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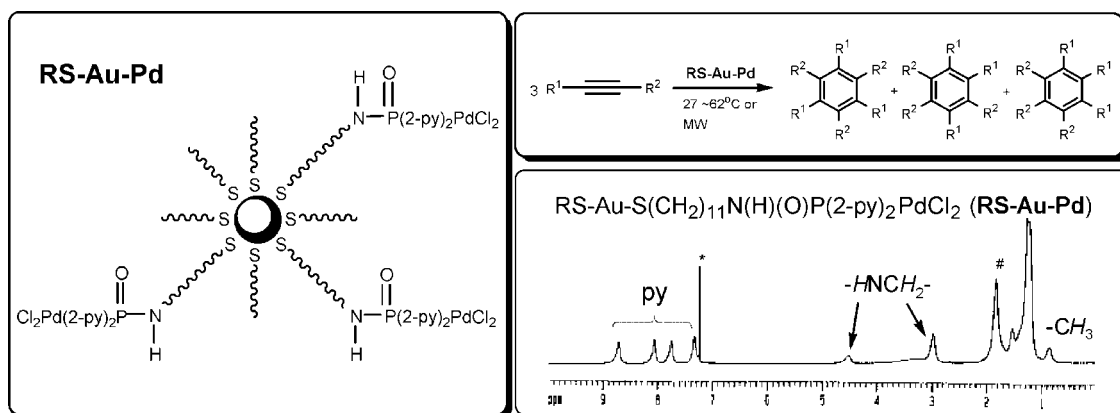
# Highly Efficient and Recyclable Au Nanoparticle-Supported Palladium(II) Interphase Catalysts and Microwave-Assisted Alkyne Cyclotrimerization Reactions in Ionic Liquids

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The gold nanoparticles with core diameter of 3.9–4.7 nm were stabilized with octanethiolate and dipyridylphosphinicamido undecanethiolate. Without varying the size of central Au cores, palladium complexes were immobilized onto these Au nanoparticles through chelation to the surface-bound dipyridyls. Hybrid catalysts of this type were dissolvable and precipitable, and their structures and reactions were investigated by solution nuclear magnetic resonance (NMR) spectroscopy with a resolution typically attained for soluble systems. These surface-bound Pd(II) complexes were highly effective catalysts for [2+2+2] alkyne cyclotrimerization reactions to give highly congested benzene rings with fairly good selectivity. The catalytic reactivity of these interphase catalysts was even higher than that of their unbound counterparts. In addition, they can be easily separated and quantitatively recovered by simple filtration. The recovered catalysts can be effectively recycled many times and their electron microscopy images and NMR spectra showed negligible difference from those of freshly prepared. The complete transformation by Au-bound Pd(II) catalyst with a loading of 4 mol % can be achieved within 1 h for most alkynes. The same catalysis can be further accelerated in ionic liquid under microwave conditions to give nearly 100% of cyclotrimerized products in minutes.

## Introduction

The strategy of immobilizing homogeneous transition metal complexes to solid supports such as organic polymers,<sup>1</sup> inorganic metal,<sup>2</sup> and metal oxides<sup>3</sup> has been extensively applied in sustainable chemistry to prepare recoverable catalysts. This type

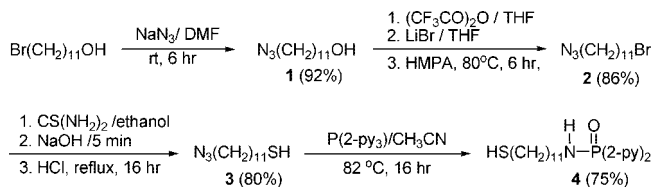
of hybrid catalyst should be in principle congregating the advantages from both heterogeneous and homogeneous systems. However, in many cases, supported catalysts suffer a series of problems due to heterogenization. This has led to alternative liquid phase methodologies to restore homogeneous reaction conditions. Hence soluble supports<sup>1,4,5</sup> have been used to obtain detailed structures of the active catalysts, and much more fundamental knowledge about the catalyst modification, degradation, as well as interactions at the interface would then become comprehensible. Since the alkanethiolate-protected gold

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nanoparticles (Au NPs) have been known not only to possess solid surfaces resembling the (111) surface of bulk gold<sup>6</sup> but also to behave like soluble molecules for their dissolvability, precipitability, and redissolvability.<sup>7</sup> Au NPs would suitably become good candidates for metal complex catalyst-supports. Some recent articles have reported the use of Au colloids as catalyst-supports in various organic transformations.<sup>8–11</sup> Herein we report the synthesis of a recyclable hybrid catalyst system consisting of Pd(II) complexes immobilized onto Au NPs through coordination to the surface alkanethiolates. Hybrid catalysts of this type are dissolvable and precipitable, so their structures and reaction chemistry can be easily investigated by solution phase nuclear magnetic resonance (NMR) spectroscopy with a resolution typically obtained on soluble systems. We have also demonstrated the excellent reactivity and sustainable recyclability of this hybrid catalyst system in a series of [2+2+2] alkyne cyclotrimerization reactions. By using transmission electron microscopy (TEM) and solution NMR it will be shown that the structures of the catalytic system remain unchanged even after 5 cycles of catalysis. In addition, the rates of these catalytic cyclotrimerization reactions can be further accelerated in ionic liquid under microwave (MW) irradiation conditions.

Most surface-bound transition metal complex catalysts are generally less reactive than their unbound analogues.<sup>3</sup> However,

### SCHEME 1. Synthesis of Spacer Ligand HS(CH<sub>2</sub>)<sub>11</sub>NHP(O)(2-py)<sub>2</sub> (4)



it is interesting to note that the Au NPs-bound Pd(II) complexes in the present study are more effective than their SiO<sub>2</sub>-bound analogues and their unbound counterparts.

## Results and Discussion

Immobilization of complexes with use of covalent tethering techniques is, at present, the most favorable approach to design stable hybrid catalysts.<sup>4a</sup> The compound dipyridylphosphinic amido undecanethiol, HS(CH<sub>2</sub>)<sub>11</sub>NHP(O)(2-py)<sub>2</sub> (4) (Scheme 1), was synthesized to be used as the tethering linker since the thiol end and the amido phosphinic dipyridyl end have been demonstrated to readily bind surface Au and molecular Pd(II), respectively.<sup>5a</sup> The Au NPs surfaces were functionalized with use of the place-exchange method<sup>12,13</sup> by treating 75 mg of octanethiolate-covered Au NPs (Au-SR, 2.7 ± 0.5 nm)<sup>6a,13b,14</sup> with various quantities of 4 (60–200 mg) in CHCl<sub>3</sub> at 70 °C for 16 h (Scheme 2). The resulting mixed thiolates-covered Au NPs RS-Au-L (7) have diameters of 3.9–4.7 nm and L:RS mole ratios ranging from 1:0.7 to 1:1.2, where RS = octanethiolate and L = S(CH<sub>2</sub>)<sub>11</sub>NHP(O)(2-py)<sub>2</sub> (see the Supporting Information). Further treatment of 7 with Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> would make the molecular Pd(II) tethered onto Au NPs via direct binding with surface dipyridyl to form a stable palladacycle. The Pd(II)-functionalized Au NPs, RS-Au-L-PdCl<sub>2</sub> (8), thus obtained has average core sizes of 3.1–4.8 nm and L-PdCl<sub>2</sub>/RS ratios of 1/0.61 to 1/1.39 (see the Supporting Information).

