

(bpy)<sub>2</sub>(OH)Ru<sup>IV</sup>ORu<sup>VO</sup>(bpy)<sub>2</sub><sup>4+</sup>/(bpy)<sub>2</sub>(OH)<sub>2</sub>Ru<sup>III</sup>ORu<sup>IV</sup>(OH)(bpy)<sub>2</sub><sup>4+</sup> couple.

The pH dependences of the dimer couples dictate that  $\Delta E^{\circ'}$  for the Cl<sup>-</sup>/Cl<sub>2</sub> interconversion should be zero at pH ≈ 3.5. As expected from the thermodynamic potentials, significant catalytic (2Cl<sup>-</sup> → Cl<sub>2</sub>) currents are observed for the dimer/Cl<sup>-</sup> system only below pH 3. Above pH 4 Cl<sub>2</sub> (or HOCl) oxidizes the Ru(III,III) or Ru(III,IV) dimers, and in basic solution OCl<sup>-</sup> can be used to drive the dimer-catalyzed oxidation of water to oxygen. The results of the pH-dependence studies lead to two significant conclusions: (1) Even at pH 2 where  $\Delta E^{\circ'} \approx 0.07$  V, significant catalytic currents are observed, showing that a remarkably low overpotential exists for the catalytic oxidation of chloride. (2) The oxidation of (bpy)<sub>2</sub>(OH)<sub>2</sub>Ru<sup>III</sup>ORu<sup>IV</sup>(OH)(bpy)<sub>2</sub><sup>4+</sup> by solutions containing chlorine at pH > 4 show that the catalytic system can operate in either direction as might have been expected on the basis of microscopic reversibility.

Oxidation of solutions containing (bpy)<sub>2</sub>Ru<sup>IV</sup>O(OH)<sub>2</sub><sup>2+</sup> at a potential sufficient to give (bpy)<sub>2</sub>Ru<sup>VI</sup>(O)<sub>2</sub><sup>2+</sup> also results in the electrocatalytic oxidation of chloride to chlorine. The details of the catalyzed reaction are similar to those described for the dimer, but the following points should be noted: (1) Loss of catalytic activity occurs over extended electrolysis times because of chloride anation to give (bpy)<sub>2</sub>Ru(OH)<sub>2</sub>Cl<sup>+</sup> and its higher oxidation state components. (2) The active oxidation catalyst appears to be Ru(VI) via the (bpy)<sub>2</sub>Ru<sup>VI</sup>(O)<sub>2</sub><sup>2+</sup>/(bpy)<sub>2</sub>Ru<sup>IV</sup>O(OH)<sub>2</sub><sup>2+</sup> couple. (3) In the absence of chloride, (bpy)<sub>2</sub>Ru<sup>VI</sup>(O)<sub>2</sub><sup>2+</sup> decomposes slowly to give O<sub>2</sub> (by GC) and an, as yet unidentified, complex of Ru(III).

Catalytic, chemically modified electrodes based on the monomer and dimeric couples have been prepared on carbon paste electrodes by the following procedures: (1) The electrodes were coated with *p*-chlorosulfonated polystyrene (-CH<sub>2</sub>(p-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl)-)<sub>n</sub>, which was hydrolyzed and deprotonated to form a polyanionic film as described elsewhere.<sup>7</sup> (2) The dimeric or monomeric catalysts were ion-exchanged into the film-coated electrodes to achieve apparent surface coverages ( $\Gamma_{app}$ )<sup>8</sup> of up to 10<sup>-10</sup> mol/cm<sup>2</sup> for the dimer and 10<sup>-9</sup> mol/cm<sup>2</sup> for the monomer. A monomer-incorporated carbon paste electrode ( $\Gamma_{app} \approx 7 \times 10^{-10}$  mol/cm<sup>2</sup>)<sup>11</sup> held at a constant potential of 1.20 V in a 0.1 M HClO<sub>4</sub> solution containing 5.0 M NaCl gave an initial catalytic current density of 8 mA/cm<sup>2</sup> that slowly decreased to 0.5 mA/cm<sup>2</sup> after 20 min. One useful feature associated with the catalytic properties of the electrodes is that the loss mechanism associated with chlorine anation can be reversed simply by cycling the potential of the coated electrode from +0.2 to +1.20 V in a 0.1 M HClO<sub>4</sub> solution free of Cl<sup>-</sup>. After several minutes, reaquation of the bound chloro groups occurs, which regenerates the diaquo catalytic sites, and the electrodes regain their full catalytic activity for the generation of Cl<sub>2</sub>.

