JOC*Note*

Merrifield Resin−$C_6H_4CH_2N_3P(MeNCH_2CH_2)_3N$: An Efficient Reusable Catalyst for Room-Temperature 1,4-Addition Reactions and a More Convenient Synthesis of Its Precursor $P(MeNCH_2CH_2)_3N$

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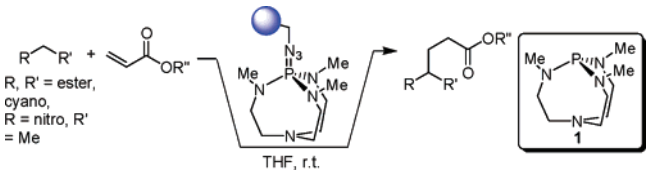
Received December 6, 2006



1,4-Additions to a variety of Michael acceptors with a wide variety of donors were efficiently catalyzed at room temperature by the title reusable Merrifield resin-supported catalyst. Advantages of this catalyst include a simple workup (filtration of the reaction mixture) and good to excellent product yields. We also report a substantially simplified synthesis of the commercially available strong nonionic base **1**, a precursor to the title polymer-bound catalyst.

The current research trend toward environmentally friendly and efficient syntheses has driven the generation of new strategies for catalyst immobilization to facilitate product recovery, catalyst reuse, reaction workup, and waste disposal.[1] Anchoring a catalyst to a polymeric matrix is a well-known approach to catalyst recovery and reuse.[1] The Michael reaction is a highly utilized tool for carbon−carbon bond formation in synthetic organic chemistry, and it is generally catalyzed by bases under nonrecyclable conditions.[2] 1,4-Additions are also useful in the synthesis of monomers,[3a,b] corrosion inhibitors,[3c] coatings,[3d] and pharmaceuticals.[3e]

A variety of solid bases for 1,4-additions have been reported, among which are $Ba(OH)_2$,[4a] KF on γ-Al_2O_3,[4b] hydrotalcites,[5] organic resins,[6a] MgLa mixed oxides,[6b] magnesium oxide fluorides,[6c] KG-60-NEt_2,[6d] [bmIm]OH,[6e] KF on α-Al_2O_3,[6f] KF-doped phosphates,[6g,h] surface-anchored amines,[6i,j] high surface area MgO,[6k] *N*-phenyl-tris(dimethylamino)iminophosphorane (P-BEMP) immobilized on polystyrene resin,[2b] and silica gel 60.[6l] Among these systems, the first eight operate at room temperature and the same is true of the last three which are commercially available. Despite these advantages, the reuse of $Ba(OH)_2$, KF on γ-Al_2O_3, KF on α-Al_2O_3, organic resins, and silica gel 60 was not addressed. Furthermore, KF-doped phosphates can be recycled only seven times; hydrotalcites, four to five times; amines anchored on silica surfaces, three times; MgLa mixed oxides, five times; magnesium oxide fluorides, four times; high surface area MgO, two times; P-BEMP, three to five times; KG-60-NEt_2, three times; and [bmIm]OH, five times. Moreover, surface-anchored amines, magnesium oxide fluorides, high surface area MgO, P-BEMP, and KG-60-NEt_2 were stated to be deactivated after their aforementioned recyclable lifetimes. [bmIm]OH requires 43% of fresh catalyst after five cycles, and organic resins and silica gel 60 were restricted to certain nitro and α-nitro ketones. Although MgLa mixed oxides, hydrotalcites, and KF-doped catalysts displayed fair recyclability, they require activation from 400 to 700 °C, which is inconvenient for industrial reactors designed for operation at low temperatures.[6f] It is clear that there is considerable room for development of more robust recyclable heterogeneous catalysts for industrial applications.

Proazaphosphatranes **1**−**3** are exceedingly strong commercially available nonionic bases known to be useful catalysts and stoichiometric reagents in a wide variety of important organic transformations,[7] including 1,4-additions.[8a−c] We recently demonstrated that a dendrimer functionalized with an

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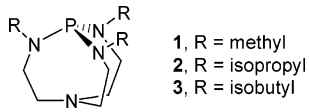
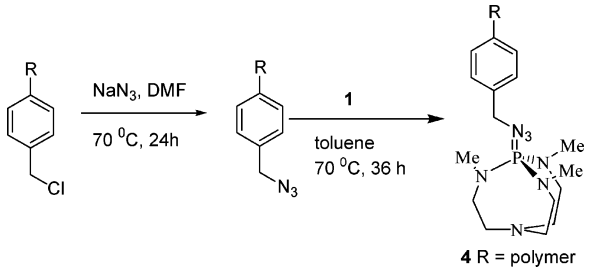
10.1021/jo062505z CCC: $37.00
Published on Web 03/17/2007

azidoproazaphosphatrane is a good catalyst for Michael and Henry reactions.[8d]



