Preparation and reactivity of metal-containing monomers

53.* Synthesis and stability of a cluster monomer $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH_2CH{=}CH_2$ in solution

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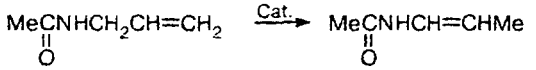
The stability of the complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH_2CH{=}CH_2$ (**1**), which contains a free unsaturated functional group in the terminal ligand $PPh_2CH_2CH{=}CH_2$, with respect to isomerization, chelation of the ligand, and other transformations in solutions was examined. No transformations of complex **1** were observed in the course of synthesis from $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9NMe_3$ or upon heating in solution. Complex **1** as well as complexes $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PHPh_2$ and $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_3$, which were formed as admixtures, were isolated in the solid state and identified by ^1H, $^1H\text{-}\{^{31}P\}$, and $^1H\text{-}\{^1H\}$ NMR, IR, and Raman spectroscopy and mass spectrometry.

Key words: osmium clusters, carbamoyl ligand, allyldiphenylphosphine, isomerization, carbonyl(phosphine)osmium, cluster monomers, ^1H and ^{31}P NMR spectroscopy.

Recently, it has been reported[2] that under mild conditions, hydridocarbonyl complexes $(\mu\text{-H})Os_3(\mu\text{-OCNR'R''})(CO)_9L$ (L = CO) can cause [1,2]-shift of the double bond in unsaturated substrates containing an amide group in the allylic position (Scheme 1).

Scheme 1



Cat. — $(\mu\text{-H})Os_3(\mu\text{-OCNR}^1R^2)(CO)_{10}$,
R^1 = H, R^2 = Allyl, Me, $(CH_2)_4Me$;
R^1 = Me, R^2 = Allyl, Me

We believed that it was of interest to investigate analogous reactions with the use of a metallopolymer in which the catalytically active cluster species are immobilized rather than with the use of free cluster species. In this connection, a demand arose for the synthesis of clusters $(\mu\text{-H})Os_3(\mu\text{-OCNR'R''})(CO)_9L$, which contain an unsaturated functional group in the terminal ligand L, as monomers for possible fixation of these clusters on a polymeric matrix by copolymerization with appropriate olefins. Complexes containing readily coordinated phosphine groups as the terminal ligand L seemed to be the most promising monomers. Generally, these complexes are very stable and can be isolated in the pure crystalline state. Carbonylphosphine mononuclear and cluster complexes often exhibit high activity and selectivity in catalytic processes. In the present work, we chose allydiphenylphosphine $PPh_2CH_2CH{=}CH_2$ as a *P*-coordinated unsaturated ligand.

The stability of the cluster monomer with respect to different transformations, which governs its behavior in polymerization, depends not only on the nature of the coordinating atom, but also on the behavior of the unsaturated functional group in the ligand and its ability either to participate in additional coordination in the cluster or to migrate. Previously,[3,4] it has been demonstrated that complexes with the nitrogen-containing unsaturated ligands $(\mu\text{-H})Os_3(\mu\text{-OCNRCH}_2CH{=}CH_2)(CO)_{10}$ (R = H or Me) were spontaneously converted into derivatives containing the *N*-prop-1-enyl ligands $(\mu\text{-H})Os_3(\mu\text{-OCNRCH}{=}CHCH_3)(CO)_{10}$ upon storage in solutions at room temperature. Analogous reactions for complexes with phosphorus-containing unsaturated ligands have not been investigated. Examples of the double bond shift in compounds containing a tetracovalent phosphorus atom, *viz.*, in allylphosphonium salts upon refluxing in benzene[5] or in the presence of alkoxides,[6] are documented. The double bond shift in the ligand of the complex $(\mu\text{-H})Os_3(\mu\text{-OCNR'R''})(CO)_9PPh_2CH_2CH{=}CH_2$ would lead to the formation of the diphenylprop-1-enylphosphine isomer

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$(\mu\text{-H})Os_3(\mu\text{-OCNR'R''})(CO)_9PPh_2CH{=}CHMe$, which is less favorable as a cluster monomer from the viewpoint of steric and electronic factors (it is known that vinyl ligands virtually cannot undergo polymerization). In addition, prop-1-enyl-containing complexes are most probably insufficiently stable due to weakening of the M—P bond as a result of the partial involvement of the donated electron pair in conjugation with the double bond of the ligand and, hence, they should undergo further conversions.

