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Catalytic isomerization of *N*-allylic substrates with chiral Os_3 clusters as potentially enantioselective reaction

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Abstract

It was shown that the [1,2]-double bond migration of *N*-allylic compounds catalyzed at ambient temperature by the chiral clusters $(\mu\text{-H})Os_3(\mu\text{-OCNR}^1R^2)(CO)_{10}$, **1**, is not accompanied by a cluster-molecule destruction or change of its configuration. Therefore, this catalytic reaction is perspective for its development as an enantioselective process. The key factor in a capability of **1** to produce the activation is the nature of carboxamido ligand. Deuterium label is not transferred from the μ-D or ND positions of the cluster-catalyst $(\mu\text{-D})Os_3(\mu\text{-OCNDMe})(CO)_{10}$, **1a**, to an alkene substrate, indicating that these hydrogen atoms do not take part in the reaction. The proposed reaction mechanism is the prototropic hydrogen transfer and involves the alkene insertion into the Os–O bond. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Osmium; Cluster; Chirality; *N*-Allylamines; Isomerization

1. Introduction

The investigation of new catalytic reaction systems involving chiral organometallic complexes is of great importance because of prospects to perform corresponding reactions enantioselectively. The chiral triosmium clusters $(\mu\text{-H})Os_3(\mu\text{-OCNR}^1R^2)(CO)_{10}$, **1**, are stereochemically rigid up to temperatures of 110–120 °C [1]. The chirality in these clusters resides in a metal triangle fitted asymmetrically into the ligand envelope. They may be further modified with chiral ligands. The ways for resolution of **1** bearing chiral ligands [1] or without them [2] into two optically active antipodes have been developed. Theoretically, catalysis by these resolved species could induce asymmetry. Unfortunately, no catalytic reactions, even photo or thermally activated, have been reported for **1**. G. Süss-Fink reported earlier that a Ru_3-analogue of **1** is catalyst for isomerization of nerol to citronellal in boiling THF [3]. Moreover, this reaction was organized as enantioselective one. We have found that nerol is unaffected by **1** at least under mild conditions.

Recently we have shown that complexes **1** are capable of producing the activation of [1,2]-double bond shift of allylamides (in particular, *N*-2-propenylacetamide) at room temperature [4]. This reaction permits access to *N*-1-propenylacetamide which is not so easy to make by other routes [5]. We have performed a closer examination of **1** and some other Os_3 clusters as catalysts for the isomerization of *N*-allylic substrates. The information derived from this research could then be used to initiate the studies of the optically active **1** as stereodifferentiating catalyst for an asymmetric isomerization.

2. Results and discussion

The nature of bridging μ-X ligand plays a key role in the catalytic isomerization of *N*-functionalized alkenes with the complexes $(\mu\text{-H})Os_3(\mu\text{-X})(CO)_{10}$ (**1**–**3** in Fig. 1).

While complete isomerization of *N*-2-propenylacetamide to *N*-1-propenylacetamide (Scheme 1) can occur in the presence of 3–10 mol% of **1** at room temperature (in CCl_4, $CHCl_3$, C_6H_6) [4] no conversion was detected with complexes $(\mu\text{-H})Os_3(\mu\text{-OOCR})(CO)_{10}$ ($R = CH_3$, **2**) and

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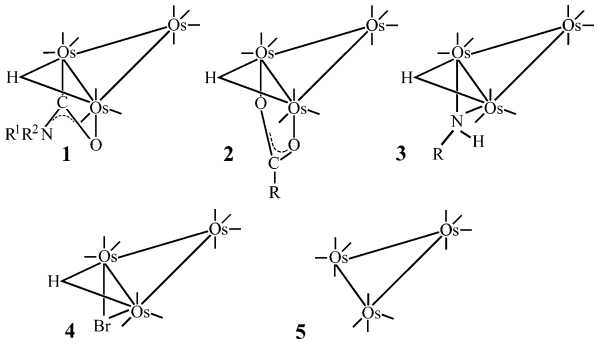
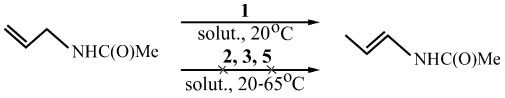


Fig. 1. The Os_3-complexes with various μ-ligands (or without them, **5**) tested as allylic double-bond shifting catalysts.



