

# Triosmium clusters with bridging terpenic thioureato-like ligands

Vladimir P. Kirin<sup>a,\*</sup>, Vladimir A. Maksakov<sup>a</sup>, Alexandr V. Virovets<sup>a</sup>,  
Sergey A. Popov<sup>b</sup>, Alexey V. Tkachev<sup>b</sup>

<sup>a</sup> Nikolaev Institute of Inorganic Chemistry, Siberian Branch of RAS, Acad Lavrentyev Avenue 3, Novosibirsk 630090, Russia

<sup>b</sup> Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of RAS, Acad Lavrentyev Avenue 9, Novosibirsk 630090, Russia

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## Abstract

The reaction of acetone-4-(2-methoxy-phenyl)thiosemicarbazone with triosmium cluster  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  results in the formation of the cluster with the  $\mu_2$  chelate-bridging ligand coordinated by S and  $\text{N}^1$  atoms, which was studied by X-ray diffraction analysis. Reaction of (3*aR*, 3*bR*, 4*aR*, 5*aS*)-5*a*-hydroxy-3,4,4-trimethyl-3*a*,3*b*,4,4*a*,5,5*a*-hexahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazole-1-carbothioic acid amide with  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  gives rise to the complex with the bridging ligand coordinated by sulphur atom. Further transformation of the complex in hot benzene results in tautomeric rearrangement of the organic ligand and the cleavage of the pyrazolinol cycle to form an open chain tautomer. Unusual silica gel induced oxidative cleavage of the cyclopropane ring in the open chain derivative and epoxidation of cycloalcan C–C bond are observed on the air.

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## 1. Introduction

We have reported earlier the reactions of the triosmium clusters with a number of the carane derivatives. These reactions proceeded quite different as compared with those of the simplest analogues. We have found CH [1] or CN [2] activation at very mild conditions and changes of the ligand coordination mode as a result of the ligands steric demands [2,3]. For example, (3*bS*, 4*aR*)-3,4,4-trimethyl-3*b*,4,4*a*,5-tetrahydro-cyclopropa[3,4]cyclopenta[1,2-*c*]pyrazole-1-carbothioic acid (2-methoxy-phenyl)-amide (amide **1**), which contains thiourea-like fragment  $\text{N}-\text{C}(=\text{S})-\text{N}$ , coordinates in triosmium cluster in the tautomeric  $\text{N}-\text{C}(=\text{NR})-\text{S}$  form [3] with the ligand coordinated only on two osmium atoms by sulphur and  $\text{N}^1$  atoms in contrast to simple analogues bridging three metal atoms [4,5]. This difference could be

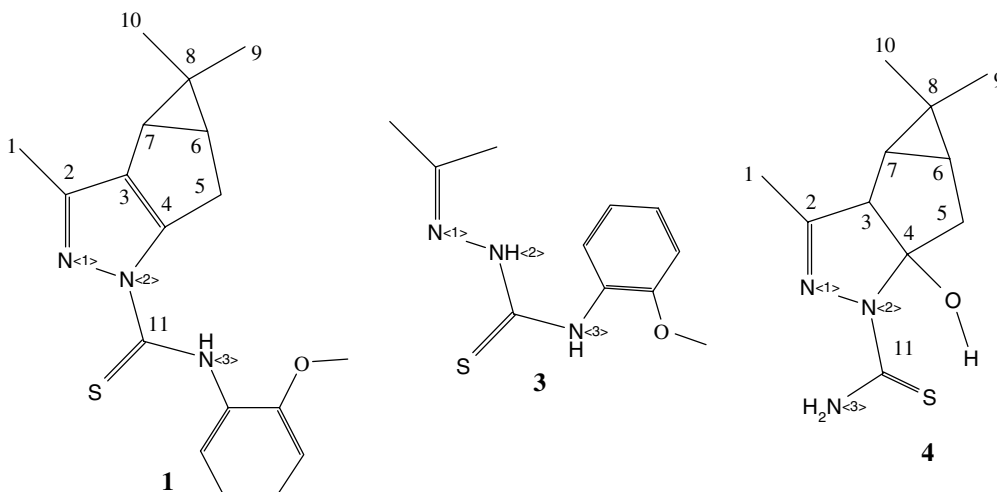
caused by (a) involving of lone electronic  $\text{N}^2$  atom pair into the aromatic-system of pyrazolic cycle; (b) the presence of the bulky substituent at the nitrogen atom  $\text{N}^3$  and decreasing of electronic density on this atom owing to electronegativity of the pyrazolic cycle; (c) steric restrictions arising at coordination of bulky tricyclic ligand on cluster core. To examine these assumptions we have investigated the reactions of cluster  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  (**2**) with acetone-4-(2-methoxy-phenyl)thiosemicarbazone (**3**) and (3*aR*, 3*bR*, 4*aR*, 5*aS*)-5*a*-hydroxy-3,4,4-trimethyl-3*a*,3*b*,4,4*a*,5,5*a*-hexahydro-cyclopropa[3,4]cyclopenta[1,2-*c*]pyrazole-1-carbothioic acid amide (**4**) (Scheme 1).

## 2. Results and discussion

Thiosemicarbazone **3** reacts with **2** similarly to amide **1**. On heating in benzene the complex **5** is formed in a good yield (74%), in which thiosemicarbazone substitutes NCMe and two CO groups and is coordinated

\* Corresponding author. Tel.: +7-383-2-343052; fax: +7-383-2-344489.

E-mail address: [kirin@che.nsk.su](mailto:kirin@che.nsk.su) (V.P. Kirin).