The TEM images of Au NPs 7 and 8 have shown that sequential immobilization processes would not cause significant size change on the central Au cores (see Supporting Information). The UV–vis spectra of RS-Au-L (7) and RS-Au-L-PdCl<sub>2</sub> (8) exhibit the characteristic surface plasmon resonance peak at ~520 nm (see Supporting Information).

Since the Pd(II)-functionalized Au NPs typically obtained under our reaction conditions are soluble in many organic solvents such as methanol, DMSO, and DMF, we could therefore use simple solution <sup>1</sup>H NMR other than the traditional atomic absorption (AA) spectroscopy to determine the average thiolate coverage and the amount of Pd(II) loading. It can be clearly seen in the <sup>1</sup>H NMR spectra (Figures 1 and 2) of thiolate-protected Au NPs, Au-SR, RS-Au-L (7) and RS-Au-L-PdCl<sub>2</sub> NPs (8), that the α-methylene proton (–CH<sub>2</sub>S–Au) resonances of the surface thiolates were broadened to an extent to become barely visible. All other proton resonances were also significantly broadened and their multiplicity could no longer be determined. The cause for peak broadening is still a subject

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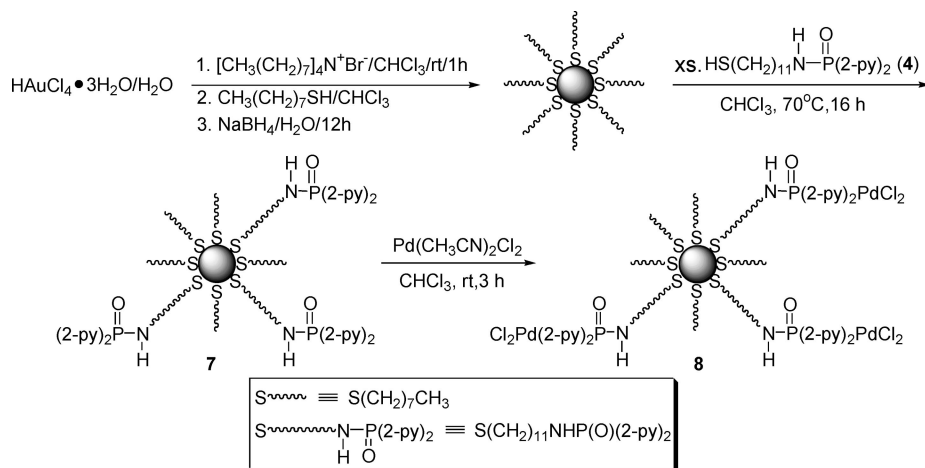
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SCHEME 2. Synthesis of Pd(II)-Functionalized Au NPs, RS-Au-L-PdCl<sub>2</sub> (8)

under discussion.<sup>15,16</sup> The Au NPs surface-bound species and their free forms can easily be distinguished by the sharpness of the multiplets and their chemical shifts (referenced to chloroform or DMSO). In addition, the IR spectra of the Au NPs-bound thiolates also showed that the  $\nu_{\text{asym}}(\text{SH})$  bands of free octanethiol (2569 cm<sup>-1</sup>) and the unbound **4** (2576 cm<sup>-1</sup>) disappeared<sup>17</sup> upon immobilization onto Au NPs (see Supporting Information).

Given that RS-Au-L-PdCl<sub>2</sub> NPs **8** are soluble in polar solvents such as DMSO, purification of these Au NPs for the use in quantitative analyses can be easily performed by washing the crude with less polar solvents such as CHCl<sub>3</sub> followed by centrifugation and filtration. In addition to TEM and AA, solution NMR spectroscopy was heavily used in the current study for quantitative analyses. The analytical data of Au NPs **7** and **8** were summarized in the Supporting Information. The mole contents of surface thiolates in 1 g of RS-Au-L (**7**) were determined to be  $4.8 \times 10^{-4}$ – $6.1 \times 10^{-4}$  mol/g of RS and  $5.0 \times 10^{-4}$ – $7.2 \times 10^{-4}$  mol/g of spacer thiolate **L**, whereas the surface contents of Pd(II) and RS in 1 g of RS-Au-L-PdCl<sub>2</sub> NPs (**8**) were found to be  $2.4 \times 10^{-4}$ – $6.0 \times 10^{-4}$  and  $3.3 \times 10^{-4}$ – $4.2 \times 10^{-4}$  mol/g, respectively. The weight percentage of immobilized Pd(II) (Pd wt %) in Au NPs **8** can then be calculated accordingly.

It can be seen in the Supporting Information that the Pd wt % of 2.5–6.4% obtained from <sup>1</sup>H NMR spectroscopy was found to be systematically smaller (<5%) than those obtained by using AA spectroscopy (Pd wt % = 2.8–6.7%). Since it would only take 10 min or less to acquire data on a <sup>1</sup>H NMR spectrometer, we used NMR instead of AA to obtain analytical data for catalyses thereafter.

The construction of highly congested benzene rings from simple alkynes is a synthetically important transformation for its extensive use in industry as well as in the laboratory.<sup>18</sup> Though many transition metals have been employed for the [2+2+2] cyclootrimerization of alkynes to polysubstituted

benzenes, only a few synthetically useful catalyst systems have been established.<sup>19,20</sup> Recent progress in this area has revealed that the Pd(II) metal center seems to be a potential candidate for its air/moisture-stability and its abounding chemistry with alkynes.<sup>21,22</sup> In the current study, molecular Pd(II) immobilized at the interphase, in a form of RS-Au-L-PdCl<sub>2</sub> NPs (**8**), was used as the active catalyst for [2+2+2] cyclootrimerization of various alkynes (R<sup>1</sup>C≡CR<sup>2</sup>, R<sup>1</sup> = R<sup>2</sup> = Me, Et, <sup>n</sup>Pr, Ph; R<sup>1</sup> = Me, R<sup>2</sup> = Et, <sup>n</sup>Pr; and R<sup>1</sup> = Ph, R<sup>2</sup> = H.). Among several solvents tested, all the catalyses were operated heterogeneously in molecular solvents (CHCl<sub>3</sub> or THF) or in ionic liquid bmimPF<sub>6</sub> for the idea of easy separation, catalyst recycling, and developing greener synthesis protocols. Under very mild reaction