We are currently investigating the mechanistic details of the Cl<sup>-</sup> oxidation reactions. Hopefully such details will give insight into both the heterogeneous oxidation of Cl<sup>-</sup> to Cl<sub>2</sub> at RuO<sub>2</sub>-impregnated electrodes and into the design of stable, chemically modified electrodes for the interconversion of Cl<sub>2</sub> and Cl<sup>-</sup>.

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**Registry No.** *cis*-(bpy)<sub>2</sub>Ru<sup>III</sup>(OH)<sub>2</sub><sup>2+</sup>, 72174-09-5; (bpy)<sub>2</sub>Ru<sup>III</sup>(OH)<sub>2</sub>ORu<sup>III</sup>(OH)<sub>2</sub>(bpy)<sub>2</sub><sup>4+</sup>, 56110-87-3; (bpy)<sub>2</sub>(OH)<sub>2</sub>Ru<sup>III</sup>ORu<sup>IV</sup>(OH)(bpy)<sub>2</sub><sup>4+</sup>, 86045-59-2; (bpy)<sub>2</sub>Ru<sup>IV</sup>O(OH)<sub>2</sub><sup>2+</sup>, 84988-22-7; (bpy)<sub>2</sub>Ru<sup>VI</sup>(O)<sub>2</sub><sup>2+</sup>, 84988-24-9; Cl<sup>-</sup>, 16887-00-6; Cl<sub>2</sub>, 7782-50-5; C, 7440-44-0.

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 (8) Apparent surface coverages ( $\Gamma_{app}$ ; moles per square centimeter) were calculated by using the equation  $\Gamma_{app} = Q_c/nFA$ .  $Q_c$  is the total charge obtained by planimetric integration of the reductive component of the Ru(III)/Ru(II) or Ru(III,IV)/Ru(III,III) cyclic voltammetric waves,  $n$  is the number of electrons per molecule reduced,  $F$  is Faraday's constant, and  $A$  is the electrode area in square centimeters.

## On the Nature of the Bicyclo[3.2.1]octa-3,6-dien-2-yl Anion. A <sup>13</sup>C NMR Spectroscopic Study<sup>†</sup>

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The title anion **1** is the most widely cited example of homoaromaticity in anionic systems.  $\pi$ -Delocalization was suggested to account for the rapid base-catalyzed H/D exchange at C-4 in bicyclo[3.2.1]octa-2,6-diene (**2**)<sup>1</sup> in comparison with bicyclo[3.2.1]oct-2-ene, and further experimental support was provided by the <sup>1</sup>H NMR spectrum of **1**.<sup>2,3</sup>

Two recent theoretical investigations<sup>4,5</sup> did not find a homoaromatic stabilization for **1** and related anions; a third one,<sup>6</sup> however, came to the opposite conclusion. Here we wish to report results that on an experimental basis give a clear insight into the nature of **1**.



**1**, R<sup>1</sup> = R<sup>2</sup> = H  
**1-d**, R<sup>1</sup> = D; R<sup>2</sup> = H  
**1-d<sub>2</sub>**, R<sup>1</sup> = R<sup>2</sup> = D  
**2**, R = H  
**2-d<sub>3</sub>**, R = D

Table I shows the <sup>13</sup>C NMR parameters of **1**,<sup>7</sup> its 2-deuterio derivative **1-d**,<sup>8</sup> its 2,4-dideuterio derivative **1-d<sub>2</sub>**,<sup>9</sup> and, for comparison, those of **2** and its 2,4,4-trideuterio derivative **2-d<sub>3</sub>**.<sup>10</sup> Based on the known chemical shifts of simple allyl anions,<sup>11,12</sup> the assignments in the spectrum of **1** are straightforward.

