

**Figure 1.** ESR spectra taken at various times for a 0.3 M COT solution in HMPA in the presence of the COT anion radical. The computer simulation was generated for a 1/6.0 ratio of  $[16]\text{annulene}^{\cdot-}$  to  $\text{COT}^{\cdot-}$ . Line widths of 0.05 and 0.15 G were used for the anion radicals of  $[16]\text{annulene}$  and COT, respectively. Spectra were recorded at 25 °C at the times indicated on the spectra. The first spectrum exhibits the presence of the COT anion radical only. The last (recorded after 250 h) shows only the anion radical of  $[16]\text{annulene}$ .

The reduction of COT (0.1–1 M) in HMPA with a very deficient (by at least 2 orders of magnitude) amount of sodium metal (under conditions where ion association is absent<sup>5</sup>) results in a solution that yields the familiar nine-line ESR spectrum of the COT anion radical. After several hours at 25 °C, the ESR spectrum of this same solution shows the presence of the anion radical of  $[16]\text{annulene}$  (Figure 1). Over a period of several days, the anion radical of COT is gradually replaced with that of  $[16]\text{annulene}$ . Quantitative aspects of this unusual reaction were followed with the use of computer simulations.

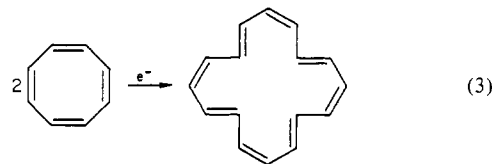
Unfortunately, the rate law for this reaction seems to be very complex, and the actual rate constants could not be obtained. Part of the problem involves the fact that the anion radicals of both  $[16]\text{annulene}$  and COT disproportionate to form the dianions and neutral molecules. Thus there are six species, which are all kinetically connected, in solution simultaneously. Despite this problem, it is clear that the rate of anion radical–neutral molecule combination is very thermally dependent. In a typical reaction, the time that it takes for the concentrations of the two anion radicals to become equal (half-life for  $\text{COT}^{\cdot-}$ ) is about 11 h at 35 °C, 41 h at 25 °C, and 520 h at 0 °C.

The thermal dimerization of COT to yield the (2 + 2) dimer does not take place at room temperature at an observable rate (this reaction takes several days at 100 °C).<sup>6</sup> After 3 days at room temperature, a solution of COT in the presence of  $\text{COT}^{\cdot-}$  shows only the anion radical of  $[16]\text{annulene}$  upon ESR analysis. However, when a portion of this same solution was kept from contact with the sodium metal for 2 weeks and then touched to the metal surface, only  $\text{COT}^{\cdot-}$  was immediately observed. Thus, the formation of  $[16]\text{annulene}$  involves the anion radical of COT and does not involve any previously formed dimer that may have existed in the solution.

Thermal (2 + 2) anion radical–neutral molecule combination reactions have synthetic potential that is well-worth exploring. This is especially true since many anion radical systems readily disproportionate, and both the newly generated anion radical and its dianion can be easily oxidized to form the neutral products. For the example described here, the anion radical product disproportionates to form the  $[16]\text{annulene}$  neutral molecule, and reaction 3 must result to some extent. However, the accumulation of a sufficient amount of neutral  $[16]\text{annulene}$  for isolation has not yet been realized.

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**Registry No.**  $[8]\text{Annulene radical anion}$ , 34510-85-5;  $[8]\text{annulene}$ , 629-20-9;  $[16]\text{annulene radical anion}$ , 37552-62-8.

### Spatially Isolated Redox Orbitals: Evidence from Low-Temperature Voltammetry

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The purpose of this report is to provide additional evidence for the concept of spatially isolated redox orbitals and to present some unusual cyclic voltammetric results.

