hydroamination reactions.

Previous studies have demonstrated that magnesium complexes[5g, 13b, 13d-f] are active species in the hydroamination processes. In this context, we have checked the activity of the magnesium doubly functionalized cyclopentadienyl complexes $[Mg\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CH_2CH_2NiPr_2)(SiMe_2NPh_2)\}X(thf)]$ (X = Bz, **2**; $N(SiMe_3)_2$ **3**) and $[Mg\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CH_2CH_2NiPr_2)(SiMe_2NPh_2)\}][BPh_4]$ (**4**) as catalysts in the intramolecular hydroamination reaction of a variety of aminoalkenes with a catalyst loading of 2-10 mol % in C_6D_6 (table 1). The catalyst activity was monitored by ^{1}H-NMR spectroscopy and the yields were determined by comparing the integration to mesitylene standard. The influence of reaction parameters, such as temperature, catalyst loading, the nature of the substrate and catalyst, upon the catalytic activity has been studied.

Doubly functionalized cyclopentadienyl complexes **2**, **3** and **4** are efficient in the cyclization of aminoalkenes. For all catalytic experiments, the activity increases with the steric bulk of the geminal substituent in the aminopentene substrates (Thorpe-Ingold effect).[33] The reaction with the diphenyl-substituted aminopentene **A** is completed in 1 h at 60 ºC with 2 % catalyst load while the reaction with the dimethyl-substituted aminopentene **C** needs 5 h at 120 ºC with 10% catalyst load to reach high conversion. The neutral magnesium complexes **2** and **3** are slightly more active than the cationic complex **4** (table 1). Their activity is comparable to that of Sadow´s tris(oxazolinyl)phenylborato magnesium complexes[5c,13j] and Hultzsch´s achiral phenoxyamine complex[5d] but less active than Hill´s diketiminate magnesium complexes[11,13i] and Hultzsch´s chiral phenoxyamine complexes.[13e] A few examples of cationic zinc[8, 19] and group 4[20] metal complexes have been reported to be active in the hydroamination of aminoalkenes, but to the best of our knowledge, this is the first example of a cationic magnesium complex employed in this type of reaction.

Both cationic and neutral magnesium complexes can produce the tandem cyclization of 2-allyl-2-methyl-penten-4-enyl-amine **D** to form, first the allyl-substituted secondary amine **H**, followed by a second bicyclization process to give the tertiary amine **I**.

Table 1**: Magnesium-catalyzed hidroamination aminoalkenes.**

Substrate	product	Cat	[Cat] (% mol)	Temp (ºC)	Time (h)	Conv[a] (%)
 **A**	 **E**	**2**	2	60	1	99
		3	2	60	1	99
		4	2	60	4	99
 **B**	 **F**	**2**	5	90	24	72
		3	5	90	30	75
		4	5	90	30	75
 **C**	 **G**	**2**	10	120	5	86
		3	10	120	5	84
		4	10	120	5	72
 **D**	 **Ha Hb**	**2**	10	120	4	39/40[b]
		4	10	120	6	44/55[b]
 **D**	 **Ha Hb**	**2**	10	120	24	22/40[b] 23 (I)
	 **I**	**4**	10	120	20	21/54[b] 24 (I)

Reaction conditions: [aminoalkene] = 1 mol L^{-1}, 0,5 mL C_6D_6. [a] NMR yield determined relative to mesitylene standard. [b](Ha/Hb) ratio.

The first cyclization process with the neutral complex **2** affords, after 4 h of reaction, a mixture of two diastereomeric products, **Ha** and **Hb,** with very low diastereoselectivity (39/40) but with cationic complex **4**, a slightly higher diastereoselectivity (44/55) was observed in a 6 h reaction. This low diastereoselectivity has been also observed for lutetium,[34] magnesium[5d] or lithium derivatives.[35]

For longer reaction times (24 h for compound **2** and 20 h for compound **4**), the formation of tertiary amine **I** by hydroamination of the secondary amine (**Ha**) is observed. In contrast to the first cyclization step, the bicyclization to form the hydroamination product **I**, induces diastereoselectivity towards one of the diastereomers (Figure 4). The *exo*, *exo*-isomer is formed by selective reaction of **Ha** while **Hb** remains unaltered during the course of this reaction. Not much alkene hydroamination catalysts can be used with secondary amine substrates[36,37] and among these examples some cationic Zr[20c,20d] or Zn[8] are found, but to the best of our knowledge, no cationic or neutral magnesium systems have been previously used in this reaction with secondary amines.

