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Organopalladium Complexes of Oxacalixarenes: Selecting the Lid for the Three-Dimensional Scaffold

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Supporting Information

ABSTRACT: The first organometallic (palladium) complexes of oxacalixarene molecules were prepared via oxidative addition of the C−I bond at the lower rim. The unique geometry of the oxacalixarene scaffold allowed for the selective introduction of new ligands at the top of the calixarene scaffold. Such coordination can be used to coordinatively link the opposing aromatic rings.

Rigid three-dimensional transition-metal calixarene complexes have received considerable attention as catalysts,[1] supramolecular hosts,[2] chemosensors[3] and in biomimetics.[4] In most cases, the metal center is coordinated to the oxygen atoms at the calixarene lower rim (Figure 1a).[5] While suitable for the early- and middle-row metals, such complexation generally limits the use of less oxophilic late transition metals because they tend to bind softer sites, such as the calixarene's π system.[6] Alternatively, the introduction of soft donors at the upper rim can lead to stable late-transition-metal complexes (Figure 1b).[7] To our knowledge, there are no examples of late-transition-metal calixarene complexes with the metal directly attached to the lower rim of a calixarene moiety. While such coordination is essential for the successful cross-coupling of the triflate groups,[8] the arylpalladium complexes were not isolated or characterized.[9] Against this background, it is surprising that the direct metalation of oxacalixarene molecules by late transition metals remained completely unexplored.[10] Only very recently have copper complexes of somewhat related pyridine-based azacalixarenes been reported;[11] however, intramolecular pyridine coordination was an integral part of the overall structure. In this work, we present the first studies of the aryl-bound palladium oxacalixarene complexes that show very interesting coordination properties relative to the calixarene cavity.

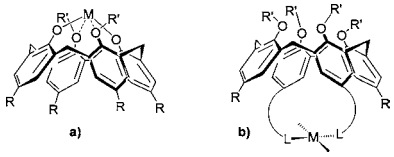
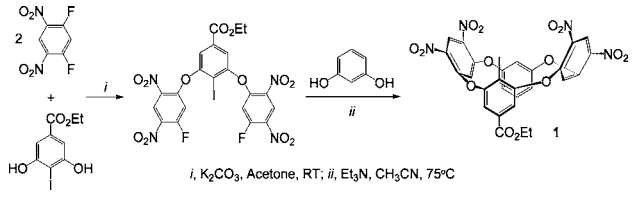


Figure 1. Metal coordination to calix[4]arenes.

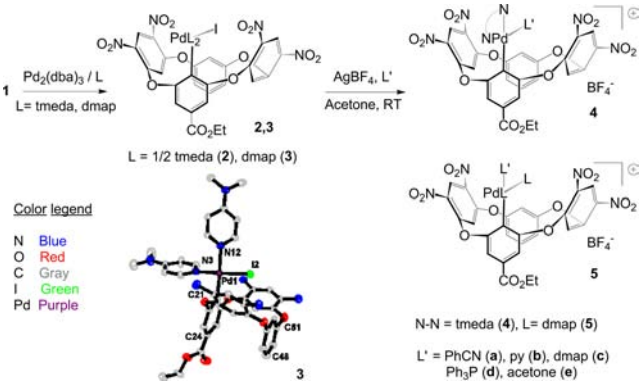
Unlike parent calix[4]arenes, oxacalixarenes can readily be assembled via a stepwise approach.[12] This method allows for the selective introduction of aromatic rings containing a readily cleavable halide function.[13] Thus, we prepared the iodocalixarene **1** in high yield using the synthetic approach shown in Scheme 1.

Scheme 1. Stepwise Synthesis of Oxacalixarene Ligands



The ethyl ester function in the para position was introduced to increase the solubility of the metal complexes. The reaction between **1** and the corresponding palladium(0) precursors resulted in clean formation of the oxidative addition products **2** and **3** (Scheme 2), which could be purified by crystallization. The

Scheme 2. Synthesis of Palladium(II) Complexes of Oxacalixarene 1



X-ray structure of complex **3** was determined and showed that the palladium atom is located in the center of a distorted square with a Pd−C distance of 1.998(4) Å. The presence of the bulky neutral donors forces the iodo ligand to "cap" the oxacalixarene cavity while the palladium center is surrounded by the nitro groups of the neighboring aromatic rings. These surroundings also prevent the associative substitution of the nitrogen-based ligands in **2** and **3**, which remain unchanged even upon stirring overnight with a 5-fold excess of Ph_3P. The cyclometalated aromatic ring and ring opposite to it are nearly parallel, with the distance between the opposing carbon atoms at the upper rim (C24---C48) being ca. 4.976 Å.

