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Mechanism of Formation of Threaded Ar_2Zn(18-crown-6) Species

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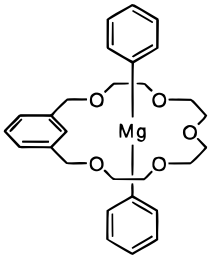
Tol_2Zn (Tol is *p*-methylphenyl) and 18-crown-6 in benzene rapidly and almost completely form a 1:1 complex (peripheral) in which Zn is probably bonded to two oxygens. A rotaxane (threaded) 1:1 species forms more slowly; at equilibrium, [rotaxane]/[peripheral] = 0.7 at 23 °C. Several observations indicate that formation and dethreading of the rotaxane require free Tol_2Zn (not incorporated into the peripheral complex). (1) Rotaxane formation is considerably more rapid when $[Tol_2Zn]_0 > [\text{18-crown-6}]_0$ than when the crown ether is initially in excess. (2) Added tetramethylethylenediamine stops both formation and dethreading of the rotaxane. (3) Pure rotaxane is stable indefinitely in a benzene solution, but dethreading occurs when some of a diorganozinc compound is added. (4) The rate of dethreading is approximately proportional to the concentrations of rotaxane and free Tol_2Zn.

Rotaxanes in which a diorganomagnesium or diorganozinc compound is threaded through a crown ether were observed several years ago by Bickelhaupt and co-workers[1] (**1**) and by Richey and co-workers[2] (**2**). Other organomagnesium and organozinc rotaxanes have since been prepared.[3] How do the rotaxanes form? Certainly not by threading of an intact diorganometal compound through the cavity of the crown ether, since even the ethyl group in **2a** or **2b** is too large to make this passage through the cavity of 18-crown-6, and the catenane (**3**) prepared by Bickelhaupt and co-workers[4] clearly cannot form by direct threading.[5]



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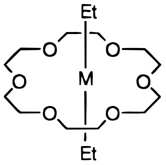
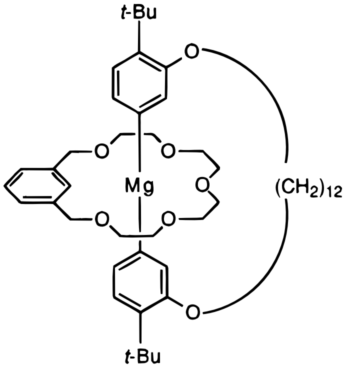


2a M = Mg
2b M = Zn



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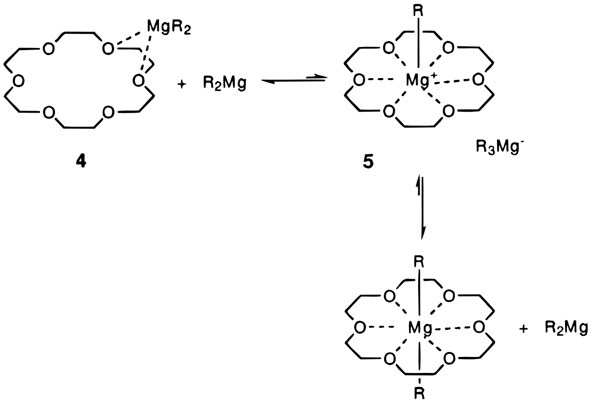
A likely process[1,3] for rotaxane formation and dethreading is outlined in eq 1. A species, such as **4**, having routine “peripheral” bonding between the Mg of R_2Mg and a few oxygens of the crown ether transfers R to a R_2Mg molecule. Loss of one R permits the Mg to penetrate the cavity of the crown ether and bond more extensively to its oxygens, as shown in **5**. Readdition of R from R_3Mg^- at the other face of the crown ether then forms the rotaxane (**6**). Other work has shown that reacting R_2Mg with some coordinating agents forms the R_3Mg^- (or $R_5Mg_2^-$, etc.) ions (eq 2) required by this suggestion.[6,7] With particularly effective coordinating



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[1] Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1988**, *110*, 4845.

[2] Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844.

[3] For a review of interactions of organomagnesium and organozinc compounds with macrocyclic compounds, see: Richey, H. G., Jr. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 1 (G. W. Gokel, Ed.), Chapter 21.

[4] Gruter, G.-J. M.; de Kanter, F. J. J.; Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1993**, *115*, 12179.

