larly interesting with regard to its use with small cations like Li^+, Ag^+, or Cu^+ to synthesize new ionic conductors. Another strategy for synthesizing polyhedric chalcogenoborates is conceivably available by starting from metal borides with preformed B_{12}, B_6, or other clusters rather than from elemental boron.

Experimental Section

All experiments were carried out in a dry nitrogen atmosphere in a glove box.

$Cs_8[B_{12}(BSe_3)_6]$ was prepared by reacting stoichiometric amounts of dicesium monoselenide (from elemental Cs and HgSe), boron (powdered, amorphous, purity 95%, Alfa-Ventron), and selenium (powdered, purity 99%, Merck) in a molar ratio of 2:9:7. In a quartz glass ampoule coated with glassy carbon the reaction mixture was heated up to 700 °C for 2 h and subsequently annealed (10 h at 600 °C, 24 h at 400 °C, 120 h at 200 °C). Powder diffraction of the resulting pale gray crystalline product showed only traces of impurities. A colorless crystal was chosen for single-crystal X-ray structure determination.

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The Self-Assembly of a Switchable [2]Rotaxane**

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Catenanes and rotaxanes are molecular compounds[1] that hold considerable promise for use in molecular devices as a consequence of the relative movements of their ring and dumbbell-shaped components. Initially researchers learned how to make simple rotaxanes,[2] followed by degenerate rotaxanes with molecular shuttling characteristics,[3] and eventually nondegenerate rotaxanes whose dynamic properties could be addressed selectively with external stimuli of a chemical, electrochemical, or photochemical nature to induce them to behave as molecular switches.[4] However, to our knowledge, no constitutionally asymmetric, two-site [2]rotaxane that exhibits 100% selectivity for one of the binding sites between ring and dumbbell-shaped components has yet been reported. Here, we describe the self-assembly of a [2]rotaxane that possesses two very dissimilar cationic binding sites within its dumbbell-shaped component—specifically, a secondary dialkylammonium center and a bipyridinium unit—each of which shows different affinities[5] toward dibenzo[24]crown-8 (DB24C8), the ring component of the [2]rotaxane. We also report the pH-controlled shuttling of the DB24C8 ring between the two very different recognition sites, or "stations", in this simple molecular shuttle.

The [2]rotaxane **2**-H·3PF_6 was self-assembled (Scheme 1) by using a template-directed threading approach.[6] A pseudorotaxane[7, 8] [DB24C8·**1**-H][PF_6]$_2$ was formed initially in solution between the DB24C8 and **1**-H·2PF_6,[9] which already contains the ammonium center and a stopper (3,5-di-*tert*-butylbenzyl) to prevent unthreading of the ring. Subsequently a single stoppering reaction with 3,5-di-*tert*-butylbenzyl bromide led to the formation of the bipyridinium dicationic unit and the dumbbell-shaped component.[10]

The ^{1}H NMR spectrum of **2**-H·3PF_6 recorded in CD_3COCD_3 at 20 °C shows signals corresponding to the formation of a [2]rotaxane. The spectrum (Figure 1b) demonstrates that the DB24C8 ring binds selectively with the secondary dialkylammonium center, since the characteristic resonance at $\delta = 4.87–4.85$ for the four CH_2 protons adjacent to the NH_2^+ group is observed. These protons experience a downfield shift of about $\Delta\delta = 0.2$ upon association with DB24C8: compare the

