Supplementary Material Available: Listings of observed and calculated structure factors, positional parameters, anisotropic thermal parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

An Example of an "Inverted" Tetrahedral Geometry at Sulfur. The Synthesis and Crystal and Molecular Structure of $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$

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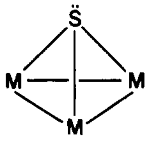
Summary: The decarbonylation of the sulfido-bridged cluster $PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$, **1**, by trimethylamine oxide leads to formation of the dimer $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **2**. The molecular structure of **2** was determined by single-crystal X-ray diffraction analysis: space group $P2_1/n$, a = 14.308 (2) Å, b = 21.753 (5) Å, c = 21.760 (4) Å, β = 96.20 (1)°, Z = 4, ρ_{calcd} = 2.83 g/cm^3. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined with 4874 reflections to the final residuals of R_F = 0.053 and R_{wF} = 0.063. Compound **2** consists of two trigonal-prismatic $PtOs_3S_2$ clusters linked on an edge by quadruply bridging sulfido ligands that serve as six-electron donors and exhibit inverted tetrahedral geometries.

Bridging ligands have been shown to be of great value for the synthesis and stabilization of transition-metal cluster compounds.[2-4] Of these the sulfido ligand has been the focus of considerable attention.[5-8] Triply bridging sulfido ligands A serve as four-electron donors while quadruply bridging sulfido ligands can serve either as four B or six C electron donors.[3] The type C geometry is best described as tetrahedral, although the M–S–M bond angles often span wide ranges due to distortions caused by the existence of metal–metal bonding.[3,9] We now wish to report the characterization of a complex containing quadruply bridging sulfido ligands that are so greatly distorted that their geometry should be described as "inverted" tetrahedral.[10,11]



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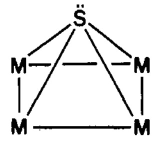

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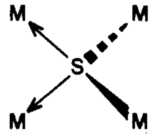

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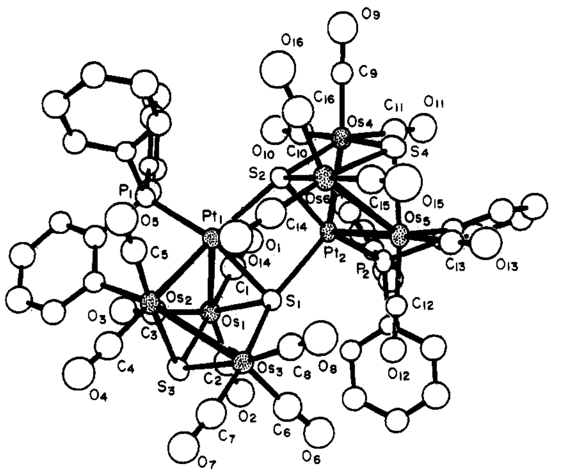

Figure 1. An ORTEP diagram of $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **2**, showing 50% probability thermal ellipsoids.

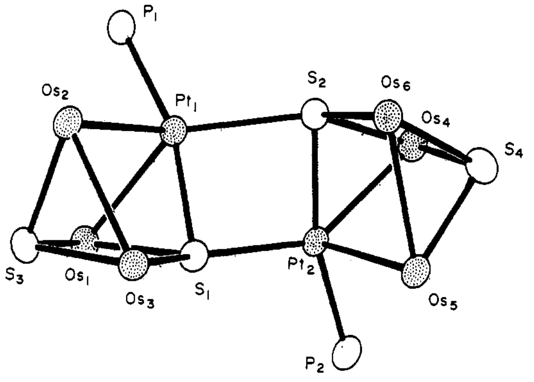

Figure 2. An ORTEP diagram of **2** with the phenyl rings and carbonyl ligands omitted.

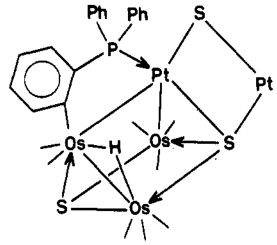

Figure 3. An electron distribution scheme showing the bonding for one half of the molecule of **2**.

