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Amide *versus* amine ligand paradigm in the direct amination of alcohols with Ru-PNP complexes†

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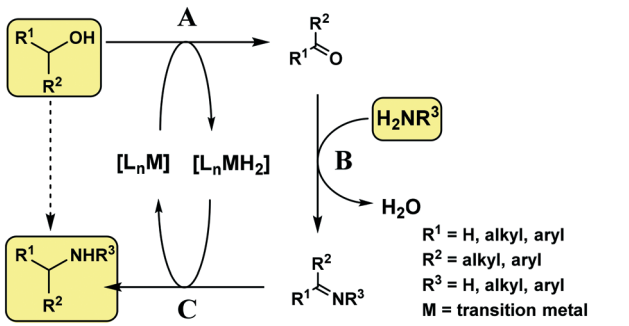
The catalytic activity of a series of Ru-PNP pincer ligand complexes was studied in the direct amination of alcohols with ammonia. It turned out that all complexes of PNP ligands bearing a secondary amine showed no activity in this hydrogen-shuttling reaction sequence, while all complexes of homologous ligands bearing a tertiary amine gave active catalysts. Further comparative studies on catalysts bearing an acridine-based PNP pincer ligand and a PNP ligand of the Xantphos family provided valuable mechanistic insight that led to the design of a highly active catalyst. It appears that in the group of ligands studied here only ligands that do not form stable Ru-amido complexes are active alcohol amination catalysts.

Introduction

In view of its synthetic potential, the homogeneously catalysed direct amination of alcohols with ammonia has gained much attention since the first example was described by Milstein in 2008.[1] Since then, several other systems have been developed that are able to convert both primary and secondary alcohols to amines.[2–6] A number of studies have revealed important information on the mechanism of the reaction,[7–9] but still there are discrepancies and parts that need further elucidation. One particularly intriguing issue concerns the large differences in activity of the systems known. The usual assumption is that catalysis proceeds *via* the "Borrowing Hydrogen"[10] or "Hydrogen Shuttling"[3] method; hydrogen is temporarily stored on the catalyst after alcohol dehydrogenation to be re-used later in the hydrogenation of the imine or enamine intermediate (Scheme 1). With reference to this dual function of the catalyst, it was already shown that the low concentration of intermediates, determined by the amount of catalyst, implies an intrinsic rate limitation. After the initial alcohol dehydrogenation step, a new cycle can only start after the catalyst has delivered the hydrogen to the intermediate imine or enamine, present only in amounts equivalent to the catalyst concentration at maximum, although dihydrogen formation would lead to higher imine concentrations and also regenerate the catalyst.[8] As the amination of alcohols involves a dehydrogenation/hydrogenation process that in part resembles a reductive amination reaction, PNP pincer-type ligands affording active catalysts for the latter reaction seem to be an ideal starting point.[11,12]

In their seminal work Milstein *et al.* employed the acridine-based PNP pincer ligand **1** (Scheme 2).[1] The same ligand was used later with $Ru_3(CO)_{12}$ in the amination of both primary and secondary bio-alcohols.[2]

Milstein and co-workers demonstrated a long-range metal–ligand cooperation, in which a hydrogen atom is



Scheme 1 Concept of "Hydrogen Shuttling". A) Alcohol dehydrogenation in which the hydrogen is stored on the catalyst, B) condensation of the carbonyl compound with the amine followed by C) hydrogenation of the imine, using the metal hydride generated in the first step.

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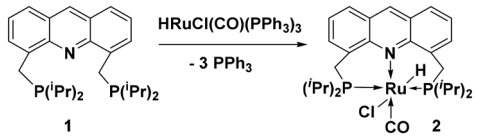


1 2

Scheme 2 Milstein's acridine PNP ligand **1** and Ru complex **2** employed in the direct amination of primary alcohols.[1]

transferred to the C9 position of the acridine ligand backbone, leading to dearomatisation and amide bonding to the Ru centre. It was suggested this might play a role in catalysis.[13] Mechanistic studies accompanied by DFT calculations, recently performed by the group of Hofmann, suggest that this is not a necessity for catalyst activity.[7]

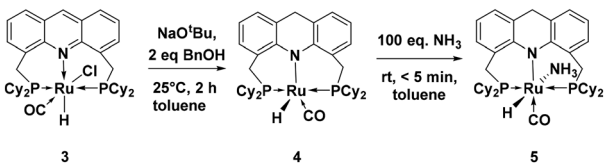
However, another prominent example of an active catalyst not providing any metal–ligand cooperativity is the analogous complex with Xantphos, reported by Beller and co-workers.[5] Investigation of further ligands revealed various Ru precursors in combination with Xantphos-type ligands that show good activity in the amination. Nevertheless, Milstein's complex (**2**) remains one of the most active catalysts so far that achieves a very high selectivity.[6,8]

Hofmann and co-workers investigated the analogous PCy_2 derivative of ligand **1**, which forms a similar Ru complex **3**.[7] Treatment of complex **3** with NaO^tBu and 2 eq. of alcohol resulted in dearomatisation of the backbone, with a saturated C9 position and amide bonding to the Ru centre (Scheme 3, **4**). Complex **4** readily forms the NH_3 adduct **5** that was also found to be the main remaining species after completion of the alcohol amination catalysis.

