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Disciplines
Chemistry

Comments
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Catalytic Reactions of Carbene Precursors on Bulk Gold Metal

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Abstract: Bulk gold metal powder, consisting of particles (5–50 μm) much larger than nanoparticles, catalyzes the coupling of carbene generated from diazoalkanes (R2C≡N2) and 3,3-diphenylcyclopropene (DPCP) to form olefins. It also catalyzes cyclopropanation reactions of these carbene precursors with styrenes. The catalytic activity of the gold powder depends on the nature of the gold particles, as determined by TEM and SEM studies. The reactions can be understood in terms of mechanisms that involve the generation of carbene R2C intermediates adsorbed on the gold surface.

1. Introduction

Although nanosized gold particles (<5 nm) supported on metal oxides catalyze a variety of reactions including CO, hydrocarbon, and alcohol oxidation,1 bulk gold metal is well-known for its poor catalytic properties.1,2 We have shown recently3 that bulk gold powder with particle sizes of ∼50 μm is capable of catalyzing oxidative reactions of isocyanides,4,5 CO,5 and amines.5,6 Gold powder also catalyzes the oxidation (O2) of CO to CO2 and glycerol to glyceric and glycolic acids in basic (~pH 14) aqueous solution.7 In the oxidative reactions of isocyanides (C≡N−R) with secondary and primary amines, there is good evidence that adsorption of the isocyanide on gold activates it toward attack by amines (Scheme 1) to give a dianimocarbene intermediate (A) that reacts rapidly with O2 to give ureas (in the case of secondary amines) and carbodiimides (in the case of primary amines). In contrast to their high reactivities on gold metal, dianimocarbene ligands in transition metal complexes are usually unreactive,8 but their nonheteroatom analogues (:CR2) are very reactive.9 Goals of the research described herein were to explore the possibility that carbene (:CR2) not containing heteroatoms could be created on the surface of bulk gold and then to compare their reactivities with those of dianimocarbene.


Scheme 1

Transition metal carbene complexes have often been prepared by treating diazoalkanes (R2C≡N2) with unsaturated metal complexes.11,12 In the present studies, we sought to determine whether or not carbene groups (:CR2) could be created on a metal surface by treating diazoalkanes with gold metal powder. We anticipated that such carbene groups would react with each other or with other reactants that were present in the mixture. By analogy with reactions of :CR2 ligands in metal complexes,10 one would expect carbene groups to couple to give olefins (2 R2CN2 → R2C=CR2 + 2 N2), in the absence of other reactants. In the presence of olefins, carbene on the gold might be expected to give cyclopropanes, as is observed in transition metal complex-catalyzed reactions of diazoalkanes and olefins.10a
Another approach to the creation of carbene ligands in transition metal complexes is the reaction (eq 1) of 3,3-diphenylcyclopropene (DPCP) with unsaturated metal complexes (L₃M).13 Perhaps the most notable use of this reaction was in the synthesis of the first generation of Grubbs’ olefin metathesis and ring-opening metathesis polymerization catalysts [(Ph₃P)₂RuCl₂] and [Cp*RuCl]₂.14a and [Cp*RuCl]₂=CHCH=CPh₂.14c In addition, vinyl carbene complexes of Co,15 Ti,16 Zr,17 Ta,18 W,19 Ru,14 Os,20 and Re21 have been prepared using DPCP. If DPCP were to form vinyl carbene groups on a gold metal surface, one would expect them to couple with each other to give triene products and/or to react with olefins to give vinyl cyclopropanes. Through studies of these reactions of diazalkanes and DPCP, we sought to gain an understanding of factors that influence the formation of carbenes on metal surfaces and also to explore the differences in reactivities of carbenes in metal complexes and on a gold metal surface. The observed reactions also extend the range of reactions that are catalyzed by bulk gold metal.

2. Results and Discussion

2.1. Characterization of Bulk Gold Powder. Gold was chosen as the catalytic metal for these reactions because it does not react with O₂ to form surface oxides.16 This means that the surface gold atoms are in only the zero oxidation state, which was expected to simplify interpretations of the role of the gold metal in its catalytic reactions. The gold powder was prepared by dissolving gold metal in aqua regia to form HAuCl₄, which was reduced with hydroquinone according to a published procedure.22 The resulting dull brown powder was treated with freshly prepared “piranha solution” (H₂SO₄/H₂O₂, 3:1), washed with water and methanol, and then dried in an oven at 110 °C [see Experimental Section]. After this treatment, the gold powder had a dull brown appearance. Electron micrographs (Figure 1a) of one sample of this dull brown Au powder showed large particle sizes (~500 nm) with attached spines (Figure 1b) that had the overall appearance of a sea urchin. The spines consist of Au nanoparticles (black in Figure 1b) (~2 nm diameter) embedded in a carbon-containing matrix. At a magnification of 440 000× (Figure 1c), fringes in the individual gold nanoparticles are visible. They are parallel to each other in each nanoparticle, but the direction of the fringes is different for each nanoparticle. The fringe spacing (0.230 nm) corresponds well with the spacing between [111] planes of FCC gold metal (0.235 nm).23–25

XRD analysis of the gold powder showed diffraction peaks corresponding to the [111], [200], [220], [311], and [222] planes of cubic gold crystals (see Figure S2 in the Supporting Information).23–25 An energy dispersive X-ray (EDX) spectrum (see Figure S1 in the Supporting Information) of the body (~500 nm) of a sea urchin particle shows that it consists of only gold. An EDX spectrum of the spines (Figure S1) also shows only Au to be present. While the EDX analysis detected only gold in the spines, low atomic weight elements are not easily detected by EDX. However, it is clear from Figure 1b,c that another material is present between the gold nanoparticles in the spines. The fringe spacing (0.682 nm) of this material does not correspond to gold. To determine the chemical composition of the material between the gold nanoparticles, the energy filtration feature of the EELS was employed to image the spines. Specifically, the spectrometer was tuned to capture the location

\[
\text{L}_3\text{M} + \text{DPCP} \rightarrow \text{L}_3\text{M} = \text{CHCH = CPh}_2
\]
of carbon. As is evident in Figure 2c, the areas (white or gray) between the gold nanoparticles contain abundant carbon (small arrow). Carbon is also visible in the bright field (Figure 2a) and dark field (Figure 2b) micrographs. Also evident in Figure 2 is carbon on the surface of the large body of the sea urchin gold. Thus, the sea urchin gold particles consist of a large gold body that is coated with a carbon-containing material. Attached to this body are spines consisting of nanogold particles embedded in a carbon-containing matrix. The carbon-containing material has a large lattice spacing (0.682 nm) which is not consistent with graphite. Perhaps it is an organic material derived from the hydroquinone used to prepare the gold powder.

