Synthesis of optically active hydridocarbonyl triosmium clusters with terpene derivatives as ligands. Molecular structure and absolute configuration of a cluster with a bridging dihydroimidazole ligand

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Reactions of the triosmium clusters $Os_3(CO)_{11}(NCMe)$ (**1**) and $Os_3(CO)_{10}(NCMe)_2$ (**2**) with terpene derivatives, *viz.*, (1*S*,3*S*,4*R*,6*R*)-3-(*N*,*N*-dimethylamino)-4-amino-3,7,7-trimethylbicyclo[4.1.0]heptane (**3**), (3b*R*,4a*R*)-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)acetic acid (**4a**), and (3b*R*,4a*R*)-3-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)propionic acid (**4b**), were studied. A complex with the terminally coordinated ligand is formed in the first step of the reaction of diamine **3** with cluster **1**. Heating of the resulting complex is accompanied by activation of one of the methyl groups of the ligand to form diastereomers with the bridging tricyclic dihydroimidazole ligand. One of these diastereomers was studied by X-ray diffraction analysis and its absolute configuration was established. Pyrazolylcarboxylic acids react with cluster **2** as simple organic acids and are coordinated as a bridge at the Os—Os bond through the carboxyl group.

Key words: triosmium clusters, terpenes, ligand activation, absolute configuration, molecular structure, ^1H and ^{13}C NMR spectroscopy.

The main idea of using molecular cluster complexes in catalysis is based on the fact that several metal centers are involved in these reactions by analogy with a number of natural metalloenzymes containing several metal atoms, which often differ in function.[1] The stereochemical characteristic features of molecular cluster complexes have not been adequately investigated. It is known that the stereochemical factors are of greater importance in coordination of different ligands in the case of carbonyl cluster complexes than in the case of mononuclear compounds because metal atoms in clusters are bound to two or more bulky $M(CO)_nL_m$ groups each. Intramolecular ligand—ligand interactions are of particular importance in coordination of bulky organic ligands to several metal atoms (μ_n-coordination of ligands). Thus intramolecular interactions between the bridging ligand and the nearest carbonyl groups in the complex $(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-NHCH(Me)CO}_2\text{Et}\}$ result in hindered rotation of the amino-acid ligand about the NH—CH bond.[2] An even more substantial steric effect is observed in M_3 clusters (M = Os or Ru) in the case of bridging coordination of bulky esters of L-hydroxyproline or L-proline containing a fairly rigid heterocycle. This leads to the formation of the only diastereomer in every case, *i.e.*, the reactions proceed stereospecifically.[3,4]

In the present work, we studied the reaction of the triosmium cluster $Os_3(CO)_{11}(NCMe)$ (**1**) with (1*S*,3*S*,4*R*,6*R*)-4-amino-3-(*N*,*N*-dimethylamino)-3,7,7-trimethylbicyclo[4.1.0]heptane (diaminocarane, **3**) and the reactions of $Os_3(CO)_{10}(NCMe)_2$ (**2**) with (3b*R*,4a*R*)-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa-[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)acetic acid (**4a**) and (3b*R*,4a*R*)-3-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)propionic acid (**4b**).

Results and Discussion

Reactions of $Os_3(CO)_{12}$ derivatives with amines have been studied in sufficient detail.[5,6] The first step involves simple replacement of the acetonitrile ligand to form clusters with terminally coordinated amines. The reactions of primary and secondary amines in the presence of an excess of the ligand afford complexes with bridging carboxamide ligands.[6] The first step of the reaction of cluster **1** with diaminocarane **3** proceeds analogously, giving rise to cluster **5**. In the IR spectrum of **5**, the region of stretching vibrations of CO groups is typical of complexes of the $Os_3(CO)_{11}L$ type, where L is a terminally coordinated ligand.[7] Like other similar complexes,[8] this cluster is unstable in solutions in the absence of an excess of the free ligand. Heating of cluster **5** in the presence of an excess of diaminocarane **3** (60 °C, 18 h) resulted in the transformation of the ligand to form

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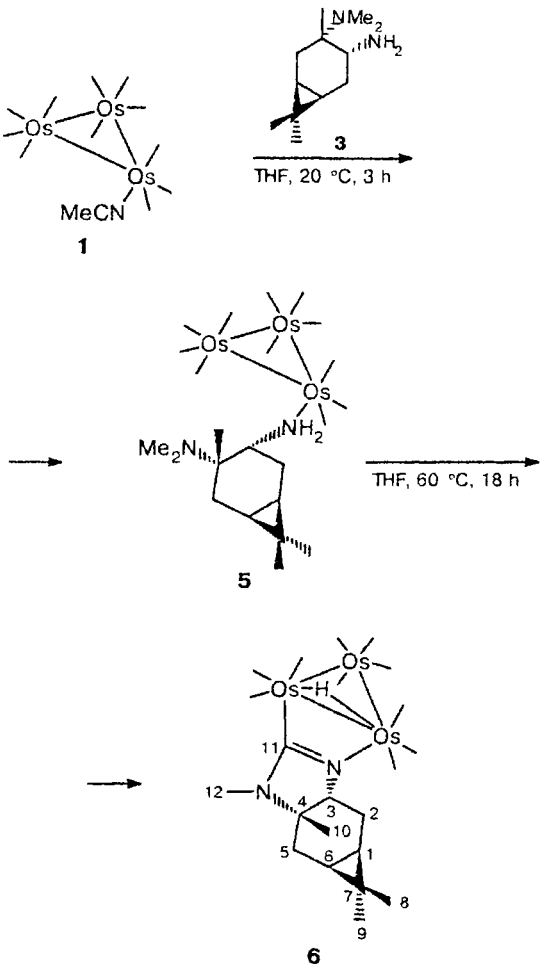
hydrido cluster **6** with the bridging tricyclic ligand containing a dihydroimidazole fragment (Scheme 1).

