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Intramolecular Catalytic Addition of Amines to Alkynes

Thomas E. Müller

Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstraße 4, D-85747 Garching

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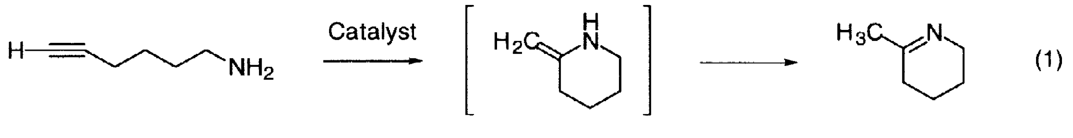
Abstract: A series of late transition metals have been found to catalyse the intramolecular addition of amines to alkynes. 6-Amino-1-hexyne is catalytically converted to 2-methyl-1,2-dehydropiperidine employing group 9, 10 or 11 metal complexes. The best results were obtained with the palladium and rhodium complexes $Pd(CH_3CN)_4(BF_4)_2$ and Rh(COD)(DIPAMP)BF_4. All catalytically active complexes have d^8 or d^{10} electron configuration.

Keywords: Addition reactions; Alkynes; Catalysis; Hydroamination

Although the catalytic addition of amines to alkenes has been the subject of numerous investigations,[1] only a few examples of homogeneously catalysed additions to alkynes have been described.[2] Even fewer examples are known where late transition metal compounds are employed.[3] We now wish to report that various metal complexes of group 9, 10 and 11 effectively catalyse the intramolecular addition of amines to alkynes.[4] The intramolecular cyclisation of 6-amino-1-hexyne (**1**) is catalysed by 1 mol% of the appropriate transition metal catalyst to generate the intermediate 2-methylene-piperidine (**2**) with an exocyclic double bond. Subsequent 1,3-hydrogen-shift leads to isomerisation of the initially formed enamine to the more stable imine and affords 2-methyl-1,2-dehydropiperidine (**3**) (eq. 1).



1 **2** **3** (1)

In a typical procedure a mixture of 6-amino-1-hexyne (100 µl, 0.88 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (2.9 mg, 8.8 µmol) and acetonitrile (25 ml) was heated at reflux for 20 hrs. The product 2-methyl-1,2-dehydropiperidine was isolated together with the remaining educt as the hydrochloride (79 mg, 67% yield). The product distribution was analysed using ^1H NMR spectroscopy. Using $Pd(CH_3CN)_4(BF_4)_2$ as catalyst, 83% of **1** was converted to **3**. The results obtained with other catalysts under similar conditions are described in Table 1.

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Table 1: Cyclisation of 6-Amino-1-hexin.

Group	Catalyst[a]	Solvent	Temp. (°C)	% Conversion
9	$Rh(COD)(DIPAMP)BF_4$	toluene	111	80
9	$Rh(COD)(DIPAMP)BF_4$	CH_2Cl_2	40	3
9	$Ir(COD)(PCy_3)(py)PF_6$	CH_2Cl_2	40	42
10	$Ni(PPh_3)_4$	THF	66	28
10	$Pd(CH_3CN)_4(BF_4)_2$	CH_3CN	82	83
10	$PtH(PEt_3)_2NO_3$	CH_2Cl_2	40	29
11	$Cu(PPh_3)_2NO_3$	CH_2Cl_2	40	18
11	$AgBF_4$	CH_2Cl_2	40	62
11	$AuCl_3$	CH_3CN	82	57

[a] Mol ratios **1** : Catalyst = 100 : 1, Time = 20 h; COD = cyclooctadiene; DIPAMP = 1,2-bis[(*o*-methoxyphenyl)(phenyl)phosphino]ethane; py = pyridine

Besides $Pd(CH_3CN)_4(BF_4)_2$, the catalytically most active complex is $Rh(COD)(DIPAMP)BF_4$ in toluene (80% conversion of **1**). The choice of the solvent is critical as the same catalyst in CH_2Cl_2 gives only 3% conversion. Various other complexes also proved to be effective. With the iridium(I) complex $Ir(COD)(PCy_3)(py)PF_6$ in CH_2Cl_2, 42% conversion was obtained. Other catalytically active complexes of group 10 metals include $Ni(PPh_3)_4$ in THF (28% conversion) and $PtH(PEt_3)_2NO_3$ in CH_2Cl_2 (29% conversion). Various complexes of all group 11 metals also catalysed the intramolecular hydroamination of **1**. Examples are the complexes $Cu(PPh_3)_2NO_3$ in CH_2Cl_2 (18% conversion), $AgBF_4$ in CH_2Cl_2 (62% conversion) and $AuCl_3$ in CH_3CN (57% conversion).

In all cases, with exception of $AgBF_4$ and $AuCl_3$, the liquid phase remained homogeneous. No reaction was noted in the absence of the metal complexes under identical reaction conditions. The reaction was also shown to be irreversible under the reaction conditions. For a successful catalysis the valence state of the metal appears to be essential, since no conversion of **1** was observed with the following nickel(II), rhodium(III), palladium(0) or gold(I) complexes: $Ni(PPh_3)_2(NO_3)_2$, $RhI_2(COD)Cl$, $Pd(P^tBu_3)_2$, $Pd(DPPF)_2$, $Pd_2Br_2(P^tBu_3)_4$ and $AuCl(PPh_3)$.

All catalytically active complexes have d^8 (metals in the 3rd period and silver) or d^{10} electron configuration (metals in the 4th and 5th period). Preliminary mechanistic studies indicate the same pathway to be valid for the intramolecular hydroamination of alkynes with all late transition metal complexes described.[5]

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