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Click reaction in the synthesis of novel thiophosphorylated ligands for electrochemical hydrogen evolution

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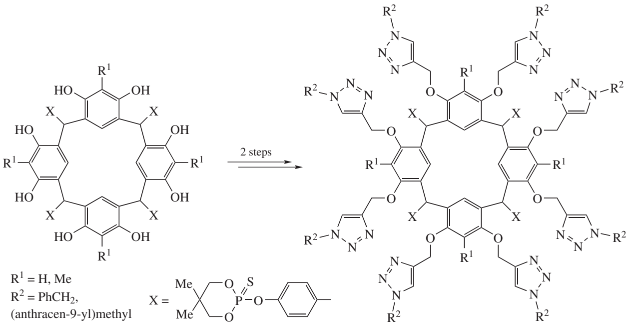
O-Propargylation of free hydroxyl groups in calix[4]resorcinols bearing thiophosphoryloxyphenyl substituents at the lower rim and possessing *cone* or *chair* conformations afforded new derivatives containing eight terminal alkyne groups. Their subsequent click reaction with azidomethylarenes led to the corresponding multifunctional triazole calix[4]resorcinols. Nickel complexes with such ligands show catalytic activity in hydrogen evolution reaction providing the decrease in potential of the direct acid reduction on glassy carbon electrode of 0.98 V.



Calix[4]resorcinols are relatively accessible macrocyclic compounds suitable for functionalization at *ortho*-positions of aromatic rings, hydroxyl groups on the upper rim of molecule, and functional substituents on a calixarene framework. Structural modification of calix[4]resorcinols by various functional groups alters selectivity and/or enhances the binding efficiency of different substrates along with an increase in their solubility, which extends potential applications of these macrocyclic ligands.[1–3]

Hydrolytically stable macrocycles with P–C bonds are most promising for further use. We previously synthesized new calix[4]-resorcinols bearing hydrolytically stable thiophosphoryl group as a substituent through the condensation of resorcinol and its derivatives with properly functionalized hydroxybenzaldehydes.[4–7] Nickel complexes of such compounds turned to be effective catalysts of electrochemical molecular hydrogen evolution from acid solutions.[8–10] We recently discovered that the modification of thiophosphorylated calix[4]resorcinols by aminomethyl groups *via* Mannich reaction improves the characteristics of such catalytic process and makes it possible to create even more effective catalytic systems with the maximum gain in energy.[11] To extend these studies, we suggested that functionalization of thiophosphorylated calix[4]resorcinols using popular click reaction[12–14] would provide derivatives with improved catalytic performance in question.

In this work, novel triazole-containing derivatives of thiophosphorylated calix[4]resorcinols were obtained employing the click reaction and catalytic activity of nickel complexes of the synthesized ligands in electrochemical hydrogen evolution from acid solutions was tested. O-Alkylation of calix[4]resorcinols **1a**,**b** and **1c** in *cone* and *chair* conformations, respectively, with propargyl bromide in the presence of freshly calcined K_2CO_3 afforded new calix[4]resorcinols **2a–c** bearing eight alkyne terminal groups in up to 99% yields (Scheme 1). The reaction was monitored by MALDI mass spectrometry and was stopped as soon as the mass spectrum showed only one peak for the corresponding target macrocycle (~24 h). Subsequent click reaction of compounds **2a–c** with benzyl azide or 9-(azidomethyl) anthracene in THF/H_2O (1:1) in the presence of $CuSO_4$/sodium ascorbate catalytic system at heating (60–65 °C, 24 h) gave novel calix- [4]resorcinols **3a–d** in yields up to 94% (see Scheme 1). The structures of synthesized compounds were proved by NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P), MALDI mass spectrometry and elemental analysis. The IR spectra of target products do not exhibit intrinsic absorption bands of C≡C and C≡C–H groups, which confirms the completion of the reaction.[†]

Note that NMR spectra of products **2a**,**b**, **3a**,**b**,**d**, which arise from the upper-rim modification of calixarenes **1a**,**b** in *cone* conformation as starting compounds, indicate the *boat* conformation. This is a general feature when bulky substituents are present in calixarene, and it is well documented.[4–6,15–18] In our case, there is a strong broadening of the signals for the protons and carbon atoms of resorcinol residues of a calixarene scaffold. In addition, in the case of bulky substituents, the situation is complicated by different opening angles of phenolic groups of the calixarene platform, which depend on the spatial arrangement of substituents. All these factors result in the variable chemical shifts of the signals in NMR spectra as observed in case of compound **3d**.

