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[10] X-ray structural analysis was performed on an Enraf Nonius CAD4 diffractometer with graphite monochromated $Cu_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data collection and refinement for $C_{128}H_{174}I_2N_8O_9$ at 173 K: transparent plate $0.20 \times 0.40 \times 0.5$ mm^3, triclinic, space group $P\bar{1}$ no. 2, $a = 15.407(5)$, $b = 27.122(5)$, $c = 14.688(5)$ Å, $\alpha = 94.65(2)$, $\beta = 90.83(2)$, $\gamma = 75.88(2)^\circ$, $V = 5933(3)$ Å^3, $Z = 2$, $M_r = 2222.64$, $\rho_{calcd} = 1.244$ g cm^{-3}, $\mu = 5.9$ cm^{-1}, $\theta_{max} = 65$, 21077 reflections were collected ($\pm h$, $\pm k$, $+l$), of which 20151 were unique ($R_{int} = 0.06$) and 11677 observed ($F_o > 4\sigma(F_o)$). The structure was solved by direct methods using SIR92 (A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined on *F* using SHELXL-96 software (G. M. Sheldrick, *SHELXL-96*, University of Göttingen, Germany, **1996**). Data were corrected for Lorentz and polarization effects. Absorption correction was applied by Ψ scan measurements (min/max transmission factor = 0.75). The terminal aliphatic chains on the phenol oxygen atoms were affected by severe static disorder arising from several slightly different orientations. It proved impossible to rationalize the disorder in terms of different orientations with different site occupancy factors and the refinement was carried out with geometrical constraints on the chains. All non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogen atoms were taken in their calculated positions "riding" on their parent atoms (1346 parameters, 30 constraints). Final $R_1 = 0.092$ and $wR_2 = 0.294$ with GOF = 0.984. Largest difference peak and hole 1.77 and -2.92 e Å^{-3}, respectively. Geometrical calculations were obtained by PARST95 (M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141315. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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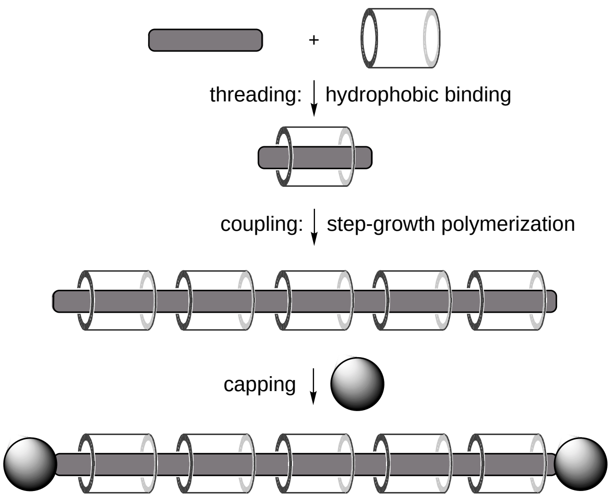
Insulated Molecular Wires: Synthesis of Conjugated Polyrotaxanes by Suzuki Coupling in Water[**]

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 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



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

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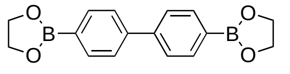
[**] We are grateful to Carol A. Stanier for valuable discussion and to Professor Christopher J. Schofield for providing facilities for gel electrophoresis. Disodium 1-aminonaphthalene-3,6-disulfonate was generously provided by Dr. M. G. Hutchings of BASF plc (Cheadle Hulme, UK). This project is funded by the Engineering and Physical Sciences Research Council (UK).

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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 Pd(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 ^{1}H NMR spectrum of this polypseudorotaxane in D$_2$O (Figure 1a) indicates that there are 1.2 ± 0.3 macrocycles 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.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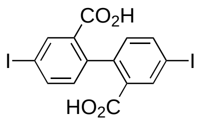
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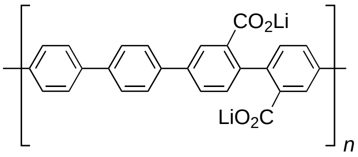
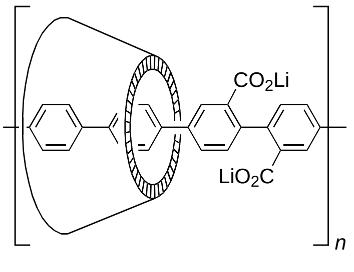

