

Organometallic chemistry and catalysis on gold metal surfaces

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Abstract

As in transition metal complexes, $C\equiv N-R$ ligands adsorbed on powdered gold undergo attack by amines to give putative diamino-carbene groups on the gold surface. This reaction forms the basis for the discovery of a gold metal-catalyzed reaction of $C\equiv N-R$, primary amines ($R'NH_2$) and O_2 to give carbodiimides ($R'-N=C=N-R$). An analogous reaction of $C\equiv O$, RNH_2 , and O_2 gives isocyanates ($R-N=C=O$), which react with additional amine to give urea ($(RNH)_2C=O$) products. The gold-catalyzed reaction of $C\equiv N-R$ with secondary amines (HNR'_2) and O_2 gives mixed ureas $RNH(C=O)NR'_2$. In another type of gold-catalyzed reaction, secondary amines $HN(CH_2R)_2$ react with O_2 to undergo dehydrogenation to the imine product, $RCH=N(CH_2R)$. Of special interest is the high catalytic activity of gold powder, which is otherwise well-known for its poor catalytic properties.

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1. Introduction

Transformations of organic molecules are often catalyzed by metals supported on high surface-area oxides such as SiO_2 , Al_2O_3 , or TiO_2 . Despite the widespread use of these heterogeneous catalysts in industrial applications, very little is known about the mechanistic details of the reactions that occur on the metal surfaces. Proposed mechanisms for surface metal-catalyzed reactions [1,2] are typically based on reactions of organic molecules that occur in solution-soluble transition metal complexes, where experimental methods are able to yield more details of reaction pathways. Often the coordination mode of the reacting organic molecule can be established by X-ray diffraction and NMR studies. Moreover, intermediates on the path to products can sometimes be characterized. On the other hand, in studies of supported metal-catalyzed reactions, X-ray diffraction and NMR techniques are not generally useful for characterizing either the initially-adsorbed reactant nor intermediates that lead to the products. This

means that the nature of organic reactant binding to a metal surface is dependent on interpretations of a variety of results from spectroscopic investigations.

The purpose of the studies described in this paper was to compare and contrast the binding and subsequent reactions of specific organic molecules in metal complexes and on metal surfaces. More specifically, we hoped to understand whether or not principles that are useful in understanding reactions of organic ligands in organometallic complexes can be applied to the same organic molecules adsorbed on a metal surface. Gold was chosen as the metal surface because it does not react with air (O_2) to form a surface oxide at room temperature, which means that organic molecules adsorb only to $Au(0)$ atoms, and not to gold in some positive oxidation state. While this simplifies studies of organic molecule adsorption on a metal surface, the gold surface is therefore also so unreactive that it is a poor catalyst as is well-known [3]. However, as will become evident, gold metal is not as catalytically inactive as was previously assumed.

For the purpose of the proposed studies, it was necessary to choose an organic reacting molecule that contained a signature infrared absorption that would identify it when

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it was adsorbed on the gold surface and would shift to another frequency when it reacted to give a new species on the surface. Our initial studies, described below, began with isocyanide molecules ($C\equiv N-R$) which exhibit a strong, characteristic $\nu(N\equiv C)$ infrared absorption, which has been used extensively in characterizing metal complexes with isocyanide ligands [4–10] and is also useful for identifying isocyanides adsorbed on metal surfaces [11]. Of course, the choice of an organic reactant for study on a metal surface was also guided by a well-developed understanding of its reactivity in metal complexes that could be compared with its reactivity on the gold metal surface.

Although gold metal has been traditionally known as a poor catalyst [3], there has been tremendous recent interest in nano-sized gold particles that have been shown to catalyze a variety of reactions including the following [3,12–17]: CO oxidation, epoxidation of propene, oxidation of various hydrocarbons and alcohols, the water–gas shift reaction, alkyne and alkene hydrogenation, and several others. The catalytic activities of these nanogold catalysts depend upon their stabilization as particles of less than 5 nm size. This is typically accomplished by forming them on a metal oxide support, which is often TiO_2 but may also be many others (e.g., Fe_2O_3 , CeO_2 , ZrO_2 , SiO_2 , Al_2O_3 , CoO_x , and MnO_x). The method used for preparing supported nanogold is very important for achieving an active catalyst, and it is frequently not possible to reproduce catalytic activity from one preparation to the next [3]. Because of the surprising catalytic activity of nanogold, numerous studies have sought to understand why nano-sized gold particles are so much more active than large (bulk) gold particles. This is a field of continuing research activity that is regularly reviewed [3,12–17].

None of the forms of gold metal that are used in the studies described in this paper are nanogold. In order to avoid complications that may arise from the presence of a metal oxide support, we have used either gold powder or a gold film. The gold powder was prepared by the simple reduction of an aqueous solution of $HAuCl_4$ with hydroquinone [18]. The resulting gold powder has a very low surface area ($0.35\text{ m}^2/\text{g}$), and its particle diameters are in the range of 1000 nm, as determined by electron microscopy [19]. This gold powder was re-used many times for both the adsorption and catalysis studies. Typically, the gold powder was cleaned before each use by treatment with “piranha” solution (concentrated $H_2SO_4/30\%$ aqueous H_2O_2) [20,21], which restored the powder to its original catalytic reactivity. If the gold powder were only washed with a solvent, e.g., MeOH, between catalytic runs, its activity would be slightly decreased ($\sim 10\%$). There was no evidence for nano-sized gold particles in the gold powder that was prepared and cleaned in this manner. The electron micrographs showed no particles that were less than 5 nm in size. A further test for nanogold particles involved using the gold powder as a potential catalyst for the reaction, $CO + 1/2 O_2 \rightarrow CO_2$. Nanogold particles are known

to catalyze this reaction even below room temperature [3]; however, no reaction was observed between CO and O_2 (1.0 atm total) in the presence of 1.0 g of gold powder at 45 °C in MeCN, which are conditions typically used for our catalytic studies. Thus, it seems very unlikely that nanogold particles are present in the gold powder. Moreover, gold powder had been previously shown to be a poor catalyst for the oxidation of CO [22–24].

