Isomerization and conformational transformations of the *N*-allyl-*N*-methylcarbamoyl bridging ligand in the $(\mu\text{-H})Os_3\{\mu\text{-OCN(Me)CH}_2\text{CH=CH}_2\}(CO)_{10}$ complex

V. A. Ershova,[a] V. A. Maksakov,[a] A. V. Golovin,[b] S. V. Tkachev,[a] and L. A. Sheludyakova[a]*

[a]Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 35 5960. E-mail: ersh@che.nsk.su

[b]G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 5 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 35 5766

The $(\mu\text{-H})Os_3\{\mu\text{-OCN(Me)CH}_2\text{CH=CH}_2\}(CO)_{10}$ complex containing an allylic fragment in the *N,N*-dialkylsubstituted carbamoyl bridging ligand was synthesized. The stereochemical behavior of this complex in solution was investigated. As follows from the NMR spectral data, the complex undergoes reversible conformational (about the amide C—N bond) and irreversible allylic isomerization. Both conformers were isolated in the solid state by chromatography at a reduced temperature. The allylic isomerization occurs stereospecifically to produce the $(\mu\text{-H})Os_3\{\mu\text{-OCN(Me)CH=CHMe}\}(CO)_{10}$ complex with the *trans*-oriented olefinic hydrogen atoms.

Key words: Os_3 clusters, carbamoyl ligand; allylic isomerization; conformation.

A change in the reactivity of ligands in complex formation is one of the most interesting aspects of the chemistry of complex compounds, in particular, cluster complexes. Studies in this direction are important from the viewpoint of the homogeneous catalysis on metallocomplex catalysts and make it possible to get data now lacking on stereochemical and electronic properties of complexes.

We have recently reported[1] on the allylic isomerization under mild conditions of the allylcarbamoyl $\mu\text{-OCNHCH}_2\text{CH=CH}_2$ ligand coordinated as a bridge in the $(\mu\text{-H})Os_3(\mu\text{-OCNHCH}_2\text{CH=CH}_2)(CO)_{10}$ cluster (**1**). It is noteworthy that under the same conditions, free allylamides and allylamines are not isomerized. The isomerization is accompanied by the unusual stereochemical behavior of the ligand. The formed $(\mu\text{-H})Os_3(\mu\text{-OCNHCH=CHMe})(CO)_{10}$ cluster (**2**) was isolated in the form of *cis*- and *trans*-isomers relative to the CH=CH bond, and each of them exists in two conformations (*Z* and *E*) relative to the amide N—CO bond. Stereochemical criteria are often predominant for the estimation of the reactivity of compounds and should be taken into account in the discussion of possible reaction mechanisms. Therefore, the data on the stereochemical behavior of the ligands in complexes **1** and **2** should be considered both from the viewpoint of their similarity and difference with common organic amide and in comparison to other carbamoyl complexes.

The main similarity between the $\mu\text{-OCNR'R''}$ ligands in the $(\mu\text{-H})M_3(\mu\text{-OCNR'R''})(CO)_{10}$ (M = Ru, Os; R', R'' = H, Alk, Ar) clusters and noncoordinated amides is the planar arrangement of the amide fragment, lengthening of the C=O bond as compared to those in aldehydes and ketones, and a decrease in the N—CO distance to the length of the multiple bond,[2–6] as in the pyridine molecule.[7] Therefore, the carbamoyl clusters can exist, in principle, in the form of two conformers. However, the clusters containing the *N*-monosubstituted amide $\mu\text{-OCNHR}$ ligand, including cluster **1**, exist in the form of a single rotamer both at ~20 °C and in a wider temperature range.

In the temperature range from −70 to +90 °C, no signals of the second, and likely less favorable, isomer were observed in the ^{13}C NMR spectra of the $(\mu\text{-H})Os_3(\mu\text{-CONHCH}_2\text{COOEt})(CO)_{10}$ complex (see Ref. 8) and its substituted derivative $(\mu\text{-H})Os_3(\mu\text{-CONHCH}_2\text{COOEt})(CO)_9(NH_2CH_2COOEt)$.[9] The existence of the single isomeric form for all similar complexes probably is determined by the considerable difference in the free energies of two conformations.