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$$2R_2Mg + \text{coord} \rightarrow RMg(\text{coord})^+ + R_3Mg^- \qquad (2)$$

agents, ion formation can be quantitative. In fact, extensive formation of such ions and rapid exchanges often make it difficult to observe NMR spectra of rotaxanes in solutions of R_2Mg compounds and crown ethers.[2,7] R_2Zn compounds are less prone than R_2Mg compounds to undergo the analogous disproportionation to $RZn(\text{coord})^+$ and organozincate anions. Disproportionation occurs significantly in favorable cases,[8,9] however, and in some cases where it is not observed spectroscopically may occur sufficiently to be significant in the process in eq 1.

The objective of this study was to investigate the mechanism of threading and dethreading of such rotaxanes. For several reasons, we decided to study organozinc rather than organomagnesium systems. (1) The complication of the presence of significant amounts of ions can be avoided since formation of $RZn(\text{coord})^+$ and R_3Zn^- is less favorable than that of the corresponding magnesium ions. (2) Achievement of equilibria of R_2Zn compounds and crown ethers with rotaxanes is slower than of the corresponding equilibria involving R_2Mg compounds, which generally are established before there is time to obtain routine NMR spectra. (3) R_2Zn compounds are generally easier than R_2Mg compounds to obtain in essentially pure form.

Results

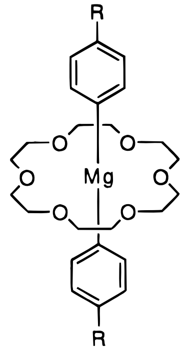
We choose to study 18-crown-6 and Tol_2Zn (Tol is *p*-methylphenyl) or Ph_2Zn. Solid Ph_2Zn(18-crown-6) rotaxane (**7a**) had been characterized by a crystal structure determination,[9]and ^1H NMR observations had shown that benzene-d_6 solutions of 18-crown-6 and Tol_2Zn or Ph_2Zn form significant (and similar) amounts of rotaxanes. Benzene was chosen as the solvent: organozinc compounds are stable in this solvent and benzene-d_6 is relatively inexpensive.

NMR Studies of Equilibria in Tol_2Zn−18-Crown-6 Solutions. ^1H NMR spectra of benzene-d_6 solutions[10] prepared from Tol_2Zn and 18-crown-6 exhibit two crown ether absorptions and two sets of Tol absorptions. The intensities of one set of Tol absorptions and one crown ether absorption indicate a 2:1 ratio of the Tol and crown ether units giving rise to them. The positions of these absorptions are essentially invariant as the reactant composition is altered. The Tol to crown ether ratio of 2, the failure of these groups to exchange rapidly with others in the solution, and other evidence[9] indicate a rotaxane structure. The absorptions attributed to the rotaxane increase with time, but this change ceases as equilibrium is reached (as detailed below, half-times for achieving equilibrium vary from less than a day to many months).

Table 1. ^{13}C NMR Absorptions[a] of *p*-Tolyl Groups in Benzene-d_6 Solutions of $(Tol)_2Zn$ and Coordinating Agents

coordinating agent	CZn	*o*-C	*m*-C	*p*-C	CH_3
	144.67	128.82	137.90	137.86	21.62
1.42 DME	149.79	139.25	129.28	135.66	21.71
1.46 18C6	151.91	139.82	129.27	135.30	21.80

[a] Absorptions in ppm (δ) relative to internal benzene (C_6D_6) taken as δ 128.0.



7a R = H
7b R = CH_3

The positions of the other set of Tol absorptions and the other crown ether absorption differ from those of Tol_2Zn and the crown ether alone and vary with the solution composition. The zinc of an organozinc compound is generally bonded to ether oxygens when these are available; formation and cleavage of Zn−O bonds is ordinarily rapid, however, so NMR spectra routinely show averaged absorptions for coordinated and free ether molecules and for the organic groups of coordinated and free R_2Zn.[11] It is likely, therefore, that oxygens of the crown ether coordinate in a peripheral fashion to the Zn of Tol_2Zn, as shown in **4** for coordination to Mg. In fact, the Tol ^{13}C NMR absorptions (Table 1) of a solution prepared from 18-crown-6 and Tol_2Zn, although significantly different from those of a solution of Tol_2Zn alone, are strikingly similar (except for the CZn absorption) to those of a solution prepared from dimethoxyethane and Tol_2Zn. This similarity suggests that coordination of Zn to two O atoms predominates in both solutions.

