excellent, which is unusual for such reactions. The stepwise procedure allows the highest *ee* values to be obtained together with high chemical yields.[23] These results show the wide scope of such aldol reactions, with certain limitations for bulky and/or conjugated aldehydes (results not optimized). The use of bulkier trialkylsilyloxyfurans slightly improved the d.r.; further optimization studies are in progress. Furthermore these findings may provide some evidence for amplification of *ee* values of biomolecules (by chemical reactions) in the chemical origins of life. Indeed, conditions for aldol reactions may have been found in prebiotic systems. More experiments are nevertheless needed to set a mathematical model for such a mechanism.[24] Such a process could also be involved in other asymmetric reactions.[23, 25, 26]

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Interconversion between μ-η^2,η^2-C$_{60}$ and μ_3-η^2,η^2,η^2-C$_{60}$ on a Carbido Pentaosmium Cluster Framework**

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Exohedral metallofullerenes have recently attracted much attention concerning the effects of metal coordination on the chemical and physical properties of C$_{60}$.[1] Most approaches to forming metal complexes have been based on metal–C$_{60}$ π-complex chemistry, which has resulted in η^2-C$_{60}$, μ-η^2,η^2-C$_{60}$, and μ_3-η^2,η^2,η^2-C$_{60}$ ligands in monometallic (for most metals),[2] bimetallic (Re$_2$, Ru$_2$, Ir$_2$),[3] and metal cluster complexes (Ru$_3$, Os$_3$, Ru$_5$C, Ru$_6$C, PtRu$_5$C),[4, 5] respectively. Metal clusters can potentially accommodate all these C$_{60}$ bonding modes, but the interaction of C$_{60}$ with cluster frameworks has been, thus far, dominated by the face-capping cyclohexatriene-like bonding mode, μ_3-η^2,η^2,η^2-C$_{60}$. The μ-η^2,η^2-C$_{60}$ bonding mode has never been observed on a cluster framework, although it has been postulated as an intermediate for the transformation of [Os$_3$(CO)$_{11}$(η^2-C$_{60}$)] to [Os$_3$(CO)$_9$(μ_3-η^2,η^2,η^2-C$_{60}$)] by loss of carbonyl ligands.[5c] The interconversion among the three kinds of the C$_{60}$ ligands remains to be established in the area of C$_{60}$–metal cluster chemistry. We have recently observed the elusive μ-η^2,η^2-C$_{60}$ bonding mode on an Os$_5$C cluster framework, and furthermore demonstrated that the two C$_{60}$ bonding modes μ-η^2,η^2 and μ_3-η^2,η^2,η^2 are interconvertible.

Reaction of [Os$_5$C(CO)$_{12}$(PPh$_3$)(NCMe)$_2$] with C$_{60}$ in refluxing ClC$_6$H$_5$ produced a mixture of **1** and **2** (see the Experimental Section). The conversion of **1** into **2** could be effected by heating a solution of **1** in ClC$_6$H$_5$ at 80 °C under 1 atm of carbon monoxide. Upon thermolysis at 132 °C, **2** was cleanly reconverted into **1** by loss of a carbonyl ligand (Scheme 1).

[Os$_5$C(CO)$_{11}$(PPh$_3$)(μ_3-η^2,η^2,η^2-C$_{60}$)] **1**

[Os$_5$C(CO)$_{12}$(PPh$_3$)(μ-η^2,η^2-C$_{60}$)] **2**

The solid-state structure of **1** is isomorphous to that of the ruthenium analogue [Ru$_5$C(CO)$_{11}$(PPh$_3$)(μ_3-η^2,η^2,η^2-C$_{60}$)].[4b] The structure of **2** (Figure 1) reveals a very intriguing feature