Scheme 1. Differentiation in the catalytic ability of the complexes **1**–**3** and **5** towards the *N*-2-propenylacetamide isomerization.

$(\mu\text{-H})Os_3(\mu\text{-NHR})(CO)_{10}$ ($R = CH_2CHCH_2$, **3**) containing other types of 3-electron μ-X donor under the same conditions. Earlier A.J. Deeming and S. Hasso reported the inertness of the complex having 3e-bridging bromo ligand $[(\mu\text{-H})Os_3(\mu\text{-Br})(CO)]_{10}$, **4**, in a double-bond migration of alkenes [6]. In addition, the pure carbonyl complex $Os_3(CO)_{12}$ (**5**, without bridging ligands) is inactive at 20–40 °C in the isomerization of *N*-2-propenylacetamide, too (Scheme 1).

The ^{1}H-NMR spectral monitoring of this reaction mixture with 3 mol% of $(\mu\text{-H})Os_3(\mu\text{-O=CNHMe})(CO)_{10}$, **1a**, showed that initial lines of *N*-2-propenylamido substrate disappear gradually and the spectrum of *N*-1-propenylacetamide (*cis*- and *trans*-isomers, about 1:3.5) appears simultaneously [4]. As can be seen from the spectra, the cluster molecule **1a** remains intact. This is evident from the CH_3 and μ-H signal intensities for **1a**, which remained constant up to the end of the reaction. Obviously this catalytic reaction is of the molecular type. Besides, these and above data point out that a vacant site in the complex-catalyst arises most likely due to reversible breaking of an Os-bridging atom bond rather than to CO dissociation.

The nature of substituents R^1 and R^2 in **1** is unimportant for catalysis, except that it has an influence on the reaction rate. Complexes with *N*,*N*-disubstituted carboxamido ligand (for instance with $R^1 = R^2 = Me$ (**1b**) or $R^1 = Me$, $R^2 = Allyl$ (**1c**)) are also catalytically active. It is of no importance whether or not the NH hydrogen is present in the bridging ligand, and so the NH atom of the cluster-catalyst **1** does not take part in transfer of the CH-hydrogen formally from the position '1' to '3' in a substrate.

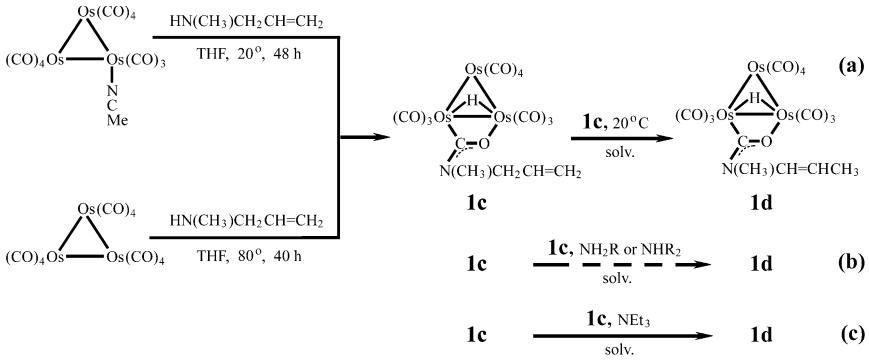
The complex $(\mu\text{-H})Os_3(\mu\text{-O=CNMeCH}_2\text{CH=CH}_2)(CO)_{10}$, **1c**, is an interesting case. Not only does this complex act as catalyst and initiates the double bond shift (Scheme 1), but at the same time it behaves as a so-called 'cluster substrate' since it contains an *N*-allylic moiety in the μ-ligand and isomerizes by itself into $(\mu\text{-H})Os_3(\mu\text{-O=CNMeCH=CHCH}_3)(CO)_{10}$, **1d**, in solution. Preliminary kinetic measurements indicated that this **1c**-to-**1d** conversion is not monomolecular process [4].

