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Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines IV-Reactions between RuH(NO)(Cyttp) and Alkynes (Cyttp: Bis(dicyclohexylphosphino-propyl)phenylphosphine)

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The types of the products of the reactions between RuH(NO)(Cyttp) and alkynes are sensitive to the nature of alkynes. Terminal, nonactivated alkynes (HC≡CR, R=Ph, hexyl and CH_2OH) produce acetylide complexes and terminal (HC≡CR, R=C(O)Me, COOEt) or internal activated ones (RC≡CR, R=COOMe) lead to form alkenyl complexes. On the other hand, internal nonactivated alkynes (RC≡CR, R=Ph) do not show reactivity toward RuH(NO)(Cyttp). These products can be rationalized by the *cis*-concerted mechanism but the radical pathway appears to work in the reaction of propargyl chloride. Form the spectroscopic date, the trigonal bipyramidal structure with a linear NO group is proposed for these products.

Introduction

The reactions between alkynes and transition metal complexes have drawn attention due to their implication in the catalytic processes such as hydrogenation, oligomerization, and polymerization. There are several important reactions in this field; substitution, isomerization to vinylidenes, metallocyclization with other acetylene molecules or small molecules (CO and RNC), and the insertion reactions of alkynes to metal hydride or alkyl bonds. These reactions and catalytic reactions are well reviewed several places in the literature.[1-7] One of the interesting parts in these reactions is that the products of the reactions between metal hydrides and alkynes are closely related with the nature of metal hydrides and alkynes. In other words, various types of products such as acetylides and alkenyl complexes were reported depending upon the nature of the reactants and many mechanisms have been proposed to explain these products. These mechanisms are mainly proposed to explain the geometry of the alkenyl products but investigation on the kinetic data[8,9] and solvent effect is scarce. This has been partly attributed to easy or fast isomerization of the products. Important mechanisms proposed are concerted mechanism (*cis*[10,11] and *trans*[12]), stepwise ionic mechanism[10,13], and radical mechanism.[14,15] Therefore, at this point, as Herberich *et al.*[16] pointed out, it is difficult to predict the type of the products. In this paper, the reactions between alkynes and ruthenium hydridonitrosyl complexes including insertion reactions were investigated to clarify the mechanism of these reactions.

Experimental Section

All manipulations were performed under an argon atomsphere using standard Schlenk techniques unless stated otherwise. Solvents were all reagent grade and were distilled over argon from appropriate drying agents prior to use. Reagent grade chemicals were purchased from Aldrich Chemical Co., Inc. and used without further purification unless stated otherwise. Ruthenium trichloride hydrate was loaned from Johnson Matthey, Inc. and $RuH(NO)(PPh_3)_3$[17] and RuH(NO)(Cyttp)[18] were prepared by modified literature methods. The $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$-NMR spectra were recorded by using 5 mm tube on a Bruker AM-250 FT NMR spectrometer operating at 101.256 MHz, 250.133 MHz, and 62.896 MHz, respectively. These spectra were referenced to 85% H_3PO_4 and residual deuterium solvent peaks. Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Mass spectra were collected by Dr. David Chang of the Ohio State University on VG 720-250S double focussing mass spectrometer using FAB (Fast Atom Bombardment) method. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Az., U.S.A. or Oneida Research Servies, Inc., Whitesboro, N.

Table 1. Spectroscopic Data for Ru(CCR)(NO)(Cyttp)

R	^{31}P-NMR (C_6D_6)			^{13}C-NMR (CD_2Cl_2)				IR (Nujol Mull)	
	δP_{center}	δP_{wing}	$^2J_{pp}$	δC_α	$^2J_{pc}$	δC_β	$^3J_{pc}$	ν(NO)	ν(CC)
Ph	21.85	27.57	35.2	131(dt)	18.6, 2.3	124(t)	3.0	1605	2050
$(CH_2)_5CH_3$	23.15	28.52	35.2	132(dt)	14.1, 2.0	120(t)	2.0	1605	1940
COMe	20.38	25.94	34.4	133(t)	9.5			1600	1990
CO_2Et	20.67	26.13	35.4						
CHOH*	21.54	27.25	35.5	118(dt)	21.0, 7.2	119(s)		1605	2060

*In the proton NMR spectrum, $\delta(CH_2)$ is found as a broad singlet at 4.67 ppm. In the IR spectrum, the OH stretching band is found as a broad band centered at 3300 cm^{-1}.

Y., U.S.A. (results of many compounds were not satisfactory due to their high air-sensitivity).

[Ru(CCPh)(NO)(Cyttp)]. RuH(NO)(Cyttp) (200 mg, 0.28 mmol) was dissolved in 5 m*l* of benzene and then 0.50 m*l* of phenylacetylene (4.6 mmol) was added. The solution was stirred for 3 hours (color changed to dark green brown) and the solvent was removed under reduced pressure and 5 m*l* of acetone was added to precipitate out the green powder. The powder was collected by filtration and washed with 2m*l* of acetone three times and dried under vacuum overnight. Yield. 140 mg (62%). Mass Spec. (FAB). m/e 820 (M+1).

