Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines III-Structure and Fluxional Mechanism of fac-RuH(NO)(ttp)

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fac-RuH(NO)(ttp) is fluxional in the range between 180 K and 303 K. The structures involved in this fluxional process are found to be a mixture of two square pyramids and a trigonal bipyramid from the low temperature NMR spectra and the line shape analysis using DNMR 3 program and the activation parameters of this process were determined by using the simulated data. The mechanism of this fluxional process is proposed to be a pathway known as Turnstile Rotation.

Introduction

It has been recognized that chelating triphosphines can stop fluxional behavior by reducing the rate of intramolecular exchange and by limiting the number of chemically reasonable pathways for the rearrangement.[1,2] In spite of this expectation some fluxional complexes containing chelating triphosphines have been reported.[1,3] However, these complexes are fluxional via dissociative mechanisms. In other words, one phosphine of the chelating triphosphine exchanges its position via a dangling phosphine[3] and a coordinated monophosphine exchanges with free monophosphines while chelating triphosphines are intact. Recently, Jia and Lee found that fac-Ru(Cyttp)Cl_2 is fluxional probably via Bailar rotation.[4] In this paper, fluxionality of fac-RuH(NO)(ttp) will be reported and a possible fluxional mechanism based on the line shape analysis will be proposed.

Experimental Section

The preparation of RuH(NO)(ttp) was reported in the first paper of this series.[5] Many attempts to separate the facial isomer from the meridional one have failed. A Bruker AM-250 spectrometer was used to obtain proton (250.13 MHz) NMR spectra in 5 mm tubes. Residual solvent proton resonances were used as internal standards for the ^1H-NMR spectra. Phosphorus NMR spectra were collected on a Bruker AM-250 spectrometer (101.25 MHz) and phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer. The IR samples were prepared as Nujol mulls between KBr plates and the spectra were referenced to the sharp 1601 cm^{-1} peak of a polystyrene film. Computer simulation of line shape analysis was performed by DNMR 3 program.[6]

Results and Discussion

From the variable temperature NMR experiment, fac-RuH(NO)(ttp) was found to show fluxional behavior in the range of 180 to 303 K and this process is reversible in these temperature ranges (Figure 1 and 2). These spectral data are summarized in the Table 1 and simulation parameters are shown in Table 2. High-temperature NMR spectra cannot be obtained due to poor solubility in common organic solvents except CH_2Cl_2 and fast reaction with $CHCl_2CHCl_2$. In order to propose a fluxional mechanism and structure of fac-RuH(NO)(ttp), the following experimental and simulation data should be considered.

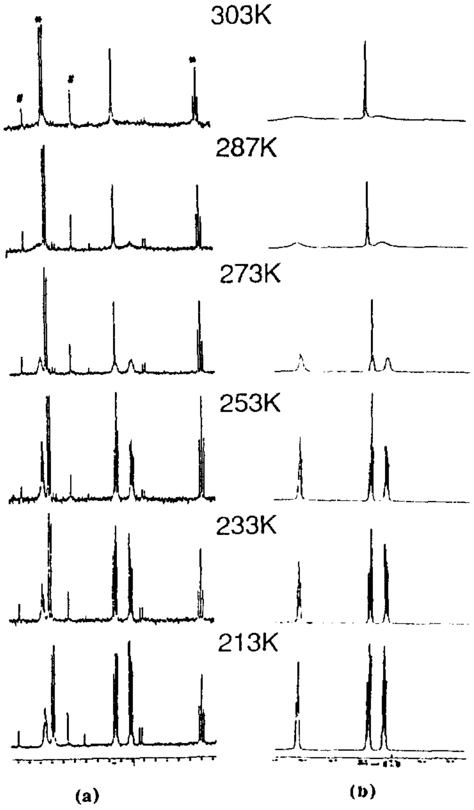


Figure 1. Variable temperature $^{31}P\{^1H\}$ NMR spectra of RuH(NO)(ttp) in CD_2Cl_2 at 101.252 MHz. (a) Experimental, (b) Calculation (facial isomer only). *: meridional isomer, $^{\#}$: impurities.

