reaction. This generalization is probably true even for systems which use cobalt(II) salts as catalyst precursors,[6c] as the carbonylate anion $[Co(CO)_4]^-$ can be formed from such compounds even at low pressures of carbon monoxide.[27]

As mentioned above, it seems unlikely that the intermediate methyl compounds $MeCo(CO)_3L$ (L = tertiary phosphine) are formed via methanol protonation by the weak acids $HCo(CO)_3L$, but homologation by phosphine-containing cobalt systems are relatively slow in the absence of either iodide ion or compounds which will generate iodide.[6c] It thus seems much more likely that the reactive alkylating agent in these cases is methyl iodide, which reacts with the small equilibrium concentrations of carbonylate anion $[Co(CO)_3L]^-$ formed by partial dissociation of $HCo(CO)_3L$. Conversion of methyl to acetyl species by treatment of the former with carbon monoxide is certainly quite facile.

Another, relative minor contribution made here is confirmation that cleavage of the acetyl compounds $MeCOCo(CO)_3L$ to give C_2-containing products involves attack by molecular hydrogen rather than by hydrides, $HCo(CO)_3L$. Our carbon-13 labeling studies are also consistent with and extend carbon-14 studies reported in 1953 using the tetracarbonyl system[28] and tend to confirm the basic features of mechanism advocated by Slocum.[6b]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (grants to M.C.B.) and the Government of Ontario (scholarship to J.T.M.) for financial support, B. W. Wojciechowski for assistance with the GC–MS studies, W. R. Pretzer for stimulating discussions, and both D. W. Slocum and D. Fahey for a corrected version of ref 6b.

Registry No. I, 24212-54-2; II, 31178-43-5; III, 14841-12-4; IV, 14054-68-3; V, 86196-53-4; VI, 86177-65-3; VII, 86177-66-4; methanol, 67-56-1.

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Cluster Synthesis. 4. The Role of Sulfido Ligands in the Synthesis of High Nuclearity Metal Carbonyl Cluster Compounds. The Synthesis of $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ and $Os_7(CO)_{20}(\mu_4\text{-}S)_2$ and the Crystal and Molecular Structure of $Os_7(CO)_{20}(\mu_4\text{-}S)_2$

Richard D. Adams,* István T. Horváth, Pradeep Mathur, Brigitte E. Segmüller, and Li-Wu Yang

Department of Chemistry, Yale University, New Haven, Connecticut 06511

Received February 4, 1983

The cluster compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ has been found to react with $Os(CO)_5$ in the presence of UV irradiation to yield the cluster $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (40% yield), and $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ has been found to combine with $Os_3(CO)_{10}(NCMe)_2$ when refluxed in octane solvent for 2 h to yield the new cluster compound $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V (16% yield). Compound V has been characterized by a single-crystal X-ray diffraction analysis: space group $P2_12_12_1$, a = 11.205 (5) Å, b = 14.461 (6) Å, c = 21.246 (16) Å, V = 3443 (6) Å^3, M_r = 1955.7 g/cm^3, Z = 4, ρ_{calcd} = 3.77 g/cm^3. The structure was solved by direct methods. Full-matrix least-squares refinement on 2315 reflections ($F^2 \geq 3.0\sigma(F^2)$) yielded the final residuals R_F = 0.055 and R_{wF} = 0.044. The structure consists of a pentagonal-bipyramidal cluster of five osmium atoms and two tetracoordinate sulfido ligands. The two sulfido ligands which are not mutually bonded and three osmium atoms form the equatorial plane. Two $Os(CO)_4$ groups bridge adjacent apical–equatorial edges of the pentagonal bipyramid on opposite sites of the equatorial plane. Two of apical–equatorial metal–metal bonds in the cluster at 2.969 (2) and 2.963 (2) Å are significantly longer than the other four, range 2.893 (2)–2.905 (2) Å. The metal–metal bonds involving the $Os(CO)_4$ groups range from 2.801 (2) to 2.825 (2) Å. Compound V contains 20 linear terminal carbonyl ligands. The importance of sulfido ligands in the synthesis of high nuclearity metal carbonyl clusters is noted and discussed.

Introduction

Recent studies have shown that atoms derived from certain elements of the main groups can play an important role in the synthesis of heteronuclear transition-metal cluster compounds. Elements such as sulfur,[1–11] selenium,[11] phosphorus,[12,13] arsenic,[13,14] carbon,[15] nitrogen,[16] and even germanium[17] have been among the most useful of these.

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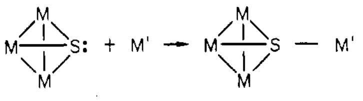
Their value is derived in large part from their ability to form relatively strong bonds to transition metals and to engage in a variety of multicoordinate bonding forms involving variable degrees of electron donations.

