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Cluster Syntheses. 2. The Role of Heteroatoms in the Formation of High Nuclearity Transition-Metal Carbonyl Cluster Compounds. The Condensation of Small Clusters

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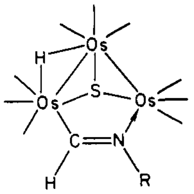
Abstract: The compounds $HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)(CO)_9$, Ia, R = C_6H_5, and Ia′, R = $C_6H_4\text{-}p\text{-}F$, lose CO and/or H_2 when heated to form the hexanuclear osmium complexes $Os_6(\mu_4\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{18}$, IIa, R = C_6H_5, and IIa′, R = $C_6H_4\text{-}p\text{-}F$, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{17}$, IIIa,b, R = C_6H_5, and IIIa′,b′, R = $C_6H_4\text{-}p\text{-}F$, which exist as two isomers, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{16}$, IVa–c, R = C_6H_5, and IVa′–c′, R = $C_6H_4\text{-}p\text{-}F$, which exist as three isomers, and $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NR)_2(CO)_{15}$, Va, R = C_6H_5, and Va′, R = $C_6H_4\text{-}p\text{-}F$. All compounds have been analyzed by IR and ^1H NMR spectroscopy. Compounds IIIa′, IVa, and Va have also been characterized by single-crystal X-ray diffraction analyses. Compounds III can be converted to IV, and IV into V. III, IV, and V are believed to be part of a sequence of cluster growth processes in which the sulfido ligands mediate the initial linking of the clusters and the subsequent formation of metal–metal bonds between them. IIIa′ contains two "open" triangular groups of three metal atoms linked by a tetrahedrally coordinated sulfido ligand. In IVa the six metal atoms are arranged in groups of four and two, with the two groups linked by a tetrahedrally coordinated sulfido ligand. In Va the six metal atoms have condensed into a central cluster of four which has the form of a butterfly tetrahedron with sulfido ligands bridging the two open triangular faces. The two remaining metal atoms are bonded to the "hinge" metal atoms of the central cluster, one to each.

Transition-metal cluster compounds have attracted a great deal of attention because of their potential use as a new class of homogeneous reaction catalysts.[1,2] However, a problem which has limited thorough investigations of their chemistry is simply their availability. Most carbonyl cluster compounds have been synthesized fortuitously through pyrolysis of low nuclearity carbonyl compounds.[3] Cluster growth occurs through formation of metal–metal bonds when carbonyl ligands are eliminated.

In an effort to develop new systematic routes for the synthesis of high nuclearity carbonyl clusters, we have been investigating the role that heteroatoms, derived from elements of the main groups, might play in cluster formation.[4,5] It is believed that heteroatoms could serve as focal points for the aggregation of metal carbonyl units and thus assist in the development and growth of the cluster.[4-7]

We have recently synthesized the sulfido cluster compounds $HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)(CO)_9$, R = C_6H_5, Ia, and $C_6H_4\text{-}p\text{-}F$, Ib.[8] When heated, these trinuclear cluster complexes lose CO and/or H_2 and condense to form hexanuclear clusters. It has been found that the sulfido ligands play an integral role in both the initial condensation process and the eventual reorganization of the metal–metal bonding.[4] The details of these reactions will be reported here.

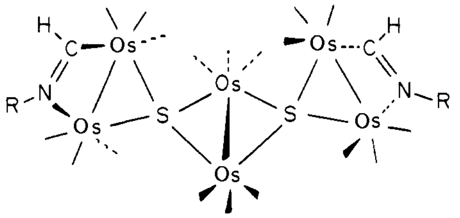


I

Results

Thermolytic decarbonylation of the trinuclear cluster compounds Ia or Ia′ in refluxing octane for 3 h yields in each case seven new hexanuclear osmium clusters which can be divided into four groups depending on the arrangement of the metal atoms.

All of the products have been characterized by IR and ^1H NMR spectroscopy and an X-ray crystallographic analysis of a representative member of each group. Members of the first group are $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NR)_2(CO)_{18}$, R = C_6H_5, IIa, and R = $C_6H_4\text{-}p\text{-}F$, IIa′. The second group consists of two isomers of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{17}$, IIIa and IIIb, R = C_6H_5, and IIIa′ and IIIb′, R = $C_6H_4\text{-}p\text{-}F$. The third group consists of three isomers of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{16}$, IVa–c, R = C_6H_5, and IVa′–c′, R = $C_6H_4\text{-}p\text{-}F$. The last group consists of $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NR)_2(CO)_{15}$, Va, R = C_6H_5, and Va′, R = $C_6H_4\text{-}p\text{-}F$. Spectra are listed in Table I.



II

Single-crystal X-ray diffraction methods have been used to establish the molecular structures of IIa,[9a] IIIa′, IVa–c, and Va. Stoichiometrically, IIa contains a combination of 2 mol of Ia less two hydrogen atoms. The metal atoms are arranged into three groups of two. The sulfido ligands have been converted from triple into tetrahedrally coordinated, quadruple bridges. These compounds apparently have no bearing on the cluster growth sequences observed among the other compounds and thus will not be further described at this time.[9]

An ORTEP diagram of the molecular structure of IIIa′ is shown in Figure 1. IIIa′ contains six osmium atoms which are arranged in two groups. Both groups are "open" clusters of three metal

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Table I. Spectroscopic Data

compd	^{1}H NMR, δ	IR ν(CO), cm^{-1}
IIa, $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HCNC_6H_5)_2(CO)_{18}$	10.92 s (2 H), 7.2 m (10 H)[a,b]	2080 m, 2073 m, 2057 s, 2051 sh, 2014 m, 2002 m, 1990 s, 1973 w[c]
IIa', $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{18}$	10.91 s (2 H), 7.2 m (8 H)[a,b]	2083 m, 2073 m, 2057 s, 2053 sh, 2015 s, 2005 m, 1991 m, 1975 w[c]
IIIa, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{17}$	12.39 s (1 H), 11.24 s (1 H), 7.3 m (10 H), −13.80 s (1 H), −17.45 s (1 H)[a]	2111 m, 2096 m, 2085 sh, 2066 s, 2054 sh, 2044 vs, 2029 vs, 2008 s, 1990 s, 1979 s, 1961 w[c]
IIIa', $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{17}$	12.40 s (1 H), 11.24 s (1 H), 7.2 m (8 H), −13.87 s (1 H), −17.46 s (1 H)[a]	2112 m, 2098 m, 2088 m, 2084 sh, 2074 w, 2066 s, 2056 s, 2052 s, 2043 vs, 2029 vs, 2011 sh, 2006 s, 2000 sh, 1991 vs, 1981 vs, 1975 sh, 1959 sh[c]
IIIb, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{17}$	11.56 s (1 H), 10.94 s (1 H), 7.3 m (10 H), −14.48 s (1 H), −17.19 s (1 H)[a]	2112 w, 2096 m, 2082 m, 2066 s, 2053 sh, 2044 vs, 2029 vs, 2006 s, 1990 s, 1979 m, 1962 w[c]
IIIb', $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{17}$	11.57 s (1 H), 10.92 s (1 H), 7.2 m (8 H), −14.51 s (1 H), −17.25 s (1 H)[a]	2110 w, 2098 w, 2088 s, 2073 w, 2065 w, 2055 s, 2038 s, 2027 s, 2011 sh, 2000 s, 1990 s, 1980 m, 1976 sh, 1964 w[c]
IVa, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{16}$	10.87 s (1 H), 10.38 s (1 H), 7.3 m (10 H), −17.57 s (1 H), −17.72 s (1 H)[a]	2099 m, 2082 sh, 2076 vs, 2054 s, 2040 m, 2022 m, 2005 s, 1997 sh, 1984 m, 1974 m, 1962 w, 1951 w[c]
IVa', $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{16}$	10.85 s (1 H), 10.44 s (1 H), 7.1 m (8 H), −17.55 s (1 H), −17.74 s (1 H)[a]	2099 w, 2081 sh, 2075 vs, 2055 vs, 2042 m, 2022 m, 2012 w, 2005 s, 1999 sh, 1986 m, 1975 w, 1955 w[c]
IVb, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{16}$	10.85 s (1 H), 10.34 s (1 H), 7.3 m (10 H), −17.53 s (1 H), −17.83 s (1 H)[a]	2098 m, 2083 s, 2075 m, 2054 vs, 2041 m, 2024 sh, 2017 s, 2002 s, 1984 m, 1975 sh, 1965 w, 1950 w[c]
IVb', $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{16}$	10.86 s (1 H), 10.42 s (1 H), 7.1 m (8 H), −17.52 s (1 H), −17.82 s (1 H)[a]	2099 m, 2083 s, 2075 m, 2053 s, 2040 m, 2024 w, 2017 m, 2002 s, 1993 m, 1990 m, 1974 m, 1954 w[c]
IVc, $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{16}$	11.02 s (1 H), 10.43 s (1 H), 7.3 m (10 H), −17.06 s (1 H), −17.73 s (1 H)[a]	2100 m, 2083 s, 2076 s, 2053 s, 2040 m, 2024 sh, 2018 m, 2001 s, 1982 m, 1975 sh, 1962 w, 1951 w[c]
IVc', $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{16}$	11.03 s (1 H), 10.44 s (1 H), 7.1 m (8 H), −17.27 s (1 H), −17.76 s (1 H)[a]	2099 w, 2083 s, 2075 s, 2056 vs, 2043 w, 2019 m, 2002 s, 1986 w, 1975 w, 1951 w w[c]
Va, $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HCNC_6H_5)_2(CO)_{15}$	10.81 s (2 H), 7.3 and 6.8 m (10 H)[a,b]	2094 s, 2031 s, 2021 s, 1998 sh, 1975 m, 1968 m, 1952 sh, 1762 bw[d]
Va', $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)_2(CO)_{15}$	10.83 s (2 H), 7.3, 7.0, and 6.8 m (8 H)[a,b]	2106 m, 2033 s, 2022 s, 1999 sh, 1977 m, 1969 m, 1955 sh, 1760 bw[d]