In solutions prepared from Tol_2Zn and 18-crown-6, the ^1H NMR absorption most shifted from that of the parent compound is that of the *ortho*-H of *p*-tolyl. A plot (Figure 1) of the position of that absorption as the 18-crown-6 to Tol_2Zn ratio is altered indicates extensive formation of a 1:1 complex. Rotaxane is also forming

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(5) Before the work with R_2Mg and R_2Zn rotaxanes, some rotaxanes had been prepared with $(CF_3)_2Hg$ and crown ethers; the crown ethers were much larger, however, and the pattern of results suggested that formation was by direct passage of intact organomercury compound into a crown ether cavity. Rebek, J., Jr.; Marshall, L. *J. Am. Chem. Soc.* **1983**, *105*, 6668. Onan, K.; Rebek, J., Jr.; Costello, T.; Marshall, L. *J. Am. Chem. Soc.* **1983**, *105*, 6759. Rebek, J., Jr.; Costello, T.; Marshall, L.; Wattley, R.; Gadwood, R. C.; Onan, K. *J. Am. Chem. Soc.* **1985**, *107*, 7481. Rebek, J., Jr.; Luis, S. V.; Marshall, L. R. *J. Am. Chem. Soc.* **1986**, *108*, 5011. Luis, S. V.; Burguete, M. I.; Salvador, R. V. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1991**, *10*, 341.

(6) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem Soc.* **1987**, *109*, 2510.

(7) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.

(8) Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6680. Also see: Tang, H.; Richey, H. G., Jr. *Organometallics* **1996**, *15*, 4891.

(9) Fabicon, R. M. Ph.D. Dissertation, The Pennsylvania State University, 1991.

(10) Most studies used initial Tol_2Zn concentrations of 0.02−0.06 M and 18-crown-6 concentrations of 0.01−0.15 M.

(11) For information on coordination of organozinc compounds to ether oxygens, see: Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 16. O'Brien, P. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 3, Chapter 4.

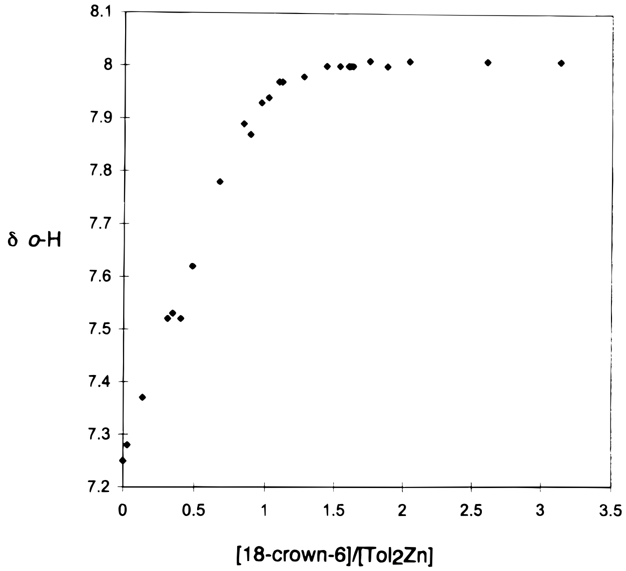

Figure 1. Plot of the chemical shift of the ^{1}H NMR absorption of the *o*-hydrogen of the *p*-tolyl groups as a function of the ratio of 18-crown-6 and Tol_2Zn concentrations (excluding the amounts of these species incorporated into the rotaxane at the time an NMR observation was made). The concentration of Tol_2Zn is ca. 0.06 M in all solutions.

in these solutions, of course, and the reactant ratios in Figure 1 are for 18-crown-6 and Tol_2Zn not incorporated in rotaxane. The slight curvature in the 1:1 composition region of the graph suggests that formation of a 1:1 complex is not quite complete. This curvature is within the experimental uncertainty but may not be completely an artifact. A solution having an 18-crown-6 to Tol_2Zn ratio of ca. 1.1 was diluted to different extents. After a 12-fold dilution, the *ortho*-H absorption had moved downfield ca. 0.04 ppm (the total range of this absorption was 0.76 ppm). This experiment suggests some dissociation of a 1:1 species but not more than a few percent at a concentration level much lower than that used in other experiments. We conclude that formation of a 1:1 peripheral complex (eq 3) is substantially complete, except perhaps at exceedingly low concentrations.

