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First Catenane Containing Phosphino Groups: A Step toward a Catenane Ligand

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Abstract: A novel [2] catenane containing a diphenylphosphino group on each ring was prepared. Synthesis of the new catenane involved the use of tetraamide rings to form an efficient pseudorotaxane intermediate. The catenane was found to be applicable as a ligand for metal-catalyzed reactions such as Suzuki-Miyaura coupling.

Keywords: amides, catenane, hydrogen bonding, ligand, phosphino group

INTRODUCTION

Over the past decade, catenanes have been the subject of much attention because of their unique structure.^[1] There have been many reports concerning the synthesis and structural analysis of catenanes, but fewer on their application as functional molecules.^[2] Balzani et al. have investigated functional catenanes for use in such applications as switching devices^[2a-c] and color-switchable dyes.^[2d] We have investigated the preparation of catenanes containing phosphorous functions for use as novel ligands in metal complex catalysis. Because catenane rings show rigidity and high mobility, catenane-based ligands may be expected to show high selectivity and wide applicability. There are examples of catenane ligands containing 2,2'-bipyridyl moieties as coordination sites,^[3] however, to the best of our knowledge, there have not yet been any reports of a [2]catenane

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with coordination sites on each ring. Very recently, phosphorous - containing catenane that is an other type reported. That has phosphineoxide moieties in thier ring structures.^[4] In this communication, we report the preparation of a novel [2]catenane possessing diphenylphosphino-group coordination sites and the application of this catenane as a ligand for metal catalysis.

RESULTS AND DISCUSSION

Amide-based [2]catenanes, studied in detail by several researchers, were selected as the mother catenane onto which phosphino groups were introduced.^[5] These can be prepared relatively easily and contain no other metal-coordination sites and no electric charges; the amide group can be inactivated by reduction and methylation if necessary.^[6]

5-(Diphenylphosphino)isophthalic acid (1) was prepared in good yield from 5-aminoisophthalic acid via diazonium salt iodination^[7] followed by palladiumcatalyzed coupling with diphenylphosphine^[8] (Scheme 1). Compound 1 was allowed to react with SOCl₂ to form an acid chloride, which then underwent amidation with 4-hydroxybenzylamine to form phosphorous-containing diphenol 2a, with oxidation of the phosphino group. (In the process of amidation of 1 and 4-hydroxybenzylamine, the phosphino group was oxidized and phosphinoxide 2a was obtained. The air oxidation was supposed, but details have not been revealed.) From 2a, catenane preparation was attempted according to the reported procedure,^[5e] but only macrocycle 3a was formed, and no interlocked compounds were obtained. It has been reported that catenane structures may be assembled via ring closure of pseudorotaxane,^[9] but in this case, it was thought that the pseudorotaxane structure could not be formed because of the bulkiness of the diphenylphosphino groups (Fig. 1a).

To avoid this steric hindrance, the preparation of a tetraamide ring catenane was investigated. The use of a tetraamide ring, which contains many hydrogen bonding sites (Fig. 1b), allows the formation of less hindered pseudorotaxane intermediates. Diamine **2b** was prepared from **1** and 4-aminobenzylamine by amidation



Scheme 1. Catenane preparation from phosphorous-containing diphenol 2a.



Figure 1. Plausible pseudorotaxane intermediates from diamide macrocycle (a) and tetraamide macrocycle (b).



Scheme 2. Preparation of tetraamide catenane ligand 4b.



Figure 2. ¹H NMR spectra of catenane ligand **4b** and macrocycle **3b** (400 MHz, DMSO- d_6 ; signals indicated by "E" represent ethanol used for PLC isolation).

using N,N'-dicyclohexylcarbodiimide/1-hydroxybenzotriazole (DCC/HOBt) as a coupling reagent,^[10] and cyclization of **2b** with sebacoyl chloride was carried out under dilution conditions (Scheme 2). The desired diphenylphosphinated [2]catenane **4b** was isolated from the product by preparative thin layer chromatography (PLC), along with macrocycle **3b**. The ¹H NMR spectra of catenane **4b** and macrocycle **3b** are shown in Fig. 2. In **4b**, the signals of the 1,4-disubstituted aromatic rings are shifted to higher field compared to those of **3b**, suggesting that a catenane structure was formed. These high field shifts of the ¹H NMR signals are characteristic of catenanes. The same results have been reported by Leigh et al.^[5e] The MALDI-TOF MS spectrum of **4b** is shown in Fig. 3. The molecular ion of the [2]catenane (M⁺, m/z = 1449.8), along with some cationized molecular ions ([M + Na]⁺, m/z = 1472.7 and [M + K]⁺, m/z = 1488.7), were observed clearly, showing that the required phosphinated catenane had been obtained.

