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Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines I-Structures of RuH(NO)P₃ (P₃ : Chelating Triphosphines)

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Chelating triphosphines were applied to freeze the fluxionality and to minimize the number of isomers found in the monophosphine analogues and this technique was proved to be useful. RuH(NO)P₃(P₃; Cyttp, ttp and etp) complexes were characterized to have similar trigonal bipyramidal structures with linear NO groups. Cyttp prefers to have a meridional geometry while etp prefers a facial one and ttp complexes are mixture of these two isomers. The crystal structure of RuH(NO)(Cyttp) has been determined to have a distorted trigonal bipyramidal structure with a linear NO in the equatorial plane. The crystals are orthorhombic, space group P_{nma}, with unit cell dimensions $a = 16.356(2)$, $b = 20.474(2)$, $c = 10.915(1)$ Å, $V = 3655$ Å³, $Z = 4$, $R = 0.035$ and $R_w = 0.034$ for the 2900 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 208 variables.

Introduction

Although hydridocarbonyl complexes have attracted much attention due to their utility in organic syntheses[1] and catalytic reactions,[2] hydridonitrosyl complexes have been remained unnoticed. Only a few complexes of this category are known (RuH(NO)L₃,[3] [IrH(NO)(PPh₃)₃]⁺,[4] CpRe(CO)(NO)H,[5] CpW(NO)₂H[6] and CpW(NO)H(CH₂SiMe₃)[7] where L is a phosphine or a phosphite) and even fewer examples of chemistry of these complexes are reported.[3,6,8] Considering the flexible nature of NO ligand (formally, 3e⁻ or 1e⁻ donor) and rich chemistry of hydride complexes, it is surprising that the che-

mistry of these complexes has not been investigated thoroughly up to date. This might be due to some fluxionality[3] and many isomers.[4] Since chelating triphosphine ligands reduce the rate of intramolecular exchange and limit the number of chemically reasonable pathways for the rearrangement,[9,10] it is expected that MH(NO)P₃ (P₃; chelating triphosphines) may stop or minimize the fluxional behavior and allowed to be studied easily by spectroscopic method at the room temperature. Also there are several advantages of chelating triphophines over monophosphines such as control of stoichiometry and coordination number due to less tendency toward dissociation.[10] This character appears to be very im-

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portant to see the change of bonding modes of NO during the reaction, if any. In other words, if the complexes follow the EAN (Effective Atomic Number) rule, the situation of bent NO can be designed by tailoring the ligands except P_3 and NO. Moreover, structural determination of $MH(NO)P_3$ will show the effect of chelating triphosphines on the structure and the bonding modes of NO group because structures of $RuH(NO)(PPh_3)_3$[11] and $[IrH(NO)(PPh_3)_3]^+$,[12,13] are already known. Since structural change was observed depending on the ring size of chelating triphosphines,[10,14] comparison of structure, bonding mode of NO of Cyttp (Bis(dicyclohexylphosphinopropyl)phenylphosphine) or ttp (Bis(diphenylphosphinopropyl)phenylphosphine) nitrosyl complexes with etp (Bis(diphenylphosphinoethyl)phenylphosphine) nitrosyl complexes can be examined to see this effect. In this paper, several new ruthenium hydridonitrosyl complexes containing chelating triphosphines were prepared and structures of these complexes will be discussed.

Experimental Section

All manipulations were performed under an argon atmosphere 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 Company, Inc. and used without further purification unless stated otherwise. Ruthenium trichloride hydrate was loaned from Johnson Matthey Inc. and $RuH(NO)(PPh_3)_3$ was prepared as described in the literature.[15] Cyttp, ttp were prepared by modified literature methods[16] and etp was purchased from the Aldrich Chemical Company, Inc. 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, tetramethylsilane (TMS) and TMS respectively. Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer. The IR samples were prepared as either Nujol mulls between KBr plates or as KBr pellets or in some proper solvents between NaCl plates and the spectra are referenced to the sharp 1601 cm^{-1} peak of a polystyrene film. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Az., U.S.A.

