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[5] Crystal data. Compound **1**: $C_{14}H_{20}FeNdN_{10}O_7$, $M_r = 640.49$, triclinic, $P\bar{1}$, $a = 8.9399(5)$, $b = 9.1967(3)$, $c = 15.4335(7)$ Å, $\alpha = 76.054(3)$, $\beta = 89.359(3)$, $\gamma = 67.756(3)^\circ$, $V = 1135.31(9)$ Å^3, $Z = 2$, $\rho = 1.874$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 2.957$ mm^{-1}, $F(000) = 632$, GoF = 1.055. A total of 18535 reflections were collected and 5364 are unique ($R_{int} = 0.0507$). The final $R1$ and $wR2$ are 0.0310 and 0.0758, respectively, for 345 parameters and 4889 reflections ($I > 2\sigma(I)$). Compound **2**: $C_{14}H_{20}CoNdN_{10}O_7$, $M_r = 643.57$, triclinic, $P\bar{1}$, $a = 8.7801(5)$, $b = 9.2011(5)$, $c = 15.4319(10)$ Å, $\alpha = 76.337(4)$, $\beta = 88.982(4)$, $\gamma = 67.542(4)^\circ$, $V = 1115.89(11)$ Å^3, $Z = 2$, $\rho = 1.915$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 3.102$ mm^{-1}, $F(000) = 634$, GoF = 1.029. A total of 14884 reflections were collected and 5118 are unique ($R_{int} = 0.1088$). The final $R1$ and $wR2$ are 0.0638 and 0.1483, respectively, for 345 parameters and 3829 reflections ($I > 2\sigma(I)$). The data of both compounds were collected on a Nonius Kappa CCD with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direction method and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147180 (**1**) and CCDC-147181 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Immobilization of Homogeneous Palladium(II) Complex Catalysts on Novel Polysiloxanes with Controllable Solubility: Important Implications for the Study of Heterogeneous Catalysis on Silica Surfaces**

Yaw-Shyan Fu and Shuchun J. Yu*

Immobilization of homogeneous transition metal complex catalysts by tethering them to silica supports has been intensively studied during the past few decades.[1] These supported homogeneous transition metal complex catalysts should in principle combine the advantages of both heterogeneous and homogeneous systems. However, the problems of significant metal leaching[2] and low catalyst selectivity[1h, 3] are major drawbacks that prevent their potential use. Due to the insoluble nature of these supported catalysts, it has been difficult to obtain detailed information about the exact chemical structures of the catalyst systems and to estimate any loss of activity resulting from heterogenization. Therefore, a major development in this field would be the development of a method that would allow silica-supported homogeneous transition metal complexes and their reactions to be investigated by NMR spectroscopy with the resolution typically attained for soluble systems.[4] Here we describe the preparation and characterization of homogeneous Pd^{II} complex catalysts tethered to a range of polysiloxanes. These materials were 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 can be systematically varied to provide catalyst systems ranging from soluble, homogeneous model compounds to heterogeneous three-dimensional networks. The structures and reaction chemistry of the soluble system were studied by NMR spectroscopy in solution, while the reactivity and regioselectivity were investigated in the catalytic [2+2+2] cyclotrimerization of alkynes.

The incomplete acid-catalyzed hydrolysis[5] of $(MeO)_3Si(CH_2)_{11}N_3$ (**1**) in THF generated silica fragments small enough to be soluble in conventional organic solvents. Subsequent silylation with trimethylsilyl chloride (TMSCl) was performed to end-cap the remaining Si-bound hydroxy groups to prevent further self-condensation of polysiloxanes (Scheme 1). The resulting polysiloxane **2** can then be readily derivatized with $P(2\text{-py})_3$ (2-py = 2-pyridyl) in situ or after isolation to afford polysiloxane **3** with $NHP(O)(2\text{-py})_2$ functionality.[6] Polysiloxanes **2** and **3** with molecular weights around 5500 and polydispersity indexes of about 1.5 were thus obtained.[7] As expected, these polymers exhibited excellent

