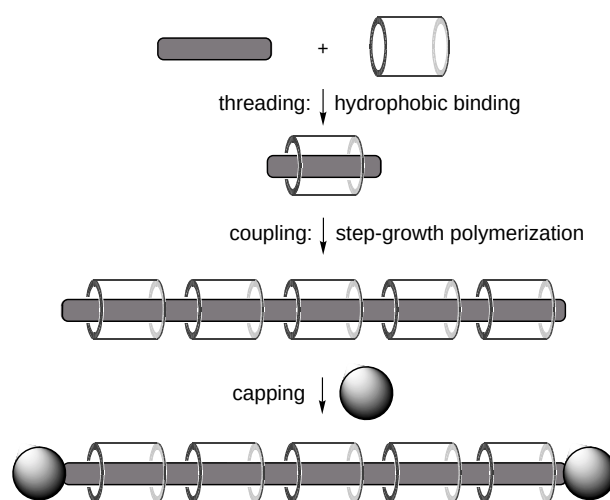


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Insulated Molecular Wires: Synthesis of Conjugated Polyrotaxanes by Suzuki Coupling in Water**

Peter N. Taylor, Michael J. O'Connell, Luke A. McNeill, Michael J. Hall, Robin T. Aplin, and Harry L. Anderson*

The semiconductivity and fluorescence of conjugated polymers result in potential applications, particularly in the area of electroluminescent display devices.^[1] We are interested in enhancing the luminescence, stability, and processability of these polymers by threading them through macrocycles to form conjugated polyrotaxanes, as a type of "insulated molecular wire".^[2,3] Recently we proposed the general route to conjugated polyrotaxanes outlined in Scheme 1. Hydrophobic binding fixes the monomer inside



Scheme 1. Hydrophobic binding directs the synthesis of an insulated molecular wire.

the cavity of a macrocycle, this 1:1 pseudorotaxane complex is then polymerized to form a conjugated polypseudorotaxane, which is coupled to bulky end groups to give the polyrotaxane. Our initial attempts at realizing this scheme used a cationic cyclophane as the macrocycle and Glaser coupling as the polymerization reaction. This failed to give polyrotaxanes higher than the [3]rotaxanes, due to problems of unthreading, aggregation, and precipitation of the growing polymer

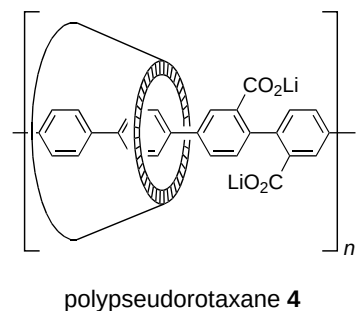
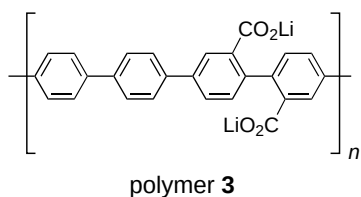
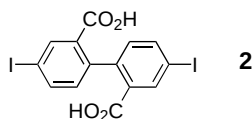
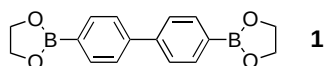
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chains.^[2b] Here we present a completely new way of implementing Scheme 1, using β -cyclodextrin (β -CD) as the macrocycle and Suzuki coupling^[4] as the polymerization reaction. Suzuki coupling works well in water,^[5] and has been used to prepare water-soluble conjugated polymers,^[5c,d] but it has not previously been used to make rotaxanes. Our new approach to polyrotaxane synthesis is remarkably successful, giving a highly threaded poly-*para*-phenylene (PPP). Insulation of the PPP backbone inside the cyclodextrins increases its fluorescence efficiency and increases its solubility (processability), suggesting that these polyrotaxanes may have real advantages over unencapsulated PPPs.

