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Diazirine-Modified Gold Nanoparticle: Template for Efficient Photoinduced Interfacial Carbene Insertion Reactions

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Received June 29, 2010. Revised Manuscript Received August 12, 2010

Photolysis of a 3-aryl-3-(trifluoromethyl)diazirine-modified monolayer-protected gold nanoparticles (**2**-C$_{12}$MPNs), with a core size of 1.8 ± 0.3 nm, in the presence of model carbene trapping reagents leads to efficient, essentially quantitative, modification of the interface via carbene insertion reactions. The utility of carbene insertion reactions as a general approach for the modification of Au-MPNs to provide a breadth of new structures available was demonstrated using acetic acid, methanol, benzyl alcohol, phenol, benzylamine, methyl acrylate, and styrene (**10a−g**, respectively) as electrophilic carbene trapping agents to form the corresponding modified **3a−g**-C$_{12}$MPNs. The 1.8 ± 0.3 nm gold nanoparticles bearing a diazirine group (**2**-C$_{12}$MPNs) were synthesized using the ligand exchange reaction with the requisite 3-aryl-3-(trifluoromethyl)diazirinealkylthiol. The **2**-C$_{12}$MPNs and the resulting products of the reaction on the MPN (**3a−g**-C$_{12}$MPN) were fully characterized by IR, ^{1}H NMR, and ^{19}F NMR spectroscopy and, when applicable, transmission electron microscopy (TEM). Verification for the **3a−g**-C$_{12}$MPNs was accomplished by comparison of the spectral data to those of obtained for the photoreactions of 3-(3-methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirine as a model with **10a−g**.

Introduction

Monolayer-protected gold nanoparticles (Au-MPNs) continue to be an active area of discovery because of their unique chemical and physical properties as well as potential applications in catalysis,[1] sensors,[2] drug delivery,[3] and nanomedicine.[4] The key to their use in any application is the ability to prepare Au-MPNs with a specific chemical functionality for the interaction or reaction required. The ability to chemically modify nanoparticles by a direct interfacial reaction of terminal functional groups, exposed on the surface of Au-MPNs, with various reactants is a critical and important goal.[5] Because of this, the chemical modification of Au-MPNs has been the subject of numerous studies, and a host of reaction types have been explored at the interface, including esterifications,[6] siloxane formation reaction,[7] nucleophilic substitutions,[8] transition-metal-catalyzed ring-opening metathesis polymerization (ROMP),[9] coupling reaction of aliphatic hydroxyl group,[10] reductive amination reaction,[11] Michael additions,[12] 1,3-dipolar cycloadditions,[13] Diels−Alder reactions,[14] Grignard reactions,[15] and olefin cross-metathesis.[16] While some reactions are efficient at ambient temperatures, many reaction types require refluxing conditions or catalysts and the low stability of the Au-MPNs in the 1−5 nm in diameter size regime to higher temperatures (> 50 °C) and some catalysts limit the efficacy. The need to perform reactions on Au-MPNs under relatively mild and low temperature conditions limits the types of reactions that can be done efficiently and quantitatively in these systems. In addition, reactions of the monolayer moieties on the Au-MPNs are typically slower (less efficient) relative to similar reactions in the solution phase because of the reaction environment provided at the interface.[12−15] Therefore, finding efficient interfacial reactions that work under mild reaction conditions is an important challenge in Au-MPNs applications. In our own attempts to extend the types of reactions that can be utilized for efficient interfacial modifications of Au-MPNs, we examined some Diels−Alder and 1,3-diploar cycloadditions. These particular reactions were found to be generally too slow to be useful at ambient temperatures but showed that high pressure conditions can be used as an efficient tool to facilitate these reactions on the Au-MPNs with high yields and with no detrimental effects on the gold core.[13c,d,14]

Photochemical reactions of suitably functionalized Au-MPNs can also be utilized to perform chemical modifications under

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(1) (a) Corma, A.; Garcia, H. *Chem. Soc. Rev.* **2008**, *37*, 2096 and references therein . (b) Juárez, R.; Corma, A.; García, H. *Green Chem.* **2009**, *11*, 949. (c) Conte, M.; Miyamura, H.; Kobayashi, S.; Chechik, V. *J. Am. Chem. Soc.* **2009**, *131*, 7189. (d) Raptis, C.; Garcia, H.; Stratakis, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3133.

(2) (a) Wang, Z.; Ma, L. *Coord. Chem. Rev.* **2009**, *253*, 1607 and references therein . (b) Sperling, R. A.; Rivera, P. G.; Zhang, F.; Zanella, M.; Parak, W. J. *Chem. Soc. Rev.* **2008**, *37*, 1896 and references therein .

(3) (a) Ghosh, P.; Han, G.; De, M.; Kim, C. K.; Rotello, V. M. *Adv. Drug Delivery Rev.* **2008**, *60*, 1307 and references therein . (b) Nakanishi, J.; Nakayama, H.; Shimizu, T.; Ishida, H.; Kikuchi, Y.; Yamaguchi, K.; Horiike, Y. *J. Am. Chem. Soc.* **2009**, *131*, 3822. (c) Elbakry, A.; Zaky, A.; Liebl, R.; Rachel, R.; Goepferich, A.; Breunig, M. *Nano Lett.* **2009**, *9*, 2059. (d) Prabaharan, M.; Grailer, J. J.; Pilla, S.; Steeber, D. A.; Gong, S. *Biomaterials* **2009**, *30*, 6065.