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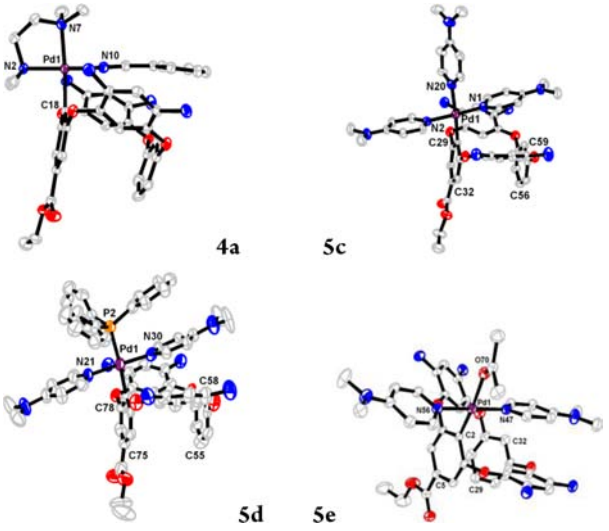


Figure 2. Molecular structures of the cations of **4a** and **5c**−**5e**. The hydrogen atoms and oxygen atoms of the nitro groups are omitted for clarity.

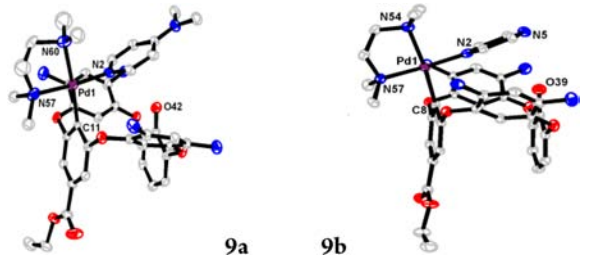
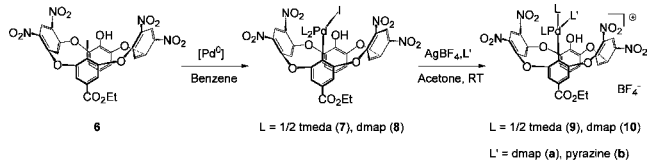


Figure 3. Molecular structures of **9a** and **9b**. The hydrogen atoms and oxygen atoms of the nitro groups are omitted for clarity.

Scheme 3. Palladium Complexes of the Hydroxyoxacalixarene 6



The enforced geometry in complexes **2** and **3**, where the iodo ligand points toward the center of the calixarene rim, opens up opportunities to introduce various ligands at this position. After removal of the iodide with $AgBF_4$, several donors can be selectively placed at the top of the calixarene scaffold, giving new cationic complexes **4** and **5** (Scheme 2). Interestingly, the aromatic groups of the cavity-oriented ligands in **4a** and **5c** (Figure 2) lie flat atop the calixarene unit, making a perfect lid at the metal-bound side of its pinched cone. The X-ray structure of **4a** shows that the presence of the large *N*,*N*-dimethylaminopyridine (dmap) ligand has a relatively minor effect on the opening of the oxacalixarene cavity compared with **3**, with the metalated ring still being roughly parallel to the opposing one. Additionally, in contrast to the chelating tetramethylenediamine (tmeda, **4**), the presence of the monodentate dmap allows for the selective placement of the incoming ligand in the position trans to the aromatic carbon atom. For example, the reaction of **3** with $AgBF_4$ followed by the addition of Ph_3P gave the triphenylphosphine complex **5d**, where the bulky phosphine ligand occupies the above position. While the stronger trans influence of Ph_3P causes elongation of the Pd−C bond [2.082(8) Å vs 1.998(4) and 2.016(6) Å in **3** and **4a**, respectively), the calixarene cavity remains largely intact (Figure 2). In all cases, the metalated ring is nearly parallel to the opposing aromatic ring of the oxacalixarene moiety, with the distance between C75 and C55 at the upper opening being 4.980 Å. Significantly, when the small and weakly bound acetone ligand is coordinated to the palladium center (**5e**), the complex geometry dramatically changes in comparison to complexes **3**, **5a**, and **5b**. In particular, the internal dmap ligand no longer points toward the center of the oxacalixarene rim. Instead, it becomes involved in apparent π-stacking interactions with one of the nitro-substituted aromatic rings of the oxacalixarene scaffold (Figure 3). Distortion of the oxacalixarene moiety is further manifested in the loss of the nearly parallel alignment of the metalated ring and ring opposite to it, leading to the significantly smaller opening of the upper rim of only 3.896 Å.

