

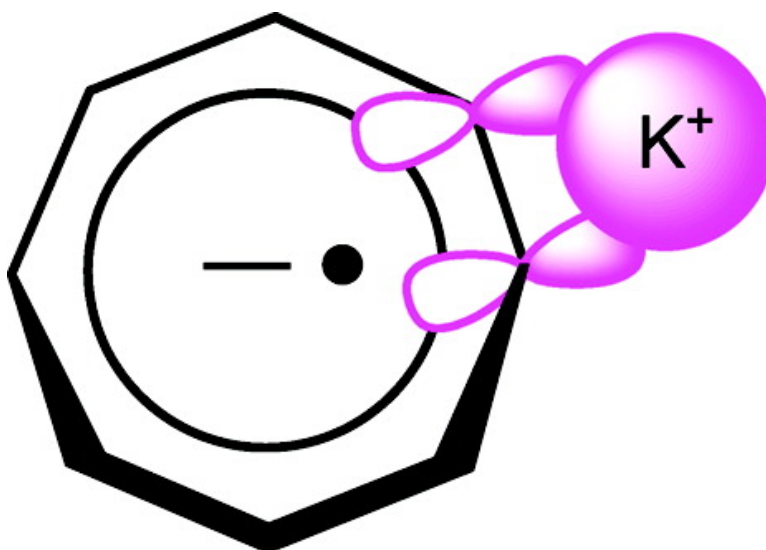
Communication

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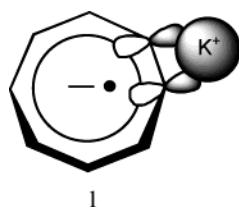
## The Cyclooctatriene- $\eta^2$ -ynyl Potassium Zwitterionic Radical: Evidence for a Potassium Organometallic

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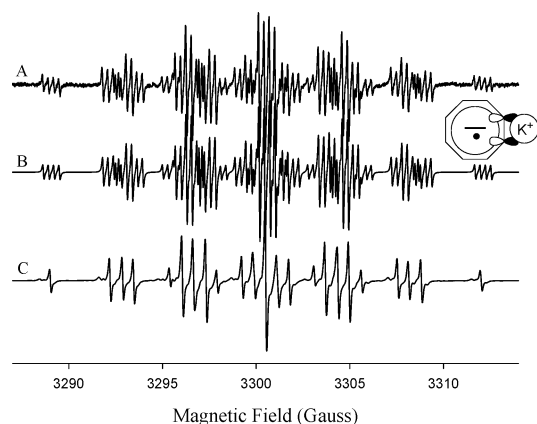
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The most fundamental interaction in molecular chemistry is the Coulombic attraction between positive and negative species. Under conditions where this interaction is mediated by a solvent, the phenomenon is called ion pairing.<sup>1</sup> Perhaps the most striking manifestation of ion pairing is represented by the unambiguous EPR observation of nuclear hyperfine splitting ( $a_M$ ) from the alkali metal counterion of organic anion radicals, such as those of naphthalene ( $C_{10}H_8$ ) and cyclooctatetraene ( $C_8H_8$ ).<sup>2</sup> The interactions between these anion radicals and the alkali metal cation are completely electrostatic in nature, and the metal cation “oscillates” over the plane of the anion radical.<sup>3</sup> The anion radical of [8]annulyne ( $C_8H_6$ )<sup>4a</sup> reveals a very unusual overlap of the empty 4s orbital of the potassium cation with the p-orbitals of the alkyne moiety, structure 1.



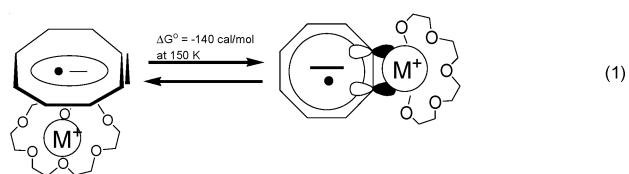
Under high vacuum, the low-temperature ( $-100\text{ }^\circ\text{C}$ ) dehydrohalogenation of bromocyclooctatetraene ( $BrC_8H_7$ ) with potassium *tert*-butoxide in tetrahydrofuran (THF)<sup>4b</sup> followed by immediate exposure to a freshly distilled potassium mirror results in the one-electron reduction of the  $C_8H_6$ , and consequent trapping of the kinetically unstable [8]annulyne as its anion radical. Upon EPR analysis, this anion radical exhibits three pairs of proton couplings and a potassium metal splitting, see Figure 1. Such a prominent  $a_K$  is unique in an annulene system,<sup>4c</sup> as the small gyromagnetic ratio of the K nucleus ( $\gamma_K = 1.2483 \times 10^3 \text{ rad G}^{-1} \text{ s}^{-1}$ ) ordinarily renders  $a_K$  too small to be observed.<sup>1,2,5</sup>