RuH(NO)(Cyttp). A solution containing 8.80 g (9.58 mmole) of $RuH(NO)(PPh_3)_3$ and 6.20 g (10.6 mmole) of Cyttp in 70 m*l* of benzene was refluxed for 30 min. After cooling down to room temperature, the solvent was removed under reduced pressure to *ca.* 1 m*l* and 20 m*l* of acetone was added to precipitate the dark yellow-brown powder. The solid was collected by filtration and washed with 5 m*l* of acetone three times and dried under vacuum overnight. Yield: 4.90 g (71%). Anal. Calcd. for $C_{36}H_{62}NOP_3Ru$: C, 60.15; H, 8.69; N, 1.95; Found: C, 60.22; H, 8.42; N, 1.86.

RuD(NO)(Cyttp). This compound was prepared by the procedure given above for RuH(NO)(Cyttp) using 3.74 g of $RuD(NO)(PPh_3)_3$[17] (4.07 mmole) and 3.25 g of Cyttp(4.46 mmole) Yield: 1.97 g (67%).

RuH(NO)(ttp). A solution containing 500 mg of RuH$(NO)(PPh_3)_3$ (0.54 mmole) and 5.0 m*l* of stock solution of ttp (0.15 M in benzene; 0.74 mmole) in 20 m*l* of acetone

was stirred for 3 hrs at room temperature. After removing solvents under reduced pressure, 15 m*l* of ether was added and light brown solid was collected by filtration and washed with 5 m*l* of ether three times and dried under vacuum overnight. Yield: 270 mg(71%). Anal. Calcd. for $C_{36}H_{38}NOP_3$Ru: C, 62.24; H, 5.51; N, 2.02; Found: C, 61.88; H, 5.47; N, 1.86.

RuH(NO)(etp). A solution containing 1.80 g of RuH(NO) $(PPh_3)_3$ (1.96 mmole) and 1.10 g of etp(2.06 mmole) in 30 m*l* of benzene was refluxed for 30 min. After cooling down to room temperature, all solvent was removed under reduced pressure and 20 m*l* of ether was added. Light red brown solid was collected by filtration and washed with 5 m*l* of ether three times and dried under vacuum overnight. Yield: 0.90 g (69%). Anal. Calcd. for $C_{34}H_{34}NOP_3Ru$: C, 61.17; H, 5.28; N, 2.10; Found: C, 61.03; H, 5.08; N, 2.00.

RuD(NO)(etp). This compound was prepared by the procedure given above for RuH(NO)(etp) using 2.00 g of RuD $(NO)(PPh_3)_3$ (2.17 mmole) and 1.20 g of etp.(2.25 mmole) Yield: 1.25 g (86%).

Crystal Structure of RuH(NO)(Cyttp). The dark brown crystals were grown from a benzene/ether/acetone solution by slow evaporation under argon stream. The crystal used for data collection was cut from a larger crystal and coated with a thin layer of epoxy. Preliminary examination of the diffraction pattern with a Syntex (Nicolet) P1 diffractometer indicated an orthorhombic crystal system with systematic absence *Okl, l* = 2*n* + 1 and *hkO, h* + *k* = 2*n* + 1. The space group possibilities are restricted to *Pc2₁n* (a non-standard setting for *Pna2₁*) and *Pcmn* (a non-standard setting for *Pnma*). The cell constants are *a* = 10.915(1) Å, *b* = 20.474(2) Å, and *c* = 16.356(2) Å and were determined at ambient temperature by a least-squares fit of the diffractometer setting angles for 25 reflections with 20° < 2θ < 29° and with Mo-Kα radiation (λ = 0.71069 Å). The θ-2θ scan method was used for data collection on the P1 diffractometer. Six standard reflections were measured after every 100 reflections and all six standards increased slightly in intensity during the course of data collection. The data were corrected for Lorentz and polarization effects and put onto an approximately absolute scale by means of a Wilson plot.[18] At this point the data is transformed to correspond to the standard setting for *Pnma*, so that the cell constants used for all further calculations are; *a* = 16.356(2) Å, *b* = 20.474(2) Å and *c* = 10.915(1) Å. No absorption correction is applied to the data because of the small value of the absorption coefficient. The structure was solved and succesfully refined in *Pnma*. With Z = 4, the presence of a crystallographic mirror plane is required and easily accomodated within the molecule. The position of ruthenium atom was obtained from a Patterson map. The remainder of the molecule was easily located by phasing on the ruthenium atom in the DIRDIF procedure.[19] The SHELX-76 package[20] was used for all full-matrix least-squares calculations. Isotropic refinement of the non-hydrogen atoms covered at an *R* factor of 0.074. After a cycle of anisotropic refinement, the majorities of the hydrogen atoms, including the hydride atom bound to ruthenium, were located on the difference electron density map. All the hydrogen atoms bound to carbon atoms were included in the model at their calculated positions with C-H = 0.98 Å and were held fixed during least-squares refinement. The hydride atom was in-
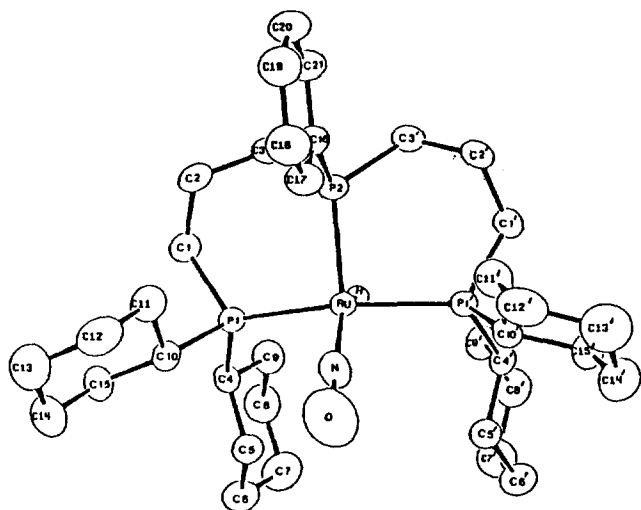
Figure 1. X-ray Crystal Structure of RuH(NO)(Cyttp) with atomic numbering scheme.