The concept of spatially isolated orbitals was originally postulated<sup>1-3</sup> to explain the occurrence of multiple-state emission<sup>3</sup> from  $[\text{Rh}(\text{bpy})_2\text{phen}]^{3+}$  and  $[\text{Rh}(\text{phen})_2\text{bpy}]^{3+}$ , compounds that exhibited two distinct  $\pi\pi^*$  emissions, one characteristic of the bpy portion of the molecule and the other of the phen. Consequently, it was suggested that the parent compounds,  $[\text{Rh}(\text{bpy})_3]^{3+}$  and  $[\text{Rh}(\text{phen})_3]^{3+}$ , also possess excited states deriving from excitation into a single chelate ring. The spectroscopy of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Os}(\text{bpy})_3]^{2+}$  would by analogy be expected to involve excited states such as  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy}^-)]^{2+}$  resulting from the presence of spatially isolated optical orbitals. While the analogous mixed-ligand complexes ( $[\text{Ru}(\text{bpy})_2\text{phen}]^{2+}$ ) did not produce direct spectroscopic evidence<sup>4</sup> for a spatially isolated redox orbital, the cyclic voltammetric pattern observed for the  $d^6$  tris bpy  $\text{Ir}(\text{III})$ <sup>5</sup> and other  $\text{Ru}(\text{II})$  complexes<sup>6</sup> and bis diimine complexes enabled us<sup>3,5</sup> to postulate that spatially isolated (single chelate ring) orbitals also exist for the  $\text{Ru}(\text{II})$  parent molecule as well as for the mixed ligand species. For the  $[\text{Ir}(\text{bpy})_3]^{3+}$  ion, a pattern of three closely spaced one-electron waves was followed by a gap of 0.6 V and three more closely spaced waves. Our model placed the first three electrons each in an orbital on a single chelate ligand<sup>11</sup> and the next three reversible one-electron waves corresponded to pairing up of the first three electrons.

Subsequently, this prediction for the optical orbital of  $[\text{Ru}(\text{bpy})_3]^{2+}$  has been supported by observation of high-resolution photoselection spectra<sup>7</sup> for  $[\text{Ru}(\text{bpy})_3]^{2+}$  and by the observation

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Table I. Half-Wave Potentials ( $E_{1/2}^R$ ) of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_3]^{2+}$ , and  $4,4'-(\text{CO}_2\text{Et})_2\text{bpy}$  in DMF Containing 0.1 M TEAH at  $-54^\circ\text{C}$ 

compound	$(E_{1/2}^R \text{ vs. } \text{Fc}^{+/0})/\text{V}$									
	2+/+	+/0	0/-	-/2-	2-/3-	3-/4-	4-/5-	5-/6-	6-/7-	7-/8-
$[\text{Ru}(\text{bpy})_3]^{2+}$	-1.76 (50)	-1.92 (60)	-2.14 (60)	-2.78 (60)	-3.00 (60)	-3.30 (50) <sup>a</sup>				
$[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_3]^{2+}$	-1.34 (50)	-1.46 (50)	-1.62 (50)	-2.02 (60)	-2.19 (60)	-2.45 (60)	-2.88 (60)	-2.97 (60)	-3.19 (60)	-3.34 (70)
$4,4'-(\text{CO}_2\text{Et})_2\text{bpy}$			-2.05 (70)	-2.40 (70)	-3.06 (80)					

<sup>a</sup> Distorted wave.

of excited-state resonance Raman<sup>8,9</sup> for the  $[\text{Ru}(\text{bpy})_3]^{2+}$  species. Further, temperature-dependent ESR data<sup>10-12</sup> for the one, two, and three-electron reduced species of  $[\text{Ru}(\text{bpy})_3]^{2+}$  demonstrated that each of the three species is an  $S = 1/2$  species and that the redox orbitals for each of the three species is localized on a single chelate ring, consistent with the circumstance occurring for the optical orbital (the excited-state species). Recently interligand charge-transfer absorptions for reduced  $[\text{Ru}(\text{bpy})_3]^{2+}$  provided additional evidence.<sup>13</sup> However, the fact that the fourth reduction wave for the  $[\text{Ru}(\text{bpy})_3]^{2+}$  was quasi-reversible and at the solvent ( $\text{CH}_3\text{CN}$ , DMF) window at room temperature precluded observation of the expected fifth and sixth waves and also prevented us from carrying out the electrochemical-ESR experiment on the four-electron reduction product.

Consequently, we have proceeded in two directions to attempt to verify the simple spatially isolated orbital model for  $[\text{Ru}(\text{bpy})_3]^{2+}$  (I) and related compounds. The first involves a chemical perturbation with the use of 4,4'-diethylcarboxy-2,2'-bipyridine ( $4,4'-(\text{CO}_2\text{Et})_2\text{bpy}$ ) ligand to form the tris Ru complex  $[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_3]^{2+}$  (II). The electrochemistry of this complex was reported by Elliott<sup>14</sup> to involve six one-electron waves at room temperature shifted anodic of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  pattern. Such a complex might allow generation of a stable four-electron reduction product for ESR study. The second was a concerted effort on our part to widen the electrochemical window by use of very careful solvent purification techniques and low-temperature electrochemical methods. The removal of trace water is a problem for both DMF and  $\text{CH}_3\text{CN}$ , therefore we have used the anthracene radical anion method<sup>15</sup> and Schlenk glassware as provided to us by Professor S. Aoyogui's laboratory at the Tokyo Institute of Technology. The results of this procedure and use of a low temperature ( $-54^\circ\text{C}$  in DMF) allows expansion of the cathodic potential window to  $-3.0 \text{ V}^{16}$  vs. NHE and produces the unique result in Figure 1. The  $[\text{Ru}(\text{bpy})_3]^{2+}$  voltammogram produces the six reversible one-electron waves predicted and spaced as expected. Even more spectacular is the voltammogram observed for compound II. In addition to the six reversible one-electron waves of the parent bpy complex, four additional one-electron waves for a total of ten one-electron waves are observed (cathodic to anodic peak separations are 50–60 mV, which is consistent with

