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Communication

Structural Consequences of Two-Fold Deprotonation of Sumanene: Embedding Two Cp-rings into a Nonplanar Carbon Framework

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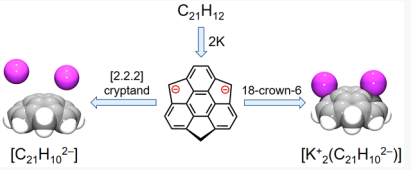
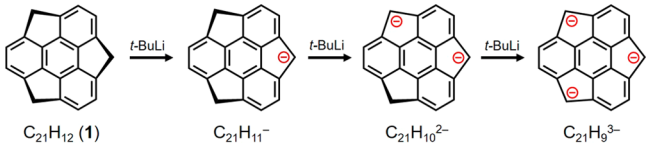
ABSTRACT: The controlled 2-fold deprotonation of bowl-shaped sumanene (**1**) with K metal provides access the sumanenyl dianion that was crystallized in the presence of [2.2.2]cryptand and 18-crown-6 ether with the corresponding potassium(I) counterions. The X-ray crystallographic study of $[\{K^+([2.2.2]cryptand)\}_2(C_{21}H_{10}^{2-})]$ (**2**) revealed the formation of a "naked" sumanenyl dianion, while in $[\{K^+(18\text{-crown-}6)\}_2(C_{21}H_{10}^{2-})]$ (**3**) two K^+ ions bind to the *exo*-surface of the bowl. The detailed structural analysis confirms the formation of two Cp-like rings embedded into a nonplanar carbon framework of $C_{21}H_{10}^{2-}$ serving as sites for alkali metal coordination in **3**.



Sumanene (**1**, $C_{21}H_{12}$), representing a C_{3v} symmetric fragment of C_{60}-fullerene, attracted significant attention due to its interesting electronic and conducting properties.[1] Sumanene can also serve as a novel bowl-shaped ligand providing its convex (*exo*-) and concave (*endo*-) surfaces for metal binding.[2]

Sumanene (**1**) has a deep and rigid carbon framework with three sp^3 hybridized carbon atoms at the benzylic positions.[1a] Therefore, the sumanenyl mono-, di-, and trianions can be generated selectively by treatment of **1** with a strong base like *t*-BuLi (Scheme 1).[3] The resulting bowl-shaped anions

Scheme 1. Stepwise Deprotonation of Sumanene

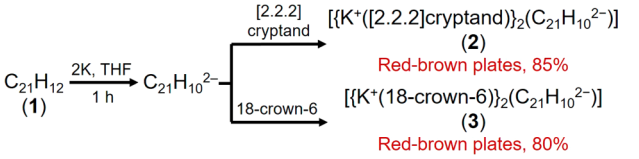


incorporate Cp-like sites into a large carbon framework and have been utilized in the formation of the convex-bound mononuclear and trinuclear zirconocene complexes.[4] Utilizing two sumanenyl monoanions, we have recently prepared a unique double concave sandwich with the Cs^+ ion trapped between two π bowls.[5] In contrast, when using an *in situ* generated mixture of sumanenyl di- and trianions, we have prepared a remarkable potassium-rich supramolecular sandwich.[6] Up to date, no dianions of sumanene have been selectively isolated and structurally characterized, thus thwarting their practical use in preparation of new organometallic complexes. Furthermore, the isolation and characterization of naked anionic species will give an insight on the aromaticity and delocalization of negative charges for π bowls.

Herein, we aim to develop the controlled preparation of sumanenyl dianions in the presence of different countercation-trapping agents, which enables the studies of structural perturbation and metal binding of bowl-shaped sumanene upon 2-fold deprotonation.

The chemical reactivity of sumanene ($C_{21}H_{12}$, **1**) with K metal was investigated in THF at room temperature (Scheme 2). The stepwise deprotonation of sumanene is accompanied

Scheme 2. Preparation of Dianionic Sumanenyl



by the aromatization of the five-membered rings of the bowl, and the process can be monitored by UV−vis and ^1H NMR spectroscopies. The reaction first proceeds through an orange-red color which is consistent with the monoanionic stage,[5,7] followed by a dark brown color indicating the formation of the sumanenyl dianion (Figures S1 and S2). By limiting the time of the K-induced reaction of **1** as 1 h and by adding [2.2.2]cryptand or 18-crown-6 ether to the resulting solution, dark red-brown crystals have been successfully isolated in good yield and fully characterized (see the Supporting Information for more details). The X-ray diffraction study confirmed the formation of two products with K^+ counterions, namely $[\{K^+([2.2.2]cryptand)\}_2(C_{21}H_{10}^{2-})]$ (**2**, crystallized with four

