Crystal data for **4**: $C_{82}H_{122}Cl_4N_2O_8Pt_2 \cdot Me_2CO$, $M_r = 1853.93$, monoclinic, space group $C2/c$, $a = 32.261(2)$, $b = 15.7989(7)$, $c = 20.0825(9)$ Å, $\beta = 119.867(1)^\circ$, $V = 8876.4(7)$ Å^3, 180(2) K; final $R1$, $wR2$, and S values are 0.052, 0.084, and 1.013 for 454 parameters. Data were collected with a Siemens SMART CCD area-detector diffractometer. Refinement was by full-matrix least squares on F^2 for all data with SHELXL-96.[15] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101757. 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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Solid-Phase Synthesis and Encoding Strategies for Olefin Polymerization Catalyst Libraries **

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Although the application of combinatorial methods in the pharmaceutical industry is fast becoming an industrial standard for the discovery and optimization of novel drug-based molecules,[1] similar methods aimed towards the identification of new materials and catalysts remain in their infancy.[2] Recent reports have appeared describing the synthesis and screening of libraries of organometallic catalysts for examining a number of transformations.[3] The application of combinatorial methods aimed toward the discovery and optimization of olefin polymerization catalysts is an area that promises to be of major importance especially to the chemical industry, which produces approximately 46 million metric tons of polyolefins annually.[4]

Since most commercial-scale polyolefin processes employ supports with high surface areas for immobilizing olefin polymerization catalysts, it is somewhat surprising that few reports have appeared examining the use of polystyrene as a catalyst support.[5] Fréchet and co-workers have recently shown that suitably modified cross-linked polystyrene can function as an efficient activator for catalysts based on Group 4 metallocenes.[6] Polystyrene with low cross-linking not only acts as a more chemically compatible support relative to silica, but also provides a "solutionlike" environment that more closely resembles the environment in which homogeneous metallocene catalysts function. In addition, a plethora of solid-phase synthetic methodologies have appeared in recent years, providing a broad knowledge base which should facilitate efforts in the field of olefin polymerization catalysis.[7]

Recent reports have shown that certain catalysts based on complexes of late transition metals with diimines exhibit olefin polymerization activities comparable to those found for early transition metal single-site metallocene-based systems.[8] These systems offer advantages over their early transition metal counterparts in that they are easily synthesized and provide a broader range of functional-group compatabilities.[9] Herein we report the first example of a combinatorial approach to the parallel synthesis of a 1,2-diimine library complexed with Ni^{II} and Pd^{II} as olefin polymerization catalysts using 1% cross-linked polystyrene as a solid support. Specifically, a general synthetic methodology has been developed that allows for the parallel synthesis and screening of ethylene polymerization catalyst libraries in a spatially addressable format.[10] Furthermore, we have discovered that it is possible to apply chemical encoding techniques to these catalysts and distinguish catalyst performance trends. Since steric bulk on the aryl rings has been shown to play a dramatic role on polymer yield and molecular weight (M_w) for these catalytic systems, we chose to synthesize aryl-substituted 1,2-diimine complexes of Ni^{II} and Pd^{II} on 1% cross-linked polystyrene. In addition, we sought to examine how electronic perturbations may affect catalyst performance.

Our synthetic approach began with a regioselective alkylation of the unsymmetrical 1,2-diimine **1** with bromomethyl polystyrene (1.05 equiv of lithium diisopropylamide (LDA), 0 °C, THF) to give the polystyrene-grafted 1,2-diimine ligand **2** (Scheme 1).[11] To incorporate a variety of functionalized aryl-substituted 1,2-diimines, a divergent approach was explored starting from diketone resin **3**, which was obtained in high yield (>95% based on recovered 2,4,6-trimethylaniline) from the hydrolysis of 1,2-diimine resin **2** with oxalic acid in THF/H_2O (5/1 v/v) at 70 °C for 12 h. This transformation was monitored by single-bead FT-IR spectroscopy ($\tilde{\nu} = 1635$ (C=N), 1712 cm^{-1} (C=O)).