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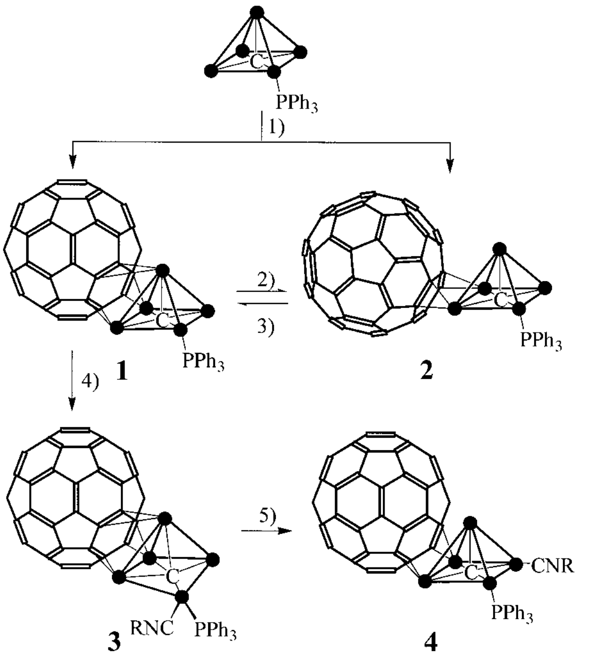

Scheme 1. 1) 1.2 Me_3NO, CH_3CN/CH_2Cl_2 (1/2), room temperature, 2 h; 2. C_{60}, ClC_6H_5, 132 °C, 1 h, 19 % for **1** and 13 % for **2;** 2) CO (1 atm), ClC_6H_5, 80 °C, 30h, 72 %; 3) ClC_6H_5, 132 °C, 6 h, 73 %; 4) RNC, ClC_6H_5, room temperature, 15 h, 84 %; 5) ClC_6H_5, 100 °C, 12 h, 64 %. R = $CH_2C_6H_5$.

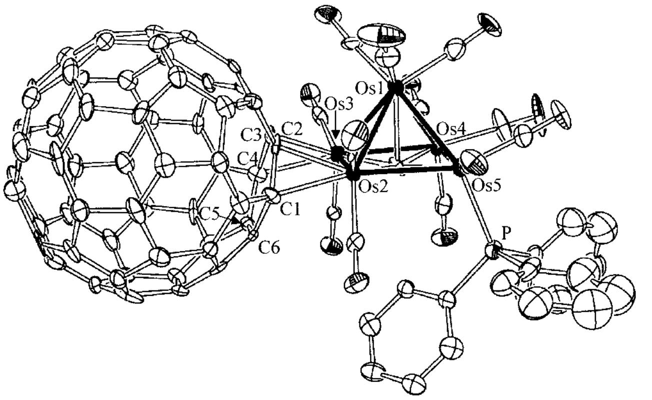

Figure 1. Molecular structure of **2**. Selected bond lengths [Å]: C1–C2 1.39(2), C2–C3 1.53(2), C3–C4 1.41(2), C4–C5 1.49(2), C5–C6 1.41(2), C6–C1 1.45(2), Os2–C1 2.23(2), Os2–C2 2.18(2), Os3–C3 2.19(1), Os3–C4 2.27(2).

of the C_{60} ligand disposition. Two adjacent double bonds in a C_6 ring of the C_{60} ligand bridge the basal Os2 and Os3 atoms in a μ-η^2,η^2 mode. Interestingly, the third uncoordinated double bond in the C_6 ring is disposed away from the Os1-Os2-Os3 triangle; the C_{60} ligand has apparently rotated by 180° upon the center of the Os2–Os3 bond during **1** → **2** conversion as compared to the C_{60} position in **1**.

This is, to our knowledge, the first example of interconversion between μ-η^2,η^2- and μ_3-η^2,η^2,η^2-C_{60} bonding modes. To understand in detail the pathways of the interconversion and the apparent accompanying C_{60} rotation on the cluster framework, the interaction of **1** with a benzyl isocyanide ligand was investigated. This would provide insight into the fate of the incoming carbonyl ligand in the transformation of **1** to **2**. Reaction of **1** with benzyl isocyanide at room temperature gave the addition product **3**. Thermolysis of this kinetic product at 100 °C resulted in the isomer **4** in high yield (Scheme 1, see the Experimental Section).

$[Os_5C(CO)_{11}(CNCH_2C_6H_5)(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})]$ **3**

$[Os_5C(CO)_{11}(CNCH_2C_6H_5)(PPh_3)(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})]$ **4**