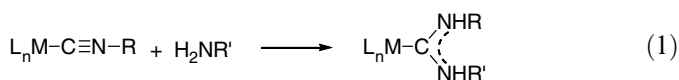
The gold films used in some of our studies were prepared by first depositing a 15 nm layer of Cr on a glass slide. Then, 300 nm of gold was vapor-deposited on the Cr. These slides were also cleaned with piranha solution between runs. Thus, all of the gold substrates used in the studies described in this paper are much larger than the supported nanogold particles that are so catalytically active. In the following sections are discussed our studies of the adsorption and catalytic reactions of isocyanides ($C\equiv N-R$), CO, and amines on bulk gold metal.

2. Isocyanides ($C\equiv N-R$) on gold: adsorption, reactions, and catalysis

Isocyanides in solution, e.g., 1,2-dichloroethane (DCE) and hexane, readily adsorb to gold metal in all of its forms (films, powders, and nanoparticles) [11]. Typically, a $\nu(N\equiv C)$ frequency for an adsorbed isocyanide that is equal to or higher than that of the free isocyanide indicates that the isocyanide is adsorbed η^1 through the carbon to one Au atom. In our own studies, we observed for *n*-BuNC adsorbed on a gold film a $\nu(N\equiv C)$ value (2224 cm^{-1}) that is 76 cm^{-1} higher than that (2148 cm^{-1}) of free *n*-BuNC in DCE solution [21]. Although the presence of only one $\nu(N\equiv C)$ band for the adsorbed isocyanide suggests that all isocyanide molecules are adsorbed on the same type of gold site, this cannot be the case because *n*-BuNC gold films that are immersed in a pure solvent, such as DCE, desorb about 55% of the *n*-BuNC within 1 min while the other 45% requires 4 h or longer. As the *n*-BuNC desorbs, the $\nu(N\equiv C)$ of the *n*-BuNC remaining on the gold increases slightly to 2232 cm^{-1} . Thus, there are two broad types of adsorbed isocyanide: (1) one that is weakly adsorbed with $\nu(N\equiv C) = 2224\text{ cm}^{-1}$ and (2) one that is strongly adsorbed with a higher $\nu(N\equiv C)$ value (2232 cm^{-1}). There are also two types of *n*-BuNC sites in powdered gold; one exhibits a $\nu(N\equiv C)$ value of 2225 cm^{-1} at saturation coverage, while the other shows a $\nu(N\equiv C)$ band at 2233 cm^{-1} for the strongly adsorbed *n*-BuNC which remains on the surface after the weakly adsorbed isocyanide is desorbed. While the $\nu(N\equiv C)$ values for the weakly and strongly adsorbed *n*-BuNC are the same on both gold film and gold powder, only 45% of *n*-BuNC is strongly adsorbed on gold film, whereas 70% is strongly adsorbed on gold powder. The much more irregular surface of gold powder would be expected to have more low-coordinate edge and corner gold atom sites than would exist on gold films with more high-coordinate gold atoms on the (111) terrace sites [25]. Gold powder would be

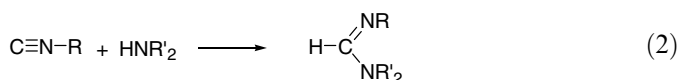
expected to bond more isocyanides more strongly at the larger number of low-coordinate sites.

In transition metal complexes, isocyanide ligands whose $\nu(\text{N}\equiv\text{C})$ values are more than 40 cm^{-1} higher than those of the free isocyanides have been observed to be attacked by amines (and other nucleophiles) [26–28] to give diaminocarbene ligands (Eq. (1)). Typically, the rate laws for



these reactions are first order in the metal complex and amine concentrations: $\text{Rate} = k[\text{L}_n\text{M}(\text{CNR})][\text{H}_2\text{NR}']$. This rate law has been interpreted as supporting a mechanism that involves nucleophilic attack on the isocyanide carbon that is activated by a metal (M) that is in a positive oxidation state and/or by ligands L that are weakly electron-donating. In some reactions, the rate law exhibits an amine concentration dependence that is higher than first order. This is interpreted to indicate the involvement of a second amine molecule, which promotes the rearrangement of the initial isocyanide–amine adduct to the diaminocarbene product [26–29].

Metal salts of Cu^+ , Ag^+ , Zn^{2+} , Cd^{2+} , and Au^{3+} are known to catalyze reactions (Eq. (2)) of isocyanides with primary and secondary amines to give formamidines [28,30]. These reactions

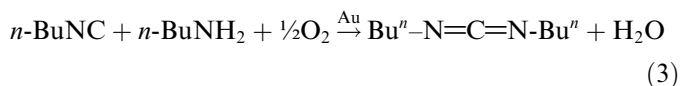


are proposed to occur by initial metal coordination of the isocyanide, which is attacked by the amine to give a diaminocarbene ligand that is displaced as the formamidine product. The last step is modeled by reactions of diaminocarbene complexes of Au(I) and Au(III) with PPh_3 or CN^- ligands that give the free formamidine product [28].

As the $\nu(\text{N}\equiv\text{C})$ value (2224 cm^{-1}) for *n*-BuNC adsorbed on gold is much more than 40 cm^{-1} higher than that (2148 cm^{-1}) of free *n*-BuNC, one expects *n*-BuNC adsorbed on gold metal to undergo attack by amines to give diaminocarbene groups on the surface, if one assumes that the 40 cm^{-1} guideline for isocyanides in metal complexes also applies to isocyanides adsorbed on metal surfaces. In fact, we observe [21] that all of the *n*-BuNC (both weakly and strongly adsorbed) is removed within 20 s from a gold film when a gold-plated slide containing adsorbed *n*-BuNC is immersed into a hexane solution containing *n*-BuNH₂. The reaction of the adsorbed *n*-BuNC is slower if the amine is less basic or more sterically bulky than *n*-BuNH₂. There was no evidence in the diffuse reflectance infrared spectrum of the resulting gold film for diaminocarbene groups, which are expected to give a $\nu(\text{N}-\text{C}=\text{N})$ absorption near 1550 cm^{-1} , which is characteristic of diaminocarbene ligands in metal complexes. Thus, the product of the reaction of the adsorbed isocyanide with the amine must have desorbed from the surface. By reacting *n*-BuNC adsorbed on 1.0 g of gold powder, which has a much larger

