spectrum (Figure 1c). The characteristic features of the antiferromagnetically coupled pairs of copper ions are almost entirely absent. Instead, a spectrum typical of magnetically isolated copper ions in sites having axial symmetry is observed. This result demonstrates conclusively that the bridge has been broken. Redissolving the solid in water largely restores the spectrum of the bridged structure (Figure 1d).

The spectrum in Figure 1c consists of only a single signal, indicating that both copper ions in the active sites of lyophilized Cu_2Cu_2SOD must be in quite similar environments. This result is surprising since Cu_2Zn_2SOD and Ag_2Cu_2SOD, where the copper is in the native copper and zinc sites, respectively, have very different ESR spectra. Ag_2Cu_2SOD in particular has an ESR spectrum typical of copper in a tetrahedral site,[14] consistent with the known geometry of the zinc site in Cu_2Zn_2SOD.[3] Breaking of the imidazolate bridge in Cu_2Cu_2SOD appears to be accompanied by alteration of the geometry around the copper atom in the zinc site to form a more favorable square-planar structure. Since this phenomenon occurs not only on lyophilization but also in solution in the presence of thiocyanate ion,[15] the two effects are probably related.

Further evidence of this relationship is found in the ESR spectrum of zinc-free SOD,[15] which lacks the rhombic distortion evident in the spectrum of Cu_2Zn_2SOD. Maintenance of the distorted geometry of the copper site in native SOD depends upon the presence of zinc in the zinc site which, by coordinating to one of the histidine imidazoles already bound to copper, produces the bridging imidazolate structure. The geometry of the copper coordination sphere is also influenced by the tertiary structure of the protein, which is sensitive to the extent of hydration. This sensitivity is revealed by the present work where lyophilization not only breaks the imidazolate bridge in the case of Cu_2Cu_2SOD but also results in the appearance of a more axial spectrum for Cu_2Zn_2SOD, even though zinc is present. In turn, binding of zinc in the zinc site affects the tertiary structure of the protein, at least around the active site, as shown by changes in the NMR spectrum of the exchangable histidine N–H protons when zinc is added to the apoprotein.[16] The geometry of the copper site is thus determined by two factors which are themselves interdependent: the tertiary structure of the protein and the presence of zinc in the zinc site.

Addition of sucrose to Cu_2Cu_2SOD solutions prior to lyophilization stabilizes the imidazolate bridge in the solid. As little as 1% (w/v) sucrose, or approximately 30 sucrose molecules per molecule of protein, is effective in maintaining the antiferromagnetic interaction between the copper ions. The presence of sucrose has no effect on the ESR spectrum of Cu_2Cu_2SOD in frozen solution. Cu_2Zn_2SOD lyophilized from either 1% or 10% (w/v) sucrose solution has ESR parameters (Table I) different from the values for both the frozen solutions and the solid lyophilized in the absence of sucrose. In particular, the $A_{\parallel}$ value of the solid in the presence of sucrose is midway between the values for the solution and the sucrose-free solid. These results indicate that, although the presence of sucrose can provide substantial stabilization of the native structure of the protein upon lyophilization, the solid does not have a structure around the copper ion which is identical with the solution structure. Saccharides have been observed previously to stabilize metalloproteins during lyophilization,[17] although the manner by which they do so has not been elucidated.

Changes in the ESR spectrum of catalase upon lyophilization have been noted,[18] and Raman spectra of deoxyhemoglobin indicate a change in the vibrational characteristics of the iron–histidine bond when the solution is frozen.[19] These results, along with those presented here, indicate that significant chemical changes can occur at the metal centers of metalloproteins because of an alteration of the normal protein–water interaction.

Acknowledgment. This work was supported by research Grant GM-16449 from the National Institute of General Medical Sciences.

Registry No. SOD, 9054-89-1; Cu, 7440-50-8; Zn, 7440-66-6.

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[14] Beem, K. M.; Richardson, D. C.; Rajagopalan, K. V. *Biochemistry* **1977**, *16*, 1930.

[15] ESR spectra of Cu_2Cu_2SOD plus thiocyanate ion in frozen aqueous solution show a single axial copper signal with $g_{\perp} = 2.065$, $g_{\parallel} = 2.259$, and $A_{\parallel} = 0.0155$ cm^{-1}.[5] The ESR spectrum of zinc-free SOD in frozen solution has $g_{\perp} = 2.076$, $g_{\parallel} = 2.269$, and $A_{\parallel} = 0.0150$ cm^{-1}.[14]

[16] Lippard, S. J.; Burger, A. R.; Ugurbil, K.; Pantoliano, M. W.; Valentine, J. S. *Biochemistry* **1977**, *16*, 1136.