[a] $CDCl_3$. [b] No hydrido resonances were observed between δ 0 and −25 at 25 or −60 °C. [c] Hexanes. [d] CH_2Cl_2.

atoms which contain only two metal–metal bonds. The metal–metal bond distances in the Os(1)–Os(2)–Os(3) group are 2.914 (1) and 2.918 (1) Å and are similar to those in $Os_3(CO)_{12}$, 2.877 (3) Å.[10] The Os(4)–Os(5)–Os(6) group contains one long bond, Os(4)–Os(5) = 2.951 (1) Å, and one short one, Os(4)–Os(6) = 2.803 (1) Å. The latter is bridged by two sulfido ligands. S(1) is a tetracoordinate, quadruple bridge, which serves as the link between the two triosmium groups while S(2) serves as a triple bridge in the Os(4)–Os(5)–Os(6) group. A tetrahedrally coordinated sulfido ligand has been observed previously in the compound $[CH_3SFe_2(CO)_6]_2S$.[11] The osmium–sulfur bond distances range from 2.404 (1) to 2.509 (1) Å and are similar to those found in other sulfidoosmium carbonyl clusters,[8,12] but on the average the metal–sulfur distances to the quadruple bridge are slightly longer than those to the triple bridge, 2.470 vs. 2.420 Å. There are 2 formimidoyl ($HCNC_6H_4$-p-F) ligands spanning the open edges of each triosmium group[8,13] and 17 linear carbonyl ligands distributed as shown in Figure 1. Bond distances and angles are listed in Tables II and III. The ^{1}H NMR spectrum shows that the molecule contains two inequivalent hydride ligands which probably serve as bridges across metal–metal bonds. Since the Os–Os bond distances in the Os(1)–Os(2)–Os(3) group are equal and similar in length to those in $Os_3(CO)_{12}$,[10] it is unlikely that either of those bonds contains a hydride bridge. The Os(4)–Os(5) bond probably contains a hydride bridge since the internuclear separation is significantly longer than the others.[14] The second

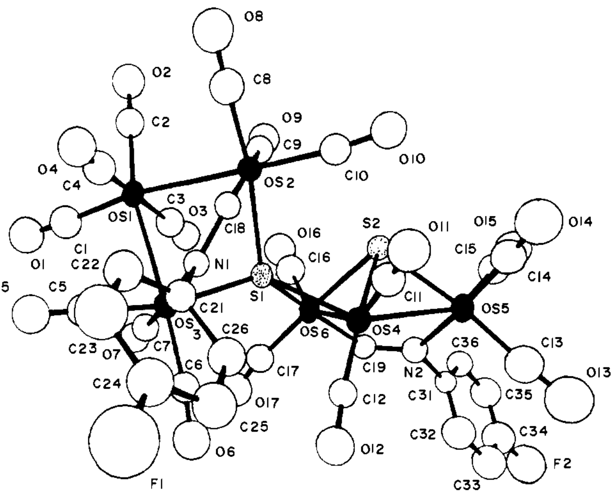

Figure 1. ORTEP diagram of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_4\text{-}p\text{-}F)_2(CO)_{17}$, IIIa', showing 50% probability thermal-motion ellipsoids.

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Table II. Interatomic Distances with esds for $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_4\text{-}p\text{-}F)_2(CO)_{17}$, IIIa′

atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.914 (1)	Os(4)–Os(5)	2.951 (1)
Os(1)–Os(3)	2.918 (1)	Os(4)–Os(6)	2.803 (1)
Os(1)–C(1)	1.92 (2)	Os(4)–S(1)	2.441 (4)
Os(1)–C(2)	1.87 (2)	Os(4)–S(2)	2.421 (3)
Os(1)–C(3)	1.93 (2)	Os(4)–C(11)	1.89 (2)
Os(1)–C(4)	1.94 (2)	Os(4)–C(12)	1.82 (1)
Os(2)–S(1)	2.447 (4)	Os(5)–S(2)	2.404 (4)
Os(2)–C(5)	1.92 (2)	Os(5)–N(2)	2.16 (1)
Os(2)–C(6)	1.89 (2)	Os(5)–C(13)	1.85 (2)
Os(2)–C(7)	1.88 (2)	Os(5)–C(14)	1.91 (2)
Os(2)–N(1)	2.12 (1)	Os(5)–C(15)	1.84 (2)
Os(3)–S(1)	2.481 (3)	Os(6)–S(1)	2.509 (4)
Os(3)–C(8)	1.88 (2)	Os(6)–S(2)	2.436 (4)
Os(3)–C(9)	1.94 (2)	Os(6)–C(16)	1.89 (2)
Os(3)–C(10)	1.92 (2)	Os(6)–C(17)	1.90 (2)
Os(3)–C(18)	2.10 (1)	Os(6)–C(19)	2.02 (2)
C(18)–N(1)	1.30 (2)	C(19)–N(2)	1.33 (2)
N(1)–C(21)	1.49 (2)	N(2)–C(31)	1.44 (2)
C(21)–C(22)	1.33 (2)	C(31)–C(32)	1.37 (2)
C(22)–C(23)	1.43 (2)	C(32)–C(33)	1.40 (2)
C(23)–C(24)	1.34 (2)	C(33)–C(34)	1.36 (2)
C(24)–C(25)	1.32 (2)	C(34)–C(35)	1.35 (2)
C(25)–C(26)	1.42 (2)	C(35)–C(36)	1.40 (2)
C(26)–C(21)	1.41 (2)	C(36)–C(31)	1.37 (2)
C(24)–F	1.43 (2)	C(34)–F	1.42 (2)
C(1)–O(1)	1.13 (2)	C(11)–O(11)	1.19 (2)
C(2)–O(2)	1.18 (2)	C(12)–O(12)	1.20 (1)
C(3)–O(3)	1.15 (2)	C(13)–O(13)	1.20 (2)
C(4)–O(4)	1.15 (2)	C(14)–O(14)	1.14 (2)
C(5)–O(5)	1.12 (2)	C(15)–O(15)	1.19 (2)
C(6)–O(6)	1.14 (2)	C(16)–O(16)	1.16 (2)
C(7)–O(7)	1.16 (2)	C(17)–O(17)	1.14 (2)
C(8)–O(8)	1.16 (2)	S(1)···S(2)	3.060 (6)
C(9)–O(9)	1.16 (2)		
C(10)–O(10)	1.15 (2)		

hydride ligand probably bridges the Os(4)–Os(6) bond. Although this bond is shorter than expected, this shortening could be due to the presence of the two sulfido bridges. Heteronuclear bridges are known to counterbalance the lengthening effect of hydrido bridges.[15] The bond angles Os(6)–Os(4)–C(2) = 116.6 (5)° and Os(4)–Os(6)–C(7) = 117.2 (5)° are large. This could be due to the steric influence of a bridging hydrido ligand.[14]

Because of their complex but strikingly similar IR and ^1H NMR spectra, it is believed that IIIa and IIIa′ are structural analogues. Also, since their IR and ^1H NMR spectra are very similar, IIIa and IIIb, and IIIa′ and IIIb′, are believed to be isomers, formed perhaps through a different permutation of metal atoms at the sulfido bridge, S(1). Isomers of IV are formed in this way, vide infra.

