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Amino-acid containing metallomonomers copolymerized into porous organic polymers: applicability to allylic alkylation catalysis

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Dedicated to Prof. Tobin J. Marks on his 60th birthday

Abstract

This paper reports the synthesis of a polymerizable dppe-derivative with eight pendent styrenyl units linked to the dppe core through four tyrosine residues. This diphosphine ligand was utilized in the synthesis of a series of P_2PdX_2 complexes ($X_2 = (R)$-BINOL, (*S*)-BINOL, Cl_2 and π-1,3-Ph_2-allyl$^+$). The compounds were used as comonomers for the synthesis of porous organic polymers (poly EDMA). Molecular imprinting effects on X_2-ligand removal were investigated. Overall, the presence of a cavity of significant size was found to be beneficial to the rate of the allylic alkylation reaction, however, chiral BINOL shaped cavities did not influence the enantio-selectivity of the reaction.

Keywords: Catalysis; Molecularly imprinted polymers; Allylation

1. Introduction

The synthesis of artificial active sites [1] for hosting transition metal catalysts with unique reactivity profiles is an important problem, but one also fraught with technical difficulties. Our first forays into this area focused on the molecular imprinting of transition metal complexes into styrene/divinylbenzene or ethylene dimethacrylate (EDMA)-based networks for creating artificial "active sites", wherein the metal complex had an associated chiral cavity whose topology could be influenced by the shape of a large, removable imprinting ligand on the metallomonomer (Scheme 1). When (*R*)-BINOL shaped cavities were created, the metal sites were capable of differentiating between (*R*)- and (*S*)-BINOL in rebinding experiments (85:15 *R*:*S*). In fact some of the sites were capable of providing up to 97:3 selectivities, though others were only 2:1 selective; the metal fragment is of course achiral [2].

Since these cavities were generally constructed of non-functionalized monomers (styrene, EDMA, etc.), we speculated that organized functionality might provide a means to improve the molecular recognition properties of the artificial active sites [3,4]; a hypothesis grounded in the fact that metalloenzymes utilize functional groups to construct and outfit their active sites [5–7]. To this end we have synthesized a series of diphosphine complexes that contain polymerizable amino acid units [8,9] for copolymerizing into the matrix of the host polymer, hoping that the basic carbonyl or H-bonding amide might provide the desired functionality to the active site [10]. We report herein the synthesis and characterization of several P_2PdX_2 [11] complexes, their polymerization into the matrix of highly crosslinked methacrylate polymers and their subsequent activation towards catalysis of the allylic alkylation reaction [12–16].

2. Results and discussion

2.1. Synthesis of a tyrosine-containing, polymerizable diphosphine ligand [17]

Synthesis of the desired compounds began with a suitably protected reactive diphosphine reagent for

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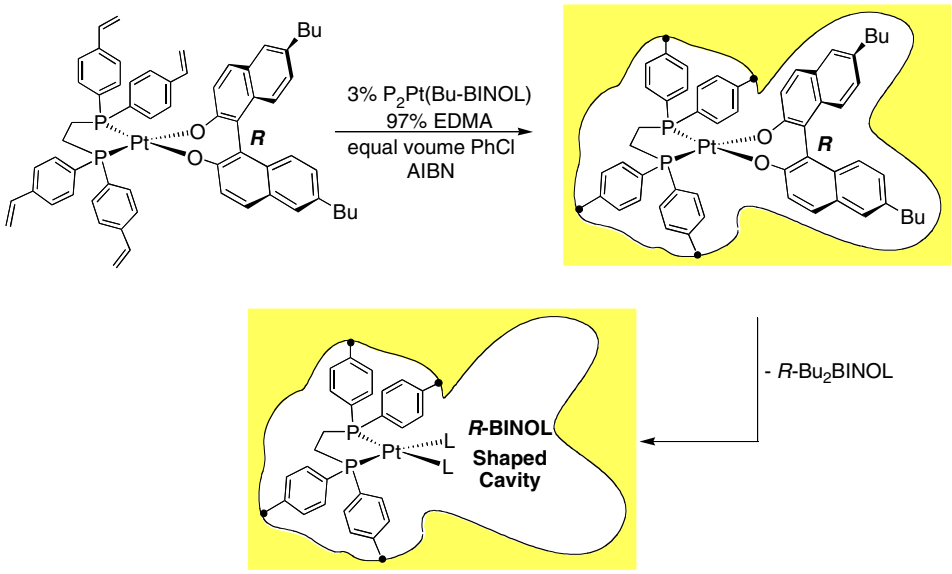
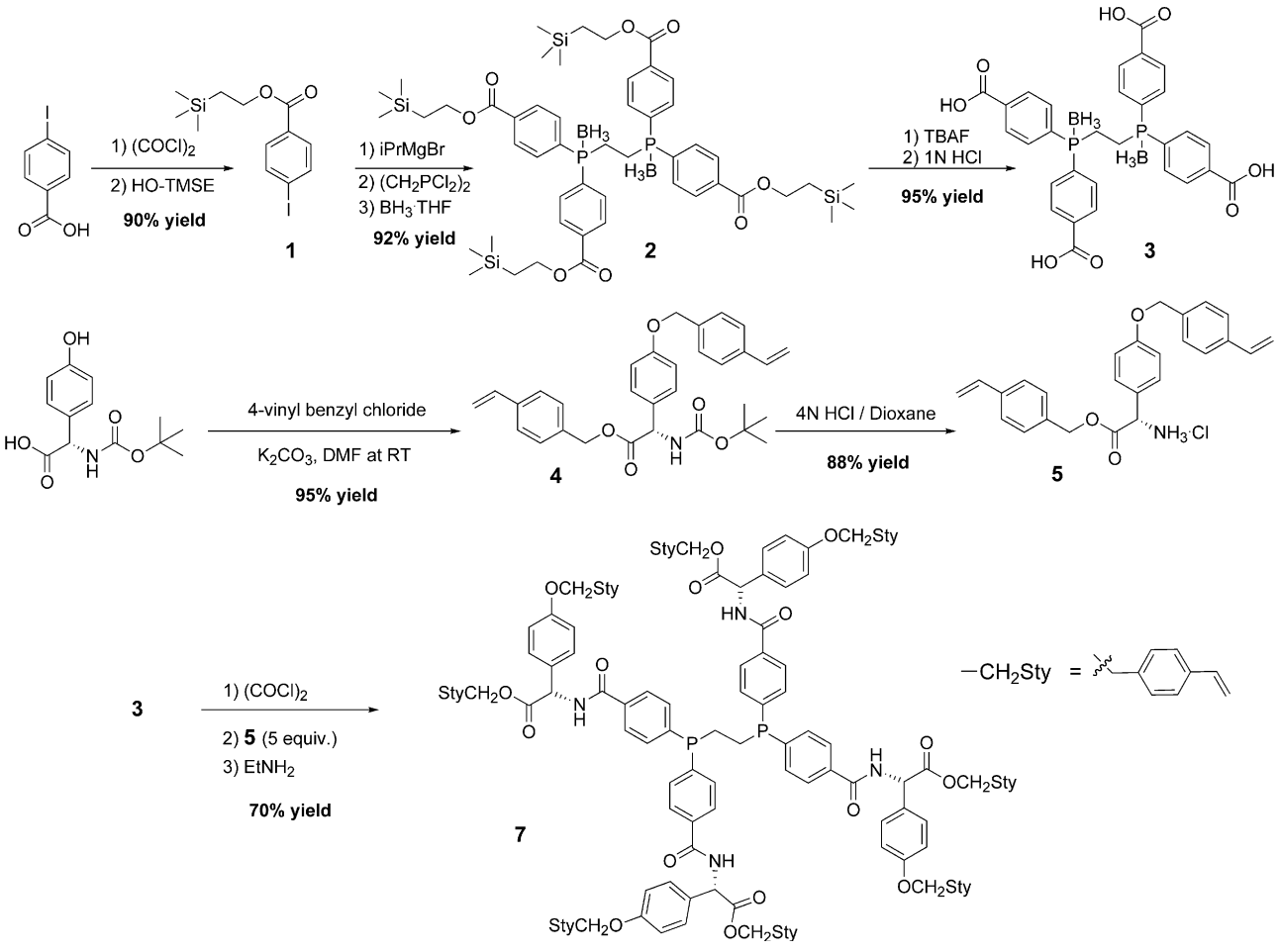