1. mer- and fac-RuH(NO)(ttp) do not interchange. (or it is too slow on the NMR time scale.)
2. No phosphorus peak assignable to a dangling phosphine

Table 1. Spectral Parameters of fac-RuH(NO)(ttp)

Temp.	δ*P* (ppm)	$^2J_{pp}$ (Hz)	δH (ppm)	$^2J_{PH}$	Solvent[b]	ν_{NO} (cm^{-1})	Medium[b]
213	35.04 (t) 22.82 (dd) 20.13 (dd)	41.0, 27.0, 22.2	−4.72 (ddd)	55.0, 38.7, 27.7	CD_2Cl_2		
233	35.15 (t) 22.67 (dd) 19.95 (dd)	41.0, 27.8, 21.9	〃	54.2, 36.8, 27.3	〃		
253	35.25 (t) 22.59 (dd) 19.85 (dd)	41.1, 27.4, 21.5	〃	53.0, 35.6, 26.0	〃		
273	35.34 (bump) 22.50 (d) 19.72 (bump)	12.4	−4.71 (dd)	27.5, 17.4	〃		
287	35 (bump) 22.55 (d) 20 (bump)	11.3	−4.72 (dd)	27.0, 18.0	〃		
303	22.52 (s)	—	−4.72 (dt)	18.0, 8.1	〃	1585	Nujol Mull

[a] NMR solvent, [b] IR medium.

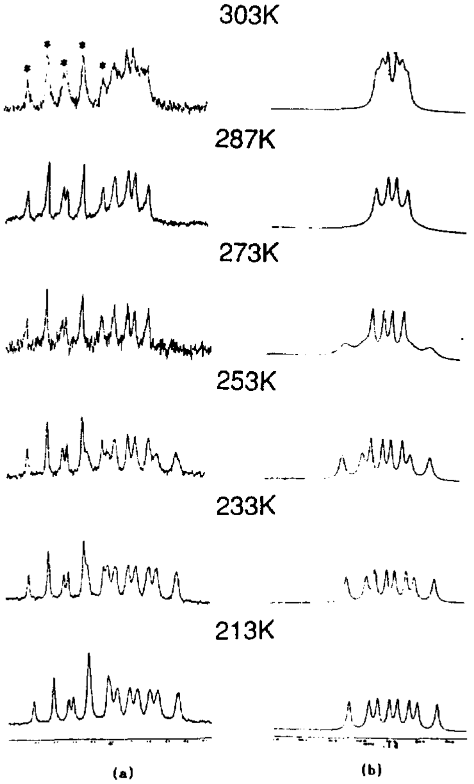


Figure 2. Variable temperature ^{1}H-NMR spectra of RuH(NO)(ttp) in CD_2Cl_2 at 250.133 MHz. (a) Experimental, (b) Calculation (facial isomer only). *: meridional isomer.

was found throughout the above-mentioned temperature range.

3. Simulation shows that three isomers are required where two of them are very similar and the outside two phosphorus peaks in the ^{31}P-NMR spectra interchange.

4. Interchange of the outside two phosphorus peaks shows that signs of two $^2J_{pp}$'s and the other $^2J_{PP}$ are different.

