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The rearrangement of the uncoordinated allyl fragment of the carboxamide ligand in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCNHCH}_2CH{=}CH_2)$ cluster

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Abstract

The rearrangement of the uncoordinated allyl fragment of the complex carboxamide ligand in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCNHCH}_2\text{-}CH{=}CH_2)$ (**1**) at room temperature has been observed. A migration of the terminal double bond to the α-position in **1** leads to the formation of four novel isomeric clusters $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCNHCH}{=}CHCH_3)$ (**2a–d**). Based on IR and ^{1}H NMR data, a conclusion has been made that the formation of isomers is attributed to the rotation of the ligand about the C=C and N–C(O) bonds.

Keywords: Allyl rearrangement; Triosmium carbonyl clusters; Cluster isomers

1. Introduction

Various types of double bond migration in olefins and their derivatives have been extensively studied for many years because of their synthetic role in the preparation of numerous organic compounds and materials. In many cases such processes are carried out only in the presence of homogeneous or heterogeneous catalysts such as acids, bases or metal complexes [1–4]. Isomerization of allylamines and allylamides has been examined to a small extent compared with other functionalised olefins. No report has previously been devoted to the allylamine, per se. There are a few reports on double bond migrations in secondary allylamines [5], whilst isomerization of tertiary *N*-substituted allylamines has been studied much more [6–9]. Generally, such reactions proceed stereospecifically and lead to the cis-isomer [7,8]. During the isomerization, the α-methylene unit needs to be deprotonated so that the use of strong bases, such as alkaline, metal amides or alkoxides, are required [6–8]. Metal complex catalysts are used for the isomerization of both tertiary allylamines [10] and allylamides [11]. In the latter case, the reactions catalyzed with Rh(II), Ru(II), and Fe(0) complexes proceed as a prolonged boiling in toluene or xylene. In general, isomerization of allylamines suggests a coordination of both olefinic and amino groups on a metal atom. As for *N*-allylamides, coordination through both the carbonyl oxygen atom and C=C double bond is also assumed [11].

This paper reports the rearrangement of the uncoordinated allyl fragment of the complex ligand in the triosmium cluster $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCNHCH}_2CH{=}CH_2)$ (**1**) at ambient temperature.

2. Results and discussion

During the development of synthetic routes to clusters which would contain an uncoordinated C=C double bond (cluster monomers), a number of trinuclear hydridocarbonyl clusters, $(\mu\text{-H})M_3(CO)_{10}(\mu\text{-SCH}_2CH{=}CH_2)$ (M = Ru, Os), $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHCH}_2CH{=}CH_2)$ and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCNHCH}_2CH{=}CH_2)$ (**1**) have been obtained with the allyl fragment involved in more complex ligands [12]. Our thin-layer chromatography (t.l.c.), IR and ^{1}H NMR studies revealed that four novel species are formed from **1** in the solution over several days. However, the compounds formed could not be isolated as individual species. T.l.c. has demonstrated that only two coloured bands were developed. These bands were eluted and the resulting solutions were characterized by IR, ^{1}H NMR, mass spectra and analytical data (see Fig. 1, Table 1 and Section 3).

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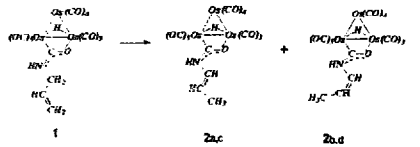
From data obtained, a general scheme of the transformation of (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH$_2$CHCH$_2$) that occurred can be presented as follows:



For both eluted fractions the IR spectra in the carbonyl stretching region are very similar to each other and to that of complex **1**. Therefore, the types of complex formed are believed to be the same as (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH$_2$CH=CH$_2$) (**1**). However, for both fractions, two relatively sharp bands at 3443, 3351 and 3433, 3345 cm^{-1} of unequal intensity have been observed in the NH stretching region, instead of the single NH-vibration mode at 3433 cm^{-1} in **1**. The relative intensity within these double bands remains essentially unchanged in a broad range of concentrations. Thus, it is reasonable to assume that two pairs of isomers have been obtained as a result of some ligand transformation.

