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

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RESULTS AND DISCUSSION

INTRODUCTION

Catalytic enantioselective 1,3-dipolar cycloadditions (1,3-DC) involving a metallo-azomethine ylide have been extensively studied since 2002. Silver(I) and copper(I)-catalyzed cycloadditions offer excellent complementary results in terms of diastereom- and enantiomericselectivity 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. 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. 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 the key intermediate, which is a precursor 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.

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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