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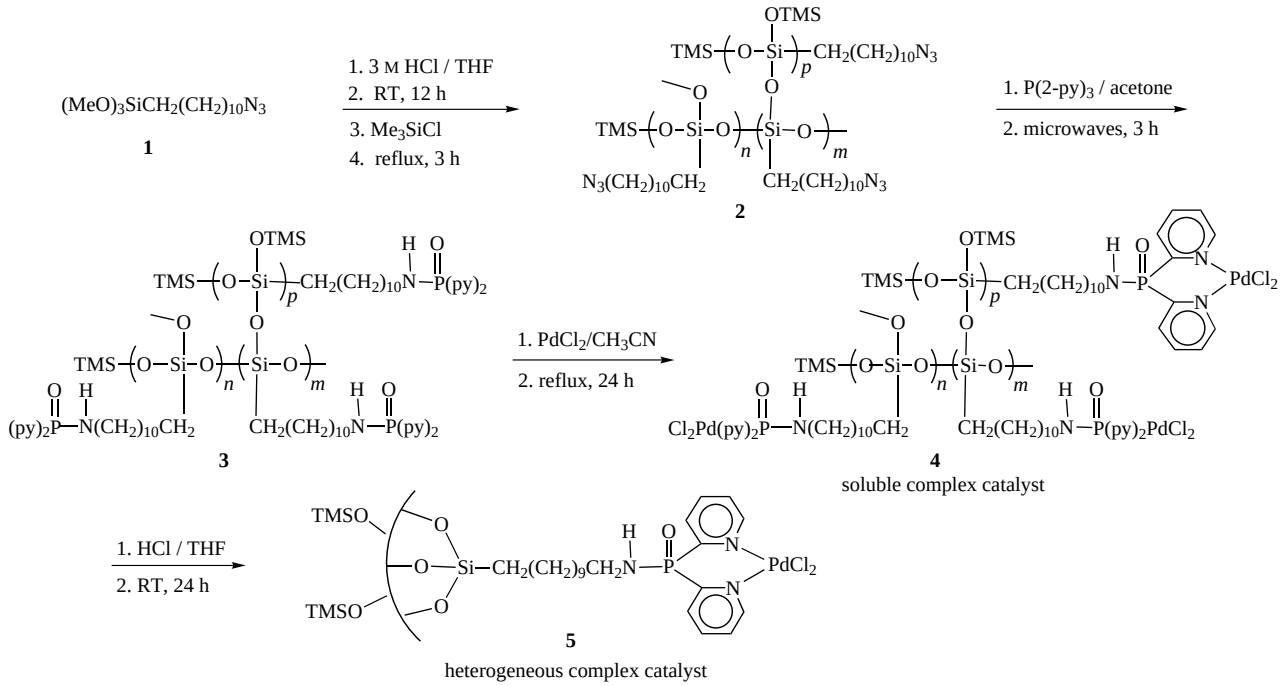

Scheme 1. Immobilization of homogeneous Pd^{II} complex catalysts on polysiloxanes with controllable solubility.

solubility and gave clear ^1H and ^{29}Si NMR spectra (Figure 1), which allowed us to determine to good accuracy the weight percent of functionalized alkyl side chains and the degree of branching.[8] Furthermore, the molecular weight and degree of branching can be controlled by varying the acid concentration and reaction time, and the TMS-end-capped polysiloxanes were highly resistant to further self-condensation, even after exposure to moist air for months.

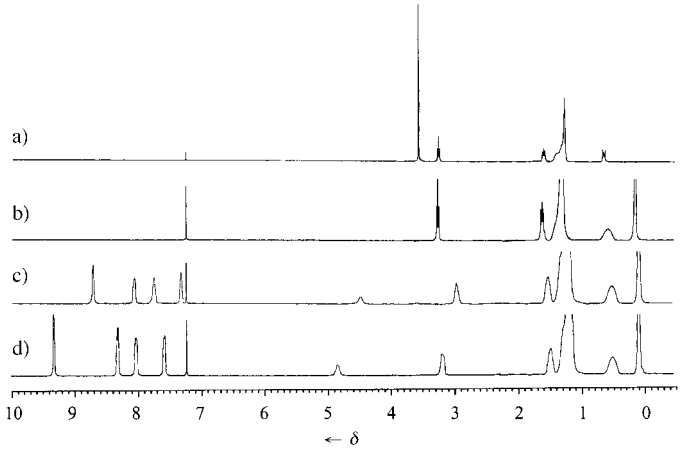

Figure 1. 400 MHz ^1H NMR spectra of a) **1**, b) **2**, c) **3**, and d) **4**.