To understand how the morphology and composition of the gold metal affects its catalytic activity, 1.0 g of the dull brown Au powder with the sea urchin morphology was used as the catalyst for the reaction (eq 2) of 0.20 mmol of ethyl diazoacetate (EDA) in 5 mL of CH₃CN at 60 °C, while stirring with a magnetic stirbar in a round-bottom tube [see Experimental Section]. After 6 h, the reaction generated a 47% yield of diethyl maleate (cis-1) and diethyl fumarate (trans-1) in a ratio of 1.1:1. When the reaction was allowed to continue for a longer time (Figure 3), there was no increase in yield even though unreacted EDA was still present. It is not clear why the sea urchin gold becomes inactive during the reaction; perhaps an EDA-derived material deposits on the gold surface. After the first reaction, the gold, which now had a shiny gold appearance, was separated by filtration and washed with large amounts of CH₃CN, CH₂Cl₂, and MeOH. After the gold was treated with piranha solution, washed (H₂O/MeOH), and dried, an SEM image (Figure 4) of the powder showed much larger gold particles that had a very different morphology. This shiny gold powder was then used in a second reaction of EDA under the same conditions as the first cycle; this reaction was much faster than the first reaction giving a quantitative yield of the products after only 7 h (Figure 3). The high activity of the gold in the second run must be due to changes in the surface composition and morphology of the gold during the first reaction and to the CH₂Cl₂/MeOH washing prior to the second run. It is possible that a small amount of carbon-containing material remains on the gold surface in the second run. Throughout the course of the second run, the cis/trans ratio of the products was always in the range 1:1–1.1:1. When the gold was regenerated and reused in additional cycles, the initial rates decreased (Figure 3), but the overall yield still reached 90% even after 6 cycles. The decrease in activity may be due to incomplete removal of organic material from the surface, even after the piranha treatment. A parallel series of recycling reactions was performed in which the catalyst was only washed with CH₂Cl₂ and MeOH (without the piranha solution) before each cycle. The results were similar to those in Figure 3 (see Figure S4 in the Supporting Information), suggesting that the piranha treatment did not have a large effect.

Typically, the gold powder was used in 10 catalytic reactions before its activity had decreased to the point where it was beneficial to recycle the gold by converting it back to HAuCl₄.

**Figure 2.** Bright field (a), dark field (b), and energy-filtered (c) transmission electron micrographs (TEMs) of spines of the sea urchin gold. Micrograph (c) was tuned for carbon. In the upper right (large arrow), lacy carbon from the Cu grid is visible.

**Figure 3.** Effect of gold regeneration by piranha treatment on catalyst activity in the self-coupling of EDA (eq 2) using 0.20 mmol of EDA and 1.0 g of Au powder (with initial sea urchin morphology) in 5 mL of CH₃CN at 60 °C. The gold powder was washed with CH₃CN (5 × 30 mL), CH₂Cl₂ (5 × 30 mL), and MeOH (5 × 30 mL) and then treated with "piranha solution" before each cycle. (●) 1st cycle, (■) 2nd cycle, (▲) 3rd cycle, (○) 4th cycle, (□) 5th cycle, (●) 6th cycle.

**Figure 4.** Scanning electron microscopy (SEM) image at 15 000× magnification of the sea urchin gold after one cycle in the catalytic reaction of EDA (eq 2).
which was again reduced to Au powder. The activity of this regenerated dull brown Au powder was often somewhat lower than that of the originally prepared gold powder. It is not clear why the activity of the Au powder varied even though it was prepared in the same way. Perhaps even the piranha treatment did not completely remove organic material that deposited on the gold surface. It seems likely that the low catalytic activity of the freshly prepared sea urchin gold was due to the carbon-containing material that coated the gold.

Even the morphology of the fresh gold powder prepared by the hydroquinone reduction of HAuCl₄ varied. In one preparation, the gold particles (Figure S3) did not have the sea urchin shape (Figure 1). Instead, it consisted of much larger particles similar to those (Figure 4) of the sea urchin gold after it had catalyzed one cycle of the EDA reaction (eq 2). This gold (Figure S3) was more reactive in the first run than the sea urchin gold. As for the sea urchin gold, its dull brown appearance changed to shiny gold during the first reaction. The activity was higher in the second run but then decreased in subsequent runs, as was observed for the sea urchin gold (Figure 3).