Scheme 1.

by a “chelate-bridging” mode by of sulphur and N<sup>1</sup> atoms: (See Scheme 2).

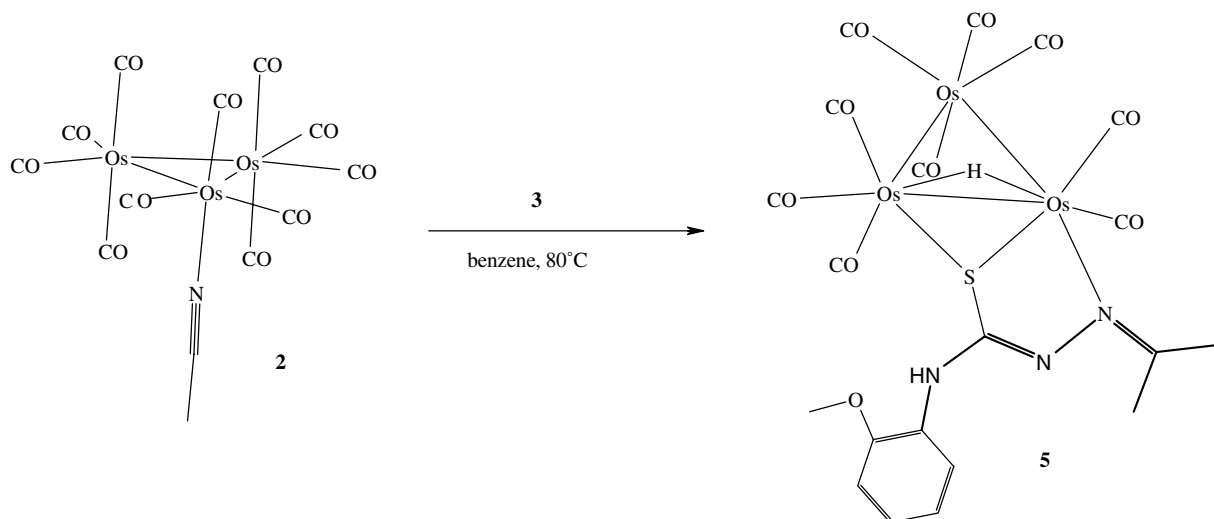
The cluster **5** has been characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectroscopy and elemental analysis, all the data are in agreement with the structure proposed (Table 1).

For this compound the single crystal has been obtained and its X-ray crystal analysis has been performed (see Fig. 1).

There is an unique fragment Os<sub>3</sub>(μ-H)(μ,η<sup>2</sup>-SCNN) presented in the molecule **5**. No similar structures were found in the Cambridge Structural Database except for recently discovered cluster with a similar fragment Os<sub>3</sub>(CO)<sub>9</sub>(μ-H)(μ,η<sup>2</sup>-SC{=NC<sub>6</sub>H<sub>4</sub>OMe}N<sub>2</sub>C<sub>10</sub>H<sub>13</sub>) (**9**) having the group N–N incorporated into pyrazole cycle [2]. The comparison of the bond lengths in chelated fragments has shown, that in **5** in comparison with **9** the

bridged Os–Os edge (2.8653 and 2.8470 Å) and Os–N (2.181 and 2.14 Å) bonds are lengthened, and N–N (1.405 and 1.47 Å), S–C (1.798 and 1.84 Å) and C(1)–N(2) (1.298 and 1.39 Å for **5** and **9** respectively) bonds are shortened noticeably. The bonds Os–S have close values in **5** and **9**. Presence of the pyrazolic cycle influences first on the bond lengths in the five-membered OsSCNN ring though the Os<sub>2</sub>S fragment is also concerned. The crystal packing of compound **5** is typically molecular, without appreciably shortened intermolecular contacts.

Unlike the above reaction, the interaction of the cluster **2** with amide **4** cleanly proceeds already at ambient temperature. According to TLC in 10 min after dissolving the reagents, there is only complex **6** as the reaction product. Unfortunately this compound is not stable on a silica gel plate in air enough to be isolated by chromatography. So complex **6** has been characterized only



Scheme 2.