The commonly used phosphane-based tethering ligands possess excellent properties for binding transition metal complexes onto silica surfaces. However, they are easily transformed into the corresponding phosphane oxides.[9] This can cause significant metal leaching and has restricted their industrial application. Hence, we designed and synthesized the aza-based ligand $SiCH_{11}NHP(O)(2\text{-py})_2$, with bidentate bis-pyridyl functionality (py-P-py 105.5°),[10] which could exhibit a large py-M-py bite angle when coordinated to metal centers and has the potential for greater catalyst stability and regioselectivity.[1b, 11] As anticipated, homogeneous Pd^{II} complexes were covalently immobilized by the ligating bis-pyridyl groups to afford the soluble, polysiloxane-supported Pd^{II} complex **4** (Scheme 1) with small specific surface areas ($\approx 25\ m^2 g^{-1}$ ($BET(N_2)$). Progressive heterogenization was conducted by further treatment of **4** with HCl to yield the insoluble counterpart **5** with larger specific surface areas ($\approx 190\ m^2 g^{-1}$ ($BET(N_2)$).

Although various Pd complexes are known to promote alkyne cyclotrimerization,[12] the problems of low chemo- and regioselectivity greatly hamper the utilization of the reaction. In the present study, both **4** and **5** were found to be excellent catalysts for various alkyne cyclotrimerization reactions (Table 1). With a catalyst loading of 4 mol%, the homogeneous reactions with **4** can be performed under milder conditions to afford polysubstituted benzenes in about 90% yields of isolated products. Conversely, reactions catalyzed by **5** had to be conducted at higher temperature since the system is heterogeneous.

A series of **4**-catalyzed cyclotrimerization reactions was also carried out in a 400 MHz solution-phase ^1H NMR probe to monitor the course of catalysis. Catalyst **4** was demonstrated to be robustly stable against decomposition and Pd leaching at 27 and 62 °C, and this made it an attractive candidate for heterogenization. In a comparative study, control experiments were performed under similar conditions with $[(PhCN)_2PdCl_2]$ as catalyst. This resulted in a suspension of $(LPdCl \cdot PdCl_2)_n$ (L = PhCN or alkyne) and a color change from yellow to dark red.[13] In contrast, neither color change nor precipitation was observed during the course of **5**-catalyzed reactions under similar conditions. Also, the lack

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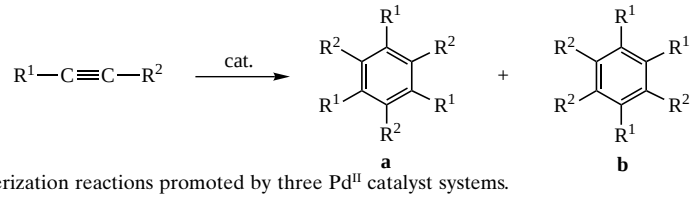

Table 1. [2+2+2] alkyne cyclotrimerization reactions promoted by three Pd^{II} catalyst systems.

Entry	Alkyne[a]		Catalyst[b]	T [°C]	t [h][c]	Yield [%][d]	Product ratio[f] **a**:**b**
	R^1	R^2			(RT/62 °C)	(RT/62 °C)	(RT/62 °C)
1	Me	Me	$[(PhCN)_2PdCl_2]$	RT	24	85	
2	Me	Me	**4**	RT/62	24/12	88/94	
3	Me	Me	**5**	62	12	94	
4	Me	*n*Pr	$[(PhCN)_2PdCl_2]$	RT	36	78	63:37
5	Me	*n*Pr	**4**	RT/62	36/16	83/96	94:6/91:9
6	Me	*n*Pr	**5**	62	16	86	90:10
7	Et	Et	$[(PhCN)_2PdCl_2]$	RT	36	83	
8	Et	Et	**4**	RT/62	36/16	88/91	
9	Et	Et	**5**	62	16	94	
10	*n*Pr	*n*Pr	$[(PhCN)_2PdCl_2]$	RT	36	81	
11	*n*Pr	*n*Pr	**4**	RT/62	36/16	90/93 (>99%, cycles 1–6)[e]	
12	*n*Pr	*n*Pr	**5**	62	16	95 (>99%, cycles 1–6)[e]	
13	Ph	H	$[(PhCN)_2PdCl_2]$	RT	36	85	52:48
14	Ph	H	**4**	RT/62	36/16	91/94	82:18/81:19
15	Ph	H	**5**	62	16	92	79:21
16	Ph	Ph	$[(PhCN)_2PdCl_2]$	RT	36	86	
17	Ph	Ph	**4**	RT/62	36/16	89/95	
18	Ph	Ph	**5**	62	16	90	