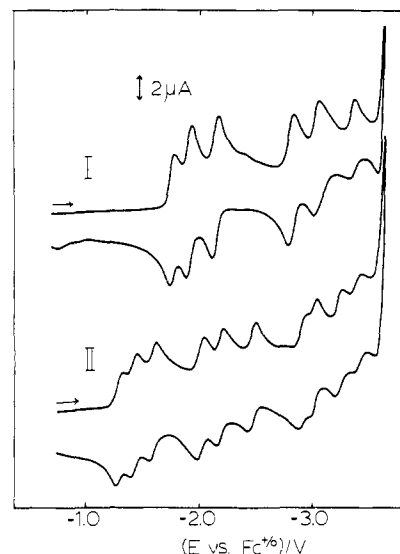


Figure 1. Cyclic voltammograms of 0.5 mM  $[\text{Ru}(\text{bpy})_3]^{2+}$  (curve I) and 0.5 mM  $[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_3]^{2+}$  (curve II) in DMF containing 0.1 M tetraethylammonium hexafluorophosphate at  $-54^\circ\text{C}$  using a scan rate of 0.1 V/s.

that of the reversible one-electron wave for the  $\text{Fc}^+/\text{Fc}$  couple).

In addition to providing verification of what surely is a unique quantum mechanical effect,<sup>17</sup> the data for compound II indicate that, at these temperatures, a molecular species with a charge of  $-8$  is produced. The concentration of II was sufficiently low that dimerization could not be responsible for the additional four waves. Uncomplexed  $4,4'-(\text{CO}_2\text{Et})_2\text{bpy}$  showed three reversible one-electron reduction waves under similar conditions.

The two ester functions per ligand likely are the site of the additional reduction processes either providing a very localized  $\pi^*$  orbital on the ester moiety or, more likely, an empty low-lying  $\pi^*$  orbital deriving from interaction of the ester system with higher lying  $\pi^*$  orbitals of the bpy system. Elliott has noted that the absorption spectra of reduced products of II are different from those of I and from the analogous 5,5'-diethylcarboxyl compound (III) and has suggested that low-energy absorption bands occurring in II derive from intramolecular charge-transfer transitions from the bpy moiety to the carboxyethyl functions.<sup>18</sup> Since the steric constraints of II and III are very different, the absence of analogous low-energy absorption bands in III is consistent with such an explanation. Our voltammogram at  $-54^\circ\text{C}$  for compound III does not exhibit any additional waves beyond those reported by Elliott consistent with the Elliott interpretation of the low-lying orbitals of II. In either case, such a possibility suggests that 12 one-electron waves are possible producing a series having a net 10- charge.

Measurement of the temperature-dependent ESR for the  $n = 4$  species generated at low temperature for the  $[\text{Ru}(\text{bpy})_3]^{2+}$  and

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(15) Basically the same purification method of DMF has been used by D. W. Clack and N. S. Hush (Clack, D. W.; Hush, N. S. *J. Am. Chem. Soc.* **1965**, *65*, 4238). After purification of DMF by this method, the removal of water from tetraethylammonium hexafluorophosphate (TEAH) is crucial. TEAH was recrystallized from methanol and vacuum-dried at  $140^\circ\text{C}$  for 1 day. Furthermore, we found that highly reduced compounds are stabilized by ion-association effect. The details of these will be given in a separate paper.

(16) Potentials were measured relative to the ferricinium/ferricenium couple ( $\text{Fc}^+/\text{Fc}$ ) whose  $E_{1/2}^h$  is 0.36 V vs. SSCE in  $\text{CH}_3\text{CN}$  at room temperature.

(17) For a related phenomena, see: Kleier, D. A.; Martin, R. L.; Wadt, W. R.; Mooman, W. R. *J. Am. Chem. Soc.* **1982**, *104*, 60.

(18) Elliott, C. M.; Hershanhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519.

at room temperature for the  $[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_3]^{2+}$  species will be completed shortly and reported later.