Scheme 1.

coupling to an amino acid ester. The diphosphine **2** was synthesized in high yield by the addition of the Grignard generated from the 4-iodobenzoate ester **1** [18] to bis(dichlorophosphino)ethane and borane protection (Scheme 2). The tetra ester was transformed to its corresponding acid **3** by the action of TBAF and acidifi-

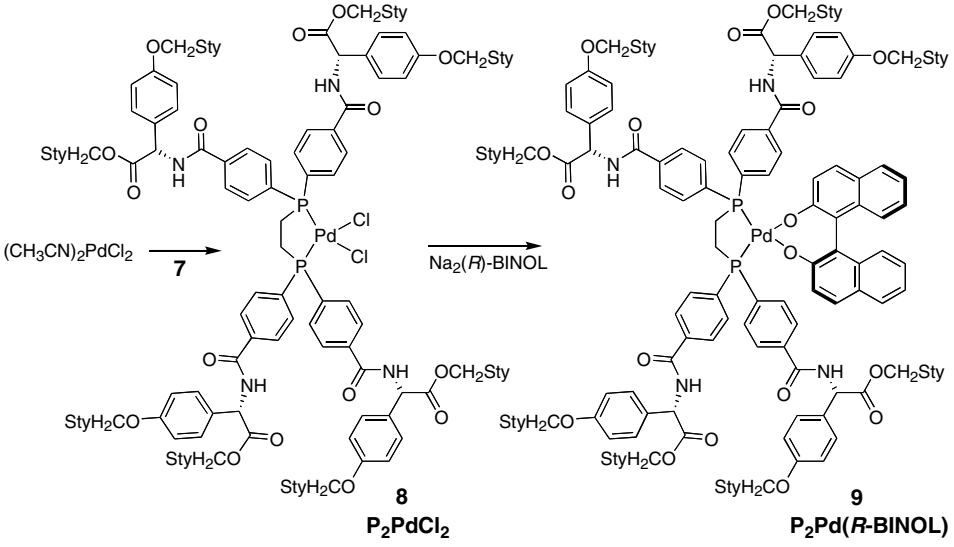


Scheme 2.

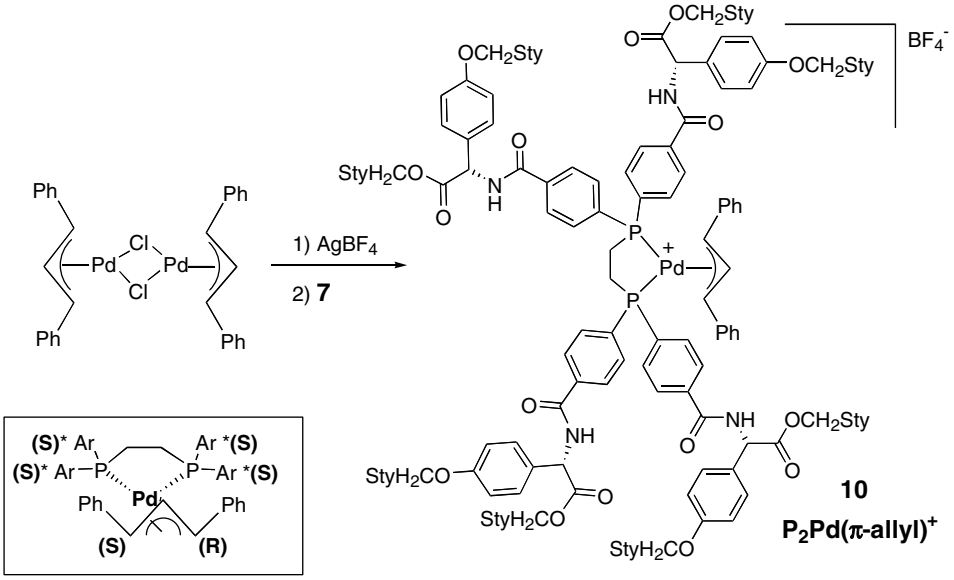
cation. The amino-acid bearing polymerizable arm **5** was prepared in two steps from *N*-Boc-L-tyrosine, first by double alkylation with 4-vinylbenzyl chloride then Boc removal. Coupling of this amino ester with the diphosphine tetra acid chloride generated from oxalyl chloride/DMF provided the borane protected product, which was most conveniently deprotected with ethylamine to yield **7**. This sequence provided multigram quantities of diphosphine **7.** Double benzylation of the amino acid was found to be critical to providing diphosphines that were soluble in organic solvents; other amino acids and alkylation schemes were abandoned due to insufficient solubility.

