

Introduction: Coinage Metals in Organic Synthesis

Bruce H. Lipshutz, and Yoshinori Yamamoto

Chem. Rev., **2008**, 108 (8), 2793-2795 • DOI: 10.1021/cr800415x • Publication Date (Web): 13 August 2008

Downloaded from <http://pubs.acs.org> on December 24, 2008

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Introduction: Coinage Metals in Organic Synthesis

Bruce H. Lipshutz and Yoshinori Yamamoto

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106 and
Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan

Received June 16, 2008



Bruce Lipshutz arrived at UC Santa Barbara as an Assistant Professor in 1979, following years of training by three exceptional mentors: Howard Alper (B.A., SUNY Binghamton); Harry Wasserman (Ph.D., Yale); and postdoctoral advisor E. J. Corey (Harvard). A majority of his 29+ year career has been devoted to developing reagents of general use for the synthetic community. The group's efforts have now turned to a mix of heterogeneous catalysis, including development of mixed metal-supported cross-coupling reagents, and homogeneous catalysis, including several "name" reactions in water using "designer surfactants". Other projects involving axially chiral biaryls and new technologies associated with, and derived from, coenzyme Q₁₀ are all well underway.

Google "coinage metals" and one is seriously tempted to change the title of this thematic issue! The lead reference is to Wikipedia and is listed under the *singular* "Group 11 element". Click on this, whereupon it teaches us that coinage metals are composed of copper, silver, and gold... and other elements as well. Really?? Then the words become even more provocative; take the bothersome next statement: "They are also known as the noble metals." Surely neither of the guest editors, nor our students, wrote this entry. Interestingly, using the same approach to information gathering, but now using the keywords "noble metals", a better outcome is forthcoming. The occupants of this privileged group are usually considered "precious"; fortunately, in such a context, this source of free information correctly makes no mention of the base metal, copper. Further evidence that the chosen title is *not* accurate is reference to the 4th member of group

Yoshinori Yamamoto is the Professor of Chemistry of Tohoku University and the Institute Director of WPI Advanced Institute of Materials Research. He was awarded the CSJ Award (1996), the Humboldt Research Award (2002), the Purple Ribbon Medal from The Cabinet (2006), and the A. C. Cope Scholar Award from American Chemical Society (2007). He was the vice president of Tohoku University and a vice president of the Chemical Society of Japan (2006–2007). He has a wide range of research interests in synthetic organic and organometallic chemistry. His recent work focused on the use of transition-metal complexes and Lewis acids as catalytic reagents in organic synthesis and synthesis of complex natural products.

11 in the Periodic Table, with symbol Rg and atomic number 111: roentgenium. Say what? With a half-life of 3.6 seconds, it's a safe bet that not much synthetic organic chemistry, nor items of currency, are to be expected anytime soon from this metal. But perhaps most striking is the (factual?) comment that "coinage metals" is an *unrecognized* term viewed as misleading by IUPAC. Yikes! What have we done here?

The idea, of course, that remains valid, is to immediately inform the reader (with all due respect to IUPAC rules) that several outstanding and especially useful reviews are contained herein featuring Cu, Ag, and Au. Among these three *munzmetalle*, **copper** (from the Latin, *cuprum*, hence its symbol) has a rich history in organometallic chemistry; we know all the names, starting with Kharasch and Gilman from the 1940s and 1950s, respectively. Many reviews over the



ensuing decades have admirably served the needs of the synthetic community, along with several monographs devoted to this vibrant and continuously evolving field. The latest compilation that incorporates both traditional and newer areas of copper chemistry, *Modern Organocopper Chemistry*, is from 2002. It's time for an update.

And that is exactly what the reader gets: starting with the metal at the top of the triad, several magnificent reviews have been scribed covering the latest developments, written by both those who have devoted decades of their careers to copper chemistry as well as those who are of more recent arrival to this field and are now accruing years of service. In line with the times, there is a heavy accent on catalytic processes, in both racemic and nonracemic manifolds. Few among us would question the role of catalysis, asymmetric catalysis in particular, in synthesis; it was the buzzword of the 1990s, and it has not lost any of its appeal eight years into the new millennium. Catalysis is quite likely to remain very much in focus; it is high on the list of approaches to minimize green chemistry's "E Factor". The first seven contributions, therefore, as outlined in the *Table of Contents*, cover several areas in which chiral copper complexes, used catalytically, have been and are today of great interest: 1,4-additions, allylic and Friedel–Crafts alkylations, 1,2-additions, and, lastly, hydrosilylations with CuH. Alternatively, induction of absolute stereochemistry is discussed based on Woodwardian substrate control, rather than Sharpless–Masamune reagent control. The explosion in applications of copper-catalyzed Huisgen azide–alkyne cycloadditions is then reviewed by one of the two groups that first discovered this amazing "click chemistry". Next, we are treated to the chemistry between copper(I) complexes and buckeyballs, which on the surface (yes, intended) might seem quite odd: reactions between an electron-rich (d^{10}) metal and an allotrope of carbon... that is deceptively electrophilic. They happen readily for a variety of good reasons, and the results are fascinating, especially structurally. And while on the topic of structure, an in-depth account follows that sheds light on what is currently known about many of the copper reagents used so routinely, the ones seen every day over arrows in reaction schemes that rarely carry any information regarding aggregation state or role and importance of associated gegenion(s). These insights rely, in particular, on sophisticated and revealing techniques in NMR spectroscopy. What a treat to then conclude this series on copper with an overview on applications of these powerful technologies to natural products synthesis. Just browsing through these, a dozen chapters with remarkably high information content, one is likely to be struck by the discoveries of recent vintage: the nature and variety of bond constructions, the advances in stereocontrol, and the exquisite chemoselectivity for which copper is so well-known. In the composite, these promise to become the "Bible" for organocopper chemistry for years to come.