To investigate the activity of catenane **4b** as a ligand, a Suzuki–Miyaura coupling reaction was carried out.^[11] In the presence of **4b** and palladium(II) acetate, bromobenzene was coupled with phenylboronic acid to give biphenyl in 69% yield (Scheme 3). This is the first report about preparation of catenane containing phosphino groups and using the catenane as a ligand of metal catalyst. Further investigations of the catenane ligand such as applications for other catalytic reactions and structure analysis of the metal–ligand complex are now in progress.

EXPERIMENTAL

Preparation of Diamine 2b

To a solution of 5-diphenylphosphinoisophthalic acid (0.70 g) and 1-hydroxybenzotriazole monohydrate (0.64 g) in DMF (6.0 mL), N,N'-dicyclohexylcarbodiimide (0.87 g) was added at 0° C and stirred for 24 h. The formed precipitate was filtered off, and the filtrate was added dropwise to a solution of 4-aminobenzylamine (0.51 g) in DMF (20 mL) and stirred for 24 h at



Figure 3. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS spectrum of catenane ligand **4b**.



Scheme 3. Suzuki–Miyaura coupling reaction with catenane **4b** as a ligand.

 0° C. After the solvent was distilled off, the residue was dissolved in chloroform and washed with 2 M NaOH. The organic layer was washed with water, dried over MgSO₄, and evaporated. Diamine **2b** was obtained in 60% yield, and the purity was high enough to use a catenane preparation.

Preparation of [2]Catenane 4b

Because of low solubility in chloroform, diamine **2b** (0.173 g) was dissolved in acetonitrile (4.0 mL) by heating and diluted by chloroform (150 mL). After adding triethylamine (0.063 g) to the diamine solution, sebacoyl chloride (0.074 g) in chloroform (50 mL) was added dropwise for 2 h. Precipitate was removed by filtration. The filtrate was washed with 1 M HCl, dried over MgSO₄, and the solvent was removed by evaporation. The residue was dissolved in a few milliliters of chloroform and allowed to stand for overnight. After filtration, [2]catenane **4b** was isolated from the filtrate by PLC in 7% yield.

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REFERENCES

- (a) Dietrich-Buchecker, C.; Sauvage, J.-P. Interlocking of molecular threads: from the statistical approach to the templated synthesis of catenands. *Chem. Rev.* 1987, 87, 795–810; (b) Amabilino, D. B.; Stoddart, J. F. Interlocked and intertwined structures and superstructures. *Chem. Rev.* 1995, 95, 2725–2828; (c) Sauvage, J.-P.; Dietrich-Buchecker, C. Eds., *Molecular Catenanes, Rotaxanes, and Knots*; Wiley-VCH: Weinheim, 1999.
- (a) Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. Switching of pseudorotaxanes and catenanes incorporating a tetrathiafulvalene unit by redox and chemical inputs. J. Org. Chem. 2000, 65, 1924–1936; (b) Balzani, V.; Credi, A.; Langford, S. J.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. Constructing molecular machinery: a chemically switchable [2]catenane. J. Am. Chem. Soc. 2000, 122, 3542–3543; (c) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. Switching devices based on interlocked molecules. Acc. Chem. Res. 2001, 34, 433–444; (d) Deng, W.-Q.; Flood, A. H.;

Stoddart, J. F.; Goddard, W. A. An electrochemical color-switchable RGB dye: Tristable [2]catenane. J. Am. Chem. Soc. 2005, 127, 15994–15995.