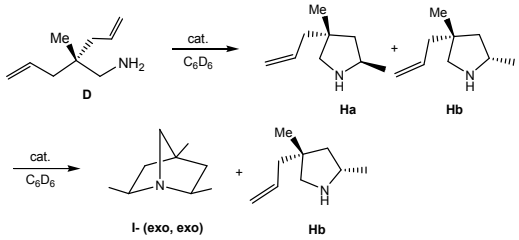


Figure 4. Bicyclization of 2-allyl-2-methylpent-4-enylamine to produce **I**-(exo, exo).

Mechanistic investigations-combined kinetic studies and stoichiometric reactions

Preliminary kinetic measurements monitored by ^{1}H-NMR spectroscopy with **2** and substrate **A** were undertaken to determine

the effect of the catalyst [cat] and substrate [S] concentrations upon reaction rate. All measurements were carried out at 25 ºC.

When the reaction rate at different [S] is determined by the differential method, a double-logarithmic plot of ln v *versus* ln [S] gave the change of order of reaction during the reaction progress (Figure S6 in the Supporting Information). A first order with respect to [S] is observed at initial times with the order falling off to nearly zero as the reaction progressed. This is consistent with an initial consumption of substrate to obtain the catalytically active species (Cat) from the precatalyst LMgBz (PCat) (see above).

Figure 5 shows the plot of [S] versus time, after approximately 20% of reaction conversion, whilst maintaining the [cat] constant, with a zero-order rate dependence with respect to [S] clearly observed.

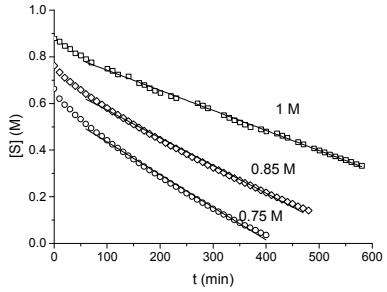


Figure 5. Zero-order plot for the hydroamination of **A** catalyzed by **2** at 25 ºC with $[PCat]_0$ = 20 mM and different initial substrate concentration.

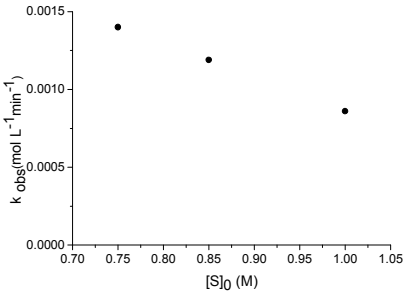


Figure 6. Plot of k_{obs} values versus initial substrate concentration plot for the hydroamination of **A** catalyzed by **2** at 25 ºC with $[PCat]_0$ = 20 mM.

The k_{obs} value decreases with increasing initial substrate concentration (Figure 6), suggesting a complex mechanism where either the substrate or the product inhibits the reaction rate (cat-S, cat-P, Figure 10). An inhibition effect by the substrate in cyclohydromination reactions has been previously reported.[38] Differential analysis of kinetic data agrees with the inhibition of the reaction by the product. So we can conclude that the increase in k values decreasing $[S]_0$ is due to the lower amount of substrate implies lower content of product which inhibits the reaction.

The dependence upon [Pcat] was examined by varying the initial concentration of the LMgBz in the range from 20 to 40 mM while keeping initial substrate concentration constant (1 M). Figure 7 shows the plot results after 20% of reaction conversion. The plot of k_{obs} value versus the initial concentration of the precatalyst shown in Figure 8 is linear confirming the first-order dependence of [cat]. However, this plot indicates that real concentration of the substance that acts as catalyst is lower than the initial concentration of the precatalyst LMgBz as similarly observed for lutetium complexes.[34] The dot line in Figure 8 should correspond to the k variation with the catalyst concentration. In contrast, a rate depression was observed when the substrate was added in two batches (Figure 9). These results are in agreement with a four-centre intermediate mechanism where the conversion of the precatalysts LMgBz into the catalytically active species in the first step is lower than 100 % and, probably, with an inhibition effect from the product when combining with the catalyst (cat-P, cat-S, Figure 10).

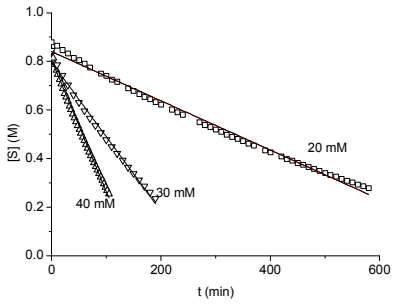


Figure 7. Zero-order plot for the hydroamination of **A** catalyzed by **2** at 25 ºC with $[S]_0$ = 1 M and different initial catalyst concentration.

