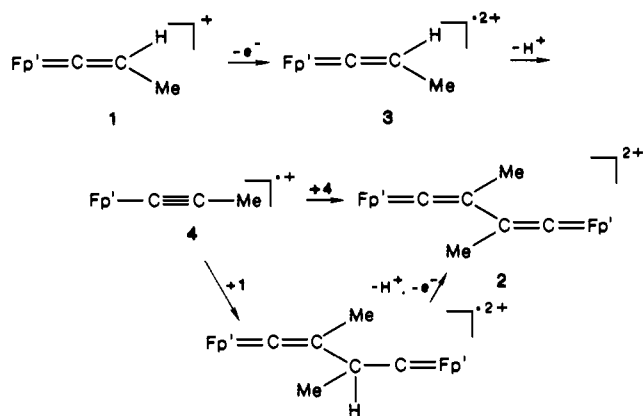


Scheme I



a few cases oxidation apparently occurs at a bound ligand, leading to C-C<sup>14a</sup> or S-S<sup>13c,d</sup> bond formation. Complex **2** may form by one-electron oxidation of **1** to a radical dication **3**, followed by deprotonation to **4** and subsequent coupling according to Scheme I. Other mechanistic possibilities including hydrogen atom abstraction from **1** to give **4** cannot be ruled out at this time. Attempts to oxidize alkynyl complex  $[\text{Fe}(\text{C}\equiv\text{CMe})(\text{dppe})(\text{Cp})]$  directly to **2** by using copper(II), silver(I), and anodic oxidation were unsuccessful, suggesting that acidic protons are required for the formation of **2**.

The oxidative coupling of vinylidene ligands is significant in several contexts. Potential oxidants  $\text{C}_7\text{H}_7^+$ ,  $\text{PhN}_2^+$ , and halogens act as electrophiles rather than oxidants toward  $[\text{Ru}(\text{C}\equiv\text{CPh})(\text{PR}_3)_2(\text{Cp})]$ ,<sup>17</sup> and aerial oxidation of ruthenium vinylidene complexes leads to oxidative cleavage of the vinylidene C=C bond.<sup>1,17d</sup> Oxidative coupling to form **2** may represent a significant difference between the iron and ruthenium systems. However, the anionic vinylidene complex  $\text{Li}[\text{Mo}(\text{C}=\text{CHCMe}_3)\{\text{P}(\text{OMe})_3\}_2(\text{Cp})]$  is oxidatively coupled to a bis(alkylidyne) complex without hydrogen loss.<sup>18</sup> The vinylidene coupling reaction may provide useful insights into the oxidative coupling of terminal alkynes using copper(II),<sup>19</sup> as well as chain-growth reactions of putative vinylidene fragments on heterogeneous catalysts.<sup>2</sup>

**Acknowledgment.** We thank the U.S. Department of Energy for financial assistance, Peter Nickias for NMR spectra, and John Gladysz for a preprint of ref 3.

**Supplementary Material Available:** Listings of bond distances and angles (Table I), positional and thermal atomic parameters (Table III), parameters for fixed atoms (Table IV), and anisotropic thermal parameters (Table V) (10 pages); observed and calculated structure factors (Table II) (34 pages). Ordering information is given on any current masthead page.

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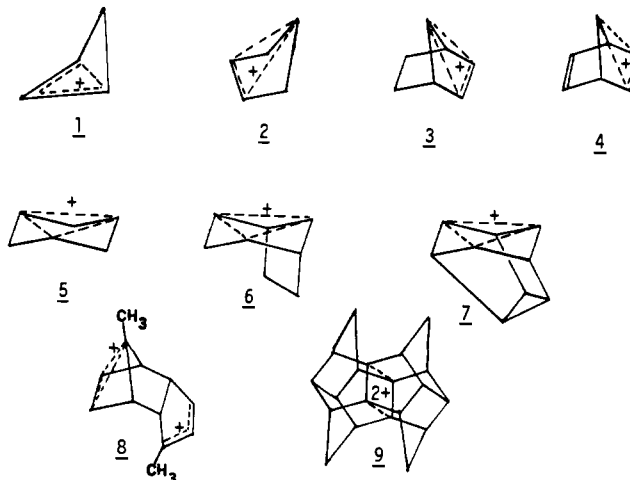
## *anti*-Tricyclo[4.2.1.1<sup>2,5</sup>]deca-3,7-diene-9,10-diyl Dication: A Sandwiched Bishomoaromatic System<sup>1a</sup>

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The homoaromaticity concept was first advanced by Winstein almost 30 years ago.<sup>2</sup> Since then it has been of great interest to experimental and theoretical chemists alike.<sup>3,4</sup> The question of homoaromatic overlap has been studied in six- $\pi$ -electron as well as two- $\pi$ -electron Hückeloid systems. The simplest two- $\pi$ -electron monohomoaromatic cation is homocyclopropenium ion **1**.<sup>5</sup> The parent bishomoaromatic 4-cyclopentenyl cation **2** is still elusive, although the bishomoaromaticity in ethano- and etheno-bridged analogues (i.e., 7-norbornenyl and 7-norbornadienyl cations **3** and **4**) is well established.<sup>6,7</sup> Even several trishomoaromatic systems such as **5**, **6**, and **7** have been prepared and characterized.<sup>8</sup>