As a consequence of a much larger  $\gamma$ ,  $\gamma_{Na} = 7.0761 \times 10^3 \text{ rad G}^{-1} \text{ s}^{-1}$ ,  $C_8H_8^{\bullet-}, Na^+$  and  $C_{10}H_8^{\bullet-}, Na^+$  yield EPR spectra revealing large  $a_{Na}$ 's.<sup>2,5</sup> Lowering the temperature increases solvation which, in turn, attenuates  $a_M$ . Even the large sodium splitting disappears when the temperature is lowered to  $-80\text{ }^\circ\text{C}$ .<sup>2,6</sup> It also disappears after the addition of 18-crown-6, which encapsulates the  $Na^+$ .<sup>7</sup> Ion pairing still persists in the presence of 18-crown-6; it simply involves the entire crown- $Na^+$  complex. Because 18-crown-6 has an even greater affinity for  $K^+$  than for  $Na^+$ , the addition of crown to potassium anion radical ion pairs is even more effective in attenuating the cation-anion magnetic interaction.<sup>7</sup> Surprisingly, EPR analysis of potassium reduced  $C_8H_6$ , to which a molar excess of 18-crown-6 has been added, reveals the presence of two species. One species exists in the absence of hyperfine splitting from the  $K^+$ , while the other species exhibits an  $a_K$  of 0.214 G, Figure 2. The ratio of the two species is independent of the amount of anion radical or crown ether present (as long as 18-crown-6 is in excess).



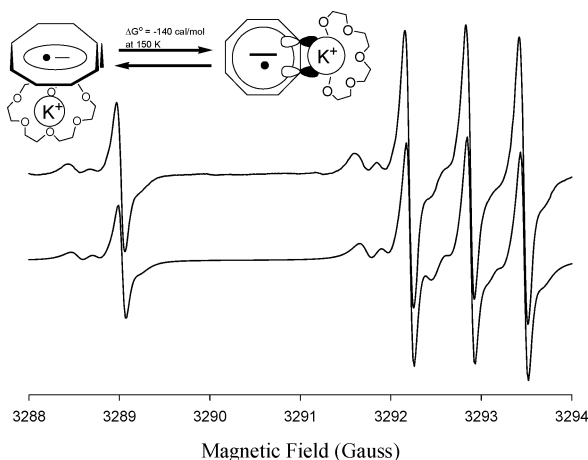
**Figure 1.** (A) X-band EPR spectrum, recorded at 150 K, of a THF solution containing the cyclooctatriene- $\eta^2$ -ynyl potassium zwitterion radical. (B) Computer generated simulation using  $a_H$ 's of 3.19 G (2 H's), 3.88 G (2 H's), and 4.455 G (2 H's), and an  $a_K$  of 0.285 G for one potassium ion. The peak-to-peak line width ( $\Delta w_{pp}$ ) is 0.07 G. (C) X-band EPR spectrum, recorded at 150 K, of a THF solution that contains the potassium reduced  $C_8H_6$  in the presence of a molar excess of 18-crown-6. The spectrum reveals two species with one exhibiting a  $K^+$  splitting (see Figure 2). The ostensibly dominant EPR signal results from coupling to three sets of proton pairs with  $a_H$ 's of 3.185, 3.855, and 4.445 G.

These two species are isomers of each other and are in thermodynamic equilibrium, reaction 1. At  $-120\text{ }^\circ\text{C}$ , the encapsulating power of the crown is insufficient to prevent the spin delocalization into the  $K^+$  ion, but it does attenuate the  $a_K$  by 0.072 G. Computer simulations reveal that  $K_{eq}$  for reaction 1 ( $M = K$ ) is  $1.6 \pm 0.1$ .



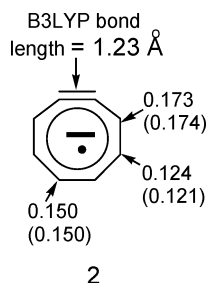
$a_{Na}$ 's are always larger than are  $a_K$ 's for ion paired species in THF. However, the B3LYP predicted distance between carbons 1 and 2 (1.23 Å) is smaller than the ionic radius of  $K^+$ , which is 1.33 Å;<sup>8</sup> this condition is not met in the case of  $Na^+$  where the ionic radius is only 0.95 Å.<sup>8</sup> Hence, an analogous hyperfine splitting from the sodium nucleus is not to be anticipated.

The low-temperature sodium metal reduction ( $-100\text{ }^\circ\text{C}$ ) of the dehydrohalogenation product of  $BrC_8H_7$  with sodium *tert*-butoxide in THF followed by EPR analysis (150 K) reveals a well-resolved ( $\Delta w_{pp} = 0.085 \text{ G}$ ) spectrum of  $C_8H_6^{\bullet-}$  that is best simulated with couplings of  $a_H = 4.455 \text{ G}$  (2 H's), 3.185 G (2 H's), and 3.88 G (2 H's). No hyperfine splitting from the sodium counterion is observed! Hence, a metal-ligand interaction, analogous to that depicted in structure 1, does not form in the  $Na^+, C_8H_6^{\bullet-}$  ion paired