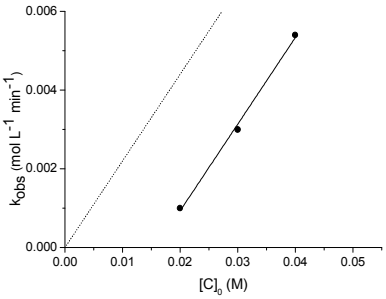


Figure 8. Plot of k_{obs} values versus initial catalyst concentration plot for the hydroamination of **A** catalyzed by **2** at 25 ºC with $[S]_0$ = 1 M.

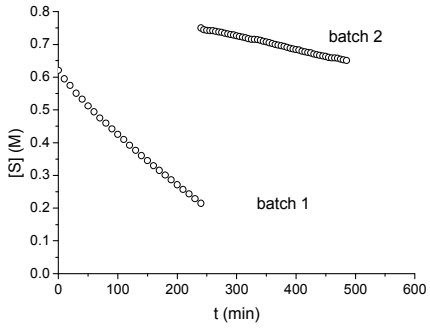


Figure 9 Time dependence of substrate concentration for the hydroamination of **A** catalyzed by **2** when adding the substrate in two batches at 25 ºC

In order to confirm this postulated mechanism obtained according to the kinetic measurements a stoichiometric reaction on the NMR-scale between substrate **A** and the precatalyst **2** in a molar ratio 1:1 was carried out a 70 ºC. Formation of toluene and the disappearance of the aminoalkene olefin proton resonances is observed at the same time as a new compound metal-pyrrolidine **T´** (Figure 10) is formed. Compound **T´** is obtained as a mixture of two diastereomers as a result of the chirality imposed by the enantiotopic face of the cyclopentadienyl ring and the chirality of one carbon atom of the pyrrolydine but no formation of **E** is detected (Figure S7 in the Supporting Information).

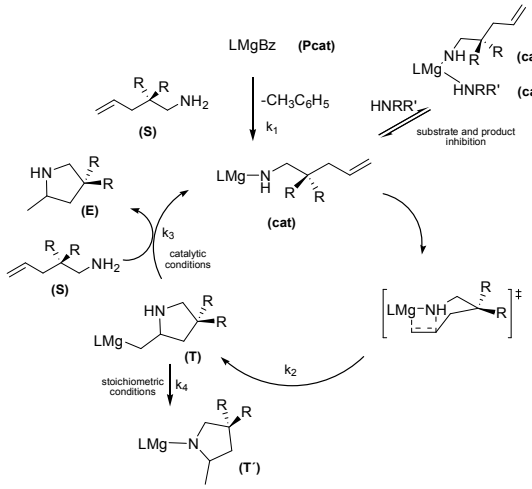


Figure 10. Plausible mechanism pathways for the hydroamination of **A** catalyzed by **2**.

According to this mechanism, the rate reaction with **2** is given by

$$-\frac{d[S]}{dt} = k_1[S][PCat] + k_3[S][T] = k_1[S][PCat] + \frac{k_3 k_2[S][Cat]}{k_4 + k_3[S]}$$

where we have considered steady state approximation for **T**; d[T]/dt=0. Under catalytic conditions $k_4 << k_3[S]$ and the equation reduces to

$$-\frac{d[S]}{dt} = k_1[S][PCat] + k_2[Cat]$$

This equation fits a first order with respect to the substrate initially. But when the reaction progresses the first term of the equation is negligible and it reduces to

$$-\frac{d[S]}{dt} = k_2[Cat]$$

Kinetic measurements were carried out in order to obtain activation parameters for the cyclohydroamination by the reaction of substrate **A** and the cationic specie **4**. A series of reactions were measured in a range of temperatures (25-50 ºC). A first order rate constant was obtained in each case from the plots of Ln[S] versus the time. The reactions carried out at 40 and 50 ºC were monitored until high conversions and the order is maintained during the course of the cyclization. The apparent rate constants are 6.1×10^{-4}, 3.7×10^{-3} and 2.1×10^{-2} min^{-1} at 25, 40 and 50 ºC respectively (Figure 11).