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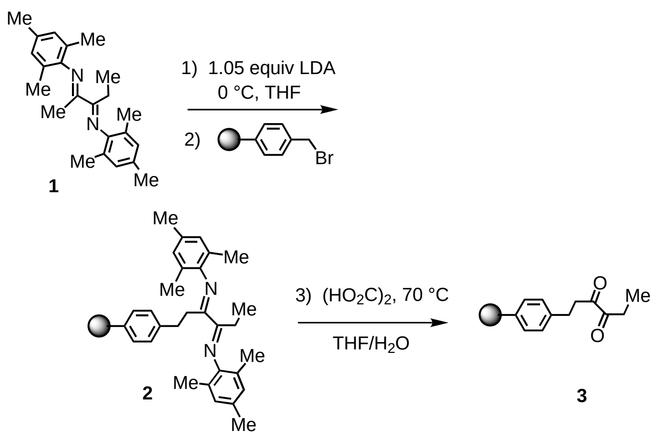
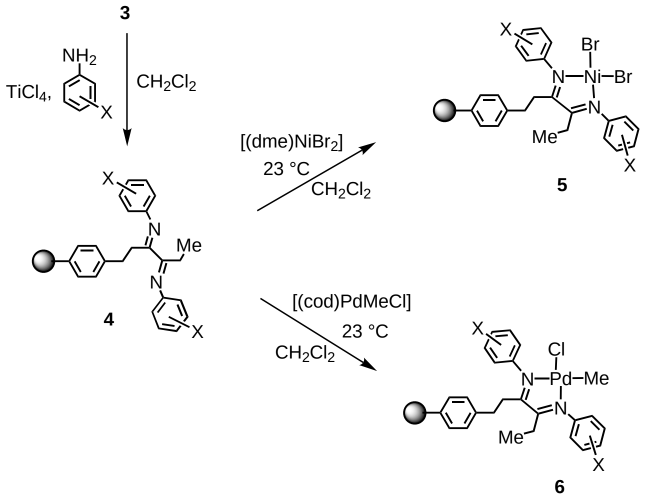


Scheme 1. Preparation of the solid-phase diketone resin **3**. The sphere represents 1 % cross-linked polystyrene.



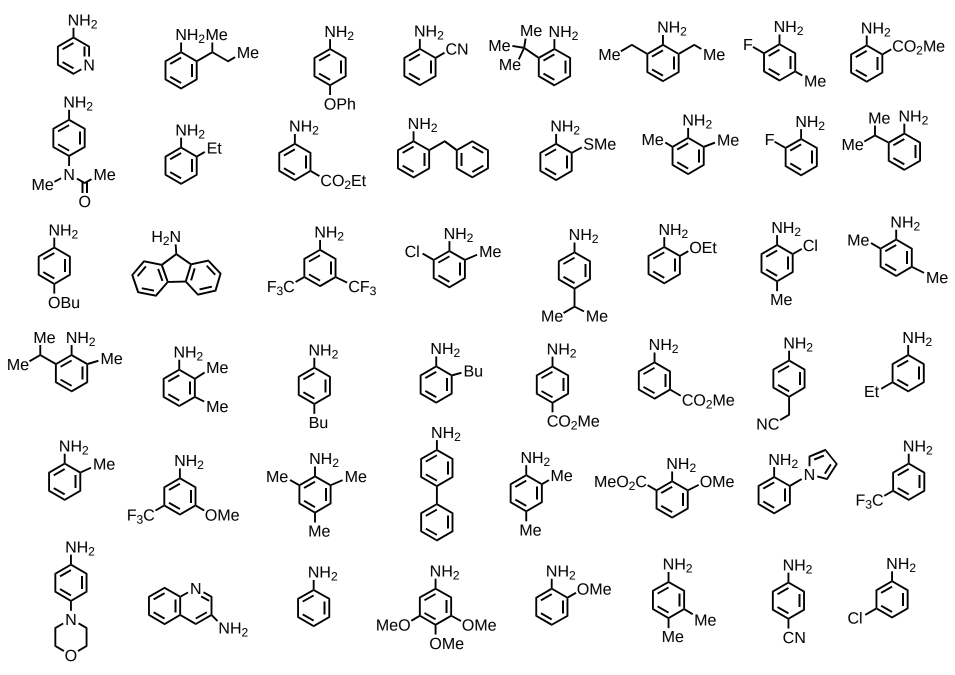
Scheme 2. Preparation of complexes **5** and **6**. dme = 1,2-dimethoxyethane, cod = 1,5-cyclooctadiene.