2.2. Synthesis of palladium metallomonomers

The reaction of **7** with $(CH_3CN)_2PdCl_2$ gave the metallomonomer **8** (Scheme 3), which provided the (*R*)- or (*S*)-BINOL-based complexes **9**-(*R*) and **9**-(*S*), respectively, on reacting with enantiomerically pure Na_2BINOL. These P_2Pd(BINOL) complexes were stable in THF, acetone and toluene but were very sensitive to chlorinated solvents. For example, **9** decomposed completely after 1 h in chlorobenzene, accompanied by formation of palladium black, diphosphine oxide and BINOL. Although formally diastereomeric, no spectroscopic differences were noted for the (*R*)- and (*S*)-



Scheme 3.



Scheme 4.

BINOL containing diastereomers **9**-(*R*) and **9**-(S). Apparently the chirality of the amino acid arms does not efficiently communicate with the BINOL stereochemistry [19].

A metallomonomer that would be an intermediate in the catalytic cycle of the allylic alkylation reaction was also desired. Synthesis of $P_2Pd(\pi\text{-allyl})^+$ BF_4^- complex [20] **10** was easily achieved by reacting the free diphosphine **7** with (1,3-diphenyl-π-allyl)palladium chloride dimer [21], after activation with $AgBF_4$ (Scheme 4). The ^{31}P NMR (Fig. 1) of this compound was unusual in that it displayed two P-resonances with a solvent-dependent chemical shift. For example in acetone, the resonances were exactly coincident, whereas in DMSO, THF and chloroform, the chemical shifts were increasingly different and AB quartets were observed. This P-inequivalence reflects diastereotopic Ps since the π-allyl fragment has mirror symmetry, while the phosphine has C_2 symmetry (Scheme 4, inset).

2.3. Synthesis of molecularly imprinted polymers

To generate a variety of active site structures, the available metallomonomers were used to synthesize four different polymers. The first pair used the (*R*)- and (*S*)-BINOL containing metallomonomers **9**-(*R*) and **9**-(*S*), BINOL cleavage of which (HCl) [2,10] provided P_2PdCl_2 catalyst precursors that should contain (*R*)- and (*S*)-BINOL shaped cavities in the outer sphere [2,15a], respectively (Scheme 5). The third polymer used the $[P_2Pd(\pi\text{-allyl})]BF_4$ metallomonomer **10**, and was designed to provide a direct entry into the catalytic cycle of an allylic alkylation reaction (Scheme 6) [22]. The fourth polymer was considered a control polymer and used the P_2PdCl_2 metallomonomer **8**, formally differing from the others in that an imprinting ligand was not present during polymer formation (Scheme 7).