[Ru(C(COMe)=CH$_2$)(NO)(Cyttp)] and [Ru(CH=CHCOMe)(NO)(Cyttp)]. RuH(NO)(Cyttp) (350 mg, 0.49 mmol) was dissolved in 5 m*l* of benzene and then 1.4 m*l* of 3-butyn-2-one stock solution (0.36 M in benzene; 0.50 mmol) was added (Color changed to dark green immediately). The solution was stirred for 10 min and the solvent was removed under reduced pressure and 5 m*l* of *n*-hexane was added to precipitate out the brown solid. The solid was collected by filtration and washed with 2 m*l* of *n*-hexane three times and dried under vacuum overnight. Yield. 270 mg (71%). Mass Spec. (FAB). m/e 786 (M-1)

[Ru(CCC(O)Me)(NO)(Cyttp)]. RuH(NO)(Cyttp) (200 mg, 0.28 mmol) was dissolved in 5 m*l* of benzene and 5.0 m*l* of 3-butyn-2-one stock solution (0.36 M in benzene; 1.8 mmol) was added (color changes to dark green immediately). The solution was stirred for 30 min and the solvent was removed under reduced pressure and 5 m*l* of *n*-hexane was added. Dark brown solid was collected by filtration and washed with 2 m*l* of *n*-hexane three times and dried under vacuum overnight. Yield. 150 mg (69%). Mass Spec. (FAB). m/e 785 (M^+).

[Ru(C(CH$_2$)(CO$_2$Et)(NO)(Cyttp)]. A solution containing 200 mg of RuH(NO)(Cyttp) (0.278 mmol) and 0.70 m*l* of stock solution of ethyl propiolate (0.42 M in benzene; 0.29 mmol) in 5 m*l* of benzene was stirred for 30 min (color changes to dark green immediately). After evaporation of the solvent under reduced pressure, 10 m*l* of methanol was added to precipitate green compound out. This solid was collected by filtration and washed with 3 m*l* of methanol three times and dried under vacuum overnight. Yield. 180 mg (79%). Mass Spec. (FAB). m/e 817 (M^+).

[Ru(C(CO$_2$Me)C(H)(CO$_2$Me)(NO)(Cyttp)]. A solution containing 200 mg of RuH(NO)(Cyttp)) (0.278 mmol) and 0.50 m*l* of dimethylacetylenedicarboxylate (4.1 mmol) in 5 m*l* of benzene was stirred for 30 min (solution turned to dark green immediately). After removal of the solvent under reduced pressure, 5 m*l* of acetone was added and green solid was collected by filtration. This solid was washed with 2 m*l* of acetone and dried under vacuum overnight. Yield. 180 mg (81%) Anal. Calcd. for $C_{42}H_{68}NO_5P_3Ru$: C, 58.59; H, 7.96; N, 1.63. Found: C, 57.84; H, 7.60; N, 1.50.

[Ru(CCCH$_2$OH)(NO)(Cyttp)]. A solution containing 200 mg of RuH(NO)(Cyttp) (0.278 mmol) and 0.40 m*l* of stock solution of propargyl alcohol (0.68 M in benzene; 0.27 mmol) in 5 m*l* of benzene was stirred for 4 hrs (color changed to dark green). After evaporation of the solvent, 5 m*l* of acetone was added to precipitate out the green solid. The solid was collected by filtration and washed with 2 m*l* of acetone three times and dried under vacuum overnigt. Yield. 130 mg (61%). Mass Spec. (FAB). m/e 774 (M+1).

[RuCl(NO)(Cyttp)]. A solution containign 200 mg of RuH(NO)(Cyttp) (0.278 mmol) and 0.55 m*l* of stock solution of propargyl chloride (0.50 M in benzene; 0.30 mmol) in 5 m*l* of benzene was stirred for 1 hr (color changes to dark yellow). After removal of all solvent, 5 m*l* of acetone was added and yellow solid was precipitated out. The solid was collected by filtration and washed with 2 m*l* of acetone three times and dried under vacuum overnight. Yield. 140 mg (67 %). Anal. Calcd. for $C_{36}H_{61}ClNOP_3Ru$: C, 57.40; H, 8.16; N, 1.86; Cl, 4.71. Found: C, 57.60; H, 7.90; N, 1.77; Cl, 4.96.