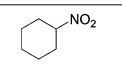
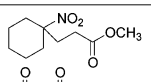
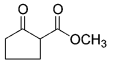
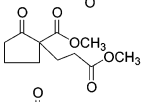
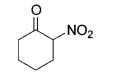
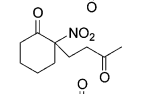
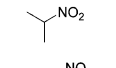
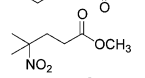
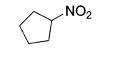
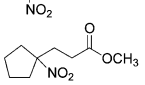
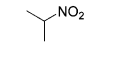
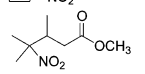
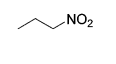
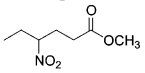
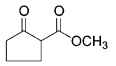
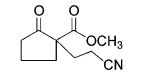
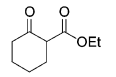
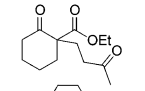
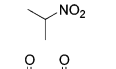
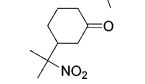
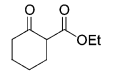
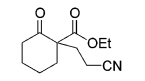
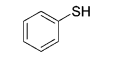
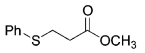
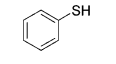
Herein, we describe an efficient and recyclable Merrifield resin-bound derivative of **1**, namely, azidoproazaphosphatrane **4**, as a room-temperature catalyst for 1,4-addition reactions. A more convenient synthesis of its precursor **1** is also described.

SCHEME 1



Catalyst **4**[9] was synthesized as shown in Scheme 1.[9a] We recently found **4** to be recyclable in the preparation of biodiesel, in general transesterifications, and in amidation reactions.[9b] The results tabulated in Tables 1 and 2 show that catalyst **4** is efficient and selective for 1,4-additions. Several structurally varying Michael donors, such as diethyl malonate, nitrocyclohexane, nitrocyclopentane, a β-ketoester, an α-nitro ketone, 2-nitropropane, 1-nitropropane, and ethyl cyanoacetate, underwent clean Michael additions with a variety of Michael acceptors including methyl vinyl ketone, methyl acrylate, methyl methacrylate, acrylonitrile, and cyclohexenone by our protocol. It is interesting to note here that the Michael adduct shown in Table 1, entry 1, was isolated in 96% yield as an NMR-pure colorless liquid without the requirement of minimal column chromatographic purification (using a short silica gel column eluted with hexanes/ethyl acetate) employed for all the other products. Simple filtration of polymer catalyst **4** in the reaction mixture associated with entry 1 of Table 1 followed by evaporation of solvent (including excess Michael acceptor) sufficed. No evidence of polymerized products was observed. These observations speak well to the practicality of **4** for the type of transformation discussed here.

TABLE 1. Substrate Scope of Room-Temperature 1,4-Additions[a]

Entry	Donor	Acceptor	t/h	Product	Yield[b]	Lit. Yield (%)
1			14		96%	100,[c] 96.8,[d] 68[e]
2			10		84%	1[f]
3			16		76%	87,[g] 96[h]
4			10		95%	54,[i] 90,[j] 72,[k] 80,[l] 78,[m] 86,[n] 87,[o] 80[p]
5			14		85%	100[q]
6			08		98%	4,[r] 61[s]
7			18		68%	62,[t] 80,[u] 65,[v] 24,[r] 45[w]
8			18		67%	55[x], 82.8[y]
9			14		89%	85-100[z]
10			16		94%	92,[aa] 99,[ab] 100[ac]
11			14		87%	71,[ad] 85,[ae] 99[af]
12			15		94%	60-96[ag]
13			15		91%	65-100[ah]