Scheme 1

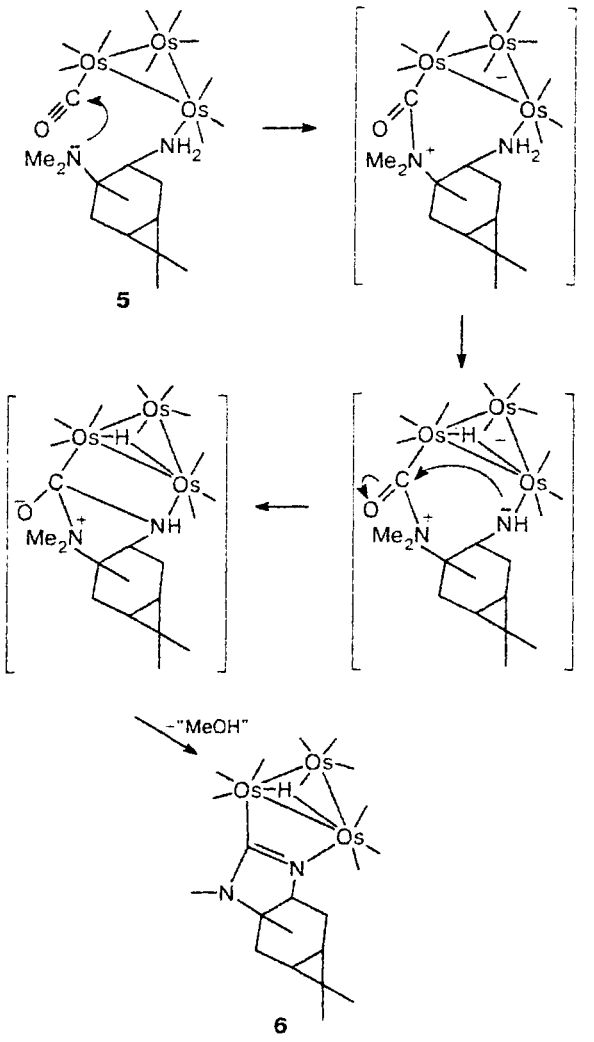


This course of the reaction was unexpected because rather drastic conditions (for example, refluxing in octane or xylene) are generally required for activation of substituents in tertiary amines on triosmium clusters.[9]

Taking into account that the key step of many reactions of amines with carbonyl complexes of transition metals involves the nucleophilic attack of the lone electron pair of the nitrogen atom on the carbon atom of the carbonyl group, it is reasonable to suggest that a scheme of formation of complex **6** involves the nucleophilic attack of the free dimethylamino group of complex **5** on the carbon atom of the carbonyl group coordinated to the adjacent osmium atom (Scheme 2).

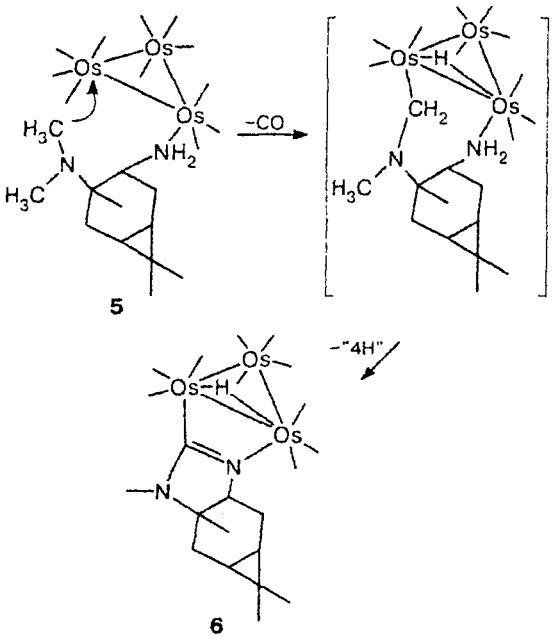
In this case, the carbonyl group of the cluster should serve as the source of the carbon atom in the dihydroimidazole ring. Hence, to verify the validity of the proposed scheme, we carried out the reaction of diaminocarane **3** with the cluster $Os_3(CO)_{11}(NCMe)$, which was synthesized from $Os_3(CO)_{12}$ enriched with ^{13}CO by ~25%. The ^{13}C NMR spectrum of the mixture of diastereomers obtained in this reaction has only 11 signals for the CO ligands of the $Os_3(CO)_{10}$ fragment (nine of ten carbonyl groups in the diastereomers have virtually identical chemical shifts), whereas no other signals are observed. Based on these data, it was concluded that the isotopic label does not appear in the dihydroimidazole ring and, hence, the key step of formation of cluster **6** involves C—H activation of the dimethylamino group (which, as mentioned above, requires rather drastic conditions[9]) rather than the nucleophilic attack at the carbon atom of the carbonyl group (Scheme 3).

Scheme 2



Apparently, the steric factors, *viz.*, the fact that one of the methyl groups of the diaminocarane ligand and the osmium atom are located in close proximity, are responsible for activation of the ligand under mild conditions. This suggestion was invoked[10] to account for

Scheme 3



the reactions of substituted pyridinealdimines with $Os_3(CO)_{10}(NCMe)_2$, in which metallation of the methyl group occurred even at room temperature to form the cluster $(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}CH_2NC_5H_3CH{=}NPr^i\}$. Further heating of this complex gave rise to the μ_3-bridging ligand accompanied by the transfer of yet another hydrogen atom to the metallocycle. In our case, the first stage of metallation of the NMe group was followed by the formation of the C=N double bond and the loss of four hydrogen atoms.

Since cluster **6** does not have a symmetry plane, it formed as two diastereomers in a ratio of ~4 : 3 (according to NMR spectral data). The major diastereomer (**6a**) was isolated in the individual form by crystallization. Its structure was studied by X-ray diffraction analysis and its absolute configuration was established. Using the nomenclature of chiral cluster complexes proposed by us previously,[3] the absolute configuration of **6a** can be described as (*R*)-1,1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-μ-hydrido-2,3-μ,η²-{(N3,C2)-(3aR,4aR,5aS,6aS)-1,5,5,6a-tetramethyl-3a,4,4a,5a,6,6a-hexahydro-1*H*-cyclopropa[*d*]benzoimidazol-2-yl}-*triangulo*-triosmium. The validity of the determined absolute configuration of the complex was confirmed by the fact that the configurations of the C(1), C(3), and C(6) atoms coincide with the known configuration for the initial noncoordinated ligand.

