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Complexation of a Bifunctional Substrate to a Heterobimetallic Complex of a Ligand with Hard and Soft Coordination Sites

Magnus Cernerud, Kenneth Wärnmark and Christina Moberg*

Department of Chemistry, Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm (Sweden)

Abstract: A heteroditopic ligand containing dipyridylmethane and crown ether binding sites and heterobimetallic complexes of the ligand have been prepared and used for studies of the binding of bifunctional substrates.

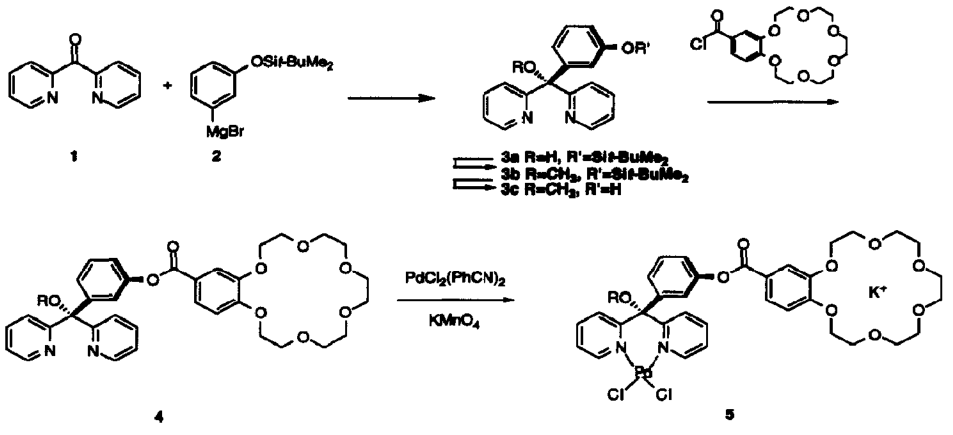
Extensive interest is currently devoted to the preparation and study of ligands containing both hard and soft binding sites.[1] Such ligands are of interest for various applications, such as the study of electron transfer processes and metal-catalyzed reactions. Several ligands have been prepared in which the hard site consists of a crown ether residue.[2] A recent example consists of a crown ether-bisphosphine complex employed as ligand in the palladium-catalyzed allylation of β-diketones.[3]

We present here the preparation of a new heteroditopic ligand containing dipyridylmethane and crown ether units as binding sites, as well as some binding studies of a heterobimetallic complex of the ligand. Dipyridylmethane was chosen as the soft coordination site since side chains containing various functional groups can be conveniently introduced on the carbon atom joining the two pyridine rings of the ligand.[4]

Di(2-pyridyl)ketone (**1**) was thus reacted with 3-(*t*-butyldimethylsilyloxy)phenyl magnesium bromide (**2**) in THF to yield, after hydrolysis, 1,1-bis(2-pyridyl)-1-(3-*t*-butyldimethylsilyloxy)phenylmethanol (**3a**, 76%). Methylation of the tertiary alcohol using NaH and CH_3I in THF to give **3b**, followed by deprotection (1M H_2SO_4) yielded phenol **3c**[5] (66% from **3a**).

This phenol can react in a variety of ways to yield functionalized dipyridylmethanes via substitution or condensation reactions. For the introduction of the crown ether, condensation with an acid chloride was chosen. Therefore, 4-carboxybenzo-18-crown-6 was transformed into its acid chloride using oxalyl chloride, followed by reaction with phenol **3c** to yield the desired ligand **4** (77%).[6]

Bimetallic complexes of ligand 4 were easily prepared. For example, reaction with bis(benzonitrile)palladium(II) chloride in CH_2Cl_2 gave a palladium(II) complex which was subsequently treated with $KMnO_4$ to give a potassium-palladium complex (5). This same complex was obtained upon reaction of the metal compounds in the reverse order. That complex formation occurred was demonstrated by ^{1}H NMR spectroscopy, showing different chemical shifts for the protons in the soft coordinating region of ligand 4 and complex 5,[7] and by the intense violet color indicating that permanganate ions were present in the chloroform solution.



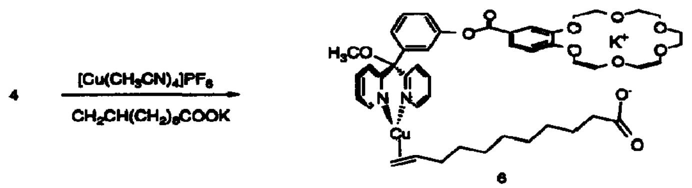
In the most stable conformation of ligand 4, as well as of its metal complexes, the phenyl ring attached to the crown ether and the carbonyl group are assumed to be coplanar to allow for conjugation, whereas the deviation from planarity of the second phenyl ring is expected to be around 50-70° in the most stable conformation.[8] To allow for simultaneous binding of a bifunctional organic substrate to the two metal atoms, this angle should be around 90°. The loss in energy caused by the required rotation[8,9] should, however, be well compensated for by coordination of a potassium carboxylate or an ammonium compound, for example, to the crown ether moiety.[10]