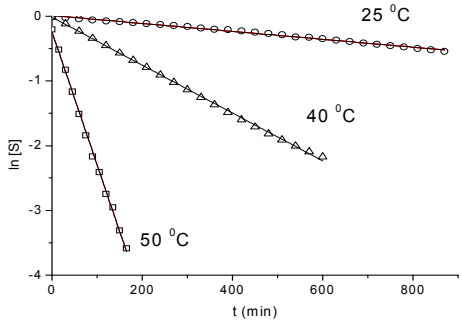


Figure 11. First-order plot for the hydroamination of **A** catalyzed by **2** $[PCat]_0$ = 20 mM and $[S]_0$ = 1 M over the temperature range 25-50 ºC.

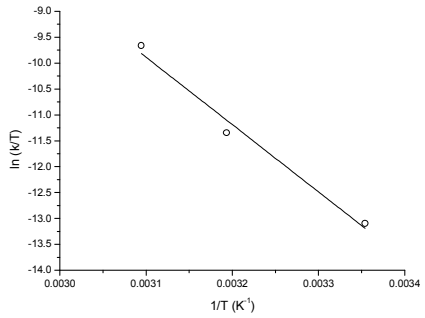


Figure 12. Eyring plot for the cyclization of A by complex **4** over the temperature range 25-50 ºC with $[PCat]_0$ = 20 mM and $[S]_0$ = 1 M.

Eyring analysis for the hydroamination of **A** with the cationic species **4** afforded $\Delta H^{\ddagger}$ = 26 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 13 cal K^{-1} mol^{-1} (Figure 12). The kinetic isotopic effect (KIE) for this reaction has been investigated. H/D KIE studies have been carried out at 40 ºC using similar reaction conditions from substrate **A** with the cationic species **4**, to give values of kobs = 3.7×10^{-3} $min^{-1}$and kobs = 5.0×10^{-4} min^{-1} respectively (Figure 13), observing a primary KIE = 7.4. This

experimental result indicates the amino proton of the substrate **A** is clearly involved in the key step of the hydroamination process.

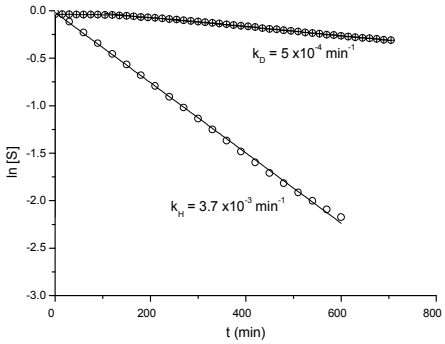


Figure 13. H/D KIE for the cyclization of **A** by complex **4** at 40ºC.

Under stoichiometric reaction conditions, no hydroamination reaction was detected when **4** and the substrate **A** were mixed in a stoichiometric molar ratio even over 3 h at 60 ºC (Figure S10 in the Supporting Information), and two or more equivalents of aminoalkene were required to induce the reaction (Figure S11 in the Supporting Information). Consequently, we suggest a plausible mechanistic proposal for the intramolecular hydroamination reaction carried out with the cationic magnesium complex **4** (Figure 14).

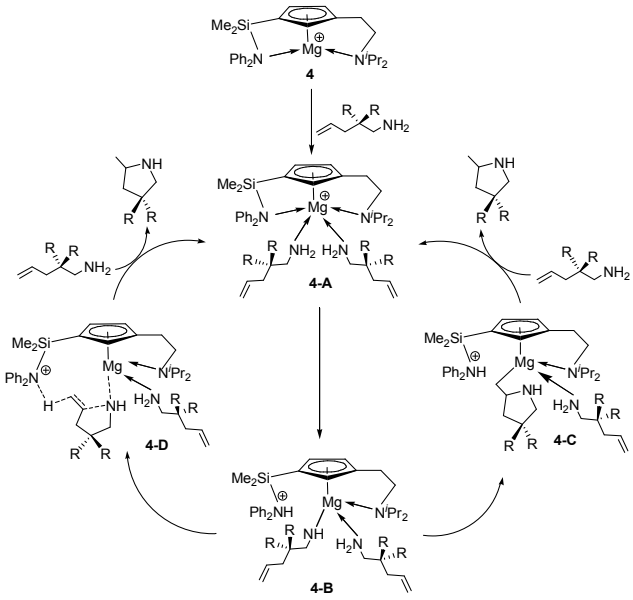


Figure 14. Plausible mechanism pathways for the hydroamination of **A** catalyzed by **4**.