Treatment of the complex $PtOs_3(CO)_{10}PPh_3(\mu_3\text{-}S)_2$, **1**,[12] with trimethylamine oxide dihydrate in THF at 0 °C for 1 h results in the formation of the orange-red product $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **2**, in 16% yield.[13] The structure of **2** was determined by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of the complete molecule is shown in Figure 1.[14] An ORTEP diagram

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[13] The reaction was performed at 0 °C over a period of 1 h. The orange product **2** was isolated by TLC on silica by using a hexane/methylene chloride solvent mixture: IR (ν(CO), cm^{-1}, in hexane) 2104 (m), 2099 (s), 2079 (s), 2073 (m), 2031 (s), 2016 (m), 2006 (s), 2003 (s), 1989 (m), 1947 (s); ^{1}H NMR (δ, $CDCl_3$) 6.70-8.00 (m, 28 H), −11.17 (d, 2 H, J_{P-H} = 9.6 Hz).

[14] Compound **2** crystallizes in the monoclinic space group $P2_1/n$: a = 14.308 (2) Å, b = 21.753 (5) Å, c = 21.760 (4) Å, β = 96.20 (1)°, V = 6733 (4) Å^3, Z = 4, ρ_{calcd} = 2.83 g/cm^3. Intensity data were collected on an Enraf-Nonius CAD4 X-ray diffractometer by using Mo K$_{\bar{\alpha}}$ radiation. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. Full-matrix least-squares refinement (4874 reflections, $F^2 \geq 3.0\ \sigma(F^2)$) yielded the final residuals R_F = 0.053 and R_{wF} = 0.063. All calculations were performed on a Digital Equipment Corp. VAX 11/750 using the Enraf-Nonius SDP program library.

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showing just the cluster framework is shown in Figure 2. Basically, the molecule consists of two trigonal-prismatic $PtOs_3S_2$ clusters that are joined on an edge by the quadruply bridging sulfido ligands S(1) and S(2). The four-membered Pt(1)–S(1)–Pt(2)–S(2) ring is slightly puckered with the dihedral angle between the two PtS_2 planes being 42°. The Pt(1)···Pt(2) distance at 3.313 (1) Å is indicative of a nonbonding interaction.[15] Within the trigonal prisms there are three metal–metal bonds (e.g., Pt(1)–Os(1) = 2.680 (1) Å, Pt(1)–Os(2) = 2.744 (1) Å, and Os(2)–Os(3) = 2.956 (1) Å). Each cluster contains one hydride ligand that is believed to bridge the elongated osmium–osmium bond. A phosphine ligand is coordinated to each platinum atom, and each has one phenyl ring ortho-metalated to an adjacent osmium atom. Each cluster contains eight linear terminal carbonyl ligands. Two osmium atoms contain three CO ligands while the one with the ortho-metalated ring (Os(2) and Os(5)) has only two.

There are a variety of resonance structures that one can devise to distribute the bonding electrons. One of these is shown in Figure 3. If the triply bridging sulfido ligands are assumed to serve as four-electron donors and the quadruply bridging sulfido ligands serve as six-electron donors, then the osmium atoms can achieve 18-electron configurations, but the platinum atoms will have only 16 electrons. However, 16-electron platinum atoms are common in mononuclear metal complexes and have been observed in cluster complexes as well.[16] It seems that the alternative in which the quadruply bridging sulfido ligands serve only as four-electron donors is highly unlikely because the still greater electron deficiency at the metal atoms would be intolerable.

The formation of the four-membered Pt_2S_2 ring produces considerable distortions on the geometry of the bridging sulfido ligands. For example, the Pt(2)–S(1)–Os(3) angle is 145.3 (3)° while the Pt(1)–S(1)–Pt(2) and Pt(1)–S(2)–Pt(2) bond angles are 85.02 (16)° and 83.81 (17)°, respectively. The Pt(1)–S(1)–Os(1) and Pt(2)–S(2)–Os(4) angles are only 68.31 (16)° and 67.28 (15)°.[17] One consequence of these distortions is that all the metal atoms lie on the same side of a plane that passes through the sulfido ligand. In tetravalent species this geometry is known as "inverted" tetrahedral.[10,11] Since all six valence electrons of the quadruply bridging sulfido ligands are involved in bonding to the metal atoms, these ligands must be regarded as tetravalent.[18] An alternative way of visualizing this situation is to determine the position of the central atom and one of the substituents with respect to a plane defined by the three other substituents. For example, atoms S(2) lies 0.32 Å from the plane defined by Pt(1), Os(4), and Os(6). Atom Pt(2) lies 1.87 Å from the plane on the opposite side.[20] If one ignores the presence of the phosphine and triply bridging sulfido ligands, the cluster has the form of two [2.2.1]propellanes that have one four-membered ring in common. Indeed, it has been the propellane class of molecules that has been the source of the greatest number of examples of inverted tetrahedral carbon structures.[10,11]

The importance of bridging sulfido ligands in the synthesis and stabilization of polynuclear metal complexes is becoming increasingly apparent as sulfidometal complexes with greater complexities are being prepared. It is clear that the ability of the sulfido ligand to adopt a wide variety of structural geometries will be a valuable feature of its ligand behavior.