For example, triply bridging sulfido ligands, I, contain a lone pair of electrons which can be used to coordinate to an additional metal atom, II, thereby providing a facile first step in cluster growth sequences, eq 1. Vahrenkamp

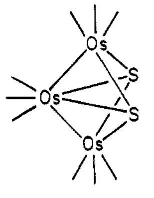


(1)

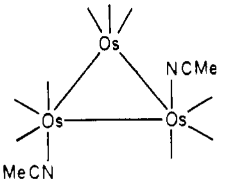
I II

has used this approach brilliantly to synthesize the first examples of chiral metal cluster compounds.[18] By expanding their coordinations to six or eight, these heteroatoms have led to the synthesis of a number of new and unusual high nuclearity transition-metal cluster compounds.[19]

Recently we have demonstrated how these heteroatoms can be used in the systematic synthesis of large clusters via the condensation of small clusters.[5-10] Herein we report a new route for the synthesis of the compound $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, III, which is readily decarbonylated to the remarkable compound $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, IV,[4,20] and the synthesis and crystal and molecular structure of new high nuclearity cluster $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V. It is significant that they have been made from the readily available compounds $Os_3(CO)_9(\mu_3\text{-}S)_2$, VI, $Os(CO)_5$, and $Os_3(CO)_{10}(NCMe)_2$, VII.



VI



VII

Results and Discussion

UV irradiation of octane solutions of $Os_3(CO)_9(\mu_3\text{-}S)_2$, VI, and $Os(CO)_5$ gives a relatively good yield, 40%, of the compound $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, III. Compound III has been synthesized previously by the addition of 1 mol of CO to $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, IV. The latter is a low-yield product obtained from the pyrolysis of $HOs_3(CO)_{10}(\mu\text{-}SPh)$.[4] Because the addition of CO to IV is quantitatively reversible, this new route to III now provides the first systematic and reasonable yield synthesis of IV.[20] The structures of III and IV were reported previously and are shown schematically.

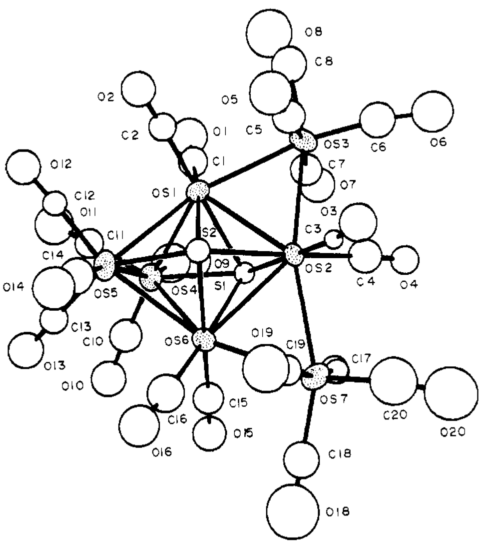


Figure 1. An ORTEP drawing of $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V, showing 50% probability thermal ellipsoids.

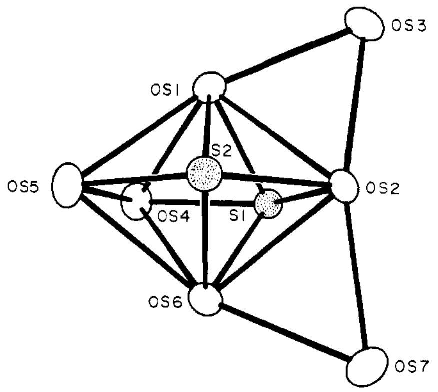
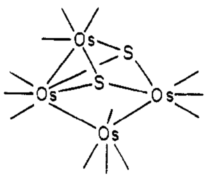
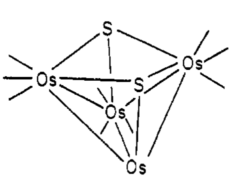


Figure 2. An ORTEP drawing of $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V, without the carbonyl ligands.



III



IV

Since the $Os(CO)_4$ group which is probably the unit added to VI does not contain bonds to the sulfur atoms, a mechanism of formation involving a direct insertion of an $Os(CO)_4$ unit (photolytically generated from $Os(CO)_5$) into one of the metal–metal bonds in VI is very likely. Alternatively, however, a mechanism involving an initial formation of a coordinate bond between a 16-electron $Os(CO)_4$ unit and a lone pair of electrons on one of the sulfido ligands should be a favorable process. Insertion of the added $Os(CO)_4$ unit into some of the original metal–sulfur bonds could with some minor additional rearrangements lead to III. Unfortunately, the present results do not allow us to distinguish between these processes.

The importance of the formation of metal–sulfur bonds is more apparent from the reaction of IV with VII to give $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V. This compound was also obtained as