(4) Boisselier, E.; Astruc, D. *Chem. Soc. Rev.* **2009**, *38*, 1759.

(5) Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293.

(6) Brust, M.; Fink, J.; Bethella, D.; Schiffrina, D. J.; Kielyb, C. *J. Chem. Soc., Chem. Commun.* **1995**, 1655.

(7) Buining, P. A.; Humbel, B. M.; Philipse, A. P.; Verkleij, A. J. *Langmuir* **1997**, *13*, 3921.

(8) Templeton, A. C.; Hostetler, M. J.; Kraft, C. T.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 1906.

(9) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462.

(10) Friggeri, A.; Van Manen, H. J.; Auletta, T.; Li, X. M.; Zapotoczny, S.; Schönherr, H.; Vancso, G. J.; Huskens, J.; Van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2001**, *123*, 6388.

(11) Otsuka, H.; Akiyama, Y.; Nagasaki, Y.; Kataoka, K. *J. Am. Chem. Soc.* **2001**, *123*, 8226.

(12) Koenig, S.; Chechik, V. *Langmuir* **2003**, *19*, 9511.

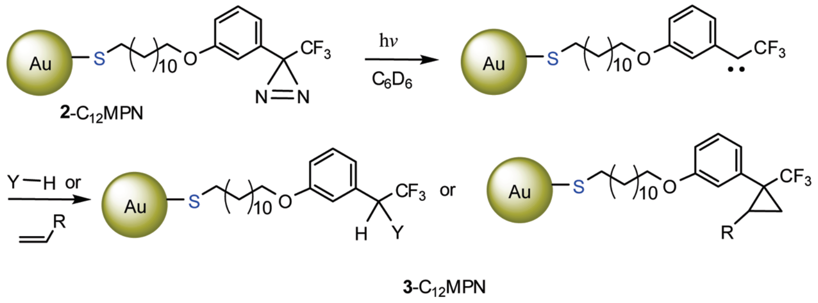
(13) (a) Fleming, D. A.; Thode, C. J.; Williams, M. E. *Chem. Mater.* **2006**, *18*, 2327. (b) Sommer, W. J.; Weck, M. *Langmuir* **2007**, *23*, 11991. (c) Zhu, J.; Lines, B. M.; Ganton, M. D.; Kerr, M. A.; Workentin, M. S. *J. Org. Chem.* **2008**, *73*, 1099. (d) Ismaili, H.; Alizadeh, A.; Snell, K. E.; Workentin, M. S. *Can. J. Chem.* **2009**, *87*, 1708.

(14) Zhu, J.; Ganton., M.; Kerr, M. A.; Workentin, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 4904.

(15) Thode, C. J.; Williams, M. E. *Langmuir* **2008**, *24*, 5988.

(16) Ornelas, C.; Méry, D.; Cloutet, E.; Aranzaes, J. R.; Astruc, D. *J. Am. Chem. Soc.* **2008**, *130*, 1495.

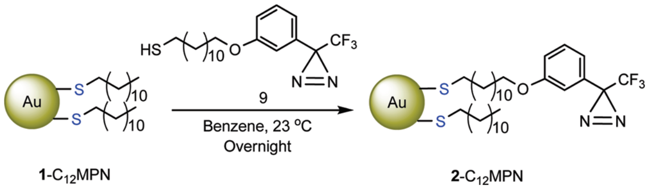
Scheme 1



ambient (or lower) temperature conditions.[17] In the continuation of our studies on exploring new methods for the modification of Au-MPNs through interfacial reactions, we report here the interfacial photoinduced carbene formation from a diazirine-modified Au-MPN and, as proof of concept, show that the subsequent carbene insertions into a selection of model trapping agents such as alcohols, amines, and alkenes is quantitative (Scheme 1). Carbene and nitrene insertion reaction approaches have been considered as feasible strategies to chemically modify surfaces or immobilize biological molecules on the functionalized surfaces.[18] Early in the advent of the use of gold monolayers, Wrighton and co-workers developed a gold self-assembled monolayer (Au-SAM) with aryl azide terminal groups that upon irradiation generated a reactive nitrene that then reacted with amines.[19] Surface modification with nylon-6,6,[20] protein immobilization on Fischer carbene-derivatized SAMs,[21] and immobilization of small natural products on a glass slide[22] are other examples of employing carbene insertion approaches on surfaces, but to date, we are not aware of any reports of generating and utilizing a reactive carbene moiety on a Au-MPN.

Diazirines are excellent carbene precursors and are well-known photophores for photoaffinity labeling and photo-cross-linking probes.[23] Diazirines readily generate reactive carbene intermediates by photoinitiated nitrogen extrusion and, as importantly, are relatively stable (chemically and thermally) prior to photolysis and hence do not undergo undesired reactions prior to photolysis or thermal activation.[23a,24] Among the diazirine derivatives, 3-aryl-3-(trifluoromethyl)diazirine has received the most widespread use because of its high thermal stability. Because of the nature of the strong C−F bonds in the CF$_3$ group, fluorine migrations to the carbene carbon do not occur, leaving a stable carbene available for quantitative insertion or addition reactions.[23a] The ground state of trifluorophenylcarbene is a triplet, which is in equilibrium with its higher energy singlet state; it is the latter that is reactive leading to the observed insertion or addition reactions.[23f,g]