Table 1  
Spectroscopic data for compounds 4–8

	IR, $\nu(\text{cm}^{-1})$	$^1\text{H}$ NMR, $\delta(\text{J Hz})$	$^{13}\text{C}$ NMR, $\delta(\text{J Hz})$
4	<sup>a</sup> 3516, 3384, 1572, 1484, 1381, 1335, 1286, 1182, 1128, 1075, 1022, 955, 902, 854	<sup>b</sup> 0.93 d ( $J=7$ Hz, H-7), 0.97 s (3H-10), 1.09 s (3H-9), 1.16 dd ( $J=7$ and 7 Hz, H-6), 1.95 d ( $J=15$ Hz, H-5a), 1.98 s (3H-1), 2.91 dd ( $J=15$ and 7 Hz, H-5b), 2.97 br.s, 5.1 br.s. (OH), 5.69 br.s (NH <sub>2</sub> )	<sup>b</sup> 14.56 (C-1), 62.33 (C-3), 107.45 (C-4), 40.36 (C-5), 30.75 (C-6), 32.14 (C-7), 20.52 (C-8), 26.66 (C-9), 14.20 (C-10), 154.45 and 155.59 (C-2 and NCSNH <sub>2</sub> )
5	<sup>c</sup> 2092 m, 2056 s, 2016 s, 2011 vs, 1997 s, 1982 m, 1972 sh, 1930 m; <sup>d</sup> 3408 w ( $\nu_{\text{N-H}}$ )	<sup>f</sup> 7.94 – 6.88 (m, 4H, C <sub>6</sub> H <sub>4</sub> ); 7.52 (br.s, 1H, NH); 3.97 (s, 3H, OMe); 2.81 and 2.46 (s, 6H, =CMe <sub>2</sub> ); –16.14 (s, 1H, $\mu\text{-H}$ )	<sup>f</sup> 188.43 (d, $J_{\text{CH}}$ 2.4), 182.07 (d, $J_{\text{CH}}$ 1.4), 179.81 (d, $J_{\text{CH}}$ 1.9), 176.74 (d, $J_{\text{CH}}$ 2.9), 174.28 (d, $J_{\text{CH}}$ 9.6), 173.44(s), 172.42 (s), 172.28 (d, 14.4), 169.85 (d, $J_{\text{CH}}$ 1.0), 169.41 (d, $J_{\text{CH}}$ 3.8) (“Os <sub>3</sub> (CO) <sub>9</sub> ” + C–S); 176.02 (sept, $J_{\text{CH}}$ 6.2, =CMe <sub>2</sub> ); 148.00 (s), 128.86 (s); 123.54 (ddd, $J_{\text{CH}}$ 162.7, 8.9, 1.7), 120.49 (dd, $J_{\text{CH}}$ 162.7, 8.2), 119.54 (dddd, $J_{\text{CH}}$ 164.1, 8.2, 5.3, 2.9), 109.93 (dd, $J_{\text{CH}}$ 159.8, 8.9) (C <sub>6</sub> H <sub>4</sub> ); 55.82 (q, $J_{\text{CH}}$ 144.9, OMe); 32.37 (qq, $J_{\text{CH}}$ 128.6, 3.1, (=CMe <sub>2</sub> ), 25.05 (qq, $J_{\text{CH}}$ 129.8, 3.3)=CMe <sub>2</sub> )
<sup>g</sup> 6	<sup>c</sup> 2110 w, 2071 s, 2063 m, 2028 s, 2019 sh, 2008 m, 1994 sh, 1989 m, 1958 w; <sup>c</sup> 3616b br.w ( $\nu_{\text{OH}}$ ), 3513br.w( $\nu_{\text{NH}}$ ), 3386 br.w ( $\nu_{\text{NHassoc}}$ )	<sup>f</sup> 6.0 and 5.7 (br.s, 1H, NH); 3.37 (m, 1H, H <sup>5<math>\alpha</math></sup> ); 2.73 (m, 1H, H <sup>3</sup> ); 2.18 (m, 1H, H <sup>5<math>\beta</math></sup> ); 2.03 and 1.96 (s, 3H, H <sup>1</sup> ); 1.48 (m, 1H, H <sup>6</sup> ); 1.15 (m, 1H, H <sup>7</sup> ); 1.22 and 1.08 (s, 3H, H <sup>10</sup> ); 1.14 and 1.09 (s, 3H, H <sup>9</sup> ); –17.19 and –17.48 (s, 1H, $\mu\text{-H}$ )	<sup>f</sup> 182.97, 181.55, 180.63, 177.11, 177.05, 174.42, 173.42, 170.88, 170.73, 170.56, 169.65, 169.51, 165.55, 162.18, 162.07, 159.07 (“Os <sub>3</sub> (CO) <sub>10</sub> ” + C <sup>11</sup> ); 123.42 (C <sup>2</sup> ), 86.27 and 84.14 (C <sup>4</sup> ), 64.78 and 63.56 (C <sup>3</sup> ), 43.01 and 42.42 (C <sup>5</sup> ), 33.21 and 33.01 (C <sup>6</sup> ), 31.69 and 31.41 (C <sup>7</sup> ), 23.49 and 20.81 (C <sup>10</sup> ), 21.16 and 20.58 (C <sup>8</sup> ), 14.83 and 14.45 (C <sup>1</sup> /C <sup>9</sup> ), 14.33 and 14.25 (C <sup>9</sup> /C <sup>1</sup> )
7	<sup>c</sup> 2111 w, 2071 s, 2063 m, 2026 s, 2016 m, 2012 sh, 1989 w, 1733 w; <sup>c</sup> 3470 w, 3377 w ( $\nu_{\text{NH}}$ )	<sup>h</sup> 5.31 (br., 2H, >NH +=NH); 3.36 (m, 1H, H <sup>3</sup> ); 3.29 (dd, 1H, 15.6, 7.0, H <sup>5<math>\alpha</math></sup> ); 2.74 (dd, 1H, 15.6, 8, H <sup>5<math>\beta</math></sup> ); 2.11 (s, 3H, H <sup>1</sup> ); 1.98 (m, 1H, H <sup>6</sup> ); 1.69 (m, 1H, H <sup>7</sup> ); 1.05 (s, 3H, H <sup>10</sup> ); 0.75 (s, 3H, H <sup>9</sup> ); –17.3 (s, 1H, $\mu\text{-H}$ )	<sup>h</sup> 202.37 (C <sup>4</sup> ); 181.43, 180.26, 180.15, 176.71, 174.13, 174.03, 170.69, 170.55, 169.46, 155.91, 152.49 (“Os <sub>3</sub> (CO) <sub>10</sub> ” + C <sup>11</sup> ); 96.53 (C <sup>2</sup> ); 63.31 (C <sup>3</sup> ); 37.93 (C <sup>5</sup> ); 32.88 (C <sup>6</sup> ); 30.69 (C <sup>7</sup> ); 26.89 (C <sup>10</sup> ); 21.54 (C <sup>8</sup> ); 15.65 (C <sup>9</sup> ); 14.62 (C <sup>1</sup> )
8	<sup>c</sup> 2112 w, 2071 s, 2062 m, 2026 s, 2016 m, 2008 m, 1988 w, 1717 w; <sup>d</sup> 3615 v.w, 3593 v.w, 3500 w, 3363 w ( $\nu_{\text{OH}}$ and $\nu_{\text{NH}}$ ); <sup>i</sup> 1743( $\nu_{\text{CO}}$ ); 1622, 1592, 1558 ( $\nu_{\text{CN}}$ and $\delta_{\text{NH}}$ ); 1461, 1453 ( $\delta_{\text{CH}}$ ); 1373, 1363, 1280	<sup>f</sup> 5.75 (br. s, 2H, NH); 4.07 (d, 1H, 1.1, H <sup>7</sup> ); 2.47 (dd, 1H, 17.6, 8.2, H <sup>5<math>\alpha</math></sup> ); 2.39 (dd, 1H, 8.2, 1.1, H <sup>6</sup> ); 2.22 (dd, 1H, 17.6, 8.2, H <sup>5<math>\beta</math></sup> ); 1.97 (s, 3H, H <sup>1</sup> ); 1.37 + 1.26 (s, 3H + 3H, H <sup>9</sup> + H <sup>10</sup> ); –17.19 (s, 1H, $\mu\text{-H}$ )	<sup>h</sup> 203.80 (s, C <sup>4</sup> ); 181.71, 180.28, 176.74, 176.72, 173.97, 173.93, 170.61, 170.51, 169.36, 169.30, 162.89 (“Os <sub>3</sub> (CO) <sub>10</sub> ” + C <sup>11</sup> ), 156.18 (t, $J_{\text{CH}}$ 6.5, C <sup>2</sup> ), 96.52 (s, C <sup>8</sup> ), 71.44 (s, C <sup>3</sup> ), 64.43 (dd, $J_{\text{CH}}$ 191.2, 4.1, C <sup>7</sup> ), 44.89 (d, $J_{\text{CH}}$ 127.4, C <sup>6</sup> ), 34.29 (dd, $J_{\text{CH}}$ 136.5, 126.4, C <sup>5</sup> ), 28.78 (q, $J_{\text{CH}}$ 124.3, C <sup>9</sup> /C <sup>10</sup> ), 27.53 (q, $J_{\text{CH}}$ 125.2, C <sup>10</sup> /C <sup>9</sup> ), 14.78 (q, $J_{\text{CH}}$ 129.6, C <sup>1</sup> )