It was concluded that the 'long range metal–ligand cooperation' is not a necessity for catalysis.[7] In this contribution we study the influence of base and ketone on a few known PNP catalyst precursors containing hydride, chloride and/or amide anions in order to establish general requirements. Subsequently several new ligands will be introduced containing secondary and tertiary amines as the central ligand atom. A simple PNP ligand with a tertiary amine and an aliphatic chain, *i.e.* no dearomatisation can take place, turned out to be one of the fastest catalysts known to date.

Results and discussion

First we studied the behaviour of Milstein's complex **2** in amination with respect to the presence of base and ketone/aldehyde. The amination of benzyl alcohol goes to completion with high selectivity to benzylamine within 8 hours at 150 °C (Chart 1A, ●). When 4 mol% of KO^tBu was added at the start of the reaction, mimicking the reactions shown in Scheme 3, catalysis was almost completely inhibited (Chart 1A, ■). The reaction with base was repeated but in this instance after 8 h, 10 mol% of benzaldehyde were added. Immediately after the addition, catalysis started and conversion went to completion within about 24 h (Chart 1B). In our earlier mechanistic studies on the amination of cyclohexanol with the $RuHCl(CO)(PPh_3)_3$/Xantphos system it was found that the dihydride $RuH_2(CO)(PPh_3)$(Xantphos) was formed by treatment with KO^tBu and alcohol.[8] This dihydride, prepared *in situ* or as an isolated complex, is inactive as catalyst precursor in the alcohol amination reaction. However, the catalytic cycle can be started by addition of the intermediate carbonyl compound (cyclohexanone in this case). This indicates the dilemma intrinsically hampering all 'borrowing hydrogen' reactions. Due to the sequence of consecutive reactions, with coupled equilibria of dehydrogenation (of the alcohol) and hydrogenation (of the imine) none of the intermediates (ketones and imines) can be present in a concentration higher than that of the catalyst. As a result, those reactions are typically slow and therefore require higher amounts of catalyst; typically 1–5 mol%. This is why increasing the steady state concentration of the intermediate



3 4 5

Scheme 3 Formation of the dearomatised complex **4** and its NH_3 adduct **5**, reported by Hofmann *et al.*[7]

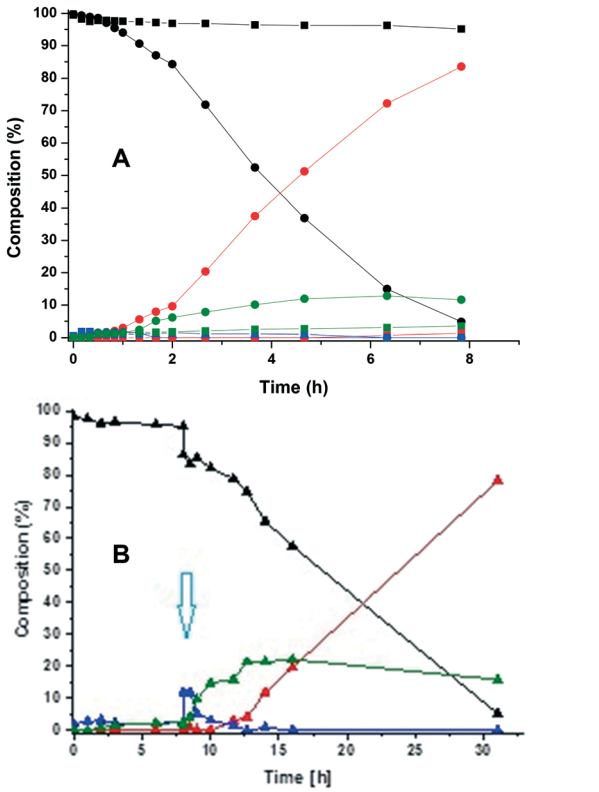


Chart 1 (A) Amination of benzylalcohol using complex **2**, with (■) and without KO^tBu (●) and (B) KO^tBu (4 mol%) added initially, followed by addition of 10 mol% benzaldehyde (arrow) after 8 h (▲). Conditions: 1 mol% complex **2**, 5 mmol benzylalcohol, 15 mL toluene, 2.5 mL NH_3, 150 °C, 8 h. Black = benzylalcohol, red = benzylamine, blue = benzaldehyde, green = dibenzylimine.

speeds up those reactions. In the present case benzaldehyde activates the catalyst in the same fashion, *i.e.* imine forms and hydrogens are transferred to the imine providing an active catalyst for the dehydrogenation again.

Further studies underline the subtle differences in the amination of primary and secondary alcohols with the different systems. While the Xantphos system $RuHCl(CO)(PPh_3)$-(Xantphos) showed a three-fold increase in activity in the amination of cyclohexanol upon addition of 10 mol% cyclohexanone,[8] the rate of amination of benzyl alcohol with **2** was only moderately increased on addition of 10 mol% of benzaldehyde (Graph S21, ESI†).

Based on the reports by Milstein[13] and Hofmann[7] one would expect that in the presence of KO^{t}Bu the dearomatised species analogous to **4** or **5** are formed. The conclusion we can draw from the lack of activity under these conditions is that, if formed, those species are not active in the direct amination of alcohols under the conditions employed here.

In analogy with Xantphos (*vide supra*) one would expect that the dihydride formed from **1** is also an inactive catalyst (Scheme 4, **6**). Treatment of $RuHCl(CO)(PPh_3)$(Xantphos) with KO^{t}Bu results in a dihydride as was shown by Williams[14] and by us.[8] In case of complex **6**, this dihydride has the possibility to undergo the dearomatisation reaction at elevated temperature to form complex **7** or its NH_3 adduct.