During analogous transformations of macrocycle **1c**, its *chair* conformation remains in all the products. Doubling of the signals for the protons of aromatic rings of resorcinol residues in calix[4]resorcinols possessing both *boat* and *chair* conformations can be observed in ^{1}H and ^{13}C NMR spectra, which indicates

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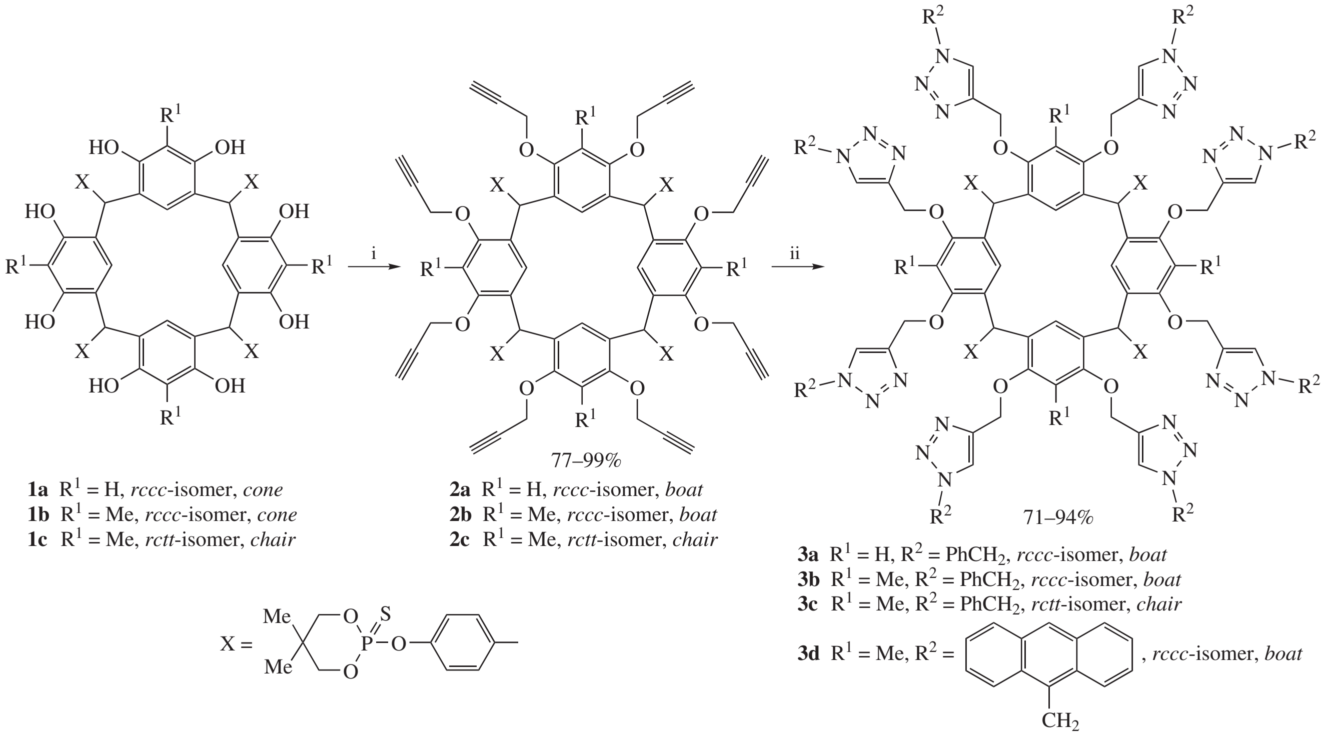
[†] For the synthesis and characteristics of compounds obtained, see Online Supplementary Materials.