Unlike copper, **silver** (*argentum*) is truly a precious metal. We learn this throughout life: is there any doubt about the



implications of being born "with a silver spoon in one's mouth"? Dare one miss a "silver anniversary"! Wikipedia does a better job with silver; there are even some interesting tidbits of coinage metal information, such as concerning the U.K. pound, originally valued as one troy pound of sterling silver (which is 92.5% silver; the rest is usually copper). While silver salts have a long and distinguished history in organic chemistry, they have typically been utilized stoichiometrically, being especially popular as halogen scavengers and oxidizing agents. More recently, however, organic synthesis has begun to warmly embrace usage of Ag in catalysis; in short, Ag chemistry is booming. The contributions covering silver-catalyzed, or mediated, transformations include cycloadditions, allylations of carbonyl and imine groups, and aldol reactions, notably along with their asymmetric versions using chiral ligands; intramolecular heterocyclizations; and C–H bond activations of terminal or silylated alkynes applied to C–C and/or C–X bond constructions. In several of these transformations, the σ - and/or π -Lewis acidity of Ag(I) is used for substrate activation. Also quite intriguing among the coinage metals is the use of silver as a partner in bimetallic catalysts, i.e., the combination of Ag and Pd, Au, Cu, Pt, Rh, or Ru, all of which are known. The role of Ag is oftentimes that of an activator of substrates; on the other hand, it can serve to convert its transition metal partners into "hotter" cationic complexes. While copper is also viewed as an integral participant in bimetallic catalysis (along with Pd), e.g., in both Sonogashira and Stille couplings, Ag, by contrast, is more frequently selected. Also reviewed are "atom transfer reactions", initiated through activation of diazo compounds and catalyzed by homogeneous silver complexes containing ligands such as tris(pyrazolyl)borate. C–H "activation" with silver? Yep, it's in here.



Gold. What is it about this metal that makes it so precious? Is it history? It does date back to prehistoric times, and yes, Wikipedia informs us that "it may have been the first metal used by humans...". It is part of our everyday speech: "The Gold Standard"; "The Gold Metal"; "The Golden Rule"; "Those were golden times." In New Zealand, even a "yes" is phrased "Good as Gold." Gold is hot, no matter what, even though other metals today are actually *far, far* more "precious": has anyone noticed the price of rhodium lately? Chemistry-wise, catalysis with gold (Latin: *aurum*; hence, Au) has truly mushroomed in just a few years time. As with Ag(I), Au(I) exhibits strong Lewis acidity (i.e., is π -electrophilic) toward unsaturated C–C bonds, as well as toward lone pairs of electrons associated with heteroatoms (i.e., is σ -electrophilic). These characteristics of Au catalysts make several types of transformations feasible, such as additions

of N, O, S, and C nucleophiles to C–C unsaturated bonds; Friedel–Crafts type reactions; activation of carbonyl and imine groups; cycloisomerizations of enynes and heteroenynes; and activation of C–H bonds of terminal alkynes (as also observed with Ag and Cu). Oxidations of unsaturated bonds can be catalyzed by gold, not only in the traditional homogeneous sense but also using nanoparticles, a promising advance in green chemistry. Moreover, like silver, it poses essentially no toxicity issues. And yes, asymmetric catalysis by nonracemic Au complexes is already here today, and undoubtedly this area is growing.

There are also contributions to this issue that individually cover all three metals. The value of each is now defined through comparisons of their reactivities and efficiencies in C–H bond functionalization by carbene and nitrene insertion, as well as in C–H oxidations using strong oxidants. Novel pathways to heterocyclic arrays found in a multitude of

complex organic targets also arise using coinage metal-derived catalysts. Coinage metal adducts containing small carbon based donors like CO and alkenes using pyrazole-based chelators serve as useful models for key reaction intermediates in catalytic and stoichiometric processes mediated by Cu, Ag, and Au.

Thus, we invite you, dear reader, to thumb through this thematic issue. However, *tenga cuidado!* Plan your time accordingly, for there is such a “wealth” of information herein, a site for one-stop shopping for coinage metal chemistry, that, like a great novel, it may be difficult to put it down. We are thrilled to have received such largesse from our colleagues who have devoted tremendous collaborative effort to bring this timely opus to the community. Indeed, it is an “embarrassment of riches”.

CR800415X