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Registry No. 1, 92763-25-2; 2, 92763-26-3; Pt, 7440-06-4; Os, 7440-04-2.

Supplementary Material Available: Tables of fractional atomic coordinates, bond distances, bond angles, and structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(15) Selected interatomic distances (Å) for 2: Pt(1)–Os(1) = 2.680 (1), Pt(1)–Os(2) = 2.744 (1), Os(2)–Os(3) = 2.956 (1), Pt(2)–Os(4) = 2.652 (1), Pt(2)–Os(5) = 2.723 (1), Os(5)–Os(6) = 2.930 (1), Pt(1)···Pt(2) = 3.313 (1), Pt(1)–S(1) = 2.365 (5), Pt(1)–S(2) = 2.583 (6), Pt(1)–P(1) = 2.235 (6), Os(1)–S(1) = 2.409 (6), Os(1)–S(3) = 2.423 (6), Os(2)–S(3) = 2.394 (6), Os(3)–S(1) = 2.484 (5), Os(3)–S(3) = 2.447 (7), Pt(2)–S(1) = 2.536 (5), Pt(2)–S(2) = 2.372 (5), Pt(2)–P(2) = 2.243 (6), Os(4)–S(2) = 2.415 (5), Os(4)–S(4) = 2.473 (7), Os(5)–S(4) = 2.384 (5), Os(6)–S(2) = 2.481 (7), Os(6)–S(4) = 2.458 (6).

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(17) Selected bond angles (deg) for 2: Pt(1)–S(1)–Os(1) = 68.31 (16), Pt(1)–S(1)–Os(3) = 102.86 (21), Os(1)–S(1)–Os(3) = 97.83 (20), Pt(1)–S(1)–Pt(2) = 85.02 (16), Pt(1)–S(2)–Os(4) = 135.0 (3), Pt(1)–S(2)–Os(6) = 122.2 (2), S(1)–Pt(1)–S(2) = 87.47 (19), Os(1)–Pt(1)–Os(2) = 78.87 (4), Pt(1)–Os(2)–Os(3) = 83.31 (4), Pt(2)–S(2)–Os(4) = 67.28 (15), Pt(2)–S(2)–Os(6) = 101.21 (22), Os(4)–S(2)–Os(6) = 97.59 (21), Pt(1)–S(2)–Pt(2) = 83.81 (17), Pt(2)–S(1)–Os(1) = 116.22 (23), Pt(2)–S(1)–Os(3) = 145.3 (3), S(1)–Pt(2)–S(2) = 88.43 (18), Os(4)–Pt(2)–Os(5) = 86.05 (4), Pt(2)–Os(5)–Os(6) = 83.05 (4).

(18) Sulfuranes[19] and the quadruply bridging sulfido ligands that act as a four-electron donors (e.g., type B) contain a lone pair of electrons on the sulfur atom. For these cases the geometry of the sulfur atom should be based on five vertices and should not be considered as inverted tetrahedra.

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(20) Atom S(1) lies 0.11 Å from the plane defined by Pt(2), Os(1), and Os(3). Atom Pt(1) lies 2.07 Å on the opposite side of that plane.

Facile C-Mercuration of Bis(diphenylphosphino)methane

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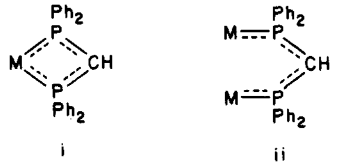
Summary: The reaction of $CH_2(PPh_2)_2$ with Hg(OAc) and $[Hg(Me_2SO)_6](O_3SCF_3)_2$ leads to $\{(AcOHg)_nCH_{2-n}[PPh_2(HgOAc)]_2\}(O_3SCF_3)_2$ (n = 1, 2), which were characterized with ^{199}Hg and ^{31}P NMR spectroscopy.

Most metal complexes of deprotonated bis(diphenylphosphino)methane (dppm) are coordinated via the *phosphorus* atoms of the ligand either in a chelating (i) or in a bridging mode (ii).[1] This is true for transition



i ii

metals including Au, Ni, Pd, and Pt[2–6] as well as for lithiated dppm that adopts structure i according to ^{31}P and ^{6}Li NMR measurements.[7] Coordination through the

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