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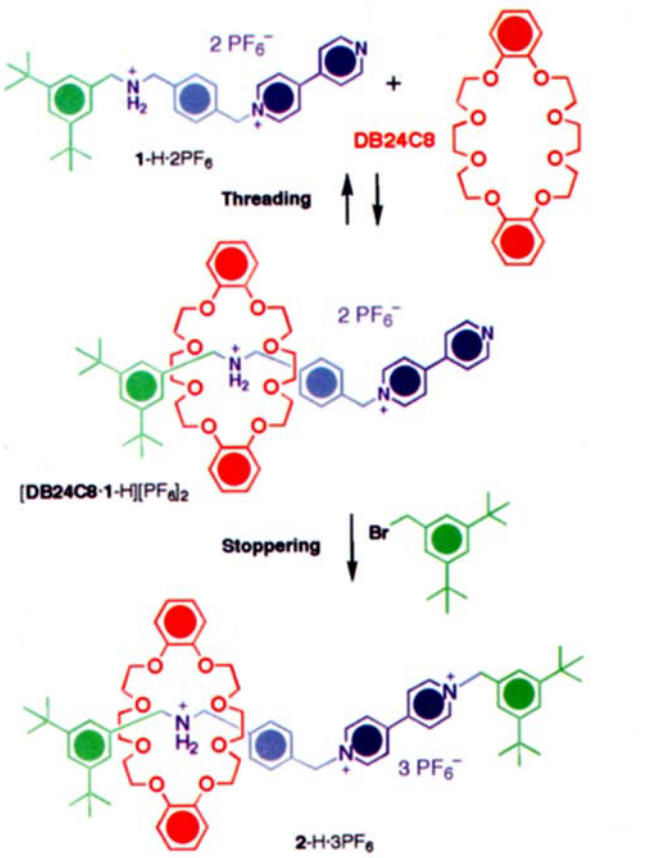


Scheme 1. The self-assembly approach to the [2]rotaxane **2**-H·3PF$_6$: threading followed by stoppering.

^{1}H NMR spectrum (Figure 1a) of the dumbbell-shaped compound **3**-H·3PF$_6$ with that of the [2]rotaxane **2**-H·3PF$_6$ (Figure 1b). This selective binding was confirmed by one-dimensional ^{1}H NMR NOE doubled-pulsed field-gradient spin-echo experiments[11]—GOESY (gradient enhanced nuclear Overhauser effect spectroscopy)—carried out at 400 MHz at room temperature. Selective irradiation of the protons (C) on the *para*-xylyl spacer closest to the NH_2^+ center showed that, in addition to the expected intramolecular NOEs, intercomponent NOEs with some of the OCH_2 protons in the DB24C8 were observed. Since the two faces of the crown ether are diastereotopic, NOEs are observed with protons on only one of its faces. The same effect was noted when the protons in *ortho* positions (A) in the stopper closest to the NH_2^+ center were irradiated selectively. Moreover, since association and dissociation between the NH_2^+ center and DB24C8 is expected to be slow on the ^{1}H NMR time scale,[8] we should observe another set of signals for a second translational isomer if the DB24C8 ring resides anywhere else along the dumbbell-shaped component other than on the NH_2^+ center. In order to establish that the [2]rotaxane **2**-H·3PF$_6$ exists as a single translational isomer, a solution of **2**-H·3PF$_6$ in CD_3COCD_3 was cooled down to −80 °C. Since no additional set of resonances could be detected, it may be concluded that the DB24C8 ring is bound to the NH_2^+ center with a selectivity of at least 98% in the temperature range between −80 °C and +31 °C.

One reason for the synthesis of interlocked molecules, such as the [2]rotaxane **2**-H·3PF$_6$ incorporating an NH_2^+ center and a bipyridinium unit, is to develop them as pH-sensitive or electrochemically driven molecular switches. Since we have established that the potentially mobile component of **2**-H^{3+}—that is the