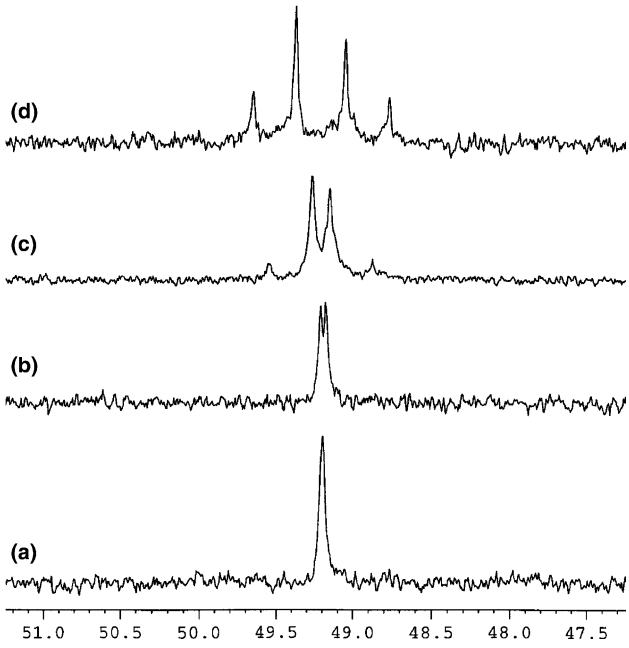
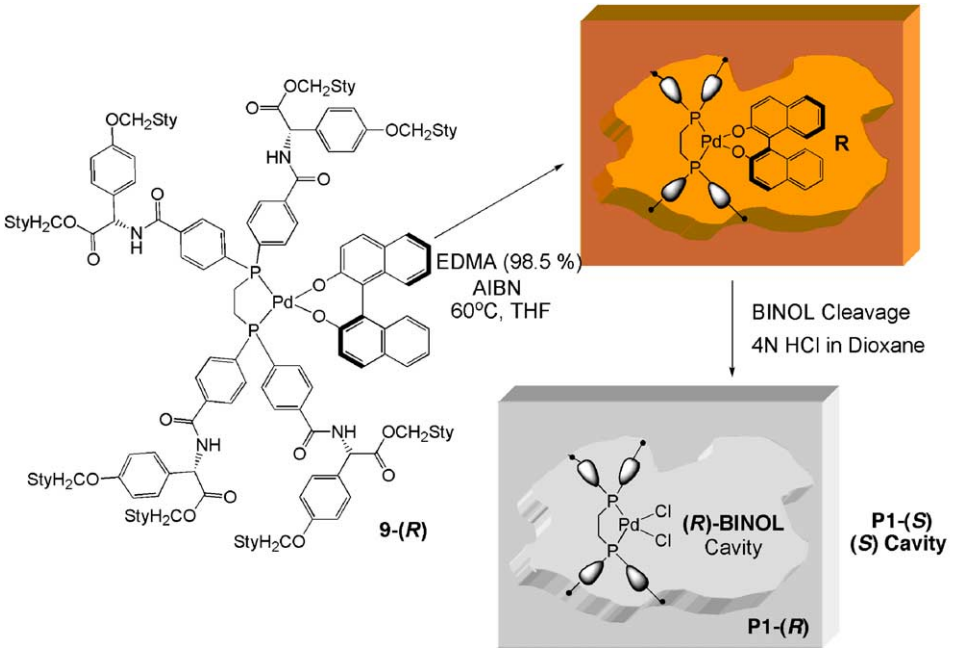
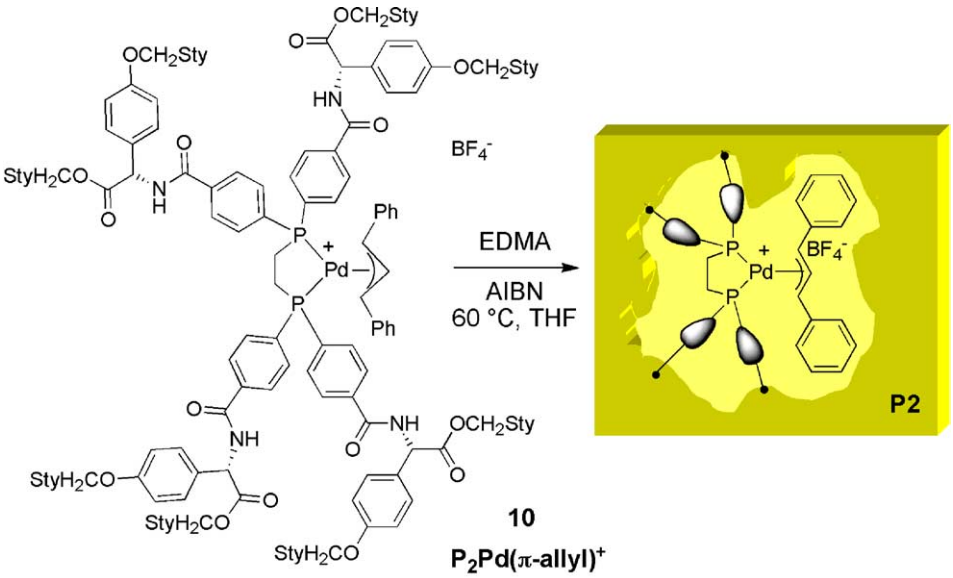


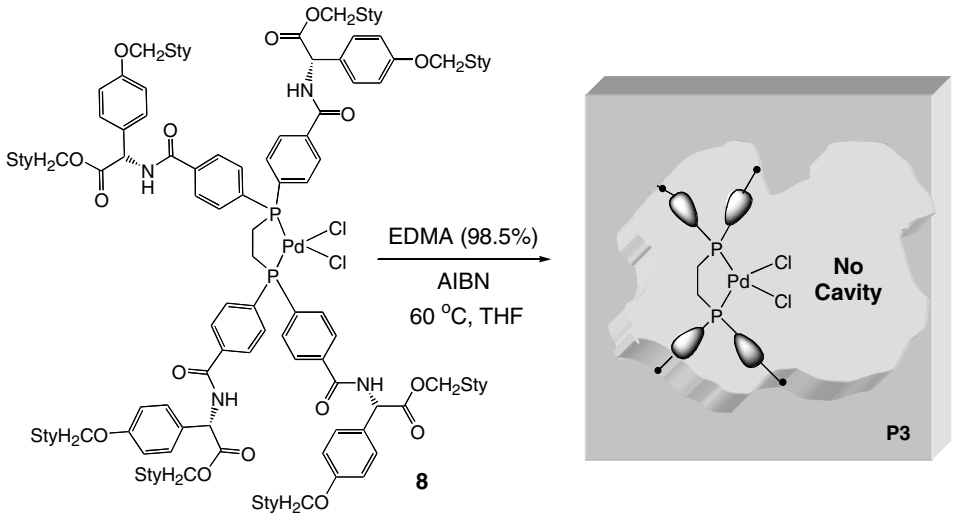
Fig. 1. ^{31}P NMR of **10** in: (a) acetone-d_6, (b) DMSO-d_6, (c) THF-d_8 and (d) $CDCl_3$. The chemical shifts have been artificially shifted for visualization purposes. The scale corresponds to spectrum A. The chemical shifts for B–D are ±1.0 ppm of that indicated.



Scheme 5.



Scheme 6.



Scheme 7.

As described elsewhere [23], the highly crosslinked polymers used in molecular imprinting are porous and have high specific surface areas (approach 500–600 m^2/g). The key to obtaining these desirable properties (from an accessibility to the interior perspective) is to carry out the free radical polymerization in the presence of a ~50% by volume diluent or porogenic solvent [24]. The role of this solvent is to create the pore structure during the gelling and subsequent phase separation of the material. The procedure generates monolithic, infinitely cross-linked networks that are insoluble in all solvents, but whose interiors can be penetrated by diffusion through a combination of macro-, meso- and micropores [25]. The molecularly imprinted P_2PdX_2 active sites were obtained by heating (N_2, 24 h, 60 °C) a mixture of the metallomonomer (1.5 mol%), ethylene dimethacrylate (EDMA) and AIBN (1 wt%) with the porogenic solvent THF [1] (1:1 by weight to all monomers). This leads to brittle polymers that are crushed into manageable pieces, soxhlet washed with THF and dried under vacuum. In the case of the BINOL containing metallomonomers **9**-(*R*) and **9**-(*S*), the light brown polymers were first crushed and the BINOL then removed by

[1] Typically chlorobenzene is used as a porogen, however, it was observed that P_2Pd-BINOL complexes are unstable in chlorinated solvents. This was confirmed upon soxhlet washing with CH_2Cl_2 (prior to HCl cleavage), which led to the observation of free BINOL, quantified to be 10% and 15% of the total amount of polymers (*R*)-**P1** and (*S*)-**P1**, respectively.