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Os(1)	−0.9466 (2)	−0.5452 (1)	−0.419 48 (8)	2.32 (7)	3.22 (8)	2.74 (8)	−0.38 (8)	−0.53 (7)	0.28 (8)
Os(2)	−0.7374 (1)	−0.4380 (1)	−0.387 10 (9)	2.59 (7)	2.12 (6)	2.36 (7)	−0.24 (7)	−0.10 (7)	0.57 (8)
Os(3)	−0.8892 (2)	−0.3809 (1)	−0.484 81 (9)	3.67 (8)	3.45 (9)	2.43 (8)	0.72 (9)	−0.12 (8)	0.86 (8)
Os(4)	−0.8505 (2)	−0.7298 (1)	−0.400 63 (9)	3.61 (8)	2.59 (7)	2.73 (9)	−0.74 (8)	0.13 (8)	−0.41 (8)
Os(5)	−0.9680 (2)	−0.6458 (1)	−0.298 20 (9)	3.21 (8)	3.30 (8)	3.04 (9)	−0.61 (8)	0.87 (8)	0.15 (8)
Os(6)	−0.7161 (2)	−0.6078 (1)	−0.313 89 (8)	2.87 (7)	1.99 (6)	1.77 (7)	0.13 (7)	−0.08 (7)	−0.22 (7)
Os(7)	−0.5397 (2)	−0.4698 (1)	−0.309 35 (9)	2.76 (7)	3.31 (8)	3.37 (9)	−0.41 (8)	−0.61 (9)	−0.64 (9)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
S(1)	−0.7337 (9)	−0.5922 (7)	−0.4290 (5)	2.1 (2)	O(20)	−0.380 (4)	−0.304 (3)	−0.322 (2)	10.4 (13)
S(2)	−0.8846 (9)	−0.4925 (7)	−0.3122 (5)	2.4 (2)	C(1)	−0.985 (4)	−0.599 (3)	−0.494 (2)	4.7 (12)
O(1)	−1.025 (3)	−0.626 (3)	−0.543 (2)	7.9 (10)	C(2)	−1.106 (3)	−0.503 (3)	−0.408 (2)	3.4 (10)
O(2)	−1.200 (3)	−0.475 (2)	−0.394 (2)	5.0 (8)	C(3)	−0.743 (3)	−0.324 (2)	−0.353 (2)	1.3 (7)
O(3)	−0.761 (3)	−0.248 (2)	−0.330 (1)	5.0 (8)	C(4)	−0.622 (4)	−0.394 (3)	−0.449 (2)	5.2 (12)
O(4)	−0.549 (2)	−0.370 (2)	−0.482 (1)	3.8 (6)	C(5)	−0.969 (4)	−0.315 (3)	−0.423 (2)	4.5 (11)
O(5)	−1.039 (3)	−0.275 (2)	−0.382 (2)	6.9 (9)	C(6)	−0.827 (4)	−0.277 (3)	−0.520 (2)	5.8 (14)
O(6)	−0.772 (3)	−0.202 (2)	−0.535 (2)	7.4 (10)	C(7)	−0.810 (4)	−0.466 (3)	−0.539 (2)	5.3 (13)
O(7)	−0.749 (3)	−0.504 (2)	−0.575 (2)	6.8 (9)	C(8)	−1.024 (5)	−0.366 (3)	−0.545 (2)	6.1 (14)
O(8)	−1.099 (4)	−0.385 (3)	−0.575 (2)	10.7 (13)	C(9)	−0.823 (5)	−0.767 (4)	−0.473 (3)	8.9 (19)
O(9)	−0.770 (3)	−0.792 (2)	−0.528 (2)	6.9 (10)	C(10)	−0.779 (4)	−0.828 (3)	−0.371 (2)	5.7 (13)
O(10)	−0.727 (3)	−0.891 (2)	−0.342 (9)	6.7 (9)	C(11)	−0.994 (4)	−0.794 (3)	−0.403 (2)	4.5 (12)
O(11)	−1.075 (3)	−0.841 (2)	−0.410 (2)	8.3 (11)	C(12)	−1.131 (3)	−0.657 (2)	−0.309 (2)	2.6 (9)
O(12)	−1.228 (3)	−0.677 (2)	−0.322 (1)	5.2 (8)	C(13)	−0.947 (4)	−0.766 (3)	−0.264 (2)	3.6 (10)
O(13)	−0.929 (3)	−0.841 (2)	−0.248 (2)	5.9 (9)	C(14)	−1.009 (4)	−0.595 (3)	−0.223 (2)	4.8 (12)
O(14)	−1.032 (3)	−0.565 (2)	−0.170 (1)	6.2 (9)	C(15)	−0.595 (4)	−0.691 (3)	−0.315 (2)	4.6 (11)
O(15)	−0.517 (3)	−0.750 (2)	−0.319 (2)	5.7 (8)	C(16)	−0.715 (4)	−0.618 (3)	−0.224 (2)	5.6 (13)
O(16)	−0.720 (3)	−0.621 (2)	−0.170 (2)	6.1 (9)	C(17)	−0.469 (4)	−0.527 (3)	−0.389 (2)	3.6 (9)
O(17)	−0.431 (2)	−0.572 (2)	−0.427 (1)	3.1 (6)	C(18)	−0.438 (4)	−0.533 (3)	−0.255 (2)	5.2 (12)
O(18)	−0.380 (4)	−0.567 (3)	−0.217 (2)	11.3 (14)	C(19)	−0.637 (4)	−0.415 (3)	−0.237 (2)	3.3 (10)
O(19)	−0.689 (3)	−0.389 (2)	−0.197 (2)	7.3 (10)	C(20)	−0.453 (5)	−0.370 (4)	−0.320 (3)	8.9 (17)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3))]$.

a minor product, not previously reported, in the pyrolysis of $HOs_3(CO)_{10}(\mu\text{-}SPh)$ (see Experimental Section).[4] The structure of V was established by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of the molecule is shown in Figure 1. An ORTEP drawing of the Os_7S_2 cluster core is shown in Figure 2. Final positional and thermal parameters are listed in Table I. Interatomic distances and angles are listed in Tables II and III, respectively. The cluster consists of a closed polyhedron of five osmium atoms and two sulfur atoms arranged in the shape of a pentagonal bipyramid. The equatorial plane consisting of atoms Os(2), Os(4), Os(5), S(1), and S(2) is essentially planar. None of these atoms deviates from their least-squares plane by more than 0.041 (2) Å. The molecule is electron precise, that is, all bonds are of a two-center–two-electron type and each metal atom achieves an 18-electron configuration, but the structure of the cluster can also be rationalized within the framework of the skeletal electron pair theory.[21] According to this theory, a pentagonal-bipyramidal cluster would require the presence of eight pairs of skeletal electrons. Assuming that the $Os(CO)_3$ groups contribute two electrons each, the sulfido ligands contribute four electrons each, Os(1) and Os(6) contribute one electron each, and Os(2) contributes two electrons, the total number of skeletal electrons is 16 or 8 pairs, as required.