The crystal structure of compound **6a** is shown in Fig. 1. The bond lengths and bond angles are given in Table 1. Both the organic ligand and the bridging hydrogen atom are coordinated to the cluster core at the same Os—Os bond, resulting in the formation of the virtually planar Os_2CN ring (the deviations of the atoms from the

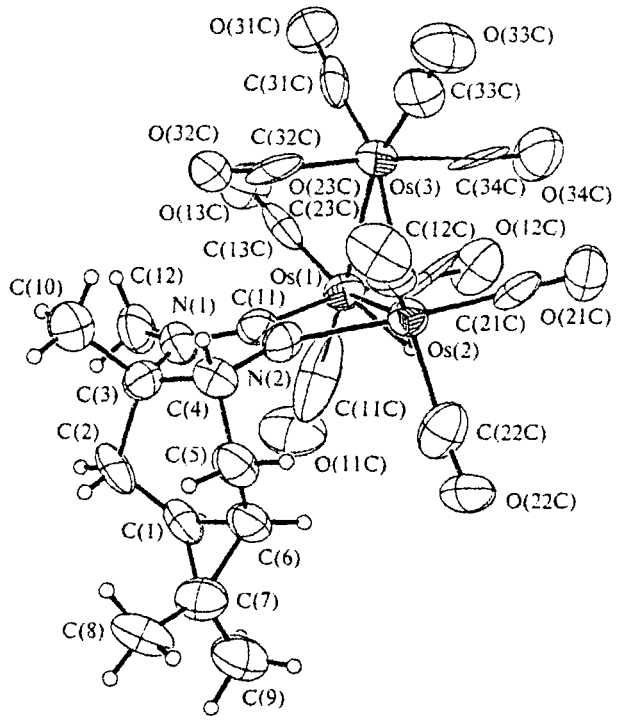


Fig. 1. Molecular structure of **6a** (thermal ellipsoids with a 50% probability).

plane do not exceed 0.021 Å). The angle between this ring and the Os_3 plane is 77.7(2)°. The angle between the Os_3 and $Os_2(\mu\text{-H})$ planes is 40(5)°. The bond lengths in the five-membered C(11)N(1)C(3)C(4)N(2) ring adjacent to the metallocycle are indicative of a definite degree of conjugation.

A search for structural data on compounds analogous to complex **6a** in the Cambridge Structural Database revealed 16 crystal structures of clusters of the general formula $Os_3(CO)_{10}(\mu\text{-H})\{\mu,\eta\text{-}C(R)N(R')\}$, in which the R and R′ fragments and the C and N atoms do not form an aromatic ring and both bridging ligands are coordinated at the same Os—Os bond. Based on the analysis of the geometric parameters of the molecules in these structures, it can be concluded that the lengths of the Os—Os bond bearing bridging ligands vary over a rather narrow range from 2.900 to 2.967 Å (the average value is 2.931 Å). Structural studies were carried out for three compounds, in which, like in complex **6a**, atoms containing a lone electron pair are bound to the carbon atom of the Os_2CN ring, *viz.*, the nitrogen atom in $Os_3(CO)_{10}(\mu\text{-H})\{\mu,\eta\text{-}(Pr^i)NCN(H)(Pr^i)\}$,[11] the oxygen atom of the carboxyl group in $Os_3(CO)_{10}(\mu\text{-H})\{\mu,\eta\text{-}(Me)NCOC(O)NHMe\}$,[12] and the sulfur atom of the heterocycle in $Os_3(CO)_{10}(\mu\text{-H})(\mu,\eta\text{-}NC_4H_4S)$.[13] The lengths of the bridging Os—Os bonds in the latter two complexes (2.924 and 2.955 Å, respectively) are close to that observed in **6a** (2.9397(9) Å). In the first complex, this bond is somewhat shortened (2.904 Å). The Os—N

Table 1. Principal bond lengths (d) and bond angles (ω) in molecule **6a**

Bond	d/Å	Bond	d/Å	Bond	d/Å
Os(1)—Os(2)	2.9397(8)	Os(3)—C(33C)	1.90(2)	N(1)—C(12)	1.45(2)
Os(1)—Os(3)	2.8754(9)	Os(3)—C(34C)	1.93(2)	N(2)—C(4)	1.49(2)
Os(1)—H(12M)	1.81(5)	C(11C)—O(11C)	1.24(3)	N(2)—C(11)	1.26(2)
Os(1)—C(11C)	1.84(3)	C(12C)—O(12C)	1.24(3)	C(1)—C(2)	1.50(2)
Os(1)—C(12C)	1.83(3)	C(13C)—O(13C)	1.17(2)	C(1)—C(6)	1.50(2)
Os(1)—C(13C)	1.85(2)	C(21C)—O(21C)	1.16(2)	C(1)—C(7)	1.52(2)
Os(1)—C(11)	2.10(1)	C(22C)—O(22C)	1.11(2)	C(2)—C(3)	1.57(2)
Os(2)—Os(3)	2.8748(9)	C(23C)—O(23C)	1.17(2)	C(3)—C(4)	1.53(2)
Os(2)—H(12M)	1.78(5)	C(31C)—O(31C)	1.20(2)	C(3)—C(10)	1.53(2)
Os(2)—C(21C)	1.84(2)	C(32C)—O(32C)	1.17(2)	C(4)—C(5)	1.53(2)
Os(2)—C(22C)	1.96(2)	C(33C)—O(33C)	1.14(2)	C(5)—C(6)	1.49(2)
Os(2)—C(23C)	1.86(2)	C(34C)—O(34C)	1.19(2)	C(6)—C(7)	1.49(2)
Os(2)—N(2)	2.08(1)	N(1)—C(3)	1.51(2)	C(7)—C(8)	1.50(2)
Os(3)—C(31C)	1.86(2)	N(1)—C(11)	1.39(2)	C(7)—C(9)	1.45(2)
Os(3)—C(32C)	1.89(2)				