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Chemistry of Exciplexes. 12. Chemistry of Heterodimers of Benzene and Anthracene[1]

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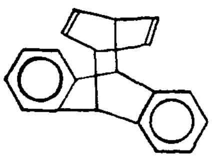
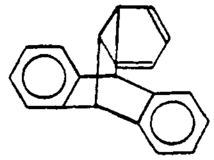
Cyclodimers of benzene with arenes are a group of energy-rich molecules which dissociate exoergically to their components.[3] There are three common types of such dimers: the $[4_{\pi_s} + 4_{\pi_s}]$, the $[4_{\pi_s} + 2_{\pi_s}]$, and the $[2_{\pi_s} + 2_{\pi_s}]$ dimers. This communication deals with the first synthesis of both meso heterodimers of anthracene with benzene in highly purified form (>99.8%), the $[4_{\pi_s} + 4_{\pi_s}]$ dimer **1** and the $[4_{\pi_s} + 2_{\pi_s}]$ dimer **2**, and their cycloreversions to anthracene and benzene.

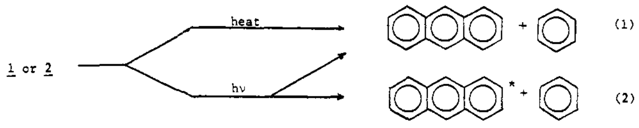


1



2

The cycloreversion of **1** is a chemical process involving $4n$ reacting electrons; that of **2** involves $4n + 2$ reacting electrons. The availability of both compounds has enabled us to study the role of conservation of orbital symmetry in cycloreversions in both the ground and the excited states.



Both **1** and **2** were synthesized by an application of photocycloaddition of substituted 1,3-cyclohexadienes (**3** and **4**, Scheme I) to anthracene[4] followed by conversion of substituents to an olefinic bond. The orientation of photocycloaddition was controlled by the choice of substrate and experimental conditions. The $[4_{\pi_s} + 4_{\pi_s}]$ adduct **5** was formed as the major adduct in the photocycloaddition of **3** to anthracene in acetonitrile, while the $[4_{\pi_s} + 2_{\pi_s}]$ adduct **7** was formed as the major adduct in the photocycloaddition of **4** to anthracene in dichloromethane. The for-

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[1] Dedicated to Professor George S. Hammond on the occasion of his 60th birthday.

[2] Hedwig Loeb Undergraduate Scholar, University of Chicago, 1981.

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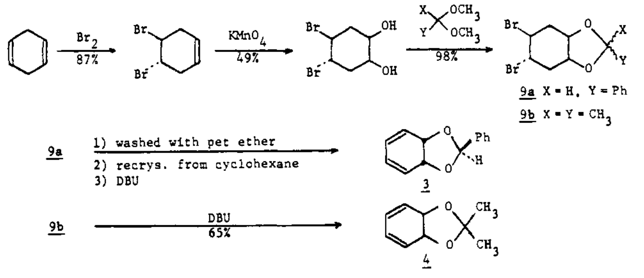
Table I

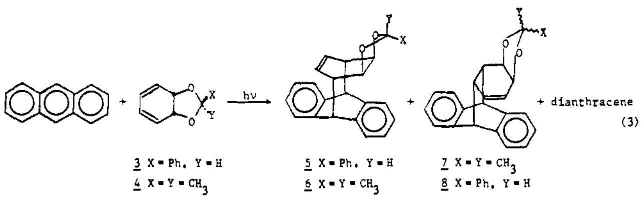
compd	thermoreversion		photoreversion		
	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Φ_{An}	Φ_f	Φ_{An^*}[a]
1	33.0 ± 0.9	16.4 ± 2.4	0.86 ± 0.06	0.31 ± 0.03	0.80 ± 0.08
2	24.3 ± 0.2	−3.0 ± 0.6	0.71 ± 0.05	0.030 ± 0.003	0.08 ± 0.01

[a] Calculated on the basis of Φ_f of anthracene being 0.39.[8]

Scheme I



mation of 7, rationalized via a stepwise mechanism, becomes significant because of solvent and other effects that disfavor the concerted pathway.[5]



(3)

$$7 \xrightarrow[\text{2) PhCH(OCH}_3)_2]{\text{1) H}_3\text{O}^+} 8 \qquad (4)$$

$$5 \xrightarrow{(CH_3)_3CLi} 1 \qquad 8 \xrightarrow{(CH_3)_3CLi} 2 \qquad (5)$$

The immediate precursors of **1** and **2**, the benzaldehyde acetals **5** and **8**, were converted to the respective heterodimers by the cycloelimination at room temperature or below of benzoate ion after abstraction of the benzylic proton from the acetal by *tert*-butyllithium (see reaction 5).[6] The ketal **7** was converted to the acetal **8** (a mixture of stereoisomers) through conventional methods. Both **1** and **2** were isolated in >98% purity by column chromatography at 0 °C and further purified by low-temperature recrystallization.[7] Their final purities were estimated by UV spectroscopy (Figure 1).