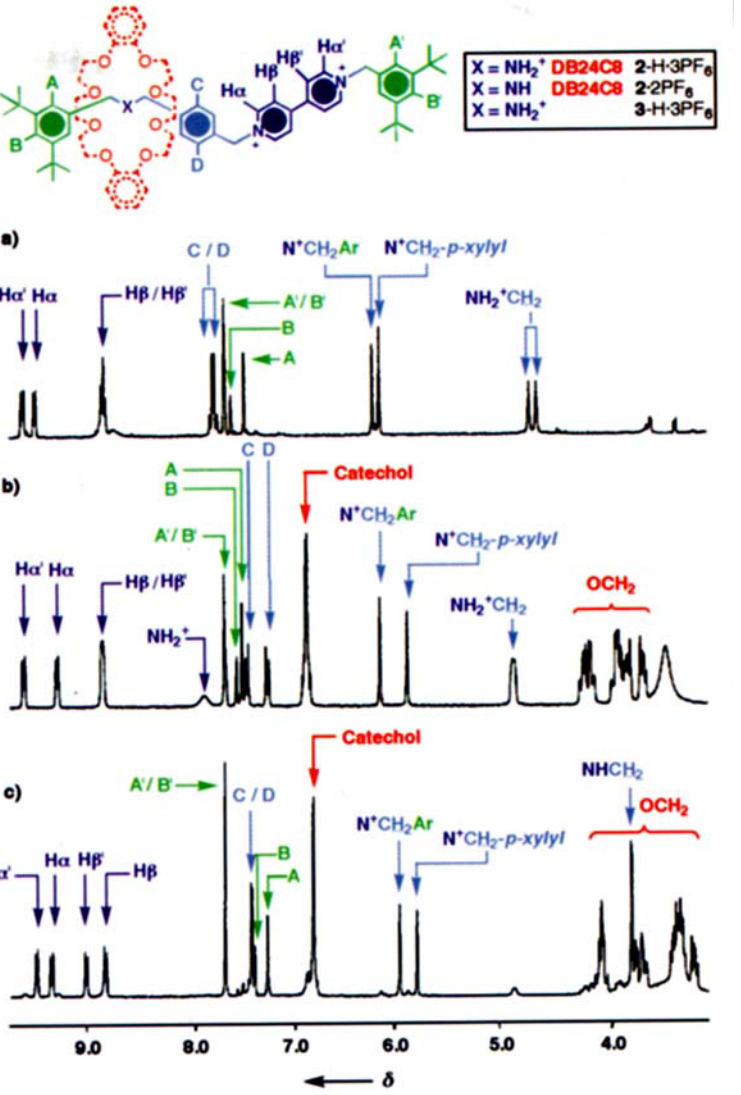
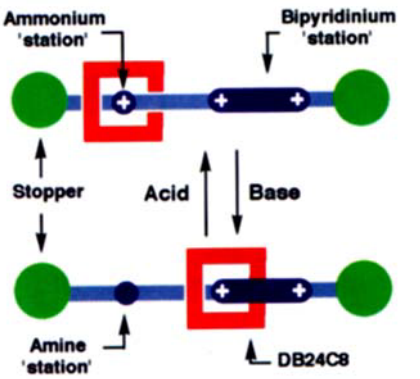


Figure 1. Partial ^{1}H NMR spectra (300 MHz, CD_3COCD_3, room temperature): a) the dumbbell-shaped compound **3**-H·3PF$_6$ (ca. 7 mM); b) the [2]rotaxane **2**-H·3PF$_6$ (ca. 4.7 mM); c) the deprotonated [2]rotaxane **2**·2PF$_6$, after addition of 1.5 μL (2.4 mol equiv) of *i*Pr$_2$NEt to the solution.

DB24C8 ring—resides initially on the NH_2^+ station, it should be possible (Scheme 2) to deprotonate the NH_2^+ center with base and "drive" the ring to the bipyridinium station. The choice of



Scheme 2. A cartoon of the switchable [2]rotaxane **2**-H·3PF$_6$ showing how the motion of the ring component (red) is driven by deprotonation or reprotonation of the ammonium/amine station in the dumbbell-shaped component (blue and green). The fact that the DB24C8 component interacts asymmetrically with the bipyridinium station is conveyed by the off-center location of the ring with respect to the station.