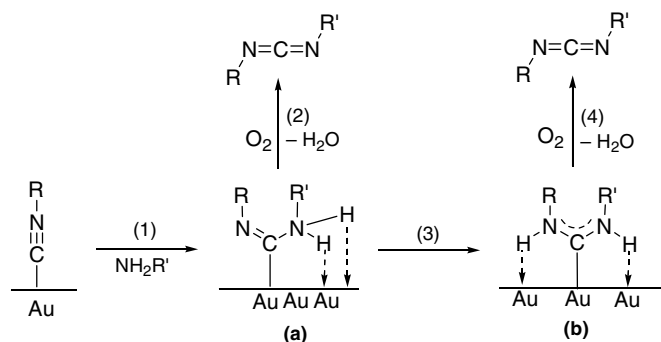
surface area than the gold film, with *n*-BuNH₂, it was possible to identify the product of the reaction. We were surprised to find that it was the carbodiimide $\text{Bu}^n-\text{N}=\text{C}=\text{N}-\text{Bu}^n$, together with a significant amount of *n*-BuNC, which presumably resulted from the rapid desorption of the weakly adsorbed *n*-BuNC. Thus, it appears that most of the reacting *n*-BuNC was the strongly adsorbed form, which would be expected to be more reactive toward nucleophiles because it has a higher $\nu(\text{N}\equiv\text{C})$ value than the weakly adsorbed *n*-BuNC.

During the studies of adsorbed *n*-BuNC with *n*-BuNH₂, we noticed that the desorbed *n*-BuNC product was also converted to the carbodiimide product if the reaction was allowed to stir for a longer time or was heated to 60°C . This meant that the reaction of *n*-BuNC with *n*-BuNH₂ to form $\text{Bu}^n-\text{N}=\text{C}=\text{N}-\text{Bu}^n$ was catalyzed by gold metal. However, the fate of the two hydrogen atoms in the *n*-BuNH₂ reactant was not evident, but it seemed possible that they were combining with O_2 to give H_2O , as the reactions were conducted in air. The catalytic reaction of *n*-BuNC with *n*-BuNH₂ in the presence of gold powder was then conducted under an argon atmosphere. Under these conditions, no carbodiimide product was formed. This meant that O_2 is a reactant and that H_2O is the likely product. Therefore, the complete gold-catalyzed reaction is represented by Eq. (3). At 60° in hexane solvent, under an air atmosphere and stirring with



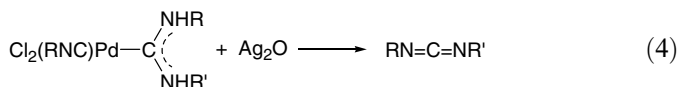
1.0 g of gold powder, *n*-BuNC (1.7×10^{-2} mmol) and *n*-BuNH₂ (17×10^{-2} mmol) react for 90 h to give a 73% yield of $\text{Bu}^n-\text{N}=\text{C}=\text{N}-\text{Bu}^n$. Since the *n*-BuNC had completely reacted, it meant that other products (27%) also formed. These products were not identified, but there were additional peaks at higher mass in the GC–MS, which might be attributed to oligomers of *n*-BuNC. If the reactions were conducted at higher concentrations of the isocyanide and amine, the percent yields decreased, presumably due to the formation of more *n*-BuNC oligomers. These lower yields mean that we have not found conditions that make this reaction useful for the synthesis of larger amounts of carbodiimides. Mixed carbodiimides $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}'$ were obtained when relatively low concentrations of a variety of isocyanides ($\text{C}\equiv\text{N}-\text{R}$) were reacted with a variety of amines ($\text{R}'\text{NH}_2$) [21,31].

Kinetic studies [21] of the gold powder-catalyzed reaction (Eq. (3)) of *n*-BuNC and *n*-BuNH₂ at 60°C in hexane show that the rate is independent of the O_2 concentration/pressure, as indicated by the observation that the rate is the same in 1 atm of air or O_2 . However, the rate is first order in the concentration of *n*-BuNH₂. These results suggest a mechanism (Scheme 1) in which the isocyanide first adsorbs on the Au surface; as in metal complexes (Eq. (1)), this makes the isocyanide susceptible to nucleophilic attack by the amine in step 1. This is the rate-determining

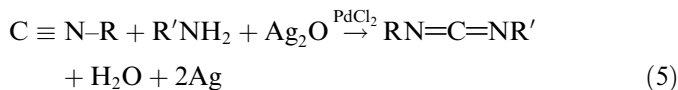


Scheme 1. Mechanism for the Au-catalyzed reaction of isocyanides ($R-N\equiv C$) with primary amines (H_2NR') and O_2 .

step in the reaction. The resulting intermediate **a** either rearranges to a diaminocarbene group **b** (as occurs in metal complexes, Eq. (1)) in step 3 or reacts with O_2 to give H_2O and the carbodiimide in step 2. Alternatively, the diaminocarbene intermediate **b** reacts with O_2 to give the products. As the overall reaction rate does not depend on the O_2 concentration, steps 2 and 4 must be fast as compared with step 1. Although step 1 is readily understandable in terms of a mechanism that is well-documented for reactions of isocyanide ligands with amines (Eq. (1)), there is no comparable metal complex model for the conversion of a diaminocarbene ligand to a carbodiimide. A reaction that presumably involves the oxidation of a diaminocarbene complex is that shown in Eq. (4) [32]. Water is suggested to be another product of the reaction,



and it seems likely that Ag metal is the reduction product especially because the stoichiometric reaction of $C\equiv N-R$ with $R'NH_2$ and Ag_2O to give carbodiimides is catalyzed by $PdCl_2$ [32], as summarized in Eq. (5). Thus, it seems possible that O_2 in Eq. (3) is an oxidizing agent like Ag^+ in Eqs. (4) and (5).

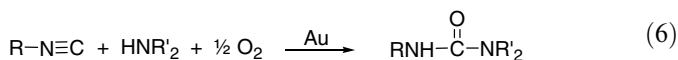


Steps 2 and 4 in Scheme 1 are unlikely to involve the generation of H_2 from intermediate **a** or **b**, because H_2 would not be converted to the H_2O product by reaction with O_2 except at temperatures above $130^\circ C$ [13,33]. However, supported nanogold is reported to catalyze the reaction of H_2 and O_2 to give H_2O_2 even below room temperature [34,35].