Scheme 2



In this paper we report the synthesis and characterization of a 3-aryl-3-(trifluoromethyl)diazirine-modified Au-MPN (**2**-C$_{12}$MPN) (Scheme 2). We demonstrate that photolysis leads to a carbene-modified MPN directly and/or via the diazo-derivative resulting from photorearrangement of the diazirine. The carbene−MPN intermediate is reactive toward X−H (X: O, N) bond insertion and alkene addition, and this can be used as a template surface to introduce new functionality at the interface (**3**-C$_{12}$MPNs) (Scheme 1). A further benefit of utilizing the 3-aryl-3-(trifluoromethyl)diazirine as the carbene precursor is that it demonstrates the usefulness of ^{19}F NMR spectroscopy to follow the course of the reactions and to further characterize the resulting products of reactions performed on Au-MPN. In fact, the use of ^{19}F NMR has some advantages over ^{1}H NMR characterization where the signals due to ligands on the Au-MPN are generally very broad.

Results and Discussion

To prepare the desired 3-aryl-3-(trifluoromethyl)diazirine-modified Au-MPN (**2**-C$_{12}$MPN), we utilized a place exchange reaction incorporating 3-aryl-3-(trifluoromethyl)diazirine dodecanethiol (**9**) onto 1.8 ± 0.3 nm dodecanethiolate-modified gold nanoparticles (**1**-C$_{12}$MPN), as illustrated in Scheme 2. The synthetic route to **9** is shown in Scheme 3. Briefly, ortho-lithiation of 3-bromoanisole **1** with *n*-butyllithium followed by trifluoroacetylation of aryllithium intermediate provided ketone **2** in 54% yield. Reaction of **2** with hydroxylamine hydrochloride gave the corresponding oxime **3** (90%) which, in turn, was treated with tosyl chloride to afford *p*-tolylsulfonyloxime **4** in quantitative yield. Exposure of **4** to liquid ammonia and the subsequent oxidation of diaziridine **5** using freshly prepared silver oxide gave diazirine **6** in 52% overall yield for two steps.[25,26] Compound **6** was converted to the corresponding phenol **7** (62%) using BBr$_3$.[27]

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(17) (a) Kell, A. J.; Stringle, D. L. B.; Workentin, M. S. *Org. Lett.* **2000**, *2*, 3381. (b) Kell, A. J.; Workentin, M. S. *Langmuir* **2001**, *17*, 7355. (c) Kell, A. J.; Montcalm, C. C.; Workentin, M. S. *Can. J. Chem.* **2003**, *81*, 484. (d) Nakanishi, J.; Nakayama, H.; Shimizu, T.; Ishida, H.; Kikuchi, Y.; Yamaguchi, K.; Horiike, Y. *J. Am. Chem. Soc.* **2009**, *131*, 3822.

(18) (a) Jonkheijm, P.; Weinrich, D.; Schröder, H.; Niemeyer, C. M.; Waldmann, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9618. (b) Browne, W. R. *Coord. Chem. Rev.* **2008**, *252*, 2470.

(19) Wollman, E. W.; Kang, D.; Frisbie, C. D.; Lorkovic, I. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 4395.

(20) Blencowe, A.; Cosstick, K.; Hayes, W. *New J. Chem.* **2006**, *30*, 53.

(21) Sawoo, S.; Dutta, P.; Chakraborty, A.; Mukhopadhyay, R.; Bouloussa, O.; Sarkar, A. *Chem. Commun.* **2008**, 5957.

(22) Kanoh, N.; Kumashiro, S.; Simizu, S.; Kondoh, Y.; Hatakeyama, S.; Tashiro, H.; Osada, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 5584.

(23) (a) Blencowe, A.; Hayes, W. *Soft Matter* **2005**, *1*, 178 and references therein . (b) Hashimoto, M.; Hatanaka, Y. *Eur. J. Org. Chem.* **2008**, 2513. (c) Hatanaka, T.; Hatanaka, Y.; Setou, M. *J. Am. Chem. Soc.* **2006**, *128*, 15092. (d) Vila-Perellö, M.; Pratt, M. R.; Tulin, F.; Muir, T. W. *J. Am. Chem. Soc.* **2007**, *129*, 8086. (e) Qiu, Z.; Lu, L.; Jian, X.; He, C. *J. Am. Chem. Soc.* **2008**, *130*, 14398. (f) Admasu, A.; Gudmundsdóttir, A. D.; Platz, M. S.; Watt, D. S.; Kwiatkowski, S.; Crocker, P. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1093. (g) Platz, M.; Admasu, A. S.; Kwiatkowski, S.; Crocker, P. J.; Imai, N.; Watt, D. S. *Bioconjugate Chem.* **1991**, *2*, 337.

