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Neutral *versus* cationic Group 3 metal alkyl catalysts: performance in intramolecular hydroamination/cyclisation†‡

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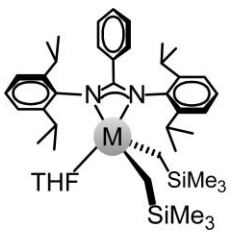
The relative catalytic activity of neutral dialkyl *versus* cationic monoalkyl Group 3 metal catalysts in the intramolecular hydroamination/cyclisation of the 2,2-dimethyl-4-pentenylamine reference substrate was investigated. This was found to depend strongly on the nature of the monoanionic ancillary ligand. With a bidentate amidinate ligand, the neutral catalysts were quite effective, but their cationic derivatives showed a much lower activity. The reaction kinetics suggest that this reflects an intrinsically higher activation barrier for the insertion of the olefinic moiety into the metal–amide bond for the cationic catalysts. In contrast, the neutral catalysts with tetradentate triamine–amide ligands showed a much lower activity than their cationic derivatives. It appears that this higher activity of the cationic triamine–amide catalysts reflects the beneficial effect of the additional available coordination space relative to the neutral species. The cationic triamine–amide yttrium catalysts are more active than the cationic amidinate catalysts of the same metal, possibly reflecting a stronger Y–amide bond in the latter, which is the more electron-deficient system.

Introduction

Neutral alkyl compounds of the trivalent Group 3 and lanthanide metals are catalytically active for a range of transformations, such as olefin polymerisation, dimerization of alkynes, olefin hydrogenation and the hydroamination or hydrophosphination of alkenes and alkynes.[1–4] In contrast to the transition metals, where such species have long been known as highly active catalysts (in particular for olefin polymerisation), *cationic* alkyl complexes of these metals have only recently become available.[5–11] Consequently, as yet little is known about the reactive properties of cationic rare earth organometallics and their relative performance in various types of catalysis *versus* their neutral congeners.

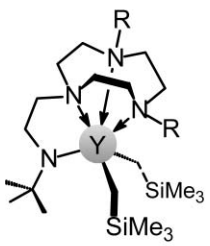
Very recently, the first example of intramolecular hydroamination/cyclisation of alkenylamines with a cationic Group 3 metal alkyl catalyst was reported, using a Sc-based catalyst with a *N*,*N*′-chelating β-diketiminato ancillary ligand.[12] In this system, the cationic monoalkyl species was shown to be significantly more active than the neutral dialkyl analogue. This result might suggest that, for this reaction, cationic catalysts are intrinsically faster than neutral catalysts (as is usually the case for catalytic olefin polymerisation).

Here we describe a comparison between neutral Group 3 metal dialkyl and cationic Group 3 metal monoalkyl catalysts with three different ancillary ligand types in the catalytic intramolecular hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine (a standard substrate for this type of reaction). It is seen that all species, neutral and cationic, are able to catalyse this particular reaction. Nevertheless, the relative rate of conversion by the cationic catalyst *versus* that by its neutral precursor depends strongly on the ancillary ligand type. This shows that, for hydroamination/cyclisation, cationic catalysts are not *per se* more active than their neutral congeners.



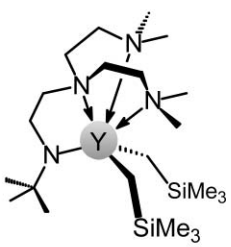
[**A**]$MR_2(THF)_n$

M = Sc, Y



[R_2**B**]YR'_2

R = Me, iPr



[**C**]YR_2

The three ancillary ligand systems chosen for this study are: the bidentate *N*,*N*′-bis(2,6-diisopropylphenyl)benzamidinate [**A**],[11b,c] tetradentate *N*,*N*′-dialkyl-triazacyclononane-amides [R_2**B**][11a] and a related non-cyclic triamine–amide [**C**].[13] All their metal bis(trimethylsilylmethyl) derivatives were shown previously to be readily converted to their corresponding monoalkyl cations by reaction with the Brønsted acid activator [$PhNMe_2H$][$B(C_6F_5)_4$].