A total of 48 commercially available anilines with varying steric and electronic substituents (Table 1) was then used to prepare the corresponding 1,2-diimine resins. We obtained the best results when employing $TiCl_4$ as a Lewis acid (15 equiv) with the appropriate aniline (30 equiv) to effect 1,2-diimine formation (Scheme 2). A thorough washing protocol was implemented after this step to minimize excess aniline and titanium contamination of the library. These solid-supported 1,2-diimines were then split and converted into a 96-member solid-phase library consisting of Ni^{II} and Pd^{II} complexes **5** and **6**, respectively, in a parallel spatially addressable format.

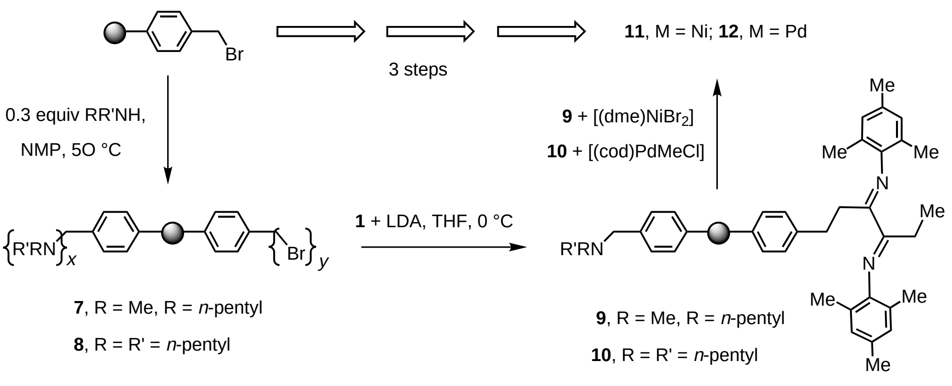
The active, cationic resin-bound Ni^{II} catalysts were generated in situ by the addition of methylalumoxane (MAO, 300 equiv) in toluene, whereas the resin-bound Pd^{II} catalysts were activated by the addition of sodium tetrakis(3,5-bistrifluoromethyl)phenyl borate (5 equiv) in dichloromethane. The beads were stirred at room temperature for 30 minutes before being exposed to ethylene in a high-pressure parallel polymerization reactor (60 psi) to ensure complete activation of the catalysts. Preliminary screening data from the library suggests that the solid-supported Ni^{II} catalysts display lower activities and produce polymers with lower molecular weight M_w relative to the corresponding solution-phase analogues which were synthesized by traditional methods and screened under identical conditions.

The polyethylene obtained from the supported catalyst, however, was isolated as discrete granules that had grown significantly in diameter (2–10 times) when compared to the initial polystyrene beads (diameter 70 μm). The polyethylene granules were isolated through a simple filtration step which allows for the convenient removal of excess MAO. In contrast to the solid-supported Ni^{II} catalysts, preliminary data suggest that the solid-supported Pd^{II} catalysts display higher activity than their solution-phase counterparts. Gel permeation chromatography (GPC) data also indicated that the molecular weights M_w and polydispersities (M_w/M_n) were nearly identical. Overall, the observed trends in relative activity and molecular weights obtained from the solid-supported catalysts were in agreement with related, previously reported systems prepared through traditional synthetic methods.[9]

Table 1. Commercially available anilines used to prepare 48 solid-phase 1,2-dimine ligands.



To implement a chemical encoding strategy,[12, 13] substochiometric amounts of secondary amines were added as tags to (bromomethyl)polystyrene (0.3 equiv of RR′NH, N-methylpyrrolidone (NMP), 50 °C; **7**: R = Me, R′ = n-pentyl; **8**: R = R′ = n-pentyl) prior to attachment of the 1,2-diimine ligands (Scheme 3). The synthetic sequence shown herein was then used to prepare the tagged, polystyrene-supported Ni^{II} and Pd^{II}



Scheme 3. Preparation of chemically tagged 1,2-diimine complexes of Ni^{II} (**11**) and Pd^{II} (**12**).

complexes **11** and **12**. The catalysts were pooled into a single reactor, activated with MAO, and exposed to 4.14 bar ethylene for 30 minutes. Upon workup, the product morphologies, when viewed under a microscope, indicated the presence of two distinct sizes of polymer products (Figure 1).

