Gold Catalysis for Organic Synthesis and Bioconjugation

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Abstract:

Gold catalysis has received considerable attention in transition metal catalysis. Owing to their excellent selectivity, high reactivity, and exceptional tolerance to air/moisture reaction conditions, gold catalysts are capable of catalyzing a variety of novel organic transformations under mild reaction conditions. We are interested to develop gold catalysis for organic synthesis and application studies on bioconjugation. We have developed unprecedented stable BINOLgold(III) complexes adopting a novel C,O-chelation mode via a modular approach by combination of 1,1'-binaphthalene-2,2'-diols (BINOLs) and cyclometallated gold(III) dichloride complexes [(C^N)AuCl₂]. X-ray crystallographic analysis revealed that the bidentate BINOL ligands tautomerized and bonded to the Au^{III} atom via C,O-chelation to form a five-membered ring instead of conventional O,O'-chelation giving a seven-membered ring. The use of these gold(III) complexes to catalyze acetalization/cycloisomerization and carboalkoxylation of orthoalkynylbenzaldehydes with trialkyl orthoformates will be presented. Bioconjugation allows covalent attachment of biophysical probes to oligosaccharides, peptides, and proteins aiming to study complex biological systems. However, modification of biomolecules is a challenging task due to a number of stringent requirements including unprotected functional groups, aqueous medium, narrow pH (6-8) and temperature (4-37 °C) range, and low biomolecule concentration (below 100 µM). For the application of gold chemistry on bioconjugation, we will present the modular assembly of cyclometalated gold(III) complexes for selective modification of cysteinecontaining and alkyne-functionalized peptides and proteins in aqueous medium. Development of new fluorescent molecules is of importance due to their diverse applications in chemical, biological and materials science. Using visible light mediated gold-catalyzed *cis*difunctionalization of alkynes, we have recently synthesized a series of fluorescent quinolinium compounds with large Stokes shift (up to 191 nm) and tunable emission wavelength (455 - 652)nm). The applications of these newly developed fluorescent quinolinium compounds as photocatalysts for visible light photoredox catalysis and fluorescent dyes for live cell molecular imaging will be presented.