5. One of $^2J_{PH}$ (55.0 Hz) indicates that one phosphorus is located trans to hydride ligand even though it is not too large as found in case of RuH(NO)(etp).[5]

It has been recognized that the chemical shift of phosphorus peak in the ^{31}P-NMR spectra is sensitive to the nature of trans ligand.[2,7] This phenomenon is clear in the square pyramidal complexes such as $RuCl_2(PR_3)_3$[8] and $RuCl_2(PPh_3)(L_2)$(L_2=dppb, dppp)[9] in which apical phosphorus (no trans ligand) peaks appear downfield relative to those of equatorial phoshorus (trans to other phosphine). In other words, high trans inflence ligands generally push the chemical shift upfield even though quantitative changes by specific ligands are not known. In the low temperature limiting spectrum (180 K), this trend can be used to assign a structure. Trigonal bipyramidal geometry is known to be a little more stable than square pyramidal one in the 5-coordinate complexes but the difference is very small. Since trans ligand effect can be applied more easily in the square pyramidal complex, a square pyramidal geometry (structure I) as shown in the proposed mechanism (Figure 3) was at first used to rationalize our assignments even though the popularity of the structure I is smaller than those of structure II in all accessible temperatures (The DNMR 3 program requires to assign popularities to the possible structures and popularities can be rationalized based on the relative stabilities of the possible structures. Therefore, it is reasonable to assign more popularity to the more stable trigonal bipyramidal structure. These relative popularities change from 0.05 (structure I), 0.94 (structure II) and 0.01 (structure III) at 180 K to 0.15, 0.35 and 0.50 at 303 K). Since H and CO show similar trans effect[10] and NO is a stronger π-acceptor than CO, it is expected that the resonance of phosphorus trans to NO (wing

Table 2. ^{31}P-NMR Parameters of fac-RuH(NO)(ttp) for Simulation

Structure	δPPh_2 (Hz)	δPPh (Hz)	$\delta' Ph_2$ (Hz)	$^2J_{P\text{-}PPh}$ Hz	$^2J_{P\text{-}P'}$ Hz	$^2J_{P'\text{-}PPh}$ Hz
I	3575	2311	2039	27.0	22.3	−41.0
II	3547	2311	2039	27.0	22.3	−41.0
III	2039	2311	3575	−41.0	22.3	27.0

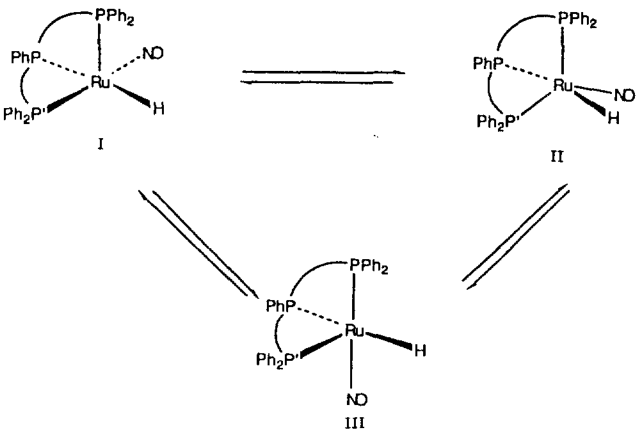
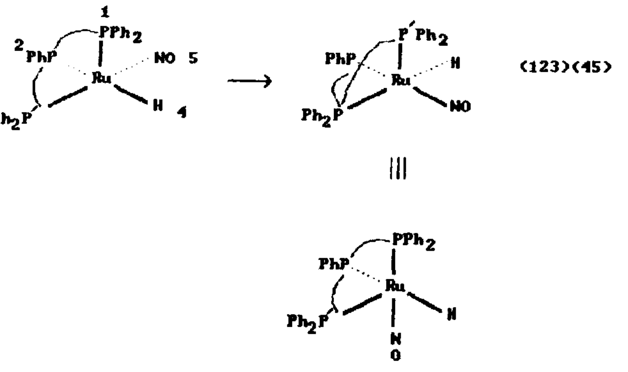


Figure 3. Proposed fluxional mechanism of fac-RuH(NO)(ttp).

Table 3. Thermodynamic Function Values of Three Exchange Processes of fac-RuH(NO)(ttp)

Process	ΔG^* kcal/mol	ΔH^* kcal/mol	ΔS^* cal/mol·K
12	6.82	6.30	−1.91
13	6.89	8.48	5.82
23	6.89	8.48	5.82



*(123)(45): rotations occur among positions specified in each parenthesis.