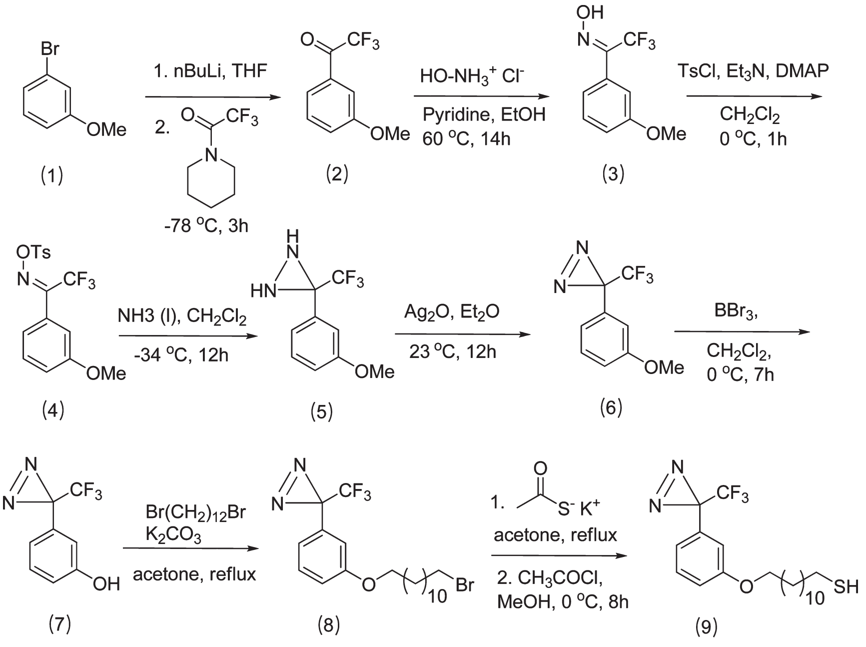
(24) Brunner, J.; Senn, H.; Richards, F. M. *J. Biol. Chem.* **1980**, *255*, 3313.

(25) Blencowe, A.; Caiulo, N.; Cosstick, K.; Fagour, W.; Heath, P.; Hayes, W. *Macromolecules* **2007**, *40*, 939.

(26) Mayer, T.; Maier, M. E. *Eur. J. Org. Chem.* **2007**, 4711.

(27) Hatanaka, Y.; Hashimoto, M.; Kurihara, H.; Nakayama, H.; Kanaoka, Y. *J. Org. Chem.* **1994**, *59*, 383.

Scheme 3



Alkylation of **7** using 1,12-dibromododecane followed by conversion of the bromide to the thioacetate, and then hydrolysis in acidic conditions afforded the desired 3-aryl-3-(trifluoromethyl)-diazirine dodecanethiol (**9**) in 73% yield.[28] The **1**-C$_{12}$MPNs were prepared using the Brust−Schiffrin two-phase method using a protocol we have previously reported.[29,13d] This protocol results in Au-MPNs with the average core diameter of 1.8 ± 0.3 nm as shown by TEM analysis (Supporting Information).

The desired **2**-C$_{12}$MPNs were prepared using a ligand exchange reaction (Scheme 2).[30] Stirring a solution of **1**-C$_{12}$MPN (200 mg) and thiol **9** (206 mg, 0.51 mmol) in benzene for 20 h gave **2**-C$_{12}$MPN. The ^{1}H NMR spectrum of the **2**-C$_{12}$MPN show broad peaks at 0.87, 0.95−1.74, and 3.89 ppm attributed to the methyl group of the CH$_3$-terminated dodecanethiolate ligands, the methylene groups of both ligands (CH$_3$-terminated dodecanethiolate and **9**), and the methylene alpha to oxygen (labeled proton e, Figure 1A), respectively. In addition, the aromatic region contains broad peaks at 6.65−6.90 ppm (protons labeled a, b, and d) and 7.27 ppm (proton c) assigned to the aromatic protons (Figure 1A). Comparison of the ^{1}H NMR spectrum of **9** to that of **2**-C$_{12}$MPN, particularly the excellent agreement of the signals due to a, b, c, d, and e that are assignable to the 3-aryl-3-(trifluoromethyl)diazirine moiety in each, illustrates the successful exchange reaction and incorporation of **9** onto **1**-C$_{12}$MPN (Figure 1A). The presence of any free, nonbound **9** would appear as sharp signals in the ^{1}H NMR spectrum of **2**-C$_{12}$MPN, while bound **9** (on **2**-C$_{12}$MPN) appear at the same chemical shift; however, the signals are more broad on the Au-MPN.[31] The purity of **2**-C$_{12}$MPN from the nonbound ligands after exchange reaction and work-up can thus be confirmed by the lack of sharp signals in the ^{1}H NMR spectrum of **2**-C$_{12}$MPN (Figure 1). The integrated areas of the methylene protons alpha to oxygen, proton labeled e (due to **9** attached to **2**-C$_{12}$MPNs), and the terminal methyl group of dodecanethiolate at 0.87 ppm (nonexchanged ligands) in the ^{1}H NMR spectrum revealed that the ratio of ligands in **2**-C$_{12}$MPNs is ca. 1:1.3 thiol **9**:dodecanethiolate. This ratio shows that ∼45% of dodecanethiolate of the **1**-C$_{12}$MPNs has been replaced by **9** through the exchange reaction and can be verified by degradation of the particles and analyzing the ^{1}H NMR spectrum of the ligands that are cleaved.[13c,d,17a−17c] Further characterization can be accomplished using ^{19}F NMR where the spectrum of **2**-C$_{12}$MPN shows a single peak at −65.7 ppm assigned to the fluorine of the CF$_3$ group, confirming the incorporation of **9** on the **2**-C$_{12}$MPNs (see inset of Figure 1).[25]

