Reaction of $Os_3(\mu\text{-}Cl)_2(CO)_{10}$ with $Ph_2PCH_2PPh_2$. The formation of a novel 12-membered macrocycle containing C, P, Cl, and Os atoms in the ring

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The reaction of $Os_3(\mu\text{-}Cl)_2(CO)_{10}$ (**1**) with $Ph_2PCH_2PPh_2$ (dppm) in a toluene solution at 65 °C results in novel osmium complexes $[Os_3(\mu\text{-}Cl)_2(CO)_9]_2(dppm)$ (**2**) and $[Os_3(\mu\text{-}Cl)_2(CO)_8]_2(dppm)_2$ (**3**). Compounds **2** and **3** were characterized by ^1H and ^{31}P NMR, and IR spectroscopy and their structures were established by X-ray analysis. In both compounds, dppm is a bridging ligand between the two cluster units. Molecule **3** can be considered as an unusual 12-membered macrocycle containing C, P, Cl, and Os atoms in the ring.

Key words: osmium heterocycle, osmium clusters, osmium carbonyl phosphines, osmium carbonyl chloride, diphosphine ligand; IR spectra, ^1H, ^{31}P NMR spectra; X-ray analysis.

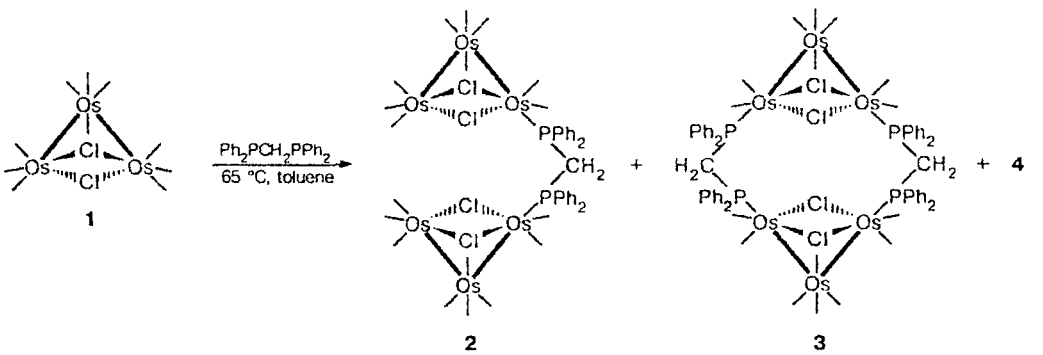
Extensive information on the reactions of trinuclear $M_3(CO)_{12}$ (M = Ru, Os) clusters with various diphosphine ligands is available in the literature at present. Depending on the reaction conditions and type of diphosphine used, cluster products with a great variety of structures are formed, in which the diphosphine ligand is a mono- or bidentate ligand; in the latter case, a chelate structure and bridging structure binding two metallocluster units can be formed.[1–7]

In this work we studied the reaction of cluster $Os_3(\mu\text{-}Cl)_2(CO)_{10}$ (**1**) with $Ph_2PCH_2PPh_2$ (dppm). The absence of a metal—metal interaction between the two Os atoms bonded only by bridging Cl atoms is a specific feature of this cluster. For this reason, reactions of cluster **1** with diphosphines can occur by two fundamentally different ways, namely, by substitution of carbonyl groups or by cleavage of chloride bridging bonds (with both retention and breakdown of the cyclic structure). Because of the enhanced ability of the dppm ligand to form chelate metallacycles and especially five-membered metallacycles with two adjacent metal atoms,[8] the reaction between dppm and cluster **1** can lead to a wide range of products with different structures.

Results and Discussion

The reaction of complex **1** with dppm (toluene, 65 °C) occurs to give predominantly a mixture of two soluble clusters $[Os_3(\mu\text{-}Cl)_2(CO)_9]_2(dppm)$ (**2**) and $[Os_3(\mu\text{-}Cl)_2(CO)_8]_2(dppm)_2$ (**3**) and a small amount of insoluble precipitate of unidentified compound **4** (Scheme 1). Clusters **2** and **3** were separated by column chromatography, characterized by ^1H and ^{31}P NMR, and IR spectroscopy, and their structures were established by X-ray analysis. Compound **2** is formed as a result of substitution of one equatorial CO group in the

Scheme 1



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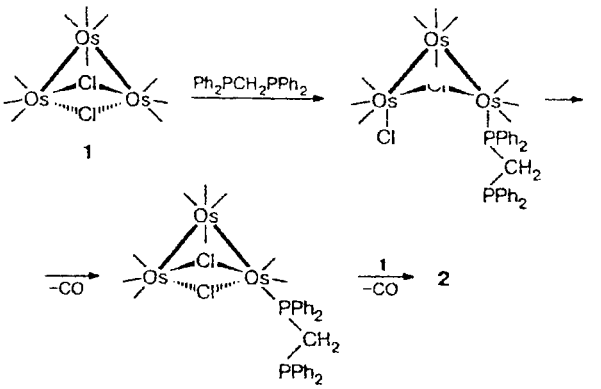
$(CO)_3Os(\mu\text{-}Cl)_2Os(CO)_3$ moiety in each of the two molecules of the initial cluster **1** by the diphosphine ligand and is the first example of compounds in the series of trinuclear Os and Ru clusters, in which dppm is a bridging ligand between the two metallocluster units. Previously, only such type of complexes with diphosphines containing at least two methylene groups between the phosphorus atoms were known, for instance, $Os_6(CO)_{22}[Ph_2P(CH_2)_nPPh_2]$ (n = 2—4) [7] and $Ru_6(CO)_{22}[Ph_2P(CH_2)_2PPh_2]$.[5] In compound **3**, both metallocluster units are bonded symmetrically already by two bridging dppm ligands, which leads to the unusual 12-membered macrocycle. The formation of such kind of structures for trinuclear clusters with diphosphine ligands is observed for the first time.