It should be noted, that during the synthesis of **1c**, even under severe conditions, (at the left of Scheme 2), this complex **1c** does not undergo isomerization until its isolation from the reaction mixture (Scheme 2(a)). These observations may be ascribed to the presence of a large excess of a secondary amine $HN(CH_3)CH_2CH=CH_2$ needed for reaction. Indeed, it was found that a primary or secondary amine added to the solution of **1c** prevents its conversion into **1d** (Scheme 2(b)). The **1c**-to-**1d** isomerization rate appears to be unaffected by a tertiary amine, NEt_3 (Scheme 2(c)). Apparently, such inhibition of catalysis by primary or secondary amines is associated with their ability to act as proton donors and to block an active center in the cluster-catalyst due to hydrogen bonding. This active center in the μ-$OCNR^1R^2$-ligand is thought to be the oxygen atom.

As a matter of fact, both **1c** and **1d** consist of the *E* and *Z* conformers with respect to amido bond (**1c**-*E*, **1c**-*Z* and **1d**-*E*, **1d**-*Z*) [7]. A sufficiently high energy barrier to rotation around this partially double bond allows to isolate each of the complexes **1c**-*E* and **1c**-*Z* in the solid state, although in solution, they exist as the equilibrium mixture since the ^{1}H-NMR spectrum of compound **1c** in $CDCl_3$ at 25 °C showed the presence of two slowly interconverting conformers in an approximate 2:3 ratio (Scheme 3). Complexes **1d**-*E*, **1d**-*Z* cannot be separated by TLC because they have identical R_f's. According to the ^{1}H-NMR data, both of them have *trans*-oriented olefinic hydrogens.

Self-activated isomerization of **1c** (Schemes 2 and 3) which has no NH-hydrogen was used to elucidate a question as to whether the μ-H atom of the catalyzing molecule participates in hydrogen transfer. It was found that the ^{1}H-NMR spectrum of *N*-1-propenyl group within isomeric products **1d**-*E*, **1d**-*Z* obtained from the μ-deuterated **1c** ($\sim$75% ^{2}H) was the same as that of undeuterated material. In an additional experiment, the more active cluster **1a** containing deuterium both in bridging position and at nitrogen was added to the undeuterated **1c** in C_6D_6–C_6H_6. After about 50% **1c**-to-**1d** conversion, the ^{2}H-NMR spectrum of this reaction mixture showed only three signals assigned to the μ-D and ND of **1a** and C_6D_6. Thus, neither the bridging deuterium atom nor the ND atom of a carboxamido complex-catalyst were incorporated into a substrate.

As mentioned above, complexes $(\mu\text{-H})Os_3(\mu\text{-NHR})(CO)_{10}$, **3**, with the bridging amido ligand (in particular, where $R=CH_2CH=CH_2$, **3a**), do not promote



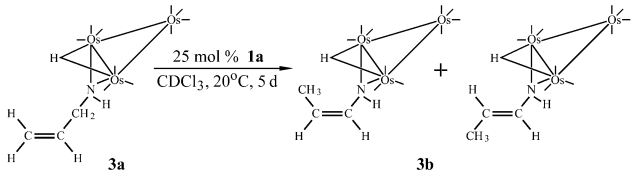
Scheme 2. Self-activated isomerization of (μ-H)Os_3(μ-O=CNMeCH$_2$CH=CH$_2$)(CO)$_{10}$, **1c**, into (μ-H)Os_3(μ-O=CNMeCH=CHCH$_3$)(CO)$_{10}$, **1d**, (a), proceeding without deceleration in the presence of a tertiary amine (c) or retarded in the presence of a primary or secondary amine (b).

the double bond migration, so **3a** is stable in solution in the absence of any catalyst. But, it plays a role of a 'cluster substrate' in the presence of **1** and, as follows from the ^{1}H-NMR data, readily converts into the mixture of *cis*- and *trans*-(μ-H)Os_3(μ-NHCH=CHCH$_3$)(CO)$_{10}$, **3b**, at ambient temperature (Scheme 4).

Note that there is no a lone electron pair on N-atom in the substrate **3a**. Therefore, the catalysis does not go through a substrate heteroatom-to-metal coordination pathway.