When 4,4'-biphenyldiboronic ester **1**^[6] and 4,4'-diiodobiphenyl-2,2'-dicarboxylic acid **2**^[7] are coupled (using phosphane-free aqueous $\text{Pd}(\text{OAc})_2$ catalyst,^[5] in the mole ratio



1:2:Pd of 1.00:0.91:0.09^[8] the product polymer **3** is mostly insoluble, as reported previously,^[9] although a fraction of the polymer is soluble enough in water, as the lithium salt, for spectroscopic characterization. When this reaction is carried out in the presence of three equivalents of β -cyclodextrin per 4,4'-biphenyldiboronic acid, a soluble polypseudorotaxane **4** is formed. This PPP complex was isolated in 71 % yield (calculated assuming one cyclodextrin per repeat unit), after precipitating with acid, dissolving in aqueous LiOH, and dialyzing^[10] to remove excess cyclodextrin, salts, and small oligomers.^[11] Integration of the aromatic and cyclodextrin regions of the ¹H NMR spectrum of this polypseudorotaxane in D₂O (Figure 1 a) indicates that there are 1.2 ± 0.3 macro-

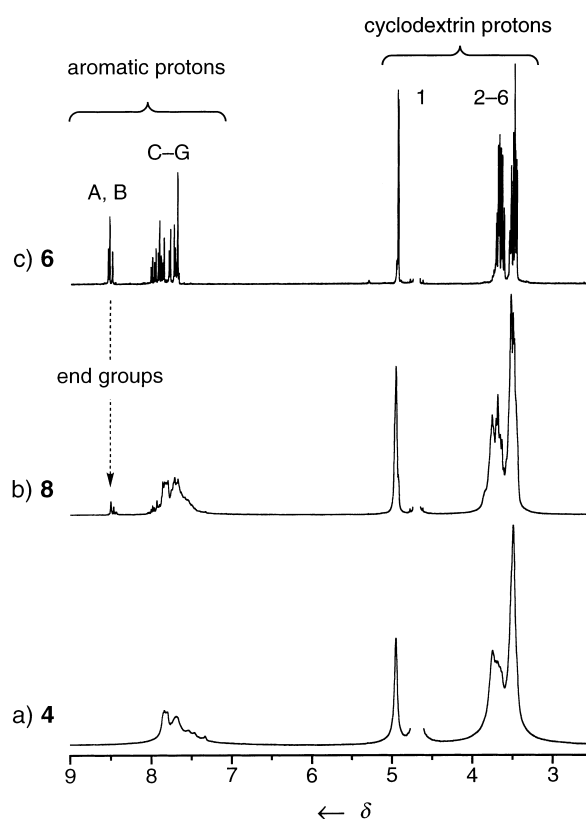
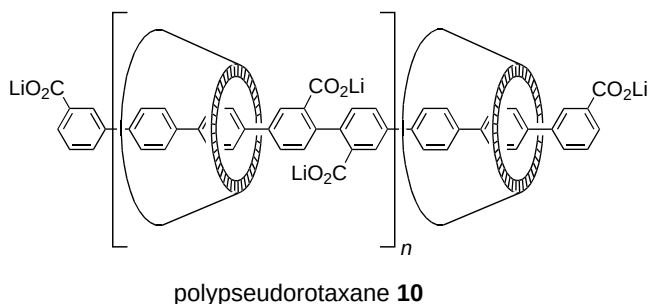
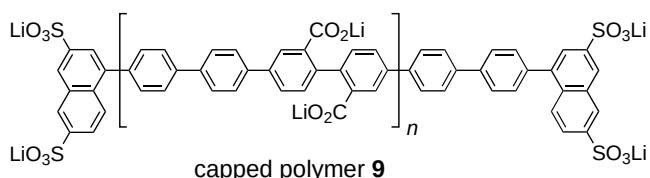
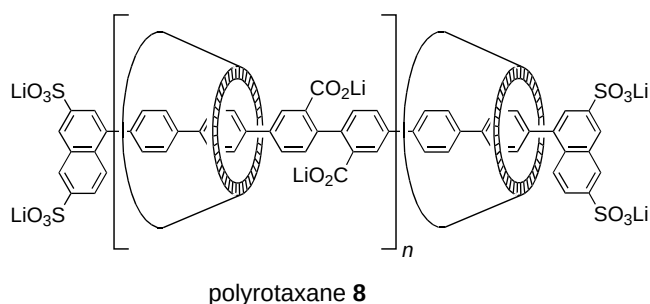
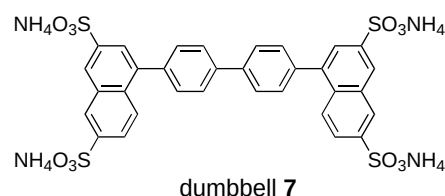
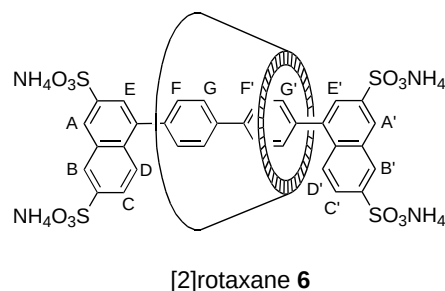
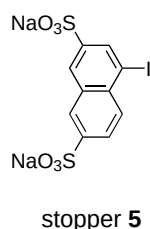