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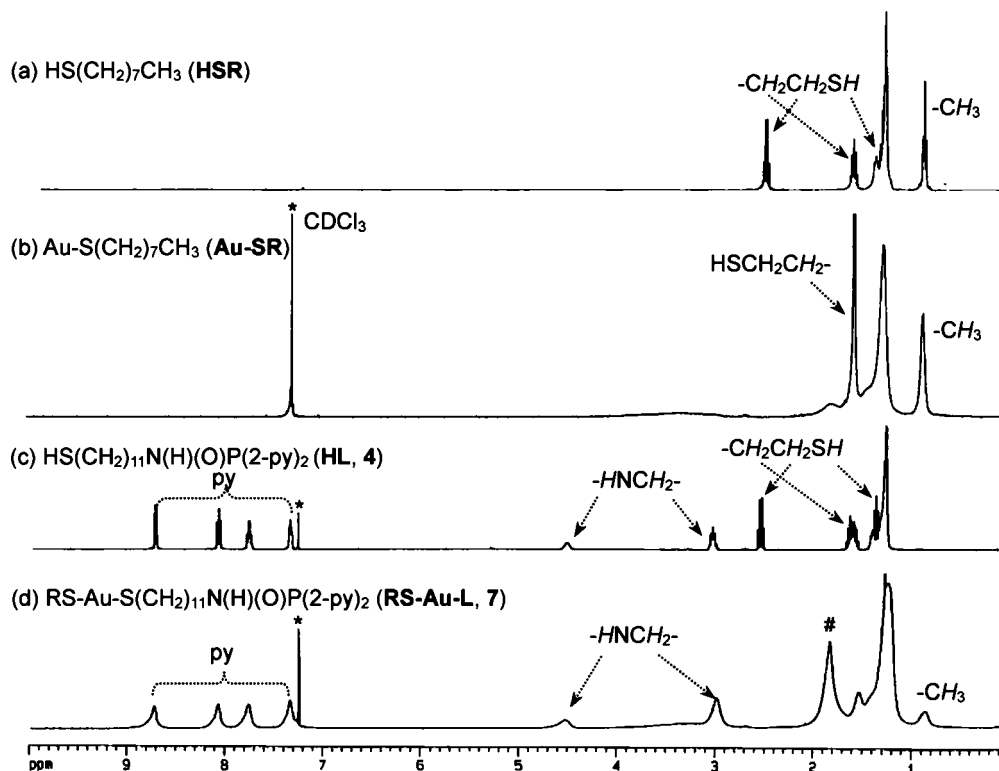
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**FIGURE 1.** The 400 MHz <sup>1</sup>H NMR (27 °C, CDCl<sub>3</sub>) spectra of (a) octanethiol (HSR), (b) octanethiolate-covered Au NPs (Au-SR), (c) phosphinic amide-functionalized alkanethiol **4** (HL), and (d) RS-Au-L NPs **7** (\* is CDCl<sub>3</sub> and # is water in the system).

conditions, complete conversions could be found for both terminal and internal alkynes to give desired products in a short reaction time without any activator such as Zn/ZnI<sub>2</sub> required for the CoBr<sub>2</sub> system<sup>23</sup> or CuCl<sub>2</sub> for the PdCl<sub>2</sub> system.<sup>22a,27b</sup> For example, in experiments conducted by using 11.6 mg of RS-Au-L-PdCl<sub>2</sub> NPs **8**, which was equivalent to 4 mol % of Pd(II) loading, 0.075 mmol of 3-hexyne was fully converted into hexaethylbenzene in 30 min at 27 °C or in 10 min at 62 °C (entry 2, Table 3). As elucidated in Table 1, the **8**-catalyzed reactions of alkynes with smaller substituents such as Me, Et, and <sup>n</sup>Pr underwent cycloaddition much more efficiently than those with a larger phenyl substituent.

It has been reported that transition metal complexes attached to self-assembled monolayers of alkanethiolates on gold colloids exhibited catalytic properties similar to those of their corresponding homogeneous catalysts.<sup>8–11</sup> It is interesting to note that in our system the hybrid catalyst RS-Au-L-PdCl<sub>2</sub> NPs (**8**) is more reactive than the unbound free forms. For example, the homogeneous analogues HO(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (**9**) and Br(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (**10**) (Scheme 3) were used as controls and they were proven to give no reactivity for cyclotrimerization of alkynes even with a Pd(II) loading of up to 20 mol % at 80 °C for over 24 h (entries 9 and 10, Table 1).<sup>24</sup> The shutoff in catalytic activity of the Pd(II) center in both **9** and **10** was most probably due to the entropically unfavorable formation of the activated complex caused by the free dangling of the long alkyl chain. This is consistent with our findings that the Au-bound Pd(II) is much more active due to immobilization

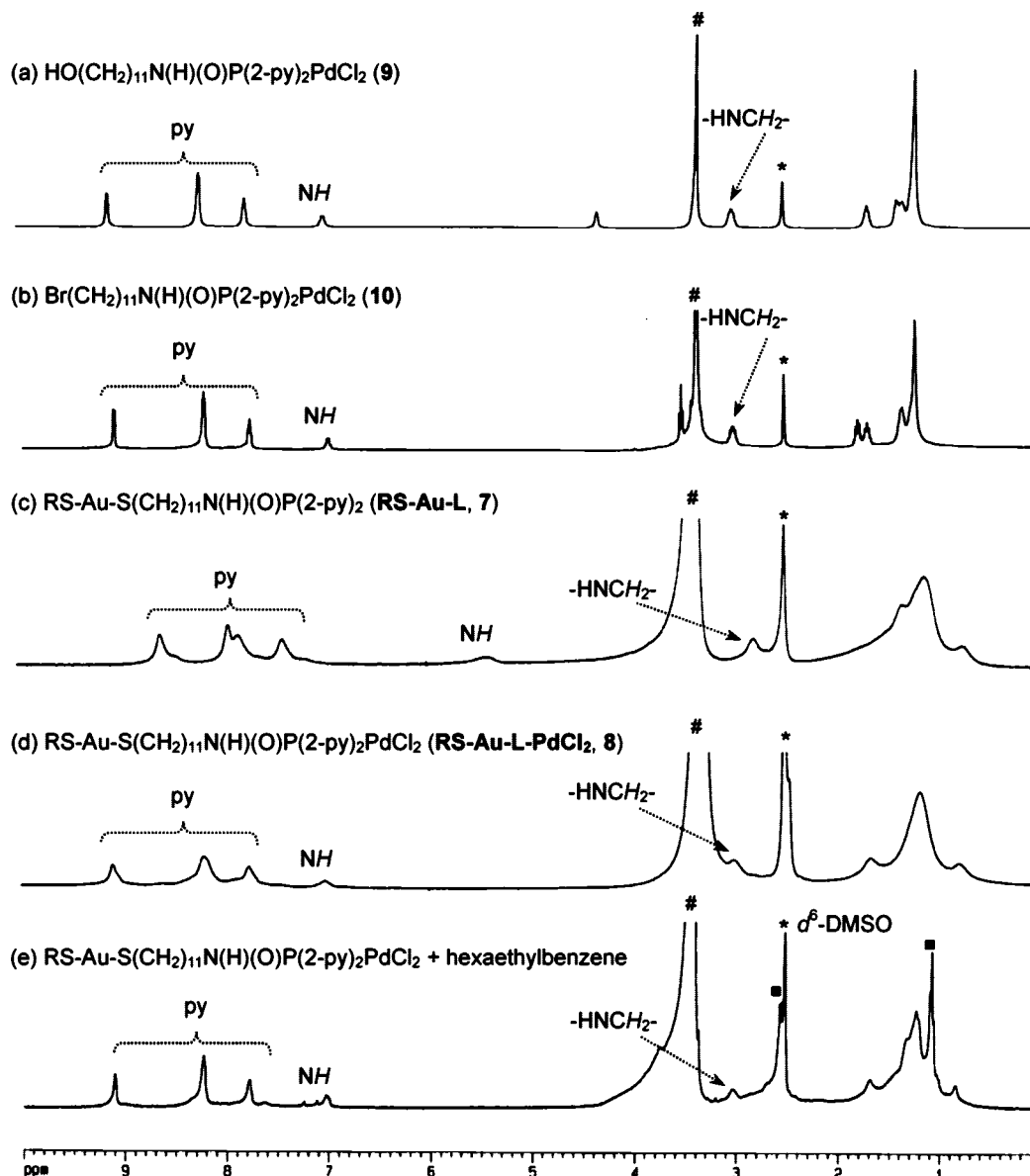
of the free end of the long alkyl chain. Also the molecular catalysts Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> and Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> bearing a short and more rigid chain were found to be effective catalysts for the same catalytic reactions. However, the catalytic efficiency of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> under homogeneous conditions was only 40–75% of that found for **8** under heterogeneous conditions for cyclotrimerization of 4-octyne, 2-pentyne, 2-hexyne, and phenylacetylene (entries 3, 5–7, and 14–17, Table 1). In cases of the most reactive 3-hexyne and the least reactive diphenylacetylene, similar catalytic reactivity was obtained for both the Au-bound and the free-form Pd(II) systems (entries 2, 4, and 11–13, Table 1).