Table 1
The allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate **11**[a]

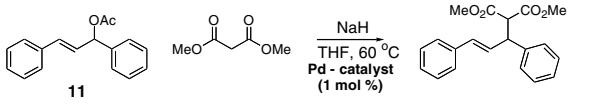
Entry	[Pd] catalyst	Catalyst (mol%)	Time (h)	Conversion (%)[b,c]
1	**8**	1	14	95
2	**10**	1	4.5	97
3	**P1**-(*R*)	1	72	75
4	**P1**-(*R*)	2	32	98
5	**P1**-(*S*)	1	72	78
6	**P2**	1	10	54[d]
7	**P3**	1	72	25
8	**P1**-(*R*) (first run)	2	32	95
9	**P1**-(*R*) (second run)		72	85
10	**P1**-(*R*) (third run)		75	20

[a] Conditions: rac-1,3-diphenyl-2-propenyl acetate (0.1 mmol); sodium dimethyl malonate (0.2 mmol); THF (2 mL); 60 °C.
[b] The conversion was determined by proton NMR.
[c] In all cases, racemic product was obtained.
[d] After 30 h, there was no additional conversion.

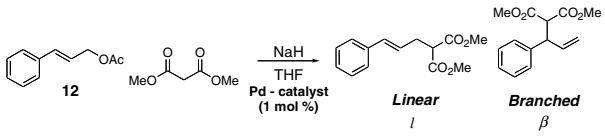
treating with 4 N HCl in dioxane, followed by soxhlet washing with THF and drying under vacuum, to yield the beige-yellow monolithic polymers, **P1**-(*R*) and **P1**-(*S*) (Scheme 5). [2] The $[P_2Pd(\pi\text{-allyl})]BF_4$ metallomonomer **10** yielded, after soxhlet washing with THF and drying, a bright yellow polymer, **P2** (Scheme 6) that was ready for direct introduction into catalytic reaction conditions. The non-imprinted reference polymer, **P3**, was synthesized under identical conditions from **8** and provided an immobilized catalyst that was compositionally identical to **P1** but presumably lacking a defined cavity (Scheme 7).

2.4. Catalysis of the allylic alkylation reaction [12b]

The effects of the cavity size/shape were measured in the allylic alkylation reaction. The alkylation of both 1,3-diphenyl propenyl acetate **11** (Eq. (1)) and 3-phenyl-propenyl-acetate **12** (Eq. (2)) with sodium dimethyl malonate were examined with the described Pd catalysts under homogeneous and heterogeneous conditions.



(1)



(2)

To measure the inherent reactivity of the new amino-acid containing diphosphine, compounds **8** and **10** were tested under homogeneous conditions (1 mol% Pd, THF, 60 °C) for the process in Eq. (1). As shown in Table 1, **8** and **10** were both competent catalysts, providing the expected products. The slower activity of **8** presumably reflected the fact that in situ reduction was necessary for entry into a productive cycle, while **10** should have already been in the cycle. Complicating the desire to call these "homogeneous" control experiments was the observation that **8** and **10** appeared to polymerize as the reaction proceeded (increasing solution viscosities). Given the low concentration of catalyst in these experiments, these results were a bit surprising, never the less, the effect was reproducible. Not surprisingly, the products of both catalysts were racemic.

As each catalyst was reactive towards alkylation, the next step was to examine the molecularly imprinted catalyst systems (Table 1, entries 3–7) [3]. Compared to results obtained with soluble catalysts, the reactivity of the polymeric catalysts was diminished. The BINOL-cavity containing catalysts **P1**-(*R*) and **P1**-(*S*) had nearly identical activities (75% and 78% conversion, respectively, entries 3 and 5), reflecting the fact that little communication was observed between the chirality on the ligand and the BINOLs. Like the solution analogs, the products were racemic, and increasing the catalyst loading to 2 mol% (entry 4) increased the rate.

Most surprising was the lack of reactivity of **P2** (entry 6). Like the solution catalyst **10**, it was expected that this system would be more reactive since the catalyst was already on the catalytic cycle. However, this catalyst inexplicably stops at only 54% conversion to product. In the case of **P3**, which does not have a defined space created by the imprinting process, we expected to see a diminished activity and this was indeed the case (entry 7, 25% conversion, 72 h). This effect has been previously ascribed to crowding of the active site by the polymer [26]. When large ligands are used in the imprinting process (and subsequently removed), equally large spaces are vacated, which ensure that the reactants can be accommodated in the site. A series of recycle experiments were also carried out to determine if catalyst reuse was feasible (entries 8–10). Unfortunately the re-

[2] Generally, HPLC analysis shows that 75–80% of the theoretical amount of BINOL is removed under these conditions.

Table 2
The allylic alkylation of 3-phenyl propenyl acetate **12**[a]

Entry	[Pd] catalyst	Catalyst (mol%)	Time (h)	Conversion (%)[c]	$l : \beta$[d]
1	**8**	1	14	>98	98:02
2	**10**	1	10 min	>99	80:20
3	**P1**-(*R*)	1	6	98	71:29
4	**P1**-(*S*)	1	6	95	70:30
5	**P1**-(*R*)[b]	1	14	90	75:25
6	**P2**	1	50	74	73:27
7	**P3**	1	72	87	75:25
8	P(^{iPr}dppePdCl$_2$)	1	24	56[e]	74:26

[a] Conditions: 3-phenylpropenyl acetate (0.1 mmol); sodium dimethyl malonate (0.2 mmol); THF (2 mL); 60 °C.
[b] 3-Phenylpropenyl acetate (0.2 mmol); sodium dimethyl malonate (0.1 mmol); THF (2 mL); 60 °C.
[c] The conversion was determined by GC.
[d] The *linear:branched* ($l : \beta$) ratio was determined by GC.
[e] Conversion measured again at 48 h showed no additional activity.

activity of **P1**-(*R*) diminished by 2/3 after the first run and was nearly unreactive by the third run.