Chart 2 shows that the system generated *in situ* from $RuH_2(CO)(PPh_3)_3$ and ligand **1** is an active catalyst for the direct amination of benzyl alcohol. This indirectly indicates that complex **7**, which is analogous to **4**, is not formed, as it was shown that complex **4** was not active. Unfortunately, attempts to unambiguously decide whether **7** is formed in the reaction of $RuH_2(CO)(PPh_3)_3$ in combination with ligand **1** failed. Reaction of complex **2** with NaH in the presence of 2 equiv. of benzyl alcohol did give the orange complex **7** as was shown by Milstein and co-workers.[13,15] Thus, the final question for this type of acridine-based Ru-PNP pincer complexes, which of the species present actually is the active one remains open and will require further studies.

A more rigid ligand of the Xantphos family was designed that bears analogous to **1** nitrogen in 10-position of the backbone instead of the usual oxygen atom (AcridanPhos **10**, Scheme 5). As the 9-position is occupied by two methyl groups, this ligand represents an analogue of the dearomatised state of the acridine-based diphosphine **1**. It lacks the methylene groups of Milstein's ligand, but unfortunately so far we did not succeed in the synthesis of the closest analogue. Upon coordination of **10** to $HRuCl(CO)(PPh_3)_3$ under ligand exchange an amide bond can be formed. This reaction was found to proceed under HCl elimination to give **11** (Scheme 5).

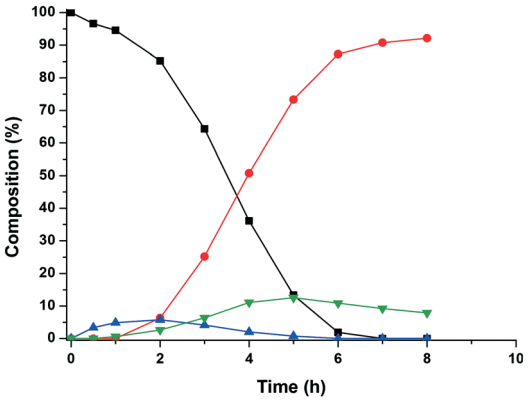


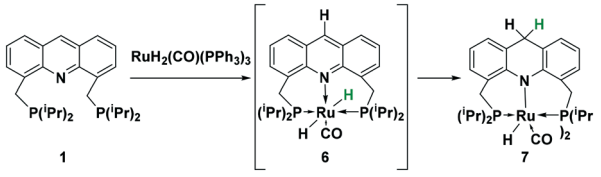
Chart 2 Amination of benzylalcohol using the *in situ* system $RuH_2(CO)(PPh_3)_3$/**1**. Conditions: 5 mmol benzylalcohol, 1 mmol% $RuH_2(CO)(PPh_3)_3$/**1**, 15 mL toluene, 2.5 mL NH_3, 150 °C. ■ = benzylalcohol, ● = benzylamine, ▲ = benzaldehyde, ▼ = dibenzylimine.

The hydride region of the ^{1}H NMR spectrum shows a double triplet with a typical *trans* H–P coupling of 103 Hz and a smaller *cis* H–P coupling of 24 Hz (Fig. S5, ESI†), confirming formation of complex **11**. The ^{31}P NMR spectrum indicates free PPh_3, a doublet, and a triplet, each with a coupling constant of 23 Hz, typical of *cis* P–P coupling constants (Fig. S6, ESI†).[6] From this, it can be concluded that indeed complex **11** was formed.

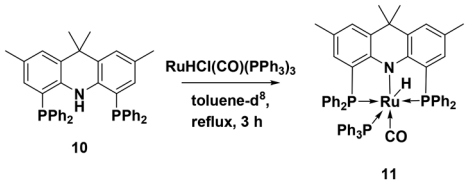
Complex **11** neither showed activity under the standard amination reaction conditions, nor in the presence of base or ketone (Graph S20, ESI†).

Based on these additional observations and taking into account the current state of knowledge we continued our studies with Ru complexes of aliphatic PNP ligands (**12**–**15**), developed in the group of Prechtl.[16–18] All these complexes are hydride, dihydride, or multi-hydride complexes, including non-classical hydrides. In the non-classical hydrides, H_2 is coordinated *via* the σ-bond (Fig. 1).[19] In these complexes H_2 and classical hydrides have been shown to be in fast exchange.[20]

Though all fairly similar, there are a few important differences between these complexes. The main one is that in complexes **13** and **15** the ligand binds as an amide with the metal; the amine is deprotonated upon complexation, forming a Ru hydride. The carbonyl-metal bond in **14** and **15**



Scheme 4 Milstein's acridine-based PNP pincer ligand (**1**) and the possible complexes **6** and **7** formed by reaction with $RuH_2(CO)(PPh_3)_3$.



Scheme 5 Reaction of AcridanPhos (**10**) with $RuHCl(CO)(PPh_3)_3$.

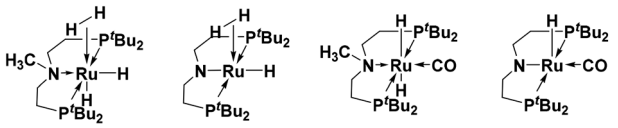


Fig. 1 Multi-hydride Ru complexes with aliphatic PNP ligands.

is most likely strong, whereas H_2 should be weakly bound in **12** and **13**, which can be easily replaced or will even dissociate thermally.[21,22] Complexes **12** and **14** bear a tertiary amine in the ligand backbone, coordinated *via* the nitrogen lone pair. Therefore, these complexes contain a second ionic ligand, in both cases a second hydride.