Table III. Selected Interatomic Angles with esds for $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_4\text{-}p\text{-}F)_2(CO)_{17}$, IIIa′

atoms	angle, deg	atoms	angle, deg
Os(2)–Os(1)–Os(3)	75.28 (2)	Os(5)–Os(4)–Os(6)	80.93 (2)
Os(1)–Os(2)–S(1)	84.49 (8)	Os(5)–Os(4)–S(1)	128.14 (8)
Os(1)–Os(3)–S(1)	83.83 (9)	Os(4)–S(2)–Os(5)	75.39 (10)
Os(2)–Os(1)–C(1)	93.8 (5)	Os(4)–S(2)–Os(6)	70.49 (10)
Os(2)–Os(1)–C(2)	166.6 (5)	Os(5)–S(2)–Os(6)	101.02 (13)
Os(2)–Os(1)–C(3)	85.5 (5)	Os(5)–Os(4)–C(11)	100.9 (5)
Os(2)–Os(1)–C(4)	85.1 (4)	Os(5)–Os(4)–C(12)	120.8 (5)
Os(3)–Os(1)–C(1)	169.1 (5)	Os(6)–Os(4)–C(11)	149.3 (4)
Os(3)–Os(1)–C(2)	91.3 (5)	Os(6)–Os(4)–C(12)	116.6 (5)
Os(3)–Os(1)–C(3)	86.8 (5)	Os(4)–Os(6)–C(16)	148.1 (5)
Os(3)–Os(1)–C(4)	85.5 (5)	Os(4)–Os(6)–C(17)	117.2 (5)
Os(1)–Os(2)–C(5)	85.2 (4)	Os(4)–Os(6)–C(19)	98.5 (4)
Os(1)–Os(2)–C(6)	173.7 (5)	Os(4)–Os(5)–C(13)	117.4 (6)
Os(1)–Os(2)–C(7)	83.4 (4)	Os(4)–Os(5)–C(14)	87.4 (5)
Os(1)–Os(2)–N(1)	90.2 (3)	Os(4)–Os(5)–C(15)	147.5 (5)
Os(1)–Os(3)–C(8)	89.4 (5)	Os(4)–Os(5)–N(2)	90.5 (4)
Os(1)–Os(3)–C(9)	85.5 (5)	S(2)–Os(4)–C(11)	101.8 (4)
Os(1)–Os(3)–C(10)	178.9 (4)	S(2)–Os(4)–C(12)	167.7 (5)
Os(1)–Os(3)–C(18)	89.0 (4)	S(2)–Os(6)–C(16)	97.3 (5)
Os(2)–S(1)–Os(3)	92.54 (13)	S(2)–Os(6)–C(17)	171.7 (5)
Os(2)–S(1)–Os(4)	124.05 (13)	S(1)–Os(4)–S(2)	78.01 (13)
Os(2)–S(1)–Os(6)	129.54 (15)	S(1)–Os(6)–S(2)	76.45 (13)
Os(3)–S(1)–Os(4)	113.61 (14)	S(1)–Os(4)–C(11)	102.2 (5)
Os(3)–S(1)–Os(6)	129.38 (14)	S(1)–Os(4)–C(12)	105.4 (5)
Os(4)–S(1)–Os(6)	68.96 (10)	S(1)–Os(6)–C(16)	109.1 (6)
Os(3)–C(18)–N(1)	122.6 (10)	S(1)–Os(6)–C(17)	98.4 (5)
Os(2)–N(1)–C(18)	122.0 (9)	S(1)–Os(6)–C(19)	152.8 (4)
Os(2)–N(1)–C(21)	121.1 (8)	Os(6)–C(19)–N(2)	123.3 (11)
C(18)–N(1)–C(21)	116.9 (11)	Os(5)–N(2)–C(19)	126.5 (11)
N(1)–C(21)–C(22)	122 (1)	Os(5)–N(2)–C(31)	115.9 (10)
N(1)–C(21)–C(26)	115 (1)	C(19)–N(2)–C(31)	117.6 (12)
C(26)–C(21)–C(22)	123 (1)	N(2)–C(31)–C(32)	120 (1)
C(21)–C(22)–C(23)	119 (2)	N(2)–C(31)–C(36)	120 (1)
C(22)–C(23)–C(24)	116 (2)	C(36)–C(31)–C(32)	120 (1)
C(23)–C(24)–C(25)	127 (2)	C(31)–C(32)–C(33)	122 (2)
C(24)–C(25)–C(26)	117 (2)	C(32)–C(33)–C(34)	115 (2)
C(25)–C(26)–C(21)	118 (2)	C(33)–C(34)–C(35)	126 (2)
C(23)–C(24)–F(1)	115 (2)	C(34)–C(35)–C(36)	117 (2)
C(25)–C(24)–F(2)	118 (2)	C(35)–C(36)–C(31)	120 (1)
Os(1)–C(1)–O(1)	175 (2)	C(33)–C(34)–F(2)	117 (2)
Os(1)–C(2)–O(2)	177 (1)	C(35)–C(34)–F(2)	116 (2)
Os(1)–C(3)–O(3)	174 (2)	Os(4)–C(11)–O(11)	176 (1)
Os(1)–C(4)–O(4)	177 (1)	Os(4)–C(12)–O(12)	177 (1)
Os(2)–C(5)–O(5)	177 (2)	Os(5)–C(13)–O(13)	174 (2)
Os(2)–C(6)–O(6)	172 (1)	Os(5)–C(14)–O(14)	178 (2)
Os(2)–C(7)–O(7)	178 (1)	Os(5)–C(15)–O(15)	175 (2)
Os(3)–C(8)–O(8)	178 (2)	Os(6)–C(16)–O(16)	177 (2)
Os(3)–C(9)–O(9)	178 (2)	Os(6)–C(17)–O(17)	172 (2)
Os(3)–C(10)–O(10)	173 (1)		

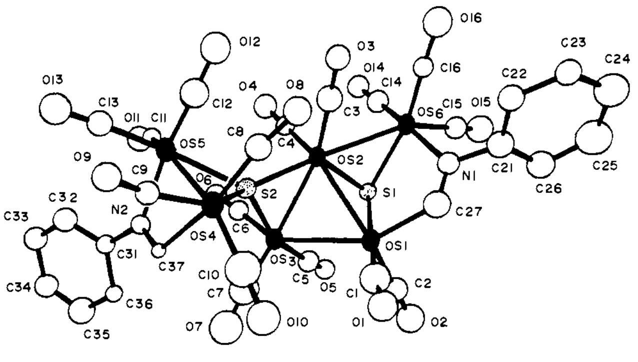

Figure 2. ORTEP diagram of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{16}$, IVa, showing 50% probability thermal-motion ellipsoids.

An ORTEP diagram of the molecular structure of IVa is shown in Figure 2. This molecule contains six osmium atoms, but these are arranged into groups of four and two. The group of four can be viewed as an open triangular unit of three, Os(1)–Os(2)–Os(6), with the fourth metal atom, Os(3), bridging the Os(1)–Os(2) bond. The Os(1)–Os(3) bond distance at 3.070 (2) Å is unusually long while the other metal–metal bonds in this group, which range from 2.839 (2) to 2.917 (2) Å, are similar to those in $Os_3(CO)_{12}$.[10] The metal atoms in the two atom group, Os(4) and Os(5), are linked by a metal–metal bond of 2.769 (2) Å. There are two sulfido ligands. S(1) serves as a triple bridge in the group of four while the tetrahedrally coordinated quadrupule bridge S(2) links the group of two to the group of four. IVa has two formimidoyl ligands. One bridges the nonbonded pair of metal atoms Os(1)···Os(6) in the group of four while the other serves as a bridge in the group of two. Structurally, these ligands are similar to those observed in related molecules.[13] Bond distances and angles are listed in Tables IV and V. There are 16 linear terminal carbonyl ligands arranged as shown in Figure 2.

The ^1H NMR spectrum of IVa indicates the presence of two inequivalent bridging hydride ligands. One probably spans the very long metal–metal bond, Os(1)–Os(3). The position of the other is not clear but the side of the Os(1)–Os(2) bond opposite the sulfido ligand S(1) has large bond angles Os(2)–Os(1)–C(1) = 124.0 (11)° and Os(1)–Os(2)–C(3) = 118.0 (10)° which could

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(15) (a) Churchill, M. R.; Lashewycz, R. *Inorg. Chem.* **1979**, *18*, 3261. (b) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Keister, J. B. *Ibid.* **1980**, *19*, 1272.