For initial studies of the binding of a bifunctional organic substrate to a bimetallic complex of ligand 4, an olefin containing a terminal carboxylic acid group was chosen. Inspection of molecular models suggested that copper(I) should serve as a suitable soft site for coordination to the olefinic part of the substrate, since this metal ion is known to coordinate olefins in a trigonal geometry with the olefin in the coordination plane,[11] an arrangement that was thought to allow for simultaneous coordination of the potassium salt of the carboxylic acid to the crown ether. This choice was further supported by the description in the literature of a copper(I)-di-(2-pyridyl)amine ethylene complex.[12]

A model reaction using dipyridylmethane derivative 3c was first performed. The addition of two equivalents of 1-hexene and 0.98 equivalents of $[Cu(CH_3CN)_4]PF_6$ to this ligand in acetone-d_6 ([ligand] = 0.04 M) resulted in the formation of a Cu(I) olefin complex, as shown by a shift of peaks in the ^1H NMR spectrum, 0.24 ppm upfield for the signals corresponding to the internal olefinic proton and ca 0.3 ppm upfield for those of the terminal protons.

The complexation to ligand **4** was also followed by ^1H NMR spectroscopy. The free ligand in MeOH-d_4 ([ligand] $\approx$ 0.04 M) was first reacted with the potassium salt of 10-undecenoic acid. This caused a shift difference of signals corresponding to the protons in the crown ether ring (ca 0.15 ppm downfield for the four protons close to the phenyl ring) and also significant chemical shift differences for some of the protons in the aromatic rings. For example, the signals for the three protons on the aromatic ring bound to the crown ether were shifted ca 0.1 ppm downfield upon complexation.[13]

The binding of 10-undecenoic acid to the Cu(I) complex of **4** was studied by the method of Higushi.[14] The Cu(I) complex of **4** was formed by the addition of $[Cu(CH_3CN)_4]PF_6$ (1 eq) to a carefully degassed solution of **4** in MeOH-d_4 ([ligand] = 0.025 M). This solution was titrated with potassium 10-undecenoate in degassed MeOH-d_4 (0.142 M, 0.3-5 eq), which caused a gradual shift change for the internal olefinic proton, from δ 5.14 to 5.69 ppm. From this study it was concluded that a 1:1 complex was formed, with an approximate complexation constant of 10^3 M^{-1}. That free Cu(I) was not involved was indicated by the fact that $[Cu(CH_3CN)_4]PF_6$ did not form a 1:1 complex when titrated with potassium 10-undecenoate. The chemical shift differences observed strongly suggest that the olefinic and carboxylate groups coordinate simultaneously to copper and potassium, respectively, forming the supramolecular complex with structure **6**.



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In the ^1H NMR spectrum of complex **6**, the signals were somewhat broadened, probably due to the fast exchange between host and guest and the presence of traces of Cu(II). A complete analysis of the spectrum was therefore not possible.

An experiment was also performed using potassium 6-heptenoate as substrate in place of potassium 10-undecenoate. In this case no shift of the signals for the vinylic protons was observed upon the addition of Cu(I) to a complex formed from the potassium salt of the acid and **4**. This demonstrates the importance of structural fit of the substrate to allow for simultaneous binding to the two sites of **4**.[15]

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6. **4**: ^{1}H NMR: (400 MHz, MeOH-d_4) δ 8.57 (ddd, J=5.0, 1.8 and 0.9 Hz, 2H), 7.95 (dt, J=7.8 and 1.7 Hz, 2H), 7.80 (td, J=8.1 and 0.9 Hz, 2H), 7.77 (dd, J=8.6 and 2.0 Hz, 1H), 7.64 (d, J=2.0 Hz, 1H), 7.46-7.41 (m, 3H), 7.39 (t, J=1.5 Hz, 1H), 7.34 (t, J=1.8 Hz, 1H), 7.17 (ddd, J=7.8, 2.3 and 1.3 Hz, 1H), 7.07 (d, J=8.6 Hz, 1H), 4.26-4.16 (m, 4H), 3.91-3.87 (m, 4H), 3.75-3.72 (m, 4H), 3.70-3.67 (m, 4H), 3.66-3.65 (m, 4H), 3.20 (s, 3H); ^{13}C NMR: (62.9 MHz, MeOH-d_4) δ 166.3, 161.5, 156.9, 152.3, 149.7, 148.6, 144.2, 139.9, 130.3, 127.3, 125.7, 125.4, 124.7, 123.5, 122.7, 122.6, 115.0, 113.1, 88.0, 71.80, 71.75, 71.59, 71.46, 70.49, 70.43, 70.31, 69.86, 53.5
7. The difference was easily seen for the protons of the pyridine rings, with a shift of 0.6 ppm downfield for the ortho-protons and 0.2-0.3 ppm downfield for the other protons.
8. This has been found by calculation and is in accord with X-ray crystallographic data: Coulter, P.; Windle, A. H. *Macromolecules* **1989**, *22*, 1129.
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