The diazirine moiety has major absorptions at 280 and 350 nm (Supporting Information). Photolysis of **2**-C$_{12}$MPN with wavelengths above 300 nm utilizing a medium-pressure Hg lamp results in photochemical nitrogen extrusion to yield the reactive carbene, which subsequently can be trapped by a variety of reagents via X−H (X: O, N) insertion or addition to alkenes.[23] In the present case, progress of the reaction (Scheme 1) can be followed using ^{19}F NMR and IR spectroscopy. As previously mentioned, the CF$_3$ moiety alpha to the diazirine group of **2**-C$_{12}$MPNs shows a sharp peak at −65.7 ppm in the ^{19}F NMR spectrum.[25] Disappearance of this peak and the emergence of the new signals in ^{19}F NMR spectrum can be used to reliably follow the reaction progress. Photolysis of the diazirine can also lead to the corresponding diazo intermediate via intramolecular rearrangement, which upon further irradiation generates the carbene (Scheme 4).[32] The diazo isomer generated from **2**-C$_{12}$MPN can be detected using IR spectroscopy by the appearance of the strong N=N=C stretch centered at 2090 cm^{-1}. The diazo stretch appears after irradiation of **2**-C$_{12}$MPNs, indicating at least partial conversion of diazirine to the diazo group; therefore, complete disappearance of the diazo peak in the IR reveals that all of the carbenes generated from either diazirine or diazo isomer has undergone insertion reaction. Conversion to the diazo-derivative is also evident in the ^{19}F NMR spectrum as described below.

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(28) Rothrock, A. R.; Donkers, R. L.; Schoenfisch, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 9362.

(29) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

(30) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782.

(31) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

(32) (a) Buterbaugh, J. S.; Toscano, J. P.; Weaver, W. L.; Gord, J. R.; Hadad, C. M.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 3580. (b) Kanoh, N.; Nakamura, T.; Honda, K.; Yamakoshi, H.; Iwabuchi, Y.; Osada, H. *Tetrahedron* **2008**, *64*, 5692.

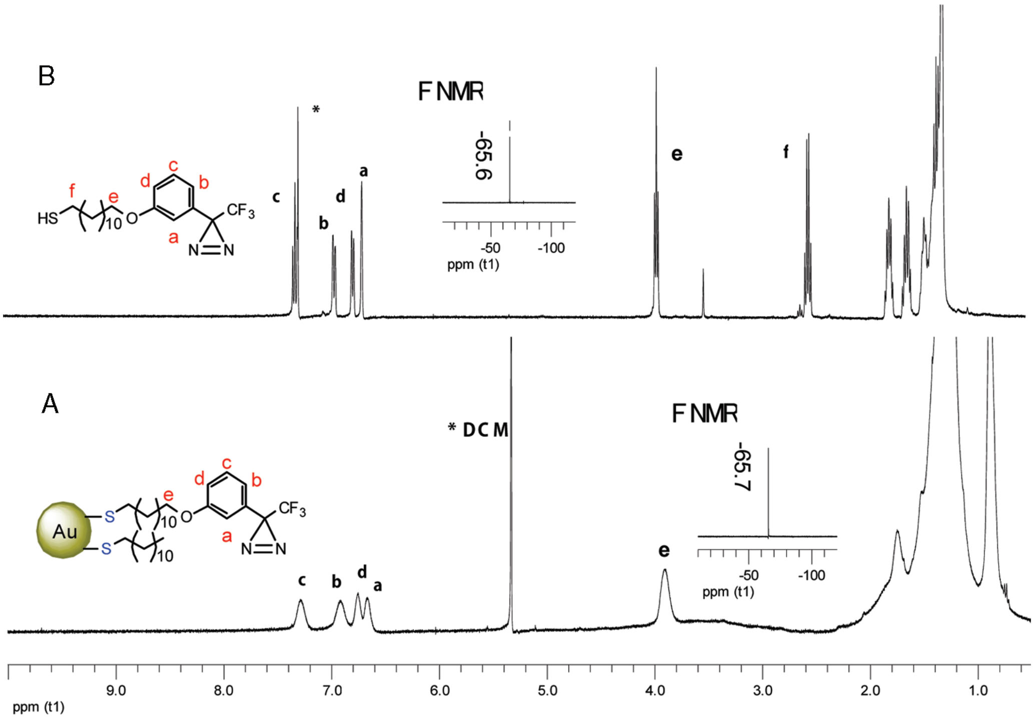
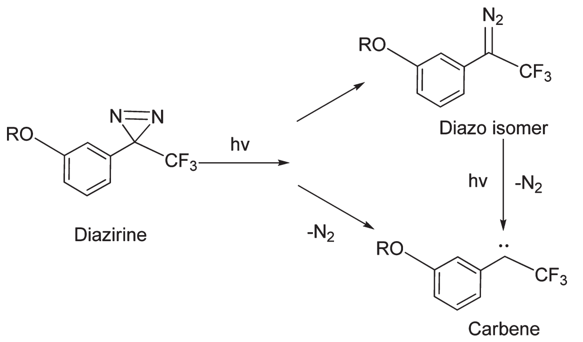


Figure 1. ^{1}H NMR spectra of (A) **2**-C_{12}MPN and (B) **9**. The asterisk denotes the signal due to residual protons in the solvent, which are CD_2Cl_2 in (A) and $CDCl_3$ in (B). Key assignments are indicated.