The molecular structure of the kinetic isomer **3** is shown in Figure 2. The μ_3-η^2,η^2,η^2-C_{60} bonding mode is unaffected, but one Os_{apical}–Os_{basal} bond in the square-pyramidal Os_5C framework of **1** has been cleaved by the addition of the two-electron donor benzyl isocyanide. The four Os atoms Os1, Os2, Os3, and Os4 form a "butterfly" framework, and the remaining osmium atom, coordinated with phosphine and isocyanide ligands, bridges the two "wing-tip" atoms Os2 and Os4. The coordination sphere of the carbido atom can be regarded as a distorted trigonal bipyramid. A similar structural feature has been previously observed in several M_5C clusters, such as $[Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}]$,[6] $[Os_5C(CO)_{15}I]^-$,[7] and $[Ru_5C(CO)_{15}(NCMe)]$.[8] It has been proposed that the site of attack by the incoming ligand is the basal metal atom in the reaction of $[Ru_5C(CO)_{15}]$ and MeCN.[8] Similarly, it can be envisaged that the Os1–Os5 bond in **1** is cleaved by attack of the benzyl isocyanide ligand on the most basic Os5 center with a phosphine ligand to form **3** (Scheme 1).

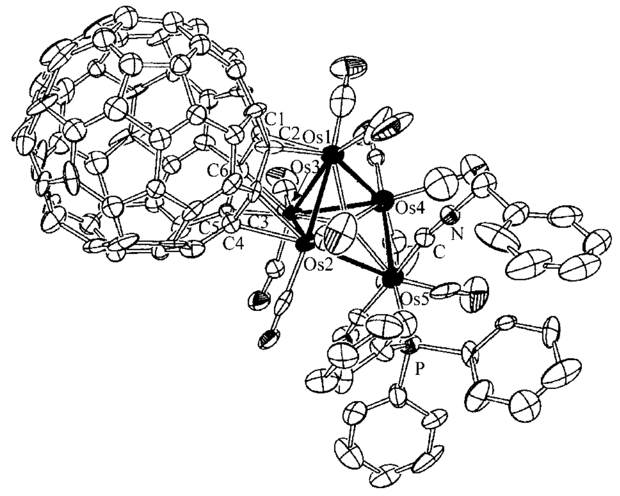

Figure 2. Molecular structure of **3**. Selected bond lengths [Å]: C1–C2 1.51(4), C2–C3 1.41(4), C3–C4 1.46(4), C4–C5 1.52(4), C5–C6 1.40(4), C6–C1 1.45(4), Os1–C1 2.27(2), Os1–C2 2.19(3), Os2–C3 2.26(3), Os2–C4 2.30(3), Os3–C5 2.17(3), Os3–C6 2.24(3).

The molecular structure of the thermodynamic isomer **4** (Figure 3) shows that the μ_3-η^2,η^2,η^2-C_{60} ligand in **3** has been converted into a μ-η^2,η^2-C_{60} ligand on a square-pyramidal Os_5C cluster framework; the two adjacent double bonds in a C_6 ring of the C_{60} ligand bridge the two basal Os2 and Os3 atoms. The two electrons needed to remove one Os–C_2 (C_{60}) bonding interaction in **3** have been provided by the formation of an Os–Os bond between two nonbonding osmium atoms. The benzyl isocyanide ligand occupies an equatorial position on the basal Os4 atom not bound by either C_{60} or PPh_3 ligands. In contrast to **2**, however, the C_6 ring positions centrally over

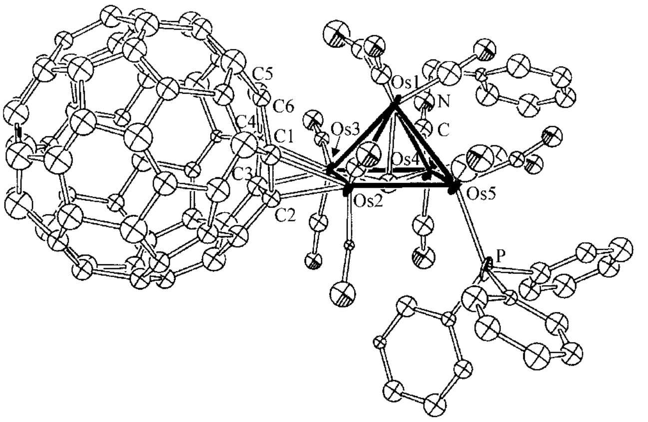

Figure 3. Molecular structure of **4**. Selected bond lengths [Å]: C1–C2 1.40(9), C2–C3 1.45(4), C3–C4 1.45(9), C4–C5 1.55(3), C5–C6 1.29(9), C6–C1 1.54(10), Os2–C1 2.27(8), Os2–C2 2.16(6), Os3–C3 2.33(8), Os3–C4 2.17(4).

the Os_3 triangle, as observed in **1**. Detailed speculation concerning the mechanism of formation of **4** from **3** is unwarranted, but the likely pathway would involve reformation of the Os1–Os5 bond, consecutive migration of the benzyl isocyanide ligand from Os5 to Os4 and of a carbonyl ligand from Os4 to Os1, and subsequent rupture of the Os1–C_2 (C_{60}) interaction.