Complexes **12–15** were examined as catalysts for the direct amination of cyclohexanol and benzyl alcohol. First, complexes **13** and **15** were employed in the direct amination of cyclohexanol. Generally, a large excess of NH_3 was employed, which is beneficial for the selectivity and conversion. As the initial complexes are hydridic, addition of ketone may provide a route for activation. Both complexes **13** and **15** appeared to be inactive (Graph S1 and S2, ESI†). These reactions were initially performed without additive, showing no activity for the first 22.5 hours. After this time, 10 mol% of cyclohexanone were added, but that did not lead to activity either. In our previous mechanistic studies it appeared that for certain complexes a base is required to yield an active complex. Usually, the base is added to abstract HCl from the complex. These complexes do not contain chloride, but the base might also be beneficial for deprotonation of the alcohol. The reactions were therefore conducted again under the same conditions but now KO^{t}Bu was added. Graph S3 and S4† in the supporting information show that this was not beneficial either. As complexes **13** and **15** are not active for secondary alcohols, benzylalcohol was used as a primary alcohol. Now the conversion reached 20% but the main product was dibenzylimine (Graph S5 and S6, ESI†). Furthermore changing the solvent from *t*-amylalcohol to toluene (Graph S7 and S8, ESI†)[23] did not result in any conversion. Having established that amides **13** and **15** are poor catalysts, we employed amine complexes **12** and **14** under the same conditions as in the amination of cyclohexanol.

Both complexes show activity, although the reaction does not go to completion within 52 h reaction time (Chart 3). Next the reactions with complexes **12** and **14** were repeated in the presence of 10 mol% of cyclohexanone (Graph S9 and S10, ESI†). Surprisingly, in the case of complex **12** and **14**, the activity strongly decreased and apparently, cyclohexanone inhibits catalysis in this case. When fresh cyclohexanone and ammonia were added after 23.5 hours to catalyst **12** the reaction was completely suppressed (Graph S11, ESI†). These type of multi-hydride Ru-PNP complexes are known to decarbonylate acetone, forming two equivalents of methane and a Ru carbonyl complex[24] Perhaps cleavage of cyclohexanone takes place

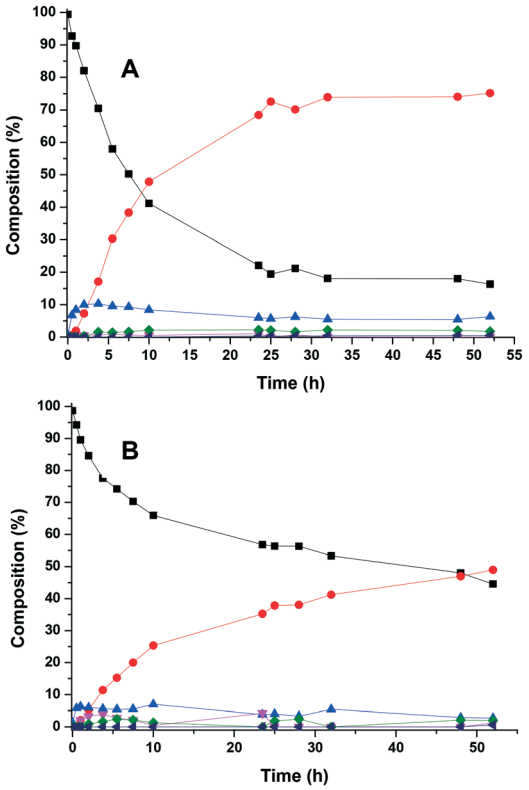
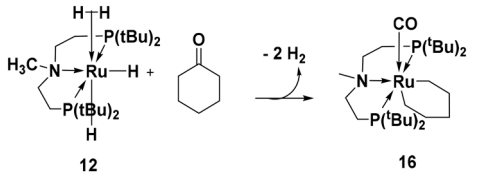


Chart 3 Amination of cyclohexanol employing complex **12** (A) and **14** (B). Conditions: 0.04 mmol catalyst, 5 mmol cyclohexanol, 15 mL *t*-amylalcohol, 2.5 mL NH_3, 150 °C. ■ = cyclohexanol, ● = cyclohexylamine, ▲ = cyclohexanone, ▼ = cyclohexylimine, ◆ = dicyclohexylimine, ◀ = dicyclohexylamine.

with formation of CO and a Ru metallacycle, the inactive complex **16** (Scheme 6).

The potential formation of the Ru metallacyclic compound **16** as a product or intermediate was investigated by MS. From the reaction mixture species **16** was detected by LIFDI-MS; the mass found agrees with the proposed structure (Fig. S1 and S2, ESI†). The relative stability of **16** might account for the observed deactivation. On the other hand, addition of an aldehyde, if decarbonylated, would lead to a much less stable Ru *n*-alkyl or aryl species, most likely not shutting down catalysis. The amination of cyclohexanol with complexes **12** and **14** was performed again with benzaldehyde as additive (Graph S12 and S13, ESI†). Now indeed, the reaction proceeded more smoothly and no deactivation was observed. For complex **14** the reaction now went to completion (Graph S12 and S13†).



