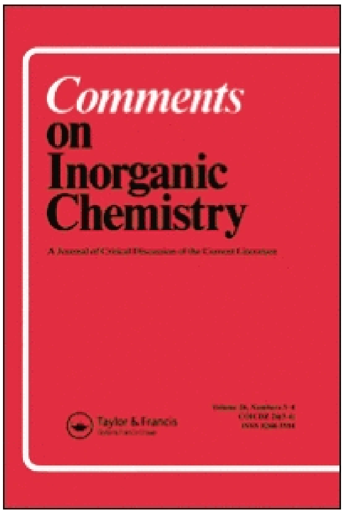

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

GROUP 11 STILL PRODUCES FASCINATING CHEMISTRY - NOVEL FINDINGS REGARDING METAL-METAL INTERACTIONS AND STRUCTURES OF CLOSED SHELL nd^{10} COPPER(I) AND GOLD(I)

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To cite this Article Fackler Jr., John P.(2010) 'GROUP 11 STILL PRODUCES FASCINATING CHEMISTRY - NOVEL FINDINGS REGARDING METAL-METAL INTERACTIONS AND STRUCTURES OF CLOSED SHELL nd^{10} COPPER(I) AND GOLD(I)', Comments on Inorganic Chemistry, 31: 3, 104 — 110

To link to this Article: DOI: 10.1080/02603594.2010.517468

URL: http://dx.doi.org/10.1080/02603594.2010.517468

Comments on Inorganic Chemistry, 31: 104–110, 2010
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ISSN: 0260-3594 print
DOI: 10.1080/02603594.2010.517468

GROUP 11 STILL PRODUCES FASCINATING CHEMISTRY – NOVEL FINDINGS REGARDING METAL-METAL INTERACTIONS AND STRUCTURES OF CLOSED SHELL nd^{10} COPPER(I) AND GOLD(I)

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INTRODUCTION

Gordon Stone was a young faculty member at Harvard while I was completing my Ph.D. down the river at MIT with Al Cotton. It wasn't until Gordon had moved back to England and I from California to Ohio that I came in contact with Gordon's chemistry again, largely in consulting. While I had made allyl palladium chloride with some Berkeley undergraduates in a synthetic inorganic chemistry course I was teaching, it wasn't until I moved to Case Western Reserve University and actively consulted at Firestone Tire and Rubber Co. in Akron, OH, on Zeigler-Natta catalysis problems that the chemistry of F. G. A. Stone became very important to me. An early Stone student, Peter Maitlis, was the Ph.D. advisor of Jung Kang, who was a leading organometallic chemistry expert at Firestone over the 25 years I consulted with them. I believe that it was this work with Kang that helped Bridgestone/Firestone to become a leading producer of today's *cis*-butadiene core golf balls. Although

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Bridgestone started producing golf balls in 1937, the development of a synthetic procedure using an inexpensive Ni catalyst[1] became very important. This polymer is formed in 95% *cis* structure in a flow reactor under adiabatic conditions. It gave Firestone an economical edge over the *cis*-polybutadiene manufacturers who had relied on the low temperature cobalt process of the 1980s. Firestone had plants that used an adiabatic process with a lithium catalyst to produce the equilibrium *cis*/*trans* product. The company was buying the small amount of the *cis* polymer it needed for tires when this new nickel-based process was discovered. Solid rubber core golf balls now have generally replaced the earlier wound rubber core balls.

The work of Stone, which described allyl and olefin interactions with group 8 and related elements, is important in the diene polymer growth processes. Olefin interactions in the growing polymer chain from multiple coordinating metal ions in a cluster catalyst were imagined to be able to control the orientation of the double bond in the product as the growing polymer wrapped around the cluster. A hexane soluble cluster containing several Ni(II) sites coordinated to a borate anion and long chain carboxylates was found which had been used in the pigment industry. I happened to become aware of this cluster in some work I did for Mooney Chemical. It turned out that this metal cluster worked in batch studies and later in continuous runs. The cluster was given the name NiOB but its structure still remains incompletely characterized since it does not crystallize. It is a precursor to the actual catalyst mixture, which also requires using tri-isobutylaluminum, TIBL, as a co-catalyst. Studies of NiOB done in our laboratory and EXAFS studies in Great Britain by David Garner identified the likely coordination of the borate and carboxylate units to four Ni(II) ions. The first polymer runs outside the pilot plant in Akron were made by cleaning out a lithium plant and introducing the new catalyst streams in weekend runs. The product easily met Firestone's *cis* polymer needs for tire manufacture. The golf ball market with a solid *cis*-butadiene core awaited the development in the 1980s of an appropriate cover to hold the core. Although a 95% *cis* polymer is also made using a neodymium catalyst, the golf ball quality of balls made with each of these two rubbers is only slightly different, making the decision by the golfer as to which golf ball to use simply a matter of price and choice. I wonder if F. G. A. Stone ever got a dozen balls from the company as I did one year.