Particular attention is drawn to the fact that each isomeric pair has only one ν(C=C) stretching band (1669 cm^{-1} and 1673 cm^{-1} for **2a**,**2c** and **2b**,**2d** respectively), which is shifted with respect to that for initial **1** (1641 cm^{-1}). We assume that such changes may be consistent with a migration of the double bond from the terminal to the α-position relative to the NH group in the allyl fragment of (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH$_2$CH=CH$_2$) (**1**) resulting in (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH=CHCH$_3$) (**2(a–d)**). If so, the separable isomeric pairs **2a**,**2c** and **2b**,**2d** could be attributed to cis/trans isomerism of the –CH=CH– fragment.

The main evidence for this conclusion is provided by ^{1}H NMR spectroscopy (Fig. 1, Table 1). The ^{1}H NMR spectra of each isomeric pair (Fig. 1, (**B**) and (**C**)) exhibit two sets of similar-looking features which differ in their intensities and chemical shifts. By convention, the major components in the spectra were attributed to isomers **2a**,**2b**, and the minor components were at-

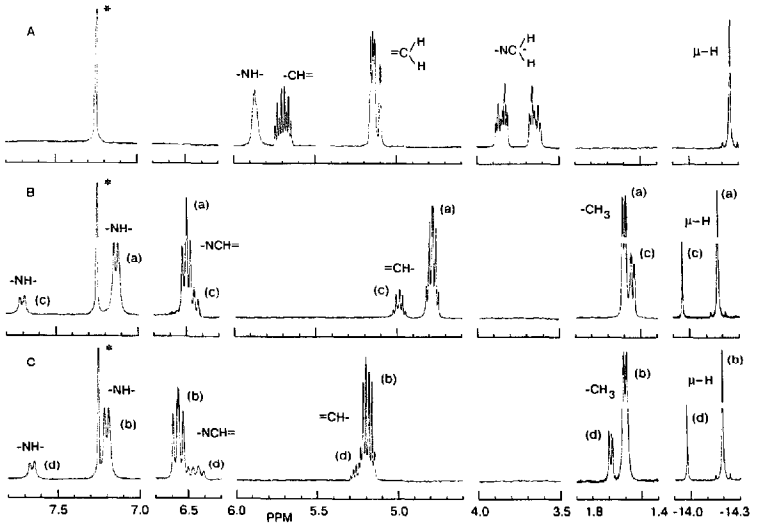


Fig. 1. ^{1}H NMR spectra of (A) the starting complex (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH$_2$CH=CH$_2$) and the four isomers of the resulting complex (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH=CHCH$_3$). (B) Spectrum of the two inseparable isomeric complexes, **a** and **c**, both with cis orientation of the olefinic protons and with higher R_f on t.l.c. (C) Spectrum of the two inseparable isomeric complexes, **b** and **d**, both with trans orientation of the olefinic protons. Recorded at 400 MHz at room temperature in $CDCl_3$ solutions. The $CHCl_3$ resonances are denoted by the asterisk.