Table IV. Interatomic Distances with esds for $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{16}$, IVa

atoms	distance, Å	atoms	distance, Å
Os(1)-Os(2)	2.865 (2)	Os(6)-C(16)	1.75 (3)
Os(1)-Os(3)	3.070 (2)	Os(6)-N(1)	2.16 (3)
Os(2)-Os(3)	2.839 (2)	C(27)-N(1)	1.21 (4)
Os(2)-Os(6)	2.917 (2)	N(1)-C(21)	1.46 (3)
Os(4)-Os(5)	2.769 (2)	C(21)-C(22)	1.43 (4)
Os(1)···Os(6)	3.757 (2)	C(22)-C(23)	1.39 (4)
Os(2)···Os(4)	4.386 (2)	C(23)-C(24)	1.39 (4)
Os(2)···Os(5)	4.337 (2)	C(24)-C(25)	1.47 (4)
Os(3)···Os(4)	4.398 (2)	C(25)-C(26)	1.45 (4)
Os(3)···Os(5)	4.401 (2)	C(26)-C(21)	1.46 (4)
Os(1)-S(1)	2.439 (7)	C(37)-N(2)	1.28 (3)
Os(2)-S(1)	2.375 (7)	N(2)-C(31)	1.45 (3)
Os(6)-S(1)	2.348 (8)	C(31)-C(32)	1.37 (4)
Os(2)-S(2)	2.372 (8)	C(32)-C(33)	1.36 (4)
Os(3)-S(2)	2.417 (7)	C(33)-C(34)	1.50 (4)
Os(4)-S(2)	2.425 (7)	C(34)-C(35)	1.33 (4)
Os(5)-S(2)	2.403 (8)	C(35)-C(36)	1.43 (4)
Os(1)-C(1)	1.81 (3)	C(36)-C(31)	1.49 (4)
Os(1)-C(2)	1.89 (3)	C(1)-O(1)	1.24 (3)
Os(1)-C(27)	2.07 (4)	C(2)-O(2)	1.18 (3)
Os(2)-C(3)	1.84 (3)	C(3)-O(3)	1.23 (3)
Os(2)-C(4)	1.85 (3)	C(4)-O(4)	1.17 (3)
Os(3)-C(5)	1.97 (3)	C(5)-O(5)	1.12 (3)
Os(3)-C(6)	1.87 (3)	C(6)-O(6)	1.19 (3)
Os(3)-C(7)	1.76 (4)	C(7)-O(7)	1.22 (5)
Os(4)-C(8)	1.84 (3)	C(8)-O(8)	1.23 (3)
Os(4)-C(9)	1.92 (3)	C(9)-O(9)	1.14 (3)
Os(4)-C(10)	1.80 (4)	C(10)-O(10)	1.26 (4)
Os(4)-C(37)	2.11 (3)	C(11)-O(11)	1.19 (3)
Os(5)-C(11)	1.87 (3)	C(12)-O(12)	1.27 (4)
Os(5)-C(12)	1.68 (4)	C(13)-O(13)	1.12 (3)
Os(5)-C(13)	1.94 (3)	C(14)-O(14)	1.24 (3)
Os(5)-N(2)	2.11 (2)	C(15)-O(15)	1.14 (3)
Os(6)-C(14)	1.77 (3)	C(16)-O(16)	1.26 (3)
Os(6)-C(15)	1.88 (3)		

Table V. Selected Interatomic Angles with esds for $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{16}$, IVa)

atoms	angle, deg	atoms	angle, deg
Os(2)-Os(1)-Os(3)	57.02 (5)	Os(1)-S(1)-Os(2)	73.0 (2)
Os(1)-Os(2)-Os(3)	65.13 (5)	Os(1)-S(1)-Os(6)	103.4 (2)
Os(1)-Os(3)-Os(2)	57.85 (5)	Os(2)-S(1)-Os(6)	76.3 (2)
Os(1)-Os(2)-Os(6)	81.04 (5)	Os(2)-S(2)-Os(3)	72.7 (2)
Os(3)-Os(2)-Os(6)	128.76 (6)	Os(2)-S(2)-Os(4)	132.2 (3)
Os(3)-Os(1)-S(1)	72.0 (2)	Os(2)-S(2)-Os(5)	130.5 (4)
Os(3)-Os(1)-C(1)	110.3 (11)	Os(3)-S(2)-Os(4)	130.5 (4)
Os(3)-Os(1)-C(2)	101.1 (10)	Os(3)-S(2)-Os(5)	131.9 (3)
Os(3)-Os(1)-C(27)	150.9 (10)	Os(4)-S(2)-Os(5)	70.0 (2)
Os(2)-Os(1)-S(1)	52.4 (2)	Os(1)-C(27)-N(1)	129 (3)
Os(2)-Os(1)-C(1)	124.0 (11)	Os(6)-N(1)-C(27)	124 (3)
Os(2)-Os(1)-C(2)	143.2 (9)	Os(6)-N(1)-C(21)	148 (2)
Os(2)-Os(1)-C(27)	94.9 (10)	C(27)-N(1)-C(21)	116 (3)
Os(1)-Os(2)-S(1)	54.5 (2)	Os(4)-C(37)-N(2)	114 (2)
Os(1)-Os(2)-S(2)	92.2 (2)	Os(5)-N(2)-C(37)	107 (2)
Os(1)-Os(2)-C(3)	118.0 (10)	Os(5)-N(2)-C(31)	129 (2)
Os(1)-Os(2)-C(4)	148.7 (8)	C(37)-N(2)-C(31)	124 (3)
Os(3)-Os(2)-S(1)	77.4 (2)	S(1)-Os(6)-N(1)	86.7 (7)
Os(3)-Os(2)-S(2)	54.4 (2)	S(1)-Os(1)-C(27)	84.9 (10)
Os(3)-Os(2)-C(3)	156.4 (9)	S(2)-Os(4)-C(37)	82.7 (6)
Os(3)-Os(2)-C(4)	93.7 (9)	S(2)-Os(5)-N(2)	83.9 (6)
Os(6)-Os(2)-S(1)	51.4 (2)	C(26)-C(21)-C(22)	122 (3)
Os(6)-Os(2)-S(2)	168.6 (2)	C(21)-C(22)-C23	119 (3)
Os(6)-Os(2)-C(3)	78.4 (9)	C(22)-C(23)-C(24)	124 (3)
Os(6)-Os(2)-C(4)	97.2 (9)	C(23)-C(24)-C(25)	117 (3)
Os(1)-Os(3)-S(2)	86.5 (2)	C(24)-C(25)-C(26)	123 (3)
Os(1)-Os(3)-C(5)	81.5 (9)	C(25)-C(26)-C(21)	114 (3)
Os(1)-Os(3)-C(6)	146.6 (10)	C(36)-C(31)-C(32)	121 (3)
Os(1)-Os(3)-C(7)	115.8 (14)	C(31)-C(32)-C(33)	122 (3)
Os(2)-Os(3)-S(2)	52.9 (2)	C(32)-C(33)-C(34)	116 (3)
Os(2)-Os(3)-C(5)	107.8 (9)	C(33)-C(34)-C(35)	124 (3)
Os(2)-Os(3)-C(6)	93.3 (10)	C(34)-C(35)-C(36)	119 (3)
Os(2)-Os(3)-C(7)	157.5 (11)	C(35)-C(36)-C(31)	117 (3)
Os(2)-Os(6)-S(1)	52.3 (2)	Os(1)-C(1)-O(1)	174 (3)
Os(2)-Os(6)-C(14)	89.2 (10)	Os(1)-C(2)-O(2)	179 (2)
Os(2)-Os(6)-C(15)	156.0 (9)	Os(2)-C(3)-O(3)	175 (3)
Os(2)-Os(6)-C(16)	109.7 (9)	Os(2)-C(4)-O(4)	176 (2)
Os(2)-Os(6)-N(1)	91.7 (7)	Os(3)-C(5)-O(5)	175 (3)
Os(5)-Os(4)-S(2)	54.6 (2)	Os(3)-C(6)-O(6)	176 (3)
Os(5)-Os(4)-C(8)	99.6 (9)	Os(3)-C(7)-O(7)	174 (4)
Os(5)-Os(4)-C(9)	93.6 (8)	Os(4)-C(8)-O(8)	172 (3)
Os(5)-Os(4)-C(10)	154.7 (11)	Os(4)-C(9)-O(9)	171 (2)
Os(5)-Os(4)-C(37)	67.5 (7)	Os(4)-C(10)-O(10)	177 (3)
Os(4)-Os(5)-S(2)	55.4 (2)	Os(5)-C(11)-O(11)	165 (3)
Os(4)-Os(5)-C(11)	158.6 (8)	Os(5)-C(12)-O(12)	178 (3)
Os(4)-Os(5)-C(12)	95.6 (11)	Os(5)-C(13)-O(13)	174 (3)
Os(4)-Os(5)-C(13)	97.5 (9)	Os(6)-C(14)-O(14)	177 (3)
Os(4)-Os(5)-N(2)	71.2 (6)	Os(6)-C(15)-O(15)	171 (3)
		Os(6)-C(16)-O(16)	179 (2)

be caused by the steric influence of a bridging hydride ligand.