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### Hexaalkylcyclotrisilanes ( $\text{R}_2\text{Si}$ )<sub>3</sub>: Hexakis(1-ethylpropyl) and Hexaisopropyl Derivatives

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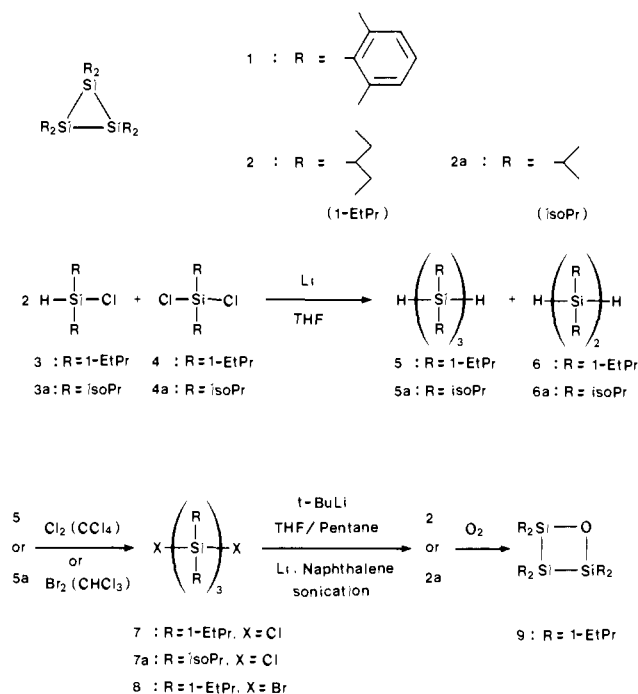
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Hexakis(2,6-dimethylphenyl)cyclotrisilane (**1**)<sup>1</sup> represents the first and thus far only compound that incorporates the silicon three-membered ring system. While the strain imposed upon this small ring is clearly and uniquely manifested in its chemical behavior, the full *aryl* substitution in **1** causes significant perturbation of the electronic structure intrinsic to the cyclotrisilane system.<sup>2</sup> With the purpose of eliminating this complication, the synthesis of the titled *alkyl* (rather than *aryl*) substituted derivatives (**2** and **2a**) has been contemplated. We record herein the high-yield synthesis and photochemical reaction of these compounds. In the present cases, the modified Kipping reaction successfully used for the synthesis of **1** is of no avail,<sup>1,3</sup> but reductive cyclization of 1,3-dichlorohexaalkyltrisilanes under the conditions precisely specified below has now been found to be highly efficient (80–90%) and also to have general applicability for those having moderately bulky alkyl substituents. Compound **2** undergoes photofragmentation to yield the corresponding disilene and silylene species.

**Synthesis of 2.** A mixture of chlorobis(1-ethylpropyl)silane (**3**) (50 mmol) and dichlorobis(1-ethylpropyl)silane (**4**) (23 mmol) in tetrahydrofuran (THF) (120 mL) is allowed to react with lithium (dispersion, 0.132 mol) at 0 °C for 3 h and then at room temperature overnight.<sup>4</sup> Two products that result from this reaction are 1,1,2,2,3,3-hexakis(1-ethylpropyl)trisilane (**5**)<sup>5</sup> (12.1 mmol, bp 196 °C (0.18 torr)) and 1,1,2,2-tetrakis(1-ethylpropyl)disilane (**6**)<sup>5</sup> (4.36 mmol, bp 120 °C (0.18 torr)) (see Scheme I). Chlorination of **5** under standard conditions proceeds smoothly at 0 °C to provide in 91% yield 1,3-dichloro-1,1,2,2,3,3-hexakis(1-ethylpropyl)trisilane (**7**)<sup>5</sup> (bp 175 °C (0.02 torr)). The corresponding dibromo compound (**8**)<sup>5</sup> (bp 196–202 °C (0.015 torr)) is also obtained in an analogous manner (90% yield).

Reductive cyclization of **7** has been examined extensively. The course of the reduction is highly sensitive to several experimental parameters, and indeed the exclusive formation of the cyclotrisilane **2** can be achieved only with a specific combination of reductants and solvent system. Thus, to a solution of **7** (1.73 mmol) in a mixed solvent (4 mL of THF and 32 mL of pentane) is added at –78 °C a 2 M solution of *tert*-butyllithium (1.72 mmol) in pentane; the resulting mixture is stirred for 45 min at –78 °C and then warmed to room temperature over a period of 2 h. Lithium (dispersion, 4.5 mmol) and naphthalene (0.19 mmol) are simultaneously added, and the reaction flask is immersed in an ultrasonic bath maintained at 40–45 °C. After 18 h, another