[Ru(CC(H)Ph)(NO)(Cyttp)]BF$_4$. A soution containing 100 mg of Ru(CCPh)(NO)(Cyttp) (0.12 mmol) in 5 m*l* of CH_2Cl_2 was cooled down to 77 K. An excess of $HBF_4 \cdot Et_2O$ was added and the solution was warmed up to room temperature slowly. The color of the solution changed to purple red. The solvent was removed under reduced pressure and 10 m*l* of ether was added to precipitate the red purple solid. The solid was collected by filtration and washed with 3 m*l* of ether three times and dried under vacuum overnight. Yield. 90 mg (81%). Anal. Calcd. for $C_{44}H_{67}BF_4NOP_3Ru \cdot HBF_4 \cdot Et_2O$: C, 53.94; H, 7.26; N, 1.31. Found: C, 53.13; H, 6.64; N, 1.45.

Results and Discussion

In Table 1, 2, 3, and 4, spectroscopic data for the products from the reactions between RuH(NO)(Cyttp) and alkynes are summarized. As expected, types of product complexes are dependent on the nature of alkynes. In general, terminal nonactivated alkynes give acetylide complexes and terminal and internal activated ones (acetylenes with electron-withdrawing groups) produce alkenyl complexes. However, propargyl chloride produces RuCl(NO)(Cyttp) only and internal nonactivated ones do not show reactivity toward RuH(NO)-

Table 2. ^{31}P-NMR Parameters of Ru(Alkenyl)(NO)(Cyttp)

Alkenyl	δP_{center}, ppm	δP_{wing}, ppm	$^2J_{PP}$, Hz	Solvent
C(COMe)CH_2, A	13.12	14.57	47.0	C_6D_6
CHCHCOMe, B	6.21	12.63	40.4	C_6D_6
C(CO_2Et)CH_2, A	13.22	14.92	43.9	C_6D_6
CHCHCO_2Et, B	7.10	13.28	40.7	C_6D_6
C(CO_2Me)CHCO_2Me	9.55	12.93	45.5	C_6D_6

Table 3. ^{1}H-NMR Parameters for Ru(Alkenyl)(NO)(Cyttp)

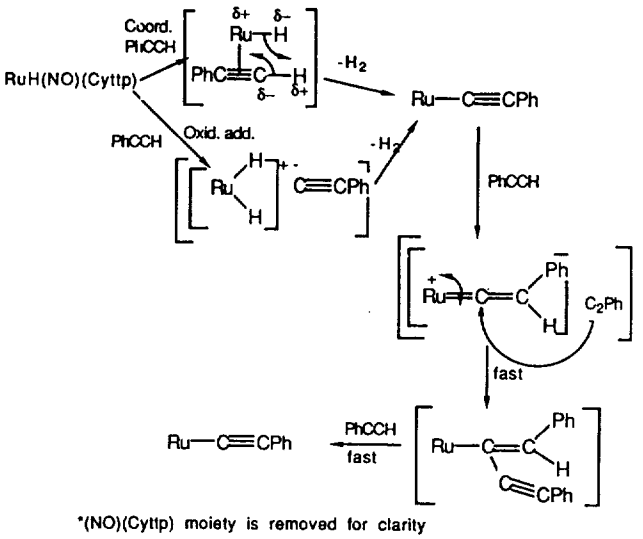
Alkenyl	δH_{vinyl} *trans*(or H_α)*	δH_{vinyl} *cis*(or H_β)*	Others	Solvent
C(COMe)CH_2, A	6.55(br, m)	6.02(br, m)	1	C_6D_6
CHCHCOMe, B	7.85(m)	6.85(br)	2	C_6D_6
C(CO_2Et)CH_2, A	6.70(br, m)	6.10(br, m)	3	CD_2Cl_2
CHCHCO_2Et, B	6.50(br)	5.80(br)	4	CD_2Cl_2
C(CO_2Me)CHCO_2Me		6.51(br, d)	5	CD_2Cl_2

1. δ(Me); 2.45 (s) 2. δ(Me); 2.66 (s) 3. δ(OCH_2); 4.02(q), δ(Me); 1.27 (t), $^3J_{HH}$=7.1 Hz 4. δ(OCH_2); 4.13 (q), δ(Me); obscured 5. δ (Me); 3.80 (s), 3.72 (s)

**Cis* and *trans* represent the relationships of vinyl protons relative to ruthenium in A-type complexes and H_α and H_β represent proton attached to C_α and C_β in the B-type complexes, respectively.

(Cyttp).