[a] Reaction conditions: donor (2 mmol), acceptor (3.0 mmol), **4** (10 mol %), THF (2 mL), room temperature. [b] Isolated yield after column chromatography unless otherwise stated. [c] See ref 8b. [d] Using benzyltrimethylammonium hydroxide at 100 °C, see ref 10a. [e] See ref 10b. [f] Using an Ir complex, see ref 10c. [g] Using basic Al_2O_3, see ref 10d. [h] Using Ph_3P, see ref 10e. [i] Using NaOH/PTC, see ref 11a. [j] Using 1,8-diazabicyclo[5.4.0]undec-7ene (DBU), see ref 11b. [k] Using a Ph_3P-supported homogeneous polymer, see ref 11c. [l] Using Amberlyst A-27, see ref 6a. [m] Using tetraethylammonium fluoride, see ref 11d. [n] Using benzyltrimethylammonium hydroxide, see ref 11e. [o] Using an electrochemical method, see ref 11f. [p] Using KF, see ref 11g. [q] Using Triton B (benzyltrimethylammonium hydroxide), see ref 12. [r] Using KF, see ref 11g. [s] Using DBU, see ref 13. [t] Using KG-60-NEt_2, see ref 6d. [u] Using NaOH, see ref 11a. [v] Using NaOH, see ref 14a. [w] Using NaOH, see ref 14b. [x] Using *t*-BuOK, see Supporting Information (SI) for ref. [y] Using Triton B, see SI for ref. [z] See SI for references. [aa] Using amino-functionalized SiO_2, see SI for ref. [ab] Using **2**, see ref 8b in ms. [ac] Using KF/Al_2O_3, see SI for ref. [ad] Using KOH, see SI for ref. [ae] Using KOH, see SI for ref. [af] Using resin-supported quaternary ammonium hydroxides, see SI for ref. [ag] See SI for references. [ah] See SI for references.

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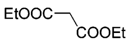
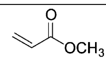
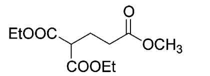
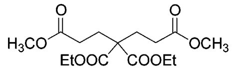
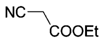
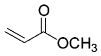
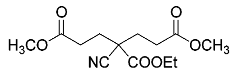
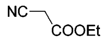
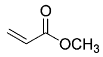
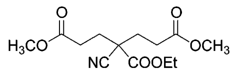
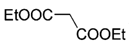
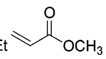
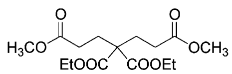
TABLE 2. 1,4-Additions with Diethyl Malonate and Ethyl Cyanoacetate[a]

Entry	Donor	Acceptor	t/h	Product	Yield[b]
1			15		7%
					42%
2			16		47%
3[c]			16		90% (Lit.: 92,[d] 70,[e] 77[f])
4[c]			14		80% (Lit.: 95[g])

[a] Reaction conditions: donor (2 mmol), acceptor (3.0 mmol), **4** (10 mol %), THF (2 mL), room temperature. [b] Isolated yield after column chromatography. [c] 5 mmol of acceptor used. [d] Using 50 mol % of [bmIm]OH, see ref 6e. [e] Using a rhenium phosphine complex, see ref 16a. [f] Using a ruthenium phosphine complex, see ref 16b. [g] Under electrochemical conditions, see ref 11f.

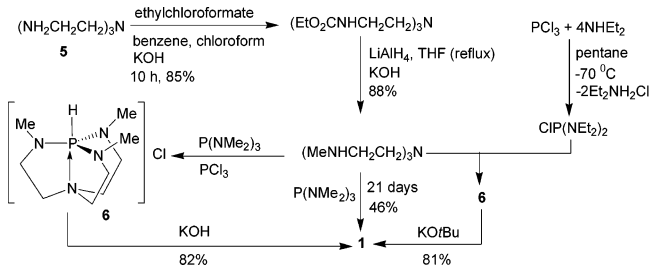
The activity of catalyst **4** was compared with the efficacy of a variety of catalytic approaches in terms of product yields (see parenthesized data in parentheses in Tables 1 and 2). From Tables 1 and 2, it is clear that the use of catalyst **4** is superior to those reported in 17 of the literature methods cited in these tables, of which all 17 approaches were different; comparable with those reported in 16 literature methods cited, of which all 16 were different; and inferior to those achieved in 13 literature methods cited, of which 13 all were different. We obtained better or comparable product yields in entries 1−11 of Table 1 with respect to those reported in the 33 literature references associated with those entries. The Michael addition of nitroalkanes is a convenient method for the preparation of useful synthetic intermediates because the nitro group can be transformed into other functionalities. It is noteworthy that the product, in entry 7 of Table 1, is an intermediate in the synthesis of the natural product, rhazinal, a potent and unusual antimitotic agent.[14a] We also investigated a heteroatom donor,[15] and good yields are reported for the sulfide products shown in entries 12 and 13 of Table 1. Amine donors gave poor conversions in our protocol.