The Os(1)–Os(2) and Os(2)–Os(6) apical–equatorial edges of the cluster contain bridging $Os(CO)_4$ groups. The metal–metal bonds to these bridging groups are very similar and span the small range, 2.801 (2)–2.825 (2) Å. However they are all significantly shorter than the Os–Os bond distances found in $Os_3(CO)_{12}$, average 2.877 (3) Å.[22]

Table II. Interatomic Distances (Å) with Esds for $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V

Os(1)–Os(2)	2.893 (2)	Os(4)–C(10)	1.75 (4)
Os(1)–Os(3)	2.825 (2)	Os(4)–C(11)	1.85 (4)
Os(1)–Os(4)	2.905 (2)	Os(5)–C(12)	1.85 (3)
Os(1)–Os(5)	2.969 (2)	Os(5)–C(13)	1.89 (3)
Os(2)–Os(3)	2.809 (2)	Os(5)–C(14)	1.83 (4)
Os(2)–Os(6)	2.915 (2)	Os(6)–C(15)	1.81 (4)
Os(2)–Os(7)	2.801 (2)	Os(6)–C(16)	1.91 (4)
Os(4)–Os(5)	2.818 (2)	Os(7)–C(17)	2.05 (3)
Os(4)–Os(6)	2.963 (2)	Os(7)–C(18)	1.86 (4)
Os(5)–Os(6)	2.895 (2)	Os(7)–C(19)	2.04 (4)
Os(6)–Os(7)	2.809 (2)	Os(7)–C(20)	1.76 (5)
Os(1)···Os(6)	3.539 (2)	C(1)–O(1)	1.22 (4)
Os(2)···Os(4)	4.414 (2)	C(2)–O(2)	1.16 (3)
Os(2)···Os(5)	4.390 (2)	C(3)–O(3)	1.21 (3)
Os(1)–S(1)	2.488 (7)	C(4)–O(4)	1.13 (4)
Os(1)–S(2)	2.501 (8)	C(5)–O(5)	1.30 (4)
Os(2)–S(1)	2.400 (8)	C(6)–O(6)	1.29 (4)
Os(2)–S(2)	2.424 (8)	C(7)–O(7)	1.16 (4)
Os(4)–S(1)	2.456 (7)	C(8)–O(8)	1.09 (5)
Os(5)–S(2)	2.424 (8)	C(9)–O(9)	1.36 (5)
Os(6)–S(1)	2.463 (8)	C(10)–O(10)	1.24 (4)
Os(6)–S(2)	2.519 (8)	C(11)–O(11)	1.15 (4)
Os(1)–C(1)	1.81 (4)	C(12)–O(12)	1.16 (3)
Os(1)–C(2)	1.91 (3)	C(13)–O(13)	1.16 (4)
Os(2)–C(3)	1.81 (3)	C(14)–O(14)	1.22 (4)
Os(2)–C(4)	1.95 (4)	C(15)–O(15)	1.23 (4)
Os(3)–C(5)	1.85 (4)	C(16)–O(16)	1.16 (4)
Os(3)–C(6)	1.82 (5)	C(17)–O(17)	1.12 (3)
Os(3)–C(7)	1.90 (4)	C(18)–O(18)	1.14 (5)
Os(3)–C(8)	1.99 (4)	C(19)–O(19)	1.11 (4)
Os(4)–C(9)	1.66 (6)	C(20)–O(20)	1.26 (5)

The metal–metal bonds within the cluster span a large range, 2.818 (2)–2.969 (2) Å. The four apical–equatorial bonds Os(1)–Os(2), Os(1)–Os(4), Os(2)–Os(6), and Os(5)–Os(6) are very similar at 2.893 (2), 2.905 (2), 2.915 (2), and 2.895 (2) Å, respectively, but the two remaining apical–equatorial bonds Os(1)–Os(5) and Os(4)–Os(6) at 2.969 (2) and 2.963 (2) Å are significantly longer. A similar,

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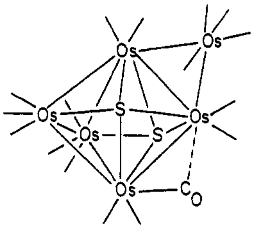
Table III. Interatomic Angles (deg) with Esds for $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V