In addition to multiplets of the phenyl protons, the ^1H NMR spectra of compounds **2** and **3** contain triplet signals of the methylene protons of coordinated dppm at δ 4.6 ($^2J_{H-P}$ = 6.2 Hz) and at δ 4.8 ($^2J_{H-P}$ = 6.7 Hz), respectively. This indicates that the phosphorus atoms in each of the compounds are equivalent. This is also in agreement with the $^{31}P\text{-}\{^1H\}$ NMR spectra in which the singlets of phosphorus atoms at δ −1.77 (for **2**) and at δ 0.52 (for **3**) are observed. The IR spectra of complexes **2** and **3** reveal the presence of ν(CO) bands of only terminal carbonyl ligands. Frequencies of several ν(CO) bands of complex **2** are shifted by ~10 cm^{-1} toward the low-frequency region as compared to corresponding frequencies of the starting complex **1**, which indicates the presence of electron-donating phosphine ligand in the cluster units. The introduction of one more phosphine ligand into the molecule **3** leads to further decrease in the ν(CO) frequencies of the $Os(CO)_2$ units observed in its IR spectrum as compared to corresponding frequencies of the starting complex **1**. However, the positions of high-frequency ν(CO) bands remain unchanged, most likely due to the fact that the phosphine ligands have virtually no electronic effect on the $Os(CO)_4$ unit.

Because of the insolubility of complex **4** in common organic solvents, we failed to record adequate NMR spectra and to grow a single crystal of this compound. However, the IR spectrum of complex **4** shows unambiguously that the number of intense ν(CO) bands is much less and that the frequencies of all of the bands are much lower (the shift value is ~100 cm^{-1}) than the corresponding parameters of the IR spectra of complexes **1**, **2**, and **3**. This is most likely due to the decrease in the number of carbonyl groups caused by their further substitution by electron-donating phosphine ligands. In contrast to the IR spectra of complexes **1**, **2**, and **3**, no high-frequency ν(CO) bands characteristic of the $Os(CO)_4$ unit is observed in the IR spectrum of **4**, which indicates that substitution of carbonyl groups by phosphine ligands occurs likely in all metallocarbonyl fragments. Along with the decrease in the ν(CO) frequencies, which is much larger than in the spectra of complexes **2** and **3**, this also indicates the presence of a larger number of phosphine ligands in compound **4**.

It should be noted that the ratio of the reaction products (see Scheme 1) is strongly dependent on the reaction conditions (concentration, temperature, and duration). As the concentration of initial reagents decreases approximately by a factor of 6, the reaction can be interrupted at a stage at which only complex **2** is formed; according to TLC data, complex **2** is the only product in this case and can be isolated in 83% yield. Thus, equatorial carbonyl groups of the $(CO)_3Os(\mu\text{-}Cl)_2Os(CO)_3$ moiety in *trans*-positions with respect to the osmium atom of the $Os(CO)_4$ unit are the sites at which initial substitution by diphosphine ligands in dichloride cluster **1** occurs. However, it cannot be ruled out that the first stage of the reaction of compound **1** with dppm includes cleavage of one of the chloride bridging bonds followed by elimination of a carbonyl group (Scheme 2).

Scheme 2



For instance, reactions of $Os_3(\mu\text{-}Cl)(\mu\text{-}H)(CO)_{10}$ with various phosphines (PPh_3, PMe_2Ph), in which stable products of addition of the phosphine due to the cleavage of the chloride bridging bond are initially produced, occur *via* this route. Upon heating, these products undergo decarbonylation at both the Os atoms bonded by the bridging bond and the Os atom of the $Os(CO)_4$ unit to give a mixture of two isomers.[9] In any case, the obtained data on the reactivity of dichloride cluster **1** toward dppm (taking into account the published data[9]) unambiguously show that the equatorial carbonyl groups mentioned above are more labile toward a diphosphine attack. This is indirectly confirmed by X-ray study of cluster **1**,[10] from which it follows that those equatorial Os—C bonds at which the substitution of CO groups by phosphine ligands occurs are somewhat lengthened. Most likely, these are the increased capability of these carbonyl groups of complex **1** to undergo substitution and performance of the reaction in excess compound **1** relative to dppm that are the deciding factors for the formation of such unusual structures as those of compounds **2** and **3**.

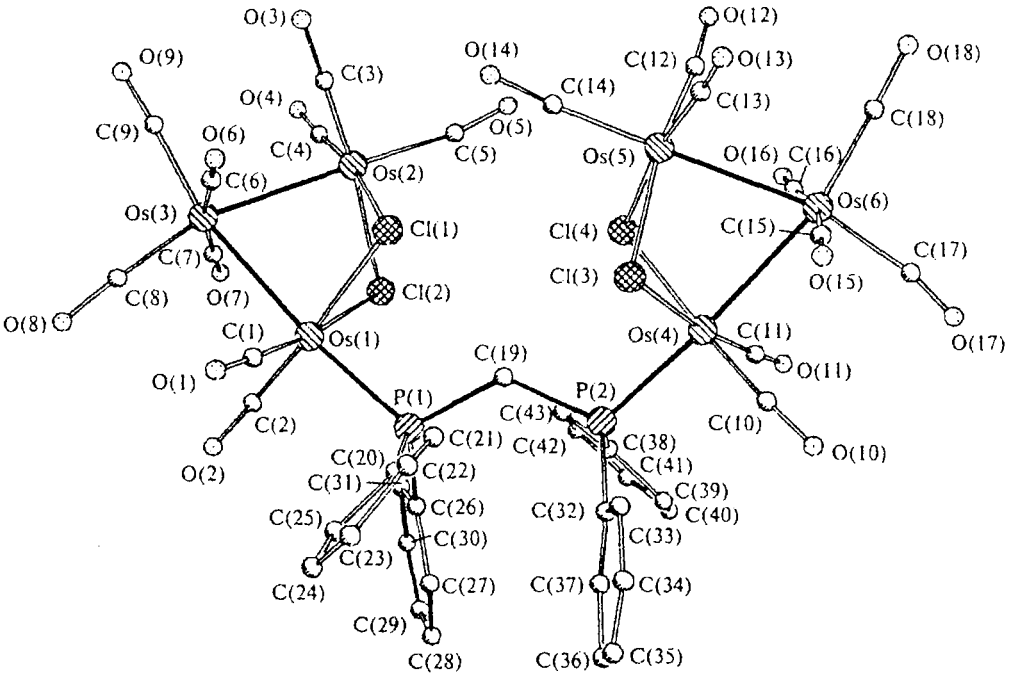


Fig. 1. Molecular structure of cluster $[Os_3(\mu\text{-}Cl)_2(CO)_9]_2(dppm)$ (**2**).