Thermal decompositions of **1** and **2** were not chemiluminescent. The kinetics of these decompositions in *n*-octane solution were determined by measuring the appearance of anthracene in the UV spectrum at several temperatures. The activation parameters are given in Table I. Clearly, conservation of orbital symmetry plays an important role in these reactions. The kinetic data indicate that the thermal cycloreversion of **1** is stepwise while that of **2** is concerted.

Both **1** and **2** undergo photodecompositions efficiently to give anthracene. At 0 °C, both compounds exhibit a fluorescence spectrum identical with that of anthracene with no benzenoid-type fluorescence from the parent compound. Although the formation of excited anthracene is energetically accessible in photocycloreversions of both **1** and **2**, **1** exhibits a Φ_f of 0.31 ± 0.03, compared to Φ_f of 0.030 ± 0.003 for **2**. The results indicate that over 90% of anthracene formed in the photodissociation of **1** is in its excited state while only a small fraction of that from **2** is excited.[8] Judging from the marked difference in the efficiencies of formation of excited anthracene, it is unlikely that the photocycloreversions of these compounds in solution proceed from a common biradical intermediate.

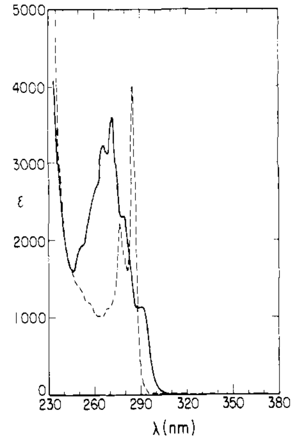


Figure 1. UV absorption of 1 (- - -) and **2** (—).

Although the principle of conversion of orbital symmetry has been applied successfully to both ground state to ground state and excited state to ground state pericyclic reactions,[9] there has been no systematic treatment of interconversions between excited-state molecules, processes known as adiabatic photoreactions or chemiluminescent photoreactions.[10] By examining the symmetry properties and configurations of various substrate and product states in cycloadditions, Woodward and Hoffmann found that the first excited state of substrate(s) correlated with the first excited state of product(s) in 4*n* cycloadditions, while the first excited state of substrate(s) correlated with an upper excited state of product(s) in 4*n* + 2 cycloadditions. The conversion of excited **1** to excited anthracene, formally a 4*n* process, is remarkably efficient and facile. By analyzing the symmetry properties of orbitals and state configurations of this conversion in two dimensions, we found indeed that there is a correlation between the first excited state of substrate(s) and product(s). Conversely, the photodissociation of **2** to excited anthracene is a formal 4*n* + 2 process, predicted by state symmetry correlation to be forbidden as a concerted process, and found to occur with low efficiency.[11] We have initiated both a theoretical treatment and a kinetic analysis for photocycloreversions of **1** and **2** to achieve a better understanding of these reactions.[12]

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(5) For these effects, see: Yang, N. C.; Yates, R. L.; Masnovi, J.; Shold, D. M.; Chiang, W. L. *Pure Appl. Chem.* **1979**, *51*, 173–180. Wang, T.-Y.; Ni, J.-D.; Masnovi, J.; Yang, N. C., unpublished results.

(6) Hines, J. N.; Peagram, M. J.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2332–2337.

(7) Both **1** and **2** decomposed in their solid state without melting to anthracene upon heating. Compound **1**: IR (KBr) 3027 and 2942 cm^{-1}; NMR (CDCl$_3$) δ 3.52 (2 H, m), 4.25 (2 H, d, *J* = 11.5 Hz), 5.91 (4 H, m), 7.03 (4 H, m) and 7.09 (4 H, m). Compound **2**: IR (CCl$_4$) 3070, 3035, 2940, and 2890 cm^{-1}; NMR (CDCl$_3$) δ 3.06 (2 H, s), 4.21 (2 H, s), 5.37 (4 H, m) and 7.20 (8 H, m). The UV spectra of **1** and **2** are given in Figure 1. Elemental analyses of these compounds were not attempted due to their low thermal stability.