Scheme 6 Reaction of Ru PNP complex **12** with cyclohexanone *via* decarbonylation.

Performing the reaction with benzylalcohol as substrate resulted in inactive systems for both complexes. However, after the addition of 10 mol% benzaldehyde, complex **12** does show some activity but is quickly deactivated as well. Only dibenzyl imine was formed in this case. Complex **14** on the other hand, remained completely inactive (Graph S16 and S17, ESI†). In conclusion, complexes **12** and **14** were shown to be active in the direct amination of cyclohexanol. Remarkably, complexes **13** and **15** with PNP ligands having a secondary amine in the backbone that form a Ru–amide bond are not active while the ones with a tertiary amine in the backbone are active.

Encouraged by the results of the alkyl amine ligands the commercially available Ru complex **17** (Fig. 2), an ester hydrogenation[25] and methanol dehydrogenation catalyst,[26,27] was tested in the amination of cyclohexanol. Complex **17** is closely related to the previously tested complexes **13** and **15**, containing the coordination sphere of catalysts **2** and **3**.

Because of the secondary amine in the backbone, **17** is likely to form an amide-metal bond under alcohol amination conditions.[28] In line with our earlier observations we expected this species to be inactive. The results with complex **17** are shown in Chart 4.

In fact, complex **17** was not active at all and could neither be activated by the addition of carbonyl compounds nor by base or by changing the solvent. Subsequently complex **18** was synthesized in which the amine in the backbone is converted to a tertiary amine (Fig. 2). Initially the same reaction parameters were employed as with all other precursors previously tested, which resulted in no activity for complex **18** (Graph S23, ESI†). However, addition of base (KO^{t}Bu) resulted in a very active system for the amination of both secondary and primary alcohols (Chart 5, also see Graph S24, ESI†). This new complex turns out to be one of the most active catalyst for the direct amination of secondary alcohols so far (TOF = 74, compare Table 1). For comparison, the TOF's of various systems determined at 20% conversion of the respective alcohol are given in Table 1.

It is apparent that the closely related complexes **14** and **18** behave quite differently in catalysis. Activation of the *trans*-dihydrido complex **14** is relatively difficult and even after addition of a carbonyl compound as hydrogen acceptor stays behind complex **18** in activity (see also ESI†). A similar behaviour was observed for $H_2Ru(CO)(PPh_3)$Xantphos, which

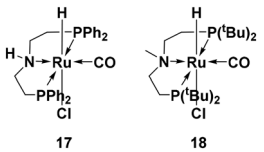


Fig. 2 Ru bis(diphenylphosphino-ethyl)amine carbonyl hydride complex (**17**) and analogous *N*-methylated complex **18** bearing P(^{t}Bu)$_2$ groups.

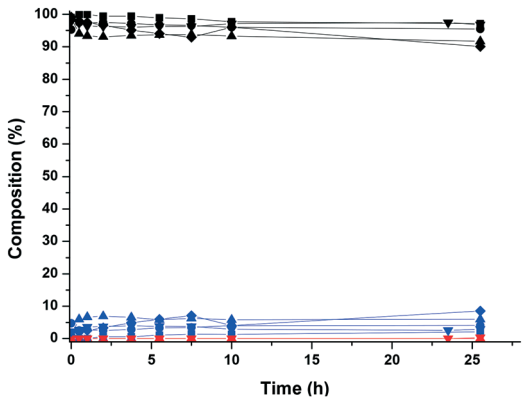


Chart 4 Amination of cyclohexanol employing complex **17**. Conditions: 0.05 mmol complex **17**, 5 mmol cyclohexanol, 15 mL *t*-amylalcohol, 2.5 mL NH_3, 150 °C, 25.5 h. ■ = no additives or changes, ● = 10 mol% benzaldehyde added, ▲ = 1 mol% KO^{t}Bu added, ▼ = 10 mol% KO^{t}Bu added, ◆ = toluene as solvent, black = cyclohexanol, red = cyclohexylamine, blue = cyclohexanone.

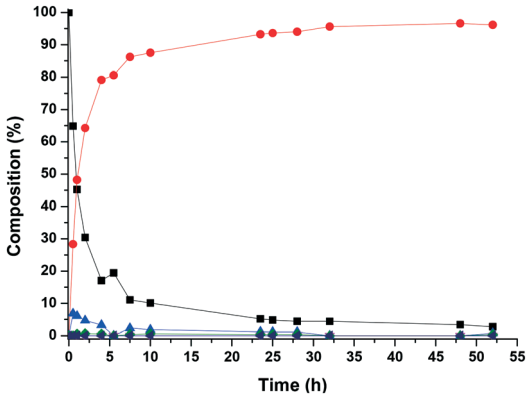


Chart 5 Amination of cyclohexanol employing complex **18** in the presence of KO^{t}Bu. Conditions: 0.04 mmol **18**, 5 mmol cyclohexanol, 0.5 mmol KO^{t}Bu, 15 mL *t*-amylalcohol, 2.5 mL NH3, 150 °C. ■ = cyclohexanol, ● = cyclohexylamine, ▲ = cyclohexanone, ▼ = cyclohexylimine, ◆ = dicyclohexylimine, ◀ = dicyclohexylamine.