IVb and IVc are spectroscopically similar to IVa and it has been shown by X-ray crystallographic methods that both are simple isomers of IVa.[9b] In IVb the bridging formimidoyl ligand in the two metal atom group is on the opposite side of the Os(4)–Os(5)–S(2) plane from that observed in IVa with the nitrogen atom bonded to Os(5) and the carbon to Os(4). IVc is similar to IVb except that the nitrogen is bonded to Os(4) and the carbon to Os(5). On the basis of their IR and ^1H NMR spectra, Table I, compounds IVa′, IVb′, and IVc′ are believed to be isomers analogous to the IVa–c series. The molecules IVa–c can be made independently by treatment of IIIa in refluxing octane although significant amounts of Ia are also formed. Once isolated, the isomers IVa–c can be interconverted. For example, treatment of IVa in refluxing octane for 8 h leads to formation of IVb and IVc.

The compounds Va and Va′ are obtained in low yield in the original preparation but can be obtained in better yields by thermolysis of the compounds IV in refluxing nonane for 6 h. The molecular structure of Va was established by a single-crystal X-ray diffraction analysis and an ORTEP drawing of it is shown in Figure 3. This compound contains six metal atoms grouped into a central cluster of four, Os(1)–Os(2)–Os(3)–Os(4), which is arranged in the form of a "butterfly tetrahedron" which contains five metal-metal bonds. The bond between the "hinge" atoms, Os(2) and Os(3), is quite short, 2.726 (1) Å, and is bridged by a carbonyl ligand, a rare occurrence in osmium clusters.[16] The osmium–osmium bonds from the hinge atoms Os(2) and Os(3) to the "wing-tips" Os(1) and Os(4) can be grouped into pairs of long, Os(1)–Os(3) = 2.992 (1) Å and Os(2)–Os(4) = 3.038 (1) Å, and short, Os(1)–Os(2) = 2.943 (1) Å and Os(3)–Os(4) = 2.942 (1) Å, bonds. The Os(1)···Os(4) distance at 3.735 (1) Å cannot involve a significant bonding interaction. The dihedral angle between the two triangular planes is 124.2°. The two remaining osmium atoms are bonded to the hinge atoms, one to each, Os(2)–Os(6) = 2.826 (1) Å and Os(3)–Os(5) = 2.819 (1) Å.

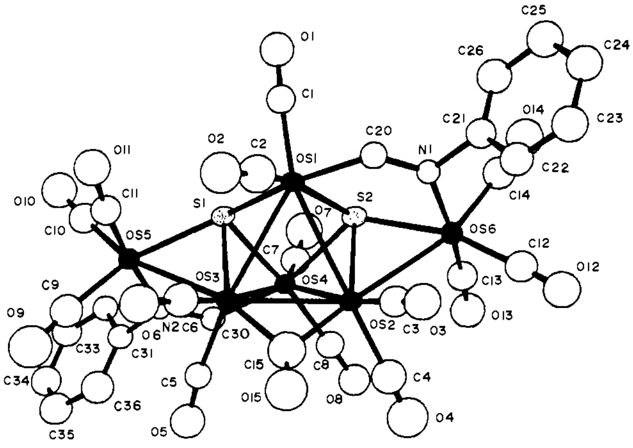

Figure 3. ORTEP diagram of $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{15}$, Va, showing 50% probability thermal-motion ellipsoids.

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(16) (a) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Kaner, D. A.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 961. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Ibid.* **1980**, 60.

The molecule contains two quadruply bridging sulfido ligands. The metal–sulfur bond distances which range from 2.364 (5) to 2.517 (5) Å are similar to those found in other osmium clusters.[8,12] The coordination geometry of the sulfido ligands is difficult to describe. We believe that these ligands serve as six-electron donors, vide infra, and therefore prefer to describe their geometry as that of highly distorted tetrahedra. Formimidoyl ligands bridge the nonbonded pairs of metal atoms Os(1)···Os(6) and Os(4)···Os(5).

There are 14 linear terminal carbonyl ligands and one symmetric bridge C(15)–O(15) which straddles the Os(2)–Os(3) metal–metal bond, Os(2)–C(15) = 2.07 (3) Å and Os(3)–C(15) = 2.03 (3) Å. As expected, this ligand has a characteristic low-energy absorption in the infrared spectrum (1762 $\mathrm{cm^{-1}}$). Overall, the molecule has C_2 symmetry (not crystallographically imposed) with the C_2 axis coincident to the C(15)–O(15) vector of the bridging CO ligand. As a result, the two formimidoyl ligands are chemically equivalent. The absence of hydride ligands was indicated by the absence of the characteristic NMR resonances both in room-temperature and low-temperature (−60 °C) spectra.

The two long metal–metal bonds in the central cluster can, perhaps, be explained by its unusual electronic configuration. If the sulfido ligands each donate 5 electrons to the central cluster, the formimidoyl ligands each donate 1 electron via their carbon atoms, and the 2 external osmium atoms each donate one; then with the 18 electrons from the carbonyl ligands and 32 electrons from the metal atoms the central cluster contains 64 electrons. However, to be electron "precise" such a cluster should have four metal–metal bonds, not five.[17] We believe the formation of two significantly weakened metal–metal bonds is an alternative manifestation of its desire to break one bond. A similar situation was observed in the isoelectronic cluster complex $\mathrm{Os_4(\mu_3\text{-}S)_2(CO)_{12}}$.[18]

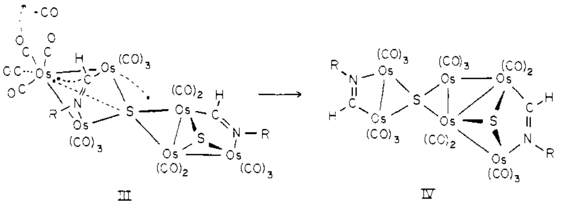
Discussion

The decarbonylation of the molecule I leads to a series of hexaosmium clusters which, except for II, appear to be related by an intimate sequence of ligand loss and cluster growth processes, eq 1. The sequence begins with the loss of 1 mol of CO from

$$\begin{array}{ll}
 & \mathrm{HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)(CO)_9},\ \mathrm{I} \\
 & \downarrow 125° \\
 & \mathrm{Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NR)_2(CO)_{18}},\ \mathrm{II} \\
 & + \\
125° & \mathrm{H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{17}},\ \mathrm{III} \\
 & + \\
150° & \mathrm{H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HC{=}NR)_2(CO)_{16}},\ \mathrm{IV} \\
 & + \\
 & \mathrm{Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NR)_2(CO)_{15}},\ \mathrm{V}
\end{array} \qquad (1)$$

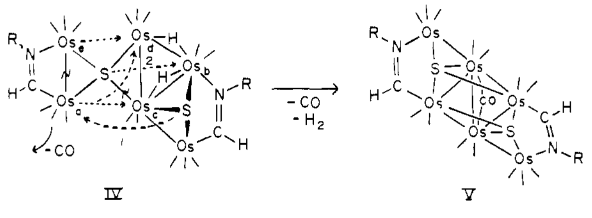
I. In the nondonor solvent which was used, the vacant coordination site is filled by donation from the lone pair of electrons of the triply bridging sulfido ligand on a second molecule of I. This sulfido ligand eventually comes to bridge two metal atoms in the added trinuclear cluster while one of the metal–sulfur bonds in its original cluster is cleaved. This cleavage produces a vacant site to which 1 mol of CO is added. The added CO ligand could come from the pool of free CO originally expelled. This would have to be followed by a loss of CO from the second cluster. Alternatively, it could move via an intercluster shift between the two trinuclear units. In any case, the product is a combination of 2 mol of I less 1 mol of CO. IIIa′ contains four metal–metal bonds; thus, there is no net formation or cleavage of metal–metal bonds. However, one sulfido ligand is transformed from a four-electron into a six-electron donor.

The compounds III appear to be immediate precursors to the group IV. This is supported by the observation that the mixture of isomers IVa–c is formed upon thermolysis of IIIa–b. Stoichiometrically, this requires the loss of another mole of CO per hexanuclear group, but this is accompanied by a transformation of the three:three grouping of metal atoms observed in the molecules III into the four:two arrangement found in the molecules IV. As shown in eq 2, CO loss from III probably occurs from the $\mathrm{Os(CO)_4}$ group. The formimidoyl ligand shifts to it to fill the vacant site, but this simply transmits the unsaturation to a neighboring $\mathrm{Os(CO)_3}$ group. That group then inserts into one of the Os–S bonds to the adjacent triosmium cluster. Two metal–metal bonds are formed and one is cleaved. Overall, there is a net loss of 1 mol of CO and addition of one metal–metal bond.



III IV (2)

The formation of V from the molecules IV is shown in eq 3.