The activity with **4** is slightly lower than that observed with the neutral derivatives (Table 1). The cationic zirconium complexes described by Scott[20d] and the cationic scandium derivatives described by Piers and Schafer[39] present higher reactivity than their neutral counterparts due to the presence of an additional alkyl/amido group in the coordination sphere of the metal catalytic precursor species. This disposition permits the protonation reaction of the cationic metal-amido or metal-alkyl complex with the substrate aminoalkene to form the suggested active species in the hydroamination process, a complex containing a metal-amidoalkene bond. In our case, the cationic magnesium complex formed after the abstraction of the alkyl ligand from the neutral complexes does not present the required magnesium-alkyl/amido bond in the corresponding catalytically starting compounds for the hydroamination process and the reaction mechanism should be different to the magnesium–alkyl **2** or magnesium–amide complex **3**. Accordingly, addition of 1 equivalent of substrate **A** to **4** does not produce the hydroamination product.

Stabilization of the cationic compound **4** is required by coordination of two molecules of amine substrate to give the **4-A** species (Figure 14), from which the amidoalkene compound **4-B** is formed by a proton migration to the silylamine. The insertion of the unsaturated C-C linkage into the magnesium-amido bond involves the formation of **4-C**. Alternatively the proton-assisted pathway evolving through the multicentre transition state **4-D** describing N-C/C-H bond formation can be proposed. In both cases the cycloamine is delivered by coordination of an additional molecule of substrate **A** to regenerate the compound **4-A**. The two alternative ways seem to be equally consistent displaying thermodynamic forces of identical magnitude according to computational calculations for similar calcium complexes.[9]

Conclusions

In summary, magnesium complexes stabilized by coordination of a cyclopentadienyl ligand with two different neutral hemilabile donor moities are stable in solution against Schlenk-type ligand redistributions. ^{1}H-^{13}C HMBC and HSQC spectra for compounds **2** and **3** demonstrate the selective formation of 1,3 substituted cyclopentadienyl derivatives. The neutral **2** and **3** and the cationic **4** compounds are active catalysts in the hydroamination of aminoalkenes. Compound **4** is the first cationic magnesium complex described as catalyst in these hydroamination reactions. Diastereoselectivity in the formation of the tertiary amine **I**-(exo, exo) by hydroamination of a secondary amine (**Ha**) is observed. Mechanistic evidences for the cationic versus the neutral magnesium derivatives are investigated.

Experimental

All manipulations were performed under an inert atmosphere using standard Schlenk-line techniques (O_2 < 3ppm) and MBraun MB-20G glovebox (O_2 < 0.6 ppm). Solvents were dried by conventional procedures and freshly distilled prior to use. Deuterated solvents were degassed by freeze–vacuum–thaw cycles and stored in the

glovebox in the presence of molecular sieves (4 Å). All reagents were purchased from Aldrich and used as received.

NMR spectra were recorded with a Bruker 400 Advance Ultrashield (^{1}H 400MHz, ^{13}C 100,6 MHz, ^{15}N 41 MHz, y ^{29}Si 79,49 MHz). All chemical shifts were determined using the residual signal of solvents and were reported versus $SiMe_4$. ^{29}Si and ^{15}N chemical shifts have been obtained by proton-heteroatom correlation, using as internal standard, TMS for ^{29}Si and ammonia for ^{15}N. The signal assignments have been developed by ^{1}H-^{13}C HSQC (Heteronuclear Single Quantum Correlation spectroscopy), ^{1}H-^{13}C HMBC (Heteronuclear Multiple-Bond Correlation spectroscopy), COSY (correlation spectroscopy) and TOCSY (total correlation spectroscopy). ^{1}H DOSY (Diffusion Ordered Spectroscopy) experiments have been carried out at 25 ºC. δ and Δ values have been calculated by monodimensional diffusion experiments (1D DOSY). Elemental analyses were performed with a PerkinElmer 2400 CHNS/O analyzer Series II and were the average of a minimum of two independent measurements.