We reported recently the generation and observation of *endo*-3,10-dimethyltricyclo[5.2.1.0<sup>2,6</sup>]deca-4,8-diene-3,10-diyl cation

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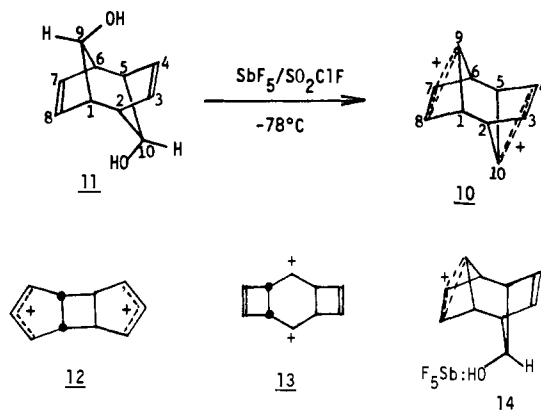
**Table I.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data of *anti*-Tricyclo[4.2.1.1<sup>2,5</sup>]deca-3,7-diene-9,10-diyl Dication, **10**, and Its Progenitor 9-*endo*-10-*endo*-Diol, **11**

substrate	$^1\text{H}$ , $\delta^a$	$^{13}\text{C}$ , $\delta^a$
dication <sup>b</sup> <b>10</b>	6.31 (br, 4 H; H <sub>3</sub> , H <sub>4</sub> , H <sub>7</sub> , H <sub>8</sub> )	131.7 (d, $J_{\text{C-H}} = 199.3$ Hz; C <sub>3</sub> , C <sub>4</sub> , C <sub>7</sub> , C <sub>8</sub> )
	3.52 (br, 2 H; H <sub>9</sub> , H <sub>10</sub> )	52.9 (d, $J_{\text{C-H}} = 219.2$ Hz; C <sub>9</sub> , C <sub>10</sub> )
	2.94 (br, 4 H; H <sub>1</sub> , H <sub>2</sub> , H <sub>5</sub> , H <sub>6</sub> )	38.1 (d, $J_{\text{C-H}} = 169.6$ Hz; C <sub>1</sub> , C <sub>2</sub> , C <sub>5</sub> , C <sub>6</sub> )
diol <sup>c</sup> <b>11</b>	6.73 (br, 4 H; H <sub>3</sub> , H <sub>4</sub> , H <sub>7</sub> , H <sub>8</sub> )	141.2 (d, $J_{\text{C-H}} = 171.1$ Hz; C <sub>3</sub> , C <sub>4</sub> , C <sub>7</sub> , C <sub>8</sub> )
	4.24 (d, 2 H, $J_{\text{H-H}} = 12.5$ Hz; OH)	83.6 (d, $J_{\text{C-H}} = 154.4$ Hz; C <sub>9</sub> , C <sub>10</sub> )
	3.95 (d, 2 H, $J_{\text{H-H}} = 12.5$ Hz; H <sub>9</sub> , H <sub>10</sub> )	44.7 (d, $J_{\text{C-H}} = 143.2$ Hz; C <sub>1</sub> , C <sub>2</sub> , C <sub>5</sub> , C <sub>6</sub> )
	2.64 (br, 4 H; H <sub>1</sub> , H <sub>2</sub> , H <sub>5</sub> , H <sub>6</sub> )	

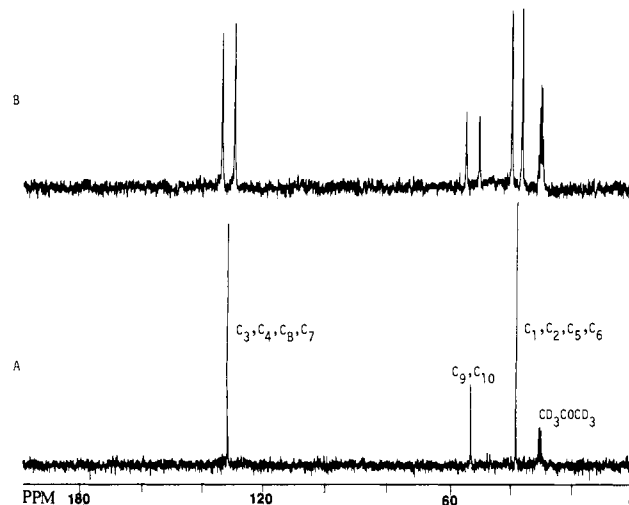
<sup>a</sup>Chemical shifts in ppm from external tetramethylsilanes: d, doublet; br, broad. <sup>b</sup>In  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-80^\circ\text{C}$ . <sup>c</sup>In  $\text{CDCl}_3$  at  $22^\circ\text{C}$ , also see ref 11a.