Although there is little basis for proposing details of steps involving O_2 in Scheme 1, evidence for amine attack on adsorbed isocyanide in step 1 is quite convincing. This step is the same as that proposed for metal ion-catalyzed reactions (Eq. (2)) of isocyanides and amines in solution. However, this homogeneous reaction gives formamidines without the involvement of O_2 . Thus, while amine attack is

a key step in both the homogeneous and Au-catalyzed reactions of isocyanides and amines, the Au surface provides a pathway for O_2 to react with the diaminocarbene intermediate that leads to a product that is very different from that obtained with the homogeneous metal ion catalysts.

Of course, carbodiimide products are only possible when the amine is a primary amine. With secondary amines, it is still possible for the amine to attack an adsorbed isocyanide, but the resulting intermediate **a** or **b** (Scheme 1) cannot react with O_2 to give a carbodiimide product. However, isocyanides do react (Eq. (6)) with secondary amines in the presence of gold powder, to



give ureas [36]. The reactions were performed under the same conditions ($60^\circ C$, hexane or MeCN solvent, 1.0 g of gold powder) that were used with the gold-catalyzed reactions of isocyanides with primary amines (Eq. (3)). The reaction occurs under 1 atm of air or O_2 , but the rate was slightly faster in the presence of pure O_2 , although this dependence was significantly less than first order in the O_2 concentration/pressure. When the reaction was run under an argon atmosphere, only a small amount ($\sim 1.5\%$) of the urea product formed, presumably due to the presence of adventitious O_2 . This formation of urea even under a very low pressure of O_2 means that the O_2 is highly reactive with intermediates on the gold surface. When *n*-BuNC was reacted with different concentrations of HNR'_2 under 1 atm of O_2 in MeCN solvent using 1.0 g of Au powder, the rate of the reaction increases as the amine concentration increases, although it was somewhat less than first order in the amine concentration. This amine dependence suggested that a key step in the reaction was nucleophilic attack of the secondary amine on the adsorbed isocyanide. Then, one would expect the rate of the catalyzed reaction to depend also on the steric and electronic properties of the amines. This is indeed observed as shown by the urea product yields (Table 1) obtained in reactions of *n*-BuNC with different secondary amines under a standard set of conditions ($60^\circ C$, MeCN solvent, 1 atm O_2 , 1.0 g gold powder). The yields were determined after 24 h of reaction. As compared with the bulky HNR'_2 , the cyclic and

Table 1
Gold metal-catalyzed reactions of *n*-BuNC with secondary amines and O_2 according to Eq. (6)^a

HNR'_2	Urea yield (%)
$HNPr'_2$	44
$HNPr'_2^b$	38
Piperidine	51
Morpholine	22
$HNPr'_2^c$	19

^a Reaction conditions: *n*-butyl isocyanide (2.0 mM), 80 mM amine, gold powder (1.0 g), O_2 (~ 1.0 L at ~ 1 atm), at $60^\circ C$ in 5 mL MeCN for 24 h.

^b Air instead of O_2 .

^c 1,1,3,3-Tetramethyl-*n*-butyl isocyanide (2.0 mM) instead of *n*-BuNC.

therefore sterically-smaller piperidine ((CH₂)₅NH) gives a higher yield (51%) of the corresponding urea. When morpholine (O(CH₂CH₂)₂NH), which is less nucleophilic but sterically-similar to piperidine, is reacted with *n*-BuNC, the yield (22%) of the urea is significantly lower. The higher p*K*_a of the protonated form of piperidine (11.2) as compared with that for morpholine (8.36) is an indicator of the higher nucleophilicity of piperidine. Therefore, both the steric and electronic properties of the amine have predictable effects on the rates of reaction.

To test for the effect of the bulkiness of the isocyanide on the rate of reaction, 1,1,3,3-tetramethyl-*n*-butyl isocyanide (CH₃)₃CCH₂C(CH₃)₂NC was reacted with HNPr₂² and O₂ under the standard conditions. As shown in the last entry in Table 1, this bulky isocyanide gives a significantly lower yield (19%) than *n*-BuNC (44%). The lower rate with the bulky isocyanide could reflect a lower isocyanide coverage on the Au surface [37] or a reduced rate of amine attack on the adsorbed isocyanide.

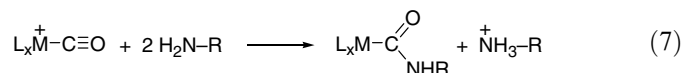
Results of the above studies can be reasonably understood in terms of a mechanism (Scheme 2) that is related to that proposed for the gold-catalyzed reactions (Eq. (3)) of isocyanides with primary amines (Scheme 1). The first step (1) in both of these mechanisms is amine attack on an adsorbed isocyanide to give an isocyanide–amine adduct **a**, which rearranges to the diaminocarbene intermediate **b**. The amine attack on adsorbed isocyanide is modeled by analogous reactions of amines with isocyanide ligands in metal complexes (Eq. (1)). The rate of this attack in both mechanisms (Schemes 1 and 2) plays a major role in influencing the overall rate of catalysis. In the reactions of *n*-BuNC with secondary amines, the rate of this first step (1) depends on the steric and electronic properties of the reacting amine, but the rate is somewhat less than first order in the amine concentration. The isocyanide–amine adduct (**a**) resulting from this attack presumably rearranges to the diaminocarbene intermediate **b** which reacts (step 3) with O₂ to give the urea product. The observed small dependence of the rate of the gold-catalyzed reaction of *n*-BuNC with HNPr₂² on the O₂ concentration suggests that step 3 (Scheme 2) is faster than step 1 but not by a large amount. Details of step 3 are not known, and there are no examples of reactions of diaminocarbene transition metal complexes with O₂ that lead to ureas. However, it is possible that the diaminocarbene groups on the gold surface add sufficient electron density to the gold metal that it adsorbs O₂, which reacts with the diaminocarbene intermediate **b** to give the urea product. Diaminocarbene ligands

are known to be strongly electron-donating ligands in transition metal complexes [38]. So, it is not unreasonable to propose that diaminocarbene groups add enough electron density to the gold metal that it reacts with O₂.

