

Catalytic Reactions of Carbene Precursors on Bulk Gold Metal

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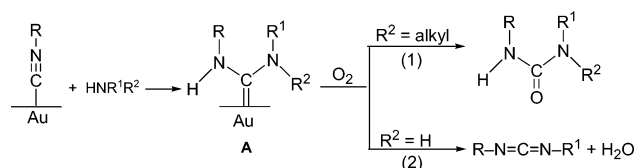
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Abstract: Bulk gold metal powder, consisting of particles (5–50 μm) much larger than nanoparticles, catalyzes the coupling of carbenes generated from diazoalkanes ($\text{R}_2\text{C}=\text{N}_2$) and 3,3-diphenylcyclopropane (DPCP) to form olefins. 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 R_2C : 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.^{1a} We have shown recently² that bulk gold powder with particle sizes of $\sim 50 \mu\text{m}$ is capable of catalyzing oxidative reactions of isocyanides,^{3,4} CO,⁵ and amines.^{6,7} Gold powder also catalyzes the oxidation (O_2) of CO to CO_2 and glycerol to glyceric and glycolic acids in basic ($\sim\text{pH}$ 14) aqueous solution.⁸ In the oxidative reactions of isocyanides ($\text{C}\equiv\text{N}-\text{R}$) 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 diaminocarbene intermediate (A) that reacts rapidly with O_2 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, diaminocarbene ligands in transition metal complexes are usually unreactive,⁹ but their nonheteroatom analogues ($:\text{CR}_2$) are very reactive.¹⁰ Goals of the research described herein were to explore the possibility that carbenes ($:\text{CR}_2$) not containing heteroatoms could be created on the surface of bulk gold and then to compare their reactivities with those of diaminocarbenes.

Scheme 1



Transition metal carbene complexes have often been prepared by treating diazoalkanes ($\text{R}_2\text{C}=\text{N}=\text{N}$) with unsaturated metal complexes.^{11,12} In the present studies, we sought to determine whether or not carbene groups ($:\text{CR}_2$) 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 $:\text{CR}_2$ ligands in metal complexes,^{10,12} one would expect carbene groups to couple to give olefins ($2 \text{R}_2\text{CN}_2 \rightarrow \text{R}_2\text{C}=\text{CR}_2 + 2 \text{N}_2$), in the absence of other reactants. In the presence of olefins, carbenes on the gold might be expected to give cyclopropanes, as is observed in transition metal complex-catalyzed reactions of diazoalkanes and olefins.^{10a}

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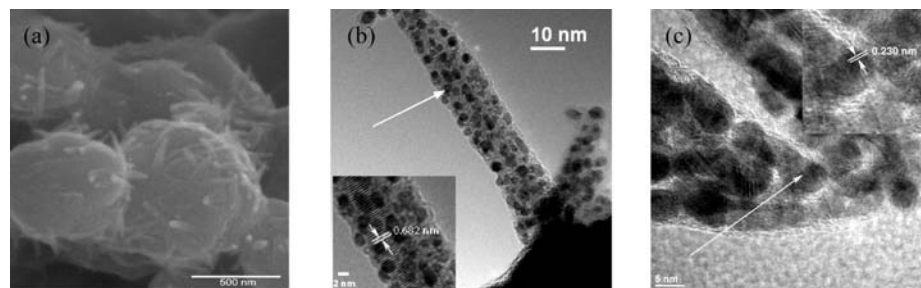
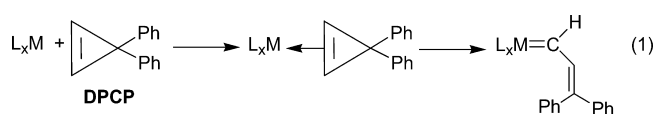


Figure 1. Electron micrographs of dull brown Au particles with sea urchin morphology. (a) Scanning electron microscopy (SEM) image measured at 50 000 \times magnification; (b) transmission electron microscopy (TEM) image measured at 64 000 \times magnification, with the inset showing an HRTEM image focusing on the lattice fringes; (c) TEM image measured at 440 000 \times , with the inset showing an HRTEM image focusing on the FCC lattice of the gold nanoparticles. The white arrows in (b) and (c) point to the areas that were magnified for the high resolution images (insets).