<sup>a</sup> In CDCl<sub>3</sub>.

<sup>b</sup> In CDCl<sub>3</sub>–CCl<sub>4</sub>1:1 v/v.

<sup>c</sup> In hexane.

<sup>d</sup> In CCl<sub>4</sub>.

<sup>e</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>f</sup> In CDCl<sub>3</sub>.

<sup>g</sup> Mixture of two rotamers.

<sup>h</sup> In C<sub>6</sub>D<sub>6</sub>.

<sup>i</sup> In KBr.

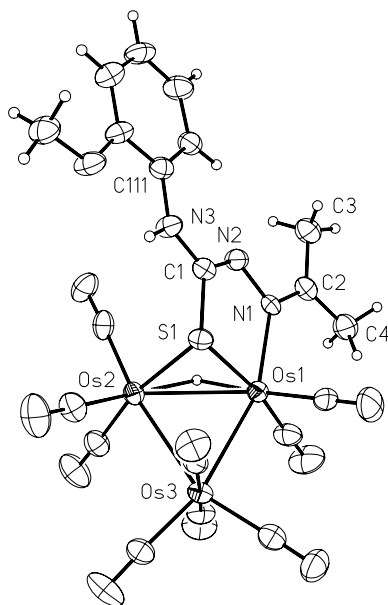
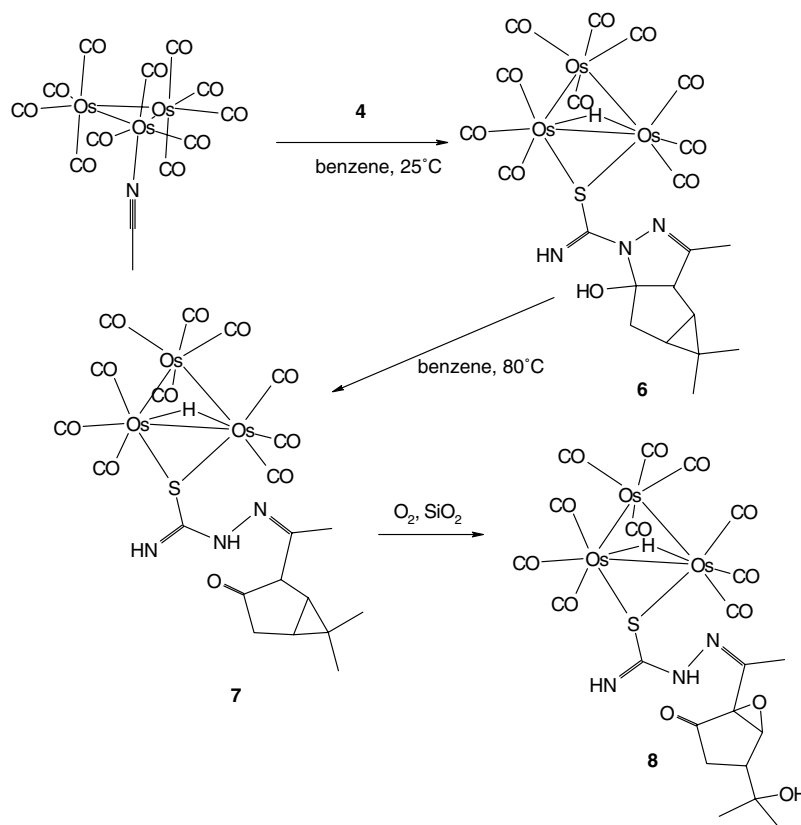