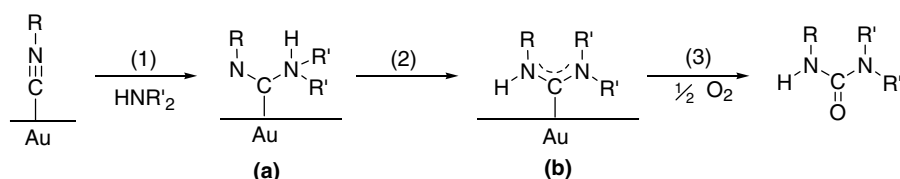
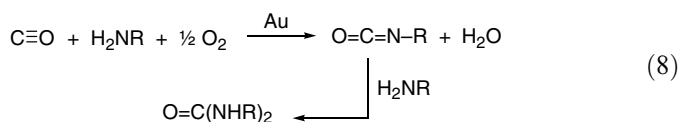
3. Carbon monoxide on gold: catalytic reactions with amines

As noted in the previous section, the susceptibility of isocyanide ligands in metal complexes to attack by amines (Eq. (1)) can be estimated from the $\nu(\text{N}\equiv\text{C})$ value of the isocyanide ligand. When this value is at least 40 cm⁻¹ higher than that of the free isocyanide, it is highly likely that amines will attack it to give diaminocarbene ligands. As the $\nu(\text{N}\equiv\text{C})$ values of isocyanides adsorbed on Au metal are approximately 80 cm⁻¹ higher than those of the free isocyanides, these isocyanides react with amines. It was these studies that led to the discovery of gold metal-catalyzed reactions of isocyanides with amines and O₂ (Eqs. (3) and (6)).

Carbon monoxide (C≡O), which is electronically-similar to isocyanides (C≡N–R), might be expected to also undergo attack by amines. In fact, reactions of amines with CO ligands in metal complexes to form carbamoyl complexes (Eq. (7)) occur when the $\nu(\text{C}\equiv\text{O})$ value of the CO



ligand is approximately 2000 cm⁻¹ or higher [39]. High $\nu(\text{C}\equiv\text{O})$ values are favored by metals (M) in positive oxidation states and/or by ligands (L) in the complex that are weakly electron-donating and/or strongly π -accepting such as CO. Although detectable amounts of CO are adsorbed on gold metal only at low temperatures (below ~150 K) [3,40], adsorbed CO has a relatively high $\nu(\text{C}\equiv\text{O})$ value of ~2100 cm⁻¹, which suggests that it would be susceptible to attack by amines. Despite the fact that little CO would adsorb on gold at room temperature, that adsorbed CO would be expected to undergo attack by primary amines. If it were to react in the same way as isocyanides with primary amines (Eq. (3)), one would expect the reaction to give organic isocyanates (Eq. (8)). The final products of the reaction would, however, be ureas



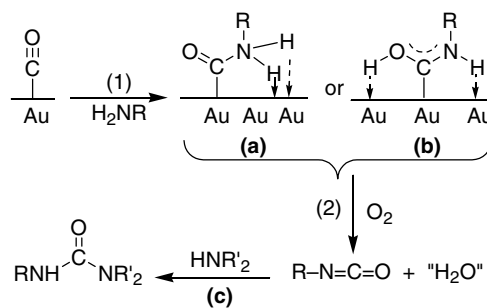
Scheme 2. Mechanism for the Au-catalyzed reaction (Eq. (6)) of isocyanides (R–N≡C) with secondary amines (HNR'₂) and O₂.

resulting from the subsequent reaction of the isocyanates with additional amine.

A series of reactions (Table 2) of CO, a primary amine, and O₂ were conducted over stirred gold powder in MeCN solvent at 45 °C [41]. The total gas pressure was approximately 1 atm with an approximately 2.5:1 ratio of CO and O₂, which were in stoichiometric excesses as compared with the amine. Ureas were the major products after a 24 h reaction time. The urea yields from reactions of three isomers of butylamine decreased as the bulkiness of the butyl group increased: *n*-BuNH₂ (46%) > *s*-BuNH₂ (12%) > *t*-BuNH₂ (2%). The less basic anilines, PhNH₂ (21%) and *p*-MeC₆H₄NH₂ (24%), gave lower yields than *n*-BuNH₂. Thus, as in the reactions of isocyanides (Eqs. (3) and (6)), the yields decrease as the size of the amine increases and its basicity decreases.

The above trends suggest that the initial step in the reaction (Scheme 3) is nucleophilic attack of the amine on adsorbed CO to give a CO–amine adduct (a) or an amino-oxocarbene (b) intermediate. It is also possible that this intermediate is deprotonated to leave an anionic carbamoyl group (–C(=O)(NHR)[–]), as occurs in metal complexes (Eq. (7)). Whatever is the nature of the intermediate, it must transfer the two hydrogen atoms initially on the amine to an oxygen atom to give the putative H₂O product (which has not been specifically identified). As for the analogous step (2 or 4 in Scheme 1) in reactions of isocyanides with primary amines and O₂ (Eq. (3)), there is little basis for proposing details for step 2 in Scheme 3. However, as noted for the isocyanide reactions, all of the possible intermediates in the reaction (a, b, or the carbamoyl group) would donate electron density to the gold which would make it more likely to activate O₂.

A key assumption in the proposed mechanism (Scheme 3) is that an isocyanate (R–N=C=O) is the initial product in the reaction; it reacts with additional amine to give the final urea product (Eq. (8)). There are several results that support the proposal that an isocyanate is the initial product: (1) The secondary amine HNPr₂² does not react with



Scheme 3.

CO and O₂ under the conditions of the primary amine reactions (Table 2). This would be expected because secondary amines are unable to form isocyanates. (2) Small amounts of the isocyanates are detected in some of the reactions (entries 1, 4, 5, 6, 8 in Table 2). (3) When equimolar PhNH₂ and HNPr₂² react with CO and O₂ in the presence of gold (entry 6 in Table 2), the product formed in highest yield (19%) is the mixed urea PhNH(C=O)NPr₂². This result is consistent with the initial formation of PhN=C=O, which subsequently reacts with HNPr₂² to give the mixed urea product. The higher known nucleophilicity [42] of HNPr₂², as compared with PhNH₂, would lead to preferential reaction of HNPr₂² with PhNCO to give PhNH(C=O)NPr₂², rather than PhNH(C=O)NHPh. Moreover, the reaction of 0.10 mmol of PhN=C=O with 0.50 mmol of both HNPr₂² and PhNH₂ under the conditions in Table 2 (but without gold) gives only the mixed urea PhNH(C=O)NPr₂². (4) When equimolar *n*-BuNH₂ and HNPr₂² are reacted (entry 7), the ratio of products *n*-BuNH(C=O)NPr₂²/*n*-BuNH₂C=O is 7.8. This is nearly the same ratio of these products (7.2) as that obtained from the reaction of *n*-BuNCO with equimolar *n*-BuNH₂ and HNPr₂² in the absence of gold; this result also supports the formation of *n*-BuNCO as an intermediate in the catalytic reaction. (5) In the reaction of equimolar *n*-BuNH₂ and PhNH₂ (entry 8), the major product is (*n*-BuNH)₂C=O (41%) with the