Since a variety of reactions, including the formation of cyclopropanes from EDA and olefins,²⁶ are catalyzed by homogeneous Au(I) and Au(III) complexes,²⁷ we studied reaction 2 under conditions that would reveal the presence of solution-soluble catalytic species, such as gold complexes or gold (nano)particles, as the actual catalysts of reaction 2. A solution of EDA (0.20 mmol) in CH₃CN (5 mL) containing mesitylene (0.06917 mmol) as a GC standard was stirred in air at 60 °C with 1.0 g of gold powder; the gold used was in its most active form, as it had been used in only one previous reaction (see Figure 3). After 45 min of reaction, the yield of the olefin products was 25% with a cis/trans ratio of 1.03:1.00. The solution was then filtered from the gold and divided into two equal parts. One part (not containing gold powder) was heated to 60 °C for 5.5 h; no additional olefin product was formed. This indicated that there were no soluble catalytic species in the solution. To the other part of the reaction solution was added the original 1.0 g of gold powder; after 5.5 h at 60 °C, the yield of the olefin was now 100% with a 1.04/1.00 cis/trans ratio. Thus, the solid gold powder is necessary for the catalysis. Similar experiments performed in the gold powder-catalyzed reactions of CO, O₂, and primary amines to give ureas⁵ and the formation of oxazoles⁵ and other uncharacterized byproducts. Although trans olefins are thermodynamically more stable than their cis isomers,²⁸ the cis/trans ratios (1.1–3) favor the cis isomer in the gold-catalyzed reactions of phenyl diazomethane, EDA, and Me-MPDA (entries 1–6). These results are similar to those obtained in self-coupling reactions of PhCH=N=N₂ catalyzed by CuX (cis/trans = 1.3–2.5)²⁸ and those of EDA catalyzed by a ruthenium porphyrin complex Ru(tmp), where tmp is 5,10,15,20-tetramesitylporphyrin (cis/trans = 15).¹²α The yield of the olefin product 4 in reactions of α-diazoacetophenone (PhCOCH=N=N₂) is affected significantly by the solvent. In acetonitrile after 24 h, this reaction (eq 3) gave a 58% yield of the olefin product 4 (consisting primarily of the trans isomer, cis/trans = 13:87) and 42% of oxazole product 6 (entry 7, and eq 3) resulting from the reaction of the carbene intermediate with the MeCN solvent; in the absence of the gold powder, there is no reaction of PhCOCH=N=N₂. In toluene after 24 h, 4 was obtained in 70% yield with a cis/trans ratio of 42:58 (entry 8); some starting material was still present when the reaction was stopped. In 1,2-dichloroethane after 24 h, the yield of 4 was the highest (86%), and the cis-isomer was the favored product (cis/trans = 52:48, entry 9).

The formation of oxazole 6 in 42% yield in the reaction (eq 3) of PhCOCH=N=N₂ with MeCN solvent (entry 7) suggested that other nitriles might give substituted oxazoles. Unfortunately, the reaction of PhCOCH=N=N₂ in benzonitrile solvent gave no oxazole product and 4 in only 42% yield (cis/trans = 2:2:1). In propionitrile under the same conditions, 4 was formed in 65% yield (cis/trans = 1:4) but none of the oxazole.

A qualitative comparison of the self-coupling reactions (Table 1) of the diazoalkanes shows that the rates of reaction decrease in the following order: PhCH=N=N₂ > EDA > PhCOCH=N=N₂ ≈ Me-MPDA >> (MeO₂C)₂C≡C=N₂. At 60 °C, phenyl diazomethane reacts completely within 15–30 min, while the diazo esters and diazo ketone (EDA, Me-MPDA, PhCOCH=N=N₂) require more than 2 h, and dimethyl diazomalonate does not react at all (entry 10). At room temperature, the reaction of PhCH=N=N₂ is complete within 30 min, but EDA requires 48 h. The overall trend in

The generally accepted mechanism for transition metal complex-catalyzed olefin formation from diazo compounds involves initial formation of a metal carbene complex (M\(_{\text{d}}\)CR\(_2\)) which undergoes nucleophilic attack by another diazo molecule; this is followed by loss of N\(_2\) and double bond formation.\(^{12a,c}\) Mechanistic studies have ruled out a process involving olefin formation from the reaction of two metal carbene complexes (M\(_{\text{d}}\)CR\(_2\)). On the other hand, it was proposed that the self-coupling of PhCOCH\(_2\)N\(_2\) on Cu powder, which yielded olefin 4, could occur either by coupling of two adjacent :CHC(O)R groups on the Cu surface or by nucleophilic attack of PhCOCH\(_2\)N\(_2\) on the adsorbed :CHC(O)R.\(^{31}\) Either of these mechanisms could be involved in our gold powder-catalyzed reactions. Studies\(^{32,33}\) of reactions of the dinuclear complexes Cp\(_2\)Ru\(_2\)(µ-CH\(_2\))(CO)\(_2\)(NCH)\(_3\)\(^{30}\) and RhM(µ-CH\(_2\))(CO)\(_3\)(dpmm)\(^2+\), where M = Ru or Os\(^{33}\) and µ-CH\(_2\) is a bridging carbene ligand, with diazoalkanes have led to the conclusion that they proceed according to the mechanism in Scheme 2. Such a mechanism is reasonable for the coupling of carbene units on the gold metal surface. To our knowledge, the only previously reported studies of gold metal-catalyzed reactions of diazoalkanes were those of