Table 1
Spectroscopic data for the coplex **1** and isomers **2a–d**

IR (cm^{-1}) [a]	^1H NMR [b]
(μ-H)Os_3(μ-O=CNHCH$_2$CH=CH$_2$)(CO)$_{10}$ **(1)**	
ν(CO) [c]: 2106w, 2067s, 2056s, 2022s, 2010s, 2006sh, 1993s, 1986m, 1978m, 1955vw, 1947vw ν(C=C) [d]: 1641w ν(NH) [d]: 3440m	5.87 (br, t (5.1), 1H, NH), 5.7 (m (5.5, 6.2, 12.8), 1H, –CH=), 5.15 (m (1.1, 4.1, 6.2, 12.8), 2H, =CH'H"), 3.85 (m (1.1, 5.1, 5.5, 15.1), 1H, NCH'), 3.65 (m (1.1, 5.1, 5.5, 15.1), 1H, NCH"), −14.26 (s, 1H, μ-H)
(μ-H)Os_3(μ-O=CNHCH=CHCH$_3$)(CO)$_{10}$ **(2a,c)** [c]	
ν(CO) [c]: 2106w, 2067s, 2056s, 2022s, 2013s, 2008sh, 1991s, 1983m, 1973m, 1958vw, 1946vw ν(C=C) [d]: 1669w ν(NH) [d]: 3443m, 3351w	7.13 (br d (10.5), 1H, NH), 6.5 (m (1.69, 8.97, 10.5), 1H, NCH), 4.78 (dq, (7.09, 8.97), 1H, =CH–), 1.60 (dd (1.69, 7.09), 3H, CH_3), −14.17 (s, 1H, μ-H) 7.71 (br d (1.68, 10.5), 1H, NH), 6.45 (m (1.68, 8.91, 10.5), 1H, NCH), 4.99 (dq (7.09, 8.97), 1H, =CH–), 1.55 (dd (1.68, 7.0), 3H, CH_3), −13.96 (s, 1H, μ-H)
(μ-H)Os_3(μ-O=CNHCH=CHCH$_3$)(CO)$_{10}$ **(2b,d)** [c]	
ν(CO) [c]: 2106w, 2067s, 2056s, 2022s, 2013s, 2008sh, 1992s, 1984m, 1973m, 1959vw, 1950vw; ν(C=C) [d]: 1673w ν(NH) [d]: 3433m, 3345w	7.20 (br d (10.5), 1H, NH), 6.56 (m (1.5, 10.5, 14.1), 1H, NCH), 5.19 (dq (7.1, 14.1), 1H, =CH–), 1.59 (dd (1.5, 7.1), 3H, CH_3), −14.19 (s, 1H, μ-H) 7.65 (br d (10.5), 1H, NH), 6.43 (m (1.5, 10.5, 13.8), 1H,NCH), 5.25 (dq (6.6, 13.8), 1H, =CH–), 1.69 (dd (1.5, 6.6) 3H, CH_3), −13.98 (s, 1H, μ-H)

[a] Abbreviations: s = strong, w = weak, v = very, sh = shoulder. [b] From $CDCl_3$ solution; data given as chemical shift (δ) (multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dq = doublet of quartets, m = multiplet, br = broad) (coupling constants (Hz)), relative intensity, assignment). [c] From hexane solution. [d] From CCl_4 solution. [e] Mixture of two isomers, the signals in ^1H NMR spectra were assigned to complexes **2a**, **2c** and **2b**, **2d** in correspondence with their intensities. More intensive signals were ascribed to **2a** and **2b**.

tributed to the isomers **2c,2d**. The proton resonance assignments in **2(a–d)** were made on the basis of the chemical shift values and the coupling constants $J(^1H–^1H)$ (Table 1) drawn out of selective $^1H–\{^1H\}$ decoupling experiments. These data confirmed that the conversion of **1** to complexes **2(a–d)** has been caused by a migration of the double bond. This conclusion is supported by a disappearance of the N–CH_2 resonance and the appearance of four resonances of the CH_3 groups. The broad triplet of N–H is converted to two pairs of doublets which are shifted 1.2–1.9 ppm downfield (see Fig. 1).

The chemical shift of the μ-H resonance, which is generally very sensitive to the nature of a counterlying bridging ligand X in Os_3(μ-H)$(CO)_{10}$(μ-X) clusters [13–16], is almost unaffected by the conversion of **1** to **2(a–d)**. Therefore, we suggest the retention of the initial (μ-H)Os_3(μ-OCNH–) unit in **2(a–d)** isomers. The coupling constant values for the –NCH=CH– unit in clusters **2(a–d)** (9 Hz and 14 Hz for **2a,2c** and **2b,2d** respectively) are indicative of the cis and trans proton arrangement around the double bond in –NCH=CH– fragment.