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(11)—Os(1)—Os(2)	65.7(4)	C(6)—C(1)—C(7)	59(1)	C(5)—C(6)—C(1)	114(1)
C(11)—Os(1)—Os(3)	86.9(4)	C(1)—C(2)—C(3)	113(1)	C(5)—C(6)—C(7)	124(1)
N(2)—Os(2)—Os(1)	66.8(3)	N(1)—C(3)—C(2)	110(1)	C(7)—C(6)—C(1)	61(1)
N(2)—Os(2)—Os(3)	88.7(3)	N(1)—C(3)—C(4)	101(1)	C(6)—C(7)—C(1)	60(1)
C(11)—N(1)—C(3)	109(1)	N(1)—C(3)—C(10)	108(1)	C(8)—C(7)—C(1)	122(2)
C(11)—N(1)—C(12)	128(1)	C(4)—C(3)—C(2)	112(1)	C(8)—C(7)—C(6)	120(1)
C(12)—N(1)—C(3)	124(1)	C(4)—C(3)—C(10)	114(1)	C(9)—C(7)—C(1)	112(2)
C(4)—N(2)—Os(2)	136.7(9)	C(10)—C(3)—C(2)	112(1)	C(9)—C(7)—C(6)	116(2)
C(11)—N(2)—Os(2)	113(1)	N(2)—C(4)—C(3)	106(1)	C(9)—C(7)—C(8)	116(1)
C(11)—N(2)—C(4)	110(1)	N(2)—C(4)—C(5)	113(1)	N(1)—C(11)—Os(1)	131(1)
C(2)—C(1)—C(6)	113(1)	C(5)—C(4)—C(3)	112(1)	N(2)—C(11)—Os(1)	114(1)
C(2)—C(1)—C(7)	121(1)	C(6)—C(5)—C(4)	111(1)	N(2)—C(11)—N(1)	115(1)

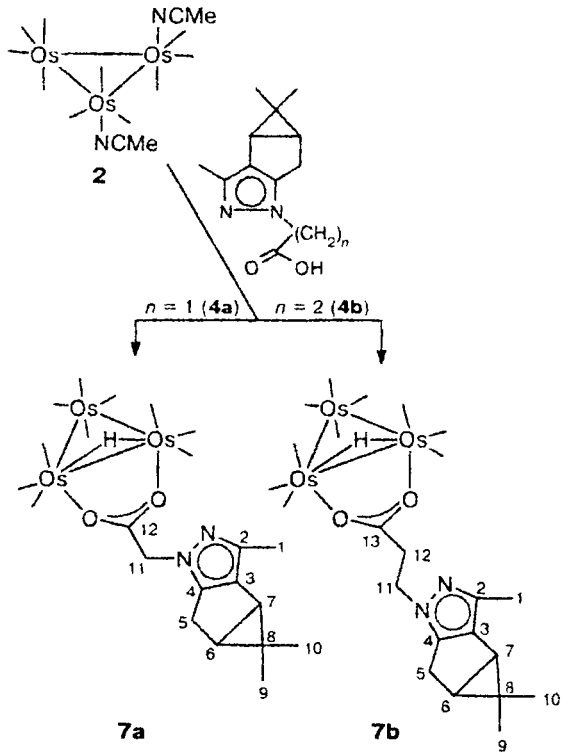
and Os—C bond lengths in **6a** are also close to those observed in analogous compounds. The angles between the Os_3 and Os_2CN planes vary over a rather narrow range from 71.4° to 80.4°, and the average value (77.7[1.7]°) coincides with that found in **6a**. Other bond lengths and bond angles in the fragment [(μ-H)$Os_3(CO)_{10}$(μ,η²-C=N—)] of molecule **6a** have values typical of trinuclear carbonyl osmium clusters.

The NMR spectral data for complexes **6a,b** agree with the structures of the complexes established by X-ray diffraction analysis. Compared to the ^{1}H NMR spectrum of the free ligand, the spectra of diastereomers **6a,b** have signals of the μ-H ligands at high field (at δ −15.71 and −15.89), which are typical of triosmium clusters containing bridging μ,η²-(C,N)R—C=N—R′ ligands[9a] or bridging nitrogen-containing heterocycles coordinated to the nitrogen and carbon atoms.[14] The spectra of both diastereomers have a signal whose intensity is half as large as that of the signal of the NMe_2 group observed in the spectrum of the free ligand. These signals are shifted upfield by 0.45 and 0.49 ppm in the spectra of **6a** and **6b**, respectively. The ^{13}C NMR spectra of the diastereomers have signals at δ 160.44 and 160.38. We assigned these signals to the carbon atoms of the dihydroimidazole ring which is σ-bound to the Os_3 metallocycle. It is worthy of note that the difference in the chemical shifts of the signals for the diastereotopic methylene protons H-2α,β (Δδ 1.37 and 1.44) and H-5α,β (Δδ 1.37 and 1.25) is larger than that in the case of the free ligand (Δδ 1.2 and 0.32). Apparently, this is associated with the anisotropy of the electromagnetic field of the carbonyl environment about the cluster.

The reactions of the analogous cluster $Os_3(CO)_{10}(NCMe)_2$ (**2**) with carboxylic acids **4a,b** containing the pyrazole ring fused with the 5-norcarane core were examined. These studies were of importance because they made it possible, first, to prepare, in one step, optically active cluster compounds with ligands possessing physiological activity and, second, to elucidate the mode of coordination of compounds containing the nitrogen atom of the pyrazole ring and the carboxy group. We believed that these ligands, which differ by one methylene group, are convenient objects for studies of stereochemical interactions between a bulky cluster fragment and a bulky ligand. Previously, we have investigated the stereochemical aspects of clusters (μ-H)$Os_3(CO)_{10}${μ-$O_2CC_5H_4Mn(CO)_3$}[15] and (μ-H)$Os_3(CO)_{10}$(μ-O_2CFc)[16] and their derivatives in which two bulky metallofragments are linked through the carboxy group. It was found that these compounds can be readily converted into chiral compounds by replacing one of CO groups by another ligand.

The reactions of $Os_3(CO)_{10}(NCMe)_2$ with pyrazolylcarboxylic acids **4a,b** readily gave clusters (Scheme 4) in which the ligand is coordinated as a bridge only through the carboxy group, as in the case of simple carboxylic acids.[17] No evidence of the formation of clusters, in which the nitrogen atom of the pyrazole ring is involved in coordination, was observed.