Table 1. Self-Coupling of Carbene Precursors Catalyzed by Gold Powder

<table>
<thead>
<tr>
<th>entry</th>
<th>carbene precursor</th>
<th>solvent</th>
<th>time (h)</th>
<th>N(_2) or O(_2) yield (%)</th>
<th>product</th>
<th>cis/trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et(_2)CC=CHN(_2) (EDA)</td>
<td>CH(_3)CN</td>
<td>2</td>
<td>N(_2) 100</td>
<td>1</td>
<td>52:48</td>
</tr>
<tr>
<td>2</td>
<td>Et(_2)CC=CHN(_2) (EDA)</td>
<td>CH(_3)CN</td>
<td>2</td>
<td>O(_2) 100</td>
<td>1</td>
<td>55:45</td>
</tr>
<tr>
<td>3</td>
<td>PhCH=CHN(_2)</td>
<td>Toluene</td>
<td>0.5</td>
<td>N(_2) 92</td>
<td>2</td>
<td>55:45</td>
</tr>
<tr>
<td>4</td>
<td>PhCH=N(_2)</td>
<td>Toluene</td>
<td>0.5</td>
<td>O(_2) 91</td>
<td>2</td>
<td>52:48</td>
</tr>
<tr>
<td>5</td>
<td>(Me-MPDA)</td>
<td>CH(_3)CN</td>
<td>24</td>
<td>N(_2) 76(^{c})</td>
<td>3</td>
<td>75:25</td>
</tr>
<tr>
<td>6</td>
<td>(Me-MPDA)</td>
<td>CH(_3)CN</td>
<td>24</td>
<td>O(_2) 34(^{d})</td>
<td>3</td>
<td>71:29</td>
</tr>
<tr>
<td>7</td>
<td>PhCOCH=CHN(_2)</td>
<td>CH(_3)CN</td>
<td>24</td>
<td>air 58(^{e})</td>
<td>4</td>
<td>13:87</td>
</tr>
<tr>
<td>8</td>
<td>PhCOCH=CHN(_2)</td>
<td>Toluene</td>
<td>24</td>
<td>air 70(^{d})</td>
<td>4</td>
<td>42:58</td>
</tr>
<tr>
<td>9</td>
<td>PhCOCH=CHN(_2)</td>
<td>CI(_2)CH(_2)Cl</td>
<td>24</td>
<td>air 86</td>
<td>4</td>
<td>52:48</td>
</tr>
<tr>
<td>10</td>
<td>MeO(_2)C=OCH(_2)</td>
<td>CH(_3)CN</td>
<td>24</td>
<td>air N.R.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Ph(_2)</td>
<td>CH(_3)CN</td>
<td>4</td>
<td>air 82</td>
<td>5</td>
<td>40:60</td>
</tr>
</tbody>
</table>

\(^{a}\) 0.2 mmol of the diazo compound, 1.0 g of gold powder, 5 mL of solvent, 60 °C. \(^{b}\) Yields were determined by \(^1\)H NMR with Ph\(_3\)CH as the internal standard. \(^{c}\) cis/trans ratios were determined by GC and \(^1\)H NMR. \(^{d}\) Low yield due to the formation of azine and some uncharacterized byproducts. \(^{e}\) Low yield due to oxazole product 6. \(^{f}\) Low yield due to incomplete reaction.
diazomethane and diazoalkanes which gave the polymers, polyethylene and polyethylene, respectively, and small amounts of the olefins, ethylene and 2-butene; colloid gold was the catalyst in these reactions. More recently, polyethylene film formation from CH₂N₂ has been investigated on gold surfaces; such films on gold have been studied for their applications in the development of sensors.

Surface science studies of CH₂ precursors (CH₂N₂ or CH₂I₂) on metal surfaces (Pt(111), Ru(001), Pd(100), Rh(111), or Cu(110)) provide evidence for CH₂ on the metal surfaces, but the nature of the attachment of the CH₂ group to one or more metal atoms has not been established. Oxygen atoms and NH groups are isoelectronic with CH₂. Their formation on Au(111) is supported by spectroscopic studies and their chemical reactions.

As described in the Introduction, 3,3-diphenylcyclopropene (DPCP) is often used for the synthesis of vinyl carbene complexes (eq 1). The goal of this aspect of the project was to determine whether or not gold atoms on a gold metal surface were also capable of promoting the rearrangement of DPCP to vinyl carbene because it gives the same type of olefin product as DPCP.

In reactions where cross-coupling occurs, it is conceivable that the cross-coupled products are formed by metathesis of the stilbene product and/or the stilbene product which was noted in the self-coupling reactions in the previous section. On the other hand, reactions of EDA with PhCOCH=CH₂ (entry 7), EDA with Me-MPDA (entry 8), and PhCOCH=CH₂ with Me-MPDA (entry 9) all afforded the corresponding cross-coupled products 10, 11, and 12, respectively. Since EDA, PhCOCH=CH₂, and Me-MPDA had similar rates of self-coupling (see previous section), they are able to cross-couple with each other.

In the reactions of DPCP with PhCH=CH₂ (entry 3), EDA (entry 4), and PhCOCH=CH₂ (entry 5), cross-coupled products 7, 8, and 9 are observed, which suggests that they have similar self-coupling rates. On the other hand, the reaction of DPCP and Me-MPDA (entry 6) gave only self-coupled products 3 and 5, which indicates that DPCP undergoes more rapid self-coupling than Me-MPDA does. All of these results from the cross-coupling studies may be summarized by assuming the following order of self-coupling rates: PhCH=CH₂ > DPCP > EDA > PhCOCH=CH₂ > Me-MPDA. Cross-coupled products are observed only in reactions of reactants that have similar self-coupling rates.

This trend in self-coupling rates is also useful for understanding the relative amounts of cross-coupled and self-coupled products in the reactions. Thus, in the reaction of PhCH=CH₂ with DPCP (entry 3), the olefin products consist of relatively little of the cross-coupled products 7 (24%) together with self-coupled products 5 (18%) and 2 (58%) in the following ratios: cis-2/trans-2/cis-7/trans-7/cis-5/trans-5 = 29:29:10:14:8:10. However, in the reaction of EDA with DPCP (entry 4), the higher amount of cross-coupled product 8 (41%) as compared with self-coupled products 1 (22%) and 5 (37%) [cis-5/trans-5/cis-8/trans-8/cis-1/trans-1 = 16:21:21:20:8:14] indicates that DPCP and EDA are closer in reactivity than DPCP and PhCH=CH₂. The amounts of cross-coupled products formed in the other reactions in Table 2 can also be explained by the trend in self-coupling rates given in the previous paragraph.

In the reaction of PhCH=CH₂ and EDA (entry 1), where there is no cross coupling, the presence of PhCH=CH₂ reduces the rate of EDA self-coupling. This is indicated by the observation that only 50% of the EDA undergoes self-coupling after 24 h, while in the absence of PhCH=CH₂ (Table 1, entry 1), EDA undergoes 100% self-coupling in only 2 h under the same conditions. Thus, it appears that the more reactive PhCH=CH₂ and/or the stilbene product adsorbs preferentially on the gold, which reduces EDA adsorption and subsequent coupling.