ORGANOMETALLIC GOLD CHEMISTRY

Although my group and the group of Hubert Schmidbaur in Germany pioneered the chemistry of Au(I) and Au(II) ylide complexes, very little work has been done with mixed ligand species, although some fascinating oxidative addition work had been reported with the mixed ligand phosphonate/ylide complex[2] $Au_2[S_2PR(OR)][(CH_2)_2PPh_2]$. A few years ago we discovered that sterically constraining amidinate ligands can produce dinuclear Au(I) and Au(II) complexes with an oxidative addition chemistry similar[3] to that of the ylides[4] (Figure 1). Hence we embarked on an effort to synthesize and characterize a mixed ligand Au_2(amidinate)-(ylide) complex. This proved to be far more difficult than anticipated. The synthetic problem ultimately was solved but the chemistry leading up to the solution requires some explanation.

We thought at first that lability of the Au-N bond in the dinuclear amidinate complex would allow us to directly react the $Au_2(\text{amidinate})_2$ with the ylide anion. This proved to be an incorrect approach. As is

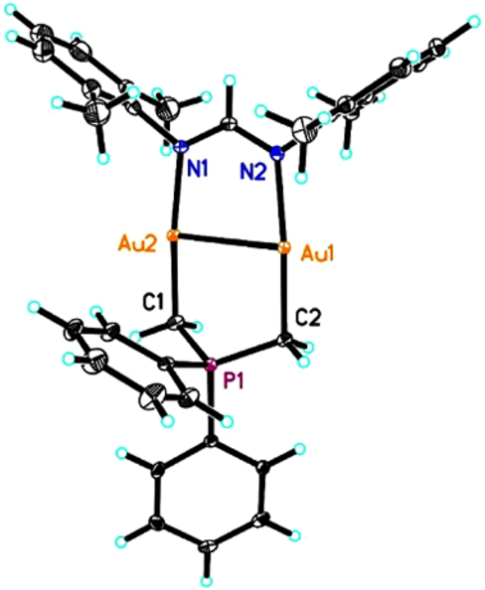

Figure 1. The structure of a mixed ligand complex of a formidinate with an ylide, $Au_2[S_2PR(OR)][(CH_2)_2PPh_2]$. The Au . . . Au distance is 2.84 Å. (Figure appears in color online.)

indicated in Figure 2, a number of interesting products result depending upon the specific synthetic conditions.

Several products in this list of new materials are particularly interesting. The species Au_2FY_2 has been characterized as the nitrate salt and is a mixed ligand species with two ylides coordinated to the Au(I) centers (Figure 3).

Using excess base a phenyl ring is ruptured from the ylide. This results in a new tetranuclear organometallic product in which the

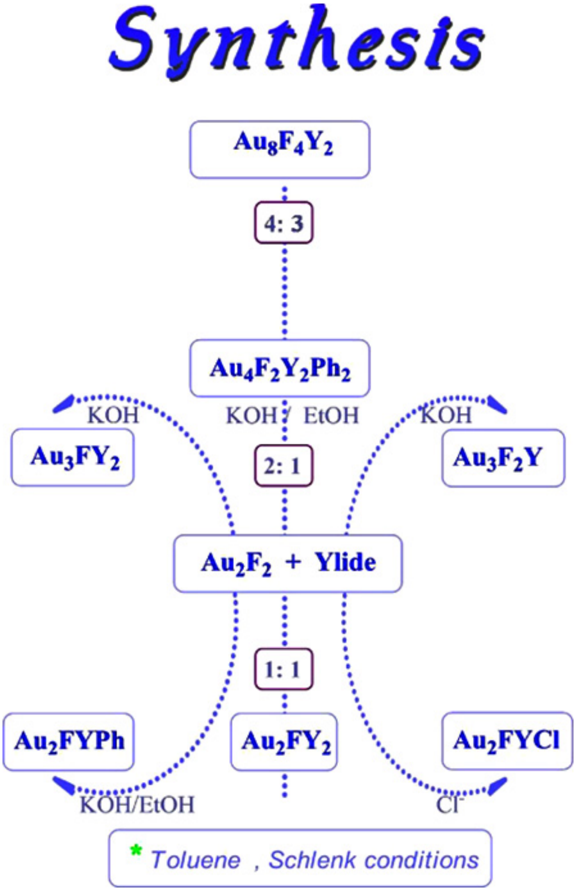

Figure 2. A line drawing of the various reactions of the Au(I) formidinate, Au_2F_2 with the methyldiphenyl phosphosphonium ylide, F = 2,6-dimethylformamidinate, Y = methyldiphenylphosphine ylide. (Figure appears in color online.)