The main difference within **2a,2c** (cis isomers), as well **2b,2d** (trans isomers), consists of the chemical shift variations of their NH-resonances (7.13 and 7.71 ppm for **2a**, **2c**; 7.2 and 7.65 ppm for **2b,2d**) (see Fig. 1, (B) and (C)). The different chemical shifts of the NH-resonances probably originated from the different orientations of the NH-proton relative to the bridging C=O or –CH= groups. Taking into account the NH–CH coupling constants, which are essentially the same for all complexes **2(a–d)** (ca. 10.5 Hz), the relative orientation of the NH and the CH groups is suggested to be always trans with no rotational isomerism about this bond. Owing to this, we have explained the chemical shift difference of the NH-resonances within **2a,2c** and **2b,2d** by a restricted rotation around the N=C(O) bond.

In initial (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH$_2$CH=CH$_2$) **(1)**, as well as in a number of analogous osmium and ruthenium clusters containing μ-O=CNHR ligand [17–20], the single resonance of the NH-group has been observed. This might imply either a rapid rotation of the NHR unit around N=C(O) bond or a complete hindering of such rotation. It has previously been reported [17] that in the related (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH$_2$CH$_3$) triosmium cluster the restricted rotation of the NHCH$_2$CH$_3$ unit of the ethylcarboxamide ligand about the N=C(O) bond causes a chemical shift difference in methylene proton resonances. However, the authors of Ref. [17] have observed a single NH proton resonance in the same cluster which is difficult to explain from the point of view of the restricted rotation of the ligand

about the N=C(O) bond. We believe that the double bond migration in the allyl residue of **1** makes possible a restricted rotation about the NH=C(O) bond in the bridging ligand.

It has been found that both isomeric pairs **2a,2c** and **2b,2d** are interconvertible on standing in solution. After the equilibrium is reached, the signal intensity ratio **2a**:**2b**:**2c**:**2d** in the mixture was found to be 6:10:1:1. One possible explanation of the rather easy cis/trans interconversion of **2a,2c** and **2b,2d** and the rotation of the NH–CH=CH–CH_3 unit about the HN=CO bond in **2(a–d)** is the formation of a CH=CH=NH=C=O fragment with a delocalised bonding.

From pure geometrical reasoning, eight isomers are principally possible for the cluster (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH=CH–CH_3). However, our analysis of Dreiding' models for all the possible cluster **2(a–d)** isomers (Fig. 2) unambiguously indicates that *cis-2* and *cis-4* complexes are forbidden because of steric restrictions. The existence of the *trans-4* complex is not feasible either for the same reasons. The stability of the *trans-2* isomer may also be diminished by the rather close contact between the bridging C=O group and the β-CH hydrogen atom in the μ-O=CNHCH=$CHCH_3$ moiety. However, the stability of this isomer may be increased by the formation of a hydrogen bond between the β-CH and the carbonyl oxygen atom. Such H-bonding though should essentially affect the chemical shifts of the β-CH and other resonances, which is not visible in the ^{1}H NMR spectrum of the isomeric mixture obtained. Consequently, on the basis of steric considerations and the absence of ligand rotation about the HN–CH bond (see above), the isomers **2(a–d)** are probably *cis-1*, *cis-3* and *trans-1*, *trans-3*.

The organic ligand in cluster **1** can be considered as the derivative of a secondary allylamine or *N*-allylformamide coordinated by its oxygen and carbon atoms to two osmium atoms. As indicated in the Section 1, both secondary allylamines and allylamides isomerize only in the presence of catalysts through C=C double bond activation under severe conditions. For cluster **1**, the coordination of the –CH=CH_2 group is unlikely because of the stereochemical rigidity of triosmium clusters with ligands of the carboxamide type [17,21,22]. At present, we do not understand why the equilibrium is shifted to the prop-1-en amine derivative, although the nitrogen atom electronic pair is partially involved in the formation of the HN=C(O) multiple bond. The presence of the latter in analogous complexes is confirmed by X-ray data [18,20,23].

This report does not intend to discuss the mechanism of the rearrangement of cluster **1** to cluster **2(a–d)** and the interconversion of isomers **2(a–d)**, since work in this direction is now in progress. Nevertheless, it is already apparent that the rearrangement discovered by us is interesting as one more type of double bond migration in allylamines.