To study the cause of catalytic reactivity enhancement in the Au nanosurface tethered Pd(II) hybrid system, we have also investigated the catalysis on bulk SiO<sub>2</sub> surfaces. It can be clearly seen in entry 8 of Table 1 that the SiO<sub>2</sub>-bound Pd(II) catalyst (Scheme 4)<sup>25</sup> only had 6–23% of reactivity of those found for **8** under exactly the same reaction conditions. However, higher conversions can be obtained when catalysis proceeded for a much longer reaction time.<sup>5a</sup> As expected for most bulk-surface supported metal complex catalysts systems, a decrease in reactivity upon progressive heterogenization was also observed for the SiO<sub>2</sub>-bound Pd(II) system. Additionally, the octanethiolate-covered Au NPs (Au-SR) were also tested for catalytic activity. As expected, the Au cores were proven to have no reactivity toward cyclotrimerization reactions.

(25) The molecular Pd(II) complex catalysts can be tethered to a range of polysiloxanes, which were specially designed to mimic the surface of silica gel, but with properties that are more readily controlled than those of silica gel. The molecular weight and degree of cross-linking of these polysiloxane materials can be systematically varied to provide catalyst systems ranging from soluble, homogeneous model compounds to heterogeneous three-dimensional networks. For the synthetic details, structural information, and reaction chemistry of the soluble form of SiO<sub>2</sub>-bound Pd(II) complex catalyst, see ref 5a.

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(24) For the case of 3-hexyne and 20 mol % of Br(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (**10**), oxidative addition of ligand C-Br was the only observable reaction in CDCl<sub>3</sub> at 62 °C after 24 h.



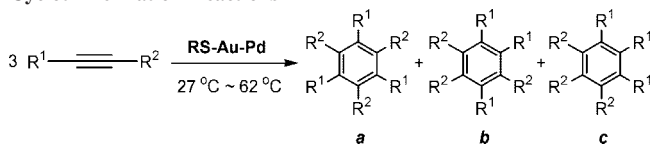
**FIGURE 2.** The 400 MHz  $^1\text{H}$  NMR (27  $^\circ\text{C}$ ,  $d_6$ -DMSO) spectra of (a) molecular catalyst **9**, (b) molecular catalyst **10**, (c) RS-Au-L NPs **7**, (d) RS-Au-L-PdCl<sub>2</sub> NPs **8**, and (e) catalyst **8** recovered from the 5th cycle of the catalytic cyclotrimerization of 3-hexyne (\* is DMSO, # is water, and ■ is the cyclotrimerized product hexaethylbenzene).

Similar observation of a significant increase in catalytic activity has also been reported for ring-opening metathesis polymerization (ROMP) of norbornene by Ru(III) catalysts supported on Au colloids or on a flat Au surface<sup>9</sup> and hydrogenation of ketones by Rh(I) catalysts organized in Langmuir–Blodgett (LB) films.<sup>26</sup> A mechanistic model connected with the orientation of the Rh(I) in a manner that favors its interaction with the substrates and the growing products was proposed by Milstein<sup>26</sup> to explain a much higher reaction rate obtained for the Rh(I) catalyst fixed on LB films. The same model has also been used by Tremel et al. in their system to explain a significant increase in catalytic activity of ROMP by the Ru(III) catalyst supported on Au colloids or on flat Au surface.<sup>9</sup> However, the real cause of reactivity enhancement in our system is not yet clear. More mechanistic insights may be

obtained from further investigation on the catalytic activity versus the length of tethering ligands.

A number of plausible mechanistic pathways for the metal-catalyzed alkyne cyclotrimerization reactions have been proposed (Scheme 5).<sup>19b,22a,b,f,g,i,27b</sup> The **8**-catalyzed cyclotrimerization of unsymmetrically substituted alkyne such as  $\text{MeC}\equiv\text{CEt}$  and  $\text{HC}\equiv\text{CPh}$  was found to give two kinds of hexasubstituted benzenes, 1,3,5- and 1,2,4- $\text{C}_6\text{R}^1\text{R}^2\text{R}^3$ , in a ratio of about 1:2 to 1:4 (entries 5 and 7, Table 1). These product distributions were in agreement with the selectivity obtained for the reported mechanism involving a metallacyclopentadiene intermediate.<sup>22f,28</sup> However, when  $\text{MeC}\equiv\text{C}^n\text{Pr}$  was used as the alkyne source, three different products were obtained in a 1,3,5-/1,2,4-/1,2,3- $\text{C}_6\text{R}^1\text{R}^2\text{R}^3$  ratio of about 1:3:1 (entry 6, Table 1), which was also consistent with another different mechanism having a cyclobutadienyl complex as reactive intermediate.<sup>22e,i,27</sup> It has been demonstrated in the literature that the product

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**TABLE 1.** RS-Au-PdCl<sub>2</sub> NPs (**8**)-Catalyzed [2+2+2] Alkyne Cyclotrimerization Reactions<sup>a</sup>

entry	alkyne R <sup>1</sup> R <sup>2</sup>	catalyst	solvent	T (°C)	time (min)	conversion <sup>c</sup> (%)	product ratio <sup>f</sup> a:b:c
1	Me Me <b>8</b>		CDCl <sub>3</sub>	27	180	99	
2	Et Et <b>8</b>		CDCl <sub>3</sub>	27	30	99	
			CDCl <sub>3</sub>	62	10	99	
			THF	62	15	99	
3	<sup>n</sup> Pr <sup>n</sup> Pr <b>8</b>		CDCl <sub>3</sub>	27	40	99	
			CDCl <sub>3</sub>	62	30	99	
			THF	62	30	99	
4	Ph Ph <b>8</b>		CDCl <sub>3</sub>	62	24 h	60	
5	Me Et <b>8</b>		CDCl <sub>3</sub>	27	180	99	33:67:0
				50	60	99	33:67:0
							(35:65:0)
6	Me <sup>n</sup> Pr <b>8</b>		CDCl <sub>3</sub>	27	90	99	18:63:19
				62	60	99	18:60:22
							(17:61:22)
7	H Ph <b>8</b>		CDCl <sub>3</sub>	27	330	99	22:78:0
				62	180	99	19:81:0
8	Et Et SiO <sub>2</sub> -PdCl <sub>2</sub> <sup>b</sup>		CHCl <sub>3</sub>	27	30	6	
				62	30	23	
				27	36 h	88 <sup>d</sup>	
				62	16 h	91 <sup>d</sup>	
9	Et Et <b>9</b>		CDCl <sub>3</sub>	27	30	NR <sup>e</sup>	
				62	10	NR <sup>e</sup>	
10	Et Et <b>10</b>		CDCl <sub>3</sub>	27	30	NR <sup>e</sup>	
				62	10	NR <sup>e</sup>	
11	Et Et Pd(PhCN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	27	30	99	
				62	10	99	
12	Et Et Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	27	30	95	
				62	30	99	
13	Ph Ph Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	62	24 h	56	
14	<sup>n</sup> Pr <sup>n</sup> Pr Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	27	40	50	
15	Me Et Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	27	180	47	35:65:0
16	Me <sup>n</sup> Pr Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	27	90	40	19:62:19
				62	60	70	18:63:19
17	H Ph Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	27	330	75	17:83:0

