thermodynamics of similar systems with various Lewis acids.

Acknowledgment. We wish to thank Professor Evans for supplying us with oxazolidinone samples. Financial support was provided by the EPSCoR program of NSF (RII861075) and the NDSU Grant-in-Aid. The NMR spectrometer was supported by a grant from the Air Force of Scientific Research (AFOSR-87-0036).

Supplementary Material Available: ^{119}Sn NMR stack plot of chelate between −60 and 40 °C, ^{119}Sn NMR stack plot of 1 and 0.5 equiv of SnCl$_4$ between −60 and 40 °C, and ^{13}C NMR stack plot of chelate between −20 and 45 °C (3 pages). Ordering information is given on any current masthead page.

A New Macrobicyclic Hard and Soft Ligand Built on Phenanthroline

Jennifer A. Wytko and Jean Weiss*

Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, URA 405 AU CNRS, Institut Le Bel, 4 rue Blaise Pascal, F-67000 Strasbourg, France

Received April 27, 1990

Summary: The synthesis of a new macrobicyclic hard and soft ligand containing an *o*-phenanthroline subunit and an aza-crown ether is described.

There is currently a growing interest in hard and soft heteroditopic ligands, which are able to complex soft transition metals as well as hard alkali cations.[1,2] Several of these ligands have been reported, and they emerge from three main approaches at the molecular level. Macrocyclic compounds combining Schiff bases and polyoxyethylene moieties have been described recently[3-6] and complete the important work on macrocyclic crown ethers incorporating pyridines and thioethers as soft sites.[7-9] Among the laterally branched compounds that have been described some years ago, phosphino-crown ethers have proven their ability to form heterodinuclear complexes.[10-12] Besides the macrocyclic and laterally branched macrocyclic approaches, the cryptate area has provided the concept of hard and soft macrobicycles combining crown ethers as hard binding sites and N or S heterocycles as sift sites.[13]

We report the synthesis of a new macrobicyclic ligand (Figure 1) which is built on a 2,9-diphenyl-1,10-phenanthroline unit used as the soft coordinating site.

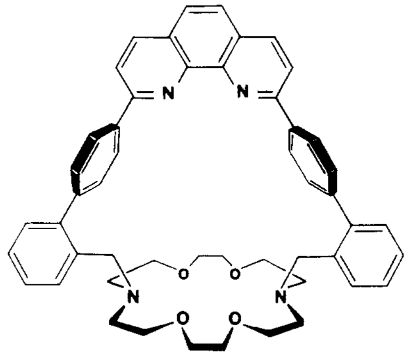

Figure 1. Rigid molecular framework incorporating both hard and soft coordination sites.

Sterically hindered phenanthrolines have been extensively studied,[14-16] and their capability of complexing and stabilizing soft cations such as copper(I) has been demonstrated.[17-19] The aza-crown ether unit [18]N$_2$O$_4$ serves as the hard binding site for an alkali cation. The biphenyl spacer ensures the rigidity of the molecular framework and, consequently, the high degree of preorganization of the ligand.

The 2,9-bis(bromophenyl)-1,10-phenanthroline (1) was obtained by previously described methods[20] by stepwise introduction of (*p*-bromophenyl)lithium at the 2- and 9-positions of *o*-phenanthroline. The diaryl bromide 1 (Figure 2) was a good precursor to form biphenyl units by "Suzuki" type cross-coupling with arylboronic acids.[21] The quantitatively protected *o*-bromobenzaldehyde **2** obtained by standard methods[22] was treated with Mg to give the Grignard reagent **3** in 95% yield. The Grignard was then slowly added to an excess of trimethylborate (THF/−78 °C/argon). After acidic workup (5% HCl/Et$_2$O) and purification by acid/base extraction, the deprotected boronic acid **4** was obtained in overall 65% yield as white crystals from CH$_2$Cl$_2$/hexane (mp 108–110 °C).