The rate of isomerization of the *N*-allylamide ligands in the clusters $(\mu\text{-H})Os_3(\mu\text{-OCNRCH}_2CH{=}CH_2)(CO)_{10}$ depends on the degree of replacement of the hydrogen atoms at the nitrogen atom.[4] Under the same conditions, the *N*,*N*-disubstituted (R = Me) complex is isomerized more slowly than its *N*-monosubstituted analog (R = H). Taking into account these factors, the complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH_2CH{=}CH_2$ (**1**) containing two methyl groups at the nitrogen atom was chosen as the target compound with the aim of decreasing the rate of its possible isomerization to form $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH{=}CHMe$ (**2**).

Yet another probable chemical conversion in a solution of cluster monomer **1** involves chelation of the ligand to form the complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_8(\mu\text{-PPh}_2CH_2CH{=}CH_2)$ (**3**), which does not contain a free unsaturated functional group capable of undergoing copolymerization. The complex $Rh_6(CO)_{14}(\mu\text{-PPh}_2CH_2CH{=}CH_2)$, which has been prepared and studied recently,[7,8] exemplifies clusters with chelate-bridging coordination of the allyldiphenylphosphine ligand.

Hence, the aim of the present work was to synthesize cluster monomer **1** and to study its ability to undergo allylic isomerization, decoordination, and chelation of the phosphorus-containing unsaturated ligand.

Results and Discussion

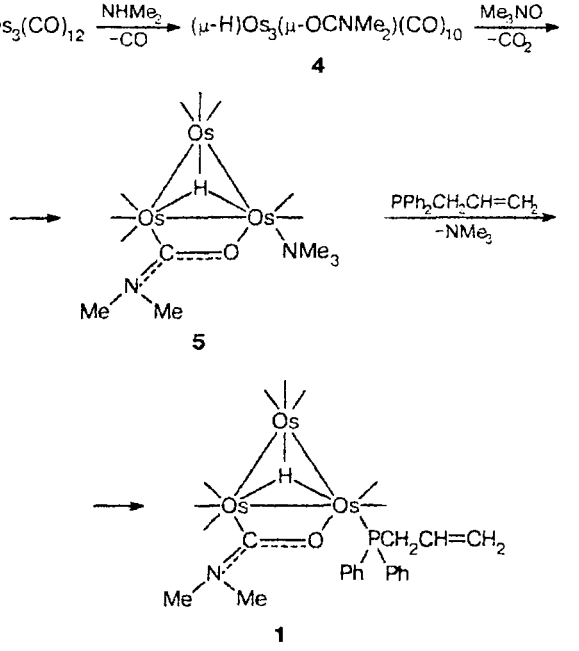
Cluster **1** was synthesized according to Scheme 2, which made it possible to introduce the ligand $PPh_2CH_2CH{=}CH_2$ into the complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_{10}$ (**4**) under very mild conditions.

Complex **4** was prepared by the reaction of $Os_3(CO)_{12}$ with liquid dimethylamine, which resulted[9–11] initially in carbonylation of the amine with the cluster followed by its coordination as a bridging carbamoyl ligand μ-$OCNMe_2$.

Oxidative replacement of one of the CO ligands in cluster **4** by NMe_3 in the reaction of **4** with a small excess of $Me_3NO \cdot 2H_2O$ proceeded smoothly. Complex **5** was isolated from the reaction mixture in virtually quantitative yield.

Complete replacement of the terminal amino ligand in complex **5** by allyldiphenylphosphine (the latter was taken in a 1.5-fold excess with respect to the stoichiometric amount) occurred in a CH_2Cl_2 solution at room temperature in ~15 h, after which TLC revealed the

Scheme 2



presence of two bright-yellow fractions, *viz.*, fraction **I** (major) and fraction **II**.