Fig. 1. Molecule **5** as 35% probability ellipsoids according to X-ray crystallography. Main bond distances (Å): Os(1)–Os(2) 2.8653(5), Os(1)–Os(3) 2.8234(5), Os(1)–S(1) 2.3731(19), Os(1)–N(1) 2.181(6), Os(2)–S(1) 2.444(2), Os(2)–Os(3) 2.8510(6), S(1)–C(1) 1.798(7), C(1)–N(2) 1.298(8), C(1)–N(3) 1.346(9), N(2)–N(1) 1.405(8), N(1)–C(2) 1.293(9), C(2)–C(3) 1.486(11), C(2)–C(4) 1.478(11), N(3)–C(111) 1.401(10).

by NMR and IR spectroscopy. IR spectrum of this cluster in the CO stretching region is characteristic for triosmium clusters with bridging thiolate ligand [6]. The OH vibration band is clearly visible at  $3613\text{ cm}^{-1}$ . The bridging coordination of the ligand by sulphur atom is confirmed by NMR data. In  $^1\text{H}$  NMR spectrum there are two very close singlet signals of  $\mu\text{-H}$  ligands ( $\approx 1:2$ ) in the area characteristic for  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SR})$  clusters [2]. Other part of the spectrum does not much differ from the spectrum of uncoordinated **4** except for doubling of the singlets of the methyl groups signals in the ratio similar to that of hydrides mentioned above. The intensity of NH signal is reduced by half in comparison with corresponding signal of free **4**. Carbon-13 NMR spectrum of the complex demonstrates two sets of signals ( $\approx 2:1$ ) whose chemical shifts and multiplicity are similar to those of free ligand **4**. The signal of  $\text{C}^{11}$  atom in complex **6** is located in the area of carbonyl carbons of the moiety  $\text{Os}_3(\text{CO})_{10}$  and so the signal was not identified.

Presence of 2 sets of signals in the NMR spectra of the complex could be explained in terms of steric hindrance: intramolecular rotation around S–C bond in the bridging ligand is inhibited by unfavourable interaction of the ligand with the carbonyl environment and results in high rotational barrier. Even in the case of the



Scheme 3.

less bulkier derivative  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-NHCHMeCOOEt})$  estimation of the intramolecular rotation barrier resulted in the value of about 55 kJ/mol [7].

In boiling benzene complex **6** is completely converted for 5 h to a number of products, cluster **7** being the main component. IR and NMR spectroscopy prove the new compound is the  $\text{Os}_3(\text{CO})_{10}(\mu\text{-SR})$  type cluster. IR spectrum of the new cluster indicates no O–H group but demonstrates the presence of a ketonic group, whereas  $^{13}\text{C}$  NMR spectrum shows the signal of organic carbonyl (202.37 ppm). Other parts of NMR spectra are similar to those of cluster **6**, so we assume the new cluster **7** is a tautomeric form of cluster **6** (Scheme 3).

Similar tautomerism for the non-coordinated compounds is known for the series of 5-hydroxy-4,5-dihydropyrazoles [8], however linear isomers can be detected only in polar solvents (like DMSO) or in case of strong electron withdrawing substituents in the hydropyrazole moiety. As the tautomeric rearrangement **6**→**7** is irreversible, the driving force of the transformation seems to arise from the decrease of steric hindrance due to formation of longer and flexible linker between  $\text{C}_{10}$  terpenoid unit and bulky  $\text{Os}_3(\text{CO})_{10}(\mu\text{-S-})$  cluster fragment.

When complex **7** is exposed to the air, a slow transformation **7**→**8** takes place. IR spectrum (CO stretching region) and  $^1\text{H}$  NMR spectrum (signal of the  $\mu\text{-H}$  ligand

–17.19 ppm) of the new complex **8** prove the presence of the moiety  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-S-})$  in the molecule. However proton and carbon NMR spectra of the organic unit differ strongly from the spectra of the ligand in clusters **6** and **7** and demonstrate disappearance of gem-dimethylcyclopropane unit and formation of the group  $-\text{CMe}_2\text{X}$  ( $\text{X}=\text{O}$  or  $\text{N}$ ) instead. Careful analysis of 2D C–H correlation NMR spectra of the new complex (See Figs. 2 and 3) allowed us to suppose the compound to be hydroxyl epoxide **8**. Formation of the small heterocycle (oxirane) is confirmed by the value of the  $\text{C}^7\text{-H}$  coupling constant in the carbon-13 NMR spectrum ( $^1J_{\text{H-C}}=191$  Hz), which is characteristic for epoxides [9], and by chemical shifts of the  $\text{C}^3$  and  $\text{C}^7$  signals (77.44 and 64.43 ppm respectively) [9]. IR spectrum of the compound **8** proves the formation of hydroxyl ( $\nu_{\text{O-H}}=3615$   $\text{cm}^{-1}$ ) and oxirane ( $\nu_{\text{C-O}}=1280$   $\text{cm}^{-1}$ ) [10].