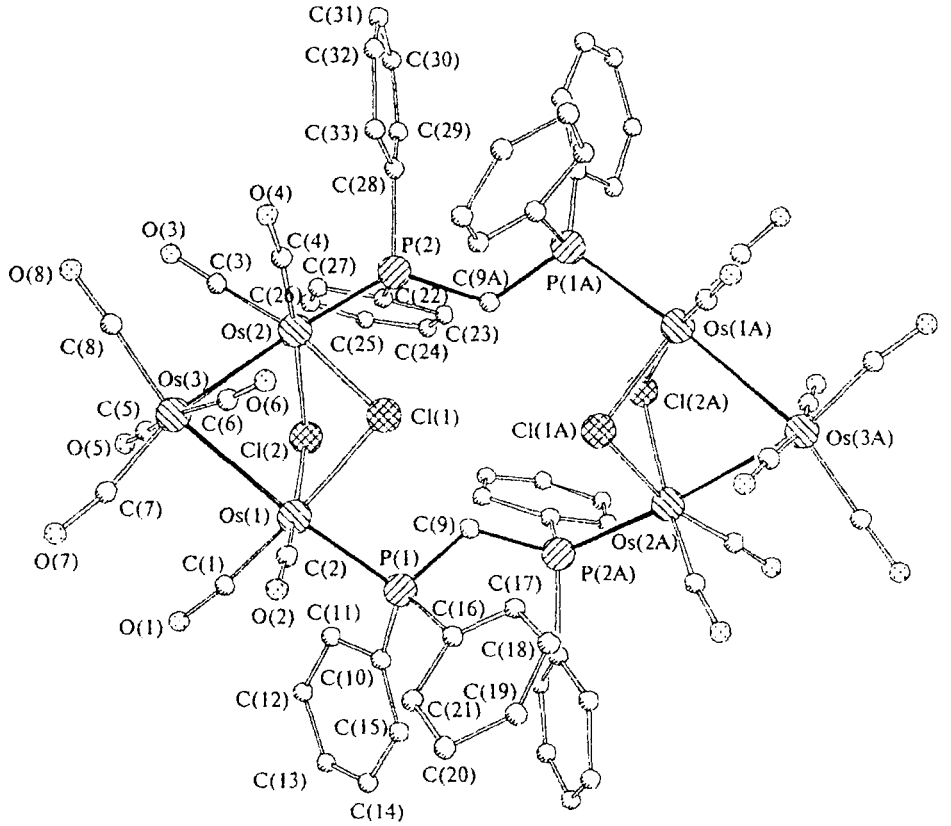


Fig. 2. Molecular structure of cluster $[Os_3(\mu\text{-}Cl)_2(CO)_8]_2(dppm)_2$ (**3**).

The structure of clusters **2** and **3** was established by X-ray analysis (Figs. 1 and 2, Tables 1—5). Molecule **2** (see Fig. 1 and Table 1) consists of two cluster moieties $(OC)_4Os(OC)_3Os(\mu\text{-}Cl)_2Os(CO)_2$ bonded by the bridg-

Table 1. Selected bond lengths (d) and bond angles (ω) in complex **2**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Os(1)—C(2)	1.84(3)	Os(3)—C(8)	1.83(3)	Os(5)—C(12)	1.89(4)	P(1)—C(19)	1.82(2)	O(8)—C(8)	1.20(3)
Os(1)—C(1)	1.88(3)	Os(3)—C(7)	1.89(3)	Os(5)—C(14)	1.91(3)	P(2)—C(32)	1.80(2)	O(9)—C(9)	1.13(3)
Os(1)—P(1)	2.394(6)	Os(3)—C(9)	1.92(3)	Os(5)—Cl(4)	2.472(5)	P(2)—C(38)	1.84(2)	O(10)—C(10)	1.12(3)
Os(1)—Cl(1)	2.489(5)	Os(3)—C(6)	2.00(3)	Os(5)—Cl(3)	2.478(6)	P(2)—C(19)	1.88(2)	O(11)—C(11)	1.14(3)
Os(1)—Cl(2)	2.508(6)	Os(4)—C(10)	1.90(3)	Os(5)—Os(6)	2.852(2)	O(1)—C(1)	1.11(3)	O(12)—C(12)	1.11(3)
Os(1)—Os(3)	2.864(2)	Os(4)—C(11)	1.90(3)	Os(6)—C(17)	1.90(4)	O(2)—C(2)	1.18(3)	O(13)—C(13)	1.20(3)
Os(2)—C(3)	1.75(3)	Os(4)—P(2)	2.393(6)	Os(6)—C(15)	1.92(3)	O(3)—C(3)	1.22(3)	O(14)—C(14)	1.15(3)
Os(2)—C(4)	1.90(2)	Os(4)—Cl(4)	2.483(6)	Os(6)—C(18)	1.92(3)	O(4)—C(4)	1.13(2)	O(15)—C(15)	1.15(3)
Os(2)—C(5)	1.97(3)	Os(4)—Cl(3)	2.504(6)	Os(6)—C(16)	1.99(4)	O(5)—C(5)	1.10(3)	O(16)—C(16)	1.11(4)
Os(2)—Cl(1)	2.473(5)	Os(4)—Os(6)	2.865(2)	P(1)—C(20)	1.76(2)	O(6)—C(6)	1.07(3)	O(17)—C(17)	1.08(3)
Os(2)—Cl(2)	2.501(6)	Os(5)—C(13)	1.79(3)	P(1)—C(26)	1.81(2)	O(7)—C(7)	1.16(3)	O(18)—C(18)	1.16(3)
Os(2)—Os(3)	2.841(2)								