polymer **3**


polypseudorotaxane **4**

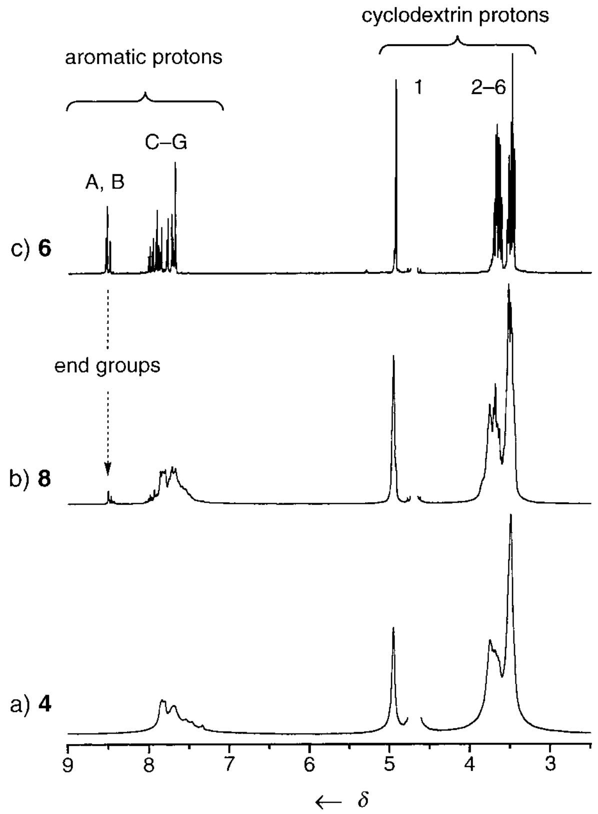
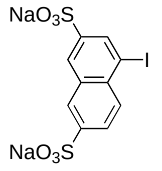


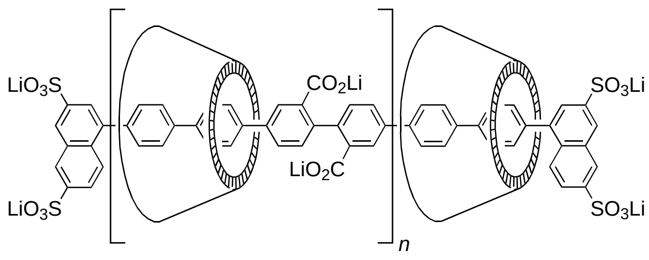
Figure 1. ^{1}H NMR spectra of a) polypseudorotaxane **4**, b) polyrotaxane **8**, and c) [2]rotaxane **6** (500 Hz in D$_2$O, with HOD peak truncated).

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**. ^{1}H 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 recystallization from aqueous methanol/ethanol. The ^{1}H NMR spectrum of **6** (Figure 1c) shows that the symmetry of the cyclodextrin is imposed on the encapsulated dumbbell, doubling the number of aromatic signals.

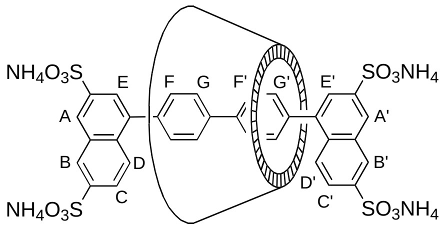
This reaction was extended to synthesize polyrotaxane **8** by coupling a mixture of **1**, **2**, **5**, and β-cyclodextrin (mole ratio **1**:**2**:**5**:Pd:β-CD of 1.00:0.74:0.37:0.07:3.0).[8] The PPP polyrotaxane **8** was isolated in 45% yield, after precipitation and extensive dialysis.[10] Although the ^{1}H NMR spectrum of **8** in D$_2$O 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



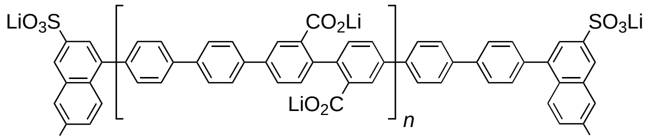
stopper **5**



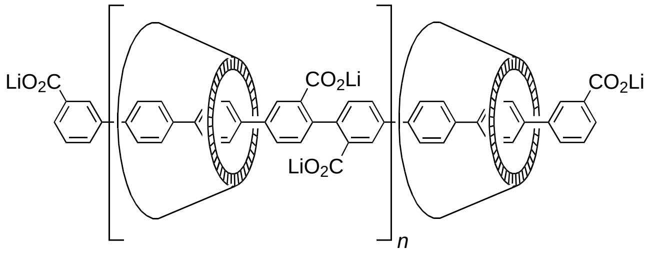
polyrotaxane **8**



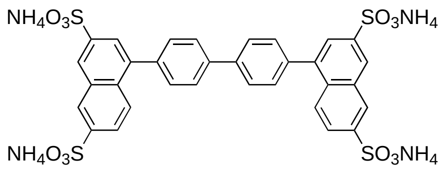
[2]rotaxane **6**



capped polymer **9**



polypseudorotaxane **10**



dumbbell **7**

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.

