

Binap-gold(I) vs Binap-silver trifluoroacetate complexes as catalysts in 1,3-dipolar cycloadditions of azomethine ylides

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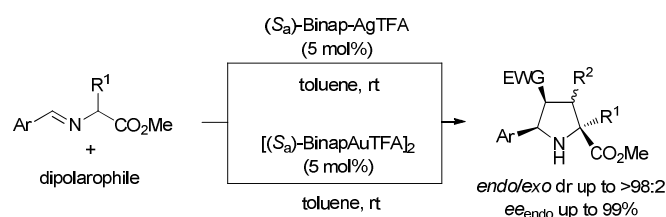
INTRODUCTION

Catalytic enantioselective 1,3-dipolar cycloadditions (1,3-DC) involving a metallo-azomethine ylide have been extensively studied since 2002.¹ Silver(I) and copper(I)-catalyzed cycloadditions offer excellent complementary results in terms of diastereo- and enantioselections and are the most frequently employed metals nowadays. Spite of the numerous published gold(III)-catalyzed processes, the diverse range of transformations developed by gold(I) complexes have demonstrated particular interest as catalysts.² Gold(I) complexes catalyze reactions under very mild conditions giving, wide functional group compatibility and high efficiency.

RESULTS AND DISCUSSION

In this work, chiral complexes were formed from Binap-AuCl and different silver salts.³ The nature of the counterion, the stoichiometry of Binap, and AuCl/Ag salt, the base, and the solvent, were studied and the best results were obtained by using Binap-AuCl/AgTFA complexes. [Binap-AuTFA]₂ complexes worked as multifunctional catalysts in the absence of an added base at room temperature in toluene. The trifluoroacetate anion generates the enolate of the iminoester and the cationic Binap-Au⁺ species were able to generate the *N*-metallated azomethine ylides. In all of the examples tested, the *endo*-diastereoselectivity was very high (up to >98:2). [Binap-AuTFA]₂ complexes induced high enantioselections by using rather sterically hindered substrates, for example *N*-phenylmaleimide and α -substituted iminoesters. Another important feature of these chiral complexes was their ability to catalyze, in the presence of a base, the 1,3-dipolar cycloaddition using (*E*)-1,2-bis(phenylsulfonyl)-ethylene as dipolarophile. A direct application of this enantioselective cycloaddition is the preparation of a

potent inhibitor of the hepatitis C virus. We also performed DFT calculations to shed light on the origins of the great stereocontrol obtained in these [Binap-AuTFA]₂ catalyzed 1,3-DC reactions.⁴



CONCLUSION

The employment of chiral gold(I) complexes in 1,3-DC has many advantages with respect to the analogous chiral silver(I) complexes, especially when sterically hindered components are involved.

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