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2)—Os(1)—C(1)	90.7(12)	C(5)—Os(2)—Os(3)	179.0(7)	Cl(4)—Os(4)—Cl(3)	80.5(2)	C(18)—Os(6)—C(16)	92.2(12)
C(2)—Os(1)—P(1)	94.2(9)	Cl(1)—Os(2)—Os(3)	86.26(13)	C(10)—Os(4)—Os(6)	90.1(7)	C(17)—Os(6)—Os(5)	164.2(9)
C(1)—Os(1)—P(1)	92.7(7)	Cl(2)—Os(2)—Os(3)	87.2(2)	C(11)—Os(4)—Os(6)	87.8(7)	C(15)—Os(6)—Os(5)	84.8(8)
C(2)—Os(1)—Cl(1)	175.5(9)	C(8)—Os(3)—C(7)	84.8(11)	P(2)—Os(4)—Os(6)	175.01(14)	C(18)—Os(6)—Os(5)	97.0(9)
C(1)—Os(1)—Cl(1)	92.1(7)	C(8)—Os(3)—C(9)	99.2(11)	Cl(4)—Os(4)—Os(6)	86.50(13)	C(16)—Os(6)—Os(5)	85.7(9)
P(1)—Os(1)—Cl(1)	89.2(2)	C(7)—Os(3)—C(9)	95.9(10)	Cl(3)—Os(4)—Os(6)	86.13(13)	C(17)—Os(6)—Os(4)	94.8(9)
C(2)—Os(1)—Cl(2)	96.3(10)	C(8)—Os(3)—C(6)	99.1(11)	C(13)—Os(5)—C(12)	90.6(12)	C(15)—Os(6)—Os(4)	86.3(7)
C(1)—Os(1)—Cl(2)	171.9(7)	C(7)—Os(3)—C(6)	171.2(10)	C(13)—Os(5)—C(14)	93.8(11)	C(18)—Os(6)—Os(4)	166.4(9)
P(1)—Os(1)—Cl(2)	90.9(2)	C(9)—Os(3)—C(6)	91.4(10)	C(12)—Os(5)—C(14)	93.2(13)	C(16)—Os(6)—Os(4)	85.0(9)
Cl(1)—Os(1)—Cl(2)	80.7(2)	C(8)—Os(3)—Os(2)	161.7(8)	C(13)—Os(5)—Cl(4)	171.5(8)	Os(5)—Os(6)—Os(4)	69.60(4)
C(2)—Os(1)—Os(3)	91.0(9)	C(7)—Os(3)—Os(2)	86.6(7)	C(12)—Os(5)—Cl(4)	93.5(9)	Os(2)—Cl(1)—Os(1)	82.6(2)
C(1)—Os(1)—Os(3)	89.3(7)	C(9)—Os(3)—Os(2)	97.7(8)	C(14)—Os(5)—Cl(4)	93.4(8)	Os(2)—Cl(2)—Os(1)	81.7(2)
P(1)—Os(1)—Os(3)	174.42(13)	C(6)—Os(3)—Os(2)	87.5(7)	C(13)—Os(5)—Cl(3)	93.8(8)	Os(5)—Cl(3)—Os(4)	81.8(2)
Cl(1)—Os(1)—Os(3)	85.47(12)	C(8)—Os(3)—Os(1)	93.2(8)	C(12)—Os(5)—Cl(3)	171.6(10)	Os(5)—Cl(4)—Os(4)	82.4(2)
Cl(2)—Os(1)—Os(3)	86.57(14)	C(7)—Os(3)—Os(1)	86.1(6)	C(14)—Os(5)—Cl(3)	93.6(8)	C(20)—P(1)—C(26)	105.7(10)
C(3)—Os(2)—C(4)	93.0(10)	C(9)—Os(3)—Os(1)	167.5(7)	Cl(4)—Os(5)—Cl(3)	81.2(2)	C(20)—P(1)—C(19)	106.4(10)
C(3)—Os(2)—C(5)	95.3(11)	C(6)—Os(3)—Os(1)	85.8(7)	C(13)—Os(5)—Os(6)	85.9(8)	C(26)—P(1)—C(19)	108.9(11)
C(4)—Os(2)—C(5)	94.1(10)	Os(2)—Os(3)—Os(1)	70.08(4)	C(12)—Os(5)—Os(6)	86.3(10)	C(20)—P(1)—Os(1)	109.5(7)
C(3)—Os(2)—Cl(1)	92.2(8)	C(10)—Os(4)—C(11)	87.2(11)	C(14)—Os(5)—Os(6)	179.4(8)	C(26)—P(1)—Os(1)	116.4(7)
C(4)—Os(2)—Cl(1)	170.8(6)	C(10)—Os(4)—P(2)	93.9(7)	Cl(4)—Os(5)—Os(6)	87.0(2)	C(19)—P(1)—Os(1)	109.4(7)
C(5)—Os(2)—Cl(1)	92.8(7)	C(11)—Os(4)—P(2)	95.4(7)	Cl(3)—Os(5)—Os(6)	86.93(14)	C(32)—P(2)—C(38)	107.1(9)
C(3)—Os(2)—Cl(2)	170.1(9)	C(10)—Os(4)—Cl(4)	175.9(7)	C(17)—Os(6)—C(15)	91.8(12)	C(32)—P(2)—C(19)	108.0(10)
C(4)—Os(2)—Cl(2)	92.6(6)	C(11)—Os(4)—Cl(4)	94.9(8)	C(17)—Os(6)—C(18)	98.7(13)	C(38)—P(2)—C(19)	106.4(10)
C(5)—Os(2)—Cl(2)	92.3(7)	P(2)—Os(4)—Cl(4)	89.4(2)	C(15)—Os(6)—C(18)	94.7(11)	C(32)—P(2)—Os(4)	113.5(6)
Cl(1)—Os(2)—Cl(2)	81.2(2)	C(10)—Os(4)—Cl(3)	97.2(8)	C(17)—Os(6)—C(16)	95.8(13)	C(38)—P(2)—Os(4)	109.9(7)
C(3)—Os(2)—Os(3)	85.1(8)	C(11)—Os(4)—Cl(3)	172.6(7)	C(15)—Os(6)—C(16)	168.9(12)	C(19)—P(2)—Os(4)	111.5(7)
C(4)—Os(2)—Os(3)	86.7(7)	P(2)—Os(4)—Cl(3)	90.4(2)			P(1)—C(19)—P(2)	128.3(12)

ing dppm ligand; the phosphorus atoms are coordinated to the osmium atoms of the $Os(\mu\text{-}Cl)_2Os$ unit. The Os(1)Os(2)Os(3)P(1) and Os(4)Os(5)Os(6)P(2)C(19) atoms lie in the planes, and the dihedral angle between the planes is 145° (Fig. 3). The P(1) and C(19) atoms deviate from the Os(1)Os(2)Os(3) plane by 0.09 Å and 0.45 Å, respectively, whereas the P(2) and C(19) atoms deviate from the Os(4)Os(5)Os(6) plane by 0.02 and 0.07 Å, respectively. The Os(1)—Os(3), Os(2)—Os(3), and Os(5)—Os(6), Os(4)—Os(6) bond lengths are nearly the same and do not differ from those in the initial dichloride **1**.[10] The Os(1)...Os(2) and Os(4)...Os(5) distances in the $Os(\mu\text{-}Cl)_2Os$ units (3.276(2) and 3.263(2) Å, respectively) are slightly longer than the corresponding distance in molecule **1** (3.233(1) Å). The Os—Cl—Os angles and Os—Cl bond lengths virtually coincide with those measured in the initial complex **1**. In cluster **2**, the Os—P bonds are 0.06 Å longer than the analogous bonds in the $Os_3(\mu\text{-}H)_2(CO)_8(1,2\text{-dppm})$[11] and $Os_3(CO)_{10}(1,2\text{-dppm})$[12] clusters containing bridging diphosphine ligands.