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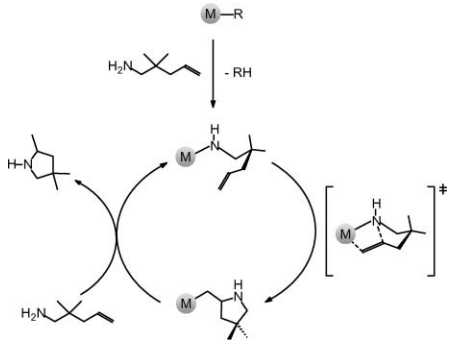
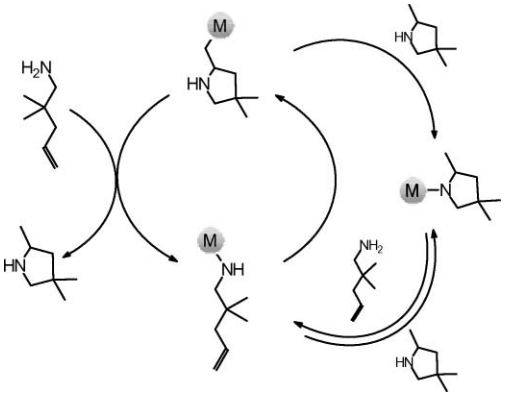
In Scheme 1, the generally applied reaction sequence for the intramolecular hydroamination/cyclisation is shown. In most cases the intramolecular insertion of the alkene into the metal–amide bond is rate-determining, leading to a zero order dependence of the rate on the substrate concentration.[14] With increasing conversion, an equilibrium between primary and secondary amide species (the latter deriving from reversible reaction with the product, see Scheme 2) can lead to deviations from this behaviour (product inhibition).[15]



Scheme 1



Scheme 2

Experimental

General

All preparations were performed under an inert nitrogen atmosphere, using standard Schlenk or glovebox techniques, unless mentioned otherwise. Deuterated benzene was vacuum transferred from Na/K alloy, prior to use. Reagent 2,2-dimethyl-4-pentylamine,[16] was synthesized as described in the literature. Complexes $\{[PhC(2,6\text{-}iPr_2C_6H_3)_2]M(CH_2SiMe_3)_2(THF)_n\}$ (M = Sc, Y),[11b,c] $[R_2\text{-}TACN\text{-}(CH_2)_2\text{-}NtBu]Y(CH_2SiMe_3)_2$ (R =Me, iPr),[11a] and $\{[Me_2N(CH_2)_2]_2N(CH_2)_2N(t\text{-}Bu)\}Y(CH_2SiMe_3)_2$,[13] were prepared according to published procedures. $[PhNMe_2H][B(C_6F_5)_4]$ (Asahi Glass Co.) was used as received. NMR spectra were recorded on Varian Gemini VXR 300 or Varian Inova 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^1H NMR spectra were referenced to resonances of residual protons in deuterated solvents. The ^{13}C NMR spectra were referenced to carbon resonances of deuterated solvents and reported in ppm relative to TMS (δ 0.0 ppm).

Procedure for intramolecular hydroamination/cyclisation

All samples for the hydroamination/cyclisation reactions were prepared in a N_2-filled glove box. Typically, an NMR tube equipped with a Teflon (Young) valve was charged with the (pre)catalyst (10 μmol), the activator $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol, where appropriate), ferrocene (as internal standard, 100 μmol), and the aminoalkene substrate 2,2-dimethyl-4-pentylamine (1000 μmol) dissolved in C_6D_6 (0.5 mL). The reactions were followed in time, either directly in the NMR spectrometer (thermostated at 50 °C unless mentioned otherwise; measurements taken in an array of regular intervals), or warmed in an electric oven at 50 °C and transferred to the spectrometer periodically. Conversions were determined by ^1H NMR following the decrease of the olefinic resonances of the substrate relative to the ferrocene internal standard (single-pulse spectra). The product 2-methyl-4,4-dimethylpyrrolidine was identified by ^1H NMR and GC-MS in comparison with literature data.

Results and discussion

Amidinate complexes

Data for the catalytic hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine by the various neutral and cationic Group 3 metal amidinate alkyl complexes are shown in Table 1 and Fig. 1.