(**8**), which encompassed an allylic cation as well as a bishomoaromatic cation framework.<sup>9</sup> More recently we also obtained<sup>10</sup> the pagodane dication, **9**, a two-electron aromatic system in a cyclobutane framework, which can be considered as a frozen Woodward-Hoffmann transition state.

In our continued interest in carbocations and new aromatic systems we wish to report the preparation and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic characterization of *anti*-tricyclo[4.2.1.1<sup>2,5</sup>]deca-3,7-diene-9,10-diyl dication (**10**), a sandwiched bishomoaromatic dication.



Careful dissolution of *anti*-tricyclo[4.2.1.1<sup>2,5</sup>]deca-3,7-diene-9-*endo*-10-*endo*-diol (**11**)<sup>11a</sup> in freshly distilled protic acid free  $\text{SbF}_5$ <sup>11b</sup> in 6-fold excess of  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  (in a dry ice/acetone bath) provided a pale-yellow solution. The 200-MHz  $^1\text{H}$  NMR spectrum<sup>12</sup> at  $-80^\circ\text{C}$  showed only three absorptions at  $\delta^1\text{H}$  6.31 (4 H), 3.52 (2 H), and 2.94 (4 H), indicating that the species in the superacid medium has the same symmetry as the progenitor tricyclo[4.2.1.1<sup>2,5</sup>]deca-3,7-diene skeleton. The  $^1\text{H}$  NMR shifts of some of the protons are in fact more shielded than those of progenitor diol (see Table I). The 50-MHz  $^{13}\text{C}$  NMR spectra (see Figure 1) of the solution at  $-80^\circ\text{C}$  again showed three



**Figure 1.** 50-MHz  $^{13}\text{C}$  NMR spectra of *anti*-tricyclo[4.2.1.1<sup>2,5</sup>]deca-3,7-diene-9,10-diyl dication, **10**, in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at  $-90^\circ\text{C}$ : (A) proton decoupled; (B) proton coupled.

absorptions at  $\delta^{13}\text{C}$  131.7 (doublet,  $J_{\text{C-H}} = 199.3$  Hz), 52.9 (doublet,  $J_{\text{C-H}} = 219.2$  Hz), and 38.1 (doublet,  $J_{\text{C-H}} = 169.6$  Hz). These shifts, which are again shielded from those of progenitor diol, clearly indicate the formation of a highly symmetrical system which can be assigned the dicationic structure **10**, in which two bishomoaromatic cation frameworks are sandwiched together. Further proof for structure **10** is based on the comparison of the observed highly shielded  $^{13}\text{C}$  NMR shifts with those of related bishomoaromatic 7-norbornenyl cation **3**<sup>6</sup> [ $\delta \text{C}_7 = 34.0$  ( $J_{\text{C-H}} = 218.9$  Hz),  $\delta \text{C}_2\text{C}_3 = 125.9$  ( $J_{\text{C-H}} = 192.8$  Hz), and  $\delta \text{C}_1\text{C}_4 = 58.0$  ( $J_{\text{C-H}} = 173.0$  Hz)]. However, the chemical shifts of **10** are much more deshielded than those in **3**. This can be rationalized by the presence of two positive charges in close proximity in **10** which probably attenuates the degree of bishomoaromatic character in the individual frameworks. Furthermore, the observation of large C-H coupling constants in **10** is also diagnostic for the formation of sandwiched bishomoaromatic cationic frameworks which compare rather well with those in **3**. Any rearranged structures such as **12** and **13** can be clearly ruled out on the basis of the magnitude of observed chemical shifts. Moreover, the dication **10** shows no temperature-dependent behavior (between  $-40$  and  $-120^\circ\text{C}$ ), clearly ruling out any sort of equilibrium process (for example, between a monocation monodonor-acceptor complex such as **14**). The dication **10** was found to be stable at  $-78^\circ\text{C}$  for several days after which it slowly degrades. When the dication **10** was quenched with cold methanol (at  $-78^\circ\text{C}$ ), a complex mixture of products were isolated after workup. This is, however, not surprising from the behavior of diol in protic acids.<sup>11b</sup> Further, stepwise quenching of dication **10** at various positions and subsequent reactions are expected to lead to complex product mixtures and decomposition.

Dication **10** can be considered as a four- $\pi$ -electron bicyclo-(polycyclo)aromatic system.<sup>13</sup> Goldstein and Hoffmann in their paper on "Symmetry, Topology, and Aromaticity"<sup>14</sup> discussed longicyclic ribbon aromatic systems. The dication **10** is the first example that can be considered as a longicyclic four-ribbon four- $\pi$ -electron [0,2,0,2] aromatic system. It appears that in four-ribbon longicyclics [0,2,0,2] the four- $\pi$ -electron interaction is the most stable one.<sup>14</sup> However, we cannot estimate the extent of such stabilization in dication **10** on the basis of the spectroscopic data.

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