[C_5H_4(CH_2CH_2N*i*Pr_2)($SiMe_2NPh_2$)] (1). Li*n*Bu (12 mL, 19.2 mmol, 1.6 M solution in hexane) was slowly added to a solution of $C_5H_5(CH_2CH_2N$*i*$Pr_2)$[21] (3.59 g, 18.6 mmol) in hexane (70 mL) at –78 ºC. The colorless solution was warmed to room temperature, and a white suspension was slowly formed and stirred for 12 h. After filtration, the solid was washed with hexane (2 x 40 mL). The resultant white solid was dissolved in THF (75 ml) and a solution of $SiMe_2Cl(NPh_2)$[22] (4,87 g, 18,6 mmol, prepared by reaction of $LiNPh_2$ with an excess of $SiMe_2Cl_2$ in hexane) dissolved in 25 ml of THF was added slowly at –78 ºC. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed under vacuum, and the residue was extracted into hexane (3 x 30 mL). After removal of the solvent a yellow oil of compound **1** was formed, which was obtained as a mixture of isomers (6.77 g, 87%). Anal. Calc. for $C_{27}H_{38}N_2Si$: C 77.45; H 9.15; N 6.69. Exp.: C 76.75; H 9.48; N 6.76. ^{1}H-NMR (400 MHz, 293 K, $CDCl_3$): δ 7.34-7.25 (m, 4H, $N(C_6H_5)_2$), 7.09-6.90 (m, 6H, $N(C_6H_5)$), 6.54, 6.49, 6.46, 6.31, 6.21, 6.16, 6.09, 4.64, 4.29, 3.81 (m, 3H, C_5H_4), 3.07-2.95 (m, 2H, $NCHMe_2$), 2.53 (m, 4H, $C_5H_4CH_2CH_2Ni$*P*r_2), 1.04 (m, 12H, $CH(CH_3)_2$), 0.28, 0.25, 0.19, 0.09, 0.05, 0.04 (s, 6H, $Si(CH_3)_2$).^{13}C-NMR (100.6 MHz, 293 K, $CDCl_3$): δ 154.6, 148.5, 148.4, 146.5, 146.4, 146.3, 145.1, 144.2, 143.2 (C_5H_4), 133.6, 133.5, 133.4, 131.9, 129.3, 129.2, 129.1, 127.4, 125.0, 124.9, 124.8, 124.4, 124.4 ($N(C_6H_5)_2$), 123.0, 122.9, 122.6, 122.5, 122.0, 121.9, 117.8 (C_5H_4), 51.1, 49.0, 48.9 ($NCHMe_2$), 47.2, 46.2, 46.0, 45.4, 45.3, 44.8 ($C_5H_4CH_2CH_2Ni$*P*r_2), 33.3, 32.8, 32.1, 27.1, 26.4, 23.7, 20.8 ($CH(CH_3)_2$), 1.1, 0.3, 0.2, –1.4 ($Si(CH_3)_2$). ^{15}N-NMR (40.5 MHz, 293 K, $CDCl_3$): δ 86.2 ($N(C_6H_5)_2$), 57.2 ($NCHMe_2$). ^{29}Si-NMR (79.5 MHz, 293 K, $CDCl_3$): δ–12.3, –7.42, –1.87, 2.1.

[Mg{η^5-C_5H_3-1,3-(CH_2CH_2N*i*Pr_2)($SiMe_2NPh_2$)}Bz(thf)] (2). A solution of $MgBz_2(thf)_2$[38] (220 mg, 0.63 mmol) in 10 mL of toluene was added to a solution of [$C_5H_4(CH_2CH_2N$*i*$Pr_2)(SiMe_2NPh_2)$] (263 mg, 0.63 mmol) in 10 mL de toluene at 0 ºC. The light brown solution was warmed to room temperature and after 1h was heated to 85 ºC for 12 h affording a pale yellow solution. The volatiles were removed under vacuum and the resultant light yellow oil was recrystallized with hexane. After cooling the saturated solution to –20 ºC compound **2** (82 mg, 24%) precipitated as colorless oil. Anal. Calc. for $C_{38}H_{52}N_2OSiMg$: C 75.41; H 8.66; N 4.63. Exp.: C 75.12; H 8.45; N 4.34. ^{1}H-NMR (400 MHz, 293 K, C_6D_6): δ 7.25-7.01 (m, 10H, $N(C_6H_5)_2$), 6.92 (d, 2H, *J* = 7.58, o-$CH_2C_6H_5$), 6.86 (t, 2H, *J* = 7.12, m-$CH_2C_6H_5$), 6.81 (t, 1H, *J* = 7.12, p-$CH_2C_6H_5$), 6.75 (m, 1H, C_5H_3), 6.17 (m, 1H, C_5H_3), 5.94 (m, 1H, C_5H_3), 2.42-2.36 (m, 4H, $C_5H_3CH_2CH_2N$ + $N(CHMe_2)_2$), 2.02-1.95 (m, 2H, $C_5H_3CH_2CH_2N$), 1.43 (d, 1H, *J* = 9.76, $CH_2C_6H_5$), 1.26 (d, 1H, *J* = 9.76, $CH_2C_6H_5$), 0.63 (s, 3H, $Si(CH_3)_2$), 0.58 (s, 3H, $Si(CH_3)_2$), 0.50 (m, 12H, $N(CH(CH_3)_2)_2$). ^{13}C-NMR (100.6 MHz, 293K, C_6D_6): δ 153.4, 149.5, 130.1, 129.6, 129.3, 129.2 ($N(C_6H_5)_2$), 129.1 ($CH_2C_6H_5$), 127.9 ($N(C_6H_5)_2$), 127.6 ($CH_2C_6H_5$), 125.2 ($N(C_6H_5)_2$), 124.8 ($CH_2C_6H_5$), 124.5, 124.1 ($N(C_6H_5)_2$), 122.0 ($CH_2C_6H_5$), 119.2 (C_5H_3), 118.8, 118.3 ($CH_2C_6H_5$), 117.5, 116.9, 110.3, 105.4 (C_5H_3), 50.4 ($NCHMe_2$), 44.6 ($C_5H_4CH_2CH_2Ni$*P*r_2), 26.7 ($C_5H_4CH_2CH_2Ni$*P*r_2), 20.0, 19.4 ($CH(CH_3)_2$), 2.0 ($Si(CH_3)_2$), 1.2 ($CH_2C_6H_5$), 1.1 ($Si(CH_3)_2$). ^{15}N-NMR (40.5 MHz, 293 K, C_6D_6): δ 87.9 ($N(C_6H_5)_2$), 56.1 ($N(CHMe_2)_2$). ^{29}Si-NMR (79.5 MHz, 293 K, C_6D_6): δ –7.3 ($Si(CH_3)_2$).