Reacting the boronic acid with the 2,9-bis(*p*-bromophenyl)-1,10-phenanthroline (1) in the remarkable "Suzuki" cross-coupling conditions[23] (Pd(PPh$_3$)$_4$/toluene-/MeOH/aqueous Na$_2$CO$_3$/argon/80 °C/12 h) afforded, after chromatography (SiO$_2$/CH$_2$Cl$_2$/1–2% ethyl acetate),

---

[1] Lehn, J.-M. *Pure Appl. Chem.* **1980**, *52*, 2441–2459.

[2] Lehn, J.-M. In *Frontiers of Science (IUPAC)*; Laider, K. J., Ed.; Pergamon Press: New York, 1982; p 265.

[3] van Staveren, C. J.; van Eerden, J.; van Veggel, F. C. J. M.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4994–5008. van Veggel, F. C. J. M.; Harkema, S.; Bos, M.; Verboom, W.; van Staveren. C. J.; Gerritsma, G. J.; Reinhoudt, D. N. *Inorg. Chem.* **1989**, *28*, 1133–1148.

[4] van Veggel, F. C. J. M.; Bos, M.; Harkema, S.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 746–748.

[5] van Staveren, C. J.; Reinhoudt, D. N.; van Eerden, J.; Harkema, S. *J. Chem. Soc., Chem. Commun.* **1987**, 974–977.

[6] Newkome, G. R.; Kiefer, G. E.; Kohli, D. K.; Xia, Y. J.; Fronczek, F.; Baker, G. R. *J. Org. Chem.* **1989**, *54*, 5105–5110.

[7] Parker, D.; Lehn, J.-M.; Rimmer, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1517–1521.

[8] Parker, D. *J. Chem. Soc., Chem. Commun.* **1985**, 1129–1131.

[9] Fergusson, G.; Matthes, K. E.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1350–1351.

[10] Powell, J.; Gregg, M. R.; Meindl, P. *Organometallics* **1989**, *8*, 2942–2947 and references cited therein.

[11] Boyce, B. A.; Carroy, A.; Lehn, J.-M.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1546–1548.

[12] Mc Lain, S. J. *J. Am. Chem. Soc.* **1983**, **105**, 6355–6357.

[13] Carroy, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1986**, 1232–1234.

[14] Kirchhoff, J. R.; Mc Millin, D. R.; Marnot, P. A.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1985**, *107*, 1138–1141.

[15] Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P.; Kintzinger, J.-P.; Maltese, P. *Nouv. J. Chim.* **1984**, *8*, 573–582.

[16] Marnot, P. A.; Ruppert, R. R.; Sauvage, J.-P. *Nouv. J. Chim.* 1981, *5*, 543–545.

[17] Mc Bryde, W. A. E. *IUPAC Chemical Data Series 17*; Pergamon Press: Paris, 1978.

[18] Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5237–5245.

[19] Brisbin, D. A.; Mc Bryde, W. A. E. *Can. J. Chem.* **1963**, *41*, 1135–1141.

[20] Chardon-Noblat, S. Ph.D. Thesis, Université Louis Pasteur de Strasbourg, France, October 1989.

[21] Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*(7), 513–519.

[22] Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley and Sons: New York, 1981.

[23] Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237–5243.