**Figure 2.** (Upper) Downfield expansion of the X-band EPR (150 K) spectrum shown in Figure 1C. The ostensive dominant spectrum is due to the  $\text{K}^+$ -crown ether complex ion paired  $\text{C}_8\text{H}_6^{\bullet-}$ . Close examination reveals the presence of a species exhibiting a metal splitting. (Bottom) Computer simulation generated by combining the spectra for the cyclooctatriene- $\eta^2$ -ynyl potassium zwitterion radical and  $\text{K}^+$ -18-crown-6, $\text{C}_8\text{H}_6^{\bullet-}$  ion pair in a 1.6/1 ratio. The spectrum for the cyclooctatriene- $\eta^2$ -ynyl potassium zwitterion radical was simulated using  $a_{\text{H}}$ 's of 3.19 G (2 H's), 3.88 G (2 H's), and 4.455 G (2 H's), and an  $a_{\text{K}}$  of 0.214 G (1 K), with  $\Delta w_{\text{pp}} = 0.17$  G. The ion paired anion radical spectrum was simulated using  $a_{\text{H}}$ 's of 3.185 G (2 H's), 3.855 G (2 H's), and 4.445 G (2 H's), with  $\Delta w_{\text{pp}} = 0.085$  G. The spectrum for the zwitterion radical is shifted 0.135 G downfield from that of the ion pair.

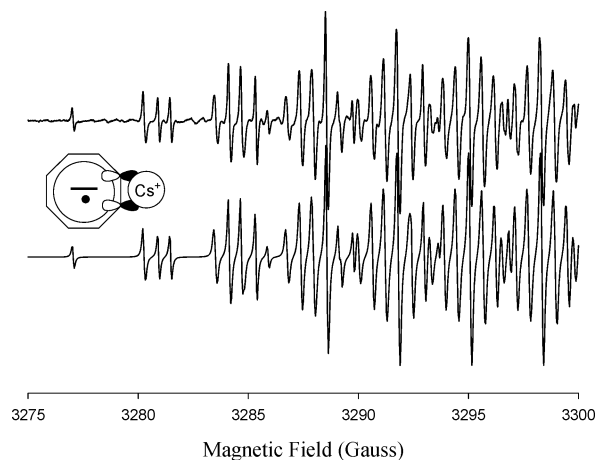
complex. Using a  $Q$  value of 26.5 G (the total spectral width for  $\text{C}_8\text{H}_8^{\bullet-}$ ),<sup>9</sup> along with the McConnell relationship ( $a_{\text{H}} = Q\rho$ ),<sup>10</sup> we obtained the  $p_z$  spin densities ( $\rho$ ) from the observed proton coupling constants. They prove to be in excellent agreement with those predicted from B3LYP/6-31G\* calculations, structure 2.<sup>11</sup>



It is expected that the larger alkali metal cations, such as  $\text{Cs}^+$ , would overlap with the alkyne moiety better than does potassium and exhibit a dramatic metal splitting upon EPR analysis. When the reduction is carried out with Cs metal, a huge Cs splitting ( $\gamma_{\text{Cs}} = 3.51 \times 10^3 \text{ rad G}^{-1} \text{ s}^{-1}$ ) of 3.26 G is observed, Figure 3. Consequently, the  $\text{Cs}^+$  (ionic radius = 1.69 Å)<sup>8</sup> must interact strongly with the alkyne moiety, as does the  $\text{K}^+$  system, yielding the cyclooctatriene- $\eta^2$ -ynyl cesium zwitterion radical.

EPR analysis of the cesium reduced  $\text{C}_8\text{H}_6$  with a molar excess of 18-crown-6 gave a result analogous to that of the potassium system where two species are present, and the relative amounts of each are independent of the concentrations of 18-crown-6 and anion radical present. The normally ion paired species, with the cation hovering over the plane of the  $\pi$ -system, shows no hyperfine splitting from the  $\text{Cs}^+$ , while the other (the cyclooctatriene- $\eta^2$ -ynyl cesium zwitterion radical) exhibits an  $a_{\text{Cs}}$  of 3.426 G (see Supporting Information). Computer simulation shows that  $K_{\text{eq}}$  for reaction 1 ( $M = \text{Cs}$ ) is  $3.5 \pm 0.1$  at  $-120$  °C.<sup>12</sup>

The alkyne moiety in  $\text{C}_8\text{H}_6^{\bullet-}$  is unique. It is highly strained and conjugated into a  $4n + 1$   $\pi$ -electron annulyne. This renders it



**Figure 3.** (Upper) Downfield half of an X-band EPR spectrum, recorded at 150 K, of a THF solution of Cs reduced  $\text{C}_8\text{H}_6$ . (Lower) Computer generated simulation using  $a_{\text{H}}$ 's of 3.20 G (2 H's), 3.879 G (2 H's), and 4.427 G (2 H's), and an  $a_{\text{Cs}}$  of 3.26 G (1 Cs), with  $\Delta w_{\text{pp}} = 0.085$  G.

susceptible to the formation of large alkali metal organometallics as shown in structure 1. The situation in the benzyne system may be analogous, and we predict that when the environmental and thermal conditions are met for the observation of the [6]annulyne anion radical, the cyclohexadiene- $\eta^2$ -ynyl potassium zwitterion radical will be found.

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**Supporting Information Available:** EPR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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