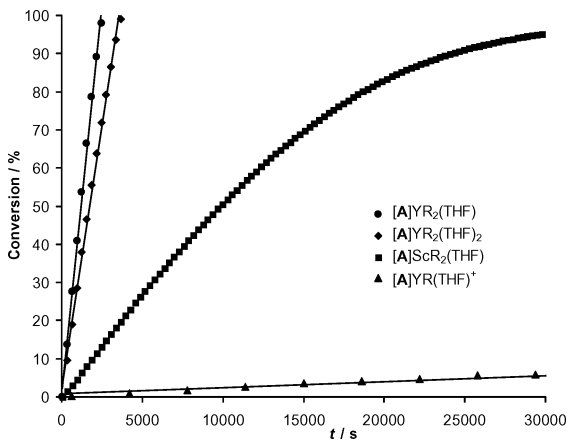


Fig. 1 Hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine with $[A]YR_2(THF)_n$ (n = 1, 2), $[A]ScR_2(THF)$ and $\{[A]YR(THF)\}^+$ catalysts in C_6D_6. A conversion of 100% corresponds to 100 turnovers.

Table 1 Catalytic hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine by neutral and cationic amidinate Group 3 metal complexes[a]

Catalyst	t/h	Conversion[b](%)	k/s^{-1}
$[A]ScR_2(THF)$	6	>90	5.14×10^{-3} [c]
$[A]YR_2(THF)$	0.8	>99	4.12×10^{-2}
$[A]YR_2(THF)_2$	1	>99	2.30×10^{-2}
$[A]ScR(THF)^+$	24	10	n.d.
$[A]YR(THF)^+$	24	13	1.45×10^{-4}

[a] Conditions: C_6D_6 solvent (0.5 ml), 50 °C, 10 μmol catalyst (and $[PhNMe_2H][B(C_5F_5)_4]$ activator where appropriate), 1.0 mmol substrate. [b] Determined by ^1H NMR. [c] Over the first 50% conversion.

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The neutral yttrium amidinate dialkyl complex [**A**]YR_2(THF) (R-CH_2SiMe_3) was found to be an efficient catalyst for the hydroamination/cyclisation reaction of the test substrate 2,2-dimethyl-4-pentenylamine, reaching full conversion of the 100 equiv. within 40 min at 50 °C. The reaction rate displays zero order dependence on the substrate concentration, an indication that the rate-determining step is likely to be the intramolecular insertion of the olefin into the Y–amide bond. Using the yttrium catalyst precursor with an additional coordinated THF molecule, [**A**]$YR_2(THF)_2$, resulted in a conversion with a rate constant that is about half of that of the mono-THF adduct, indicating a moderate inhibition by the additional Lewis base.

The corresponding neutal scandium catalyst [**A**]ScR_2(THF), with a significantly smaller metal ion (ionic radii: Sc^{3+} 0.89 Å *vs*. Y^{3+} 1.04 Å), is about one order of magnitude less active, and shows zero order dependence on the substrate concentration only over the first 50% conversion. This suggests that either product inhibition takes place (see Scheme 2), or that the product release step becomes rate-limiting at higher conversions.

Performing the reaction with the cationic amidinate catalysts, generated *in situ* by the addition of [$PhNMe_2H$][$B(C_5F_5)_4$], leads to a substantially slower substrate conversion than for the neutral analogues. This does not appear to be caused by a catalyst deactivation process or by precipitation of the ionic species from the reaction medium: visual inspection of the reaction mixtures showed that they are homogeneous (although in the absence of substrate the catalysts separate from solution as oils). The cationic yttrium catalyst [**A**]$YR(THF)^+$ again shows a reaction rate that has a zero order dependence on the substrate concentration, but with a rate constant that is more than two orders of magnitude smaller than that for the neutal catalyst [**A**]YR_2(THF). This thus appears to reflect an intrinsically higher activation energy barrier for the rate determining step (*i.e.* intramolecular insertion of the olefinic moiety into the Y–amide bond) for the cationic catalyst. For Sc the same trend is seen, with a much lower activity for the cationic catalyst.

Triamine–amide complexes

Data for the catalytic hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine by the various neutral and cationic Group 3 metal triamine–amide alkyl complexes are shown in Table 2 and Fig. 2.

The neutral dialkyl complexes with these ligands are much slower catalysts than those with the amidinate ligand shown before, and only give incomplete conversion of the 100 equiv. of substrate even after 24 h (although again no catalyst deactivation is apparent over this period). The most active of the three, [Me_2**B**]YR_2, displays an activity of the same order of magnitude as that of the cationic yttrium amidinate, and shows zero order substrate dependence over the conversion range studied.

