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Note

Intramolecular hydroamination catalysed by Ag complexes stabilised *in situ* by bidentate ligands

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ABSTRACT

A series of silver complexes generated *in situ* from $AgOSO_2CF_3$ (AgOTf) and a range of bidentate ligands were investigated as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine. A variety of P- and N-donor ligands were tested including the novel pyrazole-phosphine ligand 1-(2-(diphenylphosphino)phenyl)pyrazole. The best catalyst was formed from equimolar amounts of the P,N-donor ligand 1-(2-(diphenylphosphino)ethyl)pyrazole and AgOTf, which achieved a turnover rate of 129 h^{-1} for the cyclisation of 4-pentyn-1-amine.

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1. Introduction

Nitrogen containing heterocycles are sub-units in biologically active compounds which are important in the pharmaceutical and agrochemical industries. Their synthesis via convenient and direct approaches is therefore highly desirable. Catalysed cyclisation of alkynyl- and alkenylamines via intramolecular hydroamination has shown great potential for the energy efficient synthesis of *N*-heterocycles [1]. Lanthanide [2], early [3] and late [4–10] transition metal complexes have been shown to successfully catalyse this reaction. The advantage of late transition metals is their lower oxophilicity (compared to early transition metal or lanthanide metal catalysts), which leads to higher functional group tolerance and less sensitivity to water or oxygen exposure.

There are a number of examples of silver catalysed hydroamination reactions [5,7,9–12], however, there are only a few examples of the use of silver as a catalyst for the cyclisation of alkynylamines to form *N*-heterocycles [5,7,9,10]. These previous studies have primarily focussed on the use of silver salts rather than silver complexes as catalysts, and it has been found that these salts have a tendency to decompose at high temperatures and become inactive before the complete conversion of substrate is reached. However, a more active Ag(I) catalyst may be obtained by complexation of the silver centre with a suitable ligand, where the ligand stabilises and/or improves the efficiency of the catalytically active Ag centre [7,9,11]. Most recently, $Ag(phen)(OSO_2CF_3)$ (10 mol%), which contains the N,N-donor ligand phenanthroline (phen), has been shown to promote a conversion of 95% of 4-pentyn-1-amine (**1**) to 2-methylpyrroline (**2**) after 4 h at 70 °C, whereas $AgOSO_2CF_3$ (AgOTf) alone only promotes a conversion of 55% after the same time [9].

In this paper, we report the use of silver complexes generated *in situ* from AgOTf and a series of bidentate N,N-, P,N- and P,P-donor ligands as intramolecular hydroamination catalysts. Of particular interest for the development of efficient metal centred catalysts are mixed P,N-donor ligands which combine hard (nitrogen) and soft (phosphorus) centres [13]. Rhodium(I) and iridium(I) complexes containing the P,N-donor ligand 1-(2-(diphenylphosphino)ethyl)pyrazole (**3**) have shown high activity as hydrothiolation [14], hydroalkoxylation [15] and hydroamination [8] catalysts.

2. Results and discussion

2.1. Synthesis of 1-(2-(diphenylphosphino)phenyl)pyrazole (4)

To further investigate the use of P,N-donor ligands in hydroamination catalysis the novel pyrazole-phosphine ligand 1-(2-(diphenylphosphino)phenyl)pyrazole (**4**) was synthesised (Scheme 1). In this ligand, modelled on the previously reported ligand **3** [14], a phenyl bridge replaces the ethyl backbone. By thus expanding the range of pyrazole-phosphine ligands available we can consider the importance of the relative flexibility of the ligand backbone in catalysis. 1-Phenylpyrazole was synthesised via a condensation reaction between 1,1,3,3-tetraethoxypropane and phenylhydrazine hydrochl-

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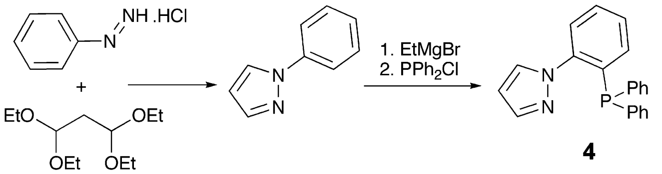


Scheme 1. Synthesis of ligand **4**.

oride [16,17]. Ethyl magnesium bromide was used to deprotonate 1-phenylpyrazole at the ortho-position, to form 2-(1-pyrazolyl)phenylmagnesiumbromide *in situ*. Addition of chlorodiphenylphosphine to the reaction mixture afforded the air stable ligand **4** cleanly, after the crude product was recrystallised from hot methanol. Ethyl magnesium bromide was used in place of *n*-butyl lithium, which has previously been used in the synthesis of 3,5-dimethyl(1-(2-(diphenylphosphino)phenyl))pyrazole [18], due to the preference of *n*-butyl lithium to deprotonate the 3 or 5 position of the pyrazole ring over the phenyl protons [19,20].

2.2. Catalysis

The efficiency of a range of Ag catalysts generated *in situ* from $AgOSO_2CF_3$ (AgOTf) and a series of bidentate ligands, including **3** and the new ligand **4**, was investigated using the intramolecular hydroamination of 4-pentyn-1-amine (**1**) to form 2-methylpyrroline (**2**) (Scheme 2). The catalysis was carried out at 60 °C in THF-d_8 under a N_2 atmosphere. Reaction progress was monitored by the acquisition of ^1H NMR spectra at regular intervals and %conversion was determined by integration of relevant peaks in the NMR spectra.