Table 1 Overview of current selective direct amination systems with respective turnover frequencies (TOF)

Complex	TOF[a] (h^{-1})	Conversion/selectivity
Complex 18	**74**	**95/99**
RuHCl(CO)(Milstein acridine)[b]	37.5	82/85
RuHCl(CO)(Triphos)[b,d]	28.6 (ref. 9)	89/90
RuHCl(Xantphos)	12.7 (ref. 8)	95/100
$Ru_3(CO)_{12}$/Milstein acridine[c]	12.4 (ref. 3)	99/100
RuHCl(CO)(PPh_3)(Sixantphos)	9.6 (ref. 6)	70/100
$Ru_3(CO)_{12}$/CatacXium Pcy[c]	8 (ref. 3)	95/91
RuHCl(CO)(PPh_3)(Xantphos)	5.6 (ref. 6)	95/100
RuHCl(CO)(PPh_3)(Thixantphos)	2.1 (ref. 6)	95/43
RuHCl(CO)(Triphos) [NaBArF][b,e]	200 (ref. 9)	100/25

[a] Turnover frequencies calculated at 20% conversion. Reactions conducted with 1 mol% complex at 150 °C with cyclohexanol as a substrate. [b] Benzylalcohol as a substrate was used as it was inactive in the amination of cyclohexanol, secondary alcohols in general.[1] [c] Prepared *in situ*, 2 mol% catalyst, 170 °C. [d] 0.28 mol% catalyst, T = 155 °C. [e] 0.2 mol% catalyst.

also required a hydride acceptor for activation, but still remained behind in activity with respect to the complex $HRuCl(CO)(PPh_3)$Xantphos.[8] For a deeper understanding of these subtle but important differences more detailed studies will have to be performed in the future.

Conclusions

Previously it was shown that aromatization/dearomatisation of the acridine backbone of Milstein's ligand might not be a prerequisite for the formation of active catalysts. We have now demonstrated that in acridine ligand **10**, in which the dearomatisation is blocked, does not form an active catalyst. In several easily accessible alkyl PNP ligands and their complexes we have shown that Ru PNP pincer complexes containing a secondary amine in the backbone that are able to form Ru-amide species under reaction conditions are invariably inactive in the direct alcohol amination with ammonia. On the contrary, the corresponding PNP ligands with a tertiary amine in the backbone form active catalysts. This leads us to postulate that in order to obtain an active catalyst, no amide bond should be present. Based on these insights a new catalyst system based on the aliphatic PNP ligand bis(di-*tert*-butyl phosphinoethyl)methylamine was prepared with the preferred precursor $RuHCl(CO)(PPh_3)_3$, which on activation with base represents one of the most active catalysts for the direct amination of alcohols with ammonia reported so far.

Experimental

General considerations

All chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise noted. Complex **17** and all other Ru-precursors were purchased from Strem and used as received. Solvents (*t*-amylalcohol, toluene) were used after drying and degassing followed by purging with Ar. Cyclohexanol was degassed and purged with Ar prior to use. KO^{t}Bu was purchased from Alfa Aesar and was used as received. Compound **10** was prepared in the group of Piet W. N. M. van Leeuwen. The autoclaves are in-house made stainless steel reactors equipped with a manometer, 50 μL sample unit and a PT100 temperature sensor. Samples are measured on a GC2010 Ultra 2 column (25 m, 0.2 mm id). Samples were subjected directly to GC without further workup. Liquid NH_3 was dosed using a Bronkhorst Liquiflow Mass Flow Controller. ^{1}H NMR, ^{31}P NMR and ^{13}C spectra were recorded on 400 MHz and 500 MHz Varian Mercury and 300 Bruker Avance II, 400 MHz and 500 MHz Bruker Avance spectrometers (s = singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, br. s. = broad singlet). Infrared spectra (IR) were measured on a Bruker Alpha spectrometer equipped with a Diamond-ATR-IR unit. Data are reported as follows: absorption $\tilde{\nu}$ [cm^{-1}], weak (w), medium (m), strong (s). LIFDI-MS (liquid injection field desorption/ionization-mass spectrometry) was performed using a Waters micromass Q-ToF-2™ mass spectrometer equipped with a LIFDI 700 ion source (Linden CMS).

Synthesis

The syntheses of compounds **12** and **13** are described in a literature procedure.[17] The synthesis of compounds **14** and **15** are described in a literature procedure.[16] Compounds **8** and **9** are described in a previous paper,[6] following a literature procedure for the synthesis of **9**.[29]

Synthesis of 4,5-bis(diphenylphosphino)-3,6,9,9-tetramethyl-9,10-dihydroacridine ligand (10). Acridine based phosphine (**10**) was synthesised from a literature known compound such as 4,5-dibromo-3,6,9,9-tetramethyl-9,10-dihydroacridine *via* lithiation and phosphination method. 3,6,9,9-Tetramethyl-9,10-dihydroacridine was prepared according to the reported methods.[30]