In the case of phenylacetylene, the type of product is not sensitive to the amount of phenylacetylene. However, when large excess of phenylacetylene is used, in addition to the acetylide complex small amount of free *cis*-and *trans*-1,4-diphenyl-1-butene-3-yne (almost 1 : 1 ratio, ^{1}H-NMR: vinyl peaks: 5.5 (d), 6.0 (d) $J_{H\text{-}H}$=11.9 Hz (*cis*), 6.1 (d) $J_{H\text{-}H}$=16.2 Hz (*trans*) 1 doublet may be obscured by the phenyl peaks) were detected by NMR in the reaction mixture. A reaction using 1 : 1 ratio of ruthenium complex to phenylacetylene also gives acetylide complexes. Resonance peaks appear in the same range for the closely related complexes reported in the literature.[19] Noncoordinating nature of these compounds was confirmed by the ^{31}P-coupled and decoupled ^{1}H and ^{13}C-NMR spectroscopy. In these spectra, the shapes of vinyl peaks assignable to these organic compounds were not changed. The amount of these compounds increased with the amount of added phenylacetylene and the reaction time. In order to explain the formation pathways of these products,



Scheme 1. Proposed mechanism for the formation of Ru(CCPh)(NO)(Cyttp).

Scheme 1 is proposed. In the first step, oxidative addition of phenylacetylene cannot be completely excluded because $[RuH_2(NO)(Cyttp)]^+$ is easily prepared by the reaction between RuH(NO)(Cyttp) and acids[20] and phenylacetylene is acidic even though it is weak. Change of bonding modes of NO group (linear mode to bending one) accomodates coordination of an acetylene in the early stage of the proposed concerted pathway. Concerted reaction between RuH(NO)-(Cyttp) and phenylacetylene is consistent with the reaction mechanism for the activated acetylenes (vide infra). The structure of the acetylide complex appears to be TBP (Trigonal Bipyramidal) with equatorial NO group because NO and CCPh are all strong *trans* influencing ligands. If either of them locates *trans* to the central phosphine, the chemical shift of this resonance shoud go upfield significantly (for this complex, ΔP(=δ P_{ceter}-δ P_{wing})=*ca.* 6 ppm). In Meek's group, these trends have been observed and this is assumed to be related with the bond distances between metal and phosphorus (remember that coordination of phosphines shifts the resonance peak downfield than free phosphine). Also, the meridional geometry of Cyttp is verified by ^{13}C-NMR spectra (virtual coupling phenomenon mentioned in the first paper[19] in this series). Since ν_{NO} does not change perceptibly from the reactant, [RuH(NO)(Cyttp)] which has a linear NO group, NO in this complex is assigned to be linear. Therefore, this complex has a structure of TBP in which a central

Table 4. ^{13}C-NMR and IR Spectra Data for Ru(Alkenyl)(NO)(Cyttp)

Alkenyl	δC_α	$^2J_{PC}$	δC_β	$^3J_{PC}$	δCO	Others	ν(NO)	ν(NO)	ν(C=C)
C(CO_2Et)CH_2, A	164.8(dt)	14.0, 7.4	125.5(dt)	7.4, 3.7	184.0(s)	58.89[1] 14.84[2]	1580	1680	1585
CHCHCO_2Et, B			128.0(br)						
C(CO_2Me)CHCO_2Me	192.7(dt)	12.7, 8.1	126.8(d)	3.3	182.9(s) 162.8(s)	51.4[1] 51.2[2]	1605	1675 1730	1520

**^{13}C-NMR and IR spectra are taken in CD_2Cl_2 and Nujol Mull, respectively. *Chemical shifts, coupling constants, and stretching frequencies are mesured in units of ppm, Hz, and cm^{-1}, respectively. 1. δ(OCH) 2. δ(Me).

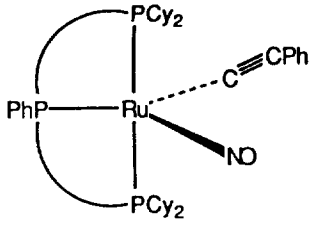
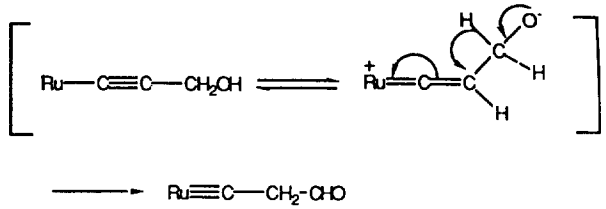


Figure 1. Proposed structure of Ru(CCPh)(NO)(Cyttp).



Scheme 2. Proposed mechanism for the rearrangement of Ru ($CCCH_2OH$)(NO)(Cyttp).

phosphine, linear NO and acetylide comprise the equatorial plane while wing phosphines occupy the axial positions (Figure 1). Similar reactions between hydride complexes and phenyl acetylene to form acetylides have been reported.[21,22]

1-Octyne gives a similar complex but reaction rates are rather slow maybe due to steric hindrance of long chain of alkyl group. Propargyl alcohol leads to form an acetylide complex which is rather surprising because -OH is more acidic than terminal acetylenic CH. This type of reaction was reported by Marder.[23] More interesting fact is that this acetylide complex slowly rearranges to form a complex containing an aldehyde group. ^{13}C and ^1H-NMR spectra show characteristic features for this complex: ^{13}C-NMR(CD_2Cl_2) 170.1 (s), δ (CHO); ^1H-NMR (CD_2Cl_2) 9.40 (t), δ(CHO) $^3J_{HH}$= 2.6 Hz; 7.7 (m) δ (CH_2); ^{31}P-NMR (C_6D_6) 24.97 (d), 19.33(t), $^2J_{PP}$=34.6 Hz. Scheme 2 is proposed for this rearrangement. Unfortunately, cabyne peaks cannot be detected due to difficulty of purification and relatively dilute concentration of ^{13}C-NMR sample. Further study to verify this pathway is still going on.