IV V (3)

Stoichiometrically, 1 mol of CO and 1 equiv of $\mathrm{H_2}$ are released. The rearrangements which ultimately lead to V are difficult to predict and prove, but a mechanism which we consider to be attractive is shown in eq 3. Dotted arrows show where bonds are formed. If CO loss occurs at osmium atom (a) in the group of two, a coordinate bond (1) could be established between that metal atom and the lone pair of electrons on the triply bridging sulfido ligand in the group of four. This sulfido ligand then becomes a six-electron donor. If the other sulfido ligand shifts to osmium atom (b) (2), this could pave the way for formation of metal–metal bonds between (a) and (c), and (a) and (d). The loss of $\mathrm{H_2}$ might occur at this stage. This would complete formation of the butterfly tetrahedron with the two quadruply bridging sulfido ligands. The formation of V would be completed by cleavage of the metal–metal bond (a)–(e) and formation of the new metal–metal bond (d)–(e). The bridging CO ligand probably originates on Os(6).

It is worth noting that in V the six metal atoms have arranged themselves into a central cluster of four which has a character and identity entirely distinct from the materials from which it was derived. In V the basic cluster grouping is that of a butterfly tetrahedron with the two external metal atoms Os(5) and Os(6) (Figure 3) being the only unincorporated portions of the original trinuclear groupings.

The sulfido ligands have played a key role in assembling the central cluster as it is found in V. First and foremost, they have served as the means for the initial linking of the two trinuclear units. Secondly, they have directed the synthesis of the new cluster by a controlled cleavage of old and formation of new metal–metal bonds. Throughout this, their great value has been derived from their ability to interconvert readily between coordination numbers of three and four, and to serve alternately as four- or six-electron donors. These features have also been observed recently in our syntheses of the high nuclearity clusters $\mathrm{Os_6(CO)_{17}(\mu_4\text{-}S)_2}$ and $\mathrm{Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)}$.[5]

Experimental Section

General Remarks. Reactions were routinely performed under a prepurified nitrogen atmosphere although all the products were air stable

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(17) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

(18) Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4115.

Table VI. Interatomic Distances with esds for $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{15}$, Va

atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.943 (1)	Os(5)–N(2)	2.11 (1)
Os(1)–Os(3)	2.992 (1)	Os(6)–C(12)	1.92 (3)
Os(2)–Os(3)	2.726 (1)	Os(6)–C(13)	1.78 (2)
Os(2)–Os(4)	3.038 (1)	Os(6)–C(14)	1.93 (3)
Os(2)–Os(6)	2.826 (1)	Os(6)–N(1)	2.15 (2)
Os(3)–Os(4)	2.942 (1)	C(20)–N(1)	1.27 (2)
Os(3)–Os(5)	2.819 (1)	N(1)–C(21)	1.50 (2)
Os(1)···Os(4)	3.735 (1)	C(21)–C(22)	1.39 (3)
Os(1)···Os(5)	4.420 (1)	C(22)–C(23)	1.36 (3)
Os(1)···Os(6)	3.847 (1)	C(23)–C(24)	1.36 (3)
Os(4)···Os(5)	3.837 (1)	C(24)–C(25)	1.42 (3)
Os(4)···Os(6)	4.447 (1)	C(25)–C(26)	1.40 (3)
Os(1)–S(1)	2.517 (5)	C(26)–C(21)	1.35 (3)
Os(3)–S(1)	2.435 (5)	C(30)–N(2)	1.32 (2)
Os(4)–S(1)	2.409 (5)	N(2)–C(31)	1.47 (2)
Os(5)–S(1)	2.364 (5)	C(31)–C(32)	1.38 (3)
Os(1)–S(2)	2.410 (5)	C(32)–C(33)	1.45 (3)
Os(2)–S(2)	2.446 (5)	C(33)–C(34)	1.38 (3)
Os(4)–S(2)	2.517 (5)	C(34)–C(35)	1.34 (3)
Os(6)–S(2)	2.378 (5)	C(35)–C(36)	1.43 (3)
Os(1)–C(1)	1.89 (2)	C(36)–C(31)	1.37 (3)
Os(1)–C(2)	1.71 (2)	C(1)–O(1)	1.16 (2)
Os(1)–C(20)	2.05 (2)	C(2)–O(2)	1.26 (2)
Os(2)–C(3)	1.86 (2)	C(3)–O(3)	1.16 (2)
Os(2)–C(4)	1.97 (3)	C(4)–O(4)	1.08 (3)
Os(2)–C(15)	2.07 (3)	C(5)–O(5)	1.13 (2)
Os(3)–C(5)	1.90 (2)	C(6)–O(6)	1.25 (2)
Os(3)–C(6)	1.77 (2)	C(7)–O(7)	1.28 (2)
Os(3)–C(15)	2.03 (3)	C(8)–O(8)	1.16 (2)
Os(4)–C(7)	1.75 (2)	C(9)–O(9)	1.19 (3)
Os(4)–C(8)	1.90 (2)	C(10)–O(10)	1.15 (2)
Os(4)–C(30)	2.05 (2)	C(11)–O(11)	1.21 (2)
Os(5)–C(9)	1.87 (3)	C(12)–O(12)	1.15 (3)
Os(5)–C(10)	1.90 (3)	C(13)–O(13)	1.25 (2)
Os(5)–C(11)	1.82 (2)	C(14)–O(14)	1.16 (3)
		C(15)–O(15)	1.22 (3)

Table VII. Interatomic Angles with esds for $Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NC_6H_5)_2(CO)_{15}$, Va