Scheme 4



The spectral characteristics of the resulting complexes (see Experimental) are in complete agreement with the proposed structures. It should be noted that free rotation of the bulky organic ligand about the cluster fragment occurs in complexes **7a,b**, as follows from their spectral data. In particular, the chemical shifts of the signals for the carbon atoms of the $Os(CO)_3$ fragments observed in the ^{13}C NMR spectra of these complexes are very similar, unlike the analogous signals in the spectra of the cluster with the bridging mercaptocaranone oxime,[18] in which the rotation of the bridging ligand is absent due to short contacts between one of the methyl groups of the ligand and the equatorial CO ligands of the $Os(CO)_3$ fragments (X-ray diffraction study).

Experimental

All reactions were carried out in freshly distilled solvents under an atmosphere of argon. The solvents were removed under reduced pressure. Commercial reagents were used without additional purification. The initial cluster complexes $Os_3(CO)_{11}(NCMe)$ (**1**)[19] and $Os_3(CO)_{10}(NCMe)_2$ (**2**)[19] as well as (1*R*,5*R*)-2-(1-hydroxyethylidene)-6,6-dimethylbicyclo[3.1.0]-hexan-3-one (**8**),[20] ethyl (3b*R*,4a*R*)-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)acetate (**9**),[21] and (1*S*,3*S*,6*R*)-3-(*N*,*N*-dimethylamino)caran-4-one oxime (**10**)[22] were prepared according to procedures reported previously. The enrichment of $Os_3(CO)_{12}$ with ^{13}CO groups was performed according to a known procedure.[23] The course of reactions was monitored by TLC. Analytical and preparative TLC were carried out on Silufol plates. The IR spectra were recorded on Specord IR-75 and Bruker IFS-66 spectrometers. The NMR spectra were measured on Bruker AM-400 (400.13 MHz for ^1H and 100.61 MHz for ^{13}C) and Bruker DRX-500 (500.13 MHz for ^1H and 125.75 MHz for ^{13}C) spectrometers at ~20 °C in $CDCl_3$ using the signal of the solvent ($CDCl_3$) as the internal standard (δ_H 7.24 and δ_C 76.90). The description of the NMR spectra follows the atomic numbering shown in Schemes 1 and 4, which do not coincide with that based on IUPAC nomenclature. The optical rotation was determined on a Palomat A polarimeter (578 nm). The mass spectra were measured on MKh-1310 (EI, 70 eV) and Finnigan MAT 8200 (EI, 70 eV) spectrometers.

4-Amino-(1*S*,3*S*,4*R*,6*R*)-3-(*N*,*N*-dimethylamino)-3,7,7-trimethylbicyclo[4.1.0]heptane (3). A solution of oxime **10** (5 g, 23.8 mmol) in anhydrous diethyl ether (30 mL) was added dropwise to a suspension of $LiAlH_4$ (3.5 g) in anhydrous diethyl ether (50 mL). The reaction mixture was refluxed for 70 h. After completion of the reaction (TLC control), wet diethyl ether (200 mL) was added dropwise to the reaction mixture and then 0.5 *M* HCl (100 mL) was added dropwise with cooling to 0 °C. The precipitate that formed was filtered off and the filtrate was extracted with HCl (100 mL). The aqueous phase was neutralized with concentrated NH_4OH to pH 13 and extracted with diethyl ether (2×200 mL). The combined extracts were washed with a saturated aqueous solution of NaCl, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting crude product (yellow oil, 1.8 g) was chromatographed on silica gel. The unconsumed amino oxime and by-products were eluted with a 20 : 1 $CHCl_3$—MeOH mixture. Diamine **3** was eluted as a viscous yellow oil with a 200 : 10 : 1 $CHCl_3$—MeOH—20% ethanolic Et_3N mixture in a yield of 1.20 g (25%), $[\alpha]^{22}_{580}$ +3° (*c* 5.45, MeOH).

IR (neat), ν/cm^{-1}: 3480, 3400 (NH_2—).

^1H NMR (400 MHz), δ: 0.56 (ddd, 1 H, H-1, J = 9.5, 9.3, and 4.5 Hz); 0.68 (ddd, 1 H, H-6, J = 9.5, 8.2, and 2.2 Hz); 0.81 (s, 3 H, H-10); 0.83 (dd, 1 H, H-2β, J = 15.6 and 4.5 Hz); 0.87 (s, 3 H, H-8); 0.92 (s, 3 H, H-9); 1.26 (br.s, 2 H, $N\underline{H}_2$—); 1.57 (ddd, 1 H, H-5β, J = 14.3, 5.7, and 2.2 Hz); 1.78 (ddd, 2 H, H-5α, J = 14.3, 10.0, and 8.2); 2.05 (dd, 2 H, H-2α, J = 15.6 and 9.3 Hz); 2.26 (s, 6 H, Me_2N); 2.37 (dd, 1 H, H-4, J = 10.0 and 5.7 Hz).

^{13}C NMR (100 MHz), δ: 15.06 (C-8); 15.19 (C-10); 17.99 (C-7); 18.94 (C-1); 20.26 (C-6); 26.95 (C-5); 28.95 (C-9); 31.45 (C-2); 40.26 (Me_2N—); 56.51 (C-3); 56.74 (C-4).

(3b*R*,4a*R*)-3-(3,4,4-Trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)propiononitrile. 3-Hydrazinopropiononitrile (2.57 g, 30.2 mmol) was added with stirring to a solution of diketone **8** (5.00 g, 30.1 mmol) in a mixture of MeOH (50 mL) and AcOH (2 mL) cooled with ice. The reaction mixture was stirred at 0 °C for 0.5 h, refluxed for 1 h, concentrated, washed with 0.5 *M* aqueous $NaHCO_3$, and extracted with CCl_4 (3×30 mL). The extract was dried with Na_2SO_4 and concentrated. The product was obtained as a pale-brown oil in a yield of 5.8 g. Then the oil was filtered through silica gel; elution with benzene gave the title compound as a

pale-yellow oil in a yield of 5.3 g (87%), $[\alpha]^{22}_{580}$ +101° (*c* 1.3, $CHCl_3$).