<sup>a</sup> Reaction conditions: alkyne (0.075 mmol) in CDCl<sub>3</sub> (1 mL), catalyst loading = 4 mol %. <sup>b</sup> Reaction conditions: alkyne (0.56 mmol) in CDCl<sub>3</sub> (3 mL), catalyst loading = 4 mol %. <sup>c</sup> Conversions were determined by <sup>1</sup>H NMR spectroscopy. <sup>d</sup> Products were purified and isolated by flash chromatography on SiO<sub>2</sub> with hexane/ethyl acetate. <sup>e</sup> NR = no observable reaction. <sup>f</sup> Isomer ratios were determined by GC-MS and numbers in parentheses were obtained by using NMR spectroscopy.

selectivity was not only highly dependent on the metal center and the solvent polarity, but also substantially affected by the size of substituents on both sides of unsymmetrical alkynes.<sup>19h,i,27b</sup> The selectivities observed in both hybrid system **8** and homogeneous system Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> are similar (entries 5–7 and 15–17, Table 1), and they are also compatible with those found for other reported Pd systems.

MW radiation is an alternative to conventional heating for transforming electromagnetic energy into heat, though many molecular solvents such as water, alcohols, DMF, and ethylene glycol have high dielectric losses and are good media for MW rapid heating. However, due to the nature of molecular solvents the MW should be applied in a pulse mode to get better temperature control.<sup>29</sup> On the contrary, room temperature ionic

liquids have proven to be better and greener solvents to couple effectively with MW in either a continuous wave mode or in a pulse mode.<sup>30</sup> In the current study, we have performed the MW-assisted **8**-catalyzed alkyne cyclotrimerization reactions in bmimPF<sub>6</sub> ionic liquid. As shown in Table 2, the MW heating method provided significant rate acceleration as compared to the conventional thermal heating method. Most of the MW-assisted, **8**-catalyzed reactions were completed within 1–5 min (entries 1–6, Table 2), whereas the same catalyses would take 10 min to 5.5 h under thermal conditions. Even with the less reactive diphenylacetylene the reaction under MW for 10 min gave 32% yield, while the same mixture at 62 °C for 10 min provided 0% conversion but would give 60% yield after 24 h. In addition to ionic bmimPF<sub>6</sub>, molecular THF was also used as the reaction media for the same microwaved catalyses. It can be clearly seen in Table 2 that the catalyses proceeded much more efficiently in bmimPF<sub>6</sub> than in THF (entries 12–15). The Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>-catalyzed cyclotrimerizations can also be substantially speeded up under MW irradiation (entries 7–11, Table 2); however, the observed reactivity was only 40–75% of those found for **8** under the same conditions.

It should also be noticed that the selectivity in relation to an isomer ratio of 1,3,5-/1,2,4-C<sub>6</sub>R<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub> remained about the same regardless with or without MW for systems starting with MeC≡CEt or HC≡CPh in either bmimPF<sub>6</sub> or THF (entries 4, 6, 9, 11, and 14 in Table 2). However, the selectivity of 1,2,3-C<sub>6</sub>R<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub> for the system starting with MeC≡C<sup>n</sup>Pr in bmimPF<sub>6</sub> has dramatically decreased under MW conditions. For example, an isomer ratio of 1,3,5-/1,2,4-/1,2,3-C<sub>6</sub>R<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub> was changed from 18:60:22 without MW to 22:75:3 with MW for catalyst **8**, and the isomer ratio was changed from 18:63:19 without MW to 25:73:2 with MW for Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>, while the selectivity of 1,2,3-C<sub>6</sub>R<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub> for the same reaction was even dropped to zero in THF to give a 1,3,5-/1,2,4-/1,2,3-C<sub>6</sub>R<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub> ratio of 55:45:0. As stated earlier it has been proposed in many publications that the two-product and the three-product systems followed different reaction pathways. The results obtained in our study implied that the MW may suppress the formation of cyclobutadienyl complex, which has been suggested as the active intermediate for the three-product mechanism. Moreover the THF solvent system probably further facilitated the formation of a palladacyclopentadiene intermediate to give only two products, 1,3,5- and 1,2,4-C<sub>6</sub>R<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub>.

There have been several recent reports on the use of MW radiation at various stages of the nucleation and growth process for synthesis of Au nanostructures.<sup>29,31</sup> We have learned from the literature that too much MW power fast absorbed by media would lead to a rapid rise in temperature and could disrupt the micelles of Au cores to cause severe size and shape changes of the aggregates.<sup>32</sup> In our study MW with 300 W of working power (2.5 GHz) was introduced to the reaction systems for 1–5 min depending on the reaction conditions. The recovered colloidal catalysts from the MW-assisted catalytic cyclotrim-