$$Tol_2Zn + crown \rightleftarrows Tol_2Zn(crown)_{peripheral} \qquad (3)$$

Since a 1:1 peripheral complex and a rotaxane have the same composition, the equilibrium between them (eq 4) should be independent of other reagents. The

$$Tol_2Zn(crown)_{peripheral} \rightleftharpoons Tol_2Zn(crown)_{rotaxane} \qquad (4)$$

amount of rotaxane is evident from its unique ^{1}H NMR absorptions. By contrast, the Tol groups and the crown ether of the peripheral complex equilibrate rapidly with excess Tol_2Zn and crown ether and, therefore, only contribute to the intensity of time-averaged NMR absorptions.[12] We now know, however, that the concentration of the peripheral complex is essentially the same as that of non-rotaxane Tol_2Zn or non-rotaxane crown ether, whichever is less. Assigning the concentration of the peripheral complex on that basis, values for K = [rotaxane]/[peripheral] of 0.71 ± 0.09 are obtained from the areas of appropriate absorptions of solutions having very different compositions (>200-fold variation in 18-crown-6). The constancy of K obtained in this manner is additional evidence that most of the limiting reagent not incorporated into the rotaxane is incorporated into a 1:1 peripheral complex. In summary, a rapidly established equilibrium of Tol_2Zn and crown ether with a peripheral complex is followed by a more slowly established and less complete equilibrium with the rotaxane.

It must be noted that K seems to differ slightly depending on which reagent is initially in excess. K's are 0.61 ± 0.03 for 9 solutions in which $[Tol_2Zn]_0 > [crown]_0$ and 0.77 ± 0.03 for 14 solutions in which $[crown]_0 > [Tol_2Zn]_0$. This small difference may be an artifact of the integration accuracy (particularly since $[18\text{-crown-}6]_0$ spanned such a wide range). Alternatively, it may indicate that eqs 3 and 4 do not completely describe the solutions. For example, small amounts of other (e.g., 2:1) peripheral complexes may be present.[12] Any deviation due to the presence of other species is small, however.

Qualitative Observations of Rates of Threading and Dethreading. Rotaxane formation ceases within a few days, at most, in solutions in which $[Tol_2Zn]_0 > [18\text{-crown-}6]_0$ but continues for many months when $[18\text{-crown-}6]_0 > [Tol_2Zn]_0$. Achievement of equilibrium is clearly slower when the crown ether is in excess,[13] a circumstance in which we now know the concentration of free Tol_2Zn (not incorporated into a peripheral complex) to be very low.

Crystalline $Ph_2Zn(18\text{-crown-}6)_{rot}$ was dissolved in benzene-d_6 to form ~ 0.02 M solutions whose ^{1}H NMR spectra show absorptions for rotaxane and a trace amount of excess crown ether only. Absorptions of the peripheral complex, which would result from dethreading, do not appear even after 2 years. Addition of ~0.1 equiv of Tol_2Zn or Et_2Zn, however, leads to dethreading; the half-times for appproaching equilibrium are only a few hours.

The effect of added TMEDA (tetramethylethylenediamine) also suggests that rotaxane formation and dethreading requires free Tol_2Zn. Even after 4 years, no rotaxane has formed in a Tol_2Zn solution containing slightly more than 1 equiv each of 18-crown-6 and TMEDA. The positions of the ^{1}H NMR absorptions are in accord with the expectation that Tol_2Zn is bonded to TMEDA. When TMEDA is added to aliquots of a Tol_2Zn−18-crown-6 solution in which equilibrium with rotaxane has been established, ^{1}H NMR spectra of the resulting solutions initially having TMEDA to Tol_2Zn ratios of 2.7, 1.7, and 0.8 show no decrease in rotaxane over 2.5 years. At equilibrium in the absence of TMEDA, similar amounts of rotaxane and peripheral complex are present so rotaxane formation and deth-

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[12] Lower temperatures might slow exchange processes sufficiently to permit seeing discrete absorptions of individual species in NMR spectra. Some efforts (using toluene-d_8 as the solvent and Tol_2Zn or (*p-tert*-butylphenyl)$_2$Zn at concentrations down to 0.01 M) led to precipitation at temperatures at which no changes (other than limited and similar broadening of *all* absorptions) were observed in ^{1}H NMR spectra.

