Synthesis and protonation of an $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CCMe_2OMe)$ cluster

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Triosmium cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CCMe_2OMe)$ (**1**) was obtained by treating $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ with $LiC{\equiv}CCMe_2OMe$. The reaction of cluster **1** with $HBF_4 \cdot Et_2O$ at −60 °C leads to the cationic complex $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\sigma,\eta^2\text{-}C{=}C{=}CMe_2)]^+BF_4^-$ (**2**) with an allenylidene ligand. The ^1H and ^{13}C NMR spectra of complex **2** reveal the temperature dependence caused by migration of hydrocarbon and carbonyl ligands. Thermodynamic parameters were obtained for the exchange process of the allenylidene ligand.

Key words: triosmium clusters, osmium carbonyls, protonation, acetylenide, carbocation.

It is known that coordination of propargyl alcohol or its derivatives with one,[1–9] two,[10–14] or three metal atoms[15–17] results in the formation of complexes that are convenient objects for the synthesis of cationic compounds and the study of problems of stabilization of an α-carbenium ion by metallic systems with different numbers of nuclei.

Recently, we have reported[16] on cationic propargyl complexes obtained on protonation of the triosmium clusters $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}2\sigma,\eta^2\text{-}HC_2R)$ and $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\sigma,2\eta^2\text{-}C{\equiv}CR)$ ($R = CH_2OH$, CMe_2OH, $C(Me){=}CH_2$) containing μ_3-alkyne and μ_3-acetylenide ligands, respectively. In this work, we present the data on the synthesis and protonation of a μ_2-acetylenide cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CCMe_2OMe)$ (**1**) in which the propargyl group forms a bridge between two osmium atoms.

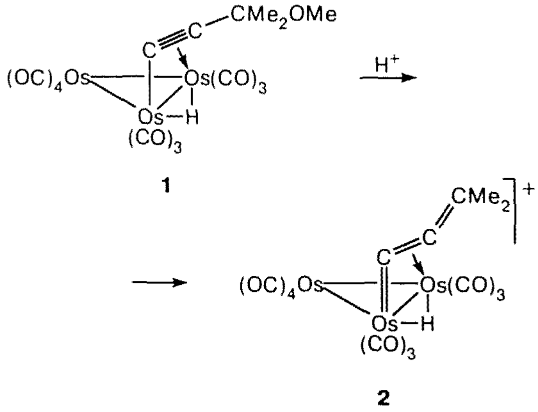
Results and Discussion

Cluster **1** was obtained using a procedure developed previously[18,19] for the synthesis of osmium clusters with the σ,π-coordinated acetylenide ligand. Cluster **1** was obtained in 50% yield in the reaction of the chlorohydride complex $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ with $LiC{\equiv}CCMe_2OMe$. Its structure was confirmed by IR and ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of compound **1**, geminal methyl groups are equivalent and appear as a single signal, which is evidence for the fast $\sigma,\pi \rightleftharpoons \pi,\sigma$ exchange of the bridge acetylenide ligand between two osmium atoms. A similar exchange has been established previously for the $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CPh)$ complex.[18,20] For both the phenylacetylenide cluster and compound **1**, the fluctuation of the hydrocarbon ligand cannot be "frozen out" even at −100 °C. Only broadening of the signal of methyl groups is observed in the case of **1**.

We have undertaken an attempt to obtain an analog of cluster **1** from the corresponding lithium acetylenide $LiC{\equiv}CCH_2OMe$. However, the target product $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CCH_2OMe)$ turned out to be unstable under the reaction conditions, and only the known complex $Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}$,[21] which was identified by the ^1H NMR spectrum, was isolated as a sole product from the reaction mixture.

Then we studied protonation of **1** with $HBF_4 \cdot OEt_2$ in CD_2Cl_2 at −90 to −60 °C. After addition of the acid to a solution of cluster **1** at −60 °C, a new set of signals appears in the ^1H NMR spectrum: at −19.82 ppm for the hydride ligand and at 2.64 and 2.18 ppm for two nonequivalent methyl groups, which testifies to the formation of the cationic cluster **2** (Scheme 1). The ^{13}C NMR spectrum of the same solution at −90 °C