RuCl(NO)(Cyttp), the product of the reaction between RuH(NO)(Cyttp) and propargyl chloride is also unexpected because all reactions of terminal nonactivated alkynes involve the terminal acetylenic≡C-H bond. However, there are several reports about the oxidative addition reaction of RC≡CX (X=halide) where C-X bond activation occurs, but to author's knowledge, there is no precedent report on the preferred activation of a C-X bond over a acetylenic≡C-H bond by the metal hydride complexes. Meanwhile, it is well-known that benzyl or allyl halide can easily undergo oxidative addition to d^8 5-coordinate complexes.[24] Since these reactions proceed by a two-step reaction, stability of benzyl or allyl cation or radical formed during the reaction may be important. Therefore, observed results in this study can be rationalized by the same token. In other words, propargyl cation or radical is more stabilized by resonance while acetylenic cation or radical is very unstable.[25] In this case, reaction mechanism of this reaction appears to be different from other cases mentioned in the study. Since this reaction was run in a nonpolar solvent, benzene, radical oxidative addition of propargyl chloride followed by reductive elimination of 1-propyne or allene and then reattack of chloride radical can be proposed. No organic compound analysis was done and some radical scarvanger such as 2,4,6-trimethylphenol did not change the reaction rate but the fact that equivalent addition of propargyl chloride lead to formation of the product quantitatively while excess addition resulted in a very complicated mixture appears to have meaningful indication.

Reactions between RuH(NO)(Cyttp) and internal or terminal activated acetylenes reach completion almost intantaneously to give alkenyl complexes. In the reactions of terminal activated alkynes, two isomers were observed depending on the reaction condition. In other words, one isomer (A) which is formed from the transfer of a hydride ligand to the terminal acetylenic carbon (≡CH) is a kinetic product (alkenyl group is -C(R)=CH_2) but the other one (B) which is formed from the transfer of a hydride ligand to the substituted acetylenic carbon(RC≡) is a thermodynamic product (alkenyl group is -CH=CHR). 3-Butyne-2-one always lead to form a mixture of two isomers. Relative ratio of two isomers is dependent on the reaction condition; high temperature favors isomer B but in refluxing benzene some decomposition was observed and one pure isomer cannot be obtained. In chloroform, both isomers exclusively convert to one complex, tentatively assigned as [Ru(C(COMe)=CH_2)Cl(NO)(Cyttp)]Cl. Even though this formula is not supported by the elemental analysis, alkenyl moiety is intact and fully characterized by NMR (^1H and ^{13}C, C-H Correlation Diagram and DEPT spectrm). At this point, the mechanism by which these two initial alkenyl isomers convert to this new alkenyl complex is not clear but this may be rationalized if there is an equilibrium between two isomers and the final product results from the reaction between isomer A and chloroform only even though the reason cannot be explained. A large excess of 3-butyne-2-one induces formation of an acetylide complex.

In the case of ethylpropiolate, isomer A is initially formed but on long storage in methylene chloride, slow isomerization to isomer B was observed. Initially formed alkenyl complexes are mainly characterized by NMR techniques. Geminal coupling (2.5 Hz) in the ^1H-NMR spectrum and ^{13}C-NMR spectra (DEPT) clearly show that the product is an alkenyl complex where Cα bears an alkyl substituent (isomer A). ^{13}C-NMR spectrum shows that Cα is located *cis* to both phosphines ($^2J_{PC}$=14.0, 7 Hz). Also, 2nd order pattern of ^{31}P-NMR spectrum indicates that NO is not *trans* to central phosphine (vide supra). ν_{NO} is not significantly different from that of the starting material but ν_{CO} shifts to a frequency lower than that of free acetylene (1720 cm^{-1}). This indicates some interaction between oxygen of the carbonyl group and the ruthenium metal atom. However, strong interaction (*i.e.* coordination through π-donation of oxygen) should accompany the change of ^{31}P-NMR spectrum (triplet should move downfield from doublet due to poor *trans* effect of oxygen). A similar IR frequency was interpreted to be due to noncoordinated carbonyl group in the reaction product with the related complex ($RuHCl(CO)(PPh_3)_3$[26]). Therefore, a TBP geometry with two Oxial wing phosphines of Cyttp and an equatorial plane comprising a central phosphine, NO and alkenyl ligands is