Figure 1. ¹H NMR spectra of a) polypseudorotaxane **4**, b) polyrotaxane **8**, and c) [2]rotaxane **6** (500 Hz in D₂O, with HOD peak truncated).

cycles per repeat unit. This threading ratio cannot be determined accurately because it gradually decreases during dialysis. As the cyclodextrins slip off the polymer chain it becomes increasingly gelatinous and insoluble.

The formation of genuine rotaxanes, rather than pseudorotaxanes, was achieved by reacting 4,4'-biphenyldiboronic ester **1** with disodium 1-iodonaphthalene-3,6-disulfonate (**5**)^[12] in the presence of β -cyclodextrin under identical aqueous Suzuki coupling conditions. This gave the [2]rotaxane **6**, together with the dumbbell **7**. ¹H NMR spectroscopy of crude reaction mixtures, after removing all free cyclodextrin by ion-exchange chromatography, showed that the ratio of **6:7** is about 1:2, which indicates that the naphthalene end groups significantly hinder cyclodextrin binding. It proved difficult to separate the [2]rotaxane **6** from dumbbell **7**, but **6** was isolated in 4 % yield by repeated recrystallization from aqueous methanol/ethanol. The ¹H NMR spectrum of **6** (Figure 1 c) shows that the symmetry of the cyclodextrin is imposed on the encapsulated dumbbell, doubling the number of aromatic signals.

This reaction was extended to synthesize polyrotaxane **8** by coupling a mixture of **1**, **2**, **5**, and β -cyclodextrin (mole ratio **1:2:5:Pd:β-CD** of 1.00:0.74:0.37:0.07:3.0).^[8] The PPP polyrotaxane **8** was isolated in 45 % yield, after precipitation and extensive dialysis.^[10] Although the ¹H NMR spectrum of **8** in D₂O is poorly resolved, it closely resembles those of **4** and **6** (as shown in Figure 1) and the resonance signals of the terminal naphthalene protons (A and B) are well separated from the other aromatic peaks. Integration of these end group



signals shows that the average degree of polymerization n is about 8 ± 2 . (This is higher than the value expected from the polymerization stoichiometry, perhaps because short oligomers are lost during purification). Integration of the cyclodextrin resonance signals shows that there are 1.1 ± 0.1 macrocycles per unsubstituted biphenyl unit. No change in this threading ratio occurred during dialysis.

The matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrum of polyrotaxane **8** (Figure 2) provides excellent evidence for its structural authenticity. All the observed peaks correspond to expected singly charged molecular ions, with up to six repeat units ($n = 3-6$) and up to nine threaded cyclodextrins ($x = 4-9$). No signals are detected for oligomers lacking naphthalene end groups. This mass spectrum confirms that some chains have more than one cyclodextrin per repeat unit, as indicated by NMR spectroscopy. The threading ratio [$y = x/(n + 1)$] ranges from 1 to 1.3, and is highest for the longest oligomers, which reflects weaker binding near the naphthalene sulfonate end groups (as deduced from the low yield of **6**). Polyacrylamide gel electrophoresis (PAGE)^[13] of **8** shows a broad band at 36–50 kDa, relative to denatured protein markers. Gel permeation chromatography (GPC) on a S200 Sephadex column gives a similar molecular weight, with a broad peak at 50 ± 4 kDa.^[14] This is higher than the molecular weight predicted from the NMR spectroscopy and MALDI TOF MS results, which may indicate that the polyrotaxane self-associates in solution.