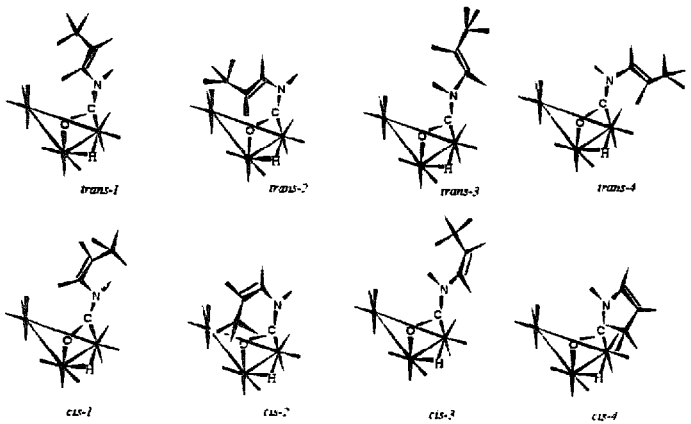


Fig. 2. Eight possible configurations of the (μ-H)$Os_3(CO)_{10}$(μ-OCNHCH=$CHCH_3$) complex arising from isomerism about the N=C(O), HN=CH, and C=C bonds. The "cis" and "trans" labellings denote the proton arrangement around the double bond in NCH=CH–CH_3 fragment.

3. Experimental section

Infrared spectra were recorded on a Specord IR-75 spectrometer. Bruker SXP-4-100 and MSL-400 spectrometers were employed in recording ^{1}H NMR spectra. Solvents and reagents were purified by standard methods.

3.1. Preparation of (μ-H)Os_3(μ-O=CNHCH$_2$CH=CH$_2$)(CO)$_{10}$ (1)

The complex $Os_3(CO)_{12}$ (0.364 g, 0.4 mmol), allylamine (0.27 g, 4.7 mmol), and tetrahydrofuran (15 cm) were degassed, sealed under vacuum in a tube and heated at 85–90 °C for 25 h. After cooling and decanting from unreacted crystalline $Os_3(CO)_{12}$ (0.07 g) followed by removal of the tetrahydrofuran and excess amine under reduced pressure, the residue was filtered through a silica column (hexane–dichloromethane 5:1). Evaporation of the solution to dryness in vacuum gave an orange amorphous residue identified by mass-, IR-, and ^{1}H NMR-spectra as (μ-H)Os_3(μ-O=CNHCH$_2$CH=CH$_2$)(CO)$_{10}$ (1) (0.263 g, 88% on reacted $Os_3(CO)_{12}$). Numerous attempts to obtain complex **1** as a crystalline solid were unsuccessful. The mass spectrum of **1** displays the parent ion at m/z 941 (on ^{187}Os) with subsequent loss of ten CO ligands.

3.2. Formation of isomers (μ-H)Os_3(μ-O=CNHCH=CH–CH$_3$)(CO)$_{10}$ (2a,2b and 2c,2d)

After leaving a chloroform solution of complex **1** for 1–2 days at ambient temperature, the ^{1}H NMR spectrum of the resulting mixture was recorded and confirmed a complete rearrangement of **1**. The resulting solution was chromatographed on thin-layer silica plates using cyclohexane–dichloromethane (5:1) as eluent. Two yellow bands gave cis- and trans-propenyl-containing complexes (μ-H)Os_3(μ-O=CNHCH=CHCH$_3$)(CO)$_{10}$ (**2a,2c** and **2b,2d** respectively) in the ratio ca. 2:3. Crystallization from CH_2Cl_2–C_6H_{14} solutions gave the products **2a,c** and **2b,d** pure spectroscopically, though not quite clean isomerically as followed by t.l.c. For crystalline mixture of isomers **2(a–d)** found: C, 17.97; H, 0.84; Os, 61.18. $C_{14}H_7NO_{11}Os_3$. Calc.: C, 17.97; H, 0.75; Os, 60.97%. Both isomeric pairs (**2a,2c** and **2b,d**) gave parent molecular ions in their mass spectra and the fragmentation pattern for **2(a–d)** compounds correspond closely to that of **1**.

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