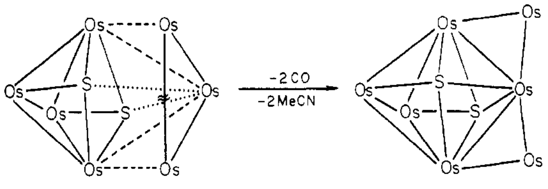
Os(2)-Os(1)-Os(3)	58.82 (5)	Os(3)-Os(2)-C(4)	79 (1)	Os(4)-Os(6)-C(16)	125 (1)
Os(2)-Os(1)-Os(4)	99.15 (6)	Os(6)-Os(2)-S(1)	54.2 (2)	Os(5)-Os(6)-S(1)	93.1 (2)
Os(2)-Os(1)-Os(5)	96.98 (6)	Os(6)-Os(2)-S(2)	55.4 (2)	Os(5)-Os(6)-S(2)	52.6 (2)
Os(3)-Os(1)-Os(4)	139.10 (7)	Os(6)-Os(2)-C(3)	124 (1)	Os(5)-Os(6)-C(15)	127 (1)
Os(3)-Os(1)-Os(5)	148.96 (7)	Os(6)-Os(2)-C(4)	125 (1)	Os(5)-Os(6)-C(16)	83 (1)
Os(4)-Os(1)-Os(5)	57.33 (5)	Os(7)-Os(2)-S(1)	93.0 (2)	Os(2)-Os(7)-C(17)	83 (1)
Os(1)-Os(2)-Os(3)	59.39 (5)	Os(7)-Os(2)-S(2)	95.6 (2)	Os(2)-Os(7)-C(18)	159 (1)
Os(1)-Os(2)-Os(6)	75.07 (5)	Os(7)-Os(2)-C(3)	87 (1)	Os(2)-Os(7)-C(19)	88 (1)
Os(1)-Os(2)-Os(7)	133.88 (6)	Os(7)-Os(2)-C(4)	86 (1)	Os(2)-Os(7)-C(20)	103 (2)
Os(3)-Os(2)-Os(6)	133.76 (6)	Os(1)-Os(3)-C(5)	88 (1)	Os(6)-Os(7)-C(17)	87 (1)
Os(3)-Os(2)-Os(7)	164.43 (7)	Os(1)-Os(3)-C(6)	170 (1)	Os(6)-Os(7)-C(18)	96 (1)
Os(6)-Os(2)-Os(7)	58.84 (5)	Os(1)-Os(3)-C(7)	82 (1)	Os(6)-Os(7)-C(19)	86 (1)
Os(1)-Os(3)-Os(2)	61.79 (5)	Os(1)-Os(3)-C(8)	104 (1)	Os(6)-Os(7)-C(20)	166 (2)
Os(1)-Os(4)-Os(5)	62.47 (5)	Os(2)-Os(3)-C(5)	85 (1)	Os(1)-S(1)-Os(2)	72.5 (2)
Os(1)-Os(4)-Os(6)	74.17 (5)	Os(2)-Os(3)-C(6)	108 (1)	Os(1)-S(1)-Os(4)	72.0 (2)
Os(5)-Os(4)-Os(6)	60.04 (5)	Os(2)-Os(3)-C(7)	88 (1)	Os(1)-S(1)-Os(6)	91.2 (3)
Os(1)-Os(5)-Os(4)	60.21 (5)	Os(2)-Os(3)-C(8)	165 (1)	Os(2)-S(1)-Os(4)	130.7 (3)
Os(1)-Os(5)-Os(6)	74.23 (5)	Os(1)-Os(4)-S(1)	54.5 (2)	Os(2)-S(1)-Os(6)	73.7 (2)
Os(4)-Os(5)-Os(6)	62.46 (5)	Os(1)-Os(4)-C(9)	104 (2)	Os(4)-S(1)-Os(6)	74.1 (2)
Os(2)-Os(6)-Os(4)	97.34 (6)	Os(1)-Os(4)-C(10)	165 (1)	Os(1)-S(2)-Os(2)	71.9 (2)
Os(2)-Os(6)-Os(5)	98.14 (6)	Os(1)-Os(4)-C(11)	98 (1)	Os(1)-S(2)-Os(5)	74.1 (2)
Os(2)-Os(6)-Os(7)	58.54 (5)	Os(5)-Os(4)-S(1)	95.1 (2)	Os(1)-S(2)-Os(6)	89.6 (3)
Os(4)-Os(6)-Os(5)	57.50 (5)	Os(5)-Os(4)-C(9)	161 (2)	Os(2)-S(2)-Os(5)	129.8 (3)
Os(4)-Os(6)-Os(7)	143.30 (7)	Os(5)-Os(4)-C(10)	106 (1)	Os(2)-S(2)-Os(6)	72.3 (2)
Os(5)-Os(6)-Os(7)	144.76 (6)	Os(5)-Os(4)-C(11)	81 (1)	Os(5)-S(2)-Os(6)	71.7 (2)
Os(2)-Os(7)-Os(6)	62.62 (5)	Os(6)-Os(4)-S(1)	53.1 (2)	S(1)-Os(1)-S(2)	83.7 (2)
Os(2)-Os(1)-S(1)	52.3 (2)	Os(6)-Os(4)-C(9)	132 (2)	S(1)-Os(2)-S(2)	87.3 (3)
Os(2)-Os(1)-S(2)	52.8 (2)	Os(6)-Os(4)-C(10)	92 (1)	S(1)-Os(6)-S(2)	83.9 (3)
Os(2)-Os(1)-C(1)	129 (1)	Os(6)-Os(4)-C(11)	139 (1)	Os(1)-C(1)-O(1)	170 (3)
Os(2)-Os(1)-C(2)	124 (1)	Os(1)-Os(5)-S(2)	54.1 (2)	Os(1)-C(2)-O(2)	172 (3)
Os(3)-Os(1)-S(1)	88.4 (2)	Os(1)-Os(5)-C(12)	91 (1)	Os(2)-C(3)-O(3)	172 (3)
Os(3)-Os(1)-S(2)	97.4 (2)	Os(1)-Os(5)-C(13)	140 (1)	Os(2)-C(4)-O(4)	176 (3)
Os(3)-Os(1)-C(1)	89 (1)	Os(1)-Os(5)-C(14)	126 (1)	Os(3)-C(5)-O(5)	172 (3)
Os(3)-Os(1)-C(2)	90 (1)	Os(4)-Os(5)-S(2)	96.9 (2)	Os(3)-C(6)-O(6)	169 (4)
Os(4)-Os(1)-S(1)	53.5 (2)	Os(4)-Os(5)-C(12)	109 (1)	Os(3)-C(7)-O(7)	167 (4)
Os(4)-Os(1)-S(2)	92.9 (2)	Os(4)-Os(5)-C(13)	81 (1)	Os(3)-C(8)-O(8)	158 (5)
Os(4)-Os(1)-C(1)	79 (1)	Os(4)-Os(5)-C(14)	166 (1)	Os(4)-C(9)-O(9)	165 (4)
Os(4)-Os(1)-C(2)	129 (1)	Os(6)-Os(5)-S(2)	55.7 (2)	Os(4)-C(10)-O(10)	171 (3)
Os(5)-Os(1)-S(1)	90.8 (2)	Os(6)-Os(5)-C(12)	165 (1)	Os(4)-C(11)-O(11)	171 (4)
Os(5)-Os(1)-S(2)	51.7 (2)	Os(6)-Os(5)-C(13)	95 (1)	Os(5)-C(12)-O(12)	168 (3)
Os(5)-Os(1)-C(1)	122 (1)	Os(6)-Os(5)-C(14)	106 (1)	Os(5)-C(13)-O(13)	175 (3)
Os(5)-Os(1)-C(2)	88 (1)	Os(2)-Os(6)-S(1)	52.2 (2)	Os(5)-C(14)-O(14)	176 (3)
Os(1)-Os(2)-S(1)	55.1 (2)	Os(2)-Os(6)-S(2)	52.4 (2)	Os(6)-C(15)-O(15)	176 (4)
Os(1)-Os(2)-S(2)	55.3 (2)	Os(2)-Os(6)-C(15)	128 (1)	Os(6)-C(16)-O(16)	177 (4)
Os(1)-Os(2)-C(3)	124 (1)	Os(2)-Os(6)-C(16)	127 (1)	Os(7)-C(17)-O(17)	168 (3)
Os(1)-Os(2)-C(4)	124 (1)	Os(4)-Os(6)-S(1)	52.9 (2)	Os(7)-C(18)-O(18)	174 (4)
Os(3)-Os(2)-S(1)	90.6 (2)	Os(4)-Os(6)-S(2)	91.2 (2)	Os(7)-C(19)-O(19)	176 (3)
Os(3)-Os(2)-S(2)	99.7 (2)	Os(4)-Os(6)-C(15)	89 (1)	Os(7)-C(20)-O(20)	171 (4)
Os(3)-Os(2)-C(3)	90 (1)				