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 (L_xM).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 $[(\text{Ph}_3\text{P})_2\text{RuCl}_2]=\text{CHCH}=\text{CPh}_2$ ^{14a} and $[\text{Cp}^*\text{RuCl}_2]=\text{CHCH}=\text{CPh}_2$.^{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 diazoalkanes 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 carbene groups 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 O_2 to form surface oxides.^{1a} 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 HAuCl_4 , which was reduced with hydroquinone according to a published procedure.²² The resulting dull brown powder was treated with freshly prepared "piranha solution" ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, 3:1), washed with water and methanol, and then dried in an oven at 110 $^\circ\text{C}$ [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 \times (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 crystallites (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

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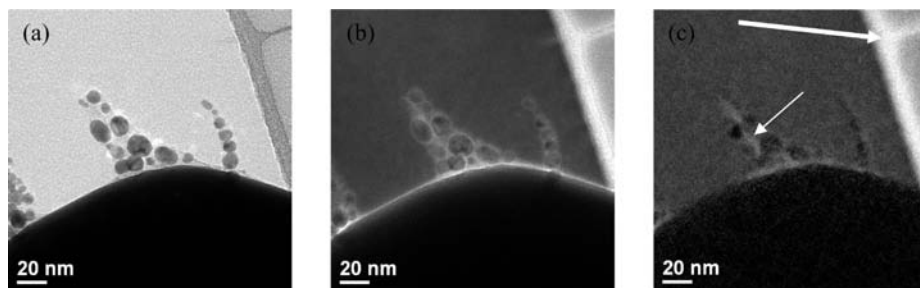
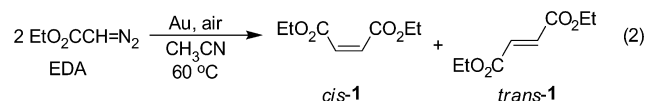


Figure 2. Bright field (a), dark field (b), and energy-filtered (c) transmission electron micrographs (TEMs) of spines of the sea urchin gold. Micrograph (c) was tuned for carbon. In the upper right (large arrow), lacy carbon from the Cu grid is visible.

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 CH_3CN 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 CH_3CN , CH_2Cl_2 , and MeOH. After the gold was treated with piranha solution, washed ($\text{H}_2\text{O}/\text{MeOH}$), 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 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

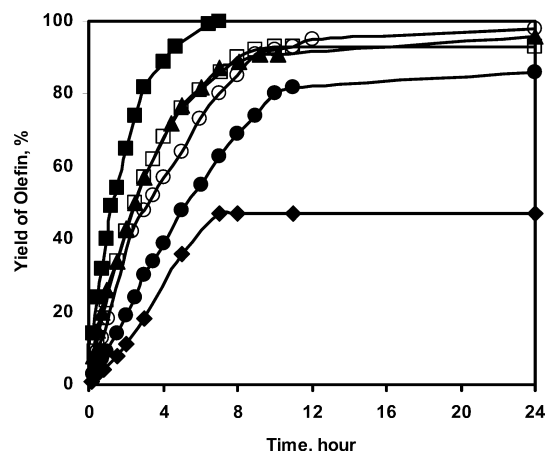


Figure 3. Effect of gold regeneration by *piranha* treatment on catalyst activity in the self-coupling of EDA (eq 2) using 0.20 mmol of EDA and 1.0 g of Au powder (with initial sea urchin morphology) in 5 mL of CH_3CN at 60 °C. The gold powder was washed with CH_3CN (5×30 mL), CH_2Cl_2 (5×30 mL), and 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.