According to the data from IR spectroscopy (in KBr), a yellow-orange complex which was isolated from the reaction mixture and corresponds to fraction **II** does not contain a double bond (the absence of bands of characteristic vibrations both of the bound and free C=C fragments in the region from 1400 to 1630 cm^{-1}). The proton-decoupled ^{31}P NMR spectrum has a singlet at δ −3.69 with respect to 85% H_3PO_4, which is indicative of the presence of a phosphorus-containing ligand in compound **II**. The ^1H NMR spectrum (Fig. 1, *a*) has a doublet of doublets in the region characteristic of hydride bridging atoms (at δ −13.51, J = 1.8 and 11.5 Hz). When coupling with ^{31}P was suppressed (Fig. 1, *b*), this doublet of doublets coalesces into a doublet with the constant equal to the smaller value of the two above-mentioned constants (1.8 Hz). The J_{HP} constant (11.5 Hz) is typical[12–14] of *cis* interactions between the μ-H and P atoms coordinated to the same metal atom in the Os_3 or Ru_3 clusters containing the ligand μ-OCNR'R''. Generally, the coordination occurs through the M atom which is bound to the oxygen atom of the bridging ligand, and the phosphorus-containing ligand occupies the equatorial position with respect to the plane of the M_3 ring.

The ^1H NMR spectrum has a group of lines in the region of aromatic protons (δ 7.42—7.6), two singlets of the nonequivalent methyl groups in the ligand μ-$OCNMe_2$ (δ 2.46 and 2.96), and two doublets with equal intensities at δ 7.72 and 6.23 along with a doublet of the μ-H hydride atom. When a sample was irradiated

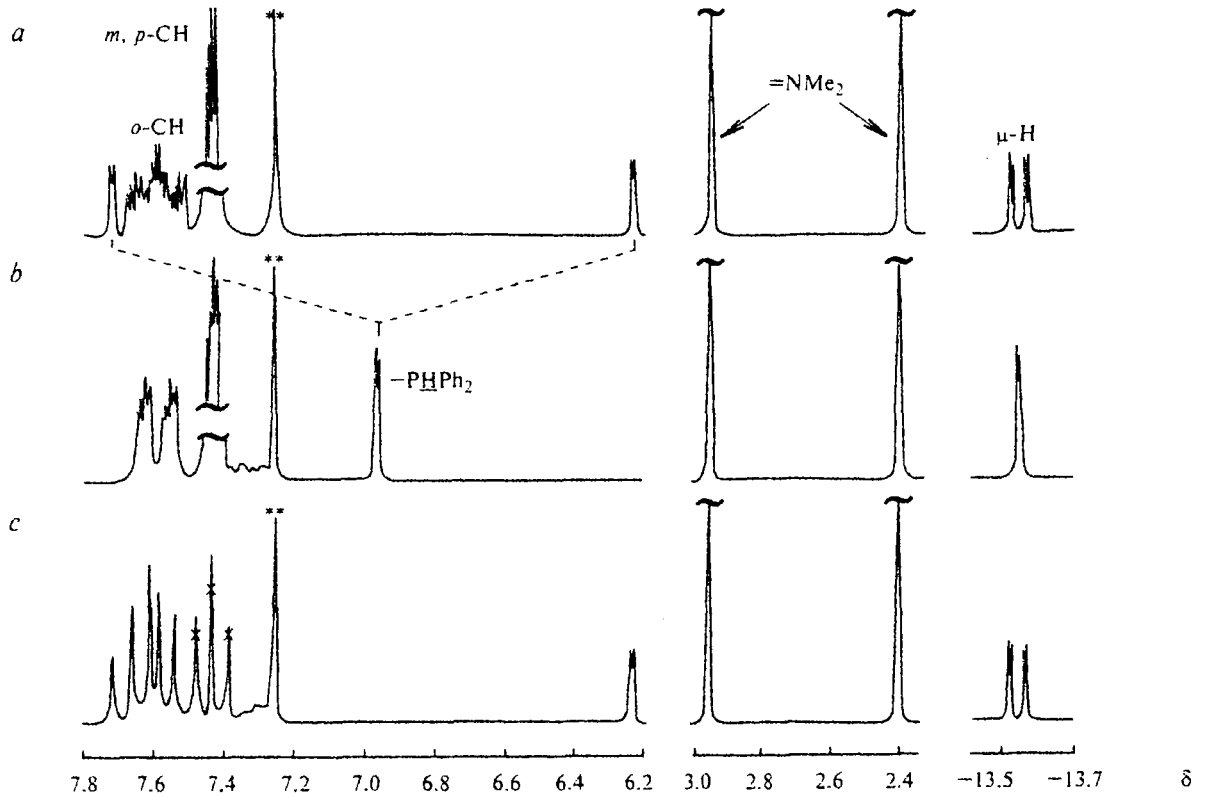


Fig. 1. ^{1}H NMR spectrum (250 MHz) of complex **6** in $CDCl_3$ (*a*) and changes in the spectrum upon suppression of coupling with ^{31}P nuclei (*b*) and with the *meta*- and *para*-protons of the phenyl groups (*c*). Signals for the residual protons of the solvent are marked with double asterisks. In the spectrum *c*, foreign signals resulting from suppression are crossed out.