Molecule **3** (see Fig. 2) can be considered as an unusual 12-membered macrocycle containing C, P, Cl, and Os atoms. Comparison of the data of X-ray study of complexes **2** and **3** shows that in cluster **3** the Os—P bonds are lengthened by 0.03 Å and the Os...Os distance in the $Os(\mu\text{-}Cl)_2Os$ unit is increased by 0.05 Å. Other interatomic distances in molecules **2** and **3** differ slightly. The Os(1)Os(2)Os(3)P(1)P(2)C(9)P(2A) atoms lie in a plane (the maximum deviation from the midplane is 0.06 Å) analogously to the Os(1A)Os(2A)Os(3A)P(1A)P(2A)C(9A)P(2) atoms. The

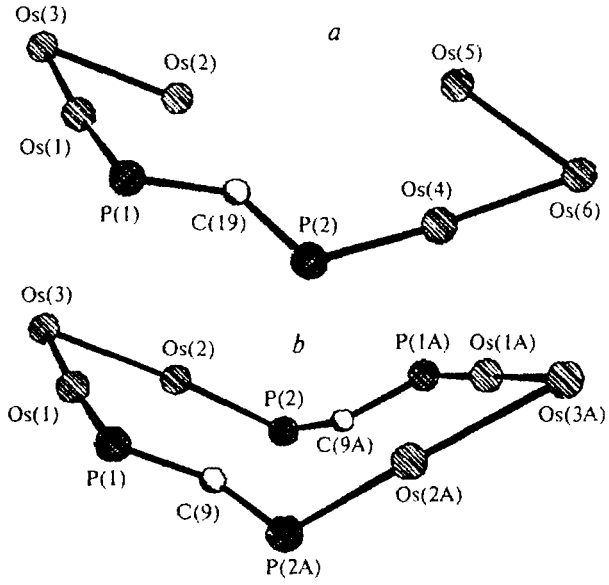


Fig. 3. View of the frameworks of clusters **2** (*a*) and **3** (*b*).

dihedral angle between these planes or the angle of folding along the P(2)...P(2A) line is 127° (see Fig. 3).

Thus, we established that the equatorial carbonyl groups in the $(CO)_3Os(\mu\text{-}Cl)_2Os(CO)_3$ moiety in *trans*-position with respect to the osmium atom of the $Os(CO)_4$ unit appear to be the most reactive in the $Os_3(\mu\text{-}Cl)_2(CO)_{10}$ osmium cluster. Therefore, the reaction between this cluster and dppm results in the formation of novel unusual non-cyclic and cyclic hexaosmium compounds, which are the first representatives of trinuclear osmium clusters where dppm is a bridging ligand between the two metallocluster units.

Experimental

All experiments were carried out in a dry Ar atmosphere using anhydrous solvents. NMR spectra were recorded on a Bruker AMX-400 spectrometer in C_6D_6 at 400.13 MHz for ^1H (relative to Me_4Si) and at 161.92 MHz for ^{31}P (relative to 85% H_3PO_4). IR spectra were recorded on a Nicolet Magna 750 spectrometer. Silpearl UV-254 silica gel was used for chromatographic separation and purification of the complexes. No optimization of yields of the products and reaction conditions was performed.

Reaction of $Os_3(\mu\text{-}Cl)_2(CO)_{10}$ (1) with bis(diphenylphosphinomethane) (dppm). A solution of dppm (158 mg, 0.4 mmol) in 2 mL of toluene was added slowly to a stirred solution of complex **1** [9] (380 mg, 0.4 mmol) in 50 mL of toluene at 65 °C. The reaction completion was monitored by

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Os(1)—C(2)	1.84(3)	Os(2)—P(2)	2.423(9)	P(1)—C(10)	1.77(4)	O(2)—C(2)	1.13(4)
Os(1)—C(1)	1.86(4)	Os(2)—Cl(1)	2.474(8)	P(1)—C(9)	1.84(3)	O(3)—C(3)	1.13(3)
Os(1)—P(1)	2.403(8)	Os(2)—Cl(2)	2.505(9)	P(1)—C(16)	1.91(3)	O(4)—C(4)	1.20(4)
Os(1)—Cl(1)	2.475(9)	Os(2)—Os(3)	2.858(2)	P(2)—C(22)	1.83(4)	O(5)—C(5)	1.20(4)
Os(1)—Cl(2)	2.501(9)	Os(3)—C(7)	1.81(4)	P(2)—C(9A)*	1.87(3)	O(6)—C(6)	1.21(5)
Os(1)—Os(3)	2.856(2)	Os(3)—C(5)	1.83(3)	P(2)—C(28)	1.90(3)	O(7)—C(7)	1.15(5)
Os(2)—C(4)	1.80(3)	Os(3)—C(6)	1.86(5)	O(1)—C(1)	1.16(4)	O(8)—C(8)	1.15(4)
Os(2)—C(3)	1.88(3)	Os(3)—C(8)	1.87(3)				