Scheme 4



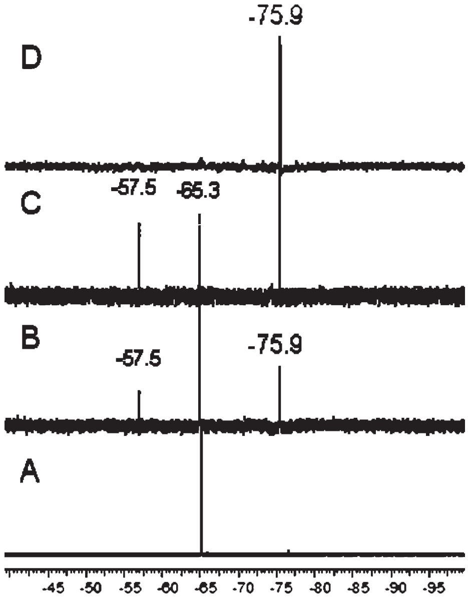
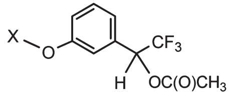
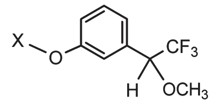
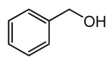
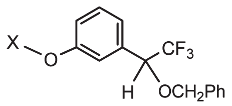
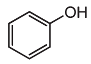
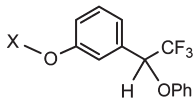
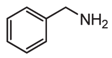
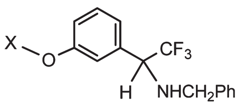
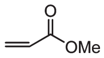
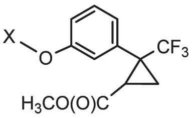
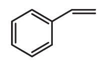
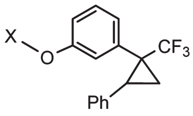


Figure 2. (A) ^{19}F NMR of **2**-C_{12}MPN; (B) 3 h and (C) 7 h after irradiaton of **2**-C_{12}MPNs in the presence of CH_3COOH. (D) ^{19}F NMR of product **3a**-C_{12}MPN.

As an initial proof of concept of using the reactive carbene to serve as a template to modify the Au-MPN, the irradiation of an argon-saturated solution of **2**-C_{12}MPN was studied in the presence of CH_3COOH in deuterated benzene (1:10−15 molar ratio, diazirine group on the **2**-C_{12}MPNs:CH_3COOH). To monitor the course of the reaction, ^{19}F NMR and IR spectra were recorded at various times throughout the reaction. Three distinctive peaks were observed in the ^{19}F NMR spectra during the course of the reaction: a peak due to the unreacted diazirine at −65.3 ppm that decreases in intensity on irradiation that is concomitant with a peak that appears at −75.9 ppm as a result of the product of the carbene insertion into the O−H of acetic acid and another at −57.5 ppm that we assign to the diazo intermediate.[25] The peak at −57.5 ppm initially grows in and then diminishes on continued photolysis with continued increase in the peak at −75.9 ppm (Figure 2). The reaction was deemed complete by the disappearance of the peaks at −65.3 and −57.5 ppm in the ^{19}F NMR spectrum. After complete reaction the ^{19}F NMR spectrum showed only a single peak at −75.9 ppm, corresponding to the CF_3 group of **3a**-C_{12}MPNs (Table 1). In addition, the IR analysis revealed the formation and consumption of diazo isomer during the reaction; the peak at 2090 cm^{-1} due to the diazo isomer appeared upon irradiation of **2**-C_{12}MPN and disappeared upon continued irradiation (see Supporting Information). Under our irradiation conditions the reaction reaches completion within 14 h at room temperature, and only products from O−H insertion are obtained. A significant point to be mentioned is that the Au core of **2**-C_{12}MPN is stable under UV irradiation in benzene and TEM taken after reaction showed no change in the Au core size. Figure 3A shows the ^{1}H NMR spectrum of **3a**-C_{12}MPN. Evidence of the carbene insertion was the emergence of new peaks (g) and (f) which

Table 1. Products of Reaction of Photolysis of the Diazirines 2-C_{12}MPN and 6 with a Variety of Carbene Trapping Agents, the Approximate Time To Complete Conversion To Form 3-C_{12}MPN and 11, Respectively, and the ^{19}F NMR Chemical Shifts of the Products 3-C_{12}MPN

Trapping Reagent	Product **3**-C_{12}MPN or **11** X = C_{12}MPN or CH_3	Time to completion 3-C_{12}MPN	11	^{19}F NMR[a] ppm
CH_3COOH **10a**	 **3a/11a**	14h	1.5h	-75.9
CH_3OH **10b**	 **3b/11b**	24h	4h	-77.4
 **10c**	 **3c/11c**	14h	3.5h	-76.7
 **10d**	 **3d/11d**	17h	5h	-77.4
 **10e**	 **3e/11e**	26h	8h	-74.2
 **10f**	 **3f/11f**	13h	2h	-65.2, -70.4
 **10g**	 **3g/11g**	14h	2h	-63.6, -70.0

[a] ^{19}F NMR of **3**-C_{12}MPNs.

are attributed to the methyl and proton alpha to the CF_3 group of the product, respectively. The broadness of the peaks often makes the ^{1}H NMR assignments of functionalized MPNs a difficult task. However, comparing the ^{1}H NMR peaks of functionalized MPNs with those of the model compound allows for a more confident assignment. To this end, we used compound **6** as a model diazirine, and it was irradiated in the presence of the same reagents, in this case CH_3COOH to yield compound **11a** (Scheme 5 and Table 1). The model products **11** can be fully characterized via ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and IR as well as by mass spectroscopy. Comparing the NMR data obtained from **11** to that of the **3**-C_{12}MPN allows the validation of the product of the interfacial reactions performed on **2**-C_{12}MPN. In the ^{1}H NMR spectra (Figure 3) the spectral alignment between **3a**-C_{12}MPNs and **11a**, particularly the protons indicated, confirms the modification of **2**-C_{12}MPNs with acetic acid. Further, they both give the same single peak at −76 ppm in their ^{19}F NMR spectra (Figure 3). The only difference is that the reaction of **6** with acetic acid went to completion in 90 min, almost 10 times faster than the corresponding reaction of **2**-C_{12}MPN with similar optical density between 350 and 360 nm. This is likely due to efficient quenching of the excited state of the diazirine on **2**-C_{12}MPN by the gold core.[33]