Next, the activity of the soluble catalysts was examined for the alkylation of 3-phenyl-propenyl acetate **12** (Eq. (2), Table 2). In general, the catalysts were more active toward **12** than **11**, with π-allyl **10** being especially so. Both **8** and **10** displayed viscosity spikes, however, the reaction with **10** was completed (<10 min) before catalyst polymerization apparently begins. [3] The *linear:branched* ($l : \beta$) ratio for **8** was also higher than that observed with any of the other catalysts. [4] The polymeric catalysts, **P1**-(*R*) and **P1**-(*S*) again displayed similar reactivities (entries 3 and 4), **P2** again being slower than **P1**.

To gain insight into the possible role of the amino acid unit on catalytic reactivity, a second P_2PdCl_2 metallomonomer was examined. The readily synthesized [2,16f] (^{iPr}dppe)PdCl$_2$ contains polymerizable groups directly bonded to the dppe and like **P3** is meant to represent an active site with no imprinted cavities, but one also lacking the polar substructure of the amino acid modified metallomonomer. In the event P(^{iPr}dppe)PdCl$_2$ had an activity very similar to **P3** (entry 8) except that it ceased functioning at 56% conversion while **P3** continued on to completion. We do not have a satisfactory explanation for this observation.

3. Summary

This paper reports the synthesis of a polymerizable amino acid containing diphosphine ligand along with its coordination chemistry to the $PdCl_2$, Pd(BINOL) and Pd(π-allyl)$^+$ fragments. These metallomonomers were used as comonomers in the synthesis of permanently porous EDMA-based polymers; the polymers in turn served as catalysts for the alkylation of allylic acetates.

These studies represent one of the few approaches to the functionalization of transition metal active sites, though it appears that allylic alkylation reactions don't respond to this feature in an obviously interpretable manner. What is apparent from these experiments, however, is the benefit of the sacrificial ligand approach to catalyst synthesis. Removal of large ligands from the metallomonomer post-polymerization ensures that the catalyst has sufficient room in the active site to accommodate the reactants necessary to accomplish catalysis [15a,26]. Contrasting this general observation is the behavior of the π-allyl metallomonomer **10**, which we expected to provide active sites perfectly able to accommodate the structure of an intermediate π-allyl during catalysis. Solving this apparent dichotomy is the subject of continuing efforts.

4. Experimental

4.1. Compound *1*

Oxalyl chloride (21.0 mL, 243 mmol) was added to a solution of 4-iodobenzoic acid (20.0 g, 80.9 mmol) in dichloromethane (150 mL) at room temperature, followed by the addition of few drops of dry DMF. The reaction mixture was then stirred overnight and dichloromethane and excess of oxalyl chloride were removed under reduced pressure. The white solid was dried en vacuo for 24 h. This residue was dissolved in dichloromethane (100 mL). 2-Trimethylsilyl ethanol (12.2 g, 101 mmol) was added and the mixture was cooled to 0 °C. Pyridine (10.1 mL, 121 mmol) was added slowly over 30 min and the reaction mixture was allowed to warm to room temperature and was stirred for an additional 4 h. Dichloromethane was evaporated and

[3] Use of [dppePd(hexenyl-π-allyl)]$^+$ generated in situ from hexenyl acetate and Pd(DBA)$_2$ gave 96:4 $l : \beta$ selectivity and 98.5% conversion after 5 h, see [20a].
[4] As a comparison, the observed regioselectivity with a dppePd(π-allyl) catalyst generated in situ was 89/11, see [22b].

the residue was re-dissolved in diethyl ether (150 mL). The pyridinium salt was then filtered off and the ethereal solution was washed with 2 N HCl (2 × 50 mL), water (2 × 50 mL), saturated NaCl (50 mL), dried over magnesium sulfate, filtered and concentrated. The residue was purified by flash chromatography on silica (EtOAc/Hexanes; 1:3) to give 25.35 g of the desired product. Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, $J = 1.95$ and 6.60 Hz, 2H), 7.77 (dd, $J = 1.95$ and 6.60 Hz, 2H), 4.44 (t, $J = 8.50$ Hz, 2H), 1.15 (t, $J = 8.50$ Hz, 2H), 0.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 133.5, 133.2, 78.2, 63.8, 17.5, −1.5.

4.2. Compound **2**

To a solution of **1** (5.0 g, 14 mmol) in dry THF (25 mL) isopropyl magnesium bromide 1 M in THF (15.8 mL, 1.10 eq) was added over 5 min at −25 °C. The reaction mixture was stirred for an additional hour at this temperature. A solution of bis(dichlorophosphino)ethane (1.08 g, 3.60 mmol) in dry and degassed THF (5 mL) was added at −25 °C and the reaction mixture was stirred for 3 h at the same temperature, and then quenched with degassed methanol (0.5 mL). BH_3:THF (8 mL, 8 mmol) was added at −25 °C and the reaction mixture was allowed to warm to room temperature and stirred overnight. THF was removed under reduced pressure and the product was precipitated by the addition of ethanol. The white precipitate was filtered, washed with ethanol and dried on the vacuum line for 24 h to give 3.30 g of the desired product. Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.13$ Hz, 2H), 7.73 (m, 8H), 4.46 (t, $J = 8.34$ Hz, 8H), 2.43 (d, $J = 2.40$ Hz, 4H), 1.15 (t, $J = 8.34$ Hz, 8H), 0.11 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 133.9, 132.6, 132.1 (t, $J = 4.9$ Hz), 129.9 (t, $J = 4.9$ Hz), 77.1, 19.2 (t, $J = 18.4$ Hz), 17.4, −1.3, −1.5, −1.8; ^{31}P NMR (161.86 MHz, $CDCl_3$) δ 21.0 (s, 2P).