at a frequency of the ^{31}P signal (see Fig. 1, *b*), these two rather distant signals coalesce (δ 6.7, J_{HH} = 1.8 Hz). Thus, they are undoubtedly components of a doublet due to splitting at the ^{31}P nucleus. The high value of the constant (J_{HP} = 372 Hz) is indicative of direct phosphorus—hydrogen interaction. This situation can occur if secondary phosphine $PHPh_2$ serves as a terminal ligand; thus, fraction **II** is the complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PHPh_2$ (**6**). Additional splitting (1.8 Hz) occurs due to interaction with the μ-H atom. These conclusions agree also with the ratio of the integrated intensities of the doublet in the ^{1}H-{^{31}P} NMR spectrum (see Fig. 1, *b*) to those of the multiplet for the aromatic protons and the signal for the μ-H hydride atom (1 : 10 : 1).

It is noteworthy that NMR spectral studies using the double resonance method made it possible to observe the chemical nonequivalence of the *ortho* protons in the different phenyl rings, which was not detected in the spectrum of the noncoordinated ligand. This is attributable to the fact that molecule **6** is chiral, like other related complexes with the μ-carbamoyl ligand.[15] In the ^{1}H NMR spectrum (see Fig. 1, *a*), a multiplet at δ ~7.6 with an intensity of 4 H was assigned to signals for the *ortho* protons because it is known[16] that *meta* and *para* protons are little sensitive to the effect of the substituent and are often observed as one group of lines (in the case under consideration, the intensity is 6 H, δ 7.43). The ^{1}H-{^{31}P} NMR spectrum (see Fig. 1, *b*) has two multiplets of the same shapes and with equal intensities (2 H) at δ 7.53 and 7.62 instead of a multiplet for the *ortho* protons. In the case of selective homonuclear suppression of coupling with the *meta* and *para* protons, two doublets with equal constants J_{HP} = 18 Hz appear in the above-mentioned region. In the ^{1}H NMR spectrum of the related complex $(\mu\text{-H})Os_3(\mu\text{-OCNHC}_6H_4\text{-}p\text{-Me})(CO)_9P(CH_3)_2Ph$ measured previously,[13] the methyl groups of the terminal phosphine ligand were nonequivalent.

The major fraction **I** of the reaction products was isolated as a bright-orange crystalline substance. Unexpectedly, the ^{1}H NMR spectrum of its solution in $CDCl_3$ appeared to be more complex and as a whole did not correspond to the individual target complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH_2CH{=}CH_2$ (**1**). The high-field portion of the spectrum (the region of the resonance of the hydride bridging atoms) has two doublets at δ −13.50 (J_{HP} = 10 Hz) and −13.04 (J_{HP} = 9 Hz) with an intensity ratio of ~4 : 1. The ^{31}P-{^{1}H} NMR spectrum has two signals at δ 14.58 and 20.79 with respect to 85% H_3PO_4, which belong to two different carbonylphosphine complexes **Ia** and **Ib**. These com-