The selective introduction of various ligands at the top of the calixarene cavity can lead to the development of new supramolecular structures, recognition of small donor molecules, and catalysis. Because the oxacalixarene scaffold is generally predisposed to place the incoming ligand in the area between the two opposing aromatic rings, we decided to explore an oxacalixarene system where an additional binding group is attached to the aromatic ring opposed to the carbopalladated one. To this end, we prepared the oxacalixarene **6**, which has the phenolic moiety at the aromatic ring opposed to the iodine anchor. Upon the addition of the palladium(0) precursor, complexes **7** and **8** were obtained as dark-yellow crystalline materials (Scheme 3). The ^{1}H NMR spectra of the new complexes were similar to those in **2** and **3** except for the lack of a signal of the aromatic hydrogen atom, replaced by the OH group. The X-ray structure of the dmap complex **8** was also similar to that of **3**. The addition of $AgBF_4$ in acetone in the presence of a donor molecule gave the corresponding cationic complexes **9** and **10** (Scheme 3). Although the hydroxy group can participate in hydrogen bonding with the $-NMe_2$ substituent of the dmap ligand, no such interaction was observed in the X-ray structure of the tmeda complex **9a** (Figure 3), suggesting that the tilt at the palladium center, which minimizes steric repulsions with the calixarene scaffold, prevents formation of the hydrogen bond. Similarly, using a smaller pyrazine ligand did not provide evidence for such interaction in **9b** (Figure 3). It is likely that a more flexible hydrogen donor in place of the OH group is required to provide a better fit to the incoming nitrogen donor.

Interestingly, when complex **8** bearing the monodentate dmap ligands was treated with $AgBF_4$ in acetone in the presence of dmap, a light-gray precipitate of the presumed cationic **10a** was formed. The solid was insoluble in tetrahydrofuran or CH_2Cl_2; however, it was possible to dissolve it in dimethyl sulfoxide (DMSO), hot MeOH, or *N*,*N*-dimethylformamide (DMF). In the last two cases, dissolution took place after several minutes. The ^{1}H NMR spectrum of the DMSO-d_6 solution of the precipitate showed very broad lines for both the calixarene scaffold and the palladium-coordinated dmap ligands. Because all other palladium complexes reported in this work, including the structurally similar **5c**, showed very good solubility in acetone and exhibited sharp signals in the ^{1}H NMR spectra, we tentatively propose that the observed precipitate of **10a** has a polymeric structure because of the hydrogen bonding between the dmap ligands and the phenolic OH group. Because there are three dmap molecules per palladium, we do not know which of

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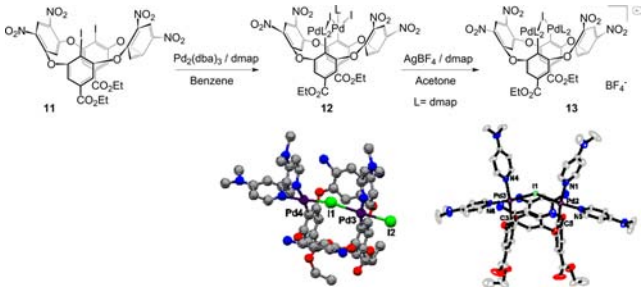
Scheme 4. Synthesis of the Iodo-Bridged Bimetallic Palladium Complexes 12 and 13[a]



[a]All hydrogen atoms and oxygen atoms of the nitro groups are omitted for clarity.

the three interacts with the formally acidic hydrogen atom. When no dmap was added to a solution in the reaction between **8** and $AgBF_4$, no precipitate was observed and the ^1H NMR spectrum revealed relatively sharp signals of the cationic palladium intermediate. An addition of Ph_3P instead of dmap leads to a new complex that shows sharp signals in both ^1H and ^{31}P NMR spectra. The chemical shift of the phosphine ligand at 16.4 ppm is very similar to that in **5d**, suggesting that it occupies the position trans to the aryl group. Thus, the presence of the dmap ligand at this position appears to be essential for the formation of insoluble **10a**. Dissolution of **10a** in DMF followed by reprecipitation with diethyl ether did not change the ^1H NMR spectrum (broad signals in DMSO-d_6), suggesting that its proposed polymeric structure is thermodynamically controlled.

Finally, we decided to explore the chemistry of oxacalixarenes bearing two metal centers at the opposing aromatic rings. Because of the constrained geometry of oxacalixarenes, such complexation can lead to the ligand bridges between the two metals at the top of the calixarene cavity. Thus, we prepared the diodocalixarene **11** and treated it with $Pd_2(dba)_3$/dmap (Scheme 4). Under these conditions, a new complex **12** was formed in high yield, which showed the presence of three different dmap ligands by ^1H NMR spectroscopy. X-ray analysis of **12**[14] revealed that there are two palladium atoms bound to the opposing aromatic rings of the oxacalixarene moiety. Importantly, one of the iodo ligands is coordinated to *both* metals, demonstrating the feasibility of the placement of bridging ligands between the two metal centers over the oxacalixarene cavity. Removal of the second iodide with $AgBF_4$ in the presence of an additional dmap molecule led to the formation of complex **13** (Scheme 4), which showed the symmetrical arrangement of the coordinated ligands in the NMR spectra. The X-ray structure confirmed that the remaining iodo ligand is equally shared by the palladium atoms in the overall symmetrical environment.

In summary, we prepared the first transition-metal (palladium) complexes of oxacalixarene molecules. These complexes can be modified to selectively bind various external ligands that behave as a lid at the wide opening of the calixarene scaffold. To our knowledge, such complexation is unprecedented in calixarene chemistry and its utilization in molecular recognition and catalysis is presently being explored in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for compounds **1**−**13** and X-ray analysis data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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