Table 2
Gold metal-catalyzed reactions of primary amines with CO and O₂ according to Eq. (8)^a

Entry	Amine (mmol)	Products	
		Urea (%)	Isocyanate (%)
1	<i>n</i> -BuNH ₂ (0.5)	46	<1, trace
2	<i>s</i> -BuNH ₂ (0.5)	12	0
3	<i>t</i> -BuNH ₂ (0.5)	2	0
4	PhNH ₂ (0.5)	21	3
5	<i>p</i> -MeC ₆ H ₄ NH ₂ (0.5)	24	3
6	PhNH ₂ /HNPr ₂ ² (0.5/0.5)	19 ^b	3, PhNCO
7	<i>n</i> -BuNH ₂ /HNPr ₂ ² (0.5/0.5)	39 ^c , 5 ^d	0, <i>n</i> -BuNCO
8	<i>n</i> -BuNH ₂ /PhNH ₂ (0.5/0.5)	41 ^d , 25 ^e	2, PhNCO; trace, <i>n</i> -BuNCO

^a At 45 °C in 5 mL MeCN solvent for 24 h with 1.00 g of Au powder; CO and O₂ total pressure = ~1 atm.

^b PhNH(C=O)NPr₂².

^c (*n*-Bu)NH(C=O)NPr₂².

^d (*n*-BuNH)₂C=O.

^e PhNH(C=O)NH(Bu^{*n*}).

mixed urea $\text{PhNH}(\text{C}=\text{O})\text{NHBu}^n$ formed in 25% yield. This is readily understood by considering $n\text{-BuNH}_2$ as a stronger nucleophile than PhNH_2 , which means that $n\text{-BuNH}_2$ is more likely to attack adsorbed CO to give $n\text{-BuNCO}$, which would react preferentially with $n\text{-BuNH}_2$ to give the major product $(n\text{-BuNH})_2\text{C}=\text{O}$. The smaller amount of mixed urea product $\text{PhNH}(\text{C}=\text{O})\text{NHBu}^n$ could form by competitive attack of PhNH_2 on adsorbed CO and/or on the $n\text{-BuNCO}$ intermediate.

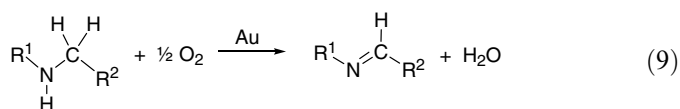
Because nanoparticles of gold are so active in catalytic reactions of CO [3,12–17], especially its oxidation with O_2 to give CO_2 , it was important to establish that nanogold was not the real catalyst of the reaction in Eq. (8). Of course, it had been shown previously that bulk gold, including gold powder, is a poor catalyst of CO oxidation [14,24], which indicates that gold nanoparticles are not present in bulk gold powder. So, it is unlikely that our gold powder contains nanoparticles. However, as a further test, we used our powdered gold to catalyze the reaction of CO (0.7 atm) with O_2 (0.3 atm) under the conditions in Table 2. This reaction gave no evidence for CO_2 at least above our detectability limit of a 0.1% yield for the reaction. Thus, it seems unlikely that nanogold particles are present in our powdered gold catalysts. It is interesting that a nanogold catalyst consisting of gold (<10 nm) supported on an ion exchange styrene–divinylbenzene polymer (Merck Ion Exchange IV) catalyzes reactions of anilines with CO (~40 atm) and O_2 (~10 atm) to give diarylureas [43]. It also catalyzes reactions of anilines with MeOH, CO, and O_2 to give carbamates $\text{ArNH}(\text{C}=\text{O})\text{OMe}$. These reactions were conducted under much more strenuous conditions (175 °C, ~50 atm gas pressure) than those used in the gold powder-catalyzed reactions (Eq. (8)) of anilines and other amines (Table 2), which suggests that the gold nanoparticles are less active than gold powder in the reaction in Eq. (8). On the other hand, the reaction of $n\text{-BuNH}_2$ with CO and O_2 under conditions in Table 2, except for the use of MeOH solvent instead of MeCN, did not give the carbamate $n\text{-BuNH}(\text{C}=\text{O})\text{OMe}$; only $(n\text{-BuNH})_2\text{C}=\text{O}$ was formed.

Another concern was that the gold powder might form soluble gold species under the conditions of the reactions, and these species might be the actual catalysts of the reaction in Eq. (8). These might be either gold (I or III) complexes resulting from oxidation of the gold metal and coordination by amine ligands or nanoparticles of a Au(0) colloid that is stabilized by adsorbed amine ligands. If a soluble form of gold were the catalyst, the reaction solution should be catalytically active after the gold powder was removed. To test for this possibility, a reaction of $n\text{-BuNH}_2$, CO, and O_2 with 1.0 g of gold powder, run under the conditions in Table 2, was stopped after 6 h when the $(n\text{-BuNH})_2\text{C}=\text{O}$ urea yield was only 13%. The reaction solution was then decanted from the gold powder, and the solution was returned to a CO/O_2 atmosphere. After reheating the solution to 45 °C with stirring for 15 h, no additional urea was formed, which shows that no catalytic

species were present in the solution, and the true catalyst was the gold powder.