Importantly, two different orientations of the μ-η^2,η^2-C_{60} ligand have been observed in **2** and **4**, which are related by 180° rotation with respect to the center of the two C_{60}-coordinated metal atoms. The reason for the two different orientations is not clear at the moment, but it seems to have an electronic origin since the steric environments around the C_{60} ligand appear to be essentially identical in **2** and **4**.

In conclusion, we have shown the first examples of the μ-η^2,η^2-C_{60} bonding mode on an Os_5C cluster framework (**2** and **4**), and demonstrated interconversion of the μ-η^2,η^2-C_{60} and μ_3-η^2,η^2,η^2-C_{60} ligands ($\mathbf{1} \rightleftarrows \mathbf{2}$) by carbonyl addition and elimination reactions. The two different dispositions of the μ-η^2,η^2-C_{60} ligand in **2** and **4** may occur by C_{60} rotation due to electronic reasons. Efforts are currently underway to understand the origin of the different structural features in **2** and **4** and to explore further reactivities of C_{60}–Os_5C clusters.

Experimental Section

Details on the syntheses of **1**–**4** as well as the interconversion of **1** and **2** are given in the Supporting Information. For the X-ray structure analyses, data were collected at $T = 293(2)$ K on a CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) using ω scans. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136396 (**1**), -136394 (**2**), -136397 (**3**), and -136395 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

1: Elemental analysis calcd for $C_{90}H_{15}O_{11}POs_5$: C 47.96, H 0.67; found: C 48.13, H 0.78; IR (CS_2): $\tilde{\nu} = 2073$(s), 2032(s), 2021(s), 2011(s) cm^{-1} (CO); ^1H NMR (300 MHz, CS_2/external CD_2Cl_2): $\delta = 7.83 - 7.73$ (m, 15 H); ^{31}P NMR (122 MHz, $Cl_2C_6H_4$/$CDCl_3$ 1/1): $\delta = 6.09$; FAB-MS (negative-ion): *m*/*z*: 2261.8 [M^-].

X-ray crystal data for **1**: Dark red, thin, needlelike crystals were obtained by slow evaporation of a solution of **1** in CS_2 at room temperature. The crystal ($0.14 \times 0.18 \times 0.20$ mm) used for data collection contained one molecule of CS_2 and a half a molecule of H_2O ($C_{90}H_{15}O_{11}POs_5 \cdot CS_2 \cdot 0.5\,H_2O$, $M_r = 2440.12$): triclinic, space group $P\bar{1}$, $a = 10.0093(2)$, $b = 13.5022(2)$, $c = 26.9630(3)$ Å, $\alpha = 77.415(1)$, $\beta = 80.705(1)$, $\gamma = 70.586(1)°$, $V = 3338.5(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.326\ g\,cm^{-3}$. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give $R = 0.1280$ and $R_w = 0.3107$ (based on F^2) for 502 variables and 5553 observed reflections with $I > 2\sigma(I)$ and $0.78 < \theta < 22.00°$.

2: Elemental analysis calcd for $C_{91}H_{15}O_{12}POs_5$: C 47.87, H 0.66; found: C 47.41, H 0.79; IR (CS_2): $\tilde{\nu} = 2072$(s), 2040(m), 2028(m, sh), 2022(s), 2007(m), 1996(w) cm^{-1} (CO); ^1H NMR (300 MHz, CS_2/external CD_2Cl_2): $\delta = 7.79 - 7.59$ (m, 15 H); ^{31}P NMR (122 MHz, CS_2/external CD_2Cl_2): $\delta = -3.87$; FAB-MS (negative-ion): *m*/*z*: 2289.8 [M^-].