although more pronounced, selective lengthening of two metal–metal bonds was observed in the structure of compound IV, one of the precursors to V.[4] Curiously, the Os(1), Os(4), Os(5), Os(6), S(1), and S(2) portion of V has the same structural arrangement as that of compound IV. The structure of V is very similar to the molecule $Os_6(CO)_{17}(\mu_4\text{-}S)_2$, VIII, which contains a cluster with the same shape and arrangement of atoms but has a semibridging carbonyl ligand in place of one of the $Os(CO)_4$ groups in V. Compound V contains 20 linear terminal carbonyl ligands. The shortest intermolecular contacts were between oxygen atoms of the carbonyl ligands, O(9)···O(17) = 2.84 (3) Å and O(16)···O(20) = 2.88 (4) Å.



VIII

Scheme I



IV + VII V

—, bond breaking; - - -, new Os–Os bonds; · · ·, new Os–S bonds

The formation of V from IV and VII seems to be that of a straight forward addition involving the cleavage of only one metal–metal bond, see Scheme I. Four new metal–metal bonds and two metal–sulfur bonds are formed. Two moles of MeCN and two moles of CO are eliminated. It is believed that metal atoms Os(2), Os(3), and Os(7) in V are derived from VII while the remainder of the molecule is derived from IV. The importance of metal–sulfur bonding in the formation of V is apparent by the formation of the new metal sulfur bonds between Os(2) and S(1) and S(2). Shifts of carbonyl ligands between certain metal atoms in VII must also have occurred in the formation of V, but these should be relatively facile processes.