4.3. Compound **3**

Tetrabutyl ammonium fluoride (1 M in THF) (16.0 mL, 16.0 mmol) was added at 0 °C to a solution of **2** (2.10 g, 2.09 mmol) in THF (20 mL). The cooling bath was then removed and the reaction mixture was stirred overnight at room temperature. About 75% of the THF was removed under reduced pressure and a solution of 1 N HCl (50 mL) was added at 0 °C. The white precipitate was collected by filtration, washed with water followed by diethyl ether and dried overnight on the vacuum line to give 1.20 g of the desired product. This material was used in the next step without any further purification. Yield: 95%; ^{1}H NMR (400 MHz, CD_3OD) δ 8.10 (d, $J = 7.8$ Hz, 8H), 7.76 (m, 8H), 2.48 (s, 4H); ^{31}P NMR (161.86 MHz, CD_3OD) δ 17.6 (s, 2P).

4.4. Compound **4**

A solution of *N*-Boc-L-tyrosine (5.00 g, 18.0 mmol) in dry DMF (80 mL) at room temperature was treated with potassium carbonate (6.23 g, 44.5 mmol; 2.50 eq), 4-vinyl benzyl chloride (9.0 mL, 53 mmol; 3.0 eq) and tetrabutyl ammonium iodide (1.20 g, 3.00 mmol). The resulting reaction mixture was stirred at room temperature overnight. Water (150 mL) was added and the solution mixture was extracted with diethyl ether (5 × 100 mL). The combined ether layers were washed with 1 N HCl (100 mL), water (100 mL), brine (50 mL), dried over magnesium sulfate, filtered and concentrated. The product was precipitated by addition of a mixture of ethanol and hexanes (1:1). The white solid was washed with hexanes and dried to give 8.70 g of the desired product. Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 6H), 7.30 (dd, $J = 8.0$ and 6.10 Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 8.0$ Hz, 2H), 6.82–6.74 (m, 2H), 5.82 (d, $J = 17.0$ Hz, 2H), 5.33 (dd, $J = 17.0$ and 6.1 Hz, 2H), 5.18 (m, 3H, 5.05 (s, 2H), 4.66 (m, 1H), 3.09 (m, 2H), 1.9 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.3, 136.6, 136.4, 136.3, 134.8, 130.4, 128.8, 128.2, 127.6, 126.4, 126.3, 114.9, 114.4, 114.0, 79.8, 69.7, 54.7, 37.4, 28.3.

4.5. Compound **5**

Compound **4** (20.0 g, 38.9 mmol) was added in portions over 30 min at room temperature to 4 N $HCl_{(aq)}$ in 1,4-dioxane (concentrated HCl/dioxane; 1:2; 444 mL). The reaction mixture was then stirred for 4 h. The precipitated white solid was filtered, washed with water (2 × 50 mL), diethyl ether (2 × 50 mL) and dried on the vacuum line for 24 h to give 15.5 g of the desired product. Yield: 88%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (s, 3H, NH_3), 7.4 (m, 6H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.1 (d, $J = 8.5$ Hz, 2d), 6.92 (d, $J = 8.5$ Hz, 2H), 6.75 (d, $J = 17.6$ Hz, 2H), 5.86 (d, $J = 17.6$ Hz, 2H), 5.29 (m, 2H), 5.15 (s, 2H), 5.07 (s, 2H), 4.3 (s, 1H), 3.24 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.2, 158.0, 137.6, 137.2, 137.1, 136.7, 136.6, 134.8, 130.9, 129.1, 128.2, 127.1, 126.6, 126.5, 115.3, 115.2, 114.8, 69.4, 67.1, 53.8, 35.5.

4.6. Compound **6**

Oxalyl chloride (1.62 mL, 18.6 mmol; 8 eq) was added slowly under argon to a suspension of **3** (1.40 g, 2.32 mmol) in dichloromethane (35 mL) at 0 °C. The reaction mixture was stirred for 30 min and then a few drops of dry DMF were added, and stirring was pursued for an additional 2 h at 0 °C. The evolution of the reaction was monitored by ^{31}P NMR (δ(^{31}P) of the tetraacid chloride product is 22.5 ppm). The reaction mixture was concentrated under reduced pressure and the residue was

dried on the vacuum line for 24 h. This material was added in dichloromethane (60 mL) to a solution of **5** (5.22 g, 11.6 mmol) and triethylamine (3.6 mL, 23 mmol) in dichloromethane (60 mL) at 0 °C and under argon. The reaction mixture was stirred at the same temperature for 5 h. About 3/4 of CH_2Cl_2 was removed and methanol (100 mL) was added. The beige solid precipitate was filtered, washed with water (50 mL), washed with methanol (2×50 mL) and dried on the vacuum line overnight to give 3.75 g of the desired product. Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 8H), 7.64 (m, 8H), 7.36 (m, 32H), 6.94 (m, 8H), 6.76 (m, 20H), 5.78 (m, 2H), 5.33–4.98 (m, 28), 3.2 (m, 8H), 2.45 (m, 4H); ^{31}P NMR (161.86 MHz, $CDCl_3$) δ 20.88 (s, 2P).

4.7. Compound 7

The solution of **6** (2.20 g, 1.01 mmol) in degassed THF (10 mL) and degassed ethylamine (15 mL) was heated at 55 °C under argon for 3 h. Methanol (10 mL) was added to complete the precipitation of the formed product. The beige solid was filtered, washed with methanol (25 mL) and dried on the vacuum line for 16 h to give 2.05 g of pure free phosphine-based monomer. Yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 8H), 7.42 (m, 42H), 6.98 (m, 8H), 6.74 (m, 18H), 5.78 (m, 8H), 5.31–5.04 (m, 18H), 4.96 (s, 8H), 3.18 (m, 8H), 2.11 (m, 4H), 1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 166.5, 166.3, 157.9, 137.9, 137.3, 136.4, 136.2, 134.5, 134.3, 132.9, 132.6, 130.3, 128.9, 128.8, 128.0, 127.9, 127.5, 127.0, 126.3, 114.9, 114.5, 114.0, 77.1, 69.7, 67.0, 53.8, 36.9; ^{31}P NMR (161.86 MHz, $CDCl_3$) δ −11.7 (s, 2P).