Rotational isomerism was mentioned[10] as one of the possible reasons for duplication of the lines of the multiplet of the NCH_2 group in the ^1H NMR spectrum of the $(\mu\text{-H})Os_3(\mu\text{-OCNHCH}_2\text{CH}_3)(CO)_{10}$ cluster. However, the equal integral intensities of these duplicated signals and the absence of duplication of the other signals, especially those of NH and μ-H, make this explanation doubtful. Thus, compound **2** can be considered to be the first reliable example of the carbamoyl complex, existing in two conformations, one of which is strongly predominant (94%).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 158—162, January, 1998.

1066-5285/98/4701-0160$20.00

Only one rotamer (*Z*-form) is also almost always predominant or observed for free *N*-monoalkylsubstituted amides.[2,11] In absolutely all cases, the data of X-ray diffraction study of the complexes with these *N*-monoalkylsubstituted ligands, for example, $(\mu\text{-H})Os_3(\mu\text{-OCNHR})(CO)_{10}$ [3,5,6,10,12] and their derivatives $(\mu\text{-H})Os_3(\mu\text{-OCNHR})(CO)_9L$ [13,14] (L is amine or phosphine), indicate the *Z*-conformation of the carbamoyl ligand. It is highly probable that this conformation is also retained in solution.

N,N-Dialkylsubstituted amides, unlike monosubstituted derivatives, usually exist in the form of two rotational isomers,[11] and not very high rotation barriers (the typical value is $\Delta G^{\neq} = 16-17$ kcal mol^{-1}) often allow their fast (in the NMR time scale) intertransformation at 90—100 °C to be observed.[15] Sometimes these amides can be isolated as individual isomers in the solid state.[2] Among clusters with *N,N*-disubstituted amido ligands, only the ruthenium and osmium complexes with methyl substituents at the N atom $(\mu\text{-H})M_3(\mu\text{-OCNMe}_2)(CO)_{10}$ (M = Ru, Os) were obtained and studied.[4,10] In the ^{1}H NMR spectra of these complexes, individual singlets of the Me groups are observed, which suggests that they are nonequivalent. For the osmium complex, the coalescence point, at which a fast exchange betweeen the positions of the Me groups would occur, was not achieved[10] upon heating almost to the decomposition temperature (120 °C). This indicates that the rotational barriers about the amide bond in the clusters are considerably higher than those in free amides.

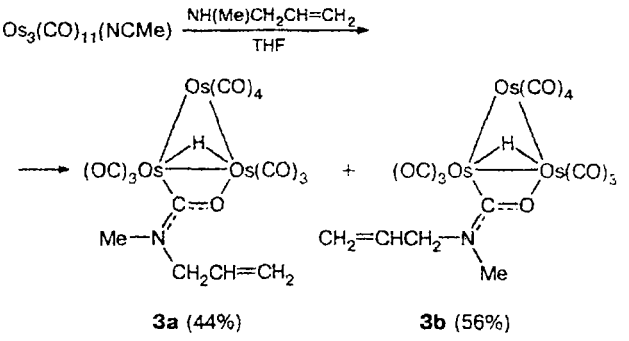
Thus, it can be assumed that a cluster with different alkyl substituents R′ and R″ at the amide N atom should exist in the form of two rotational isomers, and the isomers can be isolated in the individual state due to the high rotational barrier about the N—CO bond. The synthesis of a complex, where the allyl radical is one of the *N*-alkyl substituents (R′) and the Me group is another substituent (R″), will allow one to reveal the effect of the replacement of the hydrogen atom in the NH group in allylcarbamoyl cluster **1** by an alkyl on the allylic rearrangement.

Results and Discussion

Complex **3** with the *N*-allyl-*N*-methylcarbamoyl ligand was synthesized according to Scheme 1 (20 °C, 48 h).

The reaction mixture was chromatographed to give the single fraction of the product in the form of a broad band, which was separated into two components by elution with the same eluent at a reduced temperature (2 °C). The compounds isolated are crystalline yellow substances, unlike the previously studied complex **1**, which was not obtained in the solid state, likely due to the fast formation of admixtures of isomers of complex **2**. The IR spectra of two isolated compounds in the region of vibrations of carbonyl groups are almost identical and similar to the spectra of compounds **1** and **2** [1]