Reaction of this 'cluster substrate' **3a** with the optically active (μ-H)Os_3(μ-OC-(*S*)-NHCHMePh)-(CO)$_{10}$, **1e**, containing (*S*)-(−)-1-phenylethyl-carboxamido ligand allowed us to answer the further important question as to whether or not the optically active cluster undergoes racemization during the catalytic reaction, and whether a mechanism in principle allows to maintain the cluster configuration unchanged. For that, one of the diastereomers **1e**, namely (+)-**1e** (with higher R_f on TLC in any eluent), and also a tiny amount of the another diastereomer, (−)-**1e**, were added to **3a** in $CDCl_3$ (Fig. 2, upper spectrum).

At the end of the reaction (Fig. 2, below), the (+)-**1e**/(−)-**1e** μ-H intensity ratio remained nearly constant (within 1.5–2%), thus the detectable racemization does not occur. A relatively large amount of the complex-catalyst (~ 30% (+)-**1e** with respect to the substrate **3a**) was taken in this experiment for the more accurate NMR measurements, so the number of cycles per (+)-**1e**-molecule was modest. Nevertheless, taking into account these and above data that the deuterium label



Scheme 4. Transformation of the 'cluster substrate' **3a**, catalyzed by (μ-H)Os_3(μ-OCNHMe)(CO)$_{10}$, **1a**.

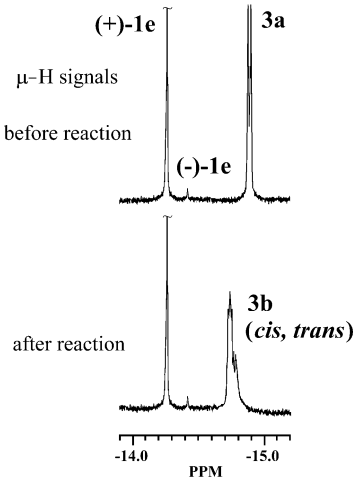
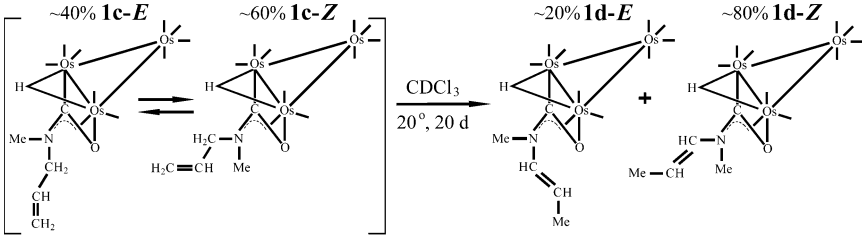


Fig. 2. ^{1}H-NMR spectral evidence of configurational stability of the optically active (μ-H)Os_3{μ-OC-(*S*)-NHCHMePh}(CO)$_{10}$, (+)-**1e** and (−)-**1e**, catalyzing the isomerization of (μ-H)Os_3(μ-NHCH$_2$CH=CH$_2$)(CO)$_{10}$, **3a**, into (μ-H)Os_3(μ-NHCH=CHCH$_3$)(CO)$_{10}$, **3b**.

does not move from the bridging position, one can suggest that both bridging ligands maintain their certain



Scheme 3. Conformational features of the **1c** into **1d** isomerization.

positions through the whole catalytic cycle. A reaction mechanism involving the insertion of alkene substrate into the Os–O bond would best provide these observations.

Further step toward an asymmetric synthesis is the experiment with the prochiral trisubstituted allylamine, *N*,*N*-diethylnerylamine. Generally, such trisubstituted olefins do not isomerize at all or at least they require the much more severe conditions with respect to the less interesting achiral mono and disubstituted substrates [8]. We found that *N*,*N*-diethylnerylamine is isomerizable into *N*,*N*-diethylcitronellamine in the presence of **1** under reasonably mild conditions (Scheme 5). This followed from ^{1}H-NMR spectrum of the reaction mixture of *N*,*N*-diethylnerylamine and 3 mol% of racemic **la** in CCl_4 after its standing at 37 °C over a week. This result indicated that prochiral trisubstituted *N*-allylic substrates can also be affected by the chiral complexes **1**, even under the mild conditions.

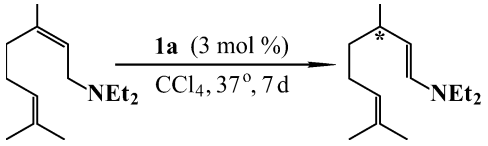
Thus, the possibility to develop the reaction as enantioselective process in which an optically active triosmium complex **1** will act as stereodifferentiating catalyst seems to be real.