MS, *m/z* (I_{rel} (%)): 215.1419 $[M]^+$ (33) (for $C_{13}H_{17}N_3$, calculated 215.1422), 200 (100), 173 (4), 159 (82), 147 (77), 132 (8), 117 (5), 106 (10), 91 (12), 77 (9), 65 (8), 54 (10), 41 (9).

IR ($CHCl_3$), ν/cm^{-1}: 2225, 1570, 1545, 1520, 1480, 1440, 1425, 1410, 1365, 1355, 1290, 1270, 1160, 1090, 1030, 990, 955, 940, 910, 830, 810.

UV (EtOH), λ_{max}/nm (ε): 239 (5060).

^{1}H NMR (400 MHz), δ: 0.67 (s, 3 H, H-9); 1.06 (s, 3 H, H-10); 1.70 (pseudo-dt, 1 H, H-6, *J* = 1.1, 6.9, and 6.9 Hz); 1.75 (dd, 1 H, H-7, *J* = 6.5 and 1.2 Hz); 2.11 (s, 3 H, H-1); 2.53 (d, 1 H, H-5α, *J* = 16.6 Hz); 2.76 (m, 2 H, H-12); ~2.81 (m, 1 H, H-5β); 4.04 (pseudo-t, 2 H, H-11, *J* = 6.3 Hz).

^{13}C NMR (100 MHz), δ: 12.21 (q, C-1); 13.50 (q, C-10); 18.81 (t, C-12); 22.20 (s, C-8); 23.14 (t, C-5); 26.12 (d, C-7); 26.15 (q, C-9); 34.03 (d, C-6); 45.12 (t, C-11); 116.73 (s, C-13); 125.66 (s, C-3); 143.10 (s, C-2); 150.92 (s, C-4).

(3b*R*,4a*R*)-(3,4,4-Trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)acetic acid (4a). A solution of compound **9** (1.24 g, 5 mmol) and KOH (50 mmol) in a mixture of MeOH (15 mL) and water (5 mL) was refluxed for 6 h. The reaction mixture was concentrated under reduced pressure, diluted with water (50 mL), and washed with benzene (30 mL). The aqueous phase was neutralized with 0.1 *M* H_2SO_4 and extracted with CH_2Cl_2 (3×30 mL). The combined extracts were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The solution of the residue in CH_2Cl_2 was filtered through silica gel, the solvent was evaporated, and the residue was recrystallized from MeCN. Acid **4a** was obtained in a yield of 0.83 g (75%), m.p. 197—199 °C (from MeCN), $[\alpha]^{26}_{580}$ +86.6° (*c* 0.9, $CHCl_3$).

MS, *m/z* (I_{rel} (%)): 220.1198 $[M]^+$ (21) (for $C_{12}H_{16}N_2O_2$, calculated 220.1212), 205 (85), 175 (9), 159 (100), 146 (10), 133 (7), 118 (6), 105 (5), 91 (16), 79 (9), 65 (9), 42 (9).

IR ($CHCl_3$), ν/cm^{-1}: 1725, 1550, 1490, 1440, 1430, 1420, 1370, 1305, 1280, 1260, 1150, 1110, 1035, 1000, 975, 880, 850, 820.

UV (EtOH), λ_{max}/nm (ε): 239 (4643).

^{1}H NMR (400 MHz), δ: 0.67 (s, 3 H, H-10); 1.04 (s, 3 H, H-9); 1.70 (pseudo-t, 1 H, H-6, *J* = 6.6 Hz); 1.77 (d, 1 H, H-7, *J* = 6.4 Hz); 2.13 (s, 3 H, H-1); 2.45 (d, 1 H, H-5α, *J* = 16.8); 2.72 (dd, 1 H, H-5β, *J* = 6.9 and 16.9 Hz); 4.61 (d, 1 H, H-11α, *J* = 17.6 Hz); 4.71 (d, 1 H, H-11β, *J* = 17.6 Hz); 12.28 (br.s, 1 H, OH).

^{13}C NMR (100 MHz), δ: 11.67 (q, C-1); 13.79 (q, C-10); 22.37 (s, C-8); 23.46 (t, C-5); 26.35 (q, C-9); 26.47 (d, C-7); 34.23 (d, C-6); 50.51 (t, C-11); 125.78 (s, C-3); 142.18 (s, C-2); 152.82 (s, C-4); 169.83 (s, C-12).

(3b*R*,4a*R*)-3-(3,4,4-Trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)propionic acid (4b). Acid **4b** was prepared analogously to **4a** starting from (3b*R*,4a*R*)-3-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)propiononitrile (1.1 g, 5 mmol) in a yield of 0.92 g (77%), m.p. 152—155 °C (from MeCN), $[\alpha]^{26}_{580}$ +76.9° (*c* 1.2, $CHCl_3$).

MS, *m/z* (I_{rel} (%)): 234.1383 $[M]^+$ (20) (for $C_{13}H_{18}N_2O_2$, calculated 234.1368), 219 (69), 201 (7), 189 (1), 173 (4), 159 (100), 147 (37), 132 (4), 117 (5), 106 (5), 91 (10), 77 (7), 65 (5), 55 (8), 41 (6).

IR ($CHCl_3$), ν/cm^{-1}: 1710, 1545, 1530, 1495, 1445, 1435, 1375, 1280, 1075, 1045, 1010, 970, 930, 890, 850, 825.

UV (EtOH), λ_{max}/nm (ε): 239 (5270).

^{1}H NMR (400 MHz), δ: 0.55 (s, 3 H, H-9); 0.99 (s, 3 H, H-10); 1.63 (dd, 1 H, H-6, *J* = 6.6 and 6.5 Hz); 1.68 (d, 1 H, H-7, *J* = 6.3 Hz); 2.09 (s, 3 H, H-1); 2.51 (d, 1 H, H-5α, *J* = 17 Hz); 2.73 (m, 1 H, H-5β); 2.70 (m, 2 H, H-12); 4.09 (t, 2 H, H-11, *J* = 6.3 Hz); 11.47 (br.s, 1 H, OH).