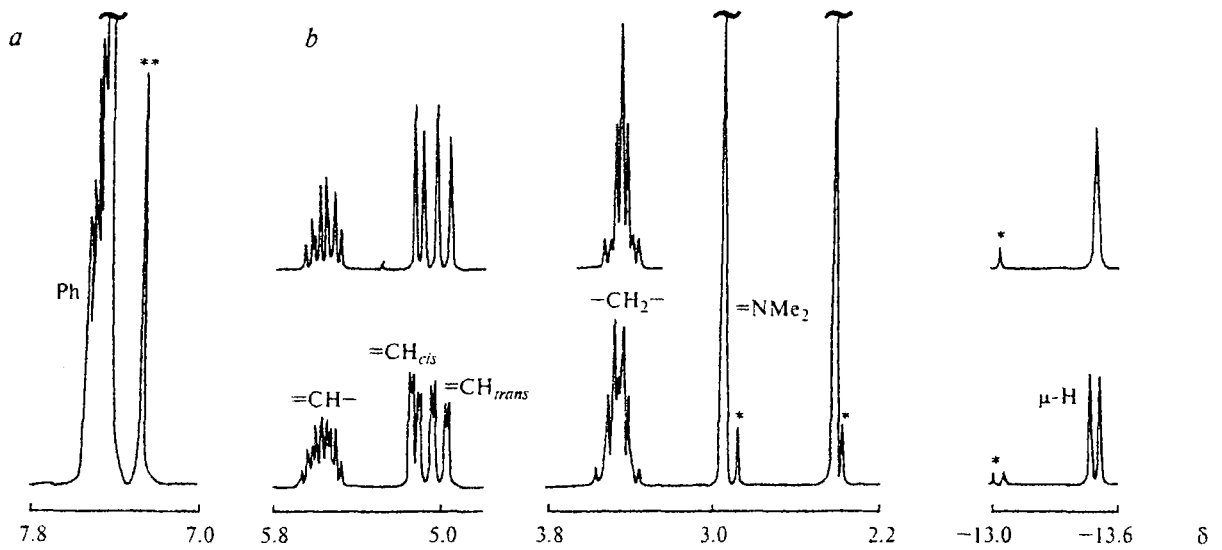


Fig. 2. ^{1}H NMR spectrum (250 MHz) of complex **1** in $CDCl_3$ (*a*) and the shapes of the signals upon suppression of coupling with ^{31}P nuclei (*b*). Signals of an admixture of complex **7** (5 mol.%), which was incompletely removed, are marked with asterisks. Signals for the residual protons of the solvent are marked with double asterisks.

plexes are similar in solubility and do not differ in the R_f value on the chromatogram. Repeated recrystallization of the mixture made it possible to increase the portion of fraction **Ia** to 95 mol.%.

The data of mass spectrometry and NMR and IR spectroscopy of product **Ia** correspond to the formula of the target complex **1** (Fig. 2, Table 1). The protons of the α-CH′H″ group are diastereotopic for the same reason as the *ortho*-protons of the phenyl group in complex **6**. In the ^{1}H-{^{31}P} NMR spectrum (see Fig. 2), these protons are manifested as an AB portion of an ABX spin system ($\delta_{H'}$ 3.49 and $\delta_{H''}$ 3.41). The absence of chelate-bridging coordination of the ligand is evidenced by the data of vibrational spectra of complex **1**. The IR spectrum of a solid sample of **1** (in KBr) has a low-intensity ν(C=C) signal of the noncoordinated double bond at 1630 cm^{-1}. In the Raman spectrum, the corresponding pronounced band is observed at 1634 cm^{-1}. The bands at 1570 cm^{-1} (w) and 1585 cm^{-1} (w) were assigned to stretching vibrations of the phenyl rings. The band at 1480 cm^{-1} (m) was assigned to deformation vibrations.

According to the data from NMR spectroscopy, product **Ib** appeared to be the complex (μ-H)Os_3(μ-$OCNMe_2$)$(CO)_9PPh_3$ (**7**). Based on the data from IR and ^{1}H NMR spectroscopy and on the R_f value in TLC, complex **7**, which was synthesized independently from **5** and PPh_3, was actually an admixture **Ib**, which was difficult to separate from the major product **1**. Complexes **6** and **7** most likely formed from **5** and small

Table 1. Data of ^{1}H NMR spectroscopy (in $CDCl_3$), IR spectroscopy (in C_6H_{12}), and mass spectrometry (with respect to ^{192}Os) for complexes **1** and **5**—**7**