Conversion **7**→**8** is induced by a silica gel support. Thus, when compound **7** has been formed, passing of the air through the reaction mixture for two days resulted only in some decomposition of the complex. The stirring the reaction mixture with Silicagel under argon atmosphere for two days has no results, whereas presence both Silicagel and air results in rapid decomposition of **7**. Exposition of isolated by TLC **7** solution to

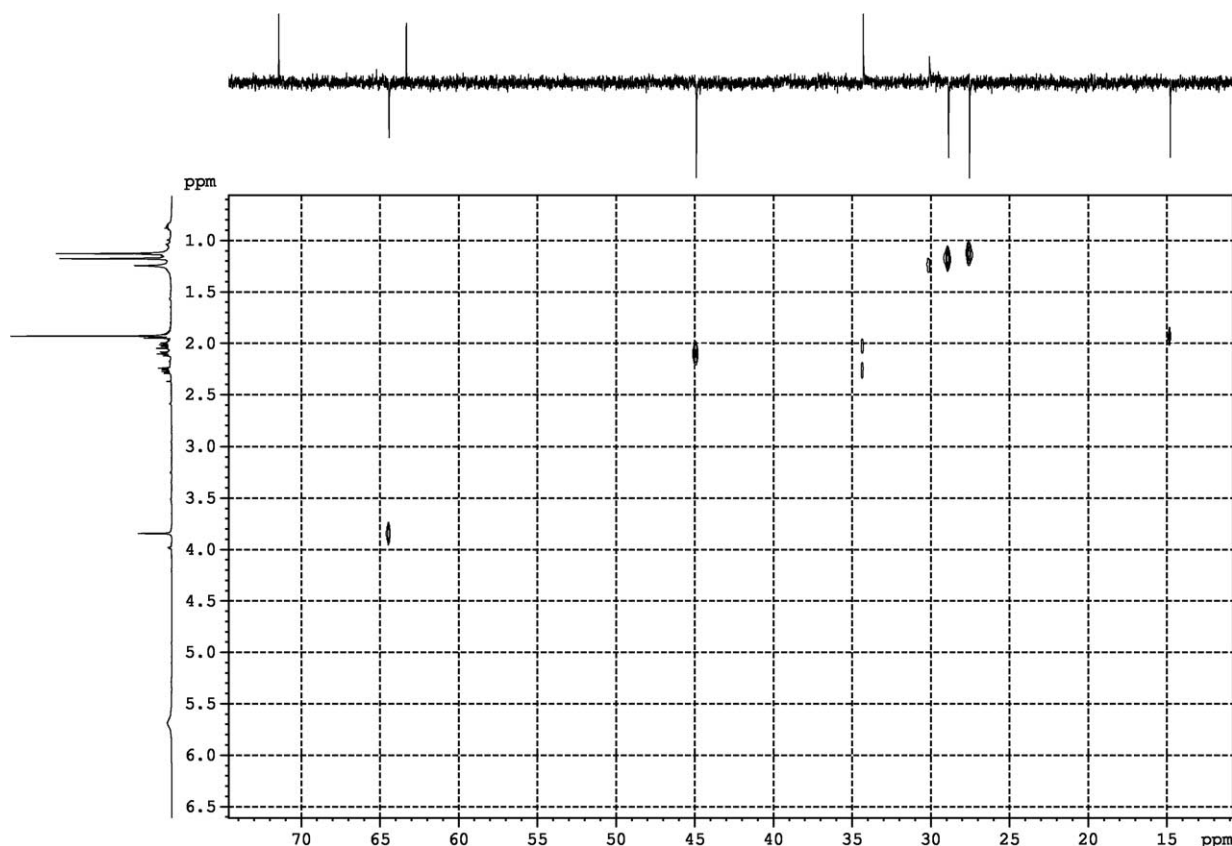


Fig. 2. D NMR spectrum of **8**: heteronuclear  $^{13}\text{C}\text{-}^1\text{H}$  correlation at the direct spin–spin coupling constants ( $J=135$  Hz).