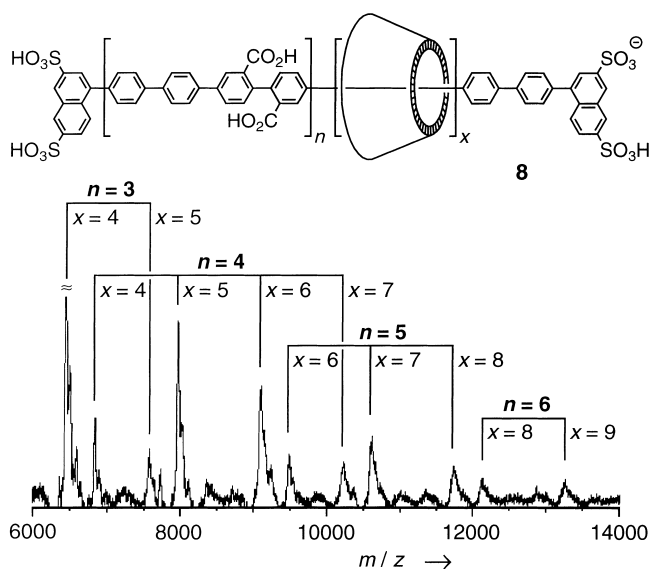


Figure 2. Negative-ion MALDI-TOF mass spectrum of the ammonium salt of polyrotaxane **8**, from a 2,5-dihydroxybenzoic acid matrix.

We have compared the polyrotaxane **8** with several model compounds. The uninsulated capped PPP **9** was prepared under identical conditions to **8**, except omitting the β -cyclodextrin. We also prepared a capped pseudorotaxane **10**, using identical conditions to the synthesis of **8**, except replacing the

end group **5** with 3-iodobenzoic acid. These end groups are too small to prevent unthreading, so the threading ratio in **10** gradually decreases during dialysis until all the cyclodextrin has been removed, leaving capped PPP **11**. This control experiment proves that **8**, which exhibits no unthreading, is a genuine polyrotaxane. The ^1H NMR spectra of the unencapsulated polymers **3**, **9**, and **11** are much broader than those of their encapsulated analogues **4**, **8**, and **10**, because encapsulation hinders aggregation.

The absorption and emission spectra of **4**, **6**, and **8** are compared in Figure 3, and the electronic spectra and fluorescence quantum yields of **3**, **4**, and **6–9** are summarized in Table 1. The peak at around 236 nm in the absorption spectra

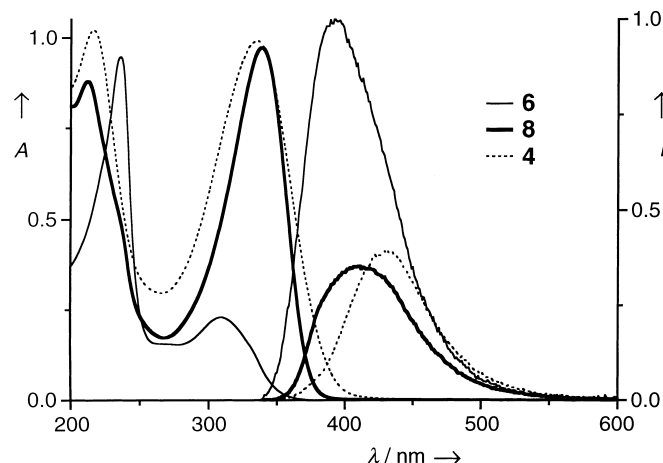


Figure 3. Absorption spectra (left) and emission spectra (right, arbitrary units) of [2]rotaxane **6** (solid), polyrotaxane **8** (bold) and polypseudorotaxane **4** (dashed), in aqueous solution. The concentrations of **6**, **8**, and **4** for the absorption spectra are 12, 26, and 25 mg L^{-1} , respectively.