[13] Erratic results in earlier efforts [ref 9 and BergStresser, G. L. M.S. Dissertation, The Pennsylvania State University, 1986] to study equilibria of diorganozinc compounds and 18-crown-6 with rotaxanes may be the consequence of not being aware of the large effect of the reactant ratio on the rate of approach to equilibrium.

reading are occurring at similar rates. The effect of TMEDA in preventing rotaxane formation could be due to Tol_2Zn(TMEDA) + 18-crown-6 being more stable than rotaxane Tol_2Zn(18-crown-6) + TMEDA. The stability of Tol_2Zn(TMEDA), a product of dethreading, should not inhibit dethreading, however, *unless removal of Tol_2Zn by this complex blocks the dethreading process.*

Kinetic Studies of Threading and Dethreading. The relation of the rate of threading or dethreading to initial concentrations could further establish the role of free Tol_2Zn. Efforts were made to study the kinetics of threading by following the appearance of rotaxane absorptions in ^{1}H NMR spectra of solutions prepared with various amounts of crown ether and Tol_2Zn. So that rates would not be inconveniently fast for the mode of observation, it was necessary to study solutions in which $[crown]_0$ exceeded $[Tol_2Zn]_0$, circumstances under which almost all Tol_2Zn is initially incorporated into a peripheral complex. The very slow rates that were observed confirm that the Tol_2Zn concentration is very low, another indication that the equilibrium constant for formation of the peripheral complex is large. The relation between rate and initial concentrations seemed erratic, however.[14] Perhaps in these experiments, in which the concentration of free Tol_2Zn is very low, even traces of impurities can greatly alter the free Tol_2Zn concentration or some very slow step can compete with the transfer of R from a peripheral complex to a Tol_2Zn molecule.

Studying rotaxane dethreading is preferable. Since the equilibrium in eq 3 lies significantly to the right, the equal amounts of Tol_2Zn and 18-crown-6 that result from dethreading will be present mainly in the form of a peripheral complex—consequently, the concentration of free Tol_2Zn will not change significantly as dethreading proceeds. Dethreading was studied by using ^{1}H NMR spectra to monitor concentrations of the peripheral complex at different times after Tol_2Zn was added to rotaxane solutions. Only data obtained before 10% of the approach to equilibrium was achieved were used so that neither reactant depletion nor the reverse reaction would be significant. Individual kinetic experiments gave good linear plots of d[peripheral]/dt versus time (R^2 generally ≥ 0.99). Defining the small concentrations of free Tol_2Zn was less precise, however, because of the small scale of the preparations necessitated by the use of a deuterated solvent and the need to correct for the Tol_2Zn removed by peripheral complex formation with the small amount of excess crown ether present when the rotaxane is dissolved. The rapidity of the reactions (most observations had to be obtained in 10−20 min), the low concentration of rotaxane dictated by its limited solubility, and the temperature range (±1 °C) also limited accuracy.

The kinetic order in Tol_2Zn was determined by plots of ln(rate of appearance of peripheral complex) versus ln$[Tol_2Zn]$ in experiments in which $[rotaxane]_0$ was held constant. The most reliable data give an order of 0.82 ($R^2 = 0.95$). The kinetic order in rotaxane was determined by similar plots of appearance of peripheral complex versus ln[rotaxane] in experiments in which $[Tol_2Zn]_0$ was held constant; the most reliable data give an order of 0.79 ($R^2 = 0.98$). Other data give poorer R^2 values but also are in accord with kinetic orders in the vicinity of one for each reactant. We conclude that the dethreading rate is approximately proportional to the first power of the concentrations of Tol_2Zn and rotaxane. Some other mode of studying rates would have to be used, however, to define the kinetic orders more precisely.

Conclusion

Tol_2Zn and 18-crown-6 rapidly form a 1:1 peripheral complex and more slowly form a rotaxane. Some free Tol_2Zn (not incorporated into a peripheral complex with the crown ether) must be present for rotaxane formation and dethreading to occur at significant rates.

Experimental Section

^{1}H NMR spectra were taken at 200 MHz except where otherwise noted. Absorptions are reported in parts per million (δ) relative to internal benzene (C_6D_5H), taken as δ 7.15 ppm, and using the following notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; b, broad. ^{13}C NMR spectra were taken at 90 MHz; absorptions are reported in parts per million (δ) relative to internal benzene (C_6D_6) taken as δ 128.0 ppm. When two species are present in a solution, their ratio indicated by areas of NMR absorptions is given and the area of an individual absorption is stated relative to others in the same species. The NMR tubes that were used generally had an extension of routine glass tubing to facilitate sealing with a flame. Samples for NMR spectroscopy were prepared in a glovebox either in the NMR tube or in a tapered vial containing a magnetic stirring bar, followed by transfer into the NMR tube. The NMR tube was sealed temporarily with a septum, removed from the glovebox, and, except where noted, frozen in liquid nitrogen and sealed at the extension with a flame.

Procedures involving organometallic compounds were performed under a nitrogen atmosphere using Schlenk techniques, a glovebox, and a vacuum line. Nitrogen was purified by passing through columns of manganese oxide oxygen scavenger and molecular sieves. Glassware was dried in an oven at 200 °C.