We propose the mechanism of the *N*-substituted alkene isomerization catalyzed by the complexes **1** which is outlined in Scheme 6 (CO ligands are omitted for simplicity). The [1,2]-double bond shift is believed to be a prototropic process. It involves the stage of insertion of alkene into the Os–O bond with the double-bond-to-Os coordination and simultaneous hydrogen bond formation between the α-CH atom and the acyl oxygen atom resulting in a five-membered cycle. Then, this C–H bond cleaves heterolytically and the acyl oxygen atom is protonated.

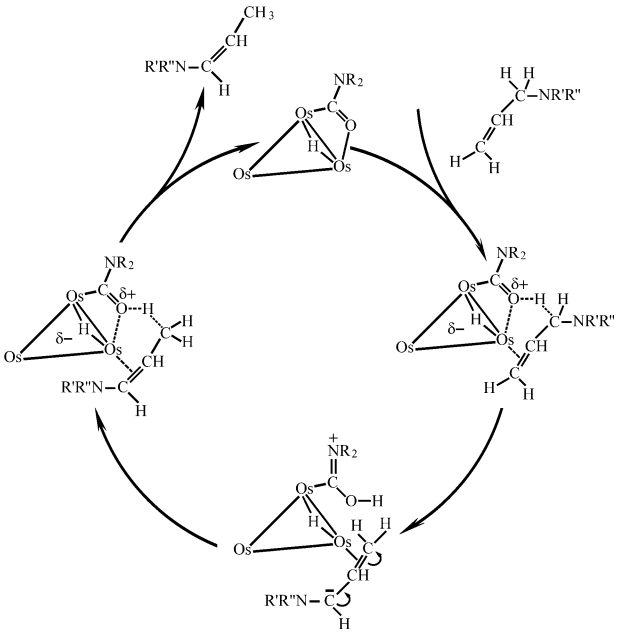
The transition state is stabilized by the +M effect of the amide nitrogen and additionally by conjugation between the double bond and the heteroatom lone pair, if any, and by a negative charge distribution onto CO ligands. After the double bond has shifted and the atoms and groups have arranged suitably, the proton comes back followed by the alkene evolution and cluster regeneration.

3. Conclusions

In the course of our investigation, a number of factors were selected which contribute to the mechanism of *N*-substituted alkenes isomerization catalyzed by the chiral carboxamido complexes $(\mu\text{-H})Os_3(\mu\text{-OCNR}^1R^2)(CO)_{10}$. Surprisingly, the μ-H atom does not participate in substrate hydrogen transfer as proved by the deuterium labeling experiments. So the proposed reaction mechanism should be considered as non-classical for a hydrido transition metal complex catalysis. The formation-breaking of a bond between the α-C–H hydrogen and the acyl oxygen proceeds instead of both the well-known metal-hydride mechanism of reversible addition-elimination of M–H to the double bond and the π-allyl metal hydride mechanism, which also would involve the μ-D-label because of hydrogen exchange between the μ-D bridging and Os–H terminal positions. As a whole, the catalytic reaction discussed above is considered to be a concerted prototropic [1,2]-double bond shift running through the insertion of an *N*-allylic substrate into the Os-bridging oxygen bond. This mechanism best explains a structural and configurational maintenance of a catalyzing chiral cluster molecule, that would be problematic in the case of both the metal–hydride and π-allyl mechanism. Now one may raise a question: if actual catalyst is a very active undetectable particle generated in a low concentration from the origin complex? This question remains for further study.



Scheme 5. The isomerization of *N*,*N*-diethylnerylamine with the complexes **1**.



Scheme 6. Proposed mechanism for an *N*-allylic substrate isomerization catalyzed by the carboxamido Os_3 cluster.

4. Experimental

4.1. General

^{1}H-NMR spectra were recorded on a Bruker DPX-250 spectrometer, and were referenced to internal

Me_4Si. NMR-experiments were conducted in sealed NMR-tubes in CCl_4, C_6D_6 or $CDCl_3$ under argon. Optical rotations for complexes **1e** were measured on a 'JASCO DIP-360' polarimeter.