atoms	angle, deg	atoms	angle, deg
Os(2)–Os(1)–Os(3)	54.69 (3)	Os(3)–Os(5)–S(1)	55.2 (1)
Os(1)–Os(2)–Os(3)	63.57 (3)	Os(3)–Os(5)–C(9)	104.3 (7)
Os(1)–Os(3)–Os(2)	61.74 (3)	Os(3)–Os(5)–C(10)	163.4 (7)
Os(1)–Os(2)–Os(4)	77.27 (3)	Os(3)–Os(5)–C(11)	89.4 (7)
Os(1)–Os(2)–Os(6)	83.63 (3)	Os(3)–Os(5)–N(2)	87.2 (4)
Os(3)–Os(2)–Os(4)	61.10 (3)	Os(2)–Os(6)–S(2)	55.3 (1)
Os(3)–Os(2)–Os(6)	143.78 (4)	Os(2)–Os(6)–C(12)	105.7 (7)
Os(4)–Os(2)–Os(6)	98.57 (3)	Os(2)–Os(6)–C(13)	92.0 (8)
Os(1)–Os(3)–Os(4)	78.01 (3)	Os(2)–Os(6)–C(14)	161.6 (7)
Os(1)–Os(3)–Os(5)	98.99 (4)	Os(2)–Os(6)–N(1)	85.1 (4)
Os(2)–Os(3)–Os(4)	64.69 (3)	Os(1)–S(1)–Os(3)	74.3 (1)
Os(2)–Os(3)–Os(5)	144.94 (4)	Os(1)–S(1)–Os(4)	98.6 (2)
Os(4)–Os(3)–Os(5)	83.49 (3)	Os(1)–S(1)–Os(5)	129.8 (2)
Os(2)–Os(4)–Os(3)	54.22 (3)	Os(3)–S(1)–Os(4)	74.8 (2)
Os(2)–Os(1)–S(1)	87.3 (1)	Os(3)–S(1)–Os(5)	72.0 (1)
Os(2)–Os(1)–S(2)	53.3 (1)	Os(4)–S(1)–Os(5)	107.0 (2)
Os(2)–Os(1)–C(1)	156.6 (6)	Os(1)–S(2)–Os(2)	74.6 (1)
Os(2)–Os(1)–C(2)	109.5 (9)	Os(1)–S(2)–Os(4)	98.6 (2)
Os(2)–Os(1)–C(20)	84.8 (6)	Os(1)–S(2)–Os(6)	106.9 (2)
Os(3)–Os(1)–S(1)	51.6 (1)	Os(2)–S(2)–Os(4)	75.5 (2)
Os(3)–Os(1)–S(2)	87.2 (1)	Os(2)–S(2)–Os(6)	71.7 (2)
Os(3)–Os(1)–C(1)	139.6 (6)	Os(4)–S(2)–Os(6)	130.6 (2)
Os(3)–Os(1)–C(2)	85.7 (9)	Os(1)–C(20)–N(1)	128 (1)
Os(3)–Os(1)–C(20)	132.3 (6)	Os(6)–N(1)–C(20)	128 (1)
Os(1)–Os(2)–S(2)	52.2 (1)	Os(6)–N(1)–C(21)	116 (1)
Os(1)–Os(2)–C(3)	95.2 (7)	C(20)–N(1)–C(21)	115 (2)
Os(1)–Os(2)–C(4)	173.0 (7)	Os(4)–C(30)–N(2)	127 (1)
Os(1)–Os(2)–C(15)	95.4 (8)	Os(5)–N(2)–C(30)	127 (1)
Os(3)–Os(2)–S(2)	92.7 (1)	Os(5)–N(2)–C(31)	120 (1)
Os(3)–Os(2)–C(3)	118.2 (6)	C(30)–N(2)–C(31)	113 (2)
Os(3)–Os(2)–C(4)	117.0 (8)	S(2)–Os(6)–N(1)	84.8 (4)
Os(3)–Os(2)–C(15)	47.8 (8)	S(2)–Os(1)–C(20)	86.8 (5)
Os(4)–Os(2)–S(2)	53.3 (1)	S(1)–Os(4)–C(30)	86.7 (6)
Os(4)–Os(2)–C(3)	172.0 (7)	S(1)–Os(5)–N(2)	85.7 (4)
Os(4)–Os(2)–C(4)	96.8 (7)	N(1)–C(21)–C(22)	117 (2)
Os(4)–Os(2)–C(15)	101.6 (7)	N(1)–C(21)–C(26)	121 (2)
Os(6)–Os(2)–S(2)	53.0 (1)	C(22)–C(21)–C(26)	122 (2)
Os(6)–Os(2)–C(3)	77.6 (7)	C(21)–C(22)–C(23)	119 (2)
Os(6)–Os(2)–C(4)	93.7 (7)	C(22)–C(23)–C(24)	121 (2)
Os(6)–Os(2)–C(15)	159.1 (7)	C(23)–C(24)–C(25)	120 (2)
Os(1)–Os(3)–S(1)	54.1 (1)	C(24)–C(25)–C(26)	119 (2)
Os(1)–Os(3)–C(5)	167.4 (6)	C(25)–C(26)–C(21)	119 (2)
Os(1)–Os(3)–C(6)	98.4 (8)	N(2)–C(31)–C(32)	116 (2)
Os(1)–Os(3)–C(15)	94.6 (8)	N(2)–C(31)–C(36)	122 (2)
Os(2)–Os(3)–S(1)	94.1 (1)	C(32)–C(31)–C(36)	121 (2)
Os(2)–Os(3)–C(5)	109.3 (6)	C(31)–C(32)–C(33)	119 (2)
Os(2)–Os(3)–C(6)	121.1 (8)	C(32)–C(33)–C(34)	118 (2)
Os(2)–Os(3)–C(15)	48.8 (7)	C(33)–C(34)–C(35)	124 (2)
Os(4)–Os(3)–S(1)	52.2 (1)	C(34)–C(35)–C(36)	118 (2)
Os(4)–Os(3)–C(5)	90.2 (5)	C(35)–C(36)–C(31)	120 (2)
Os(4)–Os(3)–C(6)	170.9 (8)	Os(1)–C(1)–O(1)	176 (2)
Os(2)–Os(3)–C(15)	105.7 (7)	Os(1)–C(2)–O(2)	171 (2)
Os(5)–Os(3)–S(1)	52.9 (1)	Os(2)–C(3)–O(3)	177 (2)
Os(5)–Os(3)–C(5)	83.9 (6)	Os(2)–C(4)–O(4)	177 (2)
Os(5)–Os(3)–C(6)	88.9 (8)	Os(3)–C(5)–O(5)	172 (2)
Os(5)–Os(3)–C(15)	165.0 (7)	Os(3)–C(6)–O(6)	171 (2)
Os(2)–Os(4)–S(1)	87.1 (1)	Os(4)–C(7)–O(7)	164 (2)
Os(2)–Os(4)–S(2)	51.2 (1)	Os(4)–C(8)–O(8)	172 (2)
Os(2)–Os(4)–C(7)	141.0 (7)	Os(5)–C(9)–O(9)	168 (2)
Os(2)–Os(4)–C(8)	82.3 (6)	Os(5)–C(10)–O(10)	174 (2)
Os(2)–Os(4)–C(30)	131.8 (5)	Os(5)–C(11)–O(11)	169 (2)
Os(3)–Os(4)–S(1)	53.0 (1)	Os(6)–C(12)–O(12)	174 (2)
Os(3)–Os(4)–S(2)	86.4 (1)	Os(6)–C(13)–O(13)	172 (2)
Os(3)–Os(4)–C(7)	158.9 (8)	Os(6)–C(14)–O(14)	178 (2)
Os(3)–Os(4)–C(8)	113.7 (6)	Os(2)–C(15)–O(15)	137 (2)
Os(3)–Os(4)–C(30)	85.0 (5)	Os(3)–C(15)–O(15)	139 (2)

in the solid state and in solutions. Reaction solvents were purified by distillation from sodium benzophenone (hexane, octane) or by storage over 4-Å molecular sieves and purging with nitrogen through a gas dispersion tube. $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)(CO)_9$ and $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCN\text{-}p\text{-}C_6H_4F)(CO)_9$ were prepared as previously described.[8] Infrared spectra were recorded on a Nicolet 7199 FT IR. Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX 270.

Thermolysis of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)(CO)_9$, Ia. A solution of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)(CO)_9$ (200 mg, 0.208 mmol) in octane (30 mL) was heated to reflux for 3 h during which time the bright yellow solution turned to an orange-brown color. The solvent was removed in vacuo. The residue was dissolved in 3 mL of methylene chloride and applied to eight thin-layer silica plates. Four elutions with hexane/methylene chloride (9/1) separated eight bands. Following the yellow starting material (Ia, 32 mg, 16%) were six closely spaced yellow bands consisting of, in descending order, IIa (5 mg, 3%), IVb (6 mg, 3%), IVa (2 mg, 1%), IVc (4 mg, 2%), IIIa (6 mg, 3%), and IIIb (5 mg, 3%). Well below this series of compounds was a green band, Va (1 mg, 1%).

Thermolysis of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_4\text{-}p\text{-}F)(CO)_9$, Ia′. In a manner similar to the thermolysis of Ia, a solution of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HCN\text{-}p\text{-}C_6H_4F)(CO)_9$ 143 mg, 0.146 mmol) in octane (30 mL) was heated to reflux for 3 h. The components of the reaction mixture were separated on thin silica plates: Ia′ (29 mg, 20%), IIa′ (1 mg, 1%), IVb′ (16 mg, 11%, IVa′ (10 mg, 7%), IVc′ (8 mg, 6%), IIIa′ (5 mg, 4%), IIIb′ (5 mg, 4%), Va′ (5 mg, 4%).

Thermolysis of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{17}$, IIIa. IIIa (5 mg, 0.003 mmol) was dissolved in octane (10 mL) and heated to reflux for 1 h. The solvent was removed in vacuo, and the brown-yellow residue was chromatographed on thin silica plates. Multiple elutions with hexane/methylene chloride (9/1) separated isomers IVa–c from the starting material. A small amount of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}NC_6H_5)(CO)_9$, Ia, was also found.

Thermolysis of $H_2Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}HCNC_6H_5)_2(CO)_{16}$, IVb. (a) In Octane: IVb (10 mg, 0.006 mmol) was dissolved in octane (10 mL) and heated to reflux for 8 h. Following removal of the solvent in vacuo, the reaction mixture was chromatographed on thin silica plates. Elution in hexane/methylene chloride (9/1) separated unreacted IVb from its isomers, IVa and IVc.

(b) In Nonane: The title compound (10 mg, 0.006 mmol) was dissolved in nonane (10 mL) and heated to reflux for 6 h. Chromatographic workup on thin silica plates in hexane/methylene chloride (9/1) afforded Va (2 mg, 20%).

Crystallographic Analyses. Crystals of IIIa′ suitable for diffraction analyses were obtained by slow crystallization from hot hexanes solutions. Crystals of IVa were obtained by slow evaporation of hexanes solutions at room temperature. Crystals of Va were obtained by slow evaporation of methylene chloride/hexanes solutions at 5 °C.