Toluene, DME (1,2-dimethoxyethane), cyclohexane, and TMEDA (tetramethylethylenediamine) were distilled from CaH_2 and stored over molecular sieves. Diethyl ether was distilled from sodium benzophenone ketyl immediately prior to use. Benzene-d_6 (Cambridge Isotopes Laboratories) was stored over molecular sieves. Et_2Zn, Mg (99.95%), and 18-crown-6 were used as supplied (Aldrich). The sample of rotaxane Ph_2Zn(18-crown-6) (**1a**) was provided by Ronaldo Fabicon.[9]

Synthesis of Di(*p*-tolyl)zinc. This compound was synthesized from a reaction of the Grignard reagent prepared from *p*-bromotoluene and $ZnCl_2$.[15] The crude solid was recrystallized twice from toluene to yield colorless crystals from which residual solvent was removed at reduced pressure: mp 172−174 °C (lit.[16] mp 169−170 °C). ^{1}H NMR: δ 2.20 (s, 3, CH_3), 7.09 (d, $J = 6.3$ Hz, 2, *m*-H), 7.23 (d, $J = 6.3$ Hz, 2, *o*-H). ^{13}C

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[14] The equilibrium expression for eq 3 is $K' = [\text{peripheral}]/[Tol_2Zn][\text{crown}]$, where $[Tol_2Zn]$ and [crown] are the concentrations of the free species (not incorporated into the peripheral complex). Since K' is large, in a solution prepared with an excess of 18-crown-6, the initial concentration of [peripheral] $\cong [Tol_2Zn]_0$ and of [crown] $\cong [\text{crown}]_0 - [Tol_2Zn]_0$. $[Tol_2Zn]$ therefore initially should $\cong [Tol_2Zn]_0/K'([\text{crown}]_0 - [Tol_2Zn]_0)$. If rate $= k[\text{peripheral}][Tol_2Zn]$, then the initial rate is expected to be $\cong k[Tol_2Zn]_0^2/K'([\text{crown}]_0 - [Tol_2Zn]_0)$.

[15] For example: de Graaf, P. W. J.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1977**, *127*, 391.

[16] Sheverdina, N. I.; Paleeva, I. E.; Zaitseva, N. A.; Kocheskov, K. A. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 623; *Chem. Abstr.* **1964**, *60*, 14531.

NMR: δ 21.62 (CH_3), 128.82 (*o*-C), 137.86 (*p*-C), 137.90 (*m*-C), 144.67 (CZn).

Synthesis of Rotaxane Tol_2Zn(18-crown-6) (7b). A mixture of Tol_2Zn (0.965 g, 3.9 mmol), 18-crown-6 (1.031 g, 3.9 mmol), and toluene (3 mL) was sealed in a glass tube. The tube was heated until most of the solid dissolved and then was centrifuged to collect the small amount of remaining solid in one end of the tube, which was then inverted to separate the solution from the solid. The tube was cooled over 1−2 h to ambient temperature and then at −20 °C until crystal formation from the solution seemed to be complete. The tube was opened, and the supernatant liquid was decanted; the yield of crystals was >90%. The crystals were recrystallized again in the same manner to give large, clear crystals: mp 108−112 °C. ^{1}H NMR: δ 2.44 (s, 3, CH_3), 2.19 (s, 12, 18-crown-6), 7.40 (d, $J = 7.9$ Hz, 2, *m*-H), 8.20 (d, $J = 7.9$ Hz, 2, *o*-H). ^{13}C NMR: δ 21.85 (CH_3), 69.45 (18-crown-6), 126.92 (*m*-C), 132.53 (*p*-C), 140.88 (*o*-H), 157.51 (CZn). ^{1}H NMR spectra also showed an absorption at δ 3.52 due to 1−3% of free 18-crown-6.

Comparison of Coordination of Tol_2Zn to DME and 18-Crown-6. Samples (total volume 0.5 mL) were prepared by adding the solvent to Tol_2Zn (5 mg, 0.02 mmol), followed by a weighed amount of a solution (5 wt %) of the coordinating agent. The reactant ratios below, determined by integration of ^{1}H NMR absorptions, are similar to those calculated on the basis of the amounts used in the preparation. For comparison, NMR spectra of benzene-d_6 solutions of the coordinating agents also are given.

DME. ^{1}H NMR: δ 3.11 (s, 3, CH_3), 3.31 (s, 2, CH_2). ^{13}C NMR: δ 58.6 (CH_3), 72.2 (CH_2).