Scheme 1 *Reagents and conditions*: i, $BrCH_2C{\equiv}CH$, K_2CO_3, MeCN, reflux; ii, $ArCH_2N_3$, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, THF/H_2O, reflux.

different, horizontal (h) and vertical (v), arrangement of opposite aromatic fragments relative to the macrocycle plane as for thiophosphorylated calix[4]resorcinols in our previous publications.[4–7]

Extensive studies in recent decades were aimed at the search for new high-performance catalytic systems for electrochemical hydrogen evolution in order to develop accessible and inexpensive catalysts for hydrogen energetics.[19–33] We recently showed that nickel complexes of thiophosphorylated calix[4]resorcinols including starting compounds **1a–c**, as well as their aminomethyl derivatives, were effective catalysts of electrochemical hydrogen evolution from acids.[8–11] The herein obtained new triazole-containing ligands **3a**,**b**,**d** were converted to the appropriate nickel complexes by analogy with the previously described[8] *in situ* reaction between equimolar amounts of a ligand and $Ni(BF_4)_2$. Using cyclic voltammetry, their catalytic activity in electrochemical hydrogen evolution from trifluoroacetic acid was studied.[‡] It was determined that in the case of complexes with ligands **3a**,**b**, the reduction potentials of Ni^{II} to Ni^0 approached –1.15 V *vs*. Ag/AgCl (Figure 1). Addition of proton donor (trifluoroacetic acid) to the solution of these complexes results in a catalytic current at the potential of nearly –1.12 V, which leads to the shift of the potential to anodic region by 60 mV (in the ligand **3b**) and 120 mV (**3a**) as compared to the catalytic potential of their precursors **1b** and **1a**, respectively. However, in this case, the catalytic efficiency is 0.04,[18] what allows one to consider the complex as the effective catalyst of this reaction. In addition, hydrogen is evolved on the surface of working electrode. The difference of the potentials between catalytic peak and the peak of heterogeneous reduction of trifluoroacetic acid on electrode amounts to 0.98 V in this case.

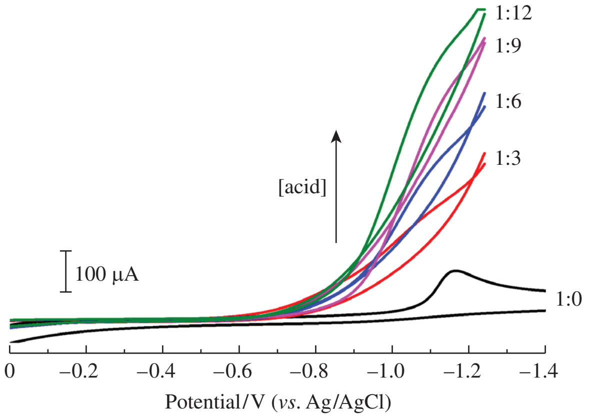


Figure 1 CVs of 1 mM $Ni(BF_4)_2$ with **3b** (1 : 1) in DMF in the presence of increasing amounts of TFA. Conditions: working electrode is glassy carbon, auxiliary electrode is Pt, supporting electrolyte is Bu_4NBF_4.

In the nickel complex of ligand **3d**, a reduction peak locates at more cathodic potential of –1.5 V (*vs*. Ag/AgCl). A current increasing is detected at the potential of –1.5 V in the presence of 10 mM (10 equiv.) of proton donor, and a further shift of the potential to cathodic range with an increase in the concentration of acid is observed, which renders this catalytic system the least attractive in this study.

In conclusion, this work demonstrates that thiophosphorylated calix[4]resorcinols can be easily and effectively modified *via* click reaction to afford new highly functionalized triazole-containing derivatives in high yields. Incorporation of triazole-containing functional groups to thiophosphorylated calix[4]resorcinol can cause the shift of the potential of catalytic hydrogen reduction to more anodic range (as compared to unsubstituted precursors) and lead to an increase in the difference between the potentials of catalytic peak and heterogeneous reduction of acid on electrode up to 0.98 V thus facilitating reduction on a nickel center. Triazole-containing calixarene ligands reveal higher catalytic activity *vs*. unmodified precursors, which seems promising for development of new high-performance catalytic systems for electrochemical hydrogen evolution processes.

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[‡] For the details of electrochemical studies, see Online Supplementary Materials.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.009.

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