^{13}C NMR (100 MHz), δ: 11.62 (q, C-1); 13.70 (q, C-10); 22.26 (s, C-8); 23.64 (t, C-5); 26.18 (d, C-7); 26.28 (q, C-9); 34.01 (d, C-6); 34.53 (t, C-12); 45.03 (t, C-11); 124.98 (s, C-3); 141.77 (s, C-2); 152.28 (s, C-4); 173.32 (s, C-11).

Reaction of $Os_3(CO)_{11}$(NCMe) with (1*S*,3*S*,4*R*,6*R*)-4-amino-3-(*N*,*N*-dimethylamino)-3,7,7-trimethylbicyclo[4.1.0]-heptane. ***A.*** A mixture of $Os_3(CO)_{11}$(NCMe) (96 mg, $1.1 \cdot 10^{-4}$ mol) and diaminocarane **3** (106 mg, $5.4 \cdot 10^{-4}$ mol) in THF (20 mL) was stirred at ~20 °C for 3 h. Then the reaction mixture was concentrated to dryness and a bright-yellow fraction was isolated from the residue by preparative TLC (pentane—benzene, 4 : 1), R_f ~0.7. Complex **5** was obtained as a yellow amorphous solid in a yield of 26 mg (23.1%). This compound slowly decomposed in the solid state and rapidly decomposed in solutions.

IR (pentane), ν/cm^{-1}: 2106 w, 2052 s, 2034 s, 2020 m, 1995 br.s, 1981 sh, 1966 sh (CO ligands).

B. A mixture of $Os_3(CO)_{11}$(NCMe) (137 mg, $1.5 \cdot 10^{-4}$ mol) and diaminocarane **3** (250 mg, $1.3 \cdot 10^{-3}$ mol) in THF (25 mL) was stirred at ~20 °C until $Os_3(CO)_{11}$(NCMe) completely disappeared (~3 h). Then the reaction mixture was heated at 60 °C for 18 h and concentrated to dryness. The bright-yellow complex, (*R*,*S*)-1,1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-μ-hydrido-2,3-μ,η^2-{(N3,C2)-(3aR,4aR,5aS,6aS)-1,5,5,6a-tetramethyl-3a,4,4a,5a,6,6a-hexahydro-1*H*-cyclopropa[*d*]benzoimidazol-2-yl}-*triangulo*-triosmium (cluster **6**), was isolated from the residue by preparative TLC (hexane—benzene, 4 : 1) as a mixture of two diastereomers (the total yield was 28 mg (18%)). The major diastereomer **6a** was obtained in the crystalline state by crystallization of the mixture of isomeric complexes **6** from pentane.

Compound **6a**. IR (hexane), ν/cm^{-1}: 2104 m, 2062 s, 2052 s, 2022 s, 2010 s, 2002 m, 1988 s, 1975 w, 1948 w (CO ligands).

^{1}H NMR (500 MHz), δ: 3.43 (s, 3 H, H-4); 2.79 (s, 3 H, H-12); 1.91 (m, 2 H, H-2α + H-5α); 1.02 (s, 3 H, H-10); 0.97 (s, 3 H, H-9); 0.96 (s, 3 H, H-8); 0.54 (m, 2 H, H-2β + H-5β); 0.18 (m, 2 H, H-1 + H-6); −15.71 (s, 1 H, μ-H).

^{13}C NMR (125 MHz), δ: 183.82, 183.32, 179.41, 175.88, 175.65, 175.45, 174.55, 173.89 ($Os_3(CO)_{10}$); 160.44 (N=C—); 72.29 (C-4); 63.95 (C-3); 29.2 (C-12); 28.29 (C-9); 26.27 (C-2); 25.14 (C-10); 21.34 (C-5); 17.86 (C-1/C-6); 17.35 (C-7); 16.21 (C-6/C-1); 14.54 (C-8).

MS, *m/z*: 1048 $[M]^+$ (with respect to ^{192}Os).

$[M]^{16}_{580}$ −1186° (*c* 0.65, $CHCl_3$).

Compound **6b**. IR (hexane), ν/cm^{-1}: 2105 m, 2060 s, 2051 s, 2020 s, 2012 s, 1999 m, 1987 s, 1973 w, 1948 w (CO ligands).

^{1}H NMR (500 MHz), δ: 3.14 (dd, 1 H, *J* = 4 and 2 Hz, H-4); 2.83 (s, 3 H, H-11); 1.97 (dd, 1 H, H-2α, *J* = 16 and 8 Hz); 1.87 (ddd, 1 H, H-5α, *J* = 16, 8, and 2 Hz); 0.99 (s, 3 H, H-21); 0.93 (s, 3 H, H-8); 0.89 (s, 3 H, H-9); 0.62 (ddd, 1 H, H-5β, *J* = 16, 9, and 4 Hz); 0.53 (dd, 1 H, H-2β, *J* = 16 and 9 Hz); 0.30 (pseudo-dt, 1 H, H-6, *J* = 9, 9, and 8 Hz); 0.23 (pseudo-dt, 1 H, H-1, *J* = 9, 9, and 8 Hz); −15.83 (s, 1 H, μ-H).

^{13}C NMR (125 MHz), δ: 183.89, 183.28, 178.58, 176.57, 175.72, 175.59, 175.11, 174.90, 174.64, 173.56 ($Os_3(CO)_{10}$); 160.38 (N=C—); 72.29 (C-4); 64.07 (C-3); 28.92 (C-12); 28.45 (C-10); 28.15 (C-9); 25.69 (C-2); 21.31 (C-5); 18.69 (C-1/C-6); 18.57 (C-7); 17.79 (C-6/C-1); 14.22 (C-8).

MS, *m/z*: 1048 $[M]^+$ (with respect to ^{192}Os).

Synthesis of isotopically labeled diastereomers 6a,b. Isotopically labeled diastereomers **6a,b** were synthesized using the

cluster $Os_3(CO)_{11}(NCMe)$ enriched with ^{13}CO. The IR spectra correspond to complexes **6a,b**.

^{13}C NMR (100 MHz), δ: 183.88, 183.29, 179.37, 178.57, 175.88, 175.63, 175.41, 175.08, 174.91, 174.59, 173.89 ($Os_3(CO)_{10}$).