In reactions where cross-coupling occurs, it is conceivable that the cross-coupled products are formed by metathesis of the self-coupled olefin products (eq 5), in which a surface carbene acts as the catalyst. That this does not occur was shown by an examination of the reaction of PhCH=CH₂ and DPCP (Table 2, entry 3), which gives 24% of the cross-coupled products 7.

When a mixture of DPCP/cis-stilbene/trans-stilbene (1:0.5:0.5) and gold powder (1.0 g) was heated in CH₂CN at 60 °C for 24 h, no cross-coupled product 7 was formed. Only the self-coupled products cis- and trans-5 (81% total yield) and unreacted cis- and trans-stilbene (in the same 1:1 cis/trans ratio) were present in the product mixture. In a study of the reaction (Table 2, entry 4) of DPCP and EDA, which gave a 41% yield...
of cross-coupled product 8, DPCP was reacted with diethyl maleate (cis-1) and diethyl fumarate (trans-1) under the above conditions. Again, no cross-coupled products were detected which rules out metathesis as the mechanism for the formation of the cross-coupled products in the reactions of different carbene precursors.

2.4. Cyclopropanation of Carbene Precursors with Olefins.

Another type of reaction that is characteristic of carbene ligands in transition metal complexes is their reaction with olefins to form cyclopropanes; there are many reactions of olefins with diazo compounds that are catalyzed by transition metal complexes. Therefore, reactions of a series of olefins and diazo compounds were investigated with gold powder as the catalyst (Table 3). The reactions were conducted at 80 °C for 24 h with a 100:1 olefin/diazo compound ratio because yields of the cyclopropanes were much lower at lower ratios. The excess olefin made the cyclopropanation reaction competitive with self-coupling of the diazo compound to give olefin 1. Uncharacterized byproducts, perhaps oligomers of styrene, were also detected in the GC of product mixtures.

As shown in Table 3 (entry 1), the reaction of EDA with styrene in toluene yielded 31% ethyl 2-phenylcyclopropanecarboxylate in a 27:73 cis/trans ratio. Using 1,2-dichloroethane as the solvent, instead of toluene, improved the yield of cyclopropanes to 45% (entry 2). Without the gold catalyst, the reaction of EDA with styrene (entry 3) gave a much lower yield (10%) of the cyclopropane products. As compared with styrene, 4-methylstyrene (4-Mestyrene) reacted with EDA to give a higher yield of cyclopropanes (54%, entry 4), while 4-methoxystyrene (4-MeOstyrene) generated a mostly uncharacterized product mixture and only a 6% yield of cyclopropanes (entry 5). 1-Hexene failed to react with EDA over gold powder either in 1,2-dichloroethane solvent or in 1-hexene as the solvent. Unreacted EDA was present in the final reaction mixture, which indicates that self-coupling of EDA to olefin 1 (Table 1) was inhibited by the 1-hexene. Cyclohexene and n-butyl vinyl ether do not react with EDA under the gold-catalyzed conditions; only the self-coupled olefins 1 are obtained in 52 and 65% yields, respectively. The reaction of PhCOCHdN2 in neat cyclohexene

Table 2. Cross Coupling of Carbene Precursors Catalyzed by Gold Powder

<table>
<thead>
<tr>
<th>entry</th>
<th>substrates</th>
<th>product</th>
<th>product ratio</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>PhCH=N2 + EDA</td>
<td>cis-2/trans-2/cis-1/trans-1</td>
<td>34:31:21:14</td>
<td>77</td>
</tr>
<tr>
<td>2d</td>
<td>PhCH=N2 + PhCO=CH=N2</td>
<td>cis-2/trans-4</td>
<td>30:27:20:23</td>
<td>81</td>
</tr>
<tr>
<td>3d</td>
<td>Ph=CH=N2 + Ph=CH=N2</td>
<td>cis-2/trans-7/cis-5/trans-5</td>
<td>29:29:10:14:10</td>
<td>51%</td>
</tr>
<tr>
<td>4d</td>
<td>Ph=CH=N2 + EDA</td>
<td>cis-5/trans-8/cis-1</td>
<td>16:21:21:20:8:14</td>
<td>75</td>
</tr>
<tr>
<td>6d</td>
<td>Ph=CH=N2 + Me-MPDA</td>
<td>cis-5/trans-3</td>
<td>25:31:31:13</td>
<td>46%</td>
</tr>
<tr>
<td>7d</td>
<td>EDA + PhCO=CH=N2</td>
<td>cis-1/trans-10/trans-10/cis-4/trans-4</td>
<td>11:5:24:20:14:25</td>
<td>69</td>
</tr>
</tbody>
</table>

- a 0.20 mmol of one substrate mixed with 0.20 mmol of another substrate, 1.0 g of gold powder, 5 mL of solvent at 60 °C for 24 h. b Ratios were determined by GC and 1H NMR. c Yields were determined by 1H NMR with Ph3CH as the internal standard. d Toluene solvent. e ClCH2CH2Cl solvent. f CH3CN solvent. g Low yields due to unidentified byproducts.