Scheme 1



and the other carbamoyl complexes,[3—6,8—10] which suggests that their structures are similar. The mass spectra contain the peaks of the same molecular ion with *m/z* 955 (with respect to the ^{192}Os isotope). The ^{1}H NMR spectra in $CDCl_3$, in general, are very similar and differ only by the chemical shifts of some signals (Fig. 1, see Experimental). The parameters of the ^{1}H NMR spectra correspond completely to the assumed formula of product **3** and suggest that **3** exists in the form of two rotational isomers **3a** and **3b**. The rotational barrier about the amide N—CO bond is sufficiently high, which allows individual signals of these isomers to be observed at room temperature and even the isomers to be isolated in the solid state. Isomers **3a** and **3b** in solution are conformationally mobile, and within several minutes the signals of the second rotamer appear in the ^{1}H NMR spectra of both complex **3a** (with the greater R_f and $\delta(\mu\text{-H})$ −13.91) and **3b** (with the lower R_f and $\delta(\mu\text{-H})$ −13.85). Based on the ratio of the intensities of the isolated nonsplit narrow signals of the NMe groups (δ 3.03 and 2.68 for **3a** and **3b**, respectively) and the singlets of μ-H, the equilibrium between the rotamers is established in ~24 h, and the ratio **3a** : **3b** becomes equal to 4 : 5. The same ratio is observed in their nonseparated mixture obtained directly from the reaction solution. Thus, the presence of the *N*-methyl substituent instead of the H atom results likely in a decrease in the difference between the energies of two conformations.

In the ^{1}H NMR spectra of benzene solutions of complexes **3a** and **3b**, both of the signals of the NMe group (δ 2.47 and 2.23, respectively) are shifted to the higher field as compared to the spectra of these complexes in $CDCl_3$, and the more downfield singlet of **3a** is shifted more strongly ($\Delta\delta$ = 0.56 ppm) than the less downfield singlet of **3b** ($\Delta\delta$ = 0.45 ppm). According to these results and by analogy to the assignment of the NMR signals of the rotational isomers of the purely organic amides,[16] the structure with the *trans*-orientation of the Me group relative to the O atom of the NC—O group corresponds to complex **3a**, and the structure with the *cis*-orientation corresponds to complex **3b**, which is present in somewhat higher amount. It is

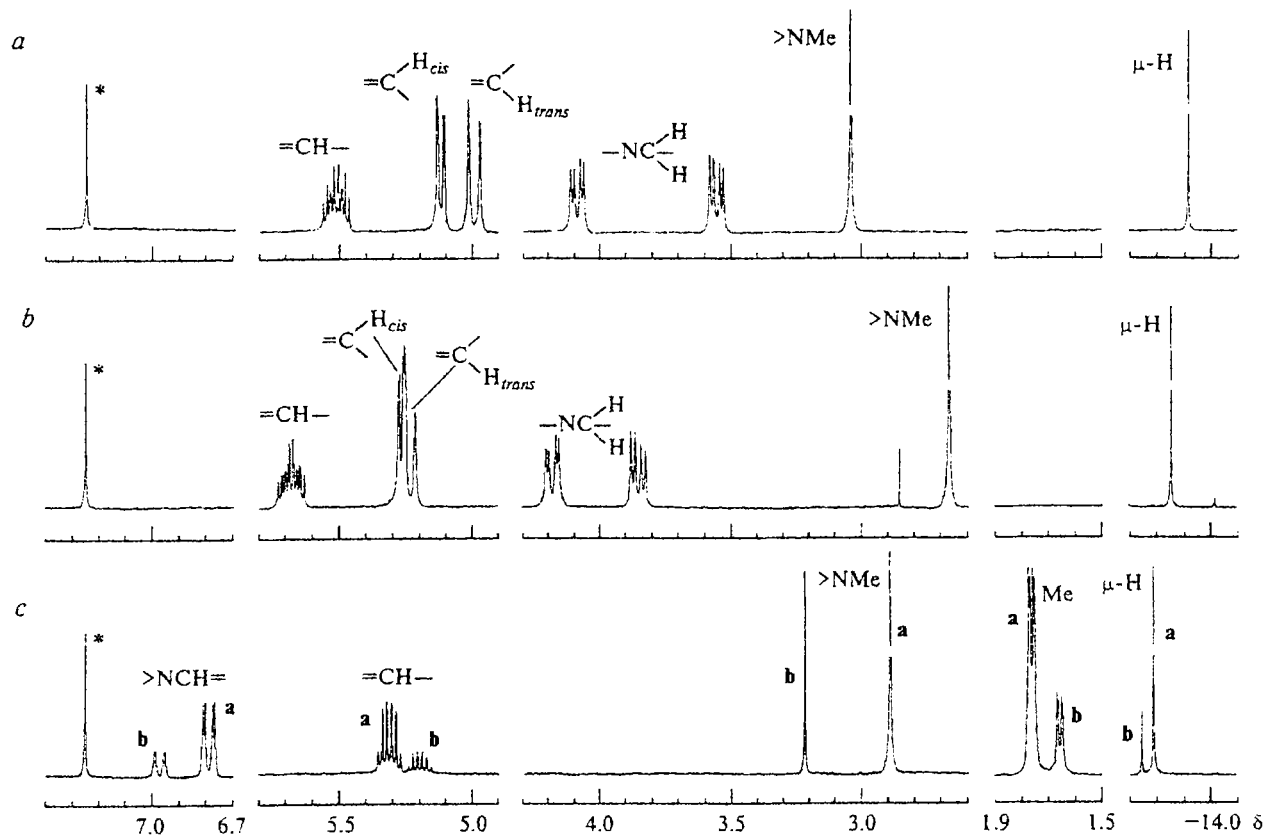
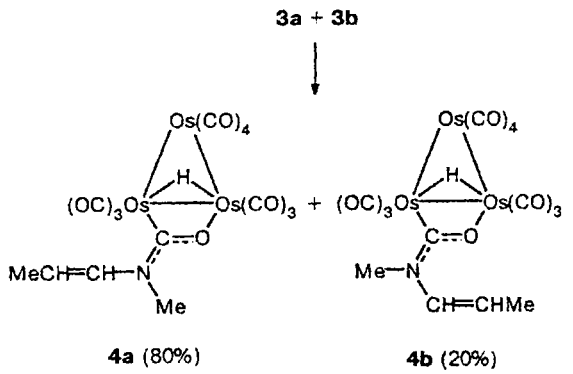