Table 1. Electronic spectra and fluorescence quantum yields.^[a]

Compound	λ_{max} abs [nm]	λ_{max} em [nm]	Φ_f
PPP 3	215, 335	430	0.18
polypseudorotaxane 4	216, 332	432	0.19
[2]rotaxane 6	236, 310	393	0.95
dumbbell 7	235, 309	415	0.64
polyrotaxane 8	216, 338	410	0.29
capped PPP 9	212, 331	429	0.21

[a] Spectra were recorded in water. Quantum yields were measured relative to anthracene in cyclohexane ($\Phi_f = 0.36$).

of **6** and **7** is due to the naphthalene end group; a small shoulder at this wavelength is also apparent in the absorption spectra of **8** and **9**. Apart from this feature, the spectra of **8** and **9** resemble those of the **3** and **4**. Comparison of the emission spectra and quantum yield of **6** with **7**, and **8** with **9**, shows that encapsulation of the chromophore results in a blue shift of about 20 nm. There is also a significant fluorescence enhancement in **8**. Several other conjugated polypseudorotaxanes have been reported,^[3f–h] but this work represents the first synthesis of conjugated polyrotaxanes. Experiments are in progress towards exploring the behavior of these new materials in electroluminescent light-emitting diodes.

Experimental Section

6: 1-Iodonaphthalene-3,6-disulfonate disodium salt **5** (183 mg, 0.40 mmol), biphenyl-4,4'-diboronic acid diethylene glycol ester **1** (65 mg, 0.22 mmol), β -cyclodextrin (1.0 g, 0.88 mmol), and $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol) were dissolved in O_2 -free Na_2CO_3 aq (3 mL, 0.2 M), and stirred at 85°C for 20 h then cooled and acidified with acetic acid. The [2]rotaxane was purified by ion-exchange chromatography (Bio-Rad AG 4-X4 resin, 1 % NH_3 aq) and recrystallized three times from $\text{H}_2\text{O}/\text{MeOH}$ and EtOH to give pure **6** as a white solid (15 mg, 4 %).

8: 1-Iodonaphthalene-3,6-disulfonate disodium salt **5** (45.8 mg, 0.10 mmol), biphenyl-4,4'-diboronic acid diethylene glycol ester **1** (79.4 mg, 0.27 mmol), 4,4'-diiodobiphenyl-2,2'-dicarboxylic acid **2** (98.8 mg, 0.20 mmol), $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol), and β -cyclodextrin (920 mg, 0.81 mmol) were dissolved in O_2 -free Li_2CO_3 aq (6 mL, 0.2 M) and heated to 85°C for under nitrogen for 20 h. Excess β -cyclodextrin was removed by precipitating the product with HCl aq (to pH 1). The resulting solid was redissolved in Li_2CO_3 aq and dialyzed.^[10] Removal of the solvent gave **8** as a glassy film (159 mg, 45 %).

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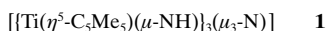
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- [10] Dialysis was carried out in a stirred cell with a 5000 nominal molecular weight limit polyethersulfone ultrafiltration membrane, using a pressure of 5 atm to force over 1 L of water through the sample. Low-molecular-weight compounds such as free cyclodextrin and **7** are rapidly removed by this procedure.
- [11] We have no information on the relative orientation of the cyclodextrin units in **4**, **8**, and **11**; our schematic representation is not intended to imply that all the macrocycles point the same way.
- [12] Disodium 1-iodonaphthalene-3,6-disulfonate (**5**) was prepared in 86 % yield by treatment of the diazonium salt of disodium 1-aminonaphthalene-3,6-disulfonate with KI.
- [13] Electrophoresis was performed in 12 % urea-PAGE gels, using the Bio-Rad minigel system, with 5 M urea in the separating gel at pH 8.8, at 100 V.
- [14] GPC solvent: aqueous 100 mM Tris/HCl, 100 mM NaCl, pH 8; molecular weight markers: 12.4–67 kDa from Sigma.

[[Ti(η^5 -C₅Me₅)(μ -NH)]₃(μ_3 -N)]: An Efficient Entry to Single and Double Cube-Type Nitrido Complexes**