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2)—Os(1)—C(1)	92(2)	C(3)—Os(2)—Cl(1)	168.3(10)	C(6)—Os(3)—Os(1)	85.6(11)	C(9A)—P(2)—Os(2)	115.0(11)
C(2)—Os(1)—P(1)	96.9(8)	P(2)—Os(2)—Cl(1)	93.4(3)	C(8)—Os(3)—Os(1)	163.8(11)	C(28)—P(2)—Os(2)	115.2(10)
C(1)—Os(1)—P(1)	93.7(9)	C(4)—Os(2)—Cl(2)	172.3(10)	C(7)—Os(3)—Os(2)	165.3(11)	O(1)—C(1)—Os(1)	173(3)
C(2)—Os(1)—Cl(1)	89.3(10)	C(3)—Os(2)—Cl(2)	96.4(10)	C(5)—Os(3)—Os(2)	84.7(9)	O(2)—C(2)—Os(1)	172(3)
C(1)—Os(1)—Cl(1)	176.2(9)	P(2)—Os(2)—Cl(2)	88.5(3)	C(6)—Os(3)—Os(2)	84.2(13)	O(3)—C(3)—Os(2)	178(3)
P(1)—Os(1)—Cl(1)	89.8(3)	Cl(1)—Os(2)—Cl(2)	78.9(3)	C(8)—Os(3)—Os(2)	93.0(11)	O(4)—C(4)—Os(2)	172(3)
C(2)—Os(1)—Cl(2)	165.7(10)	C(4)—Os(2)—Os(3)	87.0(10)	Os(1)—Os(3)—Os(2)	70.99(5)	O(5)—C(5)—Os(3)	176(3)
C(1)—Os(1)—Cl(2)	99.4(11)	C(3)—Os(2)—Os(3)	83.3(10)	Os(2)—Cl(1)—Os(1)	84.2(3)	O(6)—C(6)—Os(3)	173(4)
P(1)—Os(1)—Cl(2)	91.3(3)	P(2)—Os(2)—Os(3)	174.7(2)	Os(1)—Cl(2)—Os(2)	83.0(3)	O(7)—C(7)—Os(3)	171(4)
Cl(1)—Os(1)—Cl(2)	78.9(3)	Cl(1)—Os(2)—Os(3)	85.7(2)	C(10)—P(1)—C(9)	108(2)	O(8)—C(8)—Os(3)	178(3)
C(2)—Os(1)—Os(3)	84.7(8)	Cl(2)—Os(2)—Os(3)	86.2(2)	C(10)—P(1)—C(16)	108(2)	P(1)—C(9)—P(2A)	129(2)
C(1)—Os(1)—Os(3)	90.7(9)	C(7)—Os(3)—C(5)	92(2)	C(9)—P(1)—C(16)	104.5(14)	C(15)—C(10)—P(1)	127(3)
P(1)—Os(1)—Os(3)	175.3(2)	C(7)—Os(3)—C(6)	97(2)	C(10)—P(1)—Os(1)	116.8(12)	C(11)—C(10)—P(1)	113(3)
Cl(1)—Os(1)—Os(3)	85.8(2)	C(5)—Os(3)—C(6)	166(2)	C(9)—P(1)—Os(1)	110.0(9)	C(17)—C(16)—P(1)	122(3)
Cl(2)—Os(1)—Os(3)	86.3(2)	C(7)—Os(3)—C(8)	102(2)	C(16)—P(1)—Os(1)	109.4(9)	C(21)—C(16)—P(1)	113(3)
C(4)—Os(2)—C(3)	86.2(13)	C(5)—Os(3)—C(8)	99.0(14)	C(22)—P(2)—C(9A)	104.1(13)	C(27)—C(22)—P(2)	119(2)
C(4)—Os(2)—P(2)	98.3(10)	C(6)—Os(3)—C(8)	90(2)	C(22)—P(2)—C(28)	107(2)	C(23)—C(22)—P(2)	123(3)
C(3)—Os(2)—P(2)	97.2(10)	C(7)—Os(3)—Os(1)	94.4(11)	C(9A)—P(2)—C(28)	106.4(14)	C(33)—C(28)—P(2)	119(3)
C(4)—Os(2)—Cl(1)	97.2(9)	C(5)—Os(3)—Os(1)	82.7(8)	C(22)—P(2)—Os(2)	108.6(11)	C(29)—C(28)—P(2)	120(2)

* Equivalent positions of the atoms obtained by the symmetric transformation $y + 1, x - 1, -z$.

Table 3. Crystallographic data and parameters of the refinement for compounds **2** and **3**

Parameter	Complex **2**	Complex **3**
Empirical formula	$C_{43}H_{22}O_{18}Cl_4P_2Os_6 \cdot C_6H_6 \cdot C_5H_{12}$	$C_{66}H_{44}O_{16}Cl_4P_4Os_6 \cdot 2C_6H_6$
M	2321.80	2656.11
Space group	$P\bar{1}$	$P4_32_12$
a/Å	10.473(2)	11.904(2)
b/Å	16.273(3)	—
c/Å	20.553(4)	55.718(14)
α/deg	74.12(3)	—
β/deg	84.65(3)	—
γ/deg	89.31(3)	—
V/Å^3	3354(1)	7896(3)
Z	2	4
d_{calc}/g cm^{-3}	2.299	2.234
Diffractometer	CAD4 Enraf-Nonius	Syntex $P2_1$
Radiation (λ/Å)	Mo-Kα (0.71073)	
μ/cm^{-1}	115.90	99.00
Absorption correction	ψ-curves	DIFABS [13]
T_{min}/T_{max}	0.308/0.923	0.776/1.426
Temperature /K	293(2)	193(2)
Scan type	$\theta/(5/3)\theta$	ω
$2\theta_{max}$/deg	44	46
Number of independent reflections	7596	5151
R_1 (F-refinement for reflections with $I > 2\sigma(I)$)	0.0653 (4982 reflections)	0.0759 (3177 reflections)
wR_2 (F^2-refinement for all reflections)	0.1937 (7538 reflections)	0.2047 (5099 reflections)
Number of refined parameters	487	252

Table 4. Atomic coordinates (×10^4) and their equivalent isotropic thermal parameters (U_{eq}×10^3) in structure **2**