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the base for deprotonation of the NH_2^+ center was not straightforward, since the bipyridinium unit is very sensitive to nucleophilic bases. Addition of a slight excess of a number of bases (e.g. 2,6-lutidine, dibenzylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), quinuclidine, hexamethyldisilazane, diisopropylethylamine) to a CD_3COCD_3 solution containing equimolar amounts of DB24C8 and benzyl viologen and dibenzylammonium hexafluorophosphate allowed us to identify an appropriate base for triggering this molecular switching action of **2**-H^{3+}. The deprotonation can be followed by ^{1}H NMR spectroscopy by noting the disappearance of the multiplet assigned to the CH_2 protons adjacent to the NH_2^+ center. The stability of the bipyridinium dication was monitored by checking the signals for the α-CH and β-CH bipyridinium protons. In the presence of weak bases, such as 2,6-lutidine or dibenzylamine, although the benzyl viologen is stable, the NH_2^+ center is not deprotonated. Upon addition of a much stronger base, such as DBU, or a nucleophilic one such as quinuclidine, deprotonation does occur but the solution turns dark green, indicating the decomposition of the benzyl viologen. Eventually we found that diisopropylethylamine is the ideal base. The ^{1}H NMR spectrum (Figure 2b) shows that total deprotonation of the NH_2^+ center occurs, while the benzyl viologen is left intact—its resonances only being broadened in the presence of iPr_2NEt. Addition of trifluoroacetic acid (TFA) to this solution results in the reprotonation of the dibenzylamine (Figure 2c) and the recovery of the 1:1 complex between the dibenzylammonium cation and DB24C8. Despite the success of this association–dissociation experiment, no remarkable changes in the ^{1}H NMR spectrum that might indicate complex formation between the benzyl viologen and DB24C8 were observed. Moreover, the solution remained pale yellow all the time. Since the complex between dibenzylammonium hexafluorophosphate and DB24C8 is colorless, the pale yellow color of the 1:1:1 mixture may be a consequence of charge transfer interactions between the catechol rings of the DB24C8 and the viologen dication.[12] Clearly, once the NH_2^+ center is deprotonated, the affinity of the DB24C8 ring for the viologen is so low that most of the crown ether remains uncomplexed in solution.

This observation poses several questions: can the lack of binding be overcome in a rotaxane in which the DB24C8 ring cannot be expelled from the molecule once the NH_2^+ center is deprotonated? Would it be possible to oblige the DB24C8 ring to associate[12] with the bipyridinium unit in a cliplike manner? In order to test this hypothesis, an excess of iPr_2NEt was added to a solution of **2**-H·3PF_6 in CD_3COCD_3. Immediately, a change in the color of the solution from colorless to yellow was observed, indicative of charge transfer interactions between the catechol rings of the DB24C8 ring and the bipyridinium dication.[12] Moreover, the ^{1}H NMR spectrum (Figure 1c) of **2**·2PF_6 shows dramatic changes in chemical shifts relative to those for **2**-H·3PF_6 (Figure 1b)—especially in the resonances for the bipyridinium and *para*-xylyl protons—indicating that the DB24C8 ring interacts in an asymmetric fashion with the bipyridinium station. ^{1}H NMR spectra of the deprotonated [2]rotaxane **2**·2PF_6 from −80 °C to +31 °C in CD_3COCD_3 at 400 MHz revealed that the DB24C8 ring resides *exclusively* on the bipyridinium station. Although the spectrum broadens below −40 °C, no additional set of resonances for another translational isomer are observed. On subsequent addition of TFA to the CD_3COCD_3 solution of the [2]rotaxane **2**·2PF_6, we demonstrated that the system is reversible, since the recorded ^{1}H NMR spectrum once again shows signals for the translational isomer in which the macrocycle resides on the NH_2^+ station.