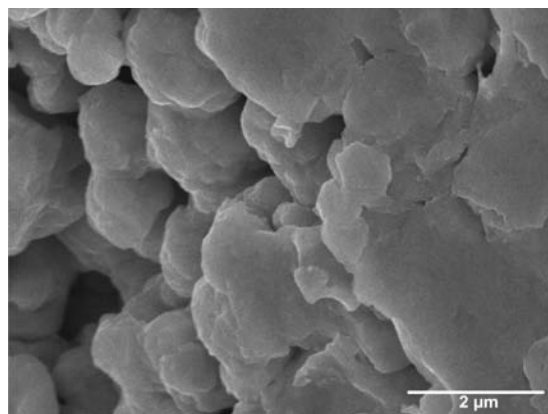
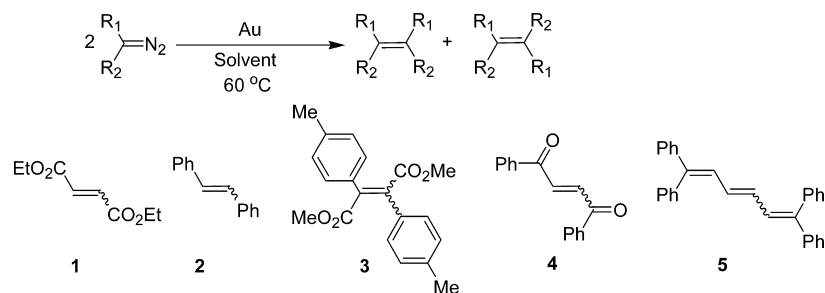
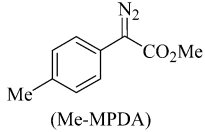
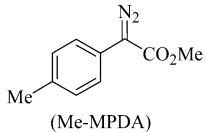
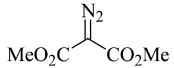



Figure 4. Scanning electron microscopy (SEM) image at 15 000× magnification of the sea urchin gold after one cycle in the catalytic reaction of EDA (eq 2).

surface, even after the *piranha* treatment. A parallel series of recycling reactions was performed in which the catalyst was only washed with CH_2Cl_2 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 HAuCl_4 ,

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

entry	carbene precursor	solvent	time (h)	N ₂ or O ₂	yield (%) ^b	product	cis/trans ^c
1	EtO ₂ CCH=N ₂ (EDA)	CH ₃ CN	2	N ₂	100	1	52:48
2	EtO ₂ CCH=N ₂ (EDA)	CH ₃ CN	2	O ₂	100	1	55:45
3	PhCH=N ₂	Toluene	0.5	N ₂	92	2	55:45
4	PhCH=N ₂	Toluene	0.5	O ₂	91	2	52:48
5	 (Me-MPDA)	CH ₃ CN	24	N ₂	76 ^d	3	75:25
6	 (Me-MPDA)	CH ₃ CN	24	O ₂	34 ^d	3	71:29
7	PhCOCH=N ₂	CH ₃ CN	24	air	58 ^e	4	13:87
8	PhCOCH=N ₂	Toluene	24	air	70 ^f	4	42:58
9	PhCOCH=N ₂	ClCH ₂ CH ₂ Cl	24	air	86	4	52:48
10		CH ₃ CN	24	air	N.R.		
11		CH ₃ CN	4	air	82	5	40:60

^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 ¹H NMR with Ph₃CH as the internal standard. ^c *Cis/trans* ratios were determined by GC and ¹H 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.

these diazoalkane reactivities is similar to that in their transition metal complex-catalyzed reactions.³⁰