18-Crown-6. ^{1}H NMR: δ 3.52 (s). ^{13}C NMR: δ 71.12.

Tol_2Zn and DME. A sample was determined by integration (CH_2 of DME, CH_3 of Tol) to have a DME:Tol_2Zn ratio of 1.46. ^{1}H NMR: (Tol_2Zn) δ 2.33 (s, 3, CH_3), 7.30 (d, $J = 7.1$ Hz, 2, *m*-H), 7.77 (d, $J = 7.4$ Hz, 2, *o*-H); (DME) δ 2.91 (s, 2, CH_2), 3.04 (s, 3, CH_3). ^{13}C NMR: (Tol_2Zn) absorptions listed in Table 1; (DME) δ 58.62 (CH_3), 71.30 (CH_2).

Tol_2Zn and 18-Crown-6. A sample was determined by integration (18-crown-6 absorption, CH_3 of Tol) to have an 18-crown-6:Tol_2Zn ratio of 1.42. Spectra were taken soon after sealing to minimize rotaxane formation. ^{1}H NMR: (Tol_2Zn) δ 2.37 (s, 3, CH_3), 7.37 (d, $J = 7.5$ Hz, 2, *m*-H), 7.98 (d, $J = 7.5$ Hz, 2, *o*-H); (18-crown-6) δ 3.42 (s). ^{13}C NMR: (Tol_2Zn) absorptions listed in Table 1; (18-crown-6) δ 71.01.

Equilibria of Tol_2Zn and 18-Crown-6 with Peripheral and Rotaxane Tol_2Zn(18-crown-6). Samples (total volume 0.5 mL) were prepared by adding the solvent (a 0.01 M solution of cyclohexane in benzene-d_6) to Tol_2Zn (7.5 mg, 0.03 mmol), followed by a weighed amount of a benzene-d_6 solution of 18-crown-6 (5 wt %). To minimize the extent of rotaxane formation, ^{1}H NMR spectra (360 MHz) were taken soon (generally 15−30 min, not counting time at liquid nitrogen temperatures) after the reagents were mixed. Even then, the initial spectra of samples having [18-crown-6]$_0$:[Tol_2Zn]$_0$ ratios <1 indicated formation of significant amounts of rotaxane (e.g., ca. 5% for a solution in which the reactant ratio was 0.96 and up to 25% for solutions in which the ratio was less than 0.4). The temperature of the samples at the time of observation was 23 ± 1 °C. In Figure 1, the position of the *o*-hydrogen absorption is plotted relative to the 18-crown-6:Tol_2Zn ratio determined by integration of the δ ~3.4 absorption that represents all crown ether (except the portion already incorporated into rotaxane) and the δ ~2.3 absorption that represents the methyl groups of all Tol_2Zn (except the portion already incorporated into rotaxane).

To permit determining the amount of rotaxane present at equilibrium, solutions were allowed to stand for many days or even months at 23 ± 1 °C. The rotaxane concentration was determined by comparing the ^{1}H NMR absorption of 18-crown-6 incorporated into the rotaxane to the cyclohexane absorption. The concentration of Tol_2Zn not incorporated into rotaxane was determined similarly using its methyl absorption, and the concentration of 18-crown-6 not incorporated into rotaxane was determined using its absorption.

Effect of TMEDA on Rotaxane Formation and Dethreading. A solution of 18-crown-6 (19 mg, 0.07 mmol) in benzene-d_6 (0.2 mL) was added to a solution of Tol_2Zn (15 mg, 0.06 mmol) and TMEDA (10% weight solution in benzene-d_6, 84 mg, 0.07 mmol) in benzene-d_6 (0.3 mL). ^{1}H NMR spectra were observed periodically, but no significant change was noted. After nearly 4 years, integration (δ 3.51, 2.36) gave a ratio of total 18-crown-6 to total Tol_2Zn of 1.17 and (δ 1.91 + 1.97, 2.15) of TMEDA to total Tol_2Zn of 1.18. ^{1}H NMR: (Tol_2Zn) δ 2.15 (s, 3, CH_3), 7.29 (d, $J = 7.7$ Hz, 2, *m*-H), 7.82 (d, $J = 7.7$ Hz, 2, *o*-H); (18-crown-6) δ 3.51 (s); (TMEDA) δ 1.91 (bs, 1), 1.97 (bs, 3).