Table 3. Gold Metal-Catalyzed Cyclopropanation of Olefins

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Carbene Precursor</th>
<th>Solvent</th>
<th>Yield A (%)</th>
<th>cis/ trans A (%)</th>
<th>Yield B (%)</th>
<th>cis/ trans B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Styrene</td>
<td>EDA</td>
<td>toluene</td>
<td>31</td>
<td>27.73</td>
<td>5</td>
<td>73.27</td>
</tr>
<tr>
<td>2</td>
<td>Styrene</td>
<td>EDA</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>45</td>
<td>25.75</td>
<td>10</td>
<td>63.37</td>
</tr>
<tr>
<td>3</td>
<td>Styrene</td>
<td>EDA</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>10&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>26.74</td>
<td>0</td>
<td>50.50</td>
</tr>
<tr>
<td>4</td>
<td>4-MeStyrene</td>
<td>EDA</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>54</td>
<td>24.76</td>
<td>5</td>
<td>50.50</td>
</tr>
<tr>
<td>5</td>
<td>4-MeStyrene</td>
<td>EDA</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>16&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>29.71</td>
<td>N.D.&lt;sup&gt;‡&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Styrene</td>
<td>PhCOCH=CH&lt;sub&gt;N&lt;/sub&gt;</td>
<td>EDA</td>
<td>35</td>
<td>40.60</td>
<td>0</td>
<td>50.50</td>
</tr>
<tr>
<td>7</td>
<td>Styrene</td>
<td>PhCOCH=CH&lt;sub&gt;N&lt;/sub&gt;</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>19</td>
<td>0.10</td>
<td>39</td>
<td>32.68</td>
</tr>
<tr>
<td>8</td>
<td>Styrene</td>
<td>PhCOCH=CH&lt;sub&gt;N&lt;/sub&gt;</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>94&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>39.61</td>
<td>5</td>
<td>50.50</td>
</tr>
<tr>
<td>9</td>
<td>Styrene</td>
<td>PhCOCH=CH&lt;sub&gt;N&lt;/sub&gt;</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>86</td>
<td>80.20</td>
<td>12</td>
<td>50.50</td>
</tr>
<tr>
<td>10</td>
<td>Styrene</td>
<td>PhCOCH=CH&lt;sub&gt;N&lt;/sub&gt;</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>13&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>45.55</td>
<td>63</td>
<td>57.43</td>
</tr>
<tr>
<td>11</td>
<td>Styrene</td>
<td>PhCOCH=CH&lt;sub&gt;N&lt;/sub&gt;</td>
<td>CICH&lt;sub&gt;2&lt;/sub&gt;CHCl</td>
<td>87&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>61.39</td>
<td>7</td>
<td>53.47</td>
</tr>
</tbody>
</table>

<sup>‡</sup> 0.1 nmol of the diazo compound, alkene/diazo = 100:1, 1.0 g of gold powder, 30 mL of solvent, 80 °C, 24 h under N<sub>2</sub>.<sup>†</sup> Yields were determined by <sup>1</sup>H NMR with Ph<sub>3</sub>CH as the internal standard, based on uncharacterized byproducts. <sup>‡</sup>Cis/trans ratios were determined by GC and <sup>1</sup>H NMR. <sup>‡</sup>No catalyst. <sup>§</sup>Low yield due to uncharacterized byproducts. <sup>δ</sup> Room temperature, 24 h.

In gold-catalyzed reactions of styrene with other diazo compounds, PhCOCH=CH<sub>N</sub> reacts with neat styrene to give a 35% yield of the cyclopropane (entry 6), but much of the styrene polymerized; less than 5% cyclopropanation was observed in the absence of Au. When PhCOCH=CH<sub>N</sub> and styrene reacted in CICH<sub>2</sub>CHCl solvent with the gold catalyst, no cyclopropanation occurred; only 10% of the self-coupled olefin 4 was detected. The Au-catalyzed reaction of Me-MPDA with styrene also gave no cyclopropanation product in toluene solvent; even the yield of the self-coupled olefin product 3 was much lower (<5%) than that (76%) in the reaction of Me-MPDA in the absence of styrene (Table 1, entry 5) which suggests that styrene inhibits the self-coupling of Me-MPDA. Attempts to prepare cyclopropenes by reaction of alkynes (PhCCH, 4-MeOC<sub>2</sub>H<sub>4</sub>CHCH, 1-hexyne, and 3-hexyne) with EDA and PhCH=N=N with 100:1 RCCH/R<sub>1</sub>R<sub>2</sub>CN<sub>2</sub> in CICH<sub>2</sub>CHCl were unsuccessful.

The highly active PhCH=N=N reacts with styrene at 80 °C over 10 h, even in the absence of gold, to give a 94% yield of 1,2-diphenylcyclopropane as a cis/trans (39:61) mixture (entry 8). In the presence of gold powder, the same reaction yielded 86% cyclopropanes with reversed diastereoselectivity (cis/trans 80:20, entry 9) and 12% stilbenes 2. Thus, the gold influences the isomer selectivity of the reaction, although it does not improve the overall cyclopropane yield. At room temperature, the reaction of PhCH=N=N and styrene yielded 13% cyclopropanes and 63% stilbenes 2 using the gold catalyst (entry 10), while 87% cyclopropanes and only 7% stilbene 2 were produced in the absence of gold (entry 11). Thus, the yield of cyclopropanes is lower in the presence of the gold catalyst, because gold is such an effective catalyst for PhCH=N=N self-coupling.

3,3-Diphenylcyclopropane (DPCP) also reacted with styrene to afford a 19% yield of cyclopropanation product 13 as the trans isomer<sup>14c</sup> (entry 7 and eq 6); in the absence of Au, no cyclopropanation was observed. To our knowledge, the only previous example of the cyclopropanation of styrene with DPCP was catalyzed by the homogeneous complex (pybox)Cl<sub>2</sub>Ru(CH=CH=CPh<sub>2</sub>)<sub>2</sub>, where pybox is 2,6-bis(4(S)-isopropylpyrazol-2-yl)pyridine.<sup>14c</sup>

In all of these gold-catalyzed cyclopropanation reactions, a competing reaction is self-coupling of the diazo compound or DPCP to give the corresponding olefin. To minimize the self-coupling reactions, it is necessary to use a 100-fold excess of the olefin. Yet even then, the only olefins that gave cyclopropanation products are styrene and its substituted derivatives.