4.8. Compound 8

To a suspension of $(CH_3CN)_2PdCl_2$ (0.12 g, 0.46 mmol) in dry THF (10 mL) at room temperature was added under argon **7** (1.00 g, 0.462 mmol) in one portion. The reaction mixture was stirred for 2 h. The solution was filtered on Celite and concentrated under reduced pressure to give 1.08 g of the desired product. Yield 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 16H), 7.44 (m, 36H), 7.02 (m, 8H), 6.74 (m, 16H), 5.74 (d, $J = 17.5$ Hz, 8H), 5.28–4.83 (m, 28H), 3.41 (m, 8H), 2.5 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.4, 165.8, 165.6, 157.9, 157.7, 137.8, 137.2, 136.4, 136.2, 136.1, 134.5, 134.0, 133.5, 130.7, 130.2, 128.7, 128.1, 127.9, 127.6, 126.7, 126.4, 126.3, 115.0, 114.8, 114.5, 114.4, 114.0, 113.9, 77.2, 69.6, 67.8, 67.2, 67.0, 54.2, 54.0, 36.9; ^{31}P NMR (161.86 MHz, $CDCl_3$) δ 64.3 (s, 2P).

4.9. Compound 9

To a solution of sodium binolate, prepared from the reaction of sodium *tert*-butoxide (0.35 mmol) and BINOL (0.17 mmol) in THF (10 mL), was added at room temperature and under argon a solution of **8** (0.39 g, 0.16 mmol) in THF (5 mL). The reaction mixture was then stirred overnight. THF was removed under reduced pressure and the residue was washed with ether (25 mL), methanol (50 mL), and dried on the vacuum line for 24 h to give 0.42 g of the desired product as a brown solid. Yield: 99%; ^{1}H NMR (400 MHz, THF-d_8) δ 7.95–6.25 (m, 94H), 5.75 (m, 8H), 5.38–4.75 (m, 28H), 3.2 (m, 6H); ^{31}P NMR (161.86 MHz, THF-d_8) $\delta = 52.9$ (s, 2P).

4.10. Compound 10

To a slurry of **7** (0.91g, 0.42 mmol) in dried, distilled acetone (20 mL) was added a slurry of $AgBF_4$ (84 mg, 0.43 mmol) in acetone (20 mL) at room temperature under N_2. The reaction was stirred for 1 h. The phosphine slurry went from yellow to brownish-green upon addition of $AgBF_4$. The solution was filtered over Celite, washed with EtOAc (50 mL) and purified by column chromatography (9:1 EtOAc:hexanes) to yield a yellow-green solid. Yield: 80%; ^{1}H NMR (400 MHz, THF-d_8) δ 8.15–6.75 (m, 76H), 6.75–6.60 (m, 8H), 5.80–5.65 (m, 8H), 5.25–4.85 (m, 24 H), 4.10–3.95 (m, 1H), 3.52–3.50 (d, $J = 8$ Hz, 1H), 3.35–3.15 (m, 8H), 2.75–2.40 (m, 8H), 1.80 (d, $J = 8$ Hz, 1H) ^{31}P NMR (161.86 MHz, THF-d_8) δ 46.5 (dd, $J = 63.2$ Hz, 2P); ^{31}P NMR (161.86 MHz, acetone-d_6) δ 49.2 (s); ^{31}P NMR (161.86 MHz, DMSO-d_6) δ 49.1 (d, $J = 5.3$ Hz); ^{31}P NMR (161.86 MHz, $CDCl_3$) δ 49.2 (dd, $J = 97.9$ Hz).

4.11. Compund P1

Metallomonomer **9** (231 mg, 0.087 mmol, 1.5 mol%), AIBN (10.7 mg, 1 wt%), EDMA (1.18 g, 5.72 mmol, 98.5 mol%) and dried THF (1400 mg) were combined in a 20-mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, light-brown polymer. After Soxhlet washing with THF for 8 h and drying on the vacuum line at 50 °C overnight, 1375 mg of polymer was obtained (63.3 μmol of Pd/g of polymer). A suspension of this polymer (687.5 mg, 31.6 μmol of Pd) in THF (25 mL) was treated under argon with 4 N HCl in dioxane (2 mL). The mixture was stirred at room temperature for 8 h. The reaction was then filtered and the polymer was Soxhlet washed with THF for 16 h. Quantitative analysis of the extract showed that 83% of the BINOL was recovered from the polymer (generating 83% of $PdCl_2$ sites from the total Pd sites). The polymer was dried on the vacuum line at 60 °C for 24 h, 675 mg (26.2 μmol of Pd/g polymer) of beige-yellow **P1** was obtained.

4.12. Compound P2

Compound **P2** was prepared under the reaction conditions described for **P1**: (0.203 mg **10**, 0.0798 mmol,

1.5 mol%), AIBN (0.021 mg, 1 wt%), EDMA (1.05 g, 5.30 mmol) and dried THF (1.06 g) were combined in a 20-mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a green-yellow polymer. The resulting polymer was Soxhlet extracted with THF for 8 h and dried on the vacuum line at 60 °C for 16 h; 1.27 g of **P2** (62.6 μmol of Pd/g of polymer) was obtained.

4.13. Compound *P3*

Compound **P3** was prepared under the reaction conditions described for **P1**: (98.3 mg **8**, 0.0454 mmol), AIBN (7.2 mg, 1 wt%), EDMA (615 mg, 2.98 mmol) and dried THF (714 mg) were combined in a 20-mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a beige-yellow polymer. The resulting polymer was Soxhlet extracted with THF for 8 h and dried on the vacuum line at 60 °C for 16 h; 700 mg of **P3** (64.8 μmol of Pd/g of polymer) was obtained.

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