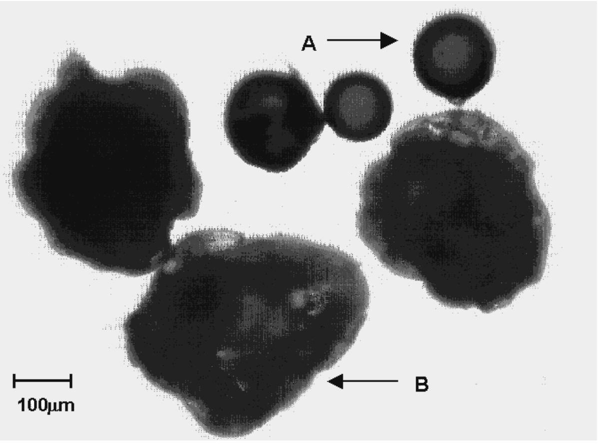


Figure 1. Microscope images of representative products obtained from a pooled polymerization. A: Product from the palladium catalyst, B: product from the nickel catalyst.

Five larger beads and five smaller beads were selected for decoding, which consisted of an amine cleavage procedure[14] coupled with HPLC and fluorescence detection (Figure 2).[12] Specifically, the beads were first treated with α-chloroethyl chloroformate, a reagent known to cleave N-benzyl-linked tertiary amines from solid supports. The cleaved secondary amines were then derivatized with dansyl chloride prior to detection by HPLC with fluorescence detection.[12] Importantly, the HPLC traces confirm a) the presence of the secondary amine tags, and b) that the larger polymer granules were prepared from the nickel catalyst, in accordance with the known relative performance trends of 1,2-diimine–Ni^{II} and 1,2-diimine–Pd^{II} olefin polymerization catalysts.[9,15] Thus, in these systems, olefin polymerization catalysts can be chemically encoded and pooled into a single reactor, and the resultant polymer granules can be decoded to deduce the synthetic history of the incipient polystyrene support.

The work described here demonstrates the feasibility of applying combinatorial techniques—including solid-supported synthesis, on-bead screening, and the potential for deconvoluting pooled libraries of catalysts—for the discovery and optimization of new catalysts. With these techniques now realized, work is currently underway to fully examine the library trends observed thus far and to expand the scope and utility of the techniques described herein to other olefin polymerization catalyst systems.

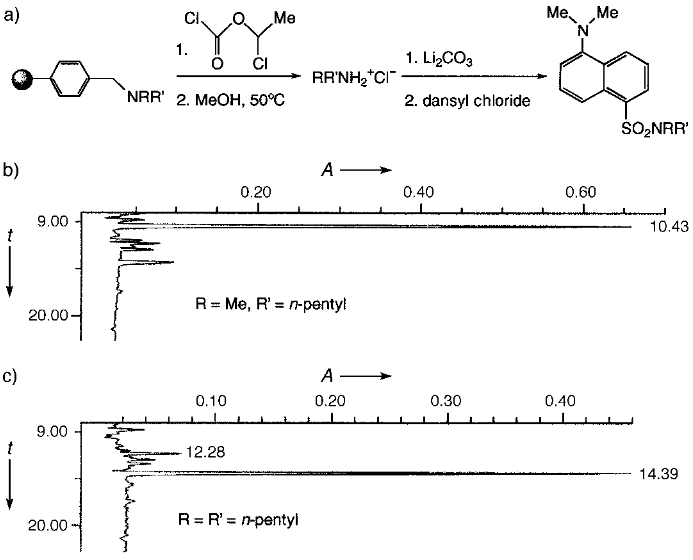


Figure 2. a) The decoding procedure. b, c) HPLC traces from the decoded products from five large beads and five small beads, respectively, formed with the nickel catalyst **11** and the palladium catalyst **12**.