Solvents were purified and dried by published procedures [9], *N*,*N*-diethylnerylamine was prepared by the literature method [10]. (*S*)-(−)-1-Phenylethylamine (Merck; GC-analytical purity > 99%; [α] 20°/*D* = −37 to −39°) was used for synthesis without purification. *N*-2-propenylacetamide was prepared as described in [11]. Complexes (μ-H)Os_3(μ-OCNMeCH_2CH=CH_2)$(CO)_{10}$, **1c,** and (μ-H)Os_3(μ-NHCH_2CH=CH_2)$(CO)_{10}$, **3a**, were obtained and characterized as reported earlier [4,7,12].

4.2. Examination of the capacity of (μ-H)Os_3(μ-NHCH_2CH=CH_2)$(CO)_{10}$ (**3a**) to catalyze the double-bond shift

Crystalline **3a** (10 mg, 0.01 mmol) was dissolved in 0.5 ml $CDC1_3$ under dry argon in an NMR tube, whereupon this tube was sealed. ^{1}H-NMR monitoring showed, that the spectrum of **3a** remains unchanged at least over 2 months at room temperature (r.t.). ^{1}H-NMR of **3a** ($CDCl_3$ δ, *J* (Hz)): 5.85 (ddt, 1H, $^3J_{trans}$, 16.1,$^3J_{cis}$ 10.3, *J* 6.5, =CH–); 5.30(dd, 1H, ^3J 10.3 J_{gem} 1.1,=CHH_{cis}); 5.24 (dd, 1H, *J* 16.1, J_{gem} 1.1,=CHH_{trans}); 3.95 (br, s, 1H, >NH); 3.46 (dd, 2H, ^3J 6.5,$^3J_{CH-NH}$ 6.9, >NCH_2–); −14.90 (d, 1H, μ-H, ^3J 2.7).

For the mixture of *N*-2-propenylacetamide and **3a** in $CDC1_3$, no detectable ^{1}H-NMR-spectral changes were observed even at equimolar ratio neither at r.t. (2 weeks) nor at 65 °C (~40 h). ^{1}H-NMR of MeC(O)NHCH_2-CH=CH_2 ($CDCl_3$, δ, *J* (Hz)): 6.13 (br s, 1H, >NH), 5.84 (m, 1H, Σ *J* = 37.5; –CH=), 5.18 (dd, 1H, ^3J 16.0, ^2J 1.5; CHH=), 5.13. (dd, 1H, ^3J 10.7, ^2J 1.5; CHH=), 3.86 (t, 2H, ^3J 5.7; CH_2<), 2.01 (c, 3H, –C(O)CH_3).

4.3. Examination of the capacity of(μ-H)Os_3(μ-OOCCH_3)$(CO)_{10}$ (**2**) and $Os_3(CO)_{12}$ (**5**) to catalyze the double-bond shift

^{1}H-NMR spectra of the mixtures of *N*-2-propenylacetamide and (μ-H)Os_3(μ-OOCCH_3)$(CO)_{10}$, **2**, or this amide and $Os_3(CO)_{12}$, **5**, in $CDCl_3$ were found to be constant even after ~40 h of exposure at 65 °C, while a catalyst/substrate ratios was taken about equmolar.

4.4. Isomerization of the 'cluster substrate' (μ-H)Os_3(μ-NHCH_2CH=CH_2)$(CO)_{10}$ (**3a**) in the presence of a carboxamido cluster (μ-H)Os_3(μ-OCNHMe)$(CO)_{10}$ (**1a**)