Table 2 Catalytic hydroamination/cyclisation of 2,2,-dimethyl-4-pentenylamine by neutral and cationic triamine–amide Group 3 metal complexes[a]

Catalyst	*t*/h	Conversion [b](%)	*k*
[Me_2**B**]YR_2	24	25	2.57×10^{-4} s^{-1}
[$i Pr_2$**B**]YR_2	24	10	n.d.
[**C**]YR_2	24	16	n.d.
[Me_2**B**]YR^+	12	>99	3.32×10^{-3} s^{-1} [c]
[$i Pr_2$**B**]YR^+	12	48	7.50×10^{-4} l mol^{-1} s^{-1}
[**C**]YR^+	12	77	1.81×10^{-3} l mol^{-1}

[a] Conditions: C_6D_6 solvent (0.5 ml), 50 °C, 10 μmol catalyst (and [$PhNMe_2H$][$B(C_5F_5)_4$] activator where appropriate), 1.0 mmol substrate. [b] Determined by ^{1}H NMR. [c] Over the first 50% conversion.

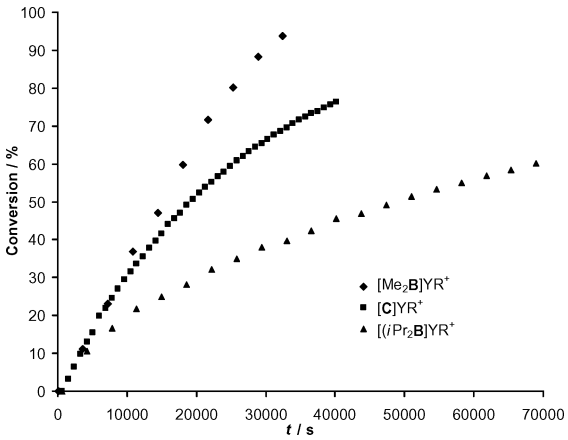

Fig. 2 Hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine with {[Me_2**B**]YR}$^+$, {[$i Pr_2$**B**]YR}$^+$ and {[**C**]YR}$^+$ catalysts in C_6D_6. A conversion of 100% corresponds to 100 turnovers.

In contrast with the amidinate systems described above, the conversion of the triamine–amide species to their cationic monoalkyl analogues results in a considerable *increase* in catalytic activity. The cationic triazacyclononane-amide catalyst {[Me_2**B**]YR}$^+$ exhibits an activity comparable to that of the neutral amidinate scandium catalyst, and also shows a zero order dependence on the substrate concentration at conversions below 50%.

Interestingly, the catalysis by the sterically more encumbered derivative {[$i Pr_2$**B**]YR}$^+$, as well as by the geometrically less constrained triamine–amide catalyst {[**C**]YR}$^+$, show a first order dependence on substrate concentration essentially over the *entire* conversion range. A plot of the rate data for {[**C**]YR}$^+$ illustrating this behaviour is shown in Fig. 3. This suggests that in these more hindered systems the protonation of the insertion product by the

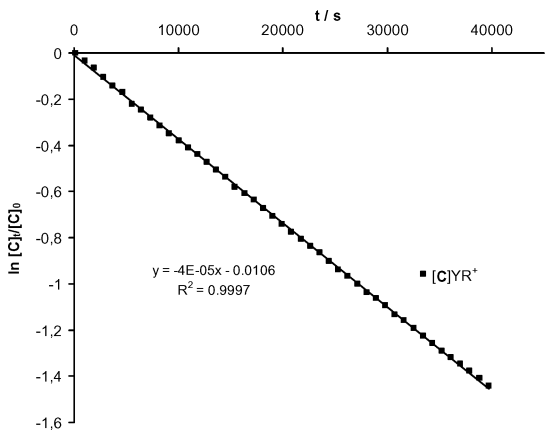

Fig. 3 Plot showing first order substrate concentration dependence of the hydroamination/cyclisation of 2,2-dimethyl-4-pentenylamine by {[**C**]YR}$^+$ catalyst in C_6D_6 solvent at 50 °C.