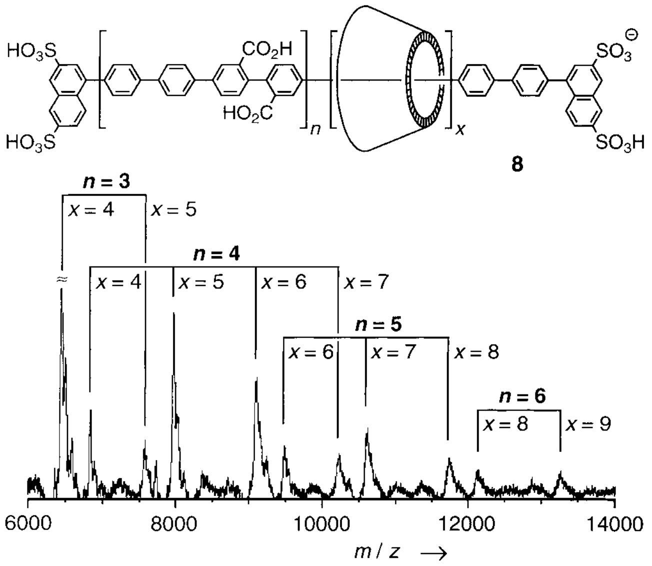


Figure 2. Negative-ion MALDI-TOF mass spectrum of the ammonium salt of polyrotaxane **8**, from a 2,5-dihydroxybenzoic acid matrix.

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 ^{1}H 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 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.

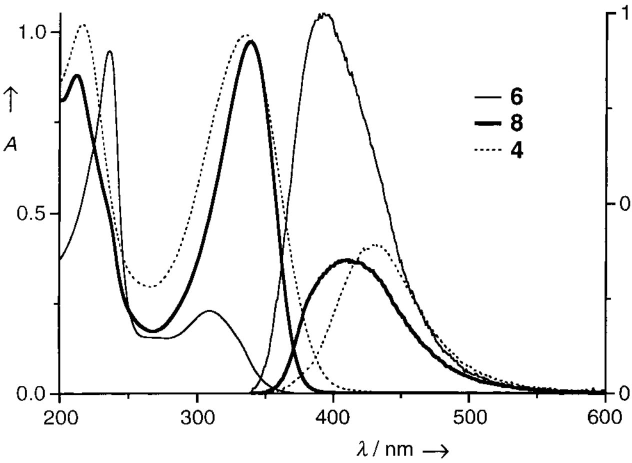


Figure 3. Absorption spectra (left) and emission spectra (right, arbitrary units) of [2]rotaxane **6** (solid), polyrotaxane **8** (bold) and polypseudorotaxane **4** (dashed), in aqueous solution. The concentrations of **6**, **8**, and **4** for the absorption spectra are 12, 26, and 25 mg L^{-1}, 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 ($\Phi_f = 0.36$).

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 Pd(OAc)$_2$ (4.5 mg, 0.02 mmol) were dissolved in O$_2$-free Na$_2$CO$_3$ 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 H$_2$O/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), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), and β-cyclodextrin (920 mg, 0.81 mmol) were dissolved in O$_2$-free Li$_2$CO$_3$ 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$_2$CO$_3$ aq and dialyzed.[10] Removal of the solvent gave **8** as a glassy film (159 mg, 45 %).

Received: May 18, 2000 [Z15146]

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[8] These mole ratios were calculated on the assumption that the Pd(OAc)$_2$ is reduced to Pd^0 by coupling boronic acid units in a reaction of the stoichiometry Pd(OAc)$_2$ + 2 ArB(OH)$_2$ $\rightarrow$ Pd^0 + Ar$_2$; M. Moreno-Mañas, M. Pérez, R. Pleixats, *J. Org. Chem.* **1996**, *61*, 2346–2351; K. A. Smith, E. M. Campi, W. R. Jackson, S. Marcuccio, C. G. M. Naeslund, G. B. Deacon, *Synlett* **1997**, 131–132.