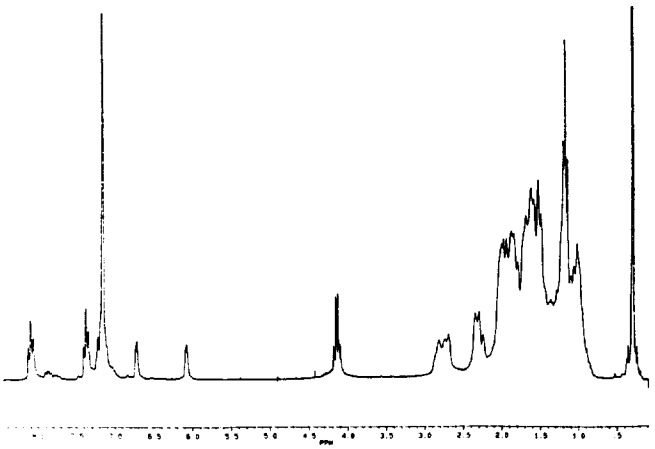


Figure 2. ^{1}H-NMR spectrum of Ru(C(CO_2Et)CH_2)(NO)(Cyttp) in C_6D_6 at 250.133 MHz.

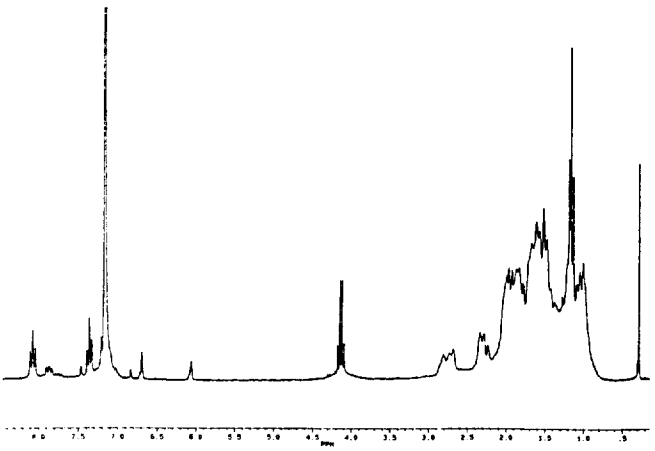
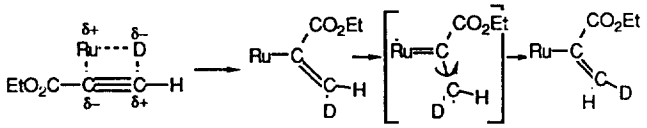
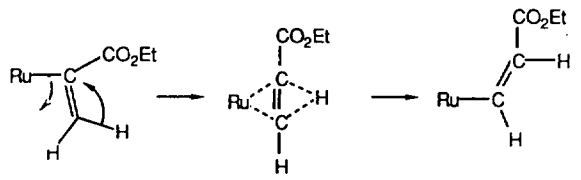


Figure 3. ^{1}H-NMR spectrum of the product of the reaction between RuD(NO)(Cyttp) and $CHCCO_2Et$ in C_6D_6 at 250.133 MHz.



Scheme 3. Proposed mechanism for the *cis-trans* Isomerization of Ru(C(CO_2Et)CH(D))(NO)(Cyttp).



Scheme 4. Proposed mechanism for the isomerization of Ru(C-(CO_2Et)CH_2)(NO)(Cyttp).

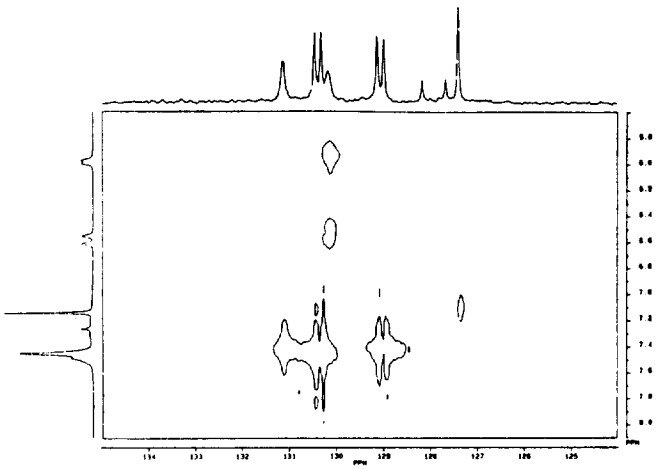


Figure 4. C-H correlation diagram of [RuCl(C(CO_2Et)CH_2)(NO)(Cyttp)]Cl in $CDCl_3$.