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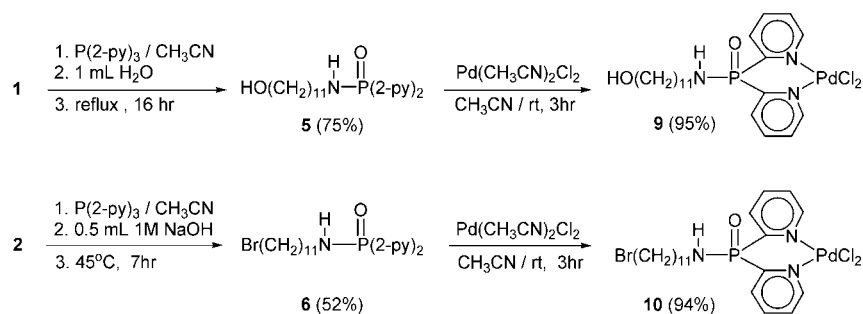
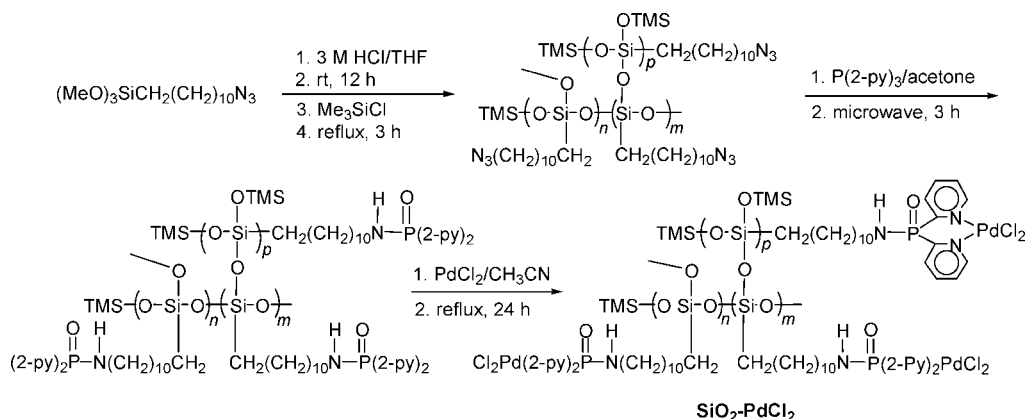
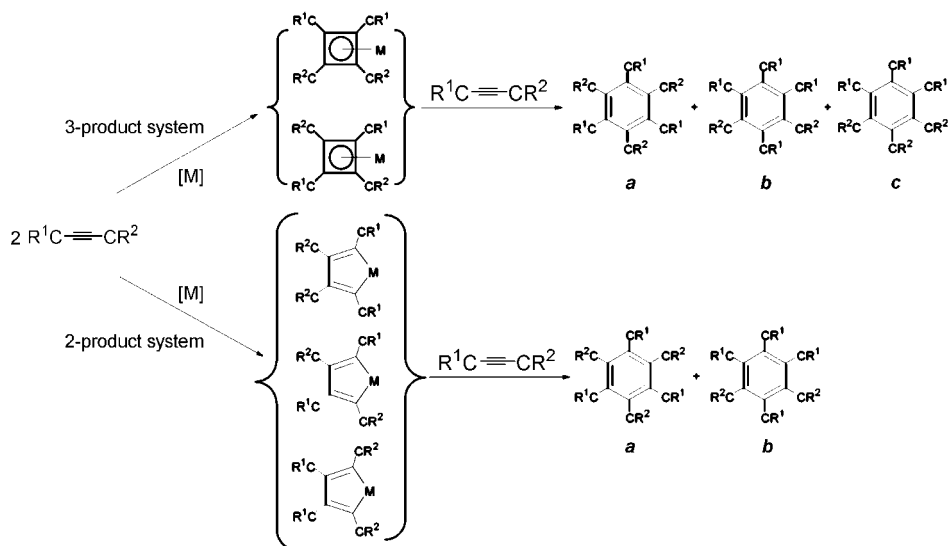
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**SCHEME 3. Syntheses of Molecular Pd(II) Complexes HO(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (9) and Br(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (10)**

 HO(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (9) and Br(CH<sub>2</sub>)<sub>11</sub>N(H)(O)P(2-py)<sub>2</sub>PdCl<sub>2</sub> (10).

**SCHEME 4. The SiO<sub>2</sub>-Bound PdCl<sub>2</sub> Catalyst**

**SCHEME 5. Plausible Mechanisms for the Metal-Catalyzed Alkyne Cyclotrimerization**


erization reaction of 3-hexyne was subjected for electron microscopy studies. The TEM images of the recovered **8** have shown no sign of MW influence on the size or shape of Au cores and the average diameter of Au NPs was comparable to those of freshly prepared **8** (see the Supporting Information).

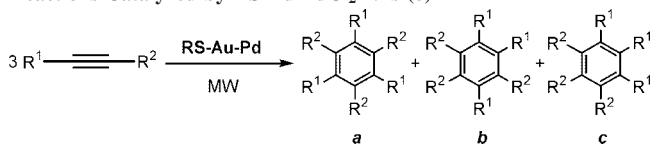
Most current homogeneous Pd catalysts cope with difficulties in quantitative separation, catalyst recovery, and catalyst deactivations by formation of inactive colloidal species at

elevated temperatures,<sup>33</sup> whereas most heterogeneous Pd catalysts suffer from low turnover frequencies and reusability<sup>34</sup> due to either particle aggregation or leaching.<sup>35–37</sup> Since the Au NPs surface bound Pd(II) complex catalysts in our study were heterogeneously suspended in either molecular CHCl<sub>3</sub>, THF, or ionic bmimPF<sub>6</sub>, they can be easily separated and quantitatively recovered from the reaction mixture through simple

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**TABLE 2.** MW-Assisted [2+2+2] Alkyne Cyclotrimerization Reactions Catalyzed by RS-Au-PdCl<sub>2</sub> NPs (**8**)<sup>a</sup>

entry	alkyne R <sup>1</sup> R <sup>2</sup>	catalyst	solvent	time (min)	conversion <sup>d</sup> (%)	product ratio <sup>e</sup> a:b:c
1	Et Et	<b>8</b>	bmimPF <sub>6</sub>	1.5	>99	
2	<sup>n</sup> Pr <sup>n</sup> Pr	<b>8</b>	bmimPF <sub>6</sub>	2.0	>99	
3	Ph Ph	<b>8</b>	bmimPF <sub>6</sub>	10	32	
4	Me Et	<b>8</b>	bmimPF <sub>6</sub>	2.0	>99	29:71:0
5	Me <sup>n</sup> Pr	<b>8</b>	bmimPF <sub>6</sub>	3.0	>99	22:75:3
6	H Ph	<b>8</b>	bmimPF <sub>6</sub>	5.0	>99	21:79:0
7	Et Et	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	bmimPF <sub>6</sub>	1.5	53	
8	<sup>n</sup> Pr <sup>n</sup> Pr	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	bmimPF <sub>6</sub>	2.0	65	
9	Me Et	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	bmimPF <sub>6</sub>	2.0	40	35:65:0
10	Me <sup>n</sup> Pr	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	bmimPF <sub>6</sub>	3.0	68	25:73:2
11	H Ph	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	bmimPF <sub>6</sub>	5.0	75	20:80:0
12	Et Et	<b>8</b>	THF <sup>b</sup>	5.0	98	
13	<sup>n</sup> Pr <sup>n</sup> Pr	<b>8</b>	THF <sup>b</sup>	7.0	99	
14	Me Et	<b>8</b>	THF <sup>c</sup>	8.5	99	29:71:0
15	Me <sup>n</sup> Pr	<b>8</b>	THF <sup>b</sup>	10	99	55:45:0

<sup>a</sup> Reaction conditions: alkyne (0.075 mmol) in bmimPF<sub>6</sub> or THF (1 mL), catalyst loading = 4 mol % under 300 W MW irradiation. <sup>b</sup> Under MW irradiation (max 300 W) and a preset temperature of 62 °C. <sup>c</sup> Under MW irradiation (max 300 W) and a preset temperature of 50 °C. <sup>d</sup> Conversions were determined by <sup>1</sup>H NMR spectroscopy. <sup>e</sup> Products were purified and isolated by flash chromatography on SiO<sub>2</sub> with hexane/ethyl acetate (10/1) as eluent and isomer ratios were determined by GC-MS.

