trations a second by-product (< 5 %) could be observed, which is most likely attributable to a square. The solvent was removed under a stream of N_2, and the resulting white precipitate was dried in vacuo (yield 93 %). ^{1}H NMR (CD_3NO_2, 300 MHz): $\delta = 9.41$ (s, 2 H; H_{pyr}), 1.79 (d, $J_{P,H} = 11.4$ Hz, 9 H; P-CH_3); ^{31}P{^{1}H} NMR (CD_3NO_2, 121 MHz): $\delta = -25.6$ (s, ^{195}Pt satellites, $J_{Pt,P} = 3269$ Hz); ^{19}F NMR (CD_3NO_2, 282 MHz): $\delta = -78.1$; ^{13}C{^{1}H} NMR (CD_3NO_2, 75 MHz): $\delta = 151.8$ (s, C_{pyr}), 122.2 (q, $J_{C,F} =$ 319 Hz, OTf), 14.7 (m,P-CH_3).

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[9] Crystal structure analysis of **3** at 200(1) K: $C_{36}H_{66}F_{18}N_6O_{18}P_6Pt_3S_6 \cdot 3CH_3NO_2$, $M_r = 2359.53$, colorless prism, $0.25 \times 0.23 \times 0.15$ mm^3, monoclinic space group $P2_1/c$, $a = 15.584(3)$, $b = 24.021(4)$, $c = 23.542(4)$ Å, $\beta = 105.146(6)^\circ$, $V = 8506(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.842$ Mg m^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 5.287$ mm^{-1}). Data were collected on a Nonius KappaCCD diffractometer in the range $1.23 < \theta < 23.28^\circ$. A total of 16528 measured reflections, 10142 unique, 6426 with $F_o^2 = 4\sigma(F_o^2)$ were used to refine 636 parameters to $R1(wR2) = 0.1134(0.2669)$, $GOF = 1.111$, F^2 refinement in SHELXL97. A multiscan absorption correction gave min. and max. transmission factors of 0.5044 and 0.3516. The residual peaks in the final difference map ranged from -1.832 to $+2.339$ e Å^{-3}.[10]

[10] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-163666.

Microencapsulated Palladium Catalysts: Allylic Substitution and Suzuki Coupling Using a Recoverable and Reusable Polymer-Supported Palladium Catalyst**

Ryo Akiyama and Shū Kobayashi*

While palladium catalysts find wide-spread utility in a variety of transformations in organic synthesis,[1] they are expensive, air-sensitive, and cannot be recovered in many cases. Immobilized palladium catalysts have been expected to solve these problems, and several polymer-supported palladium catalysts have been developed for allylic substitution,[2, 9a,b,e] oligomerization,[2c, 3, 4] decarboxylation,[2d] hydrogenation,[4, 9g] isomerization,[5] telomerization,[6] Suzuki coupling,[7, 9c,d,h] and the Mizoroki – Heck reaction,[4c, 8, 9f,h] etc. In most of these cases, however, recovery and reuse of the polymer catalysts have not been satisfactory.[9] Recently, we developed novel polymer-supported catalysts, microencapsulated scandium trifluoromethanesulfonate (MC Sc(OTf)$_3$)[10] and osmium tetroxide (MC OsO_4).[11] Our work has demonstrated a new method for immobilizing catalysts onto polymers based on physical envelopment by the polymers and on electronic interaction between the π electrons of the benzene rings of the polystyrene-based polymers and vacant orbitals of the catalysts. We now apply this new technology to immobilizing palladium catalysts. Herein, we describe the use of microencapsulated triphenylphosphane palladium for allylic substitution and Suzuki coupling. In both cases, the catalysts were recovered quantitatively and reused. Moreover, valuable information on the structure of microencapsulated catalysts was obtained.

Preparation of microencapsulated triphenylphosphane palladium was as follows:[12] polystyrene (1.0 g, M_w ca. 280000) was dissolved in cyclohexane (20 mL) at 40 °C, and to this solution was added tetrakis(triphenylphosphane)palladium(0) ([$Pd(PPh_3)_4$] 0.20 g) as a core ([$Pd(PPh_3)_4$] was dissolved). The mixture was stirred for 1 h at this temperature (and changed from brown to black), then slowly cooled to 0 °C. Coacervates (phase separation) were found to envelop the core dispersed in the medium, and hexane (30 mL) was added to harden the capsule walls. The mixture was left to stand at room temperature for 12 h, and the catalyst capsules were then washed with acetonitrile several times and dried at room temperature for 24 h. Three equivalents of triphenylphosphane (PPh_3) were recovered from the washings and one equivalent of PPh_3 remained in the catalyst capsules. We measured ^{31}P swollen-resin magic angle spinning (SR-MAS)

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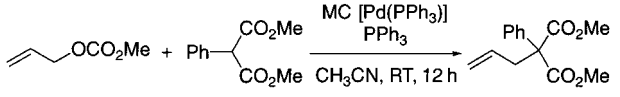
NMR spectra[13] of the catalyst capsules, and only one resonance signal arising from PPh_3 coordinating to the palladium was observed.[14] From these results, we assumed that the catalyst was encapsulated as [Pd(PPh_3)].