As a control experiment the reaction was first carried out in the presence of AgOTf with no added ligand at different loadings – 2 mol%, 5 mol% and 10 mol% (Table 1). At each of these concentrations the catalyst was initially highly active, as indicated by the consistently high turnover rates measured at 50% conversion. When using only 2 mol% AgOTf the catalytic activity dropped before complete conversion of the substrate, with no more than 90% conversion reached even after 7 days. In the presence of 5 mol% and 20 mol% of AgOTf, the rate of reaction was sufficiently fast that >98% conversion was reached quickly, before the complete decomposition of the catalyst.

With the aim of generating reactive, but stable, Ag catalysts AgOTf was reacted with each of the ligands shown in Fig. 1 in solution. The complexes thus generated *in situ* were tested for catalytic activity for the intramolecular hydroamination reaction (Table 2). Specifically, AgOTf was treated with each of the three bidentate P,N-donor ligands; 1-(2-(diphenylphosphino)ethyl)pyrazole (**3**), 1-(2-(diphenylphosphino)phenyl)pyrazole (**4**) or 2-(2-(diphenylphosphino)ethyl)-1-methylimidazole (**5**) [21], to form catalysts *in situ*. Ligands **3** and **5** were first synthesised within our research group and Ir and Rh complexes incorporating **3** and **5** have previously shown catalytic efficiency for the hydroamination reaction [14,21]. When 2 mol% of AgOTf and 2 mol% of ligand **3** were combined, a highly active and stable catalyst was generated which catalysed the complete conversion of **1** in 1.7 h with a turnover rate of 129 h^{-1}. This is the best reported result to date for the cyclisation of **1** using a silver catalyst [9]. In particular the turnover rate exceeded that of AgOTf alone (62 h^{-1}). Both the more rigid pyrazole-phosphine ligand **4** and the imidazole-phosphine ligand **5** generated poor catalysts which did not promote more than 30% conversion of substrate to product.

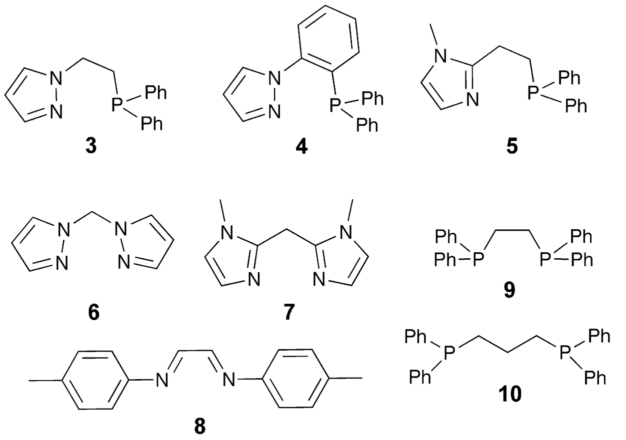
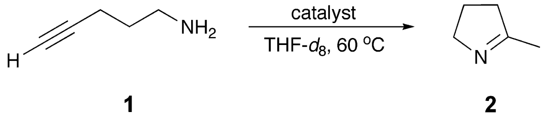


Fig. 1. Bidentate P- and N-donor ligands reacted with AgOTf to generate hydroamination catalysts *in situ*.

Table 2
Hydroamination of 4-pentyn-1-amine (**1**): relative efficiencies of Ag^+ catalysts formed *in situ* from AgOTf and various bidentate P and N-donor ligands.[a]

Catalyst	Conversion at	N_t (h^{-1})
	2 h (%)	
AgOTf + **3**	>98	129
AgOTf + **9**	90	64
AgOTf	82	62
AgOTf + **5**	43	–
AgOTf + **7**	40	–
AgOTf + **4**	37	–
AgOTf + **8**	37	–
AgOTf + **6**	28	–
AgOTf + **10**	12	–

[a] Reactions were performed using 2 mol% AgOTf and 2 mol% of ligand.



Scheme 2. Hydroamination of 4-pentyn-1-amine (**1**) to 2-methylpyrroline (**2**).

Table 1
Catalytic efficiency of AgOTf for the hydroamination of 4-pentyn-1-amine (**1**).

AgOTf (mol%)	Time at 80% conversion (h)	Time at >98% conversion (h)	N_t (h^{-1})[a]
2	1.5	164 (90%[b])	62
5	0.6	11.5	48
20	1.5	1.25	50

[a] Turnover rates (N_t, h^{-1}) = (moles of product)/(moles of catalyst)/hour, calculated at 50% coversion.

[b] Complete conversion of substrate in the presence of 2 mol% AgOTf was not observed.

Three bidentate N-donor ligands were combined with AgOTf to form complexes *in situ* which were tested as catalysts for hydroamination. The ligands studied were bis(pyrazol-1-yl)methane (**6**) [22], bis(*N*-methylimidazol-2-yl)methane (**7**) [23] and glyoxal bis(4-methylphenylimine) (**8**) [24] (Fig. 1). Ligands **6**, **7**, and **8** all formed catalysts that were initially highly active and promoted the conversion of 25% of the substrate within 15 min. The reaction rate then slowed significantly and catalysis dropped below detectable amounts, most likely due to decomposition of the Ag^+ complexes.

The activity of *in situ* silver catalysts formed from AgOTf and two bidentate phosphorus donor ligands, 1,2-bis(diphenylphos-

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