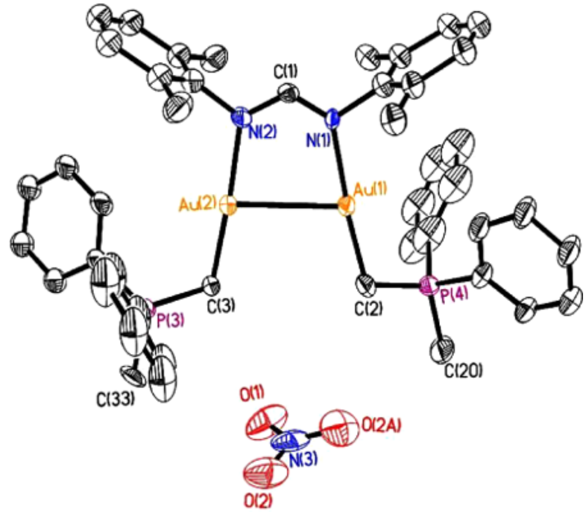

Figure 3. The cationic product, $[Au_2FY_2]NO_3$, resulting from the displacement of an amidinate ligand from the dinuclear Au_2F_2 by two equivalents of ylide, Y. The Au … Au distance is 3.00X. (Figure appears in color online.)

Au(I) captures the displaced phenyl group, $Au_4Y_2Ph_2$ (Figure 4). The solvent ethanol also plays a role in the synthesis.

Perhaps the most surprising product obtained in a low yield is the octanuclear cluster listed above as $Au_8F_4Y_2$. In reality the Y here is (Y-2H).

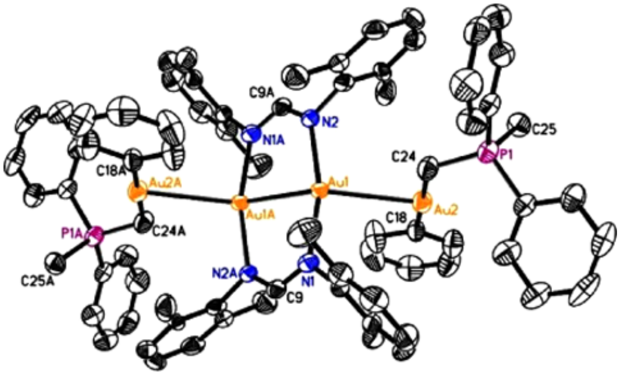

Figure 4. The tetranuclear product, $Au_4F_2Y_2Ph_2$ formed by reaction of the ylide, Y, with the formamidinate, Au_2F_2 in the presence of KOH with an alcohol solvent. The Au … Au distances: Au1-Au1A = 2.7954(16) and Au1-Au2 = 2.9758(17). (Figure appears in color online.)

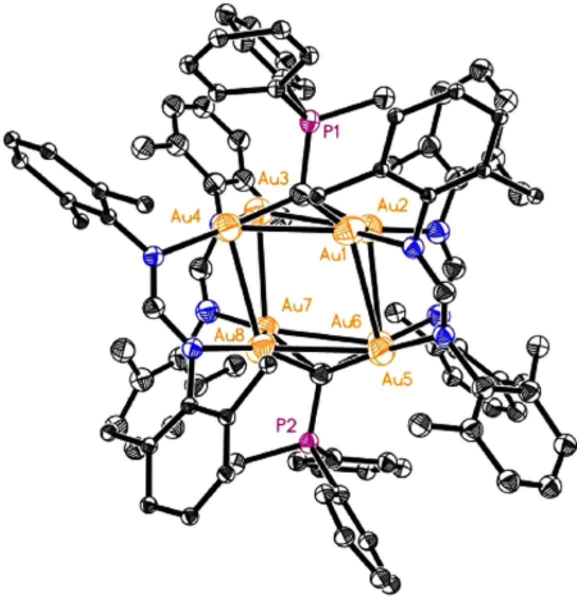

Figure 5. The cubic, octanuclear Au(I) cluster contain two hypercoordinate C linkages to gold.[5] The ave. Au . . . Au distance is 2.897X and the ave. Au-C distance is 2.1613X. (Figure appears in color online.)

The ylide has been deprotonated completely and is hyper-coordinated to four Au(I) atoms. It is correctly described as $[Au_8F_4\{\eta^5\text{-C-PPh}_2(CH_3)\}_2]$ (Figure 5). While hyper-coordinated carbon has been found previously, this appears to be the first time two hyper-coordinate carbon atoms have been found in the same cluster.

In addition we described studies of Cu(I) . . . Cu(I) interactions in some derivatives of guanidinates including the report of a short, unsupported distance of 2.67 Å in a neutral complex.[6] Factors were described that lead to Cu(I) . . . Cu(I) interactions. These include H-bonding, charge separations, and bridging ligands.

ACKNOWLEDGEMENTS

The gold studies described here have been associated with the postdoctoral studies of Doris Melgarejo and Gina Chiarella and supported by the Welch Foundation of Houston Texas, grant number A-0960.

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