X-ray crystal data for **2**: Green-brown, platelike crystals ($0.13 \times 0.22 \times 0.80$ mm) were obtained by slow diffusion of C_6H_{12} into solution of **2** in CS_2 at room temperature ($C_{91}H_{15}O_{12}POs_5$, $M_r = 2282.00$): monoclinic, space group $C2/c$, $a = 41.821(8)$, $b = 19.375(4)$, $c = 18.550(4)$ Å, $\beta = 116.04(3)°$, $V = 13\,504(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.245\ g\,cm^{-3}$; $R = 0.0606$ and $R_w = 0.1535$ (based on F^2) for 942 variables and 6750 observed reflections with $I > 2\sigma(I)$ and $1.08 < \theta < 23.00°$.

3: Elemental analysis calcd for $C_{98}H_{22}NO_{11}POs_5$: C 49.64, H 0.94, N 0.59; found: C 50.49, H 0.83, N 0.55; IR (CH_2Cl_2): $\tilde{\nu} = 2064$(s), 2046(m), 1997(s), 1990(s), 1955(w), 1933(w) cm^{-1} (CO); ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.63 - 6.98$ (m, 20 H), 4.78 (d, $J = 16.4$ Hz, 1 H), 4.49 (d, $J = 16.4$ Hz, 1 H); ^{31}P NMR (122 MHz, $Cl_2C_6H_4$/$CDCl_3$ 1/1): $\delta = -8.42$; FAB-MS (positive-ion): *m*/*z*: 2378.9 [M^+].

X-ray crystal data for **3**: Dark red-brown, needlelike crystals ($0.28 \times 0.29 \times 0.78$ mm) were obtained by slow diffusion of MeOH into a solution of **3** in CS_2/CH_2Cl_2 (1/1) at room temperature ($C_{98}H_{22}NO_{11}POs_5$, $M_r = 2371.14$): orthorhombic, space group $Fdd2$, $a = 48.766(10)$, $b = 55.356(11)$, $c = 10.054(2)$ Å, $V = 27\,140(9)$ Å^3, $Z = 16$, $\rho_{calcd} = 2.321\ g\,cm^{-3}$; $R = 0.0738$ and $R_w = 0.1760$ (based on F^2) for 985 variables and 7846 observed reflections with $I > 2\sigma(I)$ and $1.11 < \theta < 23.36°$.

4: Elemental analysis calcd for $C_{98}H_{22}NO_{11}POs_5$: C 49.64, H 0.94, N 0.59; found: C 50.35, H 0.95, N 0.58; IR (CH_2Cl_2): $\tilde{\nu} = 2046$(m), 2024(vs), 2010(s), 1991(w, br) cm^{-1} (CO); ^1H NMR (300 MHz, CS_2/external CD_2Cl_2): $\delta = 7.68 - 7.60$ (m, 20 H), 5.54 (s, 1 H), 5.47 (s, 1 H); ^{31}P NMR (122 MHz, CS_2/external CD_2Cl_2): $\delta = -2.87$; FAB-MS (positive-ion): *m*/*z*: 2378.9 [M^+].

X-ray crystal data for **4**: Brown-green, thin, platelike crystals were obtained by slow diffusion of n-C_7H_{16} into a solution of **4** in CS_2 at room temperature. The crystal ($0.12 \times 0.15 \times 0.21$ mm) used for data collection contained a half a molecule of CS_2 ($C_{98}H_{22}NO_{11}POs_5 \cdot 0.5\,CS_2$, $M_r = 2409.20$): triclinic, space group $P\bar{1}$, $a = 9.970(3)$, $b = 17.383(6)$, $c = 21.365(10)$ Å, $\alpha = 101.62(6)$, $\beta = 99.09(3)$, $\gamma = 98.49(3)°$, $V = 3519(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.274\ g\,cm^{-3}$; $R = 0.1696$ and $R_w = 0.4094$ (based on F^2) for 441 variables and 6164 observed reflections with $I > 2\sigma(I)$ and $0.99 < \theta < 22.00°$.

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Preparation, Structure, and Redox Reactions of Nine-Membered Cyclic Peroxides: A Novel Electrochromic System Undergoing Reversible Extrusion and Trapping of O_2**