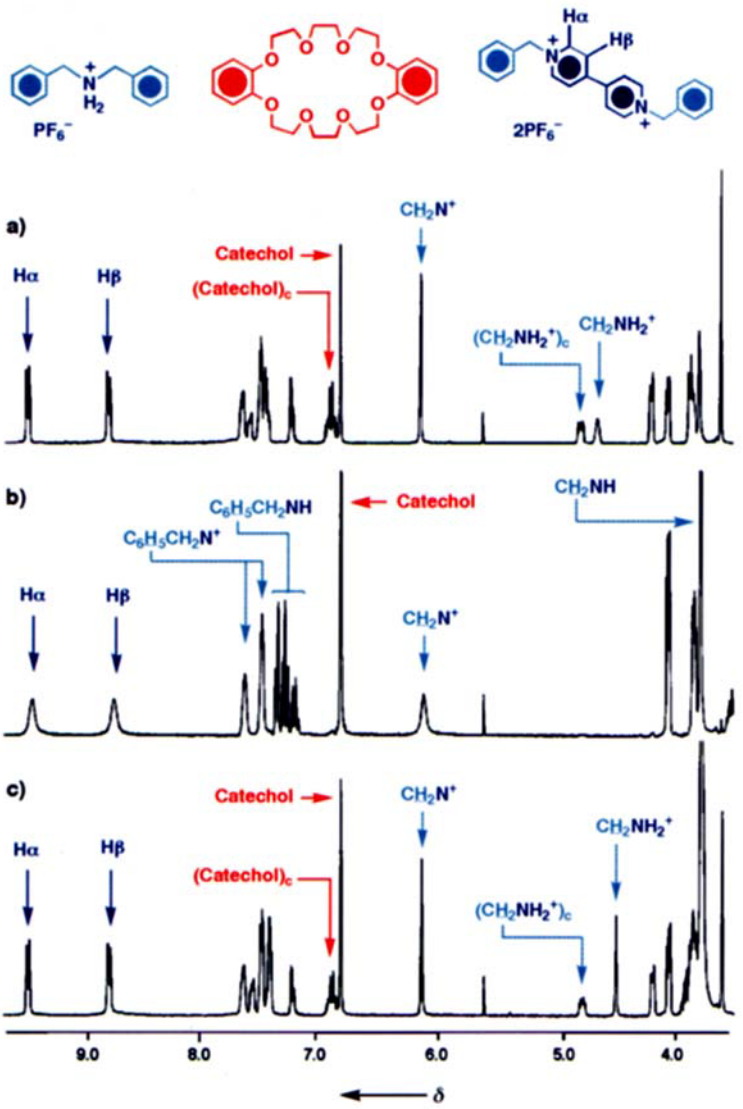

Figure 2. Partial ^{1}H NMR spectra (300 MHz, CD_3COCD_3, room temperature): a) an equimolar mixture of dibenzylammonium hexafluorophosphate, DB24C8, and benzyl viologen bis(hexafluorophoshate) (ca. 10 mM); b) after addition of 2 μL (1.4 mol equiv) of iPr_2NEt to the CD_3COCD_3 solution, and c) after subsequent addition of 2 μL (3.2 mol equiv) of TFA to the basic solution. The subscript *c* is used in the annotation to indicate signals corresponding to the 1:1 complex formed between the NH_2^+ cation and DB24C8.

In conclusion, we have shown that the dethreading and rethreading of the [2]pseudorotaxane[8] formed between the dibenzylammonium cation and DB24C8 can be controlled chemically by the addition of iPr_2NEt or TFA. However, after the dibenzylammonium cation is deprotonated, complexation of the crown ether with the benzyl viologen also present in the solution is not observed. In order to obtain an efficient switching process in which the bipyridinium dication is bound by the DB24C8 ring upon the transformation of the NH_2^+ center into a neutral amino group, a new [2]rotaxane **2**-H^{3+} was synthesized; in this compound the DB24C8 ring is bound mechanically to a dumbbell-shaped component incorporating both a secondary dialkylammonium center and a bipyridinium dicationic unit. The [2]rotaxane **2**-H·3PF_6 constitutes the most selective switchable molecular shuttle reported to date. When the NH_2^+ center is protonated, the DB24C8 ring resides *exclusively* on this station. The affinity of the crown ether for this NH_2^+ center is decreased dramatically upon the addition of a nonnucleophilic base such as iPr_2NEt—which deprotonates the NH_2^+ center—

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and the DB24C8 ring moves to the bipyridinium station. The process is reversible upon addition of TFA, which reprotonates the NH_2^+ center.