Fig. 1. ^{1}H NMR spectra (in $CDCl_3$) of conformers **3a** (*a*) and **3b** (*b*); mixture of **4a** and **4b** (*c*) (signals of residual protons are marked by asterisks; signals at δ 2.87 and −14.02 are admixture signals that often appear).

noteworthy, however, that this assignment should be confirmed by XDA data, since the anisotropic carbonyl ligands are present in the molecules considered.

Along with the intertransformation of isomers **3a** and **3b**, the allylic rearrangement similar to that observed for compound **1** (Scheme 2) occurs in a solution of complex **3**. The propenylcarbamoyl $(\mu\text{-H})Os_3[\mu\text{-OCN(Me)CH=CHCH}_3](CO)_{10}$ complex (**4**) is the product of this rearrangement ($CHCl_3$, CH_2Cl_2, or C_6H_6, 20 °C, 4—20 days).

Scheme 2



Unlike complex **2**, compound **4** exists in the form of only two conformers **4a** and **4b** rather than four conformers (*cis*—*trans*-CH=CH and *Z*—*E* isomerism). The products could not be chromatographically separated into individual fractions and were obtained as a mixture. The relative intensities of the signals of conformers **4a** and **4b** in the ^{1}H NMR spectrum indicate their ratio in the solution to be 4 : 1. The values of the spin-spin coupling constant $^3J_{CH=CH}$ are about 14 Hz for both complexes, which suggests the *trans*-arrangement of the olefinic protons. Unlike complex **2**, no transformations of the *trans*-isomers of **4** into the *cis*-isomers are observed in time or with heating to 105 °C (in deuterotoluene). Unexpectedly, the isomers exhibit no conformational mobility. No changes in the values of either chemical shifts or line half-widths are observed in the ^{1}H NMR spectra in this temperature region, which suggests that the rotational barrier about the amide bond is rather high for a conjugated system.

The existence of the strong conjugation was shown for the propenylcarbamoyl analog $(\mu\text{-H})Os_3(\mu\text{-OCNHCH=CHCH}_3)(CO)_{10}$ (**2**). The spectra of all of its four isomers exhibit[1] the spin-spin coupling constant

^3J = 10.5 Hz, which is characteristic of the restricted rotation about the α-CH—NH bond; and the typical value of the corresponding constant is 5 Hz for the free rotation about this bond in amides.[17] The bonds in a molecule of **4** should be also delocalized. It has been previously shown[18] in the comparison of *N*-methyl-*N*-vinylformamide and *N*-methyl-*N*-vinylacetamide to *N*,*N*-dimethylamide analogs that the rotational barrier about the amide bond decreases by approximately 1.5-fold and the coalescence points decrease (to 99 and 36 °C for these vinylamides, respectively) due to the conjugation of the multiple bond of the substituent with the unshared electron pair of the N atom.