**TABLE 3.** Comparative Recycling and Reuse of Catalysts RS-Au-L-PdCl<sub>2</sub> **8** and Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> in the [2+2+2] Cyclotrimerization of 3-Hexyne<sup>a</sup>

catalyst	cycle (% yield <sup>b</sup> )								
	1	2	3	4	5	6	7	8	9
<b>8</b>	>99	>99	>99	>99	90	82	75	68	57
Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	>99	82	44	20					

<sup>a</sup> Reaction conditions: alkyne (0.0375 mmol) in CDCl<sub>3</sub> (0.5 mL) at 34 °C, catalyst loading = 23.2 mg (8 mol %), reaction time = 10 min for each cycle. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy analysis.

filtration. The <sup>1</sup>H NMR spectrum of **8** recovered from the fifth cycle of catalytic cyclotrimerization of 3-hexyne showed negligible difference from that of freshly prepared **8** (Figure 2d,e). Also, the lack of any detectable Au or Pd species by AA spectroscopy in the filtrate of the reaction solution after catalysis further verified that catalyst **8** was able to resist Pd leaching under our reaction conditions. The recovered colloids after catalysis were also checked by TEM and their average particle sizes were found to be comparable to those before catalysis (see the Supporting Information). A series of catalyst recycling experiments were readily accomplished in the system containing 0.075 mol of 3-hexyne and 23.2 mg of RS-Au-L-PdCl<sub>2</sub> (**8**) (Pd-to-substrate ratio = 8 mol %) in CDCl<sub>3</sub> (0.5 mL) at 34 °C for 10 min. As shown in Table 3, the catalytic system can be effectively recycled with reactivity remaining at ~90% yield throughout the first five cycles before it gradually drop to ~60% after the ninth cycle, whereas the recycling procedure for the molecular Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> catalyst system was a lot more complicated and less efficient. The recovered Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> showed a more than 50% decrease in catalytic activity at the third cycle.

## Conclusions

In summary, we have developed a method to immobilize controllable amounts of molecular palladium(II) complex catalysts onto the surface of Au NPs. The resulting colloidal particles are readily dissolvable and precipitable, and their structures and reaction can be easily studied by solution phase NMR spectroscopy. We have also demonstrated a greener and highly efficient methodology for the construction of polysubstituted benzene rings with fairly good selectivity by using these Au NPs-bound interphase Pd(II) catalysts in ionic liquid under MW irradiation conditions. As compared to their corresponding unbound free form the Au NPs-bound Pd(II) complexes were shown to be more effective catalysts to provide significant reactivity enhancement. In addition, these hybrid catalysts can be easily separated and quantitatively recovered from reaction mixtures by simple centrifugation and filtration. The recovered catalysts can then be recycled many times without loss of reactivity.

As demonstrated herein hybrid catalysts of this type congregate the advantages from both heterogeneous and homogeneous systems. It is expected that many sustainable and applicable catalysts of this form can be made by tethering a wide range of metal complexes or even organocatalysts to a variety of metal nanosurfaces, and they may be useful for promoting many types of chemical reactions in a greener fashion.

## Experimental Section

### A. Synthesis of Molecular Palladium(II) Complex Catalysts.

**Synthesis of Palladium Complex 9.** Compound **5** (0.5 g, 1.3 mmol) was added to a solution of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (0.34 g, 1.3 mmol) in CH<sub>3</sub>CN (30 mL). The mixture was stirred for 6 h at ambient temperature. All volatiles were removed to give **9** as a yellow solid (0.70 g, 95% yield). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 27 °C): δ 1.17–1.37 (br, 16H,  $-(CH_2)_8-$ ), 1.66 (br, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.00 (br, 2H, CH<sub>2</sub>NH), 3.35 (br, 2H, CH<sub>2</sub>OH), 6.99 (br, 1H, NH), 7.76 (m, 2H, py), 8.22 (m, 4H, py), 9.11 (m, 2H, py) ppm. <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO, 27 °C): δ 25.7, 26.4, 28.9, 29.1, 29.2, 29.3, 31.4, 32.8, 41.7, 61.1, 128.4, 131.6 (<sup>3</sup>J<sub>P-C</sub> = 3.0 Hz), 140.0 (<sup>3</sup>J<sub>P-C</sub> = 9 Hz), 148.4 (<sup>1</sup>J<sub>P-C</sub> = 148.0 Hz), 156.0 (<sup>2</sup>J<sub>P-C</sub> = 88.0 Hz), ppm. <sup>31</sup>P NMR (160 MHz, d<sub>6</sub>-DMSO, 27 °C): δ 19.0 ppm. Anal. Calcd for C<sub>21</sub>H<sub>32</sub>N<sub>3</sub>PO<sub>2</sub>Cl<sub>2</sub>Pd: C, 44.50; H, 5.69; N, 7.41. Found: C, 44.12; H, 6.02; N, 7.05.

**Synthesis of Palladium Complex 10.** Compound **6** (0.5 g, 1.1 mmol) was added to a solution of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (0.29 g, 1.1 mmol) in CH<sub>3</sub>CN (30 mL). The mixture was stirred for 3 h at ambient temperature. All volatiles were removed to give **10** as a yellow solid (0.66 g, 94% yield). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 27 °C): δ 1.17–1.37 (br, 14H,  $-(CH_2)_7-$ ), 1.67 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>NH), 1.76 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Br), 3.00 (br, 2H, CH<sub>2</sub>NH), 3.50 (br, 2H, CH<sub>2</sub>Br), 6.98 (br, 1H, NH), 7.76 (m, 2H, py), 8.21 (m, 4H, py), 9.10 (m, 2H, py) ppm. <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO,

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27 °C):  $\delta$  26.3, 26.4, 27.6, 28.2, 28.7, 29.0, 31.4, 32.4, 35.3, 41.5, 45.5, 128.2, 131.5 ( $^3J_{\text{P-C}} = 16$  Hz), 139.82 ( $^3J_{\text{P-C}} = 9$  Hz), 149.1 ( $^1J_{\text{P-C}} = 147$  Hz), 155.8 ( $^2J_{\text{P-C}} = 88$  Hz) ppm.  $^{31}\text{P}$  NMR (160 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  19.1 ppm.

**B. Synthesis of Various Thiolate-Protected Au NPs. Octanethiolate-Protected Au NPs (RS-Au).** To a solution of tetraoctylammonium bromide (500 mg, 0.1 mmol) in  $\text{CHCl}_3$  (40 mL) was added a solution of tetrachloroauric acid (200 mg, 0.5 mmol) in water (15 mL). The mixture was stirred vigorously for 30 min to ensure complete transfer of  $\text{AuCl}_4 \cdot 3\text{H}_2\text{O}$ , at which point the decoloration of the aqueous phase took place while the organic phase turned orange-brown. After this, a mixture of *n*-octanethiol (200 mg, 1.4 mmol) in  $\text{CHCl}_3$  (20 mL) was added to the solution. After 10 min, a freshly prepared aqueous solution of  $\text{NaBH}_4$  (200 mg, 5.5 mmol in 20 mL of  $\text{H}_2\text{O}$ ) was added dropwise to the reaction mixture. The colloids formed instantaneously as indicated by the color change of the solution from orange to red and then to black-brown. After 12 h, the organic layer was collected. The colloidal solution was then concentrated to 3 mL, and 150 mL of ethanol was added to allow sitting at room temperature for 1 h for colloid precipitation. Precipitation from ethanol was carried out continuously until no more free ligand could be detected by  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ , no  $\alpha\text{-CH}_2$  resonance at  $\sim 2.49$  ppm) and IR spectroscopy (absence of  $\nu_{\text{asym}}(\text{SH})$  band in the region of  $2569\text{ cm}^{-1}$ ). Centrifugation gave the colloids as black solids (75 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 27 °C):  $\delta$  0.88 (br, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.57–1.80 (br, 10H,  $\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 2.46–2.51 (br, 2H,  $\text{CH}_2\text{CH}_2\text{SH}$ ), 2.9–3.5 (br, 2H,  $\text{CH}_2\text{S-Au}$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 27 °C):  $\delta$  14.1, 22.6, 22.8, 29.0–29.6, 32.0 ppm. TEM ( $2.7 \pm 0.5$  nm), the colloids contained an average number of 755 gold atoms/core<sup>38</sup> and 1470 adsorbed octanethiolate molecules per Au core.

