The First Crystalline Alkali Metal Salt of a Benzenoid Radical Anion without a Stabilizing Substituent and of a Related Dimer: X-ray Structures of the Toluene Radical Anion and of the Benzene Radical Anion Dimer Potassium-Crown Ether Salts

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We recently described the reduction of various tris(substituted cyclopentadienyl)lanthanoid compounds by potassium metal in the presence of 18-crown-6 (L) in benzene[1] or toluene.[2] This prompted us to investigate the K−L−ArH reducing system (ArH = PhMe or C_6H_6). Previously it was inferred, from EPR spectra at low temperatures, that treatment of a dilute solution of a crown ether in ArH or 1,3,5-$Me_3C_6H_3$ with a potassium mirror yielded the potassium salt of the corresponding radical anion;[3] a solid obtained from such a reaction using benzene was subjected to C_6H_6/C_6D_6 exchange and to pyrolysis.[4] Several crystalline alkali metal salts of radical anions derived from a polynuclear arene or a poly(phenyl- or trimethylsilyl)benzene have been prepared and structurally characterized.[5] Benzene (or toluene) radical anions prepared as Cs^+ salts[6] were shown to dimerize readily in THF at −70 °C, 3,3′-bis(cyclohexa-1,4-diene) (or the 1,1′-dimethyl analogue from toluene) being isolated upon hydrolysis. We now report on three crystalline products **1**−**3**, isolated from K−L−ArH systems, their preparation being summarized in Scheme 1.

The black, paramagnetic, crystalline (EPR: $g = 2.00296$) salt **1** was obtained in good yield in a slow, low-temperature reaction between K, 18-crown-6 and toluene in THF[7] (or PhMe). It was sparingly soluble in toluene. In THF it gave a deep blue solution, which readily decomposed at room temperature, the crystalline potassium enolate **3** being a significant product. The salt **1** crystallizes as a tight ion pair, shown in Figure 1.[8] The crown encapsulates the potassium cation, which is bound in an approximate η^6-fashion to the planar C_6H_5 ring, the K−C(1 to 6) distances varying from 3.044(5) Å (to C(5), a *m*-carbon atom) to 3.311 Å (to C(2)). The C−C bond lengths of the radical anion vary widely, the C(5)−C(6) bond being by far the longest and the adjacent C(5)−C(4) and C(1)−C(6) bonds, the shortest. The endocyclic bond angles range from 117.4(6)° at C(6) to 123.4(6)° at C(4).

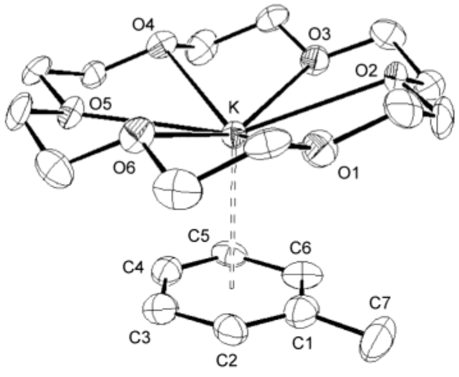
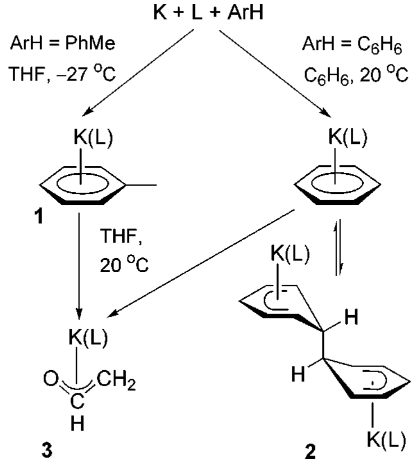


Figure 1. ORTEP drawing of **1**. 30% probability ellipsoids are shown.