0022-3263/90/1955-5200$02.50/0

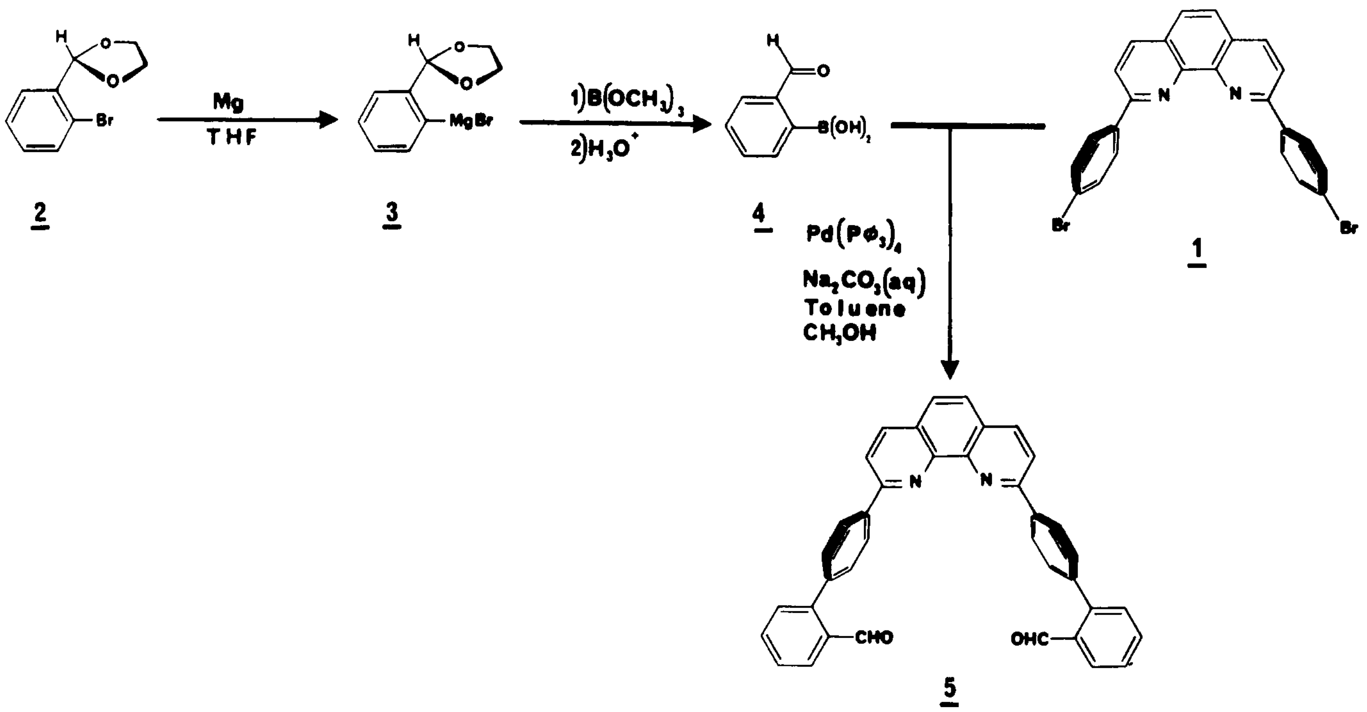

Figure 2. "Suzuki" approach to novel disubstituted phenanthrolines.