**Mixed Octanethiolate- and Dipyrldylphosphinic Amido Undecanethiolate-Protected Au NPs (RS-Au-L, 7).** Freshly prepared octanethiolate-protected Au NPs, RS-Au (75 mg) were dissolved in degassed  $\text{CHCl}_3$  (25 mL). To this solution was added ligand **4** (60 mg, 0.15 mmol), and the reaction mixture was stirred for 16 h at 70 °C. The solution was concentrated to a minimum amount (0.5 mL), then was washed with hexane ( $3 \times 50$  mL). A degassed acetone solvent (150 mL) was added and the solution was allowed to sit at room temperature for 1 h for gold colloid precipitation. Further precipitation from acetone was performed continuously until no more free ligand **4** could be detected by  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ , no  $\alpha\text{-CH}_2$  resonance at  $\sim 2.49$  ppm) and IR spectroscopy (absence of  $\nu_{\text{asym}}(\text{SH})$  band in the region of  $2576\text{ cm}^{-1}$ ). Centrifugation gave the colloids as black solid product, RS-Au-L (**7**) (60 mg).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  0.78 (br,  $\text{CH}_3$ ), 0.87–1.90 (br, methylene protons), 2.83 (br,  $\text{CH}_2\text{NH}$ ), 5.32 (m, NH), 7.42 (m, py), 7.86 (m, py), 7.95 (m, py), 8.62 (m, py) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  14.1, 22.5, 26.5, 29.5, 31.8, 117.0, 125.6, 127.8 ( $^2J_{\text{P-C}} = 21$  Hz), 136.4, 138.2, 150.1 ( $^2J_{\text{P-C}} = 20$  Hz), 156.3 ( $^1J_{\text{P-C}} = 123$  Hz) ppm.  $^{31}\text{P}$  NMR (160 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  17.4 ppm. TEM ( $3.9 \pm 0.4$  nm), the colloids contained an average number of 2278 gold atoms/core and 607 adsorbed octanethiolate molecules per Au core and 497 adsorbed bipyridylphosphinic amido *n*-undecanethiolate molecules per Au core.

**Synthesis of Palladium-Functionalized Au NPs (RS-Au-L-PdCl<sub>2</sub>, 8).** A freshly prepared mixed *n*-octanethiolate- and bipy-

ridylphosphinic amido *n*-undecanethiolate-protected Au NPs, RS-Au-L (**7**) (60 mg) was dissolved in degassed  $\text{CHCl}_3$  (30 mL). To this solution was added  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  (6 mg, 0.034 mmol), and the reaction mixture was stirred for 3 h at ambient temperature. The solution was concentrated to a minimum amount and was washed first with acetone ( $3 \times 50$  mL) then with  $\text{CHCl}_3$  ( $3 \times 50$  mL). Further precipitation from  $\text{CHCl}_3$  was performed continuously until no more free  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  was present. Centrifugation gave the colloids as black solid product, RS-Au-L-PdCl<sub>2</sub> (**8**) (40 mg).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  0.81 (br,  $\text{CH}_3$ ), 1.2–1.80 (br, methylene protons), 2.92–3.0 (m,  $\text{CH}_2\text{NH}$ ), 7.0 (m, NH), 7.77 (m, py), 8.25 (m, py), 9.10 (m, py) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  14.1, 22.3, 26.3, 29.1, 30.6, 31.5, 128.3, 131.5, 139.9, 149.0 ( $^1J_{\text{P-C}} = 122$  Hz), 155.8 ppm.  $^{31}\text{P}$  NMR (160 MHz,  $d_6$ -DMSO, 27 °C):  $\delta$  18.9 ppm. TEM ( $4.9 \pm 1$  nm), the colloids contained an average number of 4521 gold atoms/core and 287 adsorbed *n*-octanethiolate molecules/Au core and 207 adsorbed Pd(II)-functionalized *n*-undecanethiolate molecules/Au core.

**C. Catalytic [2+2+2] Alkyne Cyclotrimerization Reactions. General Procedure.** To a suspension of RS-Au-L-PdCl<sub>2</sub> (**8**) (11.6 mg, containing  $3 \times 10^{-3}$  mmol of Pd(II)) in 1.0 mL of  $\text{CDCl}_3$  was added 3-hexyne (6.2 mg, 0.075 mmol). The reaction mixture was stirred at room temperature for 30 min or at 62 °C for 10 min. After the reaction, the solids were filtered off and the filtrate was dried under vacuum for direct use in NMR and GC-MS analysis. The [2+2+2] alkyne cyclotrimerization reaction product was further purified on a short silica plug (63–200 mesh; eluting with hexane) for yield calculation. The spectroscopic characteristics of already known products were compared with published data.

**MW-Assisted [2+2+2] Alkyne Cyclotrimerization Reactions.** To a bmimPF<sub>6</sub> (1-butyl-3-methylimidazolium hexafluorophosphate, 1.0 mL) suspension of RS-Au-L-PdCl<sub>2</sub> (**8**) (11.6 mg, containing  $3 \times 10^{-3}$  mmol of Pd(II)) in a Teflon digestion vessel was added 3-hexyne (6.2 mg, 0.075 mmol). The reaction vessel was placed under 300 W MW (CEM MARS 5e, continuous wave mode) for 1.5 min. The resulting gooeey mixture was extracted with hexane ( $3 \times 5$  mL). The extract was used directly for NMR and GC-MS analysis. The cyclotrimerized products were further purified on a short silica plug (63–200 mesh; eluting with hexane) for yield calculation. The spectroscopic characteristics of already known products were compared with published data.

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**Supporting Information Available:** General Experimental Methods, detailed synthetic procedures for compounds **1–6**, TEM images of RS-Au-L NPs **7** and RS-Au-L-PdCl<sub>2</sub> NPs **8**, UV–vis spectra of compound **4** and RS-Au-L NPs **7** and RS-Au-L-PdCl<sub>2</sub> NPs **8**, analytical data for alkanethiolates-protected RS-Au NPs, RS-Au-L NPs **7**, and RS-Au-L-PdCl<sub>2</sub> NPs **8**,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **1–6**, **9**, and **10** the alkanethiolates-protected RS-Au NPs, RS-Au-L NPs **7**, and RS-Au-L-PdCl<sub>2</sub> NPs **8**, and IR spectra of compound **4** and alkanethiolates-protected RS-Au NPs, RS-Au-L NPs **7**, and RS-Au-L-PdCl<sub>2</sub> NPs **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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