Scheme 1



Treatment of potassium with 18-crown-6 in benzene at ambient temperature yielded initially a deep green-brown solution, from which the dark red salt **2** crystallized in moderate yield at ∼10 °C.[9] It was sparingly soluble in both benzene and THF, but dissociated therein to give a solution containing the radical anion $C_6H_6^{\bullet-}$, as evident from its characteristic EPR spectroscopic signal (septet, $g = 2.0067$, $a(^1H) = 3.63$ G);[10] by contrast, solid **2** revealed only a low intensity similar signal, attributed to a minute $K(L)(C_6H_6)$ contaminant. The 3,3′-bis(cyclohexa-1,4-dienediyl) ligand is the central dianion of the crystalline salt **2**, being η^5:η^5-bound in a transoid fashion to each of the two crown-encapsulated potassium cations, Figure 2;[11] the η^5-K−C distances range from 2.985(7) to 3.268(5) Å. The only previously X-ray-characterized examples of this ligand are found in $[\{Mn(CO)_3\}_2$-

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[7] Synthesis of **1**: A solution of 18-crown-6 (0.94 g, 3.6 mmol) and toluene (2 mL, 19 mmol) in 100 mL of THF was added to a K mirror (0.120 g, 3.0 mmol) at −30 °C, and the mixture was stored at −27 °C for 4 days until all K had dissolved. The solution was filtered through a glass microfiber filter, and 20 mL of hexanes were added. Crystallization for 1 day at −27 °C yielded 0.696 g (59%) of black microcrystalline **1**. X-ray quality crystals were obtained by slow crystallization from pure THF at −27 °C.

[8] Crystal data for **1** at 173 K: $C_{19}H_{32}KO_6$, FW = 395.55, orthorhombic, $Pna2_1$, $a = 19.7525(11)$ Å, $b = 9.8664(6)$ Å, $c = 10.9577(6)$ Å, $V = 2135.5(2)$ Å^3, $Z = 4$. The final R factor was 0.048 for 2245 reflections with $I > 2\sigma(I)$ (wR2 = 0.124 for all data). GOF = 1.049.

[9] Synthesis of **2** and **3**: A solution of 18-crown-6 (0.285 g, 1.1 mmol) in benzene (∼40 mL) was added to a K mirror (0.040 g 1.0 mmol) in a two-section glass apparatus sealed under vacuum. All K had dissolved after 1 h at room temperature; crystallization at +10 °C gave 0.201 g (50%) of **2** as dark red plates, mp 83−85 °C (dec). From the mother liquor 0.021 g (5%) of **3** was isolated as slightly yellow needles, mp 107−108 °C (dec).

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[11] Crystal data for **2** at 173(2) K: $C_{36}H_{60}K_2O_{12}$, FW = 763.04, orthorhombic, *Pnma*, $a = 26.1009(8)$ Å, $b = 16.3832(7)$ Å, $c = 9.1300(3)$ Å, $V = 3904.1(2)$ Å^3, $Z = 4$. The final R factor was 0.064 for 2233 reflections with $I > 2\sigma(I)$ (wR2 = 0.166 for all data). GOF = 1.062.

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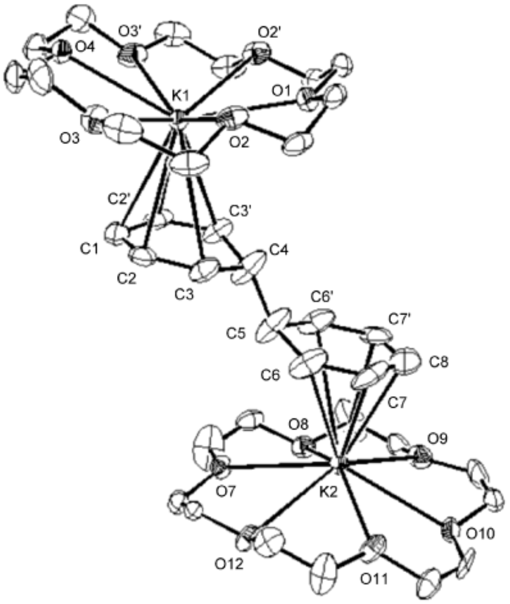

Figure 2. ORTEP drawing of **2**. 30% probability ellipsoids are shown.