In an oven dried Schlenk-tube was added 4,5-dibromo-3,6,9,9-tetramethyl-9,10-dihydroacridine (1.0 g, 2.53 mmol) and anhydrous THF (20 mL) was charged under argon atmosphere. The reaction mixture was degassed with vacuum/argon cycles and then cooled to −78 °C. To this solution was added dropwise *n*-BuLi (2.5 M in hexane, 7.59 mmol, 3.0 equiv.) *via* a syringe. The resulting reaction mixture was stirred at −78 °C for 10 min followed by the dropwise addition of chlorodiphenylphosphine (1.67 g, 7.59 mmol, 3.0 equiv.) *via* a syringe over 10 min. The reaction mixture was stirred at −78 °C for 1 h, slowly warmed to room temperature and stirred at this temperature for overnight (16 h). The reaction mixture was quenched with degassed water (3.0 mL) and the solvent was removed under vacuum. To this mixture anhydrous dichloromethane (20 mL) was added and the organic layer was washed with water (10 mL), dried over Na_2SO_4 and evaporated to dryness to give the residue. Methanol (10 mL) was added to the residue and stirred at RT for 0.5 h, the resulting white precipitate was collected by filtration and washed with methanol (5 mL) to give the desired phosphine as a white solid, yield (858 mg, 56%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$, δ = ppm): 8.74 (t, J_{HH} = 8.8 Hz, 1H, NH), 7.36–7.23 (m, 20H, 2xPPh_2), 7.20 (d, $^4J_{HH}$ = 1.6 Hz, 2H, CH backbone), 6.60 (d, $^4J_{HH}$ = 2.1 Hz, 2H, CH backbone), 2.19 (s, 6H, 2xCH_3), 1.59 (s, 6H, 2xCH_3). ^{13}C NMR (126 MHz, 298 K, $CDCl_3$, δ = ppm): 136.1, 133.9, 133.8, 133.8, 132.5, 129.3, 129.1, 128.6, 128.5, 128.4, 128.4, 127.3, 36.8, 30.3, 21.2. ^{31}P{^{1}H} NMR (202 MHz, 298 K, $CDCl_3$, δ = ppm): −20.9 (s); HRMS (ESI): $C_{41}H_{38}NP_2$ $[M + H]^+$ calcd.: 606.2480, found 606.2489.

Reaction of 10 with $RuHCl(CO)(PPh_3)_3$. AcridanPhos **10** (30.3 mg, 0.05 mmol) was weighed into a Wilmad-Young NMR tube. To this, $RuHCl(CO)(PPh_3)_3$ (47.6 mg, 0.05 mmol) was added. The solids were degassed and purged with argon. Degassed and dry toluene-d^8 was added and the mixture was heated to 130 °C for 3 h. NMR analysis confirmed complexation. ^{1}H NMR hydride region (400 MHz, 298 K, toluene-d^8, δ = ppm): −6.71 (dt, $^2J_{HP}$ = 103.6, 24). ^{31}P{^{1}H} NMR (162 MHz, 298 K, toluene-d^8, δ = ppm): 34.1 (d, $^2J_{PP}$ = 24 Hz), 31.4

(t, $^2J_{PP}$ = 24 Hz). IR(cm^{-1}): 3052 (m), 1962 (CO, s), 1584 (w), 1457 (m), 1403 (s), 1317 (m), 1260 (s), 1087 (s), 1026 (m), 998 (m), 741 (s), 691 (s). HRMS (ESI): $C_{60}H_{52}NOP_3Ru$ $[M - H^-]^+$ calcd: 996.2223, found: 996.2236.

Reaction of cyclohexanone with complex 12 resulting in complex 16. In a Teflon capped Wilmad-Young NMR tube (Wilmad 300 MHz), complex **12** (20 mg, 0.04 mmol) and cyclohexanone (5.2 μL, 0.05 mmol) were placed. To this, deuterated toluene (0.5 mL) was added and the NMR tube was close under inert atmosphere. The mixture was heated at 80 °C and NMR was recorded at t = 0, 1, 2, 4, 7, 10, 20, 24, 30, 40, 50, 60, 70 h. After 70, the solvent was remove *in vacuo* and the black liquid residue was subjected to IR and LIFDI-MS.

Compound 18 was synthesized as followed[31]. In an argon purged Schlenk tube PNP-Me ligand (160 mg, 0.43 mmol) was dissolved in toluene (6 mL). After addition of $RuHCl(CO)(PPh_3)_3$ (280 mg, 0.3 mmol) the mixture was refluxed for 5 h. After this, the solvent was removed *via* cannula and the white solid was washed with pentane (2 × 5 mL) and was stored at −34 °C. Yield: 70%. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$, δ = ppm): 2.64 (m, 4H, NCH_2), 2.53 (s, 3H, NCH_3), 2.22 (m, 4H, PCH_2), 1.56 (t, 18H, $^3J_{PH}$ = 6.6 Hz, $PC(CH_3)_3$), 1.39 (t, 18H, $^3J_{PH}$ = 6.3 Hz, $PC(CH_3)_3$), −16.03 (t, 1H, $^2J_{PH}$ = 19.7 Hz, Ru–H). $^{13}C_{apt}$ NMR (75 MHz, 298 K, $CDCl_3$, δ = ppm): 207.2 (CO), 65.8 (t, $^2J_{CP}$ = 8.8 Hz, NCH_2), 47.6 (s, NCH_3), 38.6 (t, $^1J_{CP}$ = 5.6 Hz, $P(C(CH_3)_3)$), 36.6 (t, $^1J_{CP}$ = 10.3 Hz, $P(C(CH_3)_3)$), 32.1 ($P(C(CH_3)_3)$), 31.3 (t, $^2J_{CP}$ = 2.8 Hz, $P(C(CH_3)_3)$), 31.0 (t, $^2J_{CP}$ = 2.2 Hz, $P(C(CH_3)_3)$), 23.5 (t, $^1J_{CP}$ = 5.7 Hz, PCH_2). $^{31}P\{^1H\}$ NMR (121 MHz, 298 K, $CDCl_3$, δ = ppm): 83.3 (s). IR (cm^{-1}): 3022–2824 (m), 1908 (CO, s), 1176 (m), 820 (m), 684 (m), 606 (m), 480 (m).

