Macrocyclic Receptor Molecules for Urea: The Use of Electrophiles in the (Co)complexation of Neutral Molecules

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A covalently bound carboxylic group or an electrophilic lithium ion can assist in the complexation of urea by macrocyclic polydentate ligands, provided that the macrocycle is sufficiently large to encapsulate urea. Although hitherto the work on synthetic macrocyclic polynuclear ligands almost exclusively deals with selective complexation of cations,† there is an increasing interest in the binding of neutral guest species.‡ We have recently proven that such complexes exist not only in the solid state but also in solution.†‡ Although a crystalline 18-crown-6-urea (1:5) complex has been isolated,‡ complexes of crown ethers with urea in aqueous solutions hardly exist (log K < 0.1).§ More stable complexes are formed between protonated urea (UH+X−) and macrocyclic polyethers,6 with a coordination as in the corresponding complexes with guanidinium salts.7 We are currently studying the complexation of urea with macrocyclic polyethers containing a covalently linked acidic group, which can protonate the urea molecule, a very weak base (pKb = 10.1, H2O, 25.0°C).

2-Carboxyl-1,3-xylyl crown ethers 1a-g were synthesized according to the method described by Cram et al.1 Accurate determination of the acidities of the carboxylic group in these crown ethers (1) (pKb values ±0.02) showed that the pKb value depends strongly on the ring size of the crown ether. The extremely high pKb values of 1a and 1b (5.31 and 5.71, respectively) can be attributed to the stabilization of the acid by intramolecular hydrogen bonding to a crown ether oxygen atom.8 The relatively high pKb values of 1c (4.38) and 1d (4.06) must be due to specific coordination of a water molecule in the cavity, stabilizing the hydrogen bonds indicated by dashed lines.

Figure 1. Structures of (a) the 2-carboxyl-1,3-xylyl-10-crown-9-urea complex and (b) the 2,6-pyrido-27-crown-9-bis(urea)-LiClO4 complex (the perchlorate ion is not shown). Hydrogen bonds indicated by dashed lines.

(1) de Boer, J. A. A.; Uitterlief, J. W. H. M.; Gevers, J.; Harkema, S.; Reinhoudt, D. N. J. Chem. Soc. 1983, 48, 4821-4830. (b) van Staveren, C. J.; den Herog, H. J.; Kruiis, D. N.; Uitterlief, J. W. H. M.; Kruiis, L.; Harkema, S. J. Chem. Soc., Chem. Commun. 1984, 1409-1411. (c) Newcomb, M.; Moore, S. S.; Cram, D. J. J. Am. Chem. Soc. 1979, 99, 6405-6410. 1H NMR (CDCl3) δ 3.68 (s, 1 H, CH2), 4.73 (s, 4 H, Ar CH2), 7.29 (t, 3 H, Ar H), 10.4 (br, s, 1 H, OH). 13C NMR (CDCl3) δ 147.0 (s, CH2), 138.1 (s, Ar CH2), 140.0 (s, Ar), 147.0 (s, Ar CH2).
carboxylic group. The \( P_K_b \) values of 1e–g (3.80, 3.94, and 3.93, respectively) seem to reach a limiting value and become independent of the ring size. When the \( P_K_b \) determinations of 1b, 1f, and 1g were carried out in the presence of a 100-fold excess of urea, we found a small but significant enhancement of the \( P_K_b \) values of 1f and 1g (both 0.10), an effect that hardly exists in the case of 1b (\( \Delta P_K_b \leq 0.04 \)). This increased \( P_K_b \) value can be attributed to a specific inclusion of urea. A proposed complexation which is supported by the isolation of a crystalline 1f–urea (1:1) complex. The X-ray analysis of the 1f–urea complex shows that the proton of the carboxylic group is coordinated to the urea oxygen atom via a short hydrogen bond (O–O distance 2.54 Å, O–H–O angle 167°). The total encapsulation of urea results in a complex with an apolar exterior, a property that allows for the solubilization of urea in an apolar solvent. A 0.10 M solution of 1f in CDC13 solubilized 0.05 M urea (25 °C, 17 h). In the absence of 1f no urea could be dissolved in CDC13. These results prove that the electrophilic moiety in crown ethers I can assist in the complexation of a neutral molecule, and, therefore, we assumed that other electrophiles should also be able to assist in this type of complexation.

When a dilute solution of 2,6-pyrido-27-crown-9 (2e) and an equimolar amount of lithium perchlorate was treated with 1–2 equiv of urea in ethanol, a crystalline complex (1:2) precipitated. X-ray structure analysis (Figure 1) revealed that one of the urea molecules is encapsulated in the crown ether cavity (nitrogen–oxygen distances in hydrogen bonds 2.89–3.17 Å) in a similar way as in the 1f–urea complex with the Li+ cation replacing the lithium ion of the crown ether oxygen and the oxygen atom of a second urea molecule. These Li+–O distances (1.90 Å, Li–N distance 2.02 Å). The tetrahedral coordination of the lithium cation is completed by a crown ether oxygen and the oxygen atom of a second urea molecule. These Li+–O distances (1.98 and 1.95 Å) are in agreement with values reported for other 4-fold coordinated Li+ complexes.

From these results we conclude that electrophiles such as Li+ or H+ can be vital bridging species in the cocomplexation of neutral guests by crown ethers.

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Supplementary Material Available: Tables containing listings of positional and thermal parameters of the two structures (12 pages). Ordering information is given on any current masthead page.

Oxidative addition and reductive elimination of H–H, C–H, and C–C bonds occur in many catalytic and synthetic reactions. Mechanistic studies of the reductive elimination of carbon–hydrogen and carbon–carbon bonds have been reported for several systems. Intramolecular reductive elimination can hamper the study of these reactions on a single metal center. The intramolecular reductive elimination of molecular hydrogen from a mononuclear platinum, palladium, or nickel complex has not been well characterized, although elimination of hydrogen from metal clusters has been suggested as a model for the behavior of hydrogen on surfaces. Several theoretical studies have considered the oxidative addition and reductive elimination of molecular hydrogen from bimetal complexes as a way to gain insight into the mechanism of processes that might occur on a platinum surface. These studies suggest reductive elimination proceeds via a "late" transition state that contains an n2-hydrogen ligand. Kinetic barriers predicted range between 18 and 42 kcal/mol. We report here the first experimental investigation of intramolecular, rate-determining reductive elimination of H2 from a mononuclear dihydride complex containing a metal from the nickel triad, a series of metals frequently used as heterogeneous hydrogenation catalysts.

Barrier to Reductive Elimination of Hydrogen from Dihydridobis(trimethylphosphine)platinum(II)

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