Scheme 1



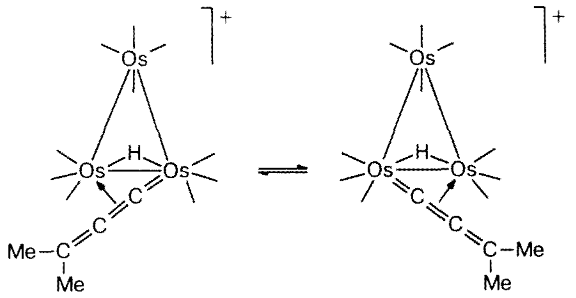
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2990—2992, December, 1996.

exhibits signals at 25.34 and 25.68 ppm for nonequivalent methyl groups, at 120.28, 153.08, and 176.79 ppm for γ-, β-, and α-carbon atoms, respectively, from the hydrocarbon ligand, and 10 signals at 157.51, 159.56, 162.99, 165.10, 165.44, 166.57, 167.80, 168.65, 170.71, and 171.18 ppm for terminal CO groups. Based on the spectral data, the structure of the Os_3 cluster with the μ_2-allenylidene ligand was assigned to the cationic complex.

It is noteworthy that this is the first example of coordination of this ligand type with a trimetallic system. Only a single example of existence of this ligand in the neutral binuclear complex $CpMo_2(CO)_4(\mu_2\text{-}C{=}C{=}CMe_2)$ is known to date.[22]

The ^1H and ^{13}C NMR spectra of cluster **2** exhibit a temperature dependence. As the temperature of the solution increases, the ^1H NMR spectrum exhibits a broadening of signals of the methyl groups, and at −5 °C the collapse is observed, which can be explained by the existence of the $\sigma,\pi \rightleftharpoons \pi,\sigma$ exchange of the bridge allenylidene ligand averaging the stoichiometric surrounding of two osmium atoms (Scheme 2).

Scheme 2



This is in accordance with the observation of one pair of satellites near the hydride signal with the spin coupling constant $^1J_{^{187}Os-^1H}$ equal to 31 Hz.[20,23] A similar fluctuation has been observed previously for dimolybdenum complexes $Cp_2Mo_2(CO)_4(\mu\text{-}C{=}CMe_2)$ and $Cp_2Mo_2(CO)_4(\mu\text{-}C{=}C{=}CMe_2)$ with vinylidene and allenylidene ligands, respectively.[22]

The following thermodynamic parameters were obtained for the process observed: $E_a = 12.4\pm0.4$ kcal mol^{-1}, $\log A = 12.27\pm0.3$, $H = 12.0\pm0.4$ kcal mol^{-1}, $S^{\#} = -3.8\pm1.5$ e.u., $G^{\#}_{298} = 13.1$ kcal mol^{-1}.

The cationic complex **2** is thermally unstable and completely transforms to the neutral nonacarbonyl cluster $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\sigma,2\eta^2\text{-}C{\equiv}CCHMe_2)$ (**3**) as the temperature of the solution increases to +10 °C. The structure of **3** was established from the IR and ^1H NMR spectral data, whose parameters are close to those for the related $M_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\sigma,2\eta^2\text{-}C{\equiv}CR)$ complexes (M = Ru, Os).[16,17,24] The temperature dependence of the ^{13}C NMR spectra is of complex character, because the processes of exchange of hydrocarbon and carbonyl ligands overlap. At −90 °C, 10 signals for the terminal CO groups appear in the ^{13}C NMR spectrum of **2**, which is in accordance with the statistical asymmetric structure of the cluster. Already at −86 °C, three of them (170.71, 168.05, and 157.57 ppm) begin to broaden, and the fourth signal enters the exchange when the temperature increases further. This signal collapses at −50 °C. The spectral picture observed indicates that a localized two-step exchange of carbonyl ligands occurs at a unique osmium atom. The exchange of three CO groups is lower in energy. This phenomenon is not observed very often in trimetallic systems. We managed to observe this process for the $Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}C\text{—}C(Ph){=}C(Ph)Re(CO)_4PMe_2Ph\}$ carbyne complex.[25] When the temperature increases, the fourth carbonyl ligand is included in the exchange. A similar two-step exchange of CO ligands at the $Os(CO)_4$ unit has been established previously in the $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}COEt)$ cluster with the bridge alkoxycarbyne ligand.[26]