suggested for this complex. The nature of NO is not clear but the presence of interaction between CO and ruthenium indicates some extent of bending even though ν_{NO} (1580 cm^{-1}) does not reflect any indication of significant bending of NO group. The same reaction by uning RuD(NO)(Cyttp) shows that there is no preferential site for the deuteride transfer between *cis* and *trans* position (Figure 2 and 3). The deuterium scrambling results indicate that ionic or radical mechanism is most probable but fast reaction rate in nonpolar solvent such as benzene, no retardation of reaction rate by addition of radical inhibitor such as 2,4,6-trimethylphenol, no evidence of radical species by ESR (electron spin resonance) and contradiction of experimental results based on the stabilities of possible vinyl radicals (Cα localized radical is more stable than Cβ form and isomer B should be formed) do not support this assumption. Therefore, *cis* concerted addition followed by isomerization can be an alternative. There are several reports of fast isomerization *via* radical[27] or phosphine catalytic reaction.[28] However, in this system thermal excitation process mentioned by Nakamura[29] (Scheme 3) appears to work since no external radical or phosphine source can be found. Storage of the product in CH_2Cl_2 for a long time induces isomerization (isomer A to B) which probably involves 1,2-hydrogen shift (Scheme 4). Isomer B has a similar chemical shift to isomer A but similar $\Delta\delta(=\delta P_{center}-\delta P_{wing})$ to acetylide complex. *Cis* relationship of two vinyl hydrogens are indicated by ^{1}H-NMR spectrum (no well-resolved *trans* or *cis* coupling constant is observed but rather broad bond ($\omega_{1/2}=2$ Hz is found) but fast equilibrium between *cis* and *trans* isomers cannot be excluded. Similarity in spectroscopic data with acetylide complexes leads to the similar structure of TBP for this isomer. Treatment with chloroform produces another complex where the alkenyl and NO groups are intact (Figure 4) as in case of 3-butyn-2-one. This complex is assigned as [RuCl(C(CO_2Et)CH_2)(NO)(Cyttp)]Cl. Futher study on this complex will be presented elsewhere. Also a large excess of ethylpropiolate produces an acetylide complex.

A reaction between RuH(NO)(Cyttp) and an internal nonactivated alkyne such as diphenylacetylene proceeds very slowly maybe due to steric hindrance. After a day, only marginal amount of acetylene was reacted. However, an internal activated alkyne such as dimethylacetylenedicarboxylate reacts very quickly to produce the *cis* (position of H with respect to Ru) insertion product. The geometry of the alkenyl group was confirmed by INEPT (Insensitive Nuclei Enhancement

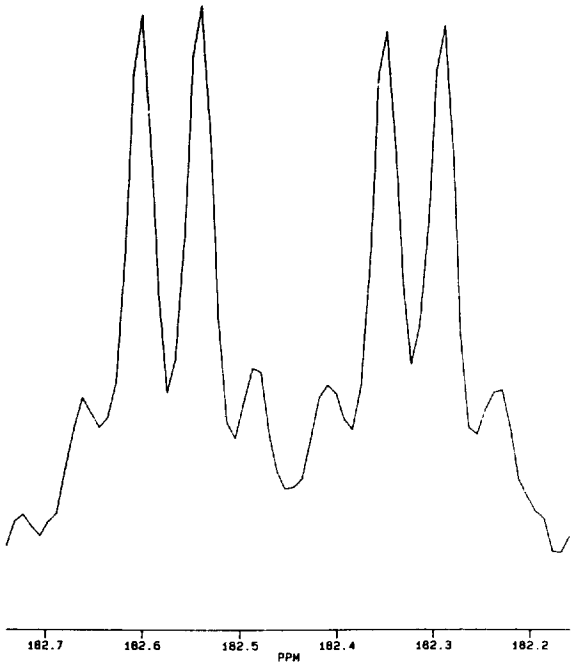
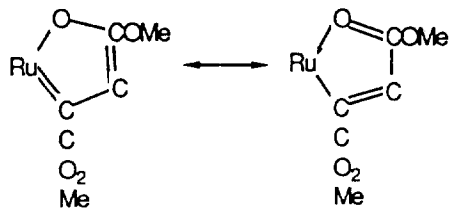


Figure 5. ^{13}C-INEPT spectrum of Ru(C(CO_2Me)CHCO_2Me)(NO)(Cyttp) in CD_2Cl_2 (Carbonyl Region Only).

by Polarization Transfer) NMR experiment (Figure 5). The result shows that the ^{13}C resonance of the carbonyl carbon bonded to the carbon not bearing vinyl proton is splitted by vinyl proton by 16.2 Hz. This value indicates these groups to be *trans* to each other.[16] Several mechanisms are possible but to be consistent throughout this sudy, *cis* concerted mechanism is the most probable. Also, δCα (192. 7 ppm) in the ^{13}C-NMR spectrum indicates one carbonyl group might coordinate to the metal center because coordination of CO of alkyne should move the chemical shift of Cα downfield due to carbene character.[30] Treatment with $CHCl_3$ produces



a similar product as in the cases of ethylpropiolate and 3-butyn-2-one and in this complex, δCα moves upfield (167.4 ppm) indicating no coordinated CO is present. Even though alkenyl and NO groups are present intact, the exact formula of this complex requires further study. Spectroscopic data for these compounds are summarized in Table 5.