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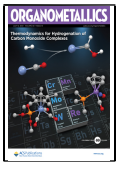

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interstitial THF molecules as **2**·4THF) and [{K^+(18-crown-6)}$_2$($C_{21}H_{10}^{2-}$)] (**3**). The ^{1}H NMR spectroscopic investigation of crystals **2** and **3** was also carried out (Figures S3 and S4), and the data are consistent with the previous *in situ* ^{1}H NMR characterization with *t*-BuLi and K metal.[3,6] Notably, the chemical shifts for the protons at the deprotonated carbon sites in **2** and **3** (5.63 and 5.61 ppm) were observed at 0.25 ppm lower field as compared to [2Li^+($C_{21}H_{10}^{2-}$)] (5.38 ppm) prepared *in situ* with *t*-BuLi.[3] It suggests that the negative charge is better delocalized in **2** and **3** than in [2Li^+($C_{21}H_{10}^{2-}$)], as the inclusion of K^+ ions into the cryptand and crown ether facilitates the formation of uncomplexed sumanenyl anions in solution.

In the crystal structure of **2** (Figure 1), the two independent K^+ ions are fully trapped by [2.2.2]cryptand molecules and

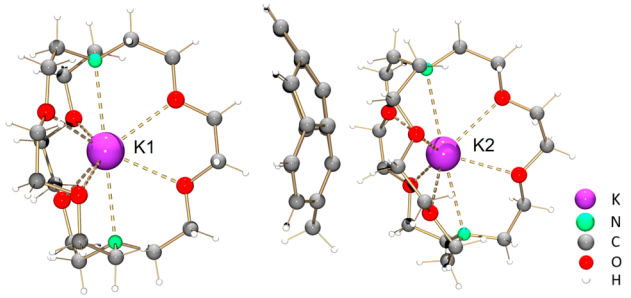


Figure 1. Crystal structure of [{K^+([2.2.2]cryptand)}$_2$($C_{21}H_{10}^{2-}$)] (**2**), ball-and-stick model.

separated from the anionic bowl, giving the first example of a "naked" sumanenyl dianion. The K···O (2.717(8)−2.948(19) Å) and K···N (2.856(11)−3.069(12) Å) distances are close to those previously reported.[8]

In the crystal structure of **3** (Figure 2), there are two independent K^+ ions that are bound in a η^5-fashion to the two

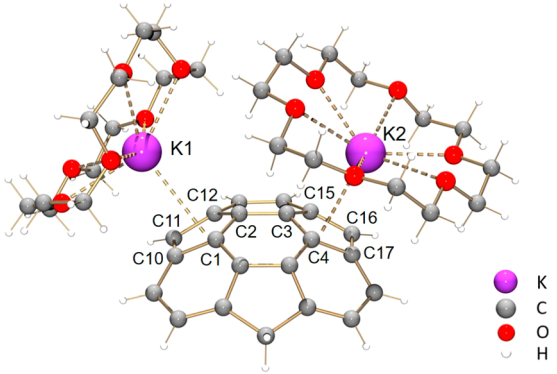


Figure 2. Crystal structure of [{K^+(18-crown-6)}$_2$($C_{21}H_{10}^{2-}$)] (**3**), ball-and-stick model.

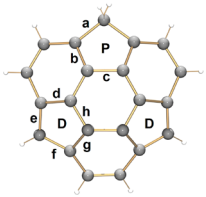
deprotonated five-membered rings at the convex surface of $C_{21}H_{10}^{2-}$. The K···C distances span a broad range of 2.947(3)−3.511(3) and 3.003(3)−3.254(3) Å, respectively (Table 1). Each K^+ ion is also hexacoordinated by an 18-crown-6 ether molecule, with the K···O distances ranging over 2.801(3)−3.045(2) Å. Notably, the K2 ion sits closer to the bowl than K1 with the K to centroid distance of 2.882(3) Å (vs. 3.031(3) Å), which could stem from the repulsion between two {K^+(18-crown-6)} cationic moieties. All K···C and K···O distances are comparable to those reported in the literature.[6,8c,e,f]

Table 1. K−C Bond Length Distances (Å) in 3

bond	distance	bond	distance
K1−C1	3.511(3)	K2−C3	3.102(3)
K1−C2	3.438(3)	K2−C4	3.003(3)
K1−C10	3.260(3)	K2−C15	3.254(3)
K1−C11	2.947(3)	K2−C16	3.165(3)
K1−C12	3.136(3)	K2−C17	3.106(3)