Solution of (μ-H)Os_3(μ-NHCH_2CH=CH_2)$(CO)_{10}$, **3a**, (42 mg, 0.046 mmol) and (μ-H)Os_3(μ-OCNH-Me)$(CO)_{10}$, **1a**, (14 mg, 0.015 mmol) in $CDCl_3$ (0.5 ml) contained in a sealed NMR tube under dry argon was left to stand at r.t. In 5 days, ^{1}H-NMR control showed that in place of original **3a** resonances the spectra of two new complexes appeared. They were identified as *cis*- and *trans*-(μ-H)Os_3(μ-NHCH=$CHCH_3$)$(CO)_{10}$ *cis*-**3b** and *trans*-**3b**, respectively. The proportion of *cis*-**3b** to *trans*-**3b** was estimated at about 1.5. This resulting mixture was chromatographed on a thin-layer silica plate with $CHCl_3$–hexane (2:3) as eluent afforded a band of **1a** and the only band of products, *cis*-**3b** plus *trans*-**3b**. Elution of this fraction with CH_2Cl_2 followed by evaporation of solvent to dryness resulted in an orange powder. ^{1}H-NMR of *cis*-**3b** plus *trans*-**3b** ($CDCl_3$, δ, *J* (Hz)): 5.36 (m., 2H, >NH–, –CH=), 4.97 (dquart, 0.4H, *J* 13.0, 6.3; $=CH_{trans}$), 4.27 (dquart, 0.6H, *J* 7.1; $=CH_{cis}$), 1.65 (d, 0.6 × 3H, *J* 7.1; –CH_3), 1.57(d, 0.4 × 3H, *J* 6.3;–CH_3), −14.74 (m, 1H, μ-H).

4.5. Preparation of(μ-D)Os_3(μ-OCNMeCH_2CH=CH)$(CO)_{10}$, μ-deuterated (**1c**)

At first, NDMeCH_2CH=CH_3 was obtained by heating its deuterium-chloride salt with burnt calcium oxide and condensed (~2 ml) directly into the dry evacuated ampoule with 100 mg (0.11 mmol) $Os_3(CO)_{12}$ followed by its sealing. This reaction mixture was allowed to stand at r.t. for 1–2 days. Next, the amine was pumped out, residue dissolved in CH_2Cl_2 and the product (63 mg, 0.066 mmol, 60% yield) was isolated by using of silica gel column chromatography with $CHCl_3$–hexane (1:3) as eluent. μ-H signal relative intensity in the ^{1}H-NMR spectrum of the product pointed out that it was ca. 75% μ-deuterated.

4.6. Isomerization of(μ-D)Os_3(μ-OCNMeCH_2CH=CH_2)$(CO)_{10}$, μ-deuterated (**1c**)

μ-Deuterated **1c** (40 mg) was dissolved in 2 ml CCl_4 and left to stand at r.t. over a week under argon. A higher-moving band of the products was isolated by chromatography on thin-layer silica plates with hexane–CCl_4 (1:2) as eluent followed by its elution with $CDCl_3$. Evaporation of the filtered eluate to dryness using a water aspirator pump gives the yellow powder (13 mg), ^{1}H-NMR spectrum demonstrated the resulting complex to be *E*/*Z*-*trans*-(μ-D)Os_3(μ-OCNMeCH=$CHCH_3$)-$(CO)_{10}$, μ-deuterated **1d**, with the same total proportion of μ-D-label (~75%) as that in the parent material. ^{1}H-NMR of **1d**-*E* ($CDCl_3$, δ, *J* (Hz)): 6.79 (dquart, 1H, ^3J 13.86, ^4J 1.58; NCH=), 5.31 (dquart, 1H, ^3J 13.86, ^3J 6.68; =CH–), 2.89 (s, 3H, NCH_3); 1.77 (dd, 3H, ^3J 6.68, ^4J 1.58; –CH_3), −13.79 (s, 1H, μ-H); **1d**-*Z*: 6.97 (dquart, 1H, ^3J 14.4, ^4J 1.6; NCH=), 5.2 (dquart, 1H, ^3J 14.4, ^3J 6.67; =CH–), 3.22 (s, 3H, NCH_3), 1.66 (dd, 3H,^3J 6.67, ^4J 1.6; CH_3), −13.76 (s, 1H, μ-H).

4.7. Isomenzation of $MeC(O)NHCH_2CH=CH_2$ in the presence of $(\mu\text{-}D)Os_3(\mu\text{-}OCNHMe)(CO)_{10}$, μ-deuterated (**1a**)

The $CDCl_3$ solution of *N*-2-propenylacetamide (10 mg, 0.1 mmol) and 38 mg (0.042 mmol, 30 mol%) of the μ-deuterated **1a** was placed into an NMR-tube and then this tube was sealed. After about 80% starting amide was isomerized (3 weeks at ~20 °C), ^{1}H-NMR spectrum was registered. It turned out, that a pattern of the *cis*/*trans* reaction product differ from that of undeuterated *cis*/*trans*-*N*-1-propenylacetamide in neither form nor in relative intensity of resonances. Apparently μ-D-**1c**-to-allylamide transfer did not take place.