[Mg{η^5-C_5H_3-1,3-(CH_2CH_2N*i*Pr_2)($SiMe_2NPh_2$)}{$N(SiMe_3)_2$}(thf)] (3). A solution of $Mg[N(SiMe_3)_2]_2(thf)_2$[40] (1.1 g, 2.24 mmol) in 20 mL of toluene was added to a solution of [$C_5H_4(CH_2CH_2N$*i*$Pr_2)(SiMe_2NPh_2)$] (0.93 g, 2.15 mmol) in 30 mL of toluene at 0 ºC. The solution was warmed to room temperature and after 1h was heated to 125 ºC for 12h. The volatiles were removed under vacuum and **3** (1.11 g, 77%) was isolated as a yellow oil. Anal. Calc. for $C_{37}H_{63}N_3Si_3OMg$: C 65.84; H 9.41; N 6.23. Exp.: C 65.45; H 8.98; N 6.17. ^{1}H-NMR (400 MHz, 293 K, C_6D_6): δ 7.57 (t, 4H, *J* = 7.25, $N(C_6H_5)_2$), 7.00 (d, 4H, *J* =7.25, $N(C_6H_5)_2$), 6.86 (t, 2H, $N(C_6H_5)_2$), 6.56 (m, 1H, C_5H_3), 6.43 (m, 1H, C_5H_3), 6.30 (m, 1H, C_5H_3), 3.38 (m, 4H, OCH_2CH_2), 3.03 (m, 2H, $C_5H_3CH_2CH_2N(CHMe_2)_2$), 2.85 (m, 2H, $C_5H_3CH_2CH_2N$), 2.68 (m, 2H, $C_5H_3CH_2CH_2N$), 1.02 (m, 16H, OCH_2CH_2 + $N(CH(CH_3)_2)_2$), 0.59 (s, 3H, $Si(CH_3)_2$), 0.53 (s, 3H, $Si(CH_3)_2$), 0.21 (s, 18H, $N(Si(CH_3)_3)_2$). ^{13}C-NMR (100.6 MHz, 293K, C_6D_6): δ 149.5, 148.9, 129.2, 129.2, 129.1, 129.1, 128.9, 125.4, 125.1, 122.1 ($N(C_6H_5)_2$), 122.3, 115.1, 114.7, 110.9, 109.5 (C_5H_3), 69.8 (OCH_2CH_2), 48.7 ($NCHMe_2$), 48.6 ($C_5H_4CH_2CH_2Ni$*P*r_2), 24.7 ($C_5H_4CH_2CH_2Ni$*P*r_2), 21.2 (OCH_2CH_2), 21.0, 20.8 ($CH(CH_3)_2$), 5.7 ($N(Si(CH_3)_3)_2$), 2.4, 1.6 ($Si(CH_3)_2$). ^{15}N-NMR (40.5 MHz, 293 K, C_6D_6): δ 88.8 ($N(C_6H_5)_2$), 56.1 ($N(CHMe_2)_2$), 37.4 ($N(Si(CH_3)_3)_2$). ^{29}Si-NMR (79.5 MHz, 293 K, C_6D_6): δ –8.0 ($Si(CH_3)_2$), –9.2 ($N(Si(CH_3)_3)_2$).