Atom	x	y	z	U_{eq}/Å^2
Os(1)	3871(1)	9831(1)	2939(1)	36(1)
Os(2)	4413(1)	9890(1)	1332(1)	46(1)
Os(3)	5143(1)	11198(1)	1904(1)	46(1)
Os(4)	2491(1)	5710(1)	3033(1)	42(1)
Os(5)	4926(1)	6165(1)	1877(1)	56(1)
Os(6)	3493(1)	4601(1)	2246(1)	59(1)
Cl(1)	5107(5)	8871(3)	2364(3)	44(2)
Cl(2)	2358(6)	9758(4)	2079(3)	50(2)
Cl(3)	4780(6)	6073(3)	3105(3)	49(2)
Cl(4)	2857(6)	6891(4)	1971(3)	53(2)
P(1)	2863(5)	8602(3)	3735(3)	37(1)
P(2)	1783(5)	6729(3)	3631(3)	35(1)
O(1)	5979(17)	9895(12)	3813(10)	75(5)
O(2)	2419(19)	11102(10)	3550(9)	84(7)
O(3)	7060(18)	10075(11)	653(9)	77(5)
O(4)	3513(18)	11310(11)	193(9)	78(6)
O(5)	3722(20)	8497(11)	679(8)	76(6)
O(6)	7597(17)	10175(11)	2227(10)	77(6)
O(7)	2504(18)	11945(13)	1622(12)	98(7)
O(8)	5290(24)	12288(12)	2873(10)	100(7)
O(9)	6488(21)	12395(13)	616(11)	101(7)
O(10)	2310(18)	4186(11)	4265(9)	77(6)
O(11)	−170(17)	5305(13)	2718(10)	82(6)
O(12)	4687(28)	6154(17)	434(12)	131(10)
O(13)	7305(19)	5124(12)	1968(12)	96(7)
O(14)	6557(18)	7801(12)	1429(9)	74(5)
O(15)	5340(18)	3997(11)	3347(9)	75(5)
O(16)	1602(25)	5530(18)	1219(12)	132(10)
O(17)	1678(23)	3201(15)	3007(15)	122(9)
O(18)	4993(25)	3781(15)	1233(11)	117(9)
C(1)	5191(26)	9855(15)	3497(12)	50(6)
C(2)	2939(29)	10598(19)	3299(15)	78(8)
C(3)	5972(26)	10008(15)	929(12)	54(6)
C(4)	3772(21)	10773(14)	635(11)	42(5)
C(5)	3906(25)	8971(17)	951(13)	59(7)
C(6)	6752(26)	10550(15)	2124(12)	50(6)
C(7)	3488(24)	11648(14)	1754(11)	44(6)
C(8)	5187(25)	11889(16)	2469(13)	59(7)
C(9)	6004(24)	11941(16)	1092(13)	55(6)
C(10)	2314(24)	4768(16)	3823(13)	54(6)
C(11)	822(29)	5426(16)	2862(13)	58(7)
C(12)	4791(30)	6167(19)	966(17)	80(9)
C(13)	6320(26)	5512(16)	1908(12)	56(6)
C(14)	5892(28)	7208(19)	1623(14)	68(8)
C(15)	4678(25)	4229(16)	2921(13)	57(7)
C(16)	2315(32)	5209(20)	1570(17)	84(9)
C(17)	2339(32)	3680(21)	2689(16)	80(9)
C(18)	4399(29)	4093(19)	1603(15)	78(8)
C(19)	2764(21)	7745(14)	3327(11)	46(6)
C(20)	3823(20)	8223(12)	4410(10)	37(5)
C(21)	4788(26)	7594(17)	4403(14)	69(7)
C(22)	5693(29)	7458(19)	4894(15)	80(8)
C(23)	5665(27)	7847(17)	5399(14)	71(8)
C(24)	4700(29)	8451(18)	5434(15)	79(8)
C(25)	3862(26)	8670(17)	4915(14)	67(7)
C(26)	1293(22)	8755(14)	4124(12)	50(6)
C(27)	896(25)	8398(16)	4808(13)	64(7)
C(28)	−389(32)	8556(21)	5056(17)	93(10)
C(29)	−1237(30)	9081(20)	4609(16)	88(9)
C(30)	−859(28)	9427(18)	3975(15)	75(8)
C(31)	428(24)	9281(15)	3682(13)	59(7)
C(32)	1825(18)	6340(12)	4536(9)	30(5)
C(33)	2970(24)	5906(16)	4782(13)	60(7)
C(34)	3129(26)	5627(17)	5481(14)	71(8)
C(35)	2158(26)	5740(16)	5922(13)	67(7)
C(36)	1038(27)	6137(18)	5703(14)	74(8)
C(37)	896(25)	6430(16)	5009(13)	64(7)
C(38)	118(21)	7026(13)	3474(11)	44(6)
C(39)	−892(25)	6441(16)	3814(13)	62(7)
C(40)	−2148(25)	6608(16)	3630(13)	63(7)
C(41)	−2372(27)	7344(17)	3150(14)	70(8)
C(42)	−1434(29)	7911(18)	2804(15)	79(8)
C(43)	−132(25)	7770(16)	2948(13)	59(7)
C(1S)*	9487(46)	11692(31)	2506(28)	150(16)
C(2S)*	9130(50)	11743(33)	3148(27)	162(18)
C(3S)*	8397(53)	12446(37)	3255(28)	174(19)
C(4S)*	8460(47)	13175(31)	2585(28)	153(17)
C(5S)*	8786(58)	13089(38)	2000(32)	188(22)
C(6S)*	9239(61)	12288(43)	1844(33)	208(25)
C(7S)*	−197(96)	11237(67)	−837(56)	332(49)
C(8S)*	−107(101)	11769(76)	−310(60)	326(53)
C(9S)*	310(131)	12584(91)	−653(70)	389(67)
C(10S)*	737(141)	12847(98)	−62(73)	461(73)
C(11S)*	1685(122)	13888(80)	−73(63)	435(63)

* For solvated molecules.

Table 5. Atomic coordinates ($\times 10^4$) and their equivalent isotropic thermal parameters ($U_{eq} \times 10^3$) in structure **3**