We believe that the increase in the rotational barrier in complex **4** upon its formation from compound **3** can be explained by the *cis*-arrangement of the H atom of the α-CH group relative to the bulky Me substituent at the N atom. The Dreiding models show that this structure of the planar propenylcarbamoyl ligand leads to steric hindrances for its rotation in the vicinity of the CO ligands.

Both singlets of the NMe group in the ^{1}H NMR spectra exhibit the upfield shifts on going from a solution in $CDCl_3$ to a benzene solution. A more downfield signal of **4b** (Δδ = 0.58: δ 3.22 in $CDCl_3$ and 2.64 in C_6D_6) is shifted more strongly than the less downfield signal of **4a** (Δδ = 0.42: δ 2.89 in $CDCl_3$ and 2.47 in C_6D_6). The assignment[16] of the signals of these isomers, as for complex **3**, shows that isomer **4a** with the *cis*-orientation of the Me group to the O atom of the bridging CO group is predominant.

Thus, we may conclude that the presence (or absence) of the hydrogen atom of the NH group does not play a fundamental role in the allylic rearrangement in the $(\mu\text{-H})Os_3(\mu\text{-OCNRCH}_2\text{CH=CH}_2)(CO)_{10}$ (R = H, Me) clusters. The replacement of this H atom by the alkyl radical results only in a decrease in the rate of the process and a change in the composition and structure of the isomeric forms of the final product. In this case, the reaction occurs stereospecifically to give *trans*-isomers relative to the olefinic bond.

Experimental

IR spectra were recorded on a Specord 75 IR spectrometer in hexane. NMR spectra were recorded on Bruker SXP-4-100 and MSL-400 spectrometers in solutions of $CDCl_3$, C_6D_6, or $C_6D_5CD_3$ ($SiMe_4$ as the internal standard). Spectra with suppression of the homonuclear proton-proton interaction were obtained to assign chemical shifts and refine spin-spin coupling constants. To simplify the analysis of the structure of complex multiplets, Lorentzian lines were transformed into substantially more narrow Gaussian lines. Mass spectra were measured on an MX-1310 mass spectrometer with the ionizing irradiation of 70 eV. Solvents and reagents were purified according to standard procedures. All complexes were synthesized in an argon atmosphere.

***N*-Allyl-*N*-methylamine** was synthesized by the method of alkyl chloride amination;[19] the method for the isolation of allylamine has been described previously.[20] CH_2=$CHCH_2Cl$ (75 mL) was added dropwise for 1 h to a solution of CuCl (2 g) in 30% aqueous $MeNH_2$ (600 mL) with cooling and vigorous stirring. The mixture was stirred for 2 h more and refluxed to remove excess methylamine, trapping it by 20% HCl. After the end of the gas evolution, the reaction mixture was cooled, acidified by concentrated HCl to a weakly acidic reaction, and concentrated to a dense wet mass in a wide beaker on a water bath. The residue was transferred to a distillation flask, and the amine was distilled with the gradual addition of a 50% aqueous solution of NaOH (this results in warming of the mixture). The distillation was continued with additional heating, and the distillate was collected in a receiver cooled with ice. The crude product was dried with fused NaOH, then with Na metal and purified on a rectification column collecting a fraction with b.p. 62.0—62.5 °C, n_D^{20} 1.4144 (Ref. 21: 62.5—63 °C, n_D^{20} 1.4168). The yield was 40%.