We further investigated catalyst **4** for use with ethyl cyanoacetate and diethyl malonate, and the results are presented in Table 2. The reaction of methyl acrylate with diethyl malonate gave a mixture of mono and disubstituted products in 7% and 42% isolated yields, respectively, whereas in the case of ethyl cyanoacetate, the reaction proceeded completely to the disubstituted adduct in 47% isolated yield. Because it appeared that catalyst **4** showed a considerable propensity for causing disubstitution, we added two more equivalents of methyl acrylate. The reaction then cleanly produced disubstituted adducts in good to excellent yields (Table 2, entries 3 and 4). The only nonmetallic catalyst reported to facilitate the synthesis of double-addition products is [bmIm]OH,[6e] and the other two are metallic, containing the metals Re or Ru.[16] Thus, our methodology offers a favorable alternative approach to the use of an ionic liquid or of metal-catalyzed processes for the synthesis of disubstituted adducts.

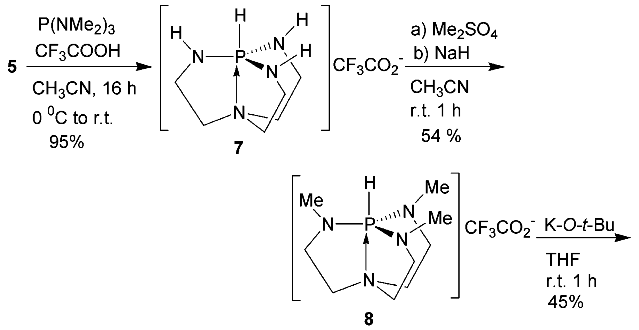
The reusability of **4** was investigated in the reaction of 2-nitropropane with methyl acrylate. Catalyst **4** was used 12 times with isolated product yields ranging from 90 to 96% (see Supporting Information). To the best of our knowledge, this number is unusually high for Michael additions. The same substrate combination has been used for determining the recyclability of triphenylphosphine supported on poly(4-*tert*-butylstyrene), a soluble polymer. By separating the product via solvent extraction, this homogeneous catalyst was recycled 5 times with product yields ranging from 31 to 71%.[11c] Thus, the present protocol for 1,4-additions appears to be the most efficacious thus far reported.

We previously reported[17] three routes for the synthesis of **1** (Scheme 2), two of which require four steps while the other needs a long reaction time (ca. 21 days). All three routes employ $LiAlH_4$ which generates copious amounts of solid waste which is often cumbersome to extract from the gellike solid produced upon hydrolysis. Here, we describe a synthesis of **1** (Scheme 3) which involves the synthesis of the trifluoroacetate salt of **7** in quantitative yield from the reaction of tren (**5**) with a 1:1 mixture of hexamethylphosphorus triamide (HMPT) and trifluoroacetic acid. Salt **7** was methylated using dimethyl sulfate in the presence of sodium hydride at room temperature in a reaction that was quite exothermic, requiring cooling for few minutes in an ice bath. The product obtained by this method also generates some P-methylated phosphonium salt (25% by ^{31}P NMR spectroscopic integration) which proved very difficult

SCHEME 2



SCHEME 3



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to separate. Thus, it was left in the reaction mixture which was then treated with potassium *tert*-butoxide. After evaporation of the THF and sublimation of the residue, white crystalline solid **1** (obtained in three facile steps) was obtained in 23% overall yield. Although this yield is lower than the yields obtained via our previously reported routes[17] (61%, 34%, 60%), the present protocol is less cumbersome and time consuming.

In conclusion, **4** efficiently facilitates room-temperature Michael additions using a variety of donors and acceptors. Catalyst **4** provides up to 12 cycles, giving good to excellent product yields for the synthesis of a variety of esters, ketones, and nitro compounds. The reactions are environmentally friendly and are easily worked up. A more convenient synthesis of **1**, the precursor to **4**, has also been developed.

Experimental Section

General Reaction Procedure. A mixture of a Michael donor (2 mmol) and acceptor (3 mmol) in THF (2 mL) was added to the polymer catalyst **1** (10 mol % of the azidophosphine moiety based on the donor). The reaction mixture was stirred at room temperature in a specified time (see Tables 1 and 2), and the polymer was filtered off and washed twice with 10 mL of THF. All volatiles were then removed from the reaction mixture under reduced pressure, followed by column chromatography of the crude product on silica gel.