The generally accepted mechanism for transition metal complex-catalyzed olefin formation from diazo compounds involves initial formation of a metal carbene complex (M=CR₂) which undergoes nucleophilic attack by another diazo molecule; this is followed by loss of N₂ 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=CR₂). On the other hand, it was proposed that the self-coupling of PhCOCH=N₂ 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=N₂ 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 Cp₂Ru₂(μ-CH₂)(CO)₂(NCMe)³⁰ and RhM(μ-CH₂)(CO)₃(dppm)²⁺, where M = Ru or Os³³ and μ-CH₂ 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

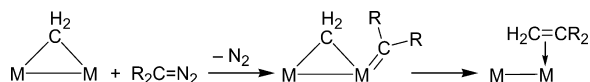
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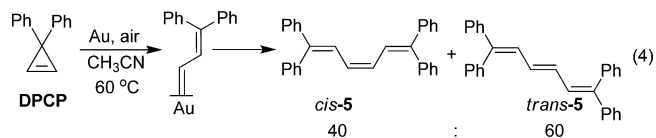
Scheme 2



diazomethane and diazoethane which gave the polymers, polymethylene and polyethylidene, respectively, and small amounts of the olefins, ethylene and 2-butene;³⁴ colloidal gold was the catalyst in these reactions. More recently, polymethylene film formation from CH_2N_2 has been investigated on gold surfaces; such films on gold have been studied for their applications in the development of sensors.³⁵

Surface science studies of CH_2 precursors (CH_2N_2 or CH_2I_2) on metal surfaces (Pt(111), Ru(001), Pd(100), Rh(111), or Cu(110)) provide evidence for CH_2 on the metal surfaces, but the nature of the attachment of the CH_2 group to one or more metal atoms has not been established.³⁶ Oxygen atoms and NH groups are isoelectronic with CH_2 . Their formation on Au(111) is supported by spectroscopic studies and their chemical reactions.³⁷

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 groups that would undergo self-coupling to give the corresponding olefin. Indeed, when DPCP was stirred with gold powder at 60 °C in CH_3CN for 4 h, an 82% yield of the triene product **5** was obtained in a 40:60 *cis/trans* ratio of isomers (eq 4 and Table 1, entry 11). In the absence of gold, no reaction occurred. In contrast, Grubbs reported that the homogeneously catalyzed self-coupling of DPCP with $[\text{Cp}^*\text{-RuCl}]_2=\text{CHCH}=\text{CPh}_2$ gave only *trans*-**5**,^{14c} while a tungsten complex $\text{WCl}_2(\text{O})[\text{P}(\text{OMe})_3]_3$ gave *cis*-**5** as the major product.^{19c} The mechanism of the gold-catalyzed coupling reaction (eq 4) is not known, but it seems likely to involve a surface-bound vinylcarbene because it gives the same type of olefin product



that is obtained from the self-coupling of diazoalkanes. To our knowledge, this is the first example of a reaction of DPCP that is catalyzed by a metal surface.

2.3. Cross-Coupling of Carbene Precursors. If surface carbene intermediates are formed in the self-coupling reactions, one might expect cross-coupled products when two different carbene precursors are present. This is observed in many cases, but not always as shown in Table 2. For example, the reactions of $\text{PhCH}=\text{N}_2$ with EDA (entry 1) and $\text{PhCH}=\text{N}_2$ with $\text{PhCOCH}=\text{N}_2$ (entry 2) gave only self-coupled products. During the course of the reaction of $\text{PhCH}=\text{N}_2$ with EDA, we observed that $\text{PhCH}=\text{N}_2$ was consumed first and converted entirely to *cis* and *trans* stilbene **2** within 2 h, but most of the EDA was still unreacted. After 24 h, the yield and *cis/trans* ratio of stilbenes did not change; however, more diethyl maleate (*cis*-**1**) and diethyl fumarate (*trans*-**1**) were produced, but still only 50% of the EDA had been converted to **1**. These results showed that the self-coupling of $\text{PhCH}=\text{N}_2$ is much faster than cross-coupling of $\text{PhCH}=\text{N}_2$ with EDA. Similarly, no cross-coupling occurred when $\text{PhCH}=\text{N}_2$ and $\text{PhCOCH}=\text{N}_2$ were present,