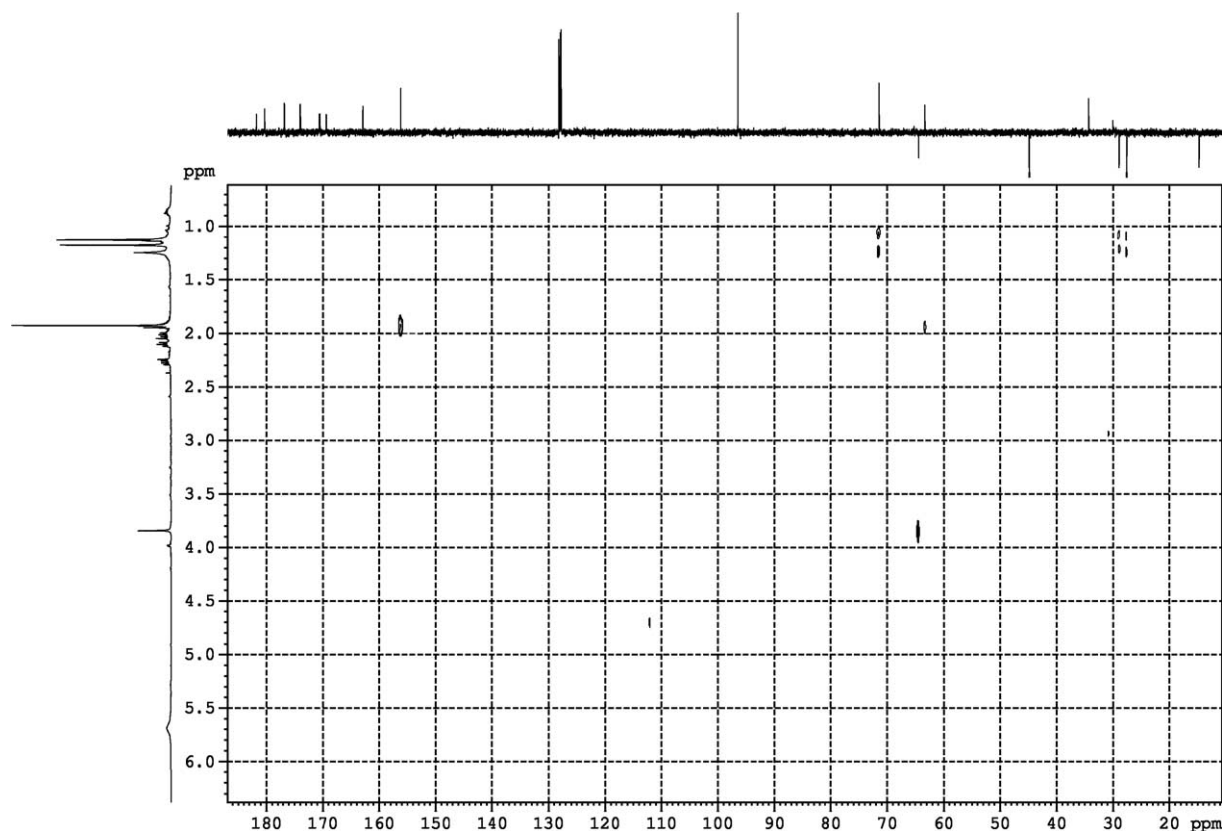


Fig. 3. D NMR spectrum of **8**: heteronuclear  $^{13}\text{C}$ - $^1\text{H}$  correlation at the long-range spin-spin coupling constants ( $J=10$  Hz).

air results in slow conversion **7**  $\rightarrow$  **8**. The transformation is completed in five days.

It should be stressed that opening of cyclopropanes is rather usual, although the oxidative cleavage of gem-dimethylcyclopropane moiety in complex **7** seems to be exceptional. Radical oxidation of the medium ring cycloalkanes with  $\text{O}(\text{P})$  results in epoxides in small yields and shows the possibility of oxidative transformation of non-functionalised cycloalkanes under quite drastic conditions [11]. Reaction **7**  $\rightarrow$  **8** demonstrates the unique example of activation of an organic ligand on a cluster core as a very complex oxidative process which takes place under mild reaction conditions.

### 3. Experimental

#### 3.1. General

All reactions were carried out in freshly distilled solvents and under argon atmosphere. The solvents were removed from reaction mixtures at the reduced pressure. Commercially available thiosemicarbazide and  $\text{Os}_3(\text{CO})_{12}$  were used without additional purification. 4-(2-Methoxyphenyl)thiosemicarbazide was prepared by

treatment of 1-isothiocyanato-2-methoxybenzene with an excess of hydrazine hydrate. The starting reagents –  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  (**2**) [12], and (1*R*,5*R*)-6,6-dimethyl-2-(1-hydroxyethylidene)-bicyclo[3.1.0]hexan-3-one (“diketone”) [13] were obtained by published procedures. Analytical and preparative thin layer chromatography (TLC) were performed on ready-made Silufo<sup>®</sup> plates. IR spectra were obtained using Specord IR-75 spectrometer. NMR spectra were recorded at ambient temperature on Bruker AM-400 ( $^1\text{H}$  400.13 MHz,  $^{13}\text{C}$  100.61 MHz) and Bruker DRX-500 ( $^1\text{H}$  500.13 MHz,  $^{13}\text{C}$  125.75 MHz) spectrometers, using the solvent signals as internal standard. Signals were assigned using the  $^{13}\text{C}$  NMR spectra recorded in the  $J$ -modulation mode (noise proton decoupling, opposite phase for signals from atoms with even and odd numbers of added protons with adjusting to the constant  $J=135$  Hz) and from data of the two-dimensional spectra (see Fig. 2): (1)  $J^1\text{H}$ - $^1\text{H}$  homonuclear correlation, (2)  $^{13}\text{C}$ - $^1\text{H}$  heteronuclear correlation on direct spin-spin coupling constants ( $J=135$  Hz), and (3)  $^{13}\text{C}$ - $^1\text{H}$  heteronuclear correlation on long-range spin-spin coupling constants ( $J=10$  Hz) (see Fig. 3). The numbering of the C-atoms shown in Scheme 1 does not coincide with the numbering of the system according to IUPAC. This numbering scheme is usual for this type of derivatives and given for NMR interpretation only.



The mass spectra were measured on Aligent 1100 HPLS-MS using electrospray ionisation technique and Finnigan MAT 8200 (EI, 70 eV) spectrometers. The optical rotation was measured on Polamat A polarimeter at the wavelength of 578 nm.

### 3.2. (3aR, 3bR, 4aR, 5aS)-5a-Hydroxy-3,4,4-trimethyl-3a,3b,4,4a,5,5a-hexahydrocyclopropa[3,4]-cyclopenta[1,2-c]pyrazole-1-carbothioic acid amide

Thiosemicarbazide (0.88 g, 4.5 mmol) was added to a stirred solution of the diketone (0.66 g, 4 mmol) in a mixture of methanol (25 ml) and glacial AcOH (1 ml). The reaction mixture was heated and allowed to stay under reflux for 3–4 h. The solvent was distilled off at reduced pressure; the residue was treated with water (40 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×30 ml). The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to give the crude product that was then purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, benzene) followed by crystallization from MeCN–CHCl<sub>3</sub> to give an analytical sample of the title compound (yield 78%) as pale-yellow crystals with m.p. 162–165 °C (dec., MeCN–CHCl<sub>3</sub>) and  $[\alpha]_{578}^{20}$  –224 (*c* 0.95, CHCl<sub>3</sub>). MS, *m/z*: 239.11036 (M<sup>+</sup>, C<sub>11</sub>H<sub>17</sub>N<sub>3</sub>OS, requires 239.10923). UV (EtOH)  $\lambda_{\max}/\text{nm}$  335 ( $\epsilon$  530), 236 ( $\epsilon$  10500), 272 ( $\epsilon$  21400).