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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-C$_5$Me$_5$)(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-C$_8$H$_8$,[1] Me$_3$ [2]), chalcogenide-bridged [{Ti(η^5-C$_5$H$_4$R)}$_4$(μ_3-S)$_4$],[3] and imido-bridged [{Ti(η^5-C$_5$H$_5$)}$_4$(μ_3-NSnMe$_3$)$_4$] complexes.[4] Our first contributions in this field were the preparation of the singular nitrido and alkylidyne complexes [{Ti(η^5-C$_5$Me$_5$)(μ_3-E)}$_4$] (E = N[5], CH[6]), which contained an almost perfect Ti$_4$E$_4$ 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 [Ti$_3$(μ-NH)$_3$(μ_3-N)],[7] in a similar way to that reported for [M$_3$(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

[{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] **1**

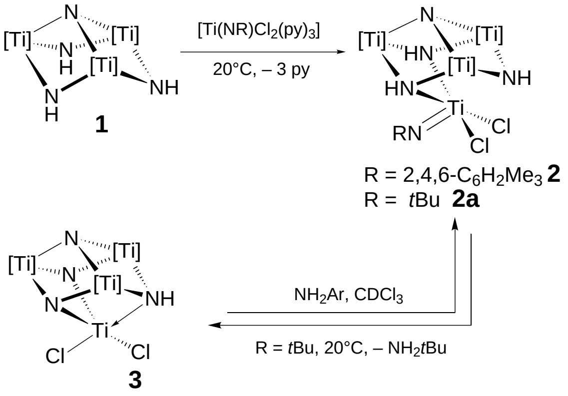
[Mo(CO)$_3$(1,3,5-Me$_3$C$_6$H$_3$)] or [M(CO)$_6$], respectively,[12] and also reacts, by N–H activation, with tris(dimethylamido)cyclopentadienyltitanium(IV) compounds[13] to give azametallocubane complexes. Herein we describe the reactions of **1** with several d^0 imido- and amidotitanium and -zirconium complexes 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 Ti$_3$N$_4$ core a very versatile building block for heterometal cluster chemistry and for molecular precursors of new ternary nitrides MTi$_x$N$_y$.

Reaction of complex **1** with [Ti(NAr)Cl$_2$(py)$_3$] (Ar = 2,4,6-C$_6$H$_2$Me$_3$)[14] in toluene at room temperature results in displacement of the pyridine (py) ligands and formation of **2** · (C$_7$H$_8$) in 51 % yield (Scheme 1). Analogous treatment of **1** with the *tert*-butylimido derivative [Ti(N*t*Bu)Cl$_2$(py)$_3$][14] in toluene afforded the complex **3** as a green precipitate in 82 %

[Ti(NAr)Cl$_2${(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] · (C$_7$H$_8$) **2** · (C$_7$H$_8$)

[TiCl$_2${(μ_3-N)$_3$(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$}] **3**

yield.[15] The addition of 2,4,6-trimethylaniline (1 equiv) to a solution of **3** in CDCl$_3$ 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).

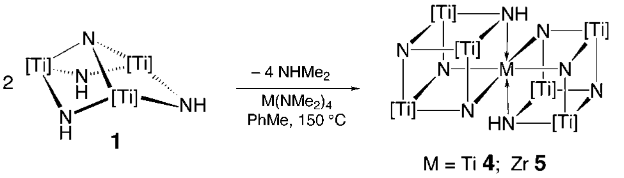


Scheme 1. Synthesis of **2** and **3** from **1**. [Ti] = Ti(η^5-C$_5$Me$_5$).

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 C$_7$H$_8$ and **5** · 1.5 C$_7$H$_8$, respectively, as dark green crystals in 69 and 60 % yield, respectively (Scheme 2). Complex **5** · 1.5 C$_7$H$_8$ was also prepared in 53 % yield through the reaction of **1** with the imido derivative [Zr(NAr′)(NHAr′)$_2$(py)$_2$] (Ar′ = 2,6-C$_6$H$_3$*i*Pr$_2$)[16] in toluene at 90 °C. Once isolated complexes **4** and **5** are not soluble in

[Ti{(μ_3-N)$_3$(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$}$_2$] · 2 C$_7$H$_8$ **4** · 2 C$_7$H$_8$

[Zr{(μ_3-N)$_3$(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$}$_2$] · 1.5 C$_7$H$_8$ **5** · 1.5 C$_7$H$_8$



Scheme 2. Synthesis of **4** and **5** from **1**. [Ti] = Ti(η^5-C$_5$Me$_5$).

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[**] This work was supported by the Spanish DGES (PB96-0672), and the Universidad de Alcalá (E027/99). C.Y. also thanks the CAM for a postdoctoral grant.