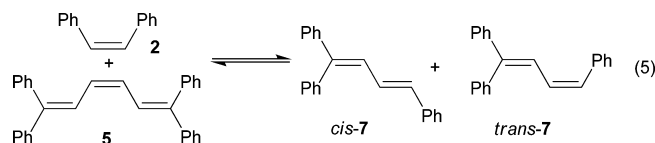
because of the fast self-coupling of $\text{PhCH}=\text{N}_2$, which was noted in the self-coupling reactions in the previous section. On the other hand, reactions of EDA with $\text{PhCOCH}=\text{N}_2$ (entry 7), EDA with Me-MPDA (entry 8), and $\text{PhCOCH}=\text{N}_2$ with Me-MPDA (entry 9) all afforded the corresponding cross-coupled products **10**, **11**, and **12**, respectively. Since EDA, $\text{PhCOCH}=\text{N}_2$, 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 $\text{PhCH}=\text{N}_2$ (entry 3), EDA (entry 4), and $\text{PhCOCH}=\text{N}_2$ (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: $\text{PhCH}=\text{N}_2 \gg \text{DPCP} > \text{EDA} > \text{PhCOCH}=\text{N}_2 > \text{Me-MPDA}$. Cross-coupled products are observed only in reactions of reactants that have similar self-coupling rates.

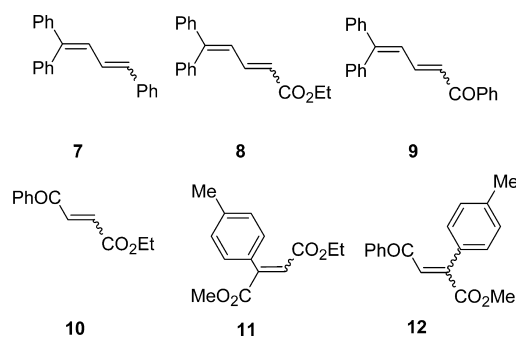
This trend in self-coupling rates is also useful for understanding the relative amounts of cross-coupled and self-coupled products in the reactions. Thus, in the reaction of $\text{PhCH}=\text{N}_2$ with DPCP (entry 3), the olefin products consist of relatively little of the cross-coupled products **7** (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 $\text{PhCH}=\text{N}_2$. 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 $\text{PhCH}=\text{N}_2$ and EDA (entry 1), where there is no cross coupling, the presence of $\text{PhCH}=\text{N}_2$ 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 $\text{PhCH}=\text{N}_2$ (Table 1, entry 1), EDA undergoes 100% self-coupling in only 2 h under the same conditions. Thus, it appears that the more reactive $\text{PhCH}=\text{N}_2$ and/or the stilbene product **2** 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 $\text{PhCH}=\text{N}_2$ 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 CH_3CN 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

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

entry	substrates	product	product ratio ^b	yield (%) ^c
1 ^d	PhCH=N ₂ + EDA	cis-2/trans-2/cis-1/trans-1	34:31:21:14	77
2 ^e	PhCH=N ₂ + PhCOCH=N ₂	cis-2/trans-2/cis-4/trans-4	30:27:20:23	81
3 ^d	PhCH=N ₂ +	cis-2/trans-2/cis-7/trans-7/cis-5/trans-5	29:29:10:14:8:10	51 ^g
4 ^f	+ EDA	cis-5/trans-5/cis-8/trans-8/cis-1/trans-1	16:21:21:20:8:14	75
5 ^e	+ PhCOCH=N ₂	cis-5/trans-5/cis-9/trans-9/cis-4/trans-4	6:12:20:22:19:20	55 ^g
6 ^f	+ Me-MPDA	cis-5/trans-5/cis-3/trans-3	25:31:31:13	46 ^g
7 ^e	EDA + PhCOCH=N ₂	cis-1/trans-1/cis-10/trans-10/cis-4/trans-4	11:5:24:20:14:25	69
8 ^f	EDA + Me-MPDA	cis-1/trans-1/cis-11/trans-11/cis-3/trans-3	10:5:30:25:22:8	76
9 ^e	PhCOCH=N ₂ + Me-MPDA	cis-4/trans-4/cis-12/trans-12/cis-3/trans-3	18:16:33:14:14:5	70

^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.