[a] Alkyne (0.56 mmol) in $CHCl_3$ (3 mL). [b] Catalyst loading = 4 mol%. [c] Time for >90% alkyne conversion at room temperature (RT) and 62 °C for catalyses by **4** and **5**. [d] Products were purified and isolated by flash chromatography on SiO_2 with hexane/ethyl acetate (10/1) as eluent. [e] >99% conversion was determined by NMR spectroscopy for each of the six catalytic cycles (16 h per cycle) at 62 °C. [f] Products were identified by NMR spectroscopy, and isomer ratios were determined by HPLC.

of any Pd species detectable by atomic adsorption spectroscopy in the filtrate of the reaction solution further verified that catalyst **5** was able to resist Pd leaching under catalytic conditions. In the case of asymmetric alkynes such as 2-hexyne and phenylacetylene, both **4** and **5** were more regioselective than $[(PhCN)_2PdCl_2]$, and this was presumably due to the formation of palladacycles. In addition, catalyst-recycling experiments were performed in $CHCl_3$ at reflux by using **4** and **5** as catalysts for the cyclic cyclotrimerization of 4-octyne to study the relative degree of catalyst deactivation (Table 1, entries 11 and 12). Both **4** and **5** exhibited excellent stability with greater than 99% 4-octyne conversion through six cycles. Also, the ^{1}H NMR spectrum in the pyridyl region of the **4**-containing solution from the last cycle showed negligible difference from that of freshly prepared **4**. This suggested that both **4** and **5** have sufficiently long catalyst lifetime to be effectively recycled.

In summary, we have demonstrated that the homogeneous palladium(II) complex catalysts were successfully immobilized on a range of polysiloxane materials with controllable solubility and degree of cross-linking. Catalysts **4** and **5** prepared in this way were found to be very active and regioselective in various alkyne cyclotrimerization reactions. Further studies of regio- and chemoselective coupling are in progress. The current system shows that a given metal catalyst can be studied and characterized progressively as its support was systematically varied from the homogeneous to the heterogeneous phase. Accordingly, these results may provide important insights into the field of heterogeneous catalysis on silica surfaces.

Experimental Section

1: $(MeO)_3Si(CH_2)_{11}Br$ (2.0 g, 5.63 mmol) was added to a solution of NaN_3 (0.493 g, 6.75 mmol) in DMF (20 mL). The mixture was stirred for 6 h. NaBr was filtered off, and the filtrate was extracted with hexane (6 × 10 mL). The extract was dried to give **1**. Yield: 1.60 g (90%). ^{1}H NMR(400 MHz, $CDCl_3$, 27 °C): $\delta = 0.63$ (t, $\equiv SiCH_2$), 1.20–1.40 (br s, $\equiv SiCH_2(CH_2)_8$), 1.58 (m, $\equiv Si(CH_2)_9CH_2$), 3.25 (t, $\equiv Si(CH_2)_{10}CH_2N_3$), 3.55 (s, $(OMe)_3Si$).