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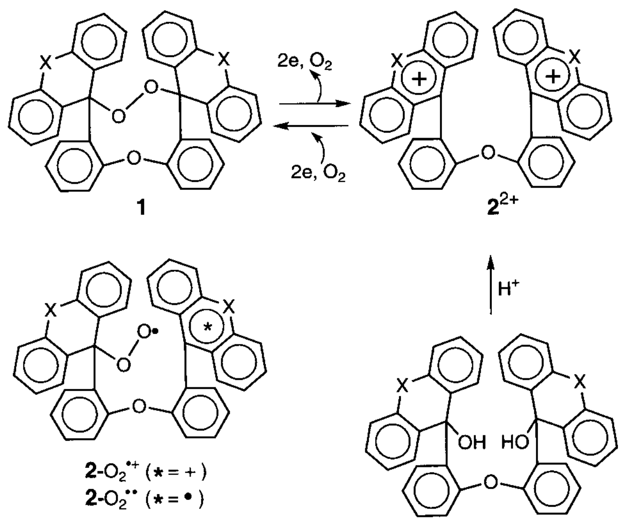
Cyclic peroxides having a medium-size ring skeleton have recently attracted much attention from a pharmacological standpoint[1] and the mechanistic studies of their electron-transfer reactions[2,3] have provided the basis for a better understanding of their biological activities. The nine-membered peroxides, however, are so rare[4] that their chemistry has not been well developed. During the course of our study on molecular systems in which the structures and properties can be controlled by electron transfer (ET)[5] we have found that the dihydrotrioxonin derivatives **1**, a new class of nine-membered cyclic peroxides having a hitherto unknown 1,2,6-trioxacyclononane skeleton, could be generated very easily. Here we report the preparation and X-ray structure of **1** along with their unique electron-transfer behavior. It is worth noting that ET induces the oxidative deoxygenation of peroxides **1** to form the dicationic dyes **2**$^{2+}$, from which compounds **1** are recovered upon 2e reduction in the presence of O_2 (Scheme 1). This system could be used to electrochemically control O_2 concentration.



Scheme 1. Interconversion between **1** and **2**$^{2+}$ by the oxidative-deoxygenation and reductive-oxygenation reactions.

Diols **3a** and **3b**[6] were prepared in 54 and 41% yield, respectively, by the reaction of 2,2′-dilithiodiphenyl ether[7] with xanthone and thioxanthone. Deeply colored salts **2a**-$(BF_4)_2$[6] [λ_{max} (lgε) 480 (sh, 3.73), 450 (3.84), 378 (4.71), 260 nm (4.86) in MeCN] and **2b**-$(BF_4)_2$[6] [531 (sh, 3.78), 498 (3.88), 387 (4.47), 282 (5.09)] were obtained in 94 and 91% yield, respectively, by treating these diols with HBF_4 in $(EtCO)_2O$.

According to the voltammetric analyses the dicationic dye undergoes facile and reversible 2e reduction (**2a**$^{2+}$: $E^{red} = +0.29$ V (2e); **2b**$^{2+}$: $E_1^{red} = +0.26$, $E_2^{red} = +0.05$ V versus the saturated calomel electrode (SCE)),[8] which indicates that the diradical **2**$^{\bullet\bullet}$ is a long-lived species in an argon atmosphere. In contrast, only irreversible reduction waves were observed in both cases when the same solutions were saturated with O_2 (Figure 1). On the basis of a detailed examination of the cyclic voltammograms, it seems likely that the cation radical intermediate **2**$^{+\bullet}$ is readily trapped by O_2 to form (**2**-O_2)$^{+\bullet}$, which is further reduced to (**2**-O_2)$^{\bullet\bullet}$ at a slightly more negative potential than **2**$^{2+}$ (ECE process). The resultant diradical (**2**-O_2)$^{\bullet\bullet}$ undergoes ring closure to the entropically disfavored nine-membered ring with unexpectedly high efficiency. Thus, peroxides **1a**[6] [λ_{max} (lgε) 291 (3.92), 284 nm (sh, 3.90) in MeCN] and **1b**[6] [285 (sh, 4.02), 267 (4.28)] were isolated as colorless crystals in 80 and 71% yield, respectively, when the **2**-$(BF_4)_2$ salts were reduced with Zn powder in aerated THF.[9]

X-ray analyses[10] on the novel heterocycles **1** (Figure 2) have revealed the extended conformation of the peroxide moiety (torsion angle for the C-O-O-C unit: 160.8(3)° for **1a**; 154.6(2)° for **1b**), and their O–O bond lengths (1.507(4) Å for **1a**; 1.502(3) Å for **1b**) are two of the longest values ever reported[11]. Yet, the electrochemical oxidation does not break this weak O–O bond, but instead breaks the adjacent C–O bonds.[3] It is also interesting to note that deoxygenation and

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