The microencapsulated [Pd(PPh_3)] (MC[Pd(PPh_3)]) thus prepared was used in the allylation reaction of allyl methyl carbonate (**1**) with dimethyl phenylmalonate (**2**). When **1** was combined with **2** in the presence of 20 mol% MC[Pd(PPh_3)], the reaction did not proceed at all. However, it was found that the reaction proceeded smoothly after adding PPh_3 (external ligand). We examined the effect of different amounts of PPh_3 (Table 1). The best results were obtained when 20 mol% of PPh_3 was used.[15] Of note is that the palladium catalyst was recovered quantitatively and reused, and that the high activity of the catalyst was maintained even after the fifth use.

Table 1. Effect of the amount of triphenylphosphane.



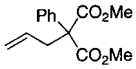
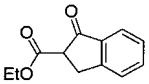
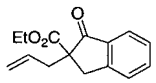
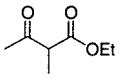
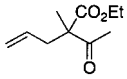
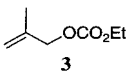
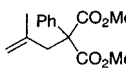
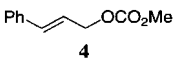
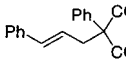
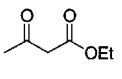
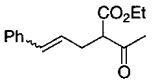
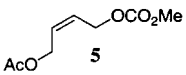
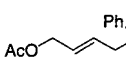
1 **2**

MC[Pd(PPh_3)] [mol%]	PPh_3 [mol%]	Yield [%] (Recovery [%]) 1st	2nd	3rd
5	0	0	–	–
5	5	97 (quant)	75 (quant)	57 (quant)
20	0	0	–	–
20	10	94 (quant)	61 (99)	30 (99)
20	20	83 (quant)	90 (quant)	84 (quant)[a]
20	40	92 (quant)	81 (99)	77 (quant)
20	60	69 (95)	58 (98)	65 (99)

[a] 4th run: 94 (quant), 5th run: 83 (quant).

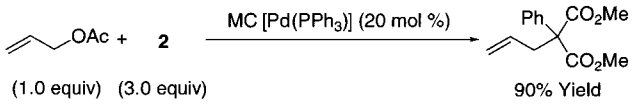
Several examples of the MC[Pd(PPh_3)]-catalyzed allylation reactions of C-nucleophiles with allylic carbonates are summarized in Table 2. Malonates and β-ketoesters smoothly reacted under these conditions to afford the corresponding allylation products in high yields. While the reaction of ethyl acetoacetate with (*E*)-cinnamyl methyl carbonate (**4**) gave a mixture of *E*/*Z* stereoisomers (*E*/*Z* = 64/36), only *E* isomers were obtained in the reactions of **2** with **4** or *Z* carbonate **5**. The recovery was quantitative in all cases and the recovered catalyst could be reused.

Table 2. Allylic substitution using MC[Pd(PPh_3)].[a]

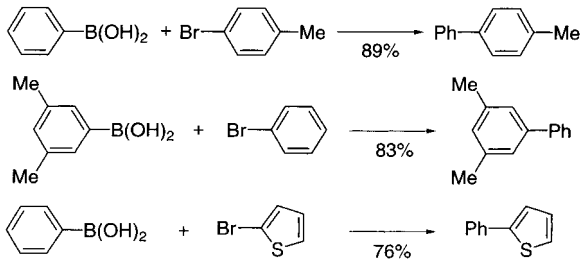
Entry	Allylic carbonate	Nucleophile	Product	Yield [%]
1	**1**	**2**		83
2	**1**			86
3	**1**			60
4	 **3**	**2**		69
5	 **4**	**2**		92[b]
6	**4**			79[c]
7	 **5**	**2**		64[b]

[a] All reactions were carried out using MC[Pd(PPh_3)] (20 mol%) and PPh_3 (20 mol%) in CH_3CN at room temperature for 12 h. [b] *E*/*Z* = > 99/< 1. [c] *E*/*Z* = 64/36.