As in homogeneous cyclopropanation reactions catalyzed by Rh<sub>2</sub>(OAc)<sub>4</sub><sup>108</sup> and metalloporphyrins,<sup>39a–c</sup> <sup>45</sup> bulk gold favors the trans product in reactions of EDA (entries 2, 4, 5, 6). Although the mechanism of the gold-catalyzed cyclopropanation reactions is not known, it seems likely that they proceed through carbene intermediates adsorbed on the gold surface, which react with the olefin (either adsorbed or in solution) to give the cyclopropane products. To our knowledge, the only other metal that is reported to catalyze cyclopropanation is copper powder, which allow the overall cyclopropane yield. At room temperature, the reaction of PhCH=N=N and styrene yielded 13% cyclopropanes and 63% stilbenes 2 using the gold catalyst (entry 10), while 87% cyclopropanes and only 7% stilbene 2 were produced in the absence of gold (entry 11). Thus, the yield of cyclopropanes is lower in the presence of the gold catalyst, because gold is such an effective catalyst for PhCH=N=N self-coupling.

3. Conclusions

Diazoolkines (R<sub>C</sub>=N<sub>2</sub>) and 3,3-diphenylcyclopropane (DPCP) are well-established precursors for the synthesis of transition metal carbene complexes. In the present studies, these precursors...
behave as if they form carbene intermediates on bulk gold metal surfaces. The catalytic activity of the gold depends significantly on the morphology and composition (including the presence of carbon-containing material) of the metal surface; the freshly prepared sea urchin morphology (with incorporated carbon) is less active than the smoother gold powder that forms during its catalysis of the self-coupling of EDA (eq 2). The reactivities of the carbene intermediates generated from R₂C≡N and DPCP are quite different than those of the diaminocarbene intermediates investigated previously² (Scheme 1). Whereas the diaminocarbene is readily oxidized (O₂) to uraeas or carbamide, the nonheteroatom carbene generated in the present studies do not react with O₂ but instead undergo self- or cross-coupling to form olefins. The higher reactivity of diaminocarbenes with O₂ may result from their stronger electron-donor properties which make the gold surfaces sufficiently electron-rich to react with O₂.² It is also possible that the differences in reactivity are due to differences in their binding to the metal surface. Diaminocarbenes are more likely to prefer coordination to one gold atom while alkylidene-type carbenes (R₂C:) may prefer to bridge two gold atoms; these binding differences are observed in transition metal complexes.¹⁰⁻¹² The carbene coupling and cyclopropanation reactions of R₂C≡N and DPCP extend the range of bulk gold catalysis to reactions that are very different than the oxidative reactions reported previously.²⁻⁸

4. Experimental Section

4.1. General Methods. Acetonitrile and 1,2-dichloroethane were heated at reflux with CaH₂ under N₂ overnight and distilled before use. Toluene was heated at reflux under N₂ over sodium benzophenone and distilled before use. HAuCl₄ was purchased from Strem Chemicals, Inc.; triethylbenzylammonium chloride (TEBAC) and ethyl diazooacetate (EDA) were purchased from Sigma Aldrich and used as received. Styrene, 4-methylstyrene, 4-methoxystyrene, acrylonitrile, 1-hexene, phenylacetylene, 1-hexyne, and 3-hexyne were purchased from Sigma-Aldrich and purified by distillation before use. It was necessary to distill these substrates from the inhibitors as they prevented the cyclopropanation reactions from occurring. Methyl(4-methylphenyl)diazooacetate (Me-MPDA),¹⁰ 3,3-diphenylcyclopropene (DPCP),¹⁸ ₄¹ α-diazooacetophenone,²² di-methyl diazomalonate,²³ and PhCH=N=N₂²⁴ were prepared according to literature procedures.

Routine H and ¹³C NMR spectra were recorded on a Varian VXR-400 or Bruker DRX-400 spectrometer. Mass spectra were measured on a Finnigan TSQ 700 spectrometer. HRMS were recorded on a Kratos MS 50 mass spectrometer. Capillary gas chromatography was performed on an HP-6890 instrument equipped with an HP-5 column and flame ionization detector. GC–MS analyses were performed on a Finnigan TSQ 700 or Magnum ITD instrument. The morphologies and size of the gold powder samples were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM measurements were performed on a JOEL 840A microscope operated at 10 kV accelerating voltage and 0.005 nA beam current. The TEM measurements with energy dispersive X-ray analysis (EDX) were performed on a Tecnai G2 F20 microscope operated at 200 kV accelerating voltage. The samples were sonicated in isopropanol alcohol/water for 5 min, and then a drop of the suspension was placed on a lacy carbon copper grid (from Ted Pella, Inc.) and dried under ambient conditions. Electron Energy Loss Spectroscopy (EELS) images were obtained on a sea urchin gold sample that was sonicated in water for 5 min. A drop of the suspension was placed on a lacy carbon copper grid (from Ted Pella, Inc.). The Electron-diffused TEM (EPTEM) instrument was tuned for carbon and once the EELS images were optimized and was used to establish the location of carbon on the sea urchin gold particles. Energy dispersive X-ray analysis was used to establish the elemental composition of the gold powders. The powder XRD diffraction data were collected on a Scintag XRD 2000 X-ray diffractometer using Cu Kα radiation.

4.2. General Procedure for the Preparation of Gold Powder. Gold powder was prepared from HAuCl₄ by reduction with hydroquinone using a procedure similar to that published previously.²² A solution of hydrogen tetrachloroaurate hydrate (10 g, 0.029 mol) in 30 mL of water was heated to 100 °C, and a solution of hydroquinone (5.74 g, 0.052 mol) in 60 mL of hot water was added slowly (during 30 min) through an addition funnel. The mixture was maintained at ∼90 °C for 1 h, cooled to room temperature, and filtered; the gold was washed with methanol to remove the quinone product until the color of the filtrate changed from dark red to colorless. The gold powder was then extracted with methanol in a Soxhlet extractor for 16 h. After drying in an oven at 110 °C for at least 1 h, the dull brown gold powder (5.63 g, 99% yield) was treated with 80 mL of freshly prepared "piranha" solution (a 3:1 mixture of concentrated H₂SO₄ and 30% aqueous H₂O₂. CAUTION: Add H₂SO₄ to H₂O₂ in an ice bath) at room temperature in a large beaker with slow stirring. Vigorous foaming and gas evolution occurred during the first 30 min.³⁵ The mixture was stirred for another 16 h and was then diluted with 400 mL of distilled water. The gold was filtered on a coarse frit, washed 10 times with 100-mL aliquots of water followed by five 50-mL methanol washings, and dried in air. The dull brown Au powder was then heated overnight in air in a 110 °C oven and then cooled to room temperature.