- (a) Ashton, P. R.; Balzani, V.; Credi, A.; Kocian, O.; Pasini, D.; Prodi, L.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. Molecular meccano, 35: Cyclophanes and [2]catenanes as ligands for transition metal complexes: Synthesis, structure, absorption spectra, and excited state and electrochemical properties. *Chem. Eur. J.* **1998**, *4*, 590–607; (b) Hu, Y.-Z.; Bossmann, S. H.; van Loyen, D.; Schwarz, O.; Dürr, H. A novel 2,2'-bipyridine[2]catenane and its ruthenium complex: Synthesis, structure, and intramolecular electron transfer—A model for the photosynthetic reaction center. *Chem. Eur. J.* **1999**, *5*, 1267–1277.
- Theil, A.; Mauve, C.; Adeline, M.-T.; Marinetti, A.; Sauvage, J.-P. Phosphoruscontaining [2]catenanes as an example of interlocking chiral structures. *Angew. Chem.* 2006, 118, 2158–2161.
- 5. (a) Hunter, C. A. Synthesis and structure elucidation of a new [2]-catenane. J. Am. Chem. Soc. 1992, 114, 5303–5311; (b) Vögtle, F.; Meier, S.; Hoss, R. One-step synthesis of a fourfold functionalized catenane. Angew. Chem., Int. Ed. Engl. 1992. 31, 1619-1622; (c) Ottens-Hildebrandt, S.; Meier, S.; Schmidt, W.; Vögtle, F. Isomeric catenanes of lactam type and their formation mechanism. Angew. Chem., Int. Ed. Engl. 1994, 33, 1767-1770; (d) Johnston, A. G.; Leigh, D. A.; Nezhat, L.; Smart, J. P.; Deegan, M. D. Structurally diverse and dynamically versatile benzylic amide [2]catenanes assembled directly from commercially available precursors. Angew. Chem., Int. Ed. Engl. 1995, 34, 1212-1216; (e) Leigh, D. A.; Moody, K.: Smart, J. P.; Watson, K. J.; Slawin, A. M. Z. Catenane chameleons: environmentsensitive translational isomerism in amphiphilic benzylic amide [2]catenanes. Angew. Chem., Int. Ed. Engl. 1996, 35, 306-310; (f) Kidd, T. J.; Leigh, D. A.; Wilson, A. J. Organic "magic rings": The hydrogen bond-directed assembly of catenanes under thermodynamic control. J. Am. Chem. Soc. 1999, 121, 1599-1600; (g) Safarowsky, O.; Vogel, E.; Vögtle, F. Amide-based [3]catenanes and [2]catenanes with aliphatic chains. Eur. J. Org. Chem. 2000, 499-505.
- Furusho, Y.; Shoji, J.; Watanabe, N.; Kihara, N.; Adachi, T.; Takata, T. Chemical modification of amide-based catenanes and rotaxanes I: Synthesis of secondary amine [2]catenanes and [2]rotaxanes by the borane reduction of secondary amide [2]catenanes and [2]rotaxanes and mobility of their components. *Bull. Chem. Soc. Jpn.* 2001, 74, 139–147.
- Zeng, F.; Zimmerman, S. C. Rapid synthesis of dendrimers by an orthogonal coupling strategy. J. Am. Chem. Soc. 1996, 118, 5326–5327.
- Herd, O.; Heßler, A.; Hingst, M.; Tepper, M.; Stelzer, O. Water soluble phosphines, VIII: Palladium-catalyzed P-C cross coupling reactions between primary or secondary phosphines and functional aryl iodides—A novel synthetic route to water-soluble phosphines. J. Organomet. Chem 1996, 522, 69–76.
- (a) Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. Glycylglycine rotaxanes— The hydrogen bond directed assembly of synthetic peptide rotaxanes. *Angew. Chem., Int. Ed. Engl.* 1997, *36*, 728–732; (b) Seel, C.; Parham, A. H.; Safarowsky, O.; Hübner, G. M.; Vögtle, F. How selective threading of amides through macrocylic lactam wheels leads to rotaxane synthesis. *J. Org. Chem.* 1999, *64*, 7236–7242.
- Fustin, C.-A.; Bailly, C.; Clarkson, G. J.; Groote, P. D.; Galow, T. H.; Leigh, D. A.; Robertson, D.; Slawin, A. M. Z.; Wong, J. K. Y. Mechanically linked polycarbonate. J. Am. Chem. Soc. 2003, 125, 2200–2207.
- Huff, B. E.; Koenig, T. M.; Mitchell, D.; Staszak, M. A. Synthesis of unsymmetrical biaryls using a modified Suzuki cross-coupling: 4-Biphenylcarboxaldehyde. *Org. Synth.* **1998**, *75*, 53–60.