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substrate is rate limiting (although a preceding intramolecular rearrangement of the insertion product to the secondary amide cannot be ruled out *a priori*).[17]

Discussion

As is evident from the results presented above, the relative catalytic activity for the hydroamination/cyclisation reaction of cationic monalkyl *versus* neutral dialkyl Group 3 metal species is highly dependent on the ancillary ligand system. For the coordinatively relatively unencumbering dihapto amidinate ligand, the catalytic activity of the cationic species is over two orders of magnitude less than that of the neutral analogue. For the coordinatevely demanding tetrahapto triamine–amide ligands, the cationic derivatives are clearly more active than the neutral species.

When directly comparing the activities of the cationic catalysts $\{[\mathbf{A}]YR(THF)\}^+$ *versus* $\{[Me_2\mathbf{B}]YR\}^+$ (which is possible, as both show zero order dependence on the substrate concentration, at least at <50% conversion), the more electron-rich triamino-amide catalyst is 22 times more active than the amidinate catalyst. Assuming that the zero order dependence on substrate concentration is an indication that the intramolecular insertion of the olefinic group into the metal–amide bond is rate-determining (as appears to be the case with most hydroamination-cyclisation catalysts), this difference could be related to the relative strength of the Y–amide bonds. This bond is expected to be stronger for the more electron deficient species, the amidinate complex, which is also the less active catalyst.

The tetradentate triamine–amide ligands occupy a significantly larger part of the coordination sphere of the metal, and also impart more electron density to the metal centre, than the bidentate amidinate ligand. It is likely that the former systems benefit from the creation of a vacant site by the removal of one of the alkyl groups from the metal centre. Nevertheless, the first order dependence on substrate concentration of the more sterically encumbered systems, with the $i\mathrm{Pr}_2\mathbf{B}$ and **C** ligands, indicates that here the product/substrate exchange step is likely to be rate limiting.[17] This indicates that direct structure–property relationships cannot always be drawn in a straightforward manner, and that the availability of kinetic data is necessary for a true comparison of catalysts.

If the suggestion that the relative strength of the metal–amide bonds is the determining factor for the activity of Group 3 metal catalysts for hydroamination/cyclisation is correct (at least for those catalysts that show zero order substrate dependence), it is unlikely that cationic Group 3 metal catalysts will be able to improve in an absolute sense on the high activities that can be obtained with neutral catalysts. An increase in activity upon going from a neutral to a cationic catalyst can then only be expected when the neutral catalyst is relatively slow due to steric or coordinative encroachment of the metal centre and where the creation of an additional free coordination site will relieve this. Although no kinetic data are available for that system, it is likely that the increased catalyst activity of the cationic scandium β-diketiminato catalyst (with 2,6-diisopropylphenyl substituents on the nitrogen atoms) relative to the neutral analogue[12] is due to the relief of steric congestion around the metal centre. For the scandium amidinate catalysts, with a ligand that is related but has a significantly smaller bite-angle, the neutral catalyst is already by far the more efficient.

Conclusions

It has been shown that both neutral and cationic Group 3 metal alkyl species, with two different types of monoanionic ancillary ligands, can catalyse the intramolecular hydroamination/cyclisation of the standard substrate 2,2-dimethyl-4-pentenylamine. For the 4-electron bidentate amidinate ligand, the neutral catalysts are considerably more active than their cationic counterparts, whereas for the 8-electron tetradentate triamine–amide ligands the reverse is the case. It appears that both the availability of sufficient room in the coordination sphere of the metal and the strength of the metal–amide bond play a role in determining the catalyst effectiveness.

From the data obtained in this study it appears that, with respect to absolute activity, cationic rare earth metal catalysts are unlikely to better the rates in hydroamination/cyclisation that can be achieved with neutral catalysts. Nevertheless, the generation of cationic species may provide a means to achieve meaningful activities with sterically demanding ancillary ligands. This approach could be useful with asymmetric ligands that aim for a high enantioselectivity in this reaction. Up until now, this has been approached mainly by using dianionic ancillary ligands (linked cyclopentadienyls,[18] bisphenolates[19]). Using cationic active species, families of sterically demanding asymmetric monoanionic multidentate ligands (*e.g.* derivatives of the bis(oxazoline)methyenyl ligands as employed by Marks and coworkers[20]) could be applied to this reaction with improved reaction rates. In this case, best activities may be expected with ligands that employ strongly donating moieties to weaken the reactive metal–amide bond.

Acknowledgements

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