A solution of Tol_2Zn (67.4 mg, 0.27 mmol) and 18-crown-6 (72.1 mg, 0.27 mmol) in benzene-d_6 (2 mL) was sealed in a tube and kept for 5 days at ambient temperature to permit the equilibrium amount of rotaxane to form. The tube was centrifuged to remove a trace of solid, and then the solution was divided into portions. Some of a solution of TMEDA (10 wt %) in benzene-d_6 was added to each. The [18-crown-6]$_0$:[Tol_2Zn]$_0$ ratios were determined by comparing the sum of the areas of the δ ~3.2 (crown ether in rotaxane) and ~3.4 (crown ether not in rotaxane) absorptions with the sum of the areas of the δ ~2.45 (methyl of tolyl in rotaxane) and ~2.35 (methyl of tolyl not in rotaxane) absorptions. The ratio of [TMEDA]$_0$ to [Tol_2Zn]$_0$ was determined by comparing the sum of the areas of the CH_2 and CH_3 absorptions of TMEDA with the sum of the δ ~2.35 and ~2.45 absorptions. The ratios by integration were similar to those calculated on the basis of the amounts used in the preparations. [Tol_2Zn]$_0$ and [18-crown-6]$_0$ were in the range 0.08−0.12 M (depending on the amount of TMEDA solution added). [18-crown-6]$_0$:[Tol_2Zn]$_0$ and [TMEDA]:[Tol_2Zn]$_0$: solution 1 (1.01 and 2.72), solution 2 (1.11 and 1.73), solution 3 (1.21 and 0.79). The ratio of rotaxane to 18-crown-6 not in rotaxane, determined by integration of the δ ~3.20 and ~3.40 absorptions, was followed for 937 days. Over that period, the ratios for solutions 1−3 were 0.35 ± 0.02

Qualitative Observations of Ph_2Zn(18-crown-6) Rotaxane Dethreading. ^{1}H NMR spectra of benzene-d_6 solutions (1 wt %) soon after preparation showed absorptions of the rotaxane and of a small amount (0.01−0.03 equiv) of free 18-crown-6. A spectrum of one solution taken after 722 days was unchanged. Small portions of solutions of Tol_2Zn or Et_2Zn were added to similar solutions. The amount of added reagent was determined by comparing areas of ^{1}H NMR absorptions (methyl of tolyl, CH_2 of ethyl) and crown ether absorptions. The $t_{1/2}$ for reaching equilibrium between rotaxane and non-rotaxane species was ~8 h with 0.09 equiv of added Tol_2Zn and ~7 h with 0.13 equiv of Et_2Zn.

Rates of Tol_2Zn(18-crown-6) Rotaxane Dethreading. Appropriate amounts of the solvent (a solution of cyclohexane (0.01 M) in benzene-d_6) and a solution (0.02 M) of Tol_2Zn(18-crown-6) rotaxane in the solvent were combined in an NMR tube, and the tube was capped with a fresh septum. A ^{1}H NMR spectrum was taken, and then some of a Tol_2Zn solution (0.05 M) in the solvent was injected into the NMR tube, which then was shaken to mix the contents. Because dethreading is rapid, ^{1}H NMR spectra were recorded as quickly as possible, at ~2.5 min intervals. The concentration of each species was determined by comparison of the indicated peak (rotaxane, δ ~3.2; 18-crown-6 not in rotaxane, δ ~3.4; Tol_2Zn not in rotaxane, δ ~2.3) with that of cyclohexane. The amount of dethreading was taken to be the concentration of non-rotaxane 18-crown-6 minus its small concentration (1−3% of the value of [rotaxane]$_0$) observed before adding Tol_2Zn. Data for formation of no more than 10% of the equilibrium amount of dethreaded products were used in determining rates. The temperature was 23 ± 1 °C. In experiments to determine kinetic order, the experimentally determined concentrations of the component intended to be constant varied slightly. To correct for this variation, small adjustments were made assuming the reaction to be first order in the "constant" component: the nearly "constant" concentrations were averaged and each individual rate constant adjusted by the small percentage that the corresponding concentration was above or below that average. Representative values of d[peripheral]/dt (mol/s) [(R^2), [rotaxane] (M), [$Tol_2Zn]_0$ (M)]: 7.56 × 10^{-8} [0.994. 0.0168, 0.00069]; 2.06 × 10^{-7} [0.998, 0.0176, 0.0038]; 7.48 × 10^{-7} [0.994, 0.0139, 0.0126]; 4.01 × 10^{-7} [0.990, 0.0085, 0.0068]; 1.82 × 10^{-7} [0.993, 0.0039, 0.0.0065], 1.39 × 10^{-7} [0.996, 0.0022, 0.0068].

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