Figure 4. Turnstile rotation of fac-RuH(NO)(ttp). *(123)(45): rotations occur among positions specified in each parenthesis.

phosphine trans to NO) appears upfield relative to that of phosphorus trans to H (central phosphine trans to H) which, in turn, is upfield relative to that of phosphorus having no trans ligand (wing phosphine in the apical site). This assignment is supported by the presence of trans $^2J_{PH}$. In structure II, it is not easy to rationalize the chemical shifts of three phosphines. In case of central phosphine trans to H, it is obvious that no chemical shift change is expected. However, it is difficult to explain why the chemical shift of the wing phosphine trans to NO does not change but the chemical shift of the wing phosphine with no trans ligand goes upfield slightly. The only reasonable explanation of these facts is that structure I and II are not ideal square pyramidal and trigonal bipyramidal, respectively. Therefore, the angle of P-Ru-N is not 180° in structure I and the angle of P-Ru-N in structure II is assumed to be the same as that in structure I by accident. Even though the X-ray structure of fac-RuH(NO)(ttp) was not obtainted yet, this possibility is supported by the highly distorted trigonal bipyramidal structure of the closely related RuH(NO)(Cyttp).[5] Finally, the upfield shift of wing phosphine with no trans ligand is rationalized by the fact that in the trigonal bipyramidal structure this phosphine feels more trans ligand effect than that in the square pyramid and chemical shift goes upfield. Therefore, structure I and II are very similar to each other except slight change of angles of P(Ph_2)-Ru-P'(Ph_2) and P(Ph_2)-Ru-N(O). NO appears to be linear from the IR stretching frequency at 303 K but the exact nature of NO group at other temperatures connot be determined due to no available IR data at these temperatures. Accordingly, similar exchange rates between structure I and III and between structure II and III can be assumed without much problem ($k_{13}=k_{23}$) and the simulated spectra are reasonably matched to the experimental ones. Simulation data were fitted by the Eyring equation and thermodynamic fuction values are summarized in Table 3. These values are comparable with those found in the intramolecular processes.[11] Most of the 5-coordinated compounds are reported to follow a pathway known as the Berry pseudorotation (BPR) mechanism.[12] However, some cyclic 5-coordinated compounds are known to follow the pathway of Turnstile Rotation (TR)[13] and in this compound, TR appears to be reasonable due to the presence of cyclic group (ttp) even though BPR cannot be completely discarded. When TR mechanism is applied to this compound, there is a combination of rotations about an approximate local C_2 axis for the pair of ligands (H and NO) and an approximate C_3 local axis for the trio (ttp) shown in the Figure 4. The rather low activation parameters (ΔG^*) might represent the highly distorted structure of fac-RuH(NO)(ttp) as reported in the case of $HM(PX_3)_4$.[14]

Conclusions

The structures of fac-RuH(NO)(ttp) involved in the fluxional process are found to be a mixture of two square pyramids and a trigonal bipyramid and the popularity of trigonal bipyramidal structure is greater than those of the other square pyramidal structures in all accessible temperatures. There are exchanges among these structures probably via the Turnstile Rotation mechanism.

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Synthesis and Characterization of Molybdenum(V) Complexes with Tridentate Schiff Bases

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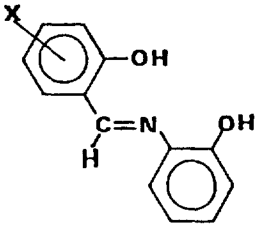
Six-coordinate molybdenum(V) complexes X[MoO(NCS)$_2$(L)], where X=PyH$^+$, Me$_4$N$^+$, Et$_4$N$^+$, n-Bu$_4$N$^+$, and L=the tridentate schiff base dianions derived from the condensation reaction between various salicylaldehydes and 2-aminophenol have been synthesized. The complexes have been characterized by elemental analysis, conductivity, UV-visible, IR, ^{1}H-NMR, and mass spectroscopy. The coordination around the molybdenum appears to be distorted octahedral. A tridentate ligand containing the ONO donor atoms occupies meridional positions with the N atom trans to the terminal oxo group. Two NCS ligands bond to the molybdenum through the N atom and are *cis* to the Mo=O$_t$ group. The electrochemical behaviors of the complexes have also been investigated by cyclic voltammetry in dimethylsulfoxide.