The structural analysis of the sumanene core perturbation upon 2-fold deprotonation can be illustrated by direct comparison of the neutral parent and the $C_{21}H_{10}^{2-}$ bowl in **2** and **3** (Table 2). The formation of the sumanenyl dianion is

Table 2. Key C−C Bond Distances (Å)[a] in $C_{21}H_{12}$ (1) and in $C_{21}H_{10}^{2-}$ (2 and 3), along with a Labeling Scheme



	1[1a]	**2**	**3**
a	1.547(4)	1.519(12)	1.547(4)
b	1.396(4)	1.376(12)	1.390(4)
c	1.381(4)	1.487(12)	1.428(4)
d	1.396(4)	1.478(12)	1.431(4)
e	1.547(4)	1.457(12)	1.431(4)
f	1.547(4)	1.374(12)	1.453(4)
g	1.396(4)	1.429(12)	1.409(4)
h	1.381(4)	1.444(12)	1.406(4)
B. D.	1.120(4)	1.222(12)	1.154(4)

[a]Values are averaged. B.D. = bowl depth. P and D stand for protonated and deprotonated rings, respectively.

accompanied by a curvature increase of the bowl core (Figure S9). In **1**, the bowl depth is about 1.12 Å, which is increased to 1.22 Å in **2** (1.15 Å in **3**). Importantly, the 2-fold deprotonation of sumanene leads to the increasing aromaticity of two five-membered rings (scheme in Table 2), which can be reflected by the C−C bond length changes. In **1**, the C−C bonds **e** and **f** are 1.55 Å, in contrast, these bond lengths in both dianions are reduced to about 1.43 Å. Meanwhile, the C−C bonds **c**, **d**, **g**, and **h** are elongated in **2** and **3**. In addition, the bond length alternation (BLA) values also clearly demonstrate aromatization of the deprotonated rings in $C_{21}H_{10}^{2-}$. In **1**, the BLA value of the five-membered rings is 0.063 Å. In contrast, the BLA values are 0.097 Å for the P-ring vs. 0.019 Å averaged for the two D-rings of the sumanenyl dianion in **3**.[9]

In the solid-state structure of **2**, the {K^+([2.2.2]cryptand} moieties interact with both *endo* and *exo* surfaces of the dianionic bowls, thus forming a 2D layer through multiple C−H··· π interactions ranging from 2.391(12) to 2.753(12) Å (Figure 3a). In **3**, only the *endo* cavities of the bowls are filled with the {K^+(18-crown-6)} moieties from the adjacent molecules, thus forming 1D columns through multiple C−H···π interactions (2.510(4)−2.547(4) Å), which are further linked into a 2D layer (C−H···π: 2.599(4) Å) (Figure 3b,c).

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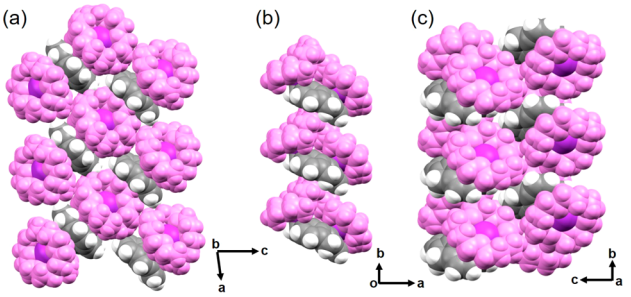

Figure 3. Solid-state structures of (a) **2** and (b, c) **3**, space-filling models.

In this work, the controlled synthesis of sumanenyl dianions has been developed and confirmed by isolation of the first crystalline products of $C_{21}H_{10}^{2-}$ with two different potassium counterions, namely {K^+([2.2.2]cryptand)} and {K^+(18-crown-6)}. Both products have been fully characterized using X-ray crystallography and spectroscopic methods. The use of different secondary ligands allowed switching metal binding "off" and "on" in **2** and **3**, respectively. The isolation of the "naked" dianion in **2** illustrated the aromatization of two five-membered rings that served as binding sites in the π-complex with two potassium cations in **3**. This work opens access to new ligand transfer agents based on dianionic sumanenyl with two Cp-like rings embedded into a curved carbon framework. These reagents can be utilized in the preparation of novel transition and lanthanide-based complexes, expanding their organometallic chemistry and applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00295.

Materials and methods, X-ray structural details, and UV−vis and NMR spectroscopy data (PDF)

Accession Codes

CCDC 2083097−2083098 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(9) A similar trend in the BLA values change is observed in **2**, although the disorder of the sumanene core (see the Supporting Information) may affect the accuracy of the calculated values in this case.

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