Compound	δ (*J*/Hz)	ν(CO)/cm^{-1}	*m/z*
1	7.51 (m, 10 H, Ph); 5.57 (m, 1 H, =CH–); 5.12 (dd, 1 H, =CH$\underline{H}_{cis}$, ^3J = 10.3, J_{gem} = 3.6, ^4J = 1.1); 5.00 (ddd, 1 H, =CH$\underline{H}_{trans}$, ^3J = 16.8, J_{gem} = 3.6, ^4J = 1.3); 3.45 (m, 2 H, –CH′H″, J_{gem} ≈ 13.6, ^3J ≈ 7.2, ^4J ≈ 1.3, J_{HP} ≈ 11); 2.96 (s, 3 H, NMe); 2.41 (s, 3 H, NMe); –13.50 (d, 1 H, μ-H, J_{HP} = 10.0)	2088 m, 2044 s, 2009 v.s, 1995 m, 1984 w, 1974 w, 1942 w, 1630 (ν(C=C), KBr)	1127
5	3.21 (s, 3 H, NMe); 2.97 (s, 9 H, NMe_3); 2.93 (s, 3 H, NMe); –12.63 (s, 1 H, μ-H)	2094 m, 2048 s, 2016 s, 2005 v.s, 1974 w, 1994 s, 1966 m, 1924 m	96
6	7.63 (m, 2 H, *o*-Ph, J_{HP} = 18.0); 7.58 (m, 2 H, *o*-Ph, J_{HP} = 18.0); 7.43 (m, 6 H, *m*-Ph, *p*-Ph); 6.97 (dd, 1 H, PH, J_{HH} = 1.8, J_{HP} = 372); 2.96 (s, 3 H, NMe); 2.46 (s, 3 H, NMe); –13.51 (dd, 1 H, μ-H, ^3J = 1.8, J_{HP} = 11.5)	2088 m, 2045 s, 2012 v.s, 1998 m, 1988 w, 1977 w, 1965 w, 1948 w	1087
7	7.45 (m, 15 H, Ph); 2.88 (s, 3 H, NMe); 2.37 (s, 3 H, NMe); –13.04 (d, 1 H, μ-H, J_{HP} = 9.0)	2090 m, 2048 s, 2014 s, 1998 m, 1978 w, 1962 m, 1948 w	1163

amounts of the corresponding phosphines $PHPh_2$ and PPh_3, which appeared in solutions due to the chemical instability of highly reactive allyldiphenylphosphine.

Therefore, analysis of the composition of the reaction solution at the end of the reaction, proceeding according to Scheme 2, demonstrated that neither spontaneous allylic isomerization of **1** nor isomerization under the action of complexes **5**—**7** of the carbamoyl type, which were present in the solution together with **1**, occurred at room temperature in 15 h. Apparently, these complexes are inert with respect to activation of the double bond shift in cluster **1** under the reaction conditions. Since complexes **5**—**7** are undoubtedly inactive due to the presence of two methyl groups at the nitrogen atom in the bridging ligand, we carried out special experiments on additional activation of the double bond in cluster **1** with the aim of examining its ability to undergo isomerization under more drastic conditions. A solution of the cluster in $CDCl_3$ was heated at 66 °C for 4 days without addition of a catalyst or in the presence of the nitrogen-monosubstituted complex $(\mu\text{-H})Os_3(\mu\text{-OCNHMe})(CO)_{10}$ (20 mol.%), which is rather active with respect to isomerization of nitrogen-containing allylic compounds.[2] The course of the reactions was monitored by NMR spectroscopy and it was demonstrated that no new complexes appeared in the solution under these conditions and the decrease in the content of fraction **I** at the end of the reactions was no higher than 3%. The unsaturated phosphine ligand in the cluster $(\mu\text{-H})Os_3(\mu\text{-OCNR'R''})(CO)_9PPh_2CH_2CH{=}CH_2$ did not exhibit the ability to undergo allylic isomerization. The additional coordination at the double bond accompanied by the replacement of one of the CO groups also did not occur.

Experimental

The IR spectra were recorded on a Specord IR-75 spectrophotometer in cyclohexane and in KBr pellets and were calibrated using polystyrene as the standard. The Raman spectrum was obtained on a Triplemate-Spex spectrometer (USA) using excitation with the 633-nm line. The ^1H and ^{31}P NMR spectra were measured on a Bruker DPX-250 spectrometer in $CDCl_3$ with Me_4Si and 85% H_3PO_4 as the internal and external standards, respectively. The spectra were analyzed using experiments with suppression of heteronuclear $^1H\text{-}\{^{31}P\}$ and $^{31}P\text{-}\{^1H\}$ couplings and with selective suppression of coupling with protons. The mass spectra were recorded on an MKh-1310 mass spectrometer; the ionizing voltage was 50 eV.