General procedure for the catalysis

Complex was weighed in the glovebox into a Schlenk tube. The Schlenk tube was removed from the glovebox (kept under Ar) and degassed solvent (15 mL) was added *via* syringe. The complex was dissolved followed by addition of cyclohexanol (520 μL, 5 mmol) *via* syringe. The mixture was transferred to the Ar-purged autoclave *via* syringe. The autoclave was closed and liquid NH_3 (2.5 mL, 97.5 mmol) was dosed to the autoclave. The whole was then heated to 150 °C. Samples were taken at t (h) = 0, 0.5, 1, 2, 3.75, 5.5, 7.5, 10, 23.5, 25, 28, 32, 48, 52.

Conflicts of interest

The authors declare no conflict of interests.

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Notes and references

1 C. Gunanathan and D. Milstein, *Angew. Chem., Int. Ed.*, 2008, **47**, 8661–8664.
2 D. Pingen, O. Diebolt and D. Vogt, *ChemCatChem*, 2013, **5**, 2905–2912.
3 D. Pingen, C. Müller and D. Vogt, *Angew. Chem., Int. Ed.*, 2010, **49**, 8130–8133.
4 S. Imm, S. Bähn, L. Neubert, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 8126–8129.
5 S. Imm, S. Bähn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 7599–7603.
6 D. Pingen, T. Lebl, M. Lutz, G. S. Nichol, P. C. J. Kamer and D. Vogt, *Organometallics*, 2014, **33**, 2798–2805.
7 X. Ye, P. N. Plessow, M. K. Brinks, M. Schelwies, T. Schaub, F. Rominger, R. Paciello, M. Limbach and P. Hofmann, *J. Am. Chem. Soc.*, 2014, **136**, 5923–5929.
8 D. Pingen, M. Lutz and D. Vogt, *Organometallics*, 2014, **33**, 1623–1629.
9 E. J. Derrah, M. Hanauer, P. N. Plessow, M. Schelwies, M. K. da Silva and T. Schaub, *Organometallics*, 2015, **34**, 1872–1881.
10 M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, **349**, 1555–1575.
11 A. Friedrich, M. Drees, M. Käss, E. Herdtweck and S. Schneider, *Inorg. Chem.*, 2010, **49**, 5482–5494.
12 M. Bertoli, A. Choualeb, D. G. Gusev, A. J. Lough, Q. Major and B. Moore, *Dalton Trans.*, 2011, **40**, 8941–8949.
13 C. Gunanathan, B. Gnanaprakasam, M. A. Iron, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2010, **132**, 14763–14765.
14 A. E. W. Ledger, P. A. Slatford, J. P. Lowe, M. F. Mahon, M. K. Whittlesey and J. M. J. Williams, *Dalton Trans.*, 2009, 716–722.
15 U. Gellrich, J. R. Khusnutdinova, G. M. Leitus and D. Milstein, *J. Am. Chem. Soc.*, 2015, **137**, 4851–4859.
16 J. H. Choi, L. E. Heim, M. Ahrens and M. H. Prechtl, *Dalton Trans.*, 2014, **43**, 17248–17254.
17 J.-H. Choi, N. E. Schloerer, J. Berger and M. H. G. Prechtl, *Dalton Trans.*, 2014, **43**, 290–299.
18 J. H. Choi and M. H. G. Prechtl, *ChemCatChem*, 2015, **7**, 1023–1028.
19 R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 789–805.
20 M. Grellier, L. Vendier, B. Chaudret, A. Albinati, S. Rizzato, S. Mason and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2005, **127**, 17592–17593.
21 C. Gunanathan, M. Hölscher and W. Leitner, *Eur. J. Inorg. Chem.*, 2011, **2011**, 3381–3386.
22 M. Grellier and S. Sabo-Etienne, *Chem. Commun.*, 2012, **48**, 34–42.

23 W. Baumann, A. Spannenberg, J. Pfeffer, T. Haas, A. Köckritz, A. Martin and J. Deutsch, *Chem. – Eur. J.*, 2013, **19**, 17702–17706.
24 R. Çelenligil-Çetin, L. A. Watson, C. Guo, B. M. Foxman and O. V. Ozerov, *Organometallics*, 2004, **24**, 186–189.
25 D. Spasyuk, S. Smith and D. G. Gusev, *Angew. Chem., Int. Ed.*, 2012, **51**, 2772–2775.
26 M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali and M. Beller, *Nature*, 2013, **495**, 85–89.
27 E. Alberico and M. Nielsen, *Chem. Commun.*, 2015, **51**, 6714–6725.
28 N. J. Oldenhuis, V. M. Dong and Z. Guan, *Tetrahedron*, 2014, **70**, 4213–4218.
29 L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz and A. L. Spek, *Organometallics*, 2000, **19**, 872–883.
30 H. Liu, N.-D. Wang and D.-M. Du, *Lett. Org. Chem.*, 2010, **7**, 114–120.
31 E. Alberico, A. J. J. Lennox, L. K. Vogt, H. Jiao, W. Baumann, H.-J. Drexler, M. Nielsen, A. Spannenberg, M. P. Checinski, H. Junge and M. Beller, *J. Am. Chem. Soc.*, 2016, **138**, 14890–14904.