Experimental Section

2-H·3PF_6: A solution of 3,5-di-*tert*-butylbenzyl bromide (300 mg, 1.06 mmol) in $CHCl_3$ (5 mL) was added to a stirred suspension of **1**-H·2PF_6 (150 mg, 0.195 mmol) and DB24C8 (200 mg, 0.446 mmol) in $CHCl_3$ (15 mL). The suspension was heated under reflux for 4 days until it became a clear solution. Upon cooling, the reaction mixture was concentrated in vacuo to give a solid residue, which was purified by column chromatography (SiO_2; gradient elution with CH_2Cl_2/MeOH in the proportions 1/0, then 9/1 and then 7/1) to afford a pale yellow solid and characterized as the hydrochloride salt **2**-H·2Cl (97 mg, 40%). After counterion exchange (NH_4PF_6/H_2O/Me_2CO), **2**-H·3PF_6 was isolated as a beige solid (116 mg, 95%); m.p. 169–173 °C; ^{1}H NMR (300 MHz, CD_3COCD_3, 20 °C): δ = 9.55 (d, 2H), 9.23 (d, 2H), 8.80 (d, 2H), 8.79 (d, 2H), 7.62 (s, 3H), 7.51 (s, 1H), 7.46 (s, 2H), 7.41, 7.21 (AA'XX' system, 4H), 6.86–6.83 (m, 8H), 6.14 (s, 2H), 5.88 (s, 2H), 4.87–4.85 (m, 4H), 4.22–3.58 (m, 24H), 1.30 (s, 18H), 1.23 (s, 18H); FABMS (*m*-NBA): *m/z* 1420 [$M - PF_6$]$^+$, 1275 [$M - 2PF_6$]$^+$, 1129 [$M - 2PF_6 - HPF_6$]$^+$.

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[9] Compound **1**-H·2PF_6 was prepared in good overall yield (49%) as follows: 3,5-di-*tert*-butylbenzaldehyde was condensed with methyl 4-aminomethylbenzoate, and the resulting imine was reduced in situ with $NaBH_4$ to give the secondary amine. After reduction of the ester function with $LiAlH_4$ and subsequent reaction of the alcohol derivative as hydrochloride salt with an excess of $SOCl_2$, the benzylic chloride in the form of the hydrochloride salt was obtained. Reaction of this compound with a fourfold excess of 4,4'-bipyridine and subsequent counterion exchange (NH_4PF_6/H_2O/Me_2CO) gave **1**-H·2PF_6.

[10] The dumbbell-shaped component of the [2]rotaxane **2**-H·3PF_6 was prepared as compound **3**-H·3PF_6 (Figure 1) in its own right by treating **1**-H·2PF_6 (50 mg, 0.065 mmol) with 3,5-di-*tert*-butylbenzyl bromide (100 mg, 0.35 mmol) in MeCN (10 mL). The reaction mixture was transferred to a Teflon ultrahigh pressure reaction vessel and subjected to a pressure of 12 kbar at 50 °C for 5 days. After removal of the solvent, the crude product was purified by column chromatography (SiO_2: gradient elution with CH_2Cl_2/MeOH 9/1 and then MeOH/2 M NH_4Cl/$MeNO_2$ 7/2/1). After counterion exchange (NH_4PF_6/H_2O/Me_2CO), the dumbbell-shaped compound **3**-H·3PF_6 was isolated as a beige solid (48 mg, 66%). M.p. 187–193 °C (decomp.); ^{1}H NMR (300 MHz, CD_3COCD_3, 20 °C): δ = 9.53 (d, 2H), 9.42 (d, 2H), 8.78 (d, 2H), 8.76 (d, 2H), 7.74, 7.70 (AA'XX' system, 4H), 7.61 (s, 3H), 7.56 (s, 1H), 7.43 (s, 2H), 6.20 (s, 2H), 6.14 (s, 2H), 4.70 (s, 2H), 4.63 (s, 2H), 1.30 (s, 18H), 1.28 (s, 18H); FABMS (*m*-NBA): *m/z* 972 [$M - PF_6$]$^+$, 827 [$M - 2PF_6$]$^+$, 681 [$M - 2PF_6 - HPF_6$]$^+$.

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[12] Complexes between catechol-containing crown ethers—such as DB24C8 and DB30C10—and bipyridinium dications—diquat, paraquat and 2,7-diazapyrenium—show an absorption band at 400 nm, indicative of the charge transfer interaction between the catechol ring of the crown ether and these bipyridinium dications. The crystal structures of some of these complexes show the π–π-stacking of the three aromatic rings leading to a stabilization of a supramolecular entity in which the macrocycle adopts a concave (or cliplike) conformation. Examples: a) H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, J. B. Wolstenholme, D. J. Williams, *J. Chem. Soc. Perkin Trans. 2* **1985**, 607–624; b) P. R. Ashton, S. J. Langford, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 1387–1388.

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