The most striking feature in the spectrum of **1** is the upfield shift of the C-6,7 resonance in comparison with **2** by 39.0 and 48.5 ppm, respectively. Two interpretations of this effect may be advanced: (i) Anion **1** is in fact the bishomoaromatic species **1d**. Then, the shielding of C-6,7 could be the consequence of the charge transfer from the allyl anion portion. (ii) Anion **1** consists of a rapidly equilibrating mixture of the allyl anion derivative **1a** and its tricyclic and tetracyclic isomers **1b** and **1c**, respectively (Scheme I). In this case, which was once considered but rejected,<sup>2</sup> C-6,7 would adopt in part the character of a cyclopropyl carbon and that of a carbanionic center, which would account for the shielding observed.

<sup>†</sup> Dedicated to Professor John D. Roberts on the occasion of his 65th birthday.

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(10) Prepared from **2** with Me<sub>2</sub>SO-*d*<sub>6</sub> and KOC(CH<sub>3</sub>)<sub>3</sub> as described.<sup>1</sup>  
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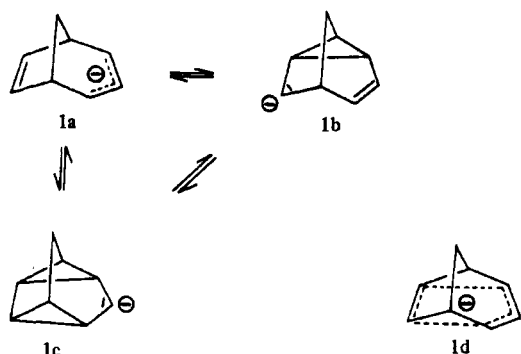
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Table I.  $^{13}\text{C}$  Chemical Shifts (ppm from  $\text{Me}_4\text{Si}$ ), One-Bond  $^{13}\text{C}$ -H Coupling Constants (Hz), and Some Deuterium Isotope Effects on the  $^{13}\text{C}$  Chemical Shifts<sup>a</sup> of **1**<sup>b</sup> and **2**

compd, solvt, temp, K	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1, <sup>c</sup> DME- <i>d</i> <sub>10</sub> , 310	40.48 (d 135)	58.76 (d 157)	120.55 (d 140)	58.76 (d 157)	40.48 (d 135)	91.37 (d 155)	91.37 (d 155)	32.17 (t 130)
1, <sup>c</sup> THF- <i>d</i> <sub>8</sub> , 310 <sup>d</sup>	40.45 40.49	58.59 58.77	120.31 120.50	58.59 58.77	40.45 40.49	91.10 91.49	91.10 91.49	31.99 32.11
1- <i>d</i> , <sup>c,e</sup> DME- <i>d</i> <sub>10</sub> , 310	40.38	58.43	120.53	58.53	40.52	90.87	90.87	32.08
2, <sup>f</sup> CDCl <sub>3</sub> , 310	40.22 38.78 <sup>g</sup>	57.54 134.17	119.63 123.99	57.64 28.78	40.36 38.43 <sup>g</sup>	88.84 130.36 <sup>h</sup>	88.84 139.82 <sup>h</sup>	31.69 40.81
	(d 145)	(d 161)	(d 160)	(t 127)	(d 141)	(d 168)	(d 169)	(t 132)
Deuterium Isotope Effects (ppm) Relative to <b>1</b> and <b>2</b> , Respectively <sup>i,j</sup>								
1- <i>d</i> , <sup>k</sup> THF- <i>d</i> <sub>8</sub> , 310	-0.14	-0.29	-0.13	-0.20	0.00	-0.07	-0.07	0.00
1- <i>d</i> , <sup>k</sup> THF- <i>d</i> <sub>8</sub> , 310	-0.14	-0.49	-0.25	-0.49	-0.14	-0.14	-0.14	0.00
2- <i>d</i> , <sup>k</sup> CDCl <sub>3</sub> , 310	-0.12	-0.15	-0.23	-0.84	-0.17	+0.04	+0.10	0.00

<sup>a</sup> Obtained from a Bruker WM 400 spectrometer operating at 100.61 MHz. <sup>b</sup> Gegenion K<sup>+</sup>. <sup>c</sup> Internal reference THF,  $\delta$  26.50 and 68.38 relative to  $\text{Me}_4\text{Si}$ . <sup>d</sup> Samples with different concentrations: upper line, lower concentration; lower line, higher concentration. <sup>e</sup> These chemical shifts are not appropriate to calculate the deuterium isotope effects, since they result from a measurement in the absence of **1**. <sup>f</sup> Internal references  $\text{Me}_4\text{Si}$ . <sup>g</sup> Assignment may be exchanged. <sup>h</sup> This assignment has been established by means of decoupling experiments. <sup>i</sup> Error  $\approx 0.01$  ppm. <sup>j</sup> Negative sign denotes shielding. <sup>k</sup> Determined from the spectra of a 1:1:1 and a 1:2:4 mixture of **1**, 1-*d*, and 1-*d*<sub>2</sub>. <sup>l</sup> Determined from the spectrum of a 1:4 mixture of **2** and 2-*d*<sub>1</sub>.