Formation of [Mg{η^5-C_5H_3-1,3-(CH_2CH_2N*i*Pr_2)($SiMe_2NPh_2$)}][BPh_4] (4).

$[HNMe_3][BPh_4]$ (4 mg, 9.9 μmol) was added in small portions to a solution of **2** (6 mg, 9.9 μmol) in C_6D_6. The white suspension was stored for 5 h at room temperature and a yellow suspension was obtained. The insoluble solid in C_6D_6 was dissolved with a drop of C_5D_5N in order to proceed to the NMR spectroscopic characterization of **4·Py**. The instability against humidity disables its characterization by elemental analysis. ^{1}H-NMR (400 MHz, 293 K,

C_6D_6/C_5D_5N): δ 7.80 (m, 5H, $B(C_6H_5)_4$), 7.50 (d, 2H, *J* = 7.12, $B(C_6H_5)_4$), 7.31 (t, 2H, *J* = 7.15, $B(C_6H_5)_4$), 7.23 (t, 1H, *J* = 7.24, $B(C_6H_5)_4$), 7.12-6.94 (m, 12H, $B(C_6H_5)_4$ + $N(C_6H_5)_2$), 6.87-6.81 (m, 8H, $N(C_6H_5)_2$), 6.62 (m, 1H, C_5H_3), 6.47 (m, 1H, C_5H_3), 6.24 (m, 1H, C_5H_3), 2.99-2.95 (m, 2H, $N(CHMe_2)_2$), 2.88 (m, 2H, $C_5H_3CH_2CH_2N$), 2.58 (m, 2H, $C_5H_3CH_2CH_2N$), 1.02 (s, 3H, $Si(CH_3)_2$), 1.00 (s, 3H, $Si(CH_3)_2$), 0.98 (m, 12H, $N(CH(CH_3)_2)_2$). ^{13}C-NMR (100.6 MHz, 293 K, C_6D_6/C_5D_5N): δ 165.5, 165.0, 164.5 ($B(C_6H_5)_4$), 149.8 ($N(C_6H_5)_2$), 136.9, 136.1, 130.2, 129.1, 129.1, 129.0, 128.9, 128.8, 128.8, 128.3, 128.3, 127.9, 127.7, 126.5, 125.9, 125.9, 125.8, 125.4, 125.3, 125.3, 122.7, 122.3, 122.0, 121.9, 121.6 ($N(C_6H_5)_2$ + $B(C_6H_5)_4$), 121.2, 115.0, 111.3, 109.4 (C_5H_3), 48.8 ($NCHMe_2$), 48.0 ($C_5H_4CH_2CH_2NiPr_2$), 32.9 ($C_5H_4CH_2CH_2NiPr_2$), 21.2, 20.1 ($CH(CH_3)_2$), 1.2, 1.1 ($Si(CH_3)_2$). ^{15}N-NMR (40.5 MHz, 293 K, C_6D_6/C_5D_5N): δ 88.1 ($N(C_6H_5)_2$), 56.1 ($N(CHMe_2)_2$). ^{29}Si-NMR (79.5 MHz, 293 K, C_6D_6/C_5D_5N): δ –7.3 ($Si(CH_3)_2$).

Hydroamination catalytic reactions. In a glovebox, a Young style NMR tube with a Teflon valve was charged with 0.30 mL of C_6D_6, 0.0556 mmol (7 mg, 7.73 μL) of mesitylene and 0.5 mmol (118 mg) of aminoalkene **A**. A solution of catalyst **2** (10 μmol; 6 mg) in 0.20 mL of C_6D_6 was added to the substrate solution and the closed NMR tube was placed in a thermostated oil bath. The reaction was monitored by NMR spectroscopy following the disappearance of the substrate relative to the internal standard mesitylene.

Acknowledgements

We acknowledge the UAH/MICINN (I3 program) and UAH (CCG2014/EXP-009) for financial support. C.G. and R.C. acknowledge the UAH for a fellowship.

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Graphical abstract

Mechanistic evidences in the catalytic hydroamination of aminoalkenes for a cationic magnesium derivative.