4. Oxidative-dehydrogenation of amines to imines

During the course of our studies of gold-catalyzed reactions of isocyanides with amines and O_2 , we discovered that secondary amines, in the absence of an isocyanide, were oxidatively dehydrogenated to imines at rates that were slower than their reactions with isocyanides. Thus, at 60 °C in MeCN solvent, the reaction of $n\text{-BuNC}$ with piperidine ($(\text{CH}_2)_5\text{NH}$) and O_2 over powdered gold (Table 1) was nearly complete before significant amounts of the piperidine oxidative-dehydrogenation product was detected. The simplest examples of the oxidative-dehydrogenation of secondary amines occurred with di-*i*-propylamine, dibenzylamine, and 1,2,3,4-tetrahydroisoquinoline (Table 3) to give the corresponding imines (Eq. (9)) [44]. The presumed



H_2O product of the reaction was not experimentally identified, but the reaction required O_2 because dibenzylamine and 1,2,3,4-tetrahydroisoquinoline did not react when the O_2 atmosphere was replaced with argon. The reactions were performed in MeCN solvent at 60 °C for 40 h or in toluene at 100 °C for 24 h. It is evident from yields of the imine products in entries 1, 2 and 3 that benzyl amines undergo oxidative-dehydrogenation more rapidly than the alkyl amine (*i*-Pr) $_2\text{NH}$. The yields of the imine products in all of the reactions were significantly higher when they were run at the higher temperature (100 °C) in toluene. A small amount of isoquinoline, resulting from dehydrogenation of the $\text{CH}_2\text{-CH}_2$ bond in the initial oxidative-dehydrogenation product 3,4-dihydroisoquinoline, was detected when the reaction in entry 3 was run for longer times at

Table 3
Gold-catalyzed aerobic oxidation of secondary amines to imines according to Eq. (9) and Scheme 4^a

Entry	Substrate	Product	Yield [%]
1			15 ^b
2			35 ^b ; 64 ^c
3			40 ^b ; 87 ^c
4			46 ^b ; 93 ^c
5			41 ^b ; 75 ^c

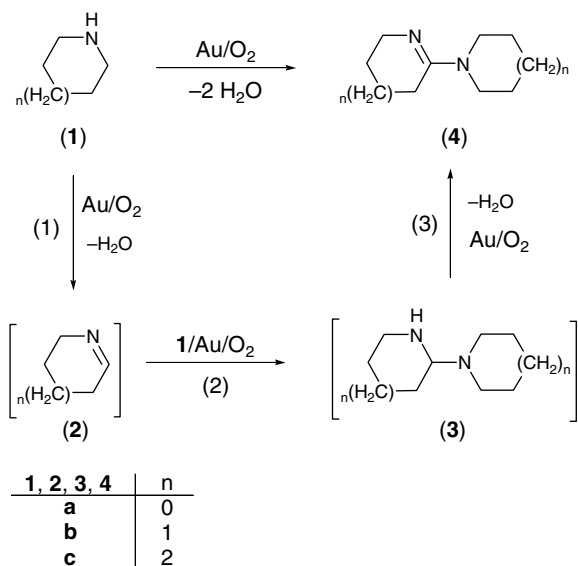
^a Reaction conditions: amine (0.20 mmol), 5 mL of solvent, gold powder (1.0 g), O_2 (~1.0 L at ~1 atm).

^b At 60 °C for 40 h in acetonitrile.

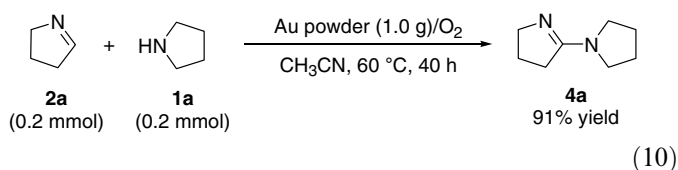
^c At 100 °C for 24 h in toluene.

100 °C. Although the oxidative-dehydrogenation of secondary amines with O₂ has been reported to be catalyzed by Ru/Al₂O₃ [45], catalysis of this reaction by bulk gold metal is surprising because of its poor catalytic activity in other reactions [3].

The cyclic secondary amines pyrrolidine ((CH₂)₄NH), piperidine ((CH₂)₅NH), and hexamethylene imine ((CH₂)₆NH), undergo a more complicated oxidative-dehydrogenation reaction that results in the coupling of two of the cyclic amines (Scheme 4). In MeCN solvent at 60 °C, the yields of the products (Table 3) decrease as the ring size increases from the 5-membered amine (46%) to the 7-membered amine (22%). The same products were obtained previously by the palladium-black catalyzed reaction of these amines under an inert atmosphere (argon), rather than O₂, at 80 °C [46]. A proposed mechanism for the coupling of the cyclic secondary amines is presented in Scheme 4. It involves initial oxidative-dehydrogenation (step 1) of the amine (1) to give the cyclic imine (2). This step is analogous to the oxidative-dehydrogenation reactions (Eq. (9)) that non-cyclic secondary amines undergo (entries 1, 2, and 3 in Table 3) under the same conditions. However, the less sterically-crowded cyclic imines react further to undergo attack by additional amine to give 3. There is no GC/MS evidence for intermediate 2 or 3 in samples of the reaction solution taken during the course of the reaction, which means that 2 and 3 must react faster than 1, and step 1 is the rate-determining step in the overall conversion of 1 to 4. To demonstrate that step 2 could occur under the conditions of the reaction, Δ¹-pyrroline (2a) was prepared [47] and reacted with 1a in the presence of gold powder under 1 atm of O₂ (Eq. (10)). This reaction gives product 4a without any evidence for intermediate 3a. As



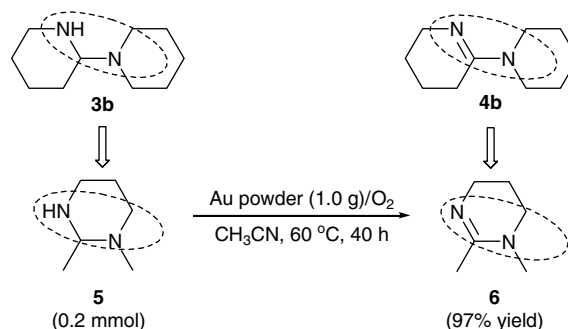
Scheme 4.



step 2 does not involve the reaction of O₂, the reaction of 2a and 1a was conducted also under an argon atmosphere. However, there was no reaction, which suggests that the equilibrium in step 2 lies to the left, which means that the oxidative-dehydrogenation of 3a to give 4a (step 3) provides the overall driving force for the conversion of 2a to 4a (Eq. (10)). (Another possible reason that the conversion of 2a to 3a does not occur in the absence of O₂ is that the O₂ activates the gold in some way.) It should also be noted that the reaction of 2a with 1a (Eq. (10)), which is nearly complete after only 20 h, is significantly faster than the overall conversion of 1a to 4a.