### 3.3. Interaction of Os<sub>3</sub>(CO)<sub>11</sub>(NCMe) with acetone-4-(2-methoxy-phenyl)thiosemicarbazone

A mixture of Os<sub>3</sub>(CO)<sub>11</sub>(NCMe) (**1**) (212 mg, 0.23 mmol) and acetone-4-(2-methoxy-phenyl)thiosemicarbazone (82 mg, 0.35 mmol) in 40 ml of benzene was heated at reflux for 8 h. Then the reaction mixture was evaporated to dryness and the residue was chromatographed on Siluphol plates, using petroleum ether:benzene:acetone=7:3:0.3 mixture as eluent. Complex **5** was obtained as a yellow amorphous solid (*R<sub>f</sub>*~0.7, 185.2 mg, 74%). Anal. Calc. for C<sub>20</sub>H<sub>15</sub>N<sub>3</sub>O<sub>10</sub>Os<sub>3</sub>S: C, 22.60; H, 1.14; Os, 53.82. Found: C, 21.72; H, 0.96; Os, 54.44. MS, *m/z*: 1064 (Os<sub>3</sub>C<sub>20</sub>N<sub>3</sub>O<sub>10</sub>Os<sub>3</sub>S, <sup>192</sup>Os, M<sup>+</sup>). The single-crystals of **5** were obtained by crystallization from benzene.

### 3.4. Interaction of Os<sub>3</sub>(CO)<sub>11</sub>(NCMe) with (3aR,3bR,4aR,5aS)-5a-hydroxy-3,4,4-trimethyl-3a,3b,4,4a,5,5a hexahydro-cyclopropa[3,4]cyclopenta[1,2-c]pyrazole-1-carbothioic acid amide

(a) A mixture of Os<sub>3</sub>(CO)<sub>11</sub>(NCMe) (85.5 mg, 0.0929 mmol) and **4** (16.7 mg, 0.0697 mmol) in 2 ml CD<sub>2</sub>Cl<sub>2</sub> was stirred at ambient temperature. On the TLC data after dissolution of all reagents in the solution there is the only complex **6**, except of starting cluster remains.

(b) A mixture of Os<sub>3</sub>(CO)<sub>11</sub>(NCMe) (97 mg, 0.105 mmol) and **4** (39 mg, 0.163 mmol) in 50 ml of benzene was stirred at room temperature for long as all starting cluster was consumed (~10 min). Then the reaction mixture was heated under reflux for 5 h, evaporated to dryness and the residue was chromatographed on Siluphol plates using petroleum ether:benzene:acetone=5:3:0.5 mixture as eluent. A bright yellow fraction with *R<sub>f</sub>*~0.2 was extracted by acetone to give **7** (60 mg, 52.2%).

(c) Solution of **7** (120 mg, 0.11 mmol) in flask filled with air was standing at room temperature for six days. Then solution was evaporated to dryness and the residue was chromatographed on Siluphol plates, eluent petroleum ether:benzene:acetone=5:3:0.5. A pale-yellow fraction was extracted with acetone to give **8** (84 mg, 68%). Anal. Calc. for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>13</sub>Os<sub>3</sub>S: C, 22.48; H, 1.53; Os, 50.86. Found: C, 22.71; H, 1.47; Os, 52.60. MS, *m/z*: 1126 (C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>13</sub>Os<sub>3</sub>S, <sup>192</sup>Os, M<sup>+</sup>).

### 3.5. X-ray analysis of **5**

The structure of **5** was solved by X-ray structural analysis. Crystal data: C<sub>20</sub>H<sub>15</sub>N<sub>3</sub>O<sub>10</sub>Os<sub>3</sub>S, *F.W.* 1060.01, monoclinic, space group *P2<sub>1</sub>/c*, *a*=9.1943(12), *b*=22.653(3), *c*=12.8709(19) Å,  $\beta$ =102.200(10), *V*=2620.2(6) Å<sup>3</sup>, *Z*=4, *d<sub>c</sub>*=2.687 g cm<sup>-3</sup>,  $\mu$ =14.649 cm<sup>-1</sup>. Data were measured at room temperature on four-cycle Nonius CAD4 diffractometer using Mo K $\alpha$  radiation ( $\lambda$ =0.7107 Å) from orange plate crystal of 0.40.36×0.04 mm size. Total 4888 reflections was measured up to  $2\theta_{\max}$ =50°, of which 4588 are unique, *R<sub>int</sub>*=0.0281. Absorption corrections were applied by integration from crystal shape, *T*=0.0370–0.5189. Structure was solved by direct methods and refined by full-matrix least-squares method in anisotropic for all non-hydrogen atoms approximation using SHELX 97 program set. Final residuals are: *R<sub>1</sub>*=0.0217 for 3374 *F<sub>hkl</sub>* ≥ 4 $\sigma$ (*F*), *wR<sub>2</sub>*=0.0508, GoF=0.897 for all unique reflections.

## 4. Supplementary material

Atomic coordinates, details of diffraction experiment and full tables of bond distances and angles for **5** are deposited in Cambridge Crystallographic Data Centre, CCDC No. 193254 for compound.

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