4.3.1. Using Piranha Solution. After use in a catalytic reaction, the gold powder was filtered from HAuCl₄ by reduction with hydroquinone using a procedure similar to that published previously.²² A solution of hydrogen tetrachloroaurate hydrate (10 g, 0.029 mol) in 30 mL of water was heated to 100 °C, and a solution of hydroquinone (5.74 g, 0.052 mol) in 60 mL of hot water was added slowly (during 30 min) through an addition funnel. The mixture was maintained at ∼90 °C for 1 h, cooled to room temperature, and filtered; the gold was washed with methanol to remove the quinone product until the color of the filtrate changed from dark red to colorless. The gold powder was then extracted with methanol in a Soxhlet extractor for 16 h. After drying in an oven at 110 °C for at least 1 h, the dull brown gold powder (5.63 g, 99% yield) was treated with 80 mL of freshly prepared "piranha" solution (a 3:1 mixture of concentrated H₂SO₄ and 30% aqueous H₂O₂. CAUTION: Add H₂SO₄ to H₂O₂ in an ice bath) at room temperature in a large beaker with slow stirring. Vigorous foaming and gas evolution occurred during the first 30 min.³⁵ The mixture was stirred for another 16 h and was then diluted with 400 mL of distilled water. The gold was filtered on a coarse frit, washed 10 times with 100-mL aliquots of water followed by five 50-mL methanol washings, and dried in air. The Au powder was then dried in a 110 °C oven, after which it was cooled to room temperature for the next reaction cycle.

After many uses (∼10), the gold was dissolved in aqua regia to form HAuCl₄,²² which was converted back to gold powder according to the above procedures.

4.3.2. By Washing with Solvent. Following use in a catalytic reaction, the gold powder was filtered from the reaction mixture and washed with CH₂CN (5 × 30 mL), CH₃Cl₂ (5 × 30 mL), and then methanol (5 × 30 mL). After filtration, the gold was stirred with 40 mL of freshly made piranha solution for 16 h at room temperature. The mixture was diluted with 200 mL of distilled water and filtered. The gold was washed 10 times with 100-mL aliquots of water followed by five 50-mL methanol washings and dried in air. The Au powder was then reheated overnight in air in a 110 °C oven, after which it was cooled to room temperature for the next reaction cycle.

After many uses (∼10), the gold was dissolved in aqua regia to form HAuCl₄,²² which was converted back to gold powder according to the above procedures.

4.4. General Procedure for the Gold-Catalyzed Self-Coupling Reactions under N₂ and O₂. A septum-capped glass tube (2.5 cm × 18 cm, ∼65 mL volume) charged with gold powder (1.0 g) and a stir bar was evacuated under vacuum and backfilled with nitrogen; this procedure was repeated three times. A solution of the diazo compound (0.20 mmol) or 3,3-diphenylcyclopropene (0.20 mmol) was placed in a 110 °C oven and then cooled to room temperature.


in a degassed solvent (5 mL) was added by syringe under nitrogen. The mixture was stirred vigorously at 60 °C for the desired time and then worked up by filtration to remove the gold powder. After removing the solvent by rotary evaporation, triphenylmethane (0.03–0.05 mmol, internal standard) and CDCl₃ were added to the reaction mixture residue to determine yields and cis/trans ratios of the products by ¹H NMR spectroscopy.

The reactions under an O₂ atmosphere were conducted in the same way except all the reactants were combined in air, rather than under N₂. Then, a syringe needle attached to a rubber balloon (∼1.0 L) containing O₂ was inserted into the septum covering the tube opening. The reactions were carried out and worked up as described for the reactions under N₂.

4.5. General Procedure for the Catalytic Cross-Coupling Reactions. A mixture of one diazo compound (0.20 mmol) and a different diazo compound or 3,3-diphenylcyclopropene (0.20 mmol) and gold powder (1.0 g) in acetonitrile (5 mL) was prepared in a glass tube (2.5 cm × 18 cm, ∼65 mL volume). The tube was sealed with a rubber septum allowing inclusion of air, and the mixture was stirred vigorously (magnetic stir bar) at 60 °C for 24 h. After cooling to room temperature and removing the gold powder by filtration, the solvent was removed by rotary evaporation. Triphenylmethane (∼0.05 mmol) was added to the reaction mixture residue as an internal standard for ¹H NMR analysis in CDCl₃ solvent.

4.6. General Procedure for the Catalytic Cyclopropanation Reactions. A 100-mL three-necked round-bottomed flask charged with gold powder (1.0 g) was evacuated under vacuum and backfilled with N₂; this procedure was repeated three times. Degassed solvent (15 mL) and distilled alkene (10 mmol) were added through a septum by syringe. A solution of the diazo compound (0.1 mmol) in a solvent (15 mL) in an addition funnel was added dropwise over a period of 6 h at 80 °C under a N₂ atmosphere. After the addition was complete, the mixture was stirred vigorously at 80 °C for an additional 18 h. The mixture was filtered to remove the gold powder, and the solvent was removed by rotary evaporation. Triphenylmethane (∼0.03 mmol) was added to the reaction mixture residue as an internal standard to determine the yields and cis/trans ratios of products by ¹H NMR and GC.

Acknowledgment. This research was supported by the U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University. We thank Matthew J. Kramer for useful discussions.

Supporting Information Available: Reaction product spectroscopic characterizations, PhCH=N=N₂ synthesis, figure of recycled gold activity. This material is available free of charge via the Internet at http://pubs.acs.org.