Atom	x	y	z	U_{eq}/Å^2
Os(1)	−4629(1)	−18551(1)	335(1)	24(1)
Os(2)	−6629(1)	−17335(1)	658(1)	23(1)
Os(3)	−4478(1)	−18016(1)	833(1)	29(1)
Cl(1)	−5613(7)	−16730(7)	293(1)	24(2)
Cl(2)	−6612(8)	−19119(8)	420(1)	31(2)
P(1)	−4880(8)	−18889(9)	−87(1)	27(2)
P(2)	−8457(8)	−16918(8)	489(1)	22(2)
O(1)	−3559(27)	−20792(26)	437(4)	60(9)
O(2)	−2384(25)	−17476(24)	297(4)	50(7)
O(3)	−7450(23)	−18327(22)	1122(4)	43(7)
O(4)	−6171(21)	−15251(22)	942(4)	36(6)
O(5)	−5496(21)	−20325(21)	896(4)	34(6)
O(6)	−3829(22)	−15633(24)	675(4)	45(7)
O(7)	−2195(31)	−18897(28)	921(5)	76(10)
O(8)	−4906(26)	−17128(27)	1332(5)	60(9)
C(1)	−3917(30)	−19917(31)	387(5)	26(8)
C(2)	−3274(29)	−17810(28)	311(5)	20(7)
C(3)	−7141(28)	−17976(27)	946(5)	17(7)
C(4)	−6439(27)	−16062(26)	827(5)	14(7)
C(5)	−5132(25)	−19394(27)	867(5)	14(7)
C(6)	−4024(37)	−16596(41)	731(6)	51(11)
C(7)	−3082(36)	−18600(35)	868(6)	42(10)
C(8)	−4754(32)	−17446(33)	1141(6)	34(9)
C(9)	−6287(26)	−18430(28)	−181(4)	15(7)
C(10)	−4692(34)	−20285(34)	−187(6)	39(10)
C(11)	−5203(32)	−21101(31)	−33(6)	34(9)
C(12)	−4933(41)	−22305(42)	−77(7)	63(13)
C(13)	−4278(41)	−22637(41)	−270(7)	61(13)
C(14)	−3777(33)	−21843(33)	−395(6)	37(10)
C(15)	−3997(30)	−20639(32)	−362(5)	29(9)
C(16)	−3874(27)	−17958(29)	−265(5)	19(8)
C(17)	−4186(32)	−17045(33)	−363(6)	35(9)
C(18)	−3337(35)	−16341(33)	−467(6)	39(10)
C(19)	−2255(33)	−16721(33)	−486(5)	35(9)
C(20)	−1863(36)	−17707(36)	−380(6)	46(11)
C(21)	−2761(35)	−18330(36)	−256(6)	45(11)
C(22)	−9222(28)	−18235(30)	449(5)	23(8)
C(23)	−9959(31)	−18474(34)	233(5)	31(9)
C(24)	−10526(42)	−19470(42)	236(7)	62(13)
C(25)	−10564(33)	−20164(32)	430(6)	34(9)
C(26)	−9957(39)	−19955(40)	630(7)	55(12)
C(27)	−9352(27)	−18975(26)	649(5)	15(7)
C(28)	−9384(29)	−15976(27)	678(5)	21(8)
C(29)	−10526(34)	−16303(32)	726(6)	38(10)
C(30)	−11127(27)	−15668(28)	880(5)	19(8)
C(31)	−10689(30)	−14779(31)	994(5)	28(9)
C(32)	−9544(36)	−14393(35)	952(6)	43(10)
C(33)	−8894(31)	−15131(32)	806(6)	33(9)
C(1S)*	−7291(43)	−13109(43)	1327(8)	69(14)
C(2S)*	−7999(54)	−12896(54)	1521(9)	93(18)
C(3S)*	−8778(45)	−11979(46)	1501(8)	71(14)
C(4S)*	−8810(50)	−11270(51)	1284(9)	87(17)
C(5S)*	−7883(44)	−11542(44)	1105(7)	68(13)
C(6S)*	−7260(47)	−12482(48)	1127(8)	76(15)

* For solvated molecules.

TLC (with hexane—benzene (1 : 1) mixture as eluent) by disappearance of the initial complex **1** in the reaction mixture. The formed fine-crystalline precipitate of compound **4** (100 mg) was filtered off, and the solution was concentrated with a small amount of silica gel (100/400) and chromatographed on a column with silica gel in an Ar atmosphere. After elution with a hexane—benzene (2 : 1) mixture and crystallization from hexane, 70 mg (16%) of cluster $[Os_3(\mu\text{-}Cl)_2(CO)_9]_2(dppm)$ (**2**) were obtained. Further elution with a hexane—benzene (1 : 1) mixture followed by crystallization from a benzene—methylene dichloride mixture gave 230 mg (45%) of cluster $[Os_3(\mu\text{-}Cl)_2(CO)_8]_2(dppm)_2$ (**3**).

Synthesis of complex 2. Complex **2** was obtained analogously, starting from complex **1** (20.0 mg, 0.021 mmol) in 10 mL of toluene and dppm (8.32 mg, 0.021 mmol) in 1 mL of toluene. After chromatography on a column with silica gel (with a hexane—benzene (2 : 1) mixture as eluent) followed by recrystallization from hot hexane, 20 mg (83%) of complex **2** were obtained.

Cluster $[Os_3(\mu\text{-}Cl)_2(CO)_9]_2(dppm)$ (2) is a dark-yellow crystalline substance. IR (hexane), $\nu CO/cm^{-1}$: 2101 m, 2098 sh, 2064 m, 2019 vs, 2012 s, 2003 m, 1992 w, 1981 m, 1961 w, 1951 sl. br. ^1H NMR, δ: 4.60 (t, 2 H, CH_2, $^2J_{HP}$ = 6.2 Hz); 6.83—7.39 (m, 20 H, Ph). ^{31}P NMR, δ: −1.77 (s).

Cluster $[Os_3(\mu\text{-}Cl)_2(CO)_8]_2(dppm)_2$ (3) is a dark-yellow crystalline compound. IR (CH_2Cl_2), $\nu CO/cm^{-1}$: 2101 w, 2075 vs, 2016 vs, 2000 vs, 1964 m.br, 1941 m. ^1H NMR, δ: 4.78 (t, 4 H, CH_2, $^2J_{HP}$ = 6.7 Hz); 6.81—7.45 (m, 40 H, Ph). ^{31}P NMR, δ: 0.52 (s).

Compound 4 is a dark-yellow powder. IR (Vaseline oil), $\nu CO/cm^{-1}$: 2011 w, 1999 w, 1992 s, 1982 m, 1971 s, 1946 vs, 1933 s, 1921 w, 1915 w.

X-ray study. Single crystals of compounds **2** and **3** suitable for X-ray study were obtained by crystallization from a benzene—pentane mixture (1 : 3). Crystallographic data and selected parameters of the refinement for compounds **2** and **3** are listed in Table 3. Both structures were solved by direct methods. The positions and thermal parameters of non-hydrogen atoms were refined isotropically and then anisotropically (except for C atoms for structure **2**, and C and O atoms for structure **3**) by the full-matrix least-squares method. Hydrogen atoms were not included in the refinement. The absolute structure of compound **3** was established by refining the value of the Flack parameter,[14] which was equal to 0.01(4). All calculations were carried out on a personal computer using the SHELXTL PLUS 5 [15] program package. The atomic coordinates in structures **2** and **3** are listed in Tables 4 and 5, respectively.

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