Protonation of acetylide complexes can lead to a vinylidene or a η^2-acetylene complex. In the case of Ru(CCPh)(NO)(Cyttp), protonation produces a vinylidene complex readily. The carbene character of Cα in the product can be easily confirmed by the ^{13}C and ^{1}H-NMR spectra. δCα (334.2 ppm (dt), $^2J_{PC}$=19.9, 12.6 Hz) and $\delta H_{vinylidene}$ (5.84 (td), $^4J_{JH}$=12.4, 6.2 Hz) fall in the range of reported vinylidene complexes. Other spectroscopic data are listed as follows. (^{31}P-NMR (Acetone-d_6); δP_{center}=20.64 ppm, δP_{wing}=19.14 ppm, $^2J_{PP}$=28.5 Hz, ^{13}C-NMR (Acetone-d_6); δCβ=119.6 (dt), $^3J_{PC}$=14.7, 6.7 Hz, IR (Nujol Mull); ν_{NO}=1670 cm^{-1}, $\nu_{C=C}$=1640, 1615 cm^{-1}. The nature of NO is not clear but since the cationic complex is less favorable for π-backbonding than the comparable neutral complex, ν_{NO} is reasonably assigned to linear NO and another TBP structure is proposed for this complex. In this complex, a central phosphine, a vinylidene and a NO group comprise an equatorial plane.

Conclusions

The types of the products of the reactions between RuH(NO)(Cyttp) and alkynes are sensitive to the nature of alkynes. Terminal, nonactivating alkynes produce acetylide complexes and terminal or internal activating ones lead to form alkenyl complexes. On the other hand, internal nonactivating alkynes do not show reactivity toward RuH(NO)(Cyttp). These initially formed products can be rationalized by the *cis*-concerted mechanism but radical pathwas is appeared to work in the reaction of propargyl chloride. Also, isomerization of products is observed (propargyl alcohol and ethylpropiolate cases) and new alkenyl complexes are formed observed (proprgyl alcohol and ethylpropiolate cases) and new alkenyl complexes are formed after the reaction between chloroform and initially formed alkenyl complexes. Protonation of acetylide complexes leads to the formation of an vinylidene complex as expected.

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Table 5. Spectroscopic Data for [Ru(Alkenyl)(NO)Cl(Cyttp)]Cl

Alkenyl	^{31}P-NMR($CDCl_3$)			^{1}H-NMR($CDCl_3$)		^{13}C-NMR($CDCl_3$)					IR (Nujol Mull)
	δP_{center}	δP_{wing}	$^2J_{pp}$	δH_{vinyl}	$^4J_{PH}$	δCα	$^2J_{pc}$	δCβ	δCO	$^3J_{pc}$	ν(NO)
C(COMe)CH_2	−17.86	4.75	26.0	7.0(d) 6.7(d)	15.8 5.7	168.6(td)	79.6, 10.0	135.3(s)	204.9(s)		1830
C(CO_2Et)CH_2	−16.81	4.70	25.4	6.75(d) 6.17(d)	14.9 5.9	152.6(td)	82.0, 10.8	130.5(s)	174.4(s)		1840
C(CO_2Me)CHCO_2Me	−12.73	6.29	25.8	6.55(s)		167.4(td)	78.9, 10.6	124.7(s)	175.8(s) 163.5(d)	9.2	1840

*Chemical shifts, coupling constants, and NO stretching frequencies are shown in units of ppm, Hz, and cm^{-1}, respectively

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Structure-Activity Relationship Study on Cephalosporins with Mechanism-based-Descriptors

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The polarizability and the transition state energy of a cephalosporin are assumed to be theoretical indices of the permeability through the outer membrane and of reactivity of β-lactam ring with penicillin binding proteins, respectively, in Gram-negative bacteria. They are computed by AM1 method and used as variables of quantitative structure-activity relationship study. The results justify quadratic dependence of the activity on the variables. The intersection of difference volumes between β-lactamase stable cephalosporins and unstable ones manifests that the steric hindrance of 7-side chain is responsible for the β-lactamase stability.

Introduction

The cephalosporins, a series of β-lactam antibiotics, inhibit bacterial growth by acylation of the penicillin binding protein (PBP) involved in biosynthesis of the peptidoglycan layer of bacterial cell walls.[1] The bacteria can be classified as two groups, Gram-negative and Gram-positive. Generally the former has outer membrane in it, but the latter does not. The