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(9) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

(10) For a review of these reactions, see: (a) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; p 608–609 and references therein. See also: (b) Yang, N. C.; Carr, R. V.; Li, E.; McVey, J. K.; Rice, S. A. *J. Am. Chem. Soc.* **1974**, *96*, 2297–2298. (c) Carr, R. V.; Kim, B.; McVey, J. K.; Yang, N. C.; Gerhartz, W.; Michl, J. *Chem. Phys. Lett.* **1976**, *39*, 57–60. (d) Jones, G., II; Chiang, S.-H. *Tetrahedron* **1981**, *37*, 3397–3403.

(11) An excited state of **2** corresponding to $\psi_2 \rightarrow \psi_3$ transition in the butadiene chromophore has the same symmetry properties in one dimension as those of benzene and excited anthracene. This may account for the formation of excited anthracene in low efficiency upon irradiation of **2**.

(12) It is interesting to note also that in electrocyclic reactions there is a correlation between the first excited state of substrate and product in allowed photochemical processes but not in allowed ground-state processes; see p 43, ref 9. Such a correlation is in agreement with experimental observations.[10]

Photocycloadditions of 1,2-dihydroxy-3,5-cyclohexadiene derivatives **3** and **4** to arenes and subsequent elimination of oxy substituents provide us with a convenient route to a variety of cyclodimers of benzene, energy-rich molecules expected to exhibit novel properties. The extension of this route to the synthesis of other cyclodimers, and the chemistry of these compounds, will be investigated.

Acknowledgment. We thank the National Science Foundation and the Louis Bloch Fund of the University of Chicago for the support of this work, Professor David Evans for a valuable suggestion in the syntheses of these compounds, and the National Cancer Institute for a grant to the University of Chicago Cancer Research Center to purchase the NMR spectrometer used in this work.

Heptamethylindenyl Lanthanide(III) Complexes of Lanthanum, Neodymium, and Erbium

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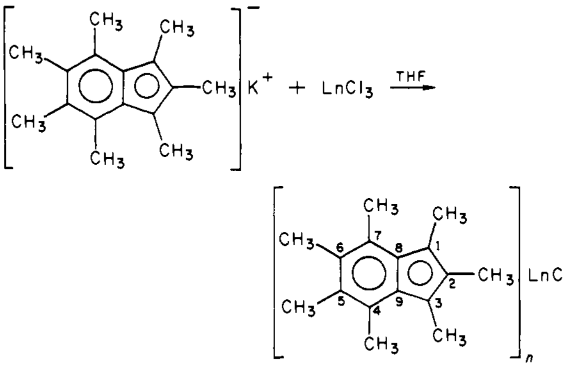
Received April 11, 1981

The π-complex chemistry of the lanthanides has been relatively undeveloped compared to that of the d-block elements.[2] For example, synthesis of all three types of organometallic compounds, LnL_3, LnL_2Cl, and $LnLCl_2$ (Ln = La–Lu, L = a π ligand such as cyclopentadienyl (Cp), methylcyclopentadienyl, or indenyl), poses a challenging problem for the design of potentially active homogeneous catalysts from lanthanide elements.[3] While compounds like $LnCp_3$ are known for a whole series of lanthanides,[4-6] the other two types of synthetic precursors, $LnCp_2Cl$ and $LnCpCl_2$ are available solely for the late members of the series (Sm–Lu).[7] It has often been claimed that this trend is due to the large ionic radii and poor ligand field–metal interaction of the early lanthanides.

One approach to circumventing this synthetic problem is to use the chelate effect to achieve enforced metal–ligand coordination. Indeed, a chelate ligand, 1,3-dicyclopentadienylpropane, has been prepared and has allowed the successful isolation of $(Cp(CH_2)_3Cp)LnR$ where Ln = La or Ce and R = Cl, C_6H_5, or $C_2C_6H_5$.[8] Unfortunately, the low solubilities of these compounds in common organic solvents limited their applications as homogeneous catalysts.