To investigate the scope of using the photogenerated interfacial carbene reaction toward X−H insertion and alkene addition as a template for the modification of **2**-C_{12}MPN, its photolysis was performed in the presence of a number of other reagents containing alcohol, amine, and alkene moieties (**10b**−**g**, Table 1). The reagents were chosen in part in this proof of concept study to have structural features that allowed for easier identification of the products using ^{1}H NMR spectroscopy, specifically having signals downfield from the alkyl H region of the spectrum. The photoreactions of **2**-C_{12}MPN in the presence of **10b**−**g** were carried out under the same conditions as described for the reaction with acetic acid above, and they were monitored using ^{19}F NMR, ^{1}H NMR, and IR spectroscopies. The reactions went to completion in 13−26 h, depending on the substrate (Table 1). Figure 4 shows the ^{1}H NMR spectra of **3b,c,e,f**-C_{12}MPN as representative examples of the **3**-C_{12}MPN products. The appearances of new peaks in ^{1}H NMR spectra confirm the efficacy of the carbene

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(33) (a) Thomas, K. G.; Kamat, P. V. *Acc. Chem. Res.* **2003**, *36*, 888. (b) Ghosh, S. K.; Pal, T. *Phys. Chem. Chem. Phys.* **2009**, 3831.

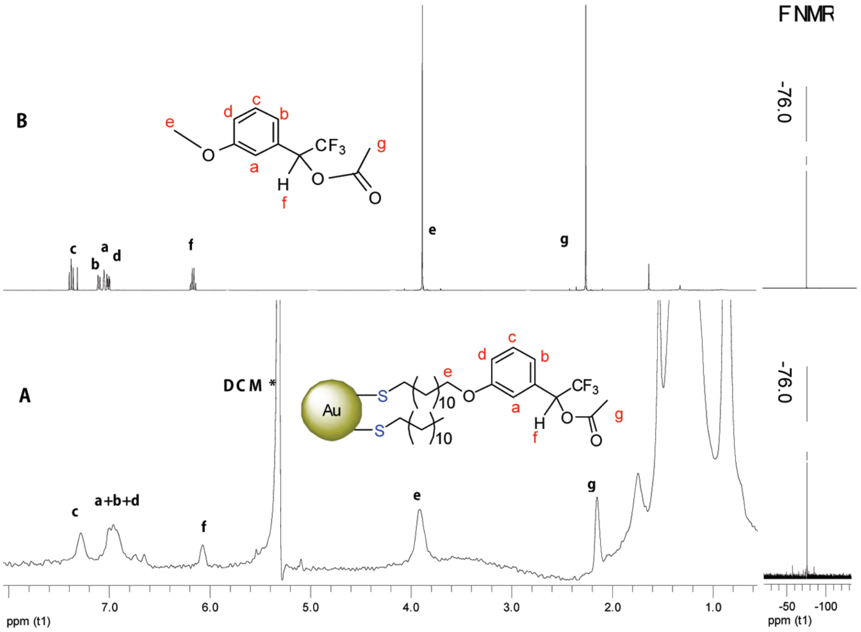


Figure 3. ^{1}H and ^{19}F NMR spectra of (A) **3a**-C$_{12}$MPN and (B) **11a**. The asterisk denotes the signal due to residual protons in the solvent CD$_2$Cl$_2$. Key assignments are indicated.

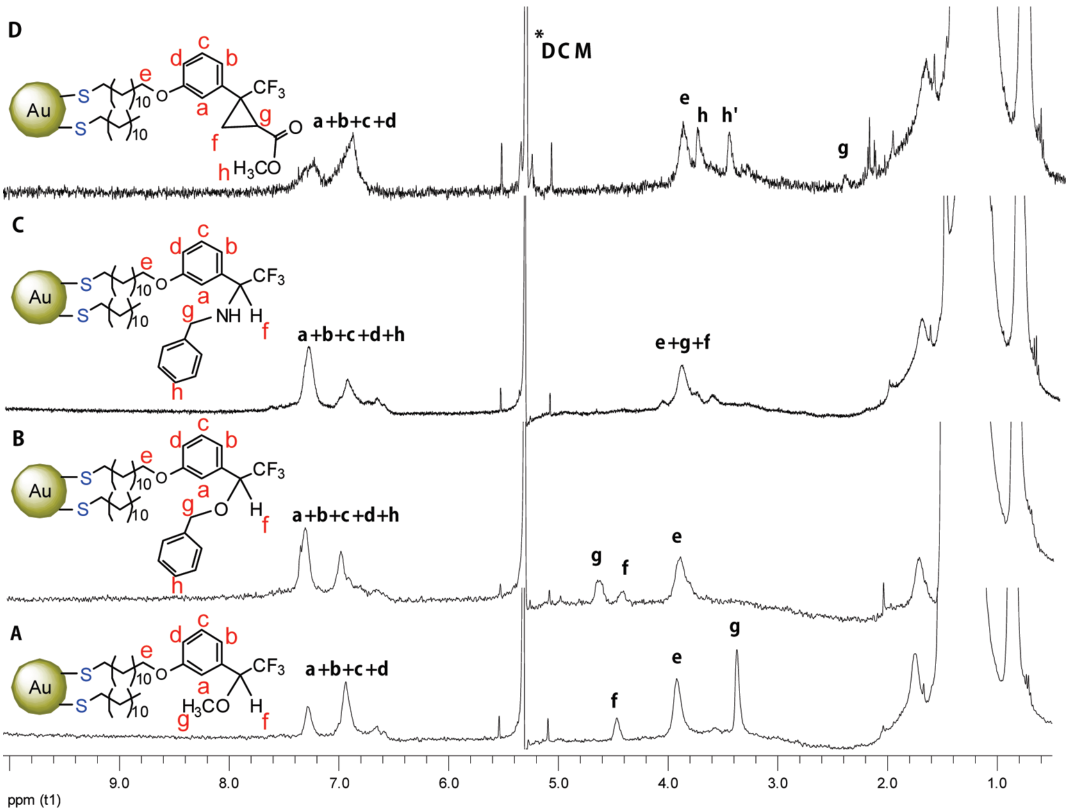
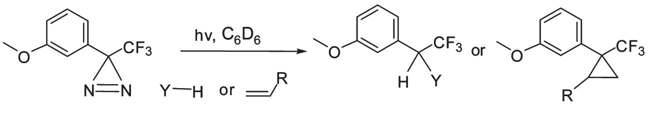