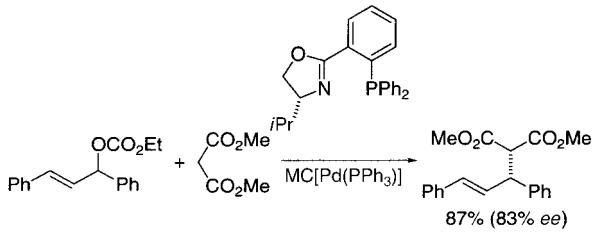
MC[Pd(PPh_3)] was successfully used in other reactions. Allyl acetate reacted with dimethyl phenylmalonate in the presence of MC[Pd(PPh_3)], PPh_3, *N*,*O*-bis(trimethylsilyl)-acetamide (BSA), and a catalytic amount of potassium acetate (KOAc), to afford the corresponding product in 90% yield (Scheme 1). In addition, Suzuki coupling reactions[16] of boronic acids with aryl bromides were found to proceed smoothly in the presence of MC[Pd(PPh_3)] to afford the corresponding products in high yields. 2-Bromothiophene also worked well. In these reactions, the best results were obtained by using tri-*o*-tolylphosphane (P(*o*-Tol)$_3$) as an external ligand (Scheme 2). Finally, a catalytic asymmetric allylation reaction was carried out using MC[Pd(PPh_3)] and a chiral ligand (Scheme 3). The reaction of 1,3-diphenyl-2-propen-1-yl ethyl carbonate (1.0 equiv) with dimethyl malonate (3.0 equiv) was performed in the presence of MC[Pd(PPh_3)] (20 mol%), 2-(*o*-diphenylphosphanophenyl)-(4*R*)-isopropyloxazoline (20 mol%),[17] BSA (3.0 equiv), and



Scheme 1. Allylic substitution of allyl acetate with **2**. Reaction carried out using MC[Pd(PPh_3)] (20 mol%), PPh_3 (20 mol%), BSA (3.0 equiv), and KOAc (0.10 equiv) in CH_3CN under reflux for 12 h.



Scheme 2. Suzuki coupling. All reactions were carried out using MC[Pd(PPh_3)] (20 mol%) and P(*o*-Tol)$_3$ (20 mol%) in CH_3CN under reflux for 6 h.



Scheme 3. Asymmetric allylic substitution. Reaction carried out using MC[Pd(PPh_3)] (20 mol%), chiral ligand (20 mol%), BSA (3.0 equiv), and KOAc (0.10 equiv) in CH_3CN under reflux for 12 h.

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KOAc (0.10 equiv) under reflux conditions in acetonitrile. The allylation adduct was obtained in 87 % yield with 83 % *ee*.

For the structure of the microencapsulated species, we assume an 18-electron Pd^0 center that is coordinated by PPh_3 and the benzene ring(s) of polystyrene. After adding an external ligand, 14- or 16-electron Pd^0 would be formed and the catalytic reaction proceeds.[18] The coordination of the external ligand to Pd^0 was confirmed by ^{31}P SR-MAS NMR analysis which revealed that the recovered catalyst in Suzuki coupling reactions contained $P(o\text{-Tol})_3$.[19]

In summary, we have immobilized triphenylphosphane palladium onto a polymer using a microencapsulating technique. The polymer-supported catalyst (MC[$Pd(PPh_3)$]) has been successfully used in several palladium-catalyzed reactions. In all cases, the reactions proceeded in high yields, and the catalyst was recovered simply by filtration and reused. It should be noted that the air-sensitivity of the palladium complex is substantially suppressed by this immobilization. Moreover, NMR spectroscopic analyses have provided valuable information on the structure of the MC catalysts.

Experimental Section

A typical experimental procedure for the allylation reaction of **1** with **2**: **1** (0.55 mmol), **2** (0.5 mmol), PPh_3 (0.1 mmol), and MC[$Pd(PPh_3)$] (0.1 mmol, 20 mol %) were combined in acetonitrile (5 mL). The mixture was stirred for 12 h at room temperature. After ethanol was added to quench the reaction, the catalyst was collected by filtration and washed with ethanol and acetonitrile, and then dried. The solvents of the filtrate were removed under reduced pressure, and the crude product was purified by preparative thin-layer chromatography (TLC) to afford the desired adduct (83 %). The recovered MC[$Pd(PPh_3)$] was reused several times without loss of activity.

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[14] MC[$Pd(PPh_3)$]: ^{31}P NMR ($CDCl_3$, SR-MAS): $\delta = 29.1$, cf. PPh_3 ($CDCl_3$): $\delta = -4.7$; $O{=}PPh_3$ ($CDCl_3$): $\delta = 55.3$, solid PPh_3 ($\delta = -8.4$) was used as an external standard.

[15] It was assumed that active Pd catalysts are located on or close to the surface of the microcapsules.[10, 11] The amount of the active catalyst is much less than 20 mol %.

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[19] The ligand exchange occurred partially.

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