Another approach which we have used is to use bulky ligands to protect the metal–ligand bonds in the expected organolanthanides. In this connection, Wayda and Evans have reported the reaction of pentamethylcyclopentadienyllithium with $NdCl_3$.[9] However, in this case, the expected $[(C_5Me_5)_2NdCl]_2$ was not formed and a lithium salt, $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$, was isolated instead. Here we report our work with a new ligand, heptamethylindenyl (Hmi), which has recently been prepared in these laboratories.[10] Both the steric bulk and the electronic character of this ligand resulting from the seven methyl groups favor stabilization of lanthanide–carbon bonds. With the aid of this ligand, the π-complexes, $(Hmi)LnCl_2$ (**1**) and $(Hmi)_3Ln$ (**3**) have been synthesized for both early and late lanthanide elements according to reaction 1. In addition, $(Hmi)_2LnCl$ (**2**) can be prepared although in the case of **2a** this complex has been shown to be a mixture of **1a**, **2a**, and **3a** by ^{13}C NMR spectroscopy.



(1)

a, Ln = La; b, Ln = Er; c, Ln = Nd

Alkali metal salts of heptamethylindenide were used as precursors of the lanthanide complexes. The alkali metal salts of Hmi can be prepared by using either lithium, sodium, or potassium. The potassium salt was most useful because of its higher reactivity toward lanthanide halides. The potassium salt was obtained by reaction of heptamethylindene with a dispersion of potassium metal in refluxing THF and could be isolated as a crystalline solid when solutions which were >0.5 M were cooled to room temperature. The lanthanide salts themselves are obtained by addition of a stoichiometric amount of KHmi (**4**) to the desired amount of $LnCl_3$ and allowing the resulting suspension to stir at 25 °C for ca. 2 days. When the ratio of KHmi to $LnCl_3$ was 3:1 (equiv/equiv), the product $Ln(Hmi)_3$ was purified by crystallization by slowly evaporating the THF solution which remained after removing by centrifugation any solids which were left after the reaction was complete. The lanthanide complexes **1** and **2** were obtained by using 1:1.05 and 2:1 ratios of KHmi to $LnCl_3$, respectively. Complexes **1** and **2** were purified by removing the initial precipitate by centrifugation, evaporating the resulting THF solution, adding a second portion of THF, again removing any insoluble material by centrifugation, and then removing the remaining THF in vacuo. Satisfactory elemental analyses were obtained for **1a**, **1b**, **2b**, **1c**, **2c**, **3c**, and **4**.[11] Complexes **3a** and **3b** analyzed correctly for lanthanide metal and hydrogen but had low values for carbon. All of the complexes **3** contained THF since no effort was made to dry them. However, the THF could easily be removed under vacuo (such dried complexes **3** seemed qualitatively less stable). Analytical samples of **3a**, **3b**, and **3c**

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[11] Anal. Calcd for $C_{32}H_{53}KO_4$ (**4**, KHmi·4THF): C, 71.06; H, 9.88; K, 7.23. Found: C, 70.54; H, 9.26; K, 8.12. Calcd for $C_{20}H_{29}Cl_2LaO$ [**1a**, $La(Hmi)Cl_2$·THF]: C, 48.50; H, 5.90; Cl, 14.32; La, 28.05. Found: C, 47.74; H, 5.64; Cl, 13.63; La, 28.19. Calcd for $C_{18}H_{25}Cl_2ErO_{0.5}$ [**1b**, Er(Hm*i*)Cl_2·0.5THF]: C, 44.34; H, 5.17; Cl, 14.54; Er, 34.31. Found: C, 43.52; H, 5.62; Cl, 14.41; Er, 34.74. Calcd for $C_{32}H_{42}ClEr$ [**2b**, Er(HM*i*)$_2$Cl]: C, 61.07; H, 6.73; Cl, 5.63; Er, 26.57. Found: C, 59.98; H, 7.10; Cl, 5.43; Er, 26.96. Calcd for $C_{60}H_{87}ErO_3$ [**3b**, $Er(Hmi)_3$·3THF]: C, 70.40; H, 8.57; Er, 16.34. Found: C, 65.98; H, 7.67; Er, 16.30. Calcd for $C_{16}H_{21}Cl_2Nd$ [**1c**, Nd(Hmi)Cl_2]: C, 44.85; H, 4.94; Cl, 16.55; Nd, 33.66. Found: C, 43.98; H, 5.44; Cl, 16.71; Nd, 33.60. Calcd for $C_{36}H_{50}ClNdO$ (**2c**, $Nd(Hmi)_2Cl$·THF): C, 63.73; H, 7.43; Cl, 5.23; Nd, 21.26. Found: C, 62.73; H, 7.24; Cl, 5.26; Nd, 21.93. Calcd for $C_{68}H_{103}NdO_5$ (**3c**, $Nd(Hmi)_3$·5THF): C, 71.34; H, 9.07; Nd, 12.60. Found: C, 70.84; H, 9.07; Nd, 12.69.

0002-7863/82/1504-0855$01.25/0