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.

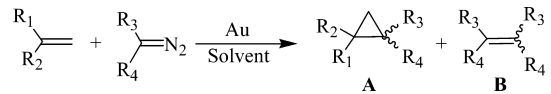
Another type of reaction that is characteristic of carbene ligands in transition metal complexes is their reaction with olefins to form cyclopropanes; there are many reactions of olefins with diazo compounds that are *catalyzed* by transition metal complexes.^{10,38} Therefore, reactions of a series 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 **A** were much lower at lower ratios. The excess olefin made the cyclopropanation reaction competitive with self-coupling of the diazo compound to give olefin **B**. 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 PhCOCH=N₂ in neat cyclohexene

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Table 3. Gold Metal-Catalyzed Cyclopropanation of Olefins^a


entry	alkene	carbene precursor	solvent	yield A (%) ^b	cis/trans ^c	yield B (%) ^b	cis/trans ^c
1	styrene	EDA	toluene	31	27:73	5	73:27
2	styrene	EDA	CICH ₂ CH ₂ Cl	45	25:75	10	63:37
3	styrene	EDA	CICH ₂ CH ₂ Cl	10 ^e	26:74	0	
4	4-Mestyrene	EDA	CICH ₂ CH ₂ Cl	54	24:76	5	
5	4-MeOstyrene	EDA	CICH ₂ CH ₂ Cl	6 ^f	29:71	N.D. ^d	
6	styrene	PhCOCH=N ₂	styrene	35	40:60	0	
7	styrene		CICH ₂ CH ₂ Cl	19	0:100	39	32:68
8	styrene	PhCH=N ₂	CICH ₂ CH ₂ Cl	94 ^e	39:61	5	50:50
9	styrene	PhCH=N ₂	CICH ₂ CH ₂ Cl	86	80:20	12	50:50
10	styrene	PhCH=N ₂	CICH ₂ CH ₂ Cl	13 ^e	45:55	63	57:43
11	styrene	PhCH=N ₂	CICH ₂ CH ₂ Cl	87 ^{e,8}	61:39	7	53:47

^a 0.1 mmol of the diazo compound, alkene/diazo = 100:1, 1.0 g of gold powder, 30 mL of solvent, 80 °C, 24 h under N₂. ^b Yields were determined by ¹H NMR with Ph₃CH as the internal standard, based on the diazo compounds. ^c Cis/trans ratios were determined by GC and ¹H NMR. ^d Not determined. ^e No catalyst. ^f Low yield due to uncharacterized byproducts. ^g Room temperature, 24 h.

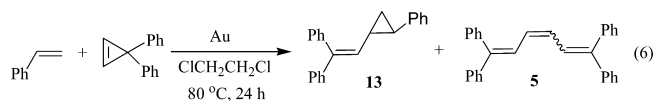
gave only the self-coupled olefins **4** in a 1.3:1.0 *cis/trans* ratio. As for the gold powder catalyzed cyclopropanation reactions, the homogeneous Fe(TTP) (TTP = *meso-tetra-p-tolylporphyrin*) catalyzes cyclopropanation reactions of styrenes with EDA much faster than reactions of nonaryl alkenes; it also catalyzes more electron-rich styrenes (e.g., 4-methylstyrene) faster than styrene itself.^{38a} On the other hand, the reaction of styrene with EDA is only slightly faster than that of 1-decene when the catalyst is Rh(TTP)(I).^{38k} Possible reasons for the differences in olefin reactivity using the iron and rhodium complexes have been discussed.^{38a}

In gold-catalyzed reactions of styrene with other diazo compounds, PhCOCH=N₂ 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=N₂ and styrene were

reacted in ClCH₂CH₂Cl 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-MeOC₆H₄CCH, 1-hexyne, and 3-hexyne) with EDA and PhCH=N₂ with 100:1 RCCH/R¹R²CN₂ in ClCH₂CH₂Cl in the presence of gold powder at 80 °C were unsuccessful.