1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ,η²-(O,O′)-{(3bR,4aR)-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)acetato}-*triangulo*-triosmium (7a). A mixture of $Os_3(CO)_{10}(NCMe)_2$ (145 mg, $1.57 \cdot 10^{-4}$ mol) and compound **4a** (350 mg, $1.59 \cdot 10^{-3}$ mol) in CH_2Cl_2 (20 mL) was stirred at ~20 °C for 5 h. Then the reaction mixture was concentrated to dryness and a bright-yellow fraction was isolated from the residue by preparative TLC in hexane, R_f ~0.3. Product **7a** was obtained in a yield of 114 mg (68%).

IR (pentane), ν/cm^{-1}: 2114 w, 2075 s, 2063 s, 2028 s, 2015 s, 1989 br.m (CO ligands).

^1H NMR (400 MHz), δ: 4.44 (d, 1 H, H-11β, J = 17.2 Hz); 4.20 (d, 1 H, H-11α, J = 17.2 Hz); 2.41 (dd, 1 H, H-5β, J = 16.4 and 6.7 Hz); 2.18 (dd, 1 H, H-5α, J = 16.4 and 1 Hz); 2.06 (s, 3 H, H-1); 1.72 (dd, 1 H, H-7, J = 6.7 and 1 Hz); 1.57 (pseudo-t, 1 H, H-6, J = 6.7 Hz); 1.04 (s, 3 H, H-9); 0.72 (s, 3 H, H-10); −10.51 (s, 1 H, μ-H).

^{13}C NMR (100 MHz), δ: 186.67 (COO); 183.82, 181.3, 175.61, 175.48, 174.11, 174.05, 173.94, 173.91, 173.88 ($Os_3(CO)_{10}$); 150.88, 143.07, 126.57, 53.2, 34.43, 27.02, 26.67, 23.73, 22.48, 14.11, 12.67.

MS, m/z: 1076 $[M]^+$ (with respect to ^{192}Os).

$[M]^{23}_{580}$ +98.5° (*c* 1.3, $CHCl_3$).

1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ,η²-(O,O′)-{(3bR,4aR)-(3,4,4-trimethyl-3b,4,4a,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)propionato}-*triangulo*-triosmium (7b). A mixture of $Os_3(CO)_{10}(NCMe)_2$ (110 mg, $1.19 \cdot 10^{-4}$ mol) and compound **4b** (212 mg, $6.54 \cdot 10^{-4}$ mol) in CH_2Cl_2 (20 mL) was heated under reflux for 4 h. Then the reaction mixture was concentrated to dryness and a bright-yellow fraction was isolated from the residue by preparative TLC in a 4 : 1 hexane—benzene mixture, R_f ~0.5. Product **7b** was obtained in a yield of 103 mg (79%).

IR (pentane), ν/cm^{-1}: 2114 w, 2075 s, 2063 s, 2028 s, 2015 s, 1989 br.m (CO ligand).

^1H NMR (500 MHz), δ: 3.84 (m, 2 H, H-11); 2.65 (m, 3 H, H-12 + H-5β); 2.37 (d, 1 H, H-5α, J = 16.5 Hz); 2.12 (s, 1 H, H-1); 1.75 (dd, 1 H, H-7, J = 6.5 and 1 Hz); 1.68 (pseudo-t, 1 H, H-6, J = 6.5 Hz); 1.04 (s, 1 H, H-10); 0.61 (s, 1 H, H-9); −10.50 (s, 1 H, μ-H).

^{13}C NMR (125 MHz), δ: 188.54 (1 C, COO); 183.28 (1 C), 181.39 (1 C), 175.7 (2 C), 174.02 (2 C), 173.94 (2 C), 173.89 (1 C), 173.83 (1 C) ($Os_3(CO)_{10}$); 45.48, 37.18, 34.09, 26.32, 26.21, 23.36, 22.25, 13.63, 12.42.

MS, m/z: 1090 $[M]^+$ (with respect to ^{192}Os).

$[M]^{23}_{580}$ +205° (*c* 1.6, $CHCl_3$).

X-ray diffraction study. Crystals of compound **6a** were prepared by crystallization of a mixture of diastereomers **6** from pentane. The crystals belong to the orthorhombic system, a = 12.647(1) Å, b = 13.370(1) Å, c = 15.848(2) Å, V = 2679.7(4) Å^3, space group $P2_12_12_1$, Z = 4, d_{calc} = 2.585 g cm^{-3}. The X-ray diffraction data were collected from a single crystal of dimensions of 0.21×0.23×0.29 mm on an automated Enraf—Nonius CAD-4 diffractometer (graphite monochromator, θ/2θ scanning technique to $2\theta_{max}$ = 50°) at room temperature. With the aim of determining the absolute configuration, the Friedel equivalents were measured for all reflection in the ranges of h = 0—15, k = 0—15, and l = 0—18 using 2θ/−ω geometry. A total of 5312 reflections (2656 pairs) were measured, of which 4698 reflections were considered as observed. The absorption correction was applied using four azimuth scanning curves, T_{min} = 0.3568, T_{max} = 1.6433. The structure was solved by the direct method using the SHELXS-86 program package[24] and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms, taking into account the secondary extinction (g = 0.00017(3)) with the use of the SHELXL-97 program package.[25] The bridging hydrogen atom at the Os—Os bond was located from the difference electron density synthesis. Its atomic coordinates and the isotropic thermal parameter were included in the final refinement. The coordinates of the remaining hydrogen atoms were calculated geometrically and refined within the framework of the rigid body model. The final values of the R factors were as follows: $R(F)$ = 0.0335, $wR(F^2)$ = 0.0666 for 3637 reflections, $F_{exp} \geq 4\sigma(F)$, $R(F)$ = 0.0525, $wR(F^2)$ = 0.0726, $GOOF$ = 0.855 for all reflections. The validity of the determined absolute configuration is supported by Flack's parameter, which is virtually equal to zero (x = −0.03(2)); the inverted structural model is characterized by Flack's parameter x = 1.02(3); $R(F)$ = 0.0400 for 3637 $F_{exp} \geq 4\sigma(F)$. The principal bond lengths and bond angles in structure **6a** are given in Table 1. The atomic coordinates were deposited with the Cambridge Structural Database.

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