Table IV. Crystallographic Data for X-ray Diffraction Study

(A) Crystal Data	
formula	$Os_7S_2O_{20}C_{20}$
temp, ±5 °C	23
space group	$P2_12_12_1$
a, Å	11.205 (5)
b, Å	14.461 (6)
c, Å	21.246 (16)
V, Å	3443 (6)
M_r	1955.7
Z	4
ρ_{calcd}, g/cm^3	3.77
(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite
detector aperture, mm	
horizontal ($A + B \tan \theta$)	
A	3.0
B	1.0
vertical	4.0
cryst faces	$0\bar{1}0$, 010, $\bar{2}12$, $2\bar{1}\bar{2}$, 212, $\bar{2}\bar{1}\bar{2}$, $01\bar{2}$, $0\bar{1}2$
cryst size, mm	0.20 × 0.15 × 0.39
cryst orientation: directn; deg from ϕ axis	normal to $01\bar{2}$; 5.6°
reflctns measd	$+h, +k, +l$
max 2θ, deg	52
scan type	moving crystal–stationary counter
ω scan width: $A + 0.347 \tan \theta$	$A = 0.90°$
background	$^1/_4$ additional scan at each end of scan
max, deg/min	6.7
min, deg/min	1.2
no. of reflctns measd	3763
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	2315
(C) Treatment of Data	
absorptn correctn	
coeff, cm^{-1}	275.6
grid	10 × 6 × 16
transmissn coeff	
max	0.093
min	0.048
P factor	0.01
final residuals	
R_F	0.055
R_{wF}	0.044
esd of unit weight	1.94
largest shift/error value on final cycle	0.05
largest peaks in final diff Fourier, e/Å^3	2.78

By an analogous procedure Vehrenkamp has utilized sulfido ligands to synthesize the cluster $Fe_2Co_2(CO)_{11}(\mu_4\text{-}S)_2$ from the dinuclear starting materials $Fe_2(CO)_6(\mu\text{-}S_2)$ and $Co_2(CO)_8$.[2b]

Experimental Section

All reactions were performed under a prepurified nitrogen atmosphere. $Os_3(CO)_{10}(CNMe)_2$,[23] $HOs(CO)_{10}(\mu\text{-}SC_6H_5)$,[24] $Os_3(CO)_9(\mu_3\text{-}S)_2$,[9] and $Os(CO)_5$[9] were prepared as previously reported. $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ was prepared from $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ as described previously.[10] IR spectra were recorded on a Nicolet 5-SX FT-IR. The percentage yields were calculated on the basis of the amount of starting material consumed in the reaction.

Photolysis of $Os_3(CO)_9(\mu_3\text{-}S)$, IV, and $Os(CO)_5$. A solution of IV (0.020 g, 0.024 mmol) and excess $Os(CO)_5$ in 40 mL of octane was photolyzed for 40 min under an N_2 atmosphere. The solvent was removed in vacuo, and the reddish brown residue was chromatographed in silica TLC plates. Elution with hexane/CH_2Cl_2 (90/10) yielded 0.011 g (0.01 mmol, 40%) of $Os_4(CO)_{13}(\mu_3\text{-}S)_2$.

Preparation of $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V. Method a. To $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, IV (38 g, 0.033 mmol), dissolved in 40 mL of octane was added $Os_3(CO)_{10}(NCMe)_2$ (140 mg, 0.150 mmol), and the mixture was heated at 120 °C for 2 h. The solvent was removed in vacuo, and the brownish green residue was placed on silica TLC plates. Elution with CH_2Cl_2/hexane (15/85) separated the unreacted, red IV and some brown $Os_6(CO)_{18}$ from the green product $Os_7S_2(CO)_{20}$, V. The product was crystallized from CH_2Cl_2/hexane at 0 °C: yield 10 mg, 16%; IR (CO) (hexane) 2127 (w), 2107 (m), 2080 (s), 2068 (w), 2057 (s), 2048 (m), 2035 (w), 2024 (sh), 2021 (s), 2011 (w), 1996 (w), 1959 (w), 1949 (w) cm^{-1}; mp 234 °C dec.

Method b. Pyrolysis of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$.[4] $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$ (160 mg, 0.17 mmol) was heated up to 250 °C (3 °C/min) under a CO atmosphere and was immediately cooled to room temperature. The dark brown residue was dissolved in methylene chloride, and the solution was placed on silica TLC plates. Elution with hexane/CH_2Cl_2 (90/10) separated the following bands: $Os_3(CO)_9(\mu_3\text{-}S)_2$, VI (45 mg, 31%); $Os_4(CO)_{12}(\mu_3\text{-}S)$[4] (20 mg, 11%); $Os_5(CO)_{15}(\mu_4\text{-}S)$[10] (45 mg, 19%); $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V (20 mg, 6%).

Crystallographic Analysis. Crystals V suitable for diffraction measurements were obtained by slowly evaporating CH_2Cl_2/hexanes solutions at room temperature. The data crystal was mounted in thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated 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.

The space group $P2_12_12_1$ was uniquely identified by the unit-cell shape and systematic absences observed in the data. Crystal data and data collection parameters are listed in Table IV. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf Nonius SDP program library (version 18). An absorption correction of a Gaussian integration type was applied to all the data. Neutral atom scattering factors were calculated by standard procedures.[26a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[26b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

The structure of V was solved by a combination of direct methods and difference Fourier techniques. The seven metal atoms were located in an electron-density map based on the phasing (MULTAN) of 194 reflections ($E \geq 1.65$). Only the osmium and sulfur atoms were refined anisotropically. The enantiomorph corresponding to positive fractional coordinates was selected originally, and with this model the values of residuals R_1 and R_2 upon convergence of the refinement were 0.058 and 0.047, respectively. At this point the other enantiomorph was tested by transforming all atomic coordinates to their negative values and refining again. With this enantiomorph refinement produced the residuals $R_1 = 0.055$ and $R_2 = 0.044$ upon convergence. This is a significant improvement, and the latter enantiomorph was deemed to be correct. The values of the fractional coordinates listed in Table I correspond to those of the latter enantiomorph. Tables II and III list interatomic distances and angles with errors obtained from the inverse matrix obtained on the final cycle of refinement.