4: $PdCl_2$ (94 mg, 0.525 mmol) was added to a solution of **3** (200 mg, 0.966 mmol of py) in CH_3CN (15 mL). The mixture was stirred at reflux for 24 h. All volatile substances were removed, and the residue was extracted with $CHCl_3$ (2 × 10 mL). The extract was dried to give **4** as a yellow solid. Yield: 260 mg (91% based on py). ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): $\delta = 0.63$ (br s, $\equiv SiCH_2$), 1.20–1.40 (br s, $\equiv SiCH_2(CH_2)_8$), 1.53 (br s, $\equiv Si(CH_2)_9CH_2$), 3.27 (br s, $\equiv Si(CH_2)_{10}CH_2NH$), 4.91 (br s, $\equiv Si(CH_2)_{11}NHP(O)$), 7.64 (br s, py), 8.07 (br s, py), 8.34 (br s, py), 9.35 (br s, py); ^{31}P NMR (160 MHz, $CDCl_3$, 27 °C): $\delta = 16.1$.

5: HCl (3 M, 1 mL) was added to a solution of **4** (100 mg) in THF (20 mL). The solution was stirred for 24 h. The mixture was filtered and dried under vacuum to give **5** as a yellow solid.

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Catalytic Enantioselective Protonation of Lithium Ester Enolates Generated by Conjugate Addition of Arylthiolate to Enoates**

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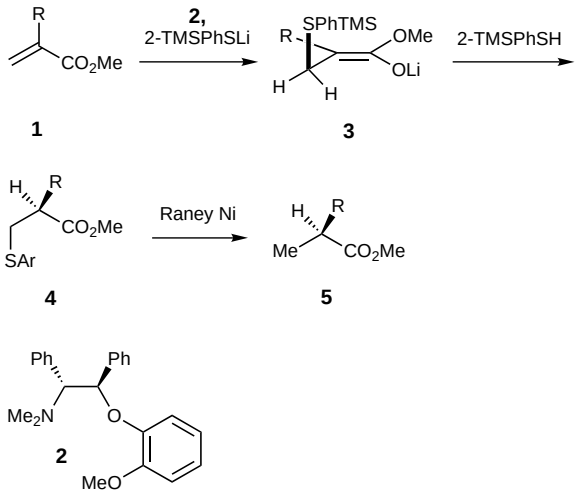
Enantioselective protonation of prochiral enolates represents a most useful advance in recent synthetic chemistry.[1, 2] In particular, catalytic enantioselective protonation has been a challenging target.[3] Generally, such reactions rely on a combination of an excess achiral proton source and a substoichiometric chiral proton source such as imides,[4] phenols,[5] alcohols,[6] amino alcohols,[7] and amines.[8] Prochiral substrates are often metal enolates, generated by the reaction of silyl enol ethers or enol acetates with an excess of an organometallic species. In spite of the recent impressive progress in this field, there have been few approaches that use a catalytic amount of a metal cation for the generation of metal enolates.[9]

We present here the chiral ligand catalyzed enantioselective protonation of a transient lithium ester enolate **3**—generated by a conjugate addition of lithium arylthiolate to propenoates **1** in the presence of the chiral amino diether **2**—to give the 3-arylsulfanyl 2-substituted propanoates **4** with high *ee* values (Scheme 1).[10] Reductive desulfurization of **4**, bearing a chiral



Scheme 1. Catalytic asymmetric addition – protonation and desulfurization. TMS = trimethylsilyl.

center at the C2 position, with Raney nickel completes the catalytic enantioselective protonation to afford the corresponding chiral propanoates **5** in high yield without racemization. The two-step procedure is characterized by an asymmetric protonation of a lithium enolate generated by a catalytic amount of a lithium cation.

The strategy for the catalytic asymmetric protonation is based on our previously developed asymmetric addition of 2-trimethylsilylbenzenethiol (2-TMSPhSH) to enoates, which is controlled by a chiral ligand.[11] The addition of a thiolate to an enoate and protonation of the resulting enolate by a thiol are highly stereoselective procedures and provide the *anti*-protonation product.[12] Furthermore, the attack of the thiolate on the 2-enoate is the rate-determining step of the addition – protonation reaction,[13] and hence protonation of the resulting enolate by thiol is rapid. Consequently, if the protonation of enolate **3** takes place before this species undergoes a conformational change, it probably proceeds in an *anti* manner to the C–S bond to afford **4** with high *ee* values.

The asymmetric addition – protonation is exemplified by the reaction of methyl 2-phenylpropenoate (**1c**, R = Ph) with 1.2 equivalents of 2-trimethylsilylbenzenethiol. The reaction

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