### Scheme I



portion of lithium (dispersion, 1.4 mmol) is added and sonication continued for another 21 h. The reaction is now completed,<sup>6</sup> and the usual workup including flash chromatography provides colorless crystals, mp 240 °C dec. The assignment of the cyclotrisilane structure to this product is based on its spectral properties: high-resolution mass spectrum (electron impact) calculated for  $\text{C}_{30}\text{H}_{66}\text{Si}_3$ ,  $m/z$  510.4472, found,  $m/z$  510.4463,  $\text{M}^+$  510 (13%), 440 (1.2), 370 (8.0), 340 (3.9), 300 (49), 271 (11), 270 (7.9), 269 (13), 230 (100), 201 (15), 200 (22), 199 (22), 169 (49), 160 (49), 131 (67), 130 (36), 129 (90); <sup>1</sup>H NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.12 (36 H, t,  $J = 7.3$  Hz,  $\text{CH}_3$ ), ca. 1.12 (6 H, CH), 1.69 (12 H, ddq,  $J = 7.3, 14.6, 7.3$  Hz), 1.93 (12 H, ddq,  $J = 4.3, 14.6, 7.3$  Hz); <sup>13</sup>C NMR (67.8 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  15.73 (dq,  $J = 121$  Hz), 27.84 (t,  $J = 129$  Hz), 30.04 (d,  $J = 118$  Hz); IR (KBr) 2955, 2920, 2865 ( $\nu$  C–H), 1460, 1375 ( $\nu$  C–H)  $\text{cm}^{-1}$ ; UV (methylcyclohexane)  $\lambda_{\text{max}}$  304 ( $\epsilon$  270), 328 (240) nm. Thus, **2** is synthesized from **7** in 90% yield. The cyclization of the dibromide **8** is less satisfactory, yielding **2** in only 60% yield. Compound **2** is rather air sensitive and is converted to the corresponding oxa compound **9**<sup>5</sup> on standing in air for several days at room temperature.

**Synthesis of 2a.** The synthetic methodology described above for **2** appears to be generally applicable. For example, hexaisopropylcyclotrisilane (**2a**) can be prepared in an equally satisfactory fashion. Treatment of a mixture of chlorodiisopropylsilane (**3a**) and dichlorodiisopropylsilane (**4a**) (1:0.34 molar ratio) with lithium (1.7 equiv) provides, in addition to 1,1,2,2-tetraisopropylidisilane (**6a**),<sup>5</sup> 1,1,2,2,3,3-hexaisopropyltrisilane (**5a**)<sup>5</sup> (40% yield), which in turn is chlorinated to yield the corresponding dichloro derivative (**7a**).<sup>5</sup> Reductive cyclization of **7a** under the conditions specified above successfully produces **2a**<sup>5</sup> in 85% yield (estimated by gas chromatography), which can be isolated virtually pure through the vacuum transfer technique. Compound **2a** is instantly converted to its (mono and di) oxa derivatives in contact with oxygen.<sup>7</sup>

**Photolysis of 2.** As compared with **1**<sup>1</sup> and a bridged compound **10**,<sup>8</sup> photoinduced fragmentation of **2** proceeds rather inefficiently.

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(2) For instance, the UV absorption of polysilanes and polygermanes is significantly affected by aryl substitution. See: Castel, A.; Rivière, P.; Saint-Roch, B.; Satgé, J.; Malrieu, J. P. *J. Organomet. Chem.* **1983**, *247*, 149.

(3) (a) Reaction of **4a** with Li leads to the corresponding cyclotrisilane (Watanabe, H.; Muraoka, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45). (b) (*t*-BuMeSi)<sub>4</sub> is prepared from *tert*-butyldichloromethylsilane (Biernbaum, M.; West, R. *Ibid.* **1977**, *131*, 179).

(4) This reaction follows a standard procedure for the silicon chain extension. For instance, see: Gilman, H.; Harrell, R. L. *J. Organomet. Chem.* **1966**, *5*, 201.

(5) See supplementary material for spectral properties of this compound.

(6) The solvent ratio (1:8 of THF and pentane) is critical. With THF alone or without *t*-BuLi a considerable amount of **5** is produced as a byproduct which is difficult to separate from **2**. Use of naphthalene (catalytic amount) is also necessary. Naphthalene appears to effect smooth lithiation of the SiCl functionality.

(7) The air sensitivity of the strained Si–Si bond depends highly on its substituents. For the case of the cyclotrisilane, see: (a) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (b) Hengge, E.; Schuster, H. G.; Peter, W. *J. Organomet. Chem.* **1980**, *186*, C45.