Acknowledgment. We wish to thank the National Science Foundation for support of this research through

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(26) "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.

Grant No. CHE 80-19041, the Alfred P. Sloan Foundation for a fellowship to R.D.A., and Engelhard Industries for a loan of osmium tetroxide.

Registry No. III, 83928-37-4; IV, 83928-36-3; V, 86177-67-5; VI, 72282-40-7; VII, 61817-93-4; $HOs_3(CO)_{10}(\mu\text{-}SPh)$, 23733-19-9; $Os(CO)_5$, 16406-49-8.

Supplementary Material Available: A table of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

Epimerization of α-Chloro Boronic Esters by Lithium and Zinc Chlorides

Donald S. Matteson* and Ender Erdik[1]

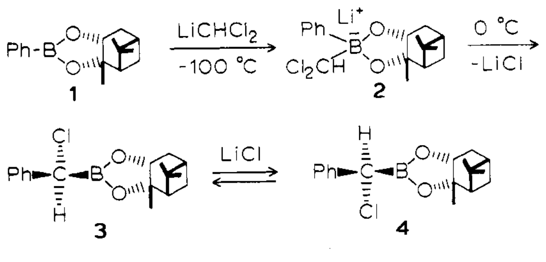
Department of Chemistry, Washington State University, Pullman, Washington 99164

Received March 11, 1983

The epimerization of (+)-pinanediol (α*S*)-α-chloro-α-phenylmethaneboronate (**3**) to the (α*R*)-isomer **4** is catalyzed by lithium chloride in tetrahydrofuran (THF). The rate is first-order in **3** and approximately 0.75 order in lithium chloride over the range 0.04–0.45 M LiCl. No epimerization takes place in the absence of lithium chloride. The rate is greatly increased by reagents which promote ionization of lithium chloride, including water and dimethyl sulfoxide. Accordingly it appears that the active catalyst is free chloride ion. Zinc chloride also catalyzes the epimerization, and the rate shows approximately 1.6-order dependence on the $ZnCl_2$ concentration, as if acid catalysis is involved together with chloride catalysis. Mixtures of lithium chloride and 0.5–1.0 equiv of zinc chloride are less active catalysts than either salt by itself, implying formation of relatively inactive $LiZnCl_3$ and Li_2ZnCl_4, but rates of epimerization by these reagents are still significant in terms of limiting the stereoselectivity of the synthesis of α-chloro boronic esters by homologation of boronic esters with (dichloromethyl)lithium. The rate of epimerization of (+)-pinanediol (α*S*)-α-chlorallylboronate by lithium chloride was 0.7 that of the α-chloro α-phenylmethaneboronate (**3**), and the rates for (+)-pinanediol 1-chloro-2-phenylethane-1-boronate and 1-chloropentane-1-boronate were about an order of magnitude less than that for **3**.

Introduction

The chirally selective reaction of pinanediol boronic esters with dichloromethylllithium to form homologous α-chloro boronic esters provides a promising new approach to directed chiral synthesis.[2] A side reaction which can decrease the stereoselectivity of this process is the epimerization of the α-chloro boronic ester product in the presence of the other reaction product lithium chloride. Thus, the reaction of (+)-pinanediol benzeneboronate (**1**) with (dichloromethyl)lithium forms the borate complex **2**, which rearranges primarily to (+)-pinanediol (α*S*)-α-chloro-α-phenylmethane boronate (**3**), which in turn epimerizes significantly to its (α*R*)-isomer (**4**) if the reaction mixture is not worked up quickly enough.[2] Although conditions were found which yielded ratios of **3** to **4** as high as 30:1,[2] the present kinetic study was undertaken in order to understand the factors which affect the rate of epimerization of **3** and related compounds, with the aim of learning how to minimize this side reaction for synthetic purposes.



Experimental Section

General Data. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Lithium chloride and zinc chloride were reagent grade and were dried to constant weight under vacuum (0.01 torr) at up to 100 °C while pulverizing with the aid of a small magnetic stirrer in a volumetric flask. The flask was cooled with an ice-water bath when THF was added to zinc chloride. Solutions were made up under argon, and all transfers of solvents or solutions were made by syringe through rubber septums with pressure equalization by argon-filled balloons. Protection from air was not entirely rigorous as the rubber septum was exchanged for a Teflon plug after filling the polarimeter cell. Slow leakage of THF through the rubber septums was observed, and solutions were used within a few days of preparation. Proton NMR spectra were measured at 60 MHz with a Varian EM-360 instrument or at 200 MHz with a Nicolet NT-200. Optical rotations were measured at 546 nm (Hg line) with a Jasco DIP-181 digital polarimeter, except for exploratory studies before this instrument became available to us, which were done with an ancient Rudolph visual instrument at 589 nm.

(+)-Pinanediol (α*S*)-α-Chlorobenzylboronate (3). A. Modified Previous Method.[2] The published procedure[2] was followed, 10-mmol scale, up to the point where the reaction mixture was kept at 0 °C for 1 h in order to rearrange **2** to **3**. If the solution was concentrated at this point and **3** was distilled directly from the residual lithium chloride as described for other α-chloro boronic esters,[3] epimerization of **3** to **4** approached the equilibrium value. To avoid this problem, the cold solution of

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