The highly active PhCH=N₂ 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=N₂ 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=N₂ self-coupling.

3,3-Diphenylcyclopropene (DPCP) also reacted with styrene to afford a 19% yield of cyclopropanation product **13** as the *trans* isomer^{14e} (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)₂Ru-(CH=CH=CPh₂), where pybox is 2,6-bis(4(S)-isopropylloxazolin-2-yl)pyridine.^{14e}

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 Rh₂(OAc)₄^{10b} and metalloporphyrins,^{38a-c} 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 has been used in a variety of organic syntheses.³⁹

3. Conclusions

Diazoalkanes (R₂C=N₂) and 3,3-diphenylcyclopropene (DPCP) are well-established precursors for the synthesis of transition metal carbene complexes. In the present studies, these precursors

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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 $R_2C=N_2$ and DPCP are quite different than those of the diaminocarbene intermediates investigated previously² (Scheme 1). Whereas the diaminocarbenes are readily oxidized (O_2) to ureas or carbodiimides, the nonheteroatom carbenes generated in the present studies do not react with O_2 but instead undergo self- or cross-coupling to form olefins. The higher reactivity of diaminocarbenes with O_2 may result from their stronger electron-donor properties which make the gold surfaces sufficiently electron-rich to react with O_2 .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 ($R_2C:$) may prefer to bridge two gold atoms; these binding differences are observed in transition metal complexes.^{10c,d} The carbene coupling and cyclopropanation reactions of $R_2C=N_2$ 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 CaH_2 under N_2 overnight and distilled before use. Toluene was heated at reflux under N_2 over sodium benzophenone and distilled before use. $H AuCl_4$ was purchased from Strem Chemicals, Inc.; triethylbenzylammonium chloride (TEBAC) and ethyl diazoacetate (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)diazoacetate (Me-MPDA),⁴⁰ 3,3-diphenylcyclopropene (DPCP),^{18,41} α -diazoacetophenone,⁴² dimethyl diazomalonate,⁴³ and $PhCH=N_2$ ⁴⁴ were prepared according to literature procedures.

Routine 1H and ^{13}C 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 morphology and size of the particles in gold powder samples were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM measurements were performed on a JEOL 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 isopropyl 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 Energy Filtered TEM (EFTEM) instrument was tuned for carbon 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 $Cu K\alpha$ radiation.

4.2. General Procedure for the Preparation of Gold Powder.

Gold powder was prepared from $H AuCl_4$ 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 H_2SO_4 and 30% aqueous H_2O_2). CAUTION: Add H_2SO_4 to H_2O_2 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.⁴⁵ 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. Regeneration/Recycling of the Gold Powder Catalyst.

4.3.1. Using Piranha Solution. After use in a catalytic reaction, the gold powder was filtered from the reaction mixture and washed with CH_3CN (5×30 mL), CH_2Cl_2 (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 heated 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 $H AuCl_4$,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 CH_3CN (5×30 mL), CH_2Cl_2 (5×30 mL), and then methanol (5×30 mL). The gold powder was dried in an oven overnight at 110 °C. After cooling to room temperature, it was used in the next cycle. The use of gold that was recycled in this way is shown in Figure S4 of the Supporting Information.

4.4. General Procedure for the Gold-Catalyzed Self-Coupling Reactions under N_2 and O_2 . A septum-capped glass tube (2.5 cm \times 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)

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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.

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

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