The solvents were dried and purified according to standard procedures. The syntheses were performed under an atmosphere of argon. Allyldiphenylphosphine was prepared according to a procedure reported previously.[17] Before use, this reagent was purified from an admixture of the corresponding phosphine oxide by chromatography on a column with dried and degassed silica gel. $Me_3NO \cdot 2H_2O$ was prepared according to a known procedure.[18]

1,2-μ-Hydrido-1,2-μ-(*N,N*-dimethylcarbamoyl)-1-trimethylamino-1,1,2,2,2,3,3,3,3,3-nonacarbonyl-*triangulo*-triosmium, $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9NMe_3$ (5). A methanolic solution of $Me_3NO \cdot 2H_2O$ (9 mL, 0.081 mmol) was added portionwise (0.1 mL) to a stirred solution of complex **4** (41 mg, 0.44 mmol) in diethyl ether (5 mL) over 20 min. The reaction mixture was kept until the spot of the initial complex **4** disappeared in TLC (dichloromethane—hexane, 1 : 4, R_f ~0.7) (~2 h) and the spot of the only product (R_f ~0.5) appeared. The mixture was diluted with hexane (1.5 vol) and passed through a short column with silica gel to remove an excess of Me_3NO. The complex was eluted from the column with dichloromethane and the combined eluates were concentrated to dryness. Complex **5** was obtained as an orange powder in a yield of 40 mg (0.042 mmol, 96%). Complex **5** crystallized as orange-red crystals from a 2 : 1 chloroform—hexane mixture in the cold (2 °C).

1-(Allyldiphenylphosphine)-1,2-μ-(*N,N*-dimethylcarbamoyl)-1,2-μ-hydrido-1,1,2,2,2,3,3,3,3,3-nonacarbonyl-*triangulo*-triosmium, $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH_2CH{=}CH_2$ (1). $PPh_2CH_2CH{=}CH_2$ (0.05 mL, 0.23 mmol) was added to a solution of complex **5** (196 mg, 0.2 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred and kept at ~20 °C for ~15 h, after which two components were detected by TLC (hexane—diethyl ether, 7 : 1), *viz.*, **I** (major) with R_f ~0.6, and **II** with R_f ~0.35. The solution was applied on Silufol plates and separated preparatively using the same eluent. Then the fractions were desorbed with CH_2Cl_2 and both fractions were concentrated to dryness without heating *in vacuo* using a water-aspirator pump. Fraction **II** (complex **6**) was obtained as dark-yellow crystals in a yield of 18 mg (0.016 mmol, 8%). Fraction **I** was obtained as a bright-orange crystalline substance in a yield of 195 mg. The ^1H NMR spectrum ($CDCl_3$) of the resulting product has two doublets at high field (δ_1 −13.50 and δ_7 −13.04) with the intensity ratio ~4 : 1. The $^{31}P\text{-}\{^1H\}$ NMR spectrum has two singlets with the same intensity ratio. Repeated recrystallization of mixture **I** from a 2 : 1 $CHCl_3$—hexane solution led to a change in the ratio between the signals of complexes **1** and **7** to 19 : 1. Complex **1** was obtained in a yield of 156 mg (0.136 mmol, 68%).

1,2-μ-(*N,N*-Dimethylcarbamoyl)-1,2-μ-hydrido-1-(triphenylphosphine)-1,1,2,2,2,3,3,3,3,3-nonacarbonyl-*triangulo*-triosmium, $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_3$ (7). All operations were carried out as described above (synthesis of complex **1**). Crystals of **7** were obtained from complex **5** (20 mg, 0.02 mmol) in a yield of 19 mg (0.016 mmol, 82%). The ^1H NMR spectrum has signals corresponding to an admixture of **Ib** in the major fraction **I** formed in the synthesis of complex **1**.

Transformations of complex $(\mu\text{-H})Os_3(\mu\text{-OCNMe}_2)(CO)_9PPh_2CH_2CH{=}CH_2$ (1) into complexes 2, 3, 6, or 7. A solution of complex **1**, which had repeatedly been recrystallized, in $CDCl_3$ (0.5 mL, ~0.01 mol L^{-1}) and an analogous solution with the addition of $(\mu\text{-H})Os_3(\mu\text{-OCNHMe})(CO)_{10}$ (the molar ratio was 1 : 2) were sealed in NMR tubes filled with argon, and the tubes were kept at 66 °C for 4 days. The spectra recorded thereafter demonstrated that the decrease in intensities of the hydride signals of **1** was not more than 2—3 mol.% for both samples. The high-field regions of the spectra have no signals for the μ-H atoms of any complexes other than the initial complexes.

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