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SYNTHESIS AND PROPERTIES OF A NOVEL CAVITY-FORMING LIGAND-SYSTEM BASED ON DIPHENYLGLYCOLURIL

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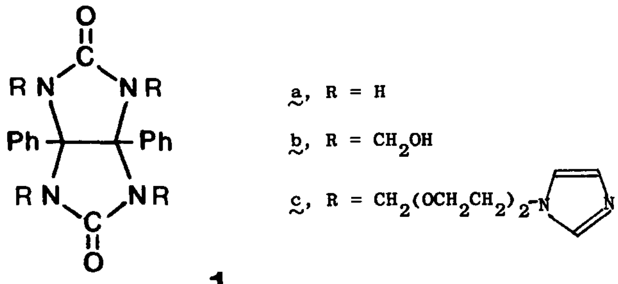
Abstract: The synthesis of a tetraimidazolyl ligand is described. Coordination to a metal centre affords a metallocryptand.

Enzymes are able to bind substrates selectively in an intramolecular cavity and position them favourably to an active centre. There is considerable interest in the design and construction of artificial systems which mimic these properties.[1]

In the present paper, we describe the synthesis of a molecule containing a cavity that is formed by coordination of a tetrapus ligand to a metal ion. The ligand is based on a glycoluril unit which has a rigid, bent configuration. Two phenyl substituents shield the convex side of this unit (1a).

Reaction of diphenylglycoluril (1a)[2] with paraformaldehyde in DMSO, using base as catalyst, yields the tetrahydroxymethyl derivative 1b (85%). The latter compound was reacted with 2-(2-chloroethoxy)ethanol in toluene using *p*-toluenesulfonic acid as catalyst. Subsequently, the product of this reaction was treated with sodium imidazolate in DMF to give the macroligand 1c as an oil (80%).[3]



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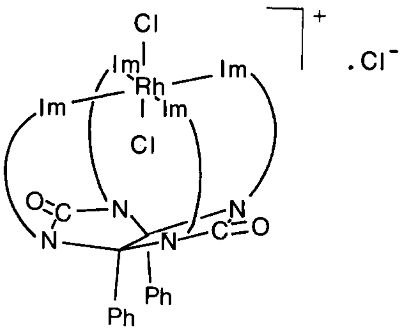
Treatment of **1c** with $RhCl_3.3H_2O$ in methanol gave the metallocryptand $[Rh(\mathbf{1c})Cl_2]Cl$ (**2**) in 57% yield. The proposed structure of this compound is confirmed by elemental analysis ($C_{48}H_{62}N_{12}O_{10}Cl_3Rh$), FAB mass spectroscopy (*m/e* 1162 $(M - Cl^- + Na^+)^+$),[4] conductivity measurements (1:1 electrolyte, Λ = 72 ohm^{-1} cm^2 mol^{-1})[5] and ^1H NMR analysis. The presence of two covalently bound *trans* chlorines is in agreement with the structure of $[RhL_4Cl_2]ClO_4$ (L = *N*-methylimidazole).[6]

Addition of **2**, dissolved in methanol to an excess of diethylether caused the complex to precipitate as a yellowish solid. According to ^1H NMR the precipitate contained exactly one equiv. of diethylether , which could not be removed by heating under vacuum (0.01 Torr) for 15 hours. We propose that the ether molecule is trapped inside the cavity which is defined by the glycoluril unit, the four ligating side arms, and the metal centre. Also a CPK model of **2** demonstrates that an ether molecule can be accomodated in the cavity. Complexation experiments in methanol indicate that charged guest molecules such as Li^+, Na^+, NH_4^+, etc. are not bound by complex **2**, probably because of electrostatic repulsion by the rhodium centre.

Reaction of the macroligand **1c** with $Pd(CH_3CN)_2Cl_2$ in methanol yields a complex (78%) analyzing as $C_{48}H_{62}N_{12}O_{10}Cl_2Pd$. The structure $[Pd(\mathbf{1c})]Cl_2$ (**3**) is supported by FAB and FD mass spectroscopy (*m/e* 1107 $(M - Cl^-)^+$, 1072 $(M - 2Cl^-)^+$),[4] conductivity measurements (1:2 electrolyte, Λ = 116 ohm^{-1} cm^2 mol^{-1}),[5] and ebulliometry (1:2 electrolyte, M = 1125 ± 75 in methanol).



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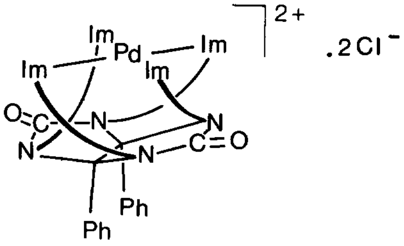

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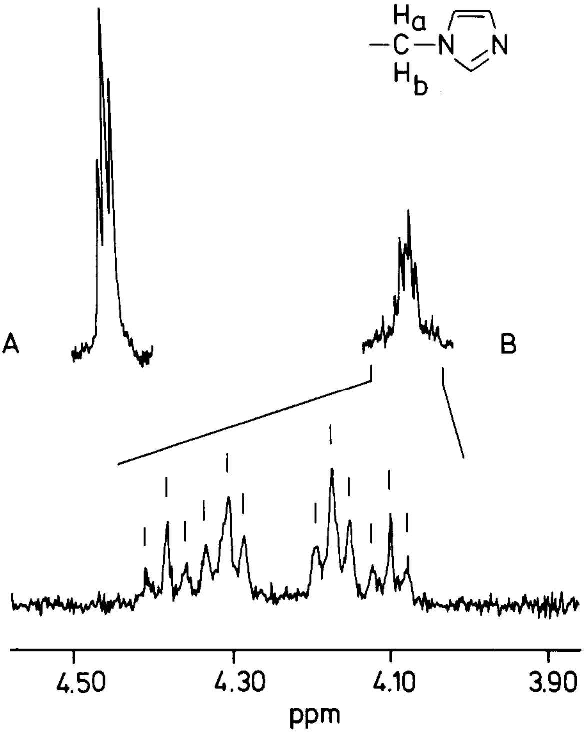
Figure 1. ^{1}*H NMR spectrum of complex* **2** *(A) and complex* **3** *(B) in the region 4 - 4.5 ppm.*



The spectroscopic properties of complex **3** differ appreciably from those of complex **2**. For instance, in the ^{1}H NMR spectrum of **3**, the CH_2Im-protons appear as an AB quartet split into triplets, implicating the protons to be chemically non-equivalent. In the rhodium complex these methylene protons show the expected AA'BB' pattern (Fig. 1). Another remarkable difference is that complex **3** does not bind guest molecules. We explain these features by the fact that in **3** no coordinated chloride is present in the cavity. The tetrapus ligand now has the possibility to stabilize the Pd(II) ion internally. CPK-models indicate that such an internal stabilization forces the molecule to take on a twisted comformation. In this structure the Pd(Im)$_4$-part is rotated either clockwise or counter-clockwise, with respect to the glycoluril unit. In this way a chiral structure is created. The ^{1}H NMR spectrum of **3** remains unaltered even at temperatures as high as 60 °C, indicating this twisted chiral structure to be relatively stable. It also shows that the two enantiomeric forms do not interconvert rapidly.

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