Cluster $(\mu\text{-H})Os_3\{\mu\text{-OCN(Me)CH}_2\text{CH=CH}_2\}(CO)_{10}$ (3). An excess of *N*-allyl-*N*-methylamine (1.5 g, 0.02 mol) was added to a solution of $Os_3(CO)_{11}(NCMe)$ (682 mg, $7.2 \cdot 10^{-4}$ mol) in THF (30 mL), and the mixture was allowed to stand at ~20 °C for 48 h. Then the solution was concentrated to a small volume using a water aspirator pump, applied onto Silufol plates, and eluted with the hexane—CH_2Cl_2 (4 : 1) mixture. The main fraction (a mixture of rotamers **3a** and **3b**) was isolated in the form of an amorphous solid. The product obtained was repeatedly fractionally chromatographed (using the same eluent) in a refrigerator chamber (2 °C). Two close zones were eluted with cold CH_2Cl_2 and evaporated *in vacuo* at a low temperature. The upper fraction (**3a**) (191 mg, 27.8%) and bottom fraction (**3b**) (134 mg, 19.5%) were obtained. The mass spectra of complexes **3a** and **3b** are identical: *m/z* 955 $[M]^+$ (with respect to the ^{192}Os isotope). IR, ν/cm^{-1}: complex **3a**, 2108 sh, 2106 w, 2091 v.w, 2066 v.s, 2054 s, 2023 v.s, 2012 v.s, 1991 m, 1984 sh, 1976 w, 1948 v.w; complex **3b**, 2104 w, 2093 v.w, 2066 v.s, 2053 s, 2022 v.s, 2010 v.s, 1990 m, 1984 sh, 1975 w, 1950 v.w. ^{1}H NMR ($CDCl_3$), δ: complex **3a**, 5.51 (dddd, 1 H, =CH—, $^3J_{trans}$ = 17.08 Hz, $^3J_{cis}$ = 10.18 Hz, $^3J_{=CH-NCH}$ = 6.23 Hz, $^3J_{=CH-NCH}$ = 5.69 Hz); 5.12 (dq, 1 H, $=CH_{cis}$, ^3J = 10.18 Hz, $J_{gem} \approx {}^4J$ = 1.3—1.4 Hz); 4.99 (dq, 1 H, $=CH_{trans}$, ^3J = 17.08 Hz, $J_{gem} \approx {}^4J$ = 1.4—1.5 Hz); 4.05 (ddt, 1 H, NCH″, J_{gem} = 14.95 Hz, ^3J = 5.69 Hz, ^4J = 1.5 Hz); 3.55 (ddt, 1 H, NCH′, J_{gem} = 14.95 Hz, ^3J = 6.23 Hz, ^4J = 1.32 Hz); 3.04 (s, 3 H, $\underline{NCH_3}$); −13.91 (s, 1 H, μ-H); complex **3b**, 5.68 (m, 1 H, =CH—, ΣJ = 39.26 Hz); 5.27 (dq, 1 H, $=CH_{cis}$, ^3J = 10.24 Hz, $J_{gem} \approx {}^4J$ = 1.25—1.35 Hz); 5.24 (dq, 1 H, $=CH_{trans}$, ^3J = 17.05 Hz, $J_{gem} \approx {}^4J$ = 1.35—1.45 Hz); 4.18 (ddt, 1 H, NCH′, J_{gem} = 15.42 Hz, ^3J = 5.3 Hz, ^4J = 1.2 Hz); 3.87 (ddt, 1 H, NCH″, J_{gem} = 15.42 Hz, ^3J = 5.3 Hz, ^4J = 1.46 Hz); 2.67 (s, 3 H, $\underline{NCH_3}$); −13.85 (s, 1 H, μ-H).

Cluster $(\mu\text{-H})Os_3\{\mu\text{-OCN(Me)CH=CH}_2\text{Me}\}(CO)_{10}$ (4). Complex **3** (100 mg) was dissolved in CH_2Cl_2, $CHCl_3$, or C_6H_6 (2 mL) and stored at ~20 °C for 4—20 days. A spot of the fraction that moved faster than the spots of the starting complexes **3a** and **3b** appeared on the control TLC (hexane—CH_2Cl_2 (4 : 1) as the eluent). The fraction was isolated by the preparative separation of the mixture on Silufol plates in the same eluent. The zone was eluted with methylene dichloride, and the solution was concentrated using a water aspirator pump. Complex **4** (a mixture of conformers) was obtained in the form of an orange powder. The yield was 80% after storage for 20 days. MS: *m/z* 955 $[M]^+$ (with respect to the ^{192}Os isotope). IR spectrum of complexes **4a**,**b**, ν/cm^{-1}: 2106 s, 2067 v.s, 2055 s, 2023 v.s, 2011 v.s, 1993 m, 1984 sh, 1977 w, 1963 v.w, 1951 v.w. ^{1}H NMR ($CDCl_3$), δ: complex **4a**, 6.79 (dq, 1 H,