Table VIII. Crystallographic Data for X-ray Difraction Studies

	(A) Cell Parameters		
compound	IIIa′	IVa	Va
formula	$Os_6S_2F_2O_{17}N_2C_{31}H_{12}$	$Os_6S_2O_{16}N_2C_{30}H_{14}$	$Os_6S_2O_{15}N_2C_{29}H_{12}$
temp, °C (±5 °C)	28	−35	26
space group	$P\bar{1}$, no. 2	$P2_1/n$, no. 14	$P\bar{1}$, no. 2
a, Å	9.865 (7)	10.461 (5)	10.391 (5)
b, Å	14.735 (6)	23.080 (11)	13.903 (6)
c, Å	15.926 (10)	16.864 (6)	14.540 (6)
α, deg	69.08 (5)	90.0	78.29 (3)
β, deg	79.63 (6)	97.60 (3)	74.90 (4)
γ, deg	86.40 (6)	90.0	70.91 (3)
V, Å^3	2127 (3)	4035 (5)	1900 (2)
M_r	1927.8	1863.8	1833.8
Z	2	4	2
ρ_{calcd}, g cm^{-3}	3.01	3.07	3.21
	(B) Measurement of Intensity Data		
radiatn	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
monochromator	graphite	graphite	graphite
detector aperture, mm			
horizontal ($A + B$ tan θ): A	3.0	3.0	3.0
B	1.0	1.0	1.0
vertical	4.0	4.0	4.0
cryst faces	$010, 0\bar{1}0, 001$ $00\bar{1}, \bar{2}01, 20\bar{1}$	$1\bar{1}\bar{1}, \bar{1}11, \bar{1}0\bar{1}$ $\bar{1}2\bar{1}, 1\bar{1}2, 12\bar{1}$	$001, 00\bar{1}, 1\bar{1}1$ $\bar{1}1\bar{1}, 010, 0\bar{1}0$
cryst size, mm	0.035 × 0.14 × 0.22	0.035 × 0.06 × 0.17	0.036 × 0.098 × 0.142
cryst orientatn directn, deg from ϕ axis	a^*, 8.5	b, 12.8	normal to $1\bar{2}0$, 5.7
reflectns measd	$h{\pm}k{\pm}l$	$hk{\pm}l$	$h{\pm}k{\pm}l$
max 2θ, deg	48	44	46
scan type	moving crystal–stationary counter		
ω scan width			
$A + 0.347 \tan\theta, A =$	0.90	0.90	0.95
background	1/4 additional scan at each end of scan		
ω scan rate (variable)			
max°/min	10.0	10.0	10.0
min°/min	1.33	1.43	1.43
no. of reflctns measd	6594	5384	5217
data used ($F^2 \geqslant 3.0\ \sigma(F)^2$)	3584	2347	3045
	(C) Treatment of Data		
absorptn correctn			
coeff, cm^{-1}	191.6	199.5	214.2
grid	14 × 4 × 12	8 × 12 × 10	14 × 10 × 6
transmissn coeff			
max	0.53	0.40	0.49
min	0.11	0.12	0.15
P factor	0.01	0.005	0.01
final residuals R_1	0.032	0.052	0.044
R_2	0.030	0.043	0.042
esd of unit weight	1.46	1.93	2.03
largest shift/error value of final cycle	0.14	0.16	0.57

All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on Enraf-Nonius CAD-4 fully automated four-circle diffractometer, using graphite monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines.

For IIIa′ and Va the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structures. For IVa the space group $P2_1/n$ was established from the systematic absences observed in the data. The data set of IVa was collected at −35 °C by using an Enraf-Nonius Model FR 524 H low-temperature accessory. Crystal data and data collections parameters are listed in Table VII. All data processing was performed on a Digital PDP 11/45 computer, using the Enraf-Nonius SDP program library (version 16). Absorption corrections of a Gaussian integration type were done for each structure. Neutral atom scattering factors were calculated by the standard procedures.[19a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[19b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_{obsd}| - |F_{calcd}|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_{obsd}^2)/2F_{obsd}$ and $\sigma(F_{obsd}^2) = [\sigma(I_{raw})^2 + (PF_{obsd}^2)^2]^{1/2}/Lp$.

The structure of IIIa′ and Va was solved by a combination of Patterson and difference Fourier syntheses. For IIIa′ the positions of two osmium atoms were obtained from the Patterson synthesis, while the remaining metal atoms and non-hydrogen atoms were located in a sequences of difference Fourier syntheses. For Va the locations of three osmium atoms were obtained from the Patterson synthesis while remaining atoms were obtained from difference Fourier syntheses.

The structure of IVa was solved by a combination of direct methods and difference Fourier techniques. The six osmium atoms were located in an electron-density map based on the phasing (MULTAN) of 176 reflections ($E \geq 1.80$).

Tables II and III list interatomic distances and angles for IIIa′, Tables IV and V list interatomic distances and angles for IVa, and Tables VI and VII list interatomic distances and angles for Va. Estimated standard deviations were obtained by using the inverse matrix obtained on the final cycle of refinement for each structure. Fractional atomic coordinates and thermal parameters are available for all three structures as well as structure factor amplitudes for Va; see supplementary material. Structure factor amplitudes for IIIa′ and IVa have been published previously.[4]

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(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV; (a) Table 2.2B, pp 99–101. (b) Table 2.3.1, pp 149–150.

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Registry No. Ia, 80399-46-8; Ia′, 79790-55-9; IIa, 84277-84-9; IIa′, 84237-76-3; IIIa, 84237-77-4; IIIa′, 84237-78-5; IIIb, 84277-85-0; IIIb′, 84366-71-2; IVa, 84237-79-6; IVa′, 84253-82-7; IVb, 84366-72-3; IVb′, 84366-74-5; IVc, 84366-73-4; IVc′, 84366-75-6; Va, 83731-69-5; Va′, 84237-80-9.

Supplementary Material Available: Tables of final fractional atomic coordinates, thermal parameters for all three structural analyses, and structure factor amplitudes are available for the structure of Va (19 pages). Ordering information is given on any current masthead page.

An Experimental Measure of Cavity Size in Macrocyclic Cyclophane-Based Host Molecules

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Abstract: The synthesis of rigid (**3a–f**) and flexible (**4a–f**) cyclophanes is described. They exhibit DNMR effects in their proton NMR spectra associated with conformational changes as in eq 1. The rates of these processes were studied as a function of the size of the alkyl group that rotates through the cyclophane's cavity. Isobutyl ester **3e** appears to be at the transition between small and large (as defined by this experimental probe) groups. The cavity of **3** closely approximates the size of an isobutyloxycarbonyl group.

There is considerable current interest in molecules possessing cavities sufficiently large to accommodate guests. Historically preeminent are the cyclodextrins.[1] Catalytic activity arising from substrate molecules' insertion into the cavity and interaction with the peripheral hydroxyl groups of the cyclodextrin has been a fruitful if simple model of enzyme catalysis.[2-4] Enlargement of the cyclodextrin cavity by attachment of simple hydrophobic residues[5] and cavity-spanning bridges[6,7] leads to substantially enhanced hydrophobic binding of guests.

Several toroidal molecules possessing faces of aromatic rings have been prepared as synthetic analogues of cyclodextrins.[8-10] While admitting to considerable structural diversity, these cyclodextrin analogues all possess hydrocarbon-like ("hydrophobic") cavities, are water soluble, and exhibit binding of aromatic substrates with varying degrees of selectivity. Construction of macrocyclic molecules whose cavities are lined with particular functional groups has been pursued by Cram[11] and Lehn.[12]

We have synthesized and examined for hydrophobic binding ability a series of [8.8]arenophanes.[13a-d] This work has raised in our minds certain questions dealing with the concept of cavity size in macrocyclic molecules, especially with regard to the possibility of constructing artificial enzymes wherein substrate binding and selectivity is determined by this structural feature. With hydrophobic complexation as a probe we have found two structural features to be of importance in defining cavity size. A rigid spacer group is required, e.g., **3a** as opposed to **4a**.[13b,c] In the absence of this rigidity the cyclophane exists in a collapsed conformation and complexation is not observed. The lateral dimensions of the cavity are important. While [8.8](1,4)-benzenophanes (e.g., **3**) cannot accommodate aromatic guests within their cavity,[13a] the analogous [8.8](2,6)naphthalenophanes can.[13d]

We report here the synthesis and conformational study of several [8.8](1,4)benzenophanes possessing rigid (**3a–g**) and flexible (**4a–g**) bridges (see Scheme I). These molecules were chosen for three reasons: they represent a synthetically accessible series of substituents of smoothly increasing size; the conformational process involving rotation of the alkoxycarbonyl group through the cavity (or more properly the dependence of this on group size) is a measure of cavity size; comparison of the rigid (**3**) with flexible (**4**) series gives a measure of the dependence of cavity size on bridge type. This latter possibility was especially interesting, as a related study of (1,4)naphthalenophanes (e.g., **6**) suggested that those cyclophanes having flexible bridges have a *larger* cavity than those with rigid bridges.[13c]

Results

The conformational model employed is summarized in eq 1. Cyclophanes of the type **3** or **4** exist in two limiting diastereomeric forms, achiral syn and chiral anti. Rotation about either phenyl's 1,4-axis interconverts the syn and anti. Two consecutive rotations of opposite rings interconverts *R* and *S anti* and is an identity operation on the syn isomer. This process also interconverts the diastereotopic protons of the ether bridges' methylene groups, H_A and H_B or $H_{A'}$ and $H_{B'}$ respectively. By virtue of the substitution pattern of **3** and **4** these rotations require passage of one alkoxycarbonyl group ("e" in eq 1) through the cavity.

Depending on the barriers involved, one may study these rotations by either classical methods for interconverting diastereomers or by dynamic NMR (DNMR[14]).

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(14) Abbreviations used here: NMR, proton NMR; DNMR, proton dynamic NMR; T_c, coalescence temperature for DNMR interconversion of two spins; $\Delta\nu$, inherent chemical shift difference (in Hz) of two nuclei in a ^{1}H NMR spectrum.

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