4.8. Preparation of $(\mu\text{-}H)Os_3(\mu\text{-}OC\text{-}(S)\text{-}NHCHMePh)(CO)_{10}$, ((+)-**1e** and (−)-**1e**)

$Os_3(CO)_{11}NCMe$ (0,623 g, 0.67 mmol) and (*S*)-(−)-α-$NH_2CHMePh$ (1,6 ml, 1.26 mmol) were dissolved in THF (15 ml) and left to stand at r.t. for 2 days. The reaction mixture was concentrated to 3–5 ml and chromatographed on thin-layer silica plates with chloroform–hexane (2:3) as eluent. Two major yellow bands of diastereoisomers **1e** were eluted with CH_2Cl_2 followed by evaporation of each filtered eluate to dryness. The yields of the recrystallized yellow solids were 160 mg (24%; upper band) and 318 (47%; lower band). For the 'upper' diastereoisomer, (+)-**1e**, $[\alpha]$ 20°/$D = +79°$ ($CHC1_3$, $c = 1$). ^{1}H-NMR ($CDCl_3$, δ): 7.30 (m, 5H, Ph), 6.05 (d, 1H, NH), 4.97 (quart, 1H, CH), 1.41 (d, 3H, CH_3), −14.27 (s, 1H, μ-H). For the 'lower' diaclereoisomer, (−)-**1e**, $[\alpha]$ 20°/$D = -120°$ ($CHC1_3$, $c = 1$). ^{1}H-NMR ($CDC1_3$ δ): 7.26 (m, 5H, Ph), 6.07 (d, 1H, NH), 4.99 (quart, 1H, CH), 1.38 (d, 3H, CH_3), −14.37 (s, 1H, μ-H).

4.9. Examination of configurational stability of the optically active $(\mu\text{-}H)Os_3(\mu\text{-}OC\text{-}(S)\text{-}NHCHMePh)(CO)_{10}$, ((+)-**1e**), catalyzing the [1,2]-double-bond shift in $(\mu\text{-}H)Os_3(\mu\text{-}NHCH_2CH=CH_2)(CO)_{10}$ (**3a**)

To a 'cluster substrate' $(\mu\text{-}H)Os_3(\mu\text{-}NHCH_2CH=CH_2)(CO)_{10}$, **3a**, (16 mg, 0.018 mmol) in $CDC1_3$ (0.5 ml) (+)-$(\mu\text{-}H)Os_3\{\mu\text{-}OC\text{-}(S)\text{-}NHCHMePh\}(CO)_{10}$, (+)-**1e**, (7 mg, 0.007 mmol) and a touch of (−)-$(\mu\text{-}H)Os_3\{\mu\text{-}OC\text{-}(S)\text{-}NHCHMePh\}(CO)_{10}$, (−)-**1e**, were added. The μ-H-singlets intensity ratio between (+)-**1e** ($\delta = -14.27$) and (−)-**1e** ($\delta = -14.37$) in the ^{1}H-NMR spectra of the reaction mixture was estimated to be diminished only by ca. 1.5% at the end of the r.t. **3a**-to-**3b** conversion (1 week).

4.10. Isomerization of *N*,*N*-diethylnerylamine in the presence of a carboxamido cluster $(\mu\text{-}H)Os_3(\mu\text{-}OCNHMe)(CO)_{10}$ (**1a**)

Two NMR tubes each were loaded with *N*,*N*-diethylnerylamine (7 mg, 0,033 mmol) and $(\mu\text{-}H)Os_3(\mu\text{-}OCNHMe)(CO)_{10}$, **1a**, (9 mg, 0.001 mmol, 3 mol%) in dry CCl_4 (0.5 ml). The first was left to stand at r.t. while the other was held at 37 °C. In a week the ^{1}H-NMR spectra showed nearly no changes in the first solution while the total isomerization of *N*,*N*-diethylnerylamine to *N*,*N*-diethylcitronellamine occurred in the second solution. The clearest indication of this conversion is an appreciable down-field shift of the *N*-diethyl CH_2 quartet (from 2.51 to 2.81 ppm) which is in accordance with the literature data [13].

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