Recyclability Protocol. Upon completion of the reaction (see Supporting Information), 5 mL of THF was added to the reaction mixture. The vial was then centrifuged for 2 h at 1000 rpm, and the vast majority of the supernatant solution was carefully removed by cannulation to avoid disturbing the catalyst. Excess THF was removed from the separated supernatant liquid via rotavapor, leaving the product which was subjected to ^{1}H and ^{13}C NMR analysis. The centrifuged catalyst, which was still submerged under a minimal volume of THF solution, was used for recycling by loading the fresh reactants and solvent.

Synthesis of 7. To a 1000 mL round-botton flask was added freshly distilled (90 mbar) tris(2-aminoethyl)amine **5** (14.9 mL, 100 mmol) followed by the addition of acetonitrile (250 mL). The reaction was magnetically stirred, and after 5 min, hexamethylphosphorus triamide (18.33 mL, 100 mmol) was syringed into the solution. After further stirring at room temperature for 15 min and after flushing with argon for about 10 min, the flask was placed in an ice-bath. To this solution was added trifluoroacetic acid (7.45 mL, 100 mmol) over a period of 1 h under argon flow using a needle outlet to release fumes generated in the flask. The ice-bath was then removed, and the solution was further stirred for 16 h at room temperature. Upon removal of volatiles under reduced pressure, a white solid was obtained which was washed with hexanes (3 × 400 mL), decanting after each wash. To the slightly sticky solid remaining was added 5 mL of THF in 200 mL of hexanes, whereupon a pale yellow solid precipitated. The flask was kept in a refrigerator for 12 h after which the supernatant was decanted, leaving a white solid which was dried under reduced pressure for 2 h providing a 95% yield (27.4 g) of product. ^{31}P NMR (162.8 MHz, CD_3CN): −44.67 ppm.

Synthesis of 8. To a 1000 mL round-bottom flask was added sodium hydride (10.0 g, 416 mmol) and **7** (28.81 g, 100 mmol) in an argon-filled glovebox followed by removal of the flask from the box and addition of 400 mL of dry acetonitrile under a flow of argon. To this stirred solution was added dimethyl sulfate (29.4 mL, 310 mmol) at room temperature over a period of 45 min under argon flow. The resulting vigorously exothermic reaction was controlled by placing the flask in an ice-bath for few minutes while the addition was interrupted. After the addition was complete (as determined by ^{31}P NMR spectroscopy) and the reaction mixture was allowed to stir for an additional 15 min, the mixture was very carefully quenched with 1 mL of water and then 5 mL of methanol. Volatiles were removed under reduced pressure while maintaining the water bath temperature below 50 °C. The crude product was washed with 3 × 500 mL of ethyl ether. The product was dissolved in THF/hexanes (50/300 by mL volume), and ethyl ether (200 mL) was added to the resulting solution. A pale yellow solid was thus obtained which was further washed with ethyl ether (2 × 500 mL) giving 23.1 g (54% yield) of product. ^{31}P NMR (162.8 MHz, CD_3CN): −9.55 ppm corresponding to **8** and P-methylated product at 47.2 ppm.

Synthesis of 1. To a 500 mL round-botton Schlenk flask was added a mixture of 75% of **8** plus 25% of P-methylated salt (i.e., 17.0 g of mixture corresponding to 40.0 mmol of **8**) potassium *tert*-butoxide (7.78 g, 69.40 mmol) in an argon-filled glovebox. The flask was then evacuated under reduced pressure after which ca. 100 mL of anhydrous THF was added to the heterogeneous reaction mixture under a flow of argon. The resulting brown solution was stirred for about 1 h at room temperature to complete the deprotonation process (as monitored by ^{31}P NMR spectroscopy). The reaction flask was then connected to a vacuum line and kept under reduced pressure for removal of volatiles, after which 200 mL of anhydrous hexane was added with further stirring for an additional 1 h at room temperature. The resulting solution was filtered through a frit under an argon atmosphere, and volatiles were removed under reduced pressure on a vacuum line. The solid remaining (6.12 g) was sublimed at 60−70 °C under 300 mTorr. The colorless crystalline solid sublimate **1** was removed from the sublimation unit in an argon-filled glovebox providing 3.91 g (45% yield). ^{31}P NMR (162.8 MHz, C_6D_6): 120.7 ppm.

Acknowledgment. The authors thank the National Science Foundation for grant support.

Supporting Information Available: References to the known compounds (all of which are known), copies of ^{1}H and ^{13}C NMR spectra for all Michael addition products, and ^{31}P NMR spectra for the preparation of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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