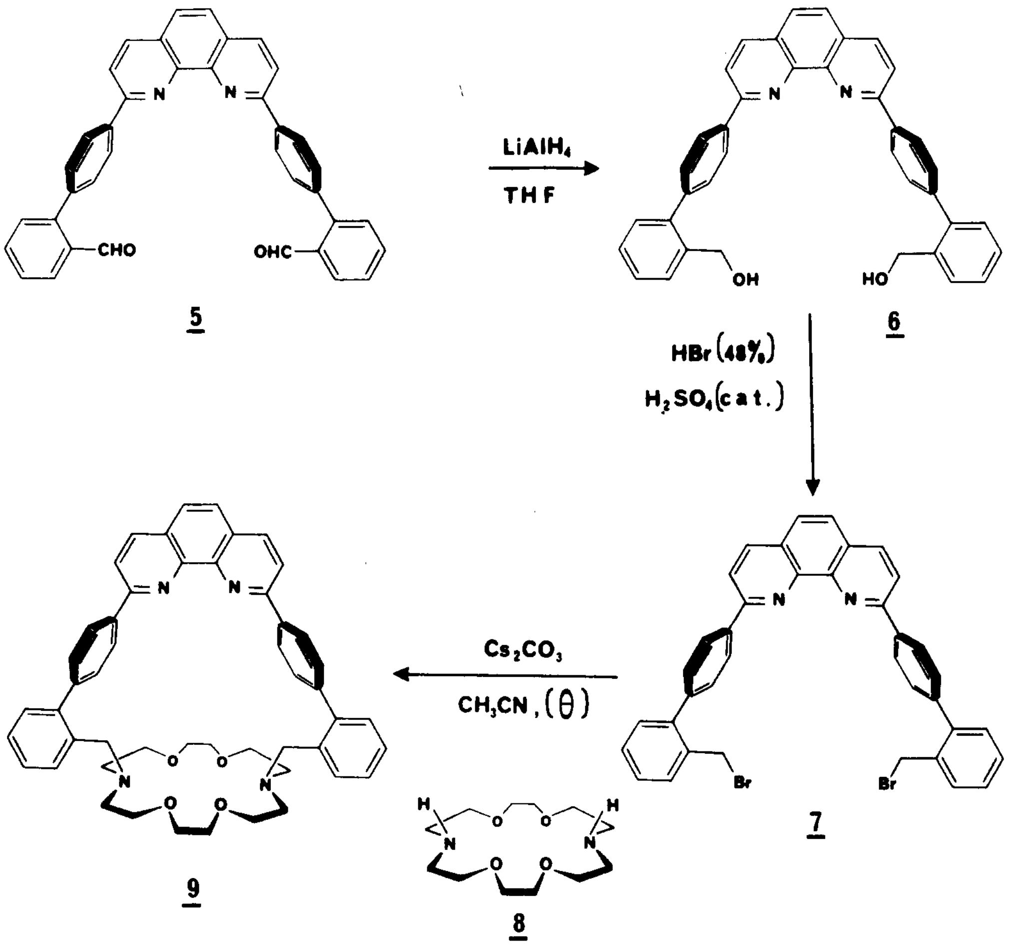

Figure 3. Ring closure of ligand **9**.

the dialdehyde **5** as a pale yellow solid (mp 237–239 °C) in 80% yield.[24]

Reduction of **5** by an excess of $LiAlH_4$ in refluxing THF afforded the diol **6** (Figure 3) as a yellow solid in 72% yield (mp 138 °C dec, SiO_2/ether–CH_2Cl_2 in 9/1 ratio/1–2% MeOH). Treatment of the diol with refluxing HBr 48% and H_2SO_4 as a catalyst gave the dibromide **7** in 35% yield (mp 249 °C dec) after chromatography (SiO_2/CH_2Cl_2/

---

[24] All new compounds gave satisfactory analytical data. ^{13}C NMR (100 MHz), ^{1}H NMR (200 MHz), CHN analysis within 0.4% error, and mass spectroscopy measurements are in agreement with the proposed structures.

traces of MeOH). The very efficient cyclization method described for 2,9-bis(bromomethyl)-1,10-phenanthrolines and aza-crown ethers to form mixed phenanthrolino-crown ether cryptates[25] has been applied to 7 and [18]N_2O_4 8. The macrocycle 8 was treated under argon with an excess of cesium carbonate in refluxing dry acetonitrile before adding dropwise a suspension of the dibromide 7. After 20 h of reaction, the inorganic materials (solids) were discarded and the crystalline ligand 9 (mp 110–111 °C) was isolated in 30% yield from the organic phase by chromatography ($SiO_2/CH_2Cl_2/MeOH$). The yield of the cyclization reaction could be compared to those obtained by Lehn and co-workers who have reported up to 70% yield for this type of reactions using Na_2CO_3 as a base.[25]

The relative flexibility of our precursor (rotation around the biphenyl bond) has directed our choice toward cesium carbonate, instead of the sodium salt. For cryptates synthesis, the size of the sodium seemed to be adequate for templation of the cyclization, but in our case benefit was taken from the ability of the cesium ion to gather fragments for S_N2 reactions.[26]

From ^1H NMR data, the geometry of the ligand 9 has been approximated, and measurements are in agreement with the proposed conformation depicted in Figure 1. The signal of the ortho proton is significantly shifted to higher fields when compared to open precursors ($\Delta\delta = -0.2$ ppm), showing that the phenyl spacer is no longer coplanar with the phenanthroline ring. The second significant shift is the shielding of the benzylic protons whose signal (singlet) appears at 3.66 ppm versus 4.54 ppm in the precursor 7. This is consistent with placing the benzylic protons very close to the shielding cone of the phenyl substituents present on the phenanthroline moiety. A slight broadening of the signals has been observed at room temperature indicating a reduced mobility of the macrobicyclic framework.