NCH=, ^3J = 13.86 Hz, ^4J = 1.58 Hz); 5.31 (dq, 1 H, =CH—, ^3J = 13.86 Hz, ^3J = 6.68 Hz); 2.89 (s, 3 H, NCH_3); 1.77 (dd, 3 H, CH_3, ^3J = 6.68 Hz, ^4J = 1.58 Hz); −13.79 (s, 1 H, μ-H); complex **4b**, 6.97 (dq, 1 H, NCH=, ^3J = 14.4 Hz, ^4J = 1.6 Hz); 5.2 (dq, 1 H, =CH—, ^3J = 14.4 Hz, ^3J = 6.67 Hz); 3.22 (s, 3 H, NCH_3); 1.66 (dd, 3 H, CH_3, ^3J = 6.67 Hz, ^4J = 1.6 Hz); −13.76 (s, 1 H, μ-H).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-33046 and 97-03-33292).

References

1. V. A. Maksakov, V. A. Ershova, V. P. Kirin, and A. V. Golovin, *J. Organomet. Chem.*, 1997, in press.
2. V. M. Potapov, *Stereokhimiya* [*Stereochemistry*], Khimiya, Moscow, 1976, 584 pp. (in Russian).
3. K. A. Azam, C. C. Yin, and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1978, 1201.
4. R. Szostak, C. E. Strouse, and H. D. Kaesz, *J. Organomet. Chem.*, 1980, **191**, 243.
5. R. D. Adams and N. M. Golembeski, *J. Organomet. Chem.*, 1979, **171**, C21.
6. N. V. Podberezskaya, V. A. Maksakov, V. A. Ershova, and S. P. Gubin, *Koord. Khim.*, 1987, **13**, 818 [*Sov. J. Coord. Chem.*, 1987, **13** (Engl. Transl.)].
7. A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, Wiley, New York, 1972.
8. V. A. Maksakov, V. A. Ershova, V. P. Kirin, N. V. Podberezskaya, and L. A. Sheludyakova, in *Blagorodnye metally: khimiya and tekhnologiya* [*Noble Metals: Chemistry and Technology*], Nauka, Novosibirsk, 1989, 125 (in Russian).
9. V. A. Maksakov, V. A. Ershova, A. V. Virovets, Yu. L. Slovokhotov, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1991, **4**, 305 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
10. Y.-X. Lin, A. Mayr, C. B. Knobler, and H. D. Kaesz, *J. Organomet. Chem.*, 1984, 272, 207.
11. W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 1970, **70**, 521.
12. R. D. Adams, N. M. Golembeski, and J. Selegue, *Inorg. Chem.*, 1981, **20**, 1242.
13. A. V. Virovets, V. A. Ershova, N. V. Podberezskaya, and V. A. Maksakov, *Metalloorg. Khim.*, 1991, **4**, 932 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
14. V. A. Maksakov, V. A. Ershova, A. V. Virovets, N. V. Podberezskaya, P. P. Semyannikov, and A. G. Buyanovskaya, *Metalloorg. Khim.*, 1993, **6**, 231 [*Organomet. Chem. USSR*, 1991, **6** (Engl. Transl.)].
15. H. Günter, NMR *Spectroscopy*, J. Wiley and Sons, Chichester, 1981.
16. F. Bovey, in *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1969, 75.
17. R. L. Shriner, R. C. Fuson, D. Y. Curtin, and T. C. Morrill, *The Systematic Identification of Organic Compounds*, J. Wiley and Sons, New York—Chichester—Brisbane—Toronto.
18. D. G. Gehring, W. A. Mosher, and G. S. Reddy, *J. Org. Chem.*, 1966, **31**, 3436.
19. N. M. Morlyan, A. G. Muradyan, L. O. Esayan, and Sh. O. Badanyan, *Arm. Khim. Zh.* [*Armenian Chem. J.*], 1975, 28, 75 (in Russian).
20. M. T. Leffler, in *Organic Syntheses, Col. Vol. II*, J. Wiley and Sons, Inc., New York, 1943, 24.
21. M. G. Vladimirova and A. D. Petrov, *Zh. Obshch. Khim.*, 1946, **16**, 2141 [*J. Gen. Chem. USSR*, 1946, 16 (Engl. Transl.)].

Received July 22, 1997