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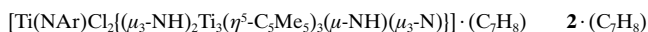
Group 4 tetrametallic derivatives of the formula [(ML_n)₄(μ_3 -E)₄] with cube-type cores remain extremely rare and are limited to halide-bridged [[TiL]₄(μ_3 -Cl)₄] (L = η^8 -C₈H₈,^[1] Me₃^[2]), chalcogenide-bridged [[Ti(η^5 -C₅H₅R)]₄(μ_3 -S)₄],^[3] and imido-bridged [[Ti(η^5 -C₅H₅)]₄(μ_3 -NSnMe₃)₄] complexes.^[4] Our first contributions in this field were the preparation of the singular nitrido and alkylidyne complexes [[Ti(η^5 -C₅Me₅)(μ_3 -E)]₄ (E = N^[5], CH^[6]), which contained an almost perfect Ti₄E₄ cube. A possible synthetic strategy to access this type of compounds would involve the incorporation of different metal complex fragments in a cuboidal core such as [Ti₃(μ -NH)₃(μ_3 -N)]₂,^[7] in a similar way to that reported for [M₃(μ -S)₃(μ_3 -S)] species.^[8–10] In this context, we have recently determined that the preorganized^[11] “organometallic ligand” **1** is able to displace mesitylene or carbonyl ligands in



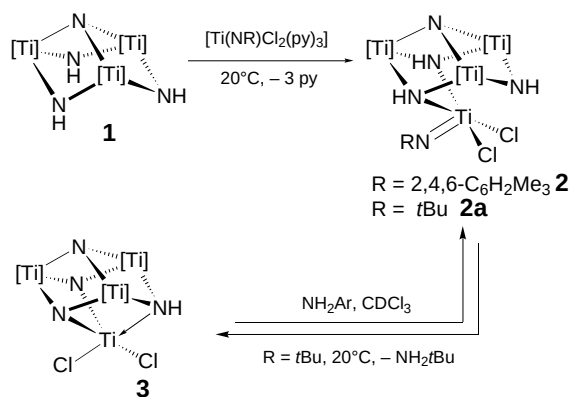
[Mo(CO)₃(1,3,5-Me₃C₆H₃)] or [M(CO)₆], respectively,^[12] and also reacts, by N–H activation, with tris(dimethylamido)cyclopentadienyltitanium(IV) compounds^[13] to give azametallocubane complexes. Herein we describe the reactions of **1** with several d⁰ imido- and amidotitanium and -zirconium com-

plexes that yield new cube-type derivatives and, for the first time, metal corner-shared double cube nitrido complexes. This synthetic method should be generally applicable and thus make the Ti₃N₄ core a very versatile building block for heterometal cluster chemistry and for molecular precursors of new ternary nitrides MTi_xN_y.

Reaction of complex **1** with [Ti(NAr)Cl₂(py)₃] (Ar = 2,4,6-C₆H₂Me₃)^[14] in toluene at room temperature results in displacement of the pyridine (py) ligands and formation of **2**·(C₇H₈) in 51 % yield (Scheme 1). Analogous treatment of **1** with the *tert*-butylimido derivative [Ti(N^tBu)Cl₂(py)₃]^[14] in toluene afforded the complex **3** as a green precipitate in 82 %



yield.^[15] The addition of 2,4,6-trimethylaniline (1 equiv) to a solution of **3** in CDCl₃ at room temperature gave **2** within several days. Complexes **2** and **3** were characterized by spectral and analytical methods, as well as by an X-ray structure determination in the case of **2** (vide infra).

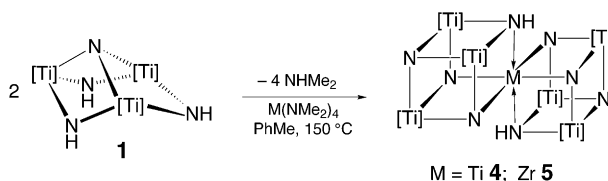


Scheme 1. Synthesis of **2** and **3** from **1**. [Ti] = Ti(η^5 -C₅Me₅).

Treatment of **1** with tetrakis(dimethylamido)titanium(IV) or -zirconium(IV) in toluene at 150 °C afforded the corner-shared double cube complexes **4**·2 C₇H₈ and **5**·1.5 C₇H₈, respec-



tively, as dark green crystals in 69 and 60 % yield, respectively (Scheme 2). Complex **5**·1.5 C₇H₈ was also prepared in 53 % yield through the reaction of **1** with the imido derivative [Zr(NAr')(NHAr')₂(py)₂] (Ar' = 2,6-C₆H₃iPr₂)^[16] in toluene at 90 °C. Once isolated complexes **4** and **5** are not soluble in



Scheme 2. Synthesis of **4** and **5** from **1**. [Ti] = Ti(η^5 -C₅Me₅).

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