As the temperature of the solution of **2** increases further to −20 °C, the $\sigma\pi \rightleftharpoons \pi\sigma$ fluctuation of the organic ligand begins, and the ^{13}C NMR spectrum had to contain three signals in a 2 : 2 : 2 ratio of intensities (due to the paired averaging at the $Os(CO)_3$ units). However, a single signal at 166.04 ppm appears in the spectrum at −10 °C in our case. The position of this signal indicates that it is a result of averaging of all 10 CO groups. Since the localized exchange combined with the fluctuation of the hydrocarbon ligand cannot result in the complete averaging of 10 signals, one can assume that the third exchange process also occurs in this case. One of the variants suggested for the ruthenium $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CCMe_3)(CO)_9$ cluster[27,28] can take place, namely: (*a*) combination of the rotation of the hydrocarbon ligand with the migration of the hydride ligand, (*b*) pyramidal rotation of CO groups in two equivalent $Os(CO)_3$ units. In our case, variant *b* is preferable, because variant *a* is inappropriate for the migration of the hydride ligand. As has been mentioned above, the spin coupling value $^1J_{^{187}Os-^1H} = 31$ Hz lies within the range typical of clusters with fluctuating hydrocarbon and rigidly bound hydride ligands.

It should be mentioned in conclusion that, unlike the $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}2\sigma,\eta^2\text{-}HC_2R)$ and $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\sigma,2\eta^2\text{-}C{\equiv}CR)$ clusters (R = CH_2OH, CMe_2OH, $C(Me){=}CH_2$) previously studied, in which the μ_3-propargyl system generates cationic complexes with the propargyl type ligands, the protonation of the $Os_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}\sigma,\eta^2\text{-}C{\equiv}CCMe_2OMe)$ cluster (**1**) with the μ_2-propargyl system results in the allenylidene ligand in the cationic complex **2**.

Experimental

All experiments were carried out in an atmosphere of argon using anhydrous solvents.

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument (CD_2Cl_2). IR spectra were obtained on a Specord IR-75 spectrophotometer in *n*-hexane.

$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CCMe_2OMe)$ (1). A solution of $LiC{\equiv}CCMe_2OMe$, obtained at −78 °C from $HC{\equiv}CCMe_2OMe$ (0.04 mL, 0.6 mmol) in THF (5 mL) and a 1.3 *M* solution of BuLi in hexane (0.28 mL), was added dropwise to a solution of $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ (0.2 g, 0.23 mmol) in hexane (50 mL) cooled to −40 °C. The mixture was stirred for 1 h at −25 °C, then several drops of water were added, and the temperature of the reaction mixture was increased to room temperature. The organic layer was washed with water to the neutral reaction, and the aqueous layer was extracted with ether. The combined extracts were dried with $MgSO_4$. The solvent was evaporated, and the residue was chromatographed on a column with silica gel 40—100 mm in hexane—benzene (3 : 1). After the solvent was evaporated, compound **1** (0.10 g, 50%) was obtained as bright-yellow crystals. IR, $\nu(CO)/cm^{-1}$: 2110 w, 2070 v.s, 2046 w, 2028 w, 2020 s, 2007 m, 1992 w, 1985 w. ^1H NMR, δ: −16.91 (s, 1 H, μ-H); 1.59 (s, 6 H, CMe_2); 3.09 (s, 3 H, OMe). ^{13}C NMR, δ: 29.1 (Me); 50.8 (CMe_2); 73.1 (C=); 77.8 (=C).

$Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\sigma,2\eta^2\text{-}C{\equiv}CCHMe_2)$ (3). A solution of cationic complex **2**, obtained by the addition of three drops of $HBF_4 \cdot OEt_2$ to a solution of compound **1** (0.1 g, 0.11 mmol) in CD_2Cl_2 (2 mL) at −60 °C, was poured in ice-cold water. The aqueous layer was extracted with ether. The organic extracts were combined, washed with water to the neutral reaction, and dried with $MgSO_4$. The solution was evaporated, and the residue was chromatographed on a column with silica gel in hexane—benzene (3 : 1). After removal of the solvent and recrystallization from hexane, pale-yellow crystalline compound **3** (0.05 g, 50%) was obtained. IR, $\nu(CO)/cm^{-1}$: 2098 m, 2072 s, 2052 s, 2020 s, 2008 v.s, 1989 m, 1946 v.w. ^1H NMR, δ: −23.4 (s, 1 H, μ-H); 1.3 (d, 3 H, $^3J_{H,H}$ = 6.7 Hz); 2.9 (sep, 1 H, $^3J_{H,H}$ = 6.8 Hz).

The authors are grateful to M. V. Galakhov for recording the spectra and calculation of thermodynamic parameters for exchange of the acetylenide ligand.

This work was financially supported by the Russian Foundation for Basic Research (Projects Nos. 94-03-08167 and 94-03-08338).

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Received June 17, 1996