Figure 4. ^{1}H NMR spectra of (A) **3b**-C$_{12}$MPN, (B) **3c**-C$_{12}$MPN, (C) **3e**-C$_{12}$MPN, and (D) **3f**-C$_{12}$MPN. The asterisk denotes the signal due to residual protons CD$_2$Cl$_2$. Key assignments are indicated.

Scheme 5



6 **11a-g**

insertion reactions at modifying the **2**-C$_{12}$MPNs (^{19}F NMR and IR data as well as ^{1}H NMR of all **3**-C$_{12}$MPN can be found in the Supporting Information). We also performed the photoreactions with **6** in the presence of **10b**−**g** to prepare **11b**−**g** (Scheme 5 and Table 1) to aid in the characterization of **3**-C$_{12}$MPN. It is these comparisons that allowed for the characterization of the ^{1}H NMR of **3**-C$_{12}$MPN and the assignment of the protons identified in Figure 4 and the ^{19}F in the products indicated in Table 1. In all cases the reactions were efficient and resulted in quantitative conversion of the diazirine. For the alkene addition reactions, the two signals observed in the ^{19}F NMR spectra are from the two diastereomers. Full characterization is provided in the Supporting Information.

It is important to note that in none of the reactions of **6** and **2**-C$_{12}$MPNs with **10a−g** was the product of the insertion of the carbene into the deuterated benzene (solvent) detected. Only in the absence of a trapping reagent was this product observed. Following 15 h of irradiation of **2**-C$_{12}$MPNs in deuterated benzene two peaks were observed in the ^{19}F NMR spectra: one at −57.5 ppm due to the diazo isomer and another at −73.9 resulting from insertion into deuterated benzene to yield cyclohepta-1,3,5-triene.[25] In none of the ^{19}F NMR spectra of **3**-C$_{12}$MPNs was this latter signal observed, suggesting that it was not a major competing process and that the carbene insertion into benzene-d_6 is much slower than X−H insertion or alkene addition. No other products of other C−H insertion reactions were found.

We have prepared and characterized 3-aryl-3-(trifluoromethyl)-diazirine-modified monolayer-protected gold nanoparticles (**2**-C$_{12}$MPN). Further, these are efficient photoprecursors to a reactive carbene at an Au-MPN interface that can undergo efficient X−H insertion and alkene additions leading to the quantitative modification of the Au-MPN. Compound **2**-C$_{12}$MPN serves as a photoreactive template Au-MPN for the introduction of structural diversity to these particle types. In this study we utilized Au-MPN with a 1.8 ± 0.3 nm core size; however, the results are likely to be general for any similarly modified MPN. Of course, the efficiency of the photoreactions can also be optimized by utilizing more intense light sources. Additionally, the ease of generation of the carbene-modified Au-MPN and its highly reactive nature makes **2**-C$_{12}$MPN useful for the modification of other surface types, including carbon nanotubes, graphene, polymers, with Au-MPN; these studies are currently in progress.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (Canada) and the University of Western Ontario for financial support. S. Lee is grateful to the exchange program between Université Pierre et Marie Curie (Paris 6, France) and the Chemistry Department of the University of Western Ontario.

Supporting Information Available: Full experimental details and characterization of compounds **2−9**, **1**-C$_{12}$MPN, **2**-C$_{12}$MPN, **3a−g**-C$_{12}$MPN and **11a−g**, ^{1}H and ^{19}F NMR spectra of **3a−g-**C$_{12}$MPN and **11a−g**, TEM of **2-**C$_{12}$MPN and **3a-**C$_{12}$MPN, IR of **2**-C$_{12}$MPN, **3a-**C$_{12}$MPN, and diazo intermediate, and UV−vis spectra of **1**-C$_{12}$MPN, **2**-C$_{12}$-MPN, and **3a-**C$_{12}$MPN. This material is available free of charge via the Internet at http://pubs.acs.org.