If 3 is indeed an intermediate in the conversion of 1 to 4, the oxidative-dehydrogenation of 3 must be fast as compared with step 1 and with the overall conversion of 1 to 4. However, compounds 3a–c are unknown, perhaps because the equilibrium in step 2 lies to the left, as suggested by the lack of a reaction between 2a and 1a (Eq. (10)) in the absence of O₂, as discussed above. So, compound 5 (in Scheme 5), which contains secondary and tertiary amine groups in the same relative positions as in 3b, was chosen as a model for the conversion of 3b to 4b. When 5 was reacted with O₂ under the standard conditions (Table 3), the formation of the imine 6 was nearly complete in only 10 h which is much faster than the oxidative-dehydrogenation of any of the secondary amines in Table 3. Therefore, step 3 in Scheme 4 is indeed likely to be much faster than the overall conversion of 1 to 4 and is consistent with step 1 being the rate-determining step in the overall conversion.

As a side note, one can understand why the oxidative-dehydrogenation of 5 to 6 is faster than that of 1b to 2b by considering the effect of amine groups on the dehydrogenation of hydrocarbons. The dehydrogenation (–H₂) of nitrogen-containing hydrocarbons, e.g., R₂N–CH₂–CH₃ → R₂N–CH=CH₂ + H₂, is thermodynamically more favorable than the dehydrogenation of simple hydrocarbon analogs, e.g., H₃C–CH₃ → H₂C=CH₂ + H₂ [48]. It has



Scheme 5.

also been found that the dehydrogenation of nitrogen-containing hydrocarbons is *kinetically* faster than the dehydrogenation of simple hydrocarbons over Pd/C and Rh/C heterogeneous catalysts at 110 °C [48]. It is therefore reasonable to assume that it is the tertiary amine group in **5** (and presumably in **3a–c**) that makes the oxidative-dehydrogenation of **5** faster than that of **1a–c** and the other amines in Table 3.

To determine whether or not the powdered gold was converted to catalytically-active soluble species such as gold colloids or gold complexes, the reaction of piperidine (**1b**) with O₂ (1 atm) in the presence of gold powder (1.0 g) at 60 °C in MeCN solvent (same conditions as in Table 3) was stopped after 6 h when the imine (**4b**) yield was only 9%. After the reaction solution was decanted from the gold powder, the solution was returned to an O₂ atmosphere and reheated to 60 °C for 15 h. The yield of **4b** remained at 9% indicating that there were no soluble gold species that were the actual catalysts of these reactions. Thus, as in the reactions of primary amines with CO and O₂, it is the bulk gold powder that is the actual catalyst of the oxidative-dehydrogenation of secondary amines.

5. Concluding comments

An initial goal of these investigations was to determine whether or not the reactivity of isocyanides adsorbed on gold metal could be predicted from our understanding of isocyanide reactivity in transition metal complexes. On the basis of the $\nu(\text{N}\equiv\text{C})$ values of isocyanides adsorbed on gold metal, it was expected that amines would attack them to give diaminocarbene groups. The observed reactions (Scheme 6) of adsorbed isocyanides with primary and secondary amines can be readily understood by assuming the amines attack the adsorbed isocyanides. High $\nu(\text{N}\equiv\text{C})$ values for isocyanides adsorbed on a variety of other metals [11] suggest that these metals too will activate isocyanides to nucleophilic attack by amines and other nucleophiles. After the initial attack, the resulting diaminocarbene reacts with O₂ by two different pathways depending on whether the amine is a secondary (path 1) or primary amine (path 2). Path (1) leads to cleavage of the Au–C bond with the formation of the urea. Although this appears to be a logical reaction, it is not a reaction that has been reported previously for diaminocarbene metal complexes. In fact, metal complexes with diaminocarbene ligands are often used as catalysts for oxidative reactions

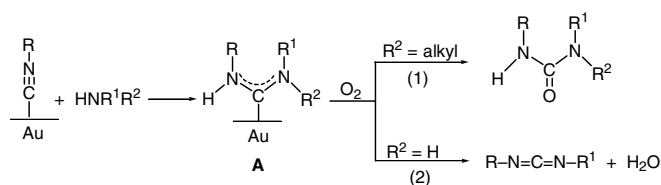
because the metal–diaminocarbene bond is so resistant to oxidative degradation [49]. Clearly, the gold metal surface must play a role in cleaving the metal–diaminocarbene bond. However, O₂ does not adsorb on bulk gold in detectable amounts at room temperature. So, it is presumably the strongly electron-donating ability of the diaminocarbene group [50] that makes the gold sufficiently electron-rich to react with O₂.

In contrast to the reactions (path 1) of diaminocarbene intermediates (**A** in Scheme 6) that lead to urea products, carbene intermediates derived from primary amines react (path 2) with O₂ by transferring two of its hydrogen atoms to O₂ to give H₂O and carbodiimide products. It is not clear why this intermediate **A** prefers to give a carbodiimide (path 2) rather than a urea (path 1). It is evident that the reactivity of diaminocarbene groups on gold metal surfaces requires further study.

By analogy with reactions of adsorbed isocyanides with amines (Scheme 6), carbon monoxide reacts (Eq. (8)) readily with primary amines and O₂ to give isocyanates (R–N=C=O). The first step in this reaction is presumably amine attack on an adsorbed CO, whose $\nu(\text{C}\equiv\text{O})$ value is sufficiently high that such an attack is expected on the basis of reactions of CO ligands in transition metal complexes. The nature of the resulting intermediate (Scheme 3) is less well-defined than that in the isocyanide reactions (Scheme 6), but it reacts with O₂ to give the isocyanate product while transferring two hydrogen atoms to O₂. It is presumably the strong electron-donating ability of the intermediate that activates the gold to react with O₂.

The final topic of this report is the oxidative-dehydrogenation of secondary amines. This is a very different type of reaction than those of isocyanides and CO. While it must involve cleavage of N–H and C–H bonds, together with a combining of hydrogen atoms with O₂, any mechanistic proposal for this reaction would be highly speculative at this stage. Attempts to catalyze the oxidative-dehydrogenation of secondary amines (Eq. (9)) [44], as well as the oxidative-amination of CO (Eq. (8)) [41], using copper and silver metal powders were unsuccessful.

One of the important results of these studies is that they demonstrate that bulk gold metal is capable of high catalytic reactivity in certain reactions. Although nano-gold catalysis is now a subject of intense current study, it is worth taking another look at the catalytic properties of bulk gold metal, the type of gold that is normally chosen for its inertness in decorative and electronic applications.



Scheme 6.

Acknowledgments

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