Experimental Section

General procedure for the solid-phase synthesis of diketone **3**: To a cooled solution (0 °C) of 1,2-diimine **1** (0.50 g, 1.49 mmol) in dry THF (15 mL) under nitrogen was added LDA (1.09 mL, 1.49 mmol, 1.5 M in THF). After the mixture was stirred at 0 °C for 2 h, (bromomethyl)polystyrene (1.06 g, 0.75 mmol) was added, and the resulting suspension was stirred for 3 h at 0 °C and then 10 h at room temperature. The resin was filtered, washed with THF (2×10 mL), H_2O (2×20 mL), and CH_2Cl_2 (2×20 mL), and dried under high vacuum to afford 1.60 g of **2**. The loading capacity of this resin was calculated to be 0.40 mmol g^{-1} based on nitrogen analysis (1.21 % N). A strong absorbance at 1635 cm^{-1} (C=N) is observed by single-bead FT-IR spectroscopy. A stirred suspension of **2** (0.25 g, 0.09 mmol) and oxalic acid (42 mg, 0.47 mmol) in THF/H_2O (10 mL, 5/1 v/v) was heated to 70 °C for 12 h. After cooling to room temperature, the resin was filtered and washed with DMF (2×10 mL), H_2O (2×10 mL), and THF (2×10 mL) to yield 0.15 g of diketone resin **3**. A strong absorbance at 1712 cm^{-1} (C=O) is observed by single-bead FT-IR spectroscopy.

General procedure for the solid-phase synthesis of 1,2-diimine resins **4** and the corresponding complexes of Ni^{II} and Pd^{II}: The reactions were performed in glass tubes in a 48-cell parallel reactor. To a suspension of diketone resins **2** (0.10 g, 0.08 mmol) in dry CH_2Cl_2 (8 mL) was added the appropriate aniline (2.40 mmol) and $TiCl_4$ (1.20 mL, 1.20 mmol, 1.0 M in CH_2Cl_2) under nitrogen. The suspensions were shaken at room temperature for 24 h, after which the resins were filtered and washed extensively with CH_2Cl_2 (3×10 mL), $NaOCH_3$ in THF/MeOH (3×10 mL), and THF

(3×10 mL), and dried under high vacuum to yield the desired 1,2-diimine resins **4**. These resins were then split and converted into the corresponding complexes of Ni^{II} (**5**) and Pd^{II} (**6**) by the addition of $[(dme)NiBr_2]$ (30 mg, 0.10 mmol) or $[(cod)PdMeCl]$ (27 mg, 0.10 mmol) in CH_2Cl_2 (10 mL), and the reaction block was shaken for 12 h. The resins were then washed with CH_2Cl_2 (4×10 mL) and dried under high vacuum to afford the desired resin-bound complexes. Loading capacities for these resins were calculated to be approximately 0.30 mmol g^{-1} based on Ni and Pd analysis.

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Dendritic Pseudorotaxanes[**]

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While dendrimers begin to find their potential applications in the fields of molecular electronics,[1] material science (high-performance polymers, catalysts, adhesives, etc.),[2] and membrane chemistry,[3] structural control[4] and synthetic efficiency still remain the major issues in dendrimer research. Three synthetic methods (convergent,[5] divergent,[6] and double-stage convergent[7]) are recognized, up to now, for the preparation of high molecular weight, monodisperse dendrimers. Recently, Zimmerman and Feng introduced a synthetic approach based on self-organization, which guarantees structural accuracy while eliminating steps from the conventional multistep approach.[8] In this case, six subunits were brought together by hydrogen bonding to construct supramolecular dendritic structures up to the fourth generation. Here, we report a concise self-organizing dendrimer synthesis in which 1:3 pseudorotaxane complexes between a triply charged ammonium salt (**1**)[9] (Scheme 1) and substituted dibenzo[24]crown-8 (DB24C8) units make up the core portions of the dendritic architectures. This is based on the finding of Stoddart et al. that DB24C8 forms pseudorotaxanes with secondary ammonium salts through noncovalent bonding.[10]

The cyclization reaction between tri(ethylene glycol) dichloride and methyl 3,4-dihydoxybenzoate at high dilution gave 4-methoxycarbonyldibenzo[24]crown-8 in 40% yield. The ester group was hydrolyzed and then esterified with a series of benzyl ether dendrons bearing primary alcohol moieties ([G1]-OH, [G2]-OH, and [G3]-OH)[5] using the redox system diethyl azodicarboxylate (DEAD) and triphenylphosphane (TPP)[11] to afford the corresponding dendrons with the macrocyclic unit at the focal points (**2**–**4**; Scheme 1). Our strategy to construct a series of self-organizing dendrimers is illustrated in Scheme 2.

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