(μ-η^5:η^5-C_6H_6−C_6H_6)] (**4**)[12] and [{Fe(η^5-C_5H_5)}$_2$(μ-η^5:η^5-C_6H_6−C_6H_6)].[13] The fold angle in each C_6H_6 moiety of **2** is much smaller (15.7 and 12.5° about the C(3)···C(3′) and C(6)···C(6′) vectors, respectively) and the C(sp^3)−C(sp^3) bond of 1.461(11) Å is much shorter than in **4** (41.8(1)° and 1.547(4) Å, respectively)[12a] attributed to the different ligand-to-metal bonding modes: ionic for **2**, but covalent for **4** (having short η^5-Mn−C bond lengths, av. 2.17 Å). It is surprising that the C(sp^3)−C(sp^3) bond of **2** is so readily cleaved in solution.

The light yellow, crystalline potassium enolate [K(L)(η^3-OCH=CH$_2$)] (**3**) was first isolated as a byproduct in the synthesis of **2** in benzene.[9] It was obtained also as a major product upon dissolving **1** or **2** (decolorized in 1 h) in THF at ambient temperature. The source of **3** was probably carbanionic attack on THF (or 18-crown-6). Cleavage of 15-crown-5 was observed in a reaction of the potassium alkalide K(15-crown-5)$_2$K with oxetane or methyloxirane, yielding $H_2C{=}CHO(C_2H_4O)_3CH_2CH_2$-OK as the main product derived from the crown ether.[14] Thus, it is established by spectroscopy and by trapping that THF is cleaved by anions (such as lithium hydrocarbyls or the lithium salt of a poly-*N*-centered nucleophile), generating the lithium enolate.[15] X-ray-characterized metal (Li,[15e−g] Ti,[15i] Y[15g,h]) OCH=CH$_2$ complexes have generally shown this ligand to function in a bridging (μ_2-[15g,h] or μ_3-[15e,f]) fashion; only in [Ti(η^5-C_5H_5)$_2$-(OCHCH$_2$)$_2$][15i] does it behave as an *O*-centered terminal ligand. The salt **3** crystallizes as a mononuclear contact ion pair shown in Figure 3,[16] in which the enolato-ligand is bound to the crown-encapsulated potassium cation (the K−O distances range from 2.79 to 2.99 Å; cf., 2.82 to 2.95 Å in **1** and 2.81 to 2.99 Å in **2**) in an unprecedented η^3-chelating fashion; that is, **3** is best described as a potassium 1-oxaallyl. The distances from the K atom to the O, C(H), and C(H$_2$) atoms are 2.6692(9), 3.0279(13), and 3.2020(17) Å, respectively; the O−C and C−C bond lengths in the enolate are 1.2814(16) and 1.345(2) Å, respectively, indicative of π-electron delocalization (all of the other structurally characterized acetaldehyde enolates[15] have the O−C bond longer than the C−C), and the O−C−C angle is 129.08(14)°.

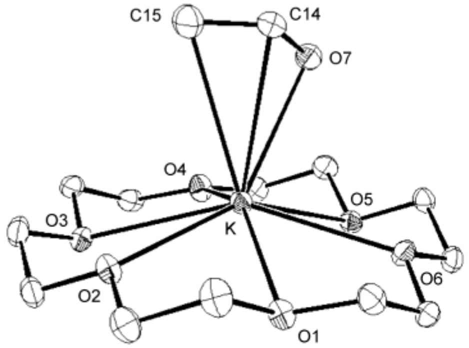

Figure 3. ORTEP drawing of **3**·1/2C_6H_6. 30% probability ellipsoids are shown. Solvate benzene molecules are omitted for clarity.

The different outcome of the reactions in the K−L−ArH systems for ArH = PhMe or C_6H_6, yielding crystalline **1** or **2**, respectively, is attributed to the low solubility of the crystalline dimer **2**, as well as electronic effects of the Me group making dimerization of **1** unfavorable.

Acknowledgment. We thank the EPSRC for support of this work.

Supporting Information Available: Tables of crystal data, structure solution and refinement, tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for salts **1**, **2**, and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Crystal data for **3**·1/2C_6H_6 at 173 K: $C_{17}H_{30}KO_7$, FW = 385.51, monoclinic, *C*2/*c*, *a* = 26.6844(6) Å, *b* = 8.5157(3) Å, *c* = 22.0803(5) Å, β = 125.751(2)°, *V* = 4072.0(2) Å^3, *Z* = 8. The final *R* factor was 0.034, for 4104 reflections with $I > 2\sigma(I)$, (wR2 = 0.091 for all data). GOF = 0.939.