Investigations concerning the complexing abilities of 9 as well as its copper(I)– and rhodium(I)–alkali complexes are under progress.

Acknowledgment. We warmly acknowledge the CNRS for financial support.

Supplementary Material Available: ^1H NMR spectra of compounds 5, 6, 7, and 9; ^{13}C NMR spectra of compounds 5 and 9; and mass spectra of compounds 5, 6, 7, and 9 (20 pages). Ordering information is given on any current masthead page.

---

[25] Rodriguez-Ubis, J. C.; Alpha, B.; Plancherel, D.; Lehn, J.-M. *Helv. Chim. Acta* **1984**, *67*, 2264–2269.

[26] Kellog, R. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 782–794.

Articles

Synthesis of 4-Alkyl-2-iodosobenzoic Acids: Potent Catalysts for the Hydrolysis of Phosphorous Esters

Charles A. Panetta,*[1a] Stephanie M. Garlick,[1c,d] H. Dupont Durst,[1b] Frederick R. Longo,[1c] and J. Richard Ward[1b]

Applied Chemistry Branch, Chemical Division, Research Directorate, U.S. Army Chemical Research, Development, and Engineering Center, Aberdeen Proving Ground, Maryland 21010-5423, and The Department of Chemistry, The University of Mississippi, University, Mississippi 38677

Received October 31, 1989

The syntheses of five new 4-alkyl-2-iodosobenzoic acids (3) are described. The iodine atom was introduced by ortho-directed lithiation of 4-alkylbenzyl alcohols followed by treatment with I_2. The catalytic effectiveness of each of the products in the hydrolysis of 4-nitrophenyl diphenyl phosphate in microemulsions was studied. The 4-methyl- and 4-ethyl-substituted products were each found to be significantly better catalysts than the standard nonalkylated 2-iodosobenzoic acid (3, R = H). These results would indicate that microemulsions of these materials may find use in detoxification procedures.

Introduction

Certain phosphate, phosphonate, and phosphinate esters are persistent acetylcholinesterase inhibitors and neurotoxic agents. Since some are used as potent pesticides and chemical warfare agents, their rates of decomposition and detoxification are of considerable importance. Efficient detoxification methods would find applications in the decontamination of environments and equipment exposed to these agents.

Many functional groups have been studied for their reactivity toward phosphate esters and, since the latter are only sparingly soluble in water, micellar and microemulsion media have often been employed. In recent years, 2-iodosobenzoic acid (IBA, 3, R = H) and several derivatives have been reported to be effective catalysts in phosphate ester decompositions.[2] Speculation on the mechanism responsible for the extraordinary reactivity of IBA has suggested that the cyclic IBA anion is the nucleophile that

---

[1] (a) NRC-CRDEC Senior Resident Research Associate, 1988–1989. Permanent address, The University of Mississippi. (b) U.S. Army Chemical Research, Development, and Engineering Center. (c) The Department of Chemistry, Drexel University, Philadelphia, PA 19104. (d) Geocenters Inc., Fort Washington, MD 20744.

[2] Moss, R. A.; Alwis, K. W.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1983**, *105*, 681. Moss, R. A.; Alwis, K. W.; Shin, J.-S. *J. Am. Chem. Soc.* **1984**, *106*, 2651. Moss, R. A.; Kim, K. Y.; Swarup, S. *J. Am. Chem. Soc.* **1986**, *108*, 788. Moss, R. A.; Scrimin, P.; Rosen, R. T. *Tetrahedron Lett.* **1987**, *28*, 257. Katritzky, A. R.; Duell, B. L.; Durst, H. D.; Knier, B. L. *J. Org. Chem.* **1988**, *53*, 3972.

0022-3263/90/1955-5202$02.50/0