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

Maria Lusser and Paul Peringer*

Institut für Anorganische und Analytische Chemie
der Universität Innsbruck, Innrain 52a
A-6020 Innsbruck, Austria

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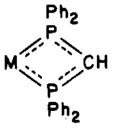
Summary: The reaction of $CH_2(PPh_2)_2$ with Hg(OAc) and $[Hg(Me_2SO)_6](O_3SCF_3)_2$ leads to $\{(AcOHg)_nCH_{2-n}[PPh_2(HgOAc)]_2\}(O_3SCF_3)_2$ (n = 1, 2), which were characterized with ^{199}Hg and ^{31}P NMR spectroscopy.

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 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



i

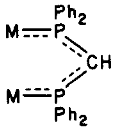


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Table I. {^{1}H} NMR Parameters of $\{(AcOHg)_nCH_{2-n}[PPh_2(HgOAc)]_2\}^{2+}$ [a]

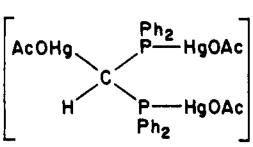
n	$\delta(^{31}P)$	$\delta(^{199}Hg_P)$	$\delta(^{199}Hg_C)$	$^1J(^{199}Hg, ^{31}P)$	$^2J(^{199}Hg, ^{31}P)$	$^3J(^{199}Hg, ^{31}P)$	T, K
1	34.1	916 d[b]	854 t[b]	8773	265	30	253
2	43.3	889 d[c]	941 t[c]	8648	234	212	273

[a] Chemical shifts are in parts per million the low field of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol of HgO/cm^3 of 60% $HClO_4$); coupling constants are in Hz; solvent, MeOH. [b] $^2J(^{199}Hg, ^1H) = 260$, $^3J(^{199}Hg, ^1H) = 300$; coupling constants determined from a ^{1}H-coupled ^{199}Hg NMR spectrum. [c] The t/d intensity ratio of **2** is nearly (due to different NOE) doubled compared with that of **1**.

methylene *carbon* is known only in a few cases.[8–12] The complexes were generated from the deprotonated ligand and appropriate metal compounds or by deprotonation of the coordinated ligand. We report here further examples of C-substitution in various mercury complexes of dppm.

The reaction of dppm with $Hg(OAc)_2$ and $[Hg(Me_2SO)_6](O_3SCF_3)_2$[13] according to eq 1 in methanol at ambient temperature affords the C-metalated product **1** almost quantitatively within a few minutes.[14] The compound was isolated and crystallized as an Me_2SO solvate.[15] The structure is evidenced by ^{199}Hg and ^{31}P NMR spectroscopy.[16] The ^{199}Hg{^{1}H} NMR spectrum (^{199}Hg, $I = 1/2$, abundance 16.8%) of **1** shows two different mercury sites: one doublet attributable to the mercury bound to phosphorus and a 1:2:1 triplet for the carbon-bound mercury being coupled to two equivalent phosphorus atoms via two bonds. This is confirmed by the ^{31}P NMR spectrum. The NMR data are summarized in Table I.

$Ph_2PCH_2PPh_2 + 2Hg(OAc)_2 + [Hg(Me_2SO)_6](O_3SCF_3)_2 \longrightarrow$

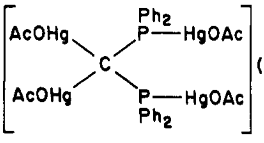


$(O_3SCF_3)_2$ + HOAc (1)

1

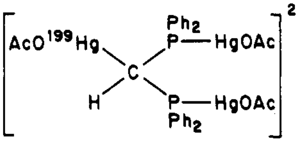
The reaction of one further equivalent of $Hg(OAc)_2$ according to eq 2 leads under the same conditions almost quantitatively to the dimercurated product **2**, which was characterized similarly to **1** (Table I).[14,17] Particulary conclusive is the nearly doubled intensity of the ^{199}Hg satellite pattern due to $^2J(^{199}Hg, ^{31}P)$ in the ^{31}P NMR spectrum according to a statistical abundance of 19.37% for the isotopomer **2a** compared with that of **1a** (11.56%).

$Ph_2PCH_2PPh_2 + 3Hg(OAc)_2 + [Hg(Me_2SO)_6](O_3SCF_3)_2 \longrightarrow$

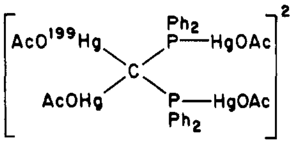


$(O_3SCF_3)_2$ + 2HOAc (2)

2



1a



2a

The mercury-199 resonance of the C-bound mercury is at high frequency relative to that of **1** in keeping with the results for the series $CH_{4-n}(HgX)_n$.[18]

The occurrence of reactions 1 and 2 under mild conditions is quite interesting since the replacement of hydrogen by mercury (mercuration) in aliphatic compounds is limited to acidic hydrocarbons, i.e., hydrogens α to electron-withdrawing groups[19] such as cyano, diazo, carbonyl, or phosphoryl[20] groups (e.g., eq 3). dppm is not acidic according to a pK_a of 29.9,[21] and deprotonation only succeeds by using very strong bases. We propose that the methylene group of dppm is activated as a result of the coordination of mercury to the diphenylphosphino groups, i.e., that $[PPh_2HgOAc]^+$ acts as an electron-withdrawing group.

$$CH_2[P(O)(OEt)_2]_2 + 2Hg(OAc)_2 \rightarrow \rightarrow (AcOHg)_2C[P(O)(OEt)_2]_2 + 2HOAc \quad (3)$$

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(14) The use of $[Hg(Me_2SO)_6](O_3SCF_3)_2$ alone in the reactions 1 and 2 leads to compounds corresponding to 1 and 2 besides other unidentified products; the use of $Hg(OAc)_2$ alone in the reactions 1 and 2 leads to products corresponding to 1 and 2 that exhibit an increased kinetic lability of the Hg–P bonds and decompose even faster.

(15) $\{(AcOHg)CH[PPh_2(HgOAc)]_2\}(O_3SCF_3)_2\cdot3Me_2SO$: mp 127–133 °C. Anal. Calcd for $C_{39}H_{48}F_6Hg_3O_{15}P_2S_5$: C, 27.6; H, 2.9; Hg, 35.5. Found: C, 27.4; H, 2.9; Hg, 34.6. The Me_2SO content was also confirmed by integration of the ^{1}H NMR spectrum.

(16) NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer.

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New Tin Heterocycles: Adducts between Acetylenes or Allenes and "Distannacyclopropanes"

H. Killing and T. N. Mitchell*

Abteilung Chemie, Universität Dortmund
4600 Dortmund 50, FRG

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Summary: 1,2,4,5-Tetrastannacyclohexanes react with 1-alkynes and 1,1-dimethylallene in the presence of tetrakis(triphenylphosphine)palladium(0) to give 4-substituted 1,3-distannacyclopentenes and 4-methylene-1,3-distannacyclopentanes, respectively. These compounds are formally adducts between the acetylene or allene and distannacyclopropanes.

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