## Scheme 1



Deuterium isotope effects on  $^{13}\text{C}$  chemical shifts have been utilized with great success to distinguish between the different types of carbocations.<sup>13</sup> A few applications in carbanion chemistry have also been published.<sup>14</sup> The spectra of the deuterated species 1-*d* and 1-*d*<sub>2</sub> decide unambiguously between the above alternatives. If **1a-c** were equilibrating, the population of these species should be changed in 1-*d* and 1-*d*<sub>2</sub> relative to **1**, since a deuterium favors its position on a cyclopropyl carbon over that on an olefinic  $\text{sp}^2$ -hybridized carbon.<sup>15</sup> Given that C-2,4 in **1a** behave as olefinic  $\text{sp}^2$ -hybridized carbons, the proportions of **1b** and **1c** should be increased in 1-*d* and 1-*d*<sub>2</sub>. Consequently, upfield shifts would be expected in the spectra of these compounds relative to that of **1** especially for the resonance of C-6,7.

As shown in Table I the deuterons in 1-*d* and 1-*d*<sub>2</sub> cause small upfield shifts of nearly all signals with a maximum of 0.49 ppm at C-2,4, the carbons binding the deuterons in 1-*d*<sub>2</sub>. On comparison with literature data<sup>16</sup> the order of magnitude characterizes

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these upfield shifts as being intrinsic rather than equilibrium effects. Thus only a single species, i.e., **1d**, is involved. This is emphasized by the finding that only one bridgehead carbon responds to the deuterium substituent in 1-*d*, probably the adjacent C-1 (-0.14 ppm), while the effect decreases to zero at the remote C-5, a situation typical for intrinsic isotope effects.<sup>17</sup> For comparison the deuterium effects of 2-*d*<sub>3</sub> have been included. Interestingly, those at C-6 and C-7 are deshielding<sup>18</sup> in contrast to the values in 1-*d* and 1-*d*<sub>2</sub>, providing evidence that in **1** there are direct bonding interactions between the allyl anion termini and the ethylenic unit, namely, a C-2-C-7 and a C-4-C-6 bond. Small shift variations on different concentrations in the same solvent and on solvent change (**1** in DME-*d*<sub>10</sub> vs. THF-*d*<sub>8</sub>) as well as the upfield shifts at low temperatures (up to 2.03 ppm at C-6,7 in 1-*d*, DME-*d*<sub>10</sub>, 213 vs. 310 K) indicate an equilibrium between solvent-separated and contact ion pairs.<sup>19</sup>

A consideration of the  $^{13}\text{C}$  chemical shifts of cyclopentadiene and cyclopentadienyl anion reveals that the conversion **2**  $\rightarrow$  **1** brings about much larger upfield shifts than predicted as the effect of the newly generated and cyclicly delocalized negative charge. The chemical shift of the five carbons of cyclopentadiene sum up to 571.6 ppm,<sup>20</sup> those of its anion to 515.6 ppm.<sup>11,20</sup> Hence a total effect of -56.0 ppm results on deprotonation of cyclopentadiene. The abstraction of a proton of C-4 in **2** causes a total effect of about -136 ppm, however, as calculated from the sums of the chemical shifts of C-2, C-3, C-4, C-6, and C-7 in **2** and **1**.

We ascribe these additional 80 ppm to the increased coordination number of C-2,4 and C-6,7 in structure **1d** as compared with standard  $\text{sp}^2$ -hybridized carbons. Because of the homoaromatic<sup>21,22</sup>  $\pi$ -bonds C-2-C-7 and C-4-C-6 these carbons should adopt hybridizations intermediate between  $\text{sp}^2$  and  $\text{sp}^3$ .

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