Introduction

Extensive studies have been carried out on oxomolybdenum(V) complexes of schiff base ligands.[1] In marked contrast, complexes with tridentate type ligands derived from salicylaldehyde and 2-aminophenol have been little studied. Recently, Yamanouchi *et al.*[2] reported the preparation and a single crystal X-ray structure determination for the type of complex (PyH)[MoOCl$_2$(sap)], (sap=N-salicylidene-2-aminophenol), and Mondal *et al.*[3] reported the preparation and electrochemical characterization of the complexes [MoO(sap)(cat)](cat=catechole) starting from [MoO$_2$(sap)]$_2$. However, the oxomolybdenum(V) complexes of the mixed ligands with the isothiocyanate and N-salicylidene-2-aminophenol or its derivatives are not as yet reported. Mazzi[4,5] prepared also the rhenium(V) complexes, [ReOCl$_n$(sap)]$^-$ (n=2, 3) and [ReO(L^1)(L^2)](L^1=sap^{2-}, L^2=monobasic bidentate ligands) depending on the stoichiometric ratios and conditions. These ligands contain potentially coordinating donor atom sets ON or ONO. It is known that the possibility of obtaining complexes with a particular structure is governed by the nature of the metal, the substituents and donor atom in the ligand, and the preparation conditions. Thus, with the aim of finding other possible stable configuration around molybdenum(V) containing the MoO^{3+} core, we have synthesized a series of complexes with isothiocyanates (PyH)[MoO(NCS)$_2$(X-sap)], where X-sap=the dibasic tridentate N-salicylidene-2-aminophenol or its 5-Me, 3-MeO, 3-EtO, or 5,6-Bz derivative, for the first time. In this paper, we report the syntheses, the structural determination by spectroscopic studies, and electrochemical behaviors of oxomolybdenum(V) complexes with the ligands illustrated (Figure 1).

Experimental



X	
H	sapH$_2$
5-Me	5-Me-sapH$_2$
3-MeO	3-MeO-sapH$_2$
3-EtO	3-EtO-sapH$_2$
5,6-Bz	5,6-Bz-sapH$_2$

Figure 1. Ligands used.

Materials. All chemicals used in synthesis were of reagent grade and were used without further purification. Pyridinium oxoisothiocyanatomolybdate(V), (PyH)$_2$[MoO(NCS)$_5$][6] and 5-methylsalicylaldehyde[7] were prepared by literature methods. All the schiff bases were prepared according to the method of Yamanouchi and identified by IR and ^{1}H-NMR.[2] All solvents were dried by standard procedures[8] and distilled before use.

Physical Measurements. Elemental analyses were carried out by Kolon R and D center, and molybdenum was determined gravimetrically as lead molybdate by literature method,[9] M. P. measurements were performed by using a Haake melting point apparatus. The IR spectra of solid samples in KBr were recorded on a Mattson Polaris FT-IR. The ^{1}H-NMR spectra in DMSO-d_6 were recorded on a Bruker AM-300 spectrometer and referenced to TMS (internal). Electronic spectra were obtained on a Pye Unicam SP-800 spectrophotometer. Electron-impact-ionization mass spectra of thermally volatilized samples were obtained by the direct-insertion probe technique on a Kratos MS-25 RFA spectrometer. Molar conductance was measured with Metrohm 660 conductometer. Cyclic voltammograms were recorded on a PAR 273 Potentiostat/Galvanostat and PAR RE 0091 X-Y re-