Table 1. Crystallographic Details for RuH(NO)(Cyttp)

Formula	$RuNOP_3C_{36}H_{62}$
Formula wt., amu	718.89
Space group	$Pnma$
a, Å	16.356(2)
b, Å	20.474(2)
c, Å	10.915(1)
Volume, Å³	3655
Z	4
Density (Calc.), g/cm³	1.31
Crystal size	0.29 mm×0.29 mm×0.41 mm
Radiation	MoKα with graphite mono-chromator, λ=0.70926 Å
Linear abs. coeff., cm⁻¹	5.76
Temperature	20℃
2θ limits	$4° \leq 2\theta \leq 55°$
Scan speed	2.0 to 24.0 deg/min in 2θ
Scan range	$(K\alpha_1 - 1.0)°$ to $(K\alpha_2 + 1.0)°$
Data Collected	$+h, +k, +l$
Unique data	4342
Unique data, with $F_o^2 > 3\sigma(F_o^2)$	2900
Final number of variables	208
$R(F)^a$	0.035
$R_w(F)^b$	0.034

$^a R(F) = \Sigma|F_o| - |F_c| /\Sigma|F_o|$. $^b R_w(F) = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

cluded in the model at its position as located in the difference electron density map. It was initially held fixed, but was later allowed to refine during the final cycles of least-squares refinement. The final refinement cycle (on F) yielded agreement indices of $R = 0.035$ and $R_w = 0.034$ for the 2900 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 208 variables (non-hydrogen atoms anisotropic, hydride atom isotropic, and all the remaining hydrogen atoms fixed). The largest peak in the final difference electron density map is 0.36 e/Å³ and is located between atoms P(1) and C(1). The minimum peak in the map

Table 2. Final Positional Parameters and B(eq) Values for the Non-Hydrogen Atoms of RuH(NO)(Cyttp)

Atom	x^a	y	z	B(eq)^b
Ru	0.09613(2)	0.250	0.06121(3)	2.16(1)
P1	0.07399(5)	0.36148(4)	0.03710(7)	2.35(3)
P2	0.05536(7)	0.250	0.26236(10)	2.42(4)
C1	0.01643(22)	0.40691(16)	0.15486(28)	3.11(15)
C2	0.02651(22)	0.38533(16)	0.28914(27)	3.10(15)
C3	−0.00878(20)	0.31776(16)	0.31540(28)	2.98(15)
C4	0.01761(20)	0.38580(15)	−0.10326(27)	2.65(13)
C5	0.06400(22)	0.36648(17)	−0.21901(27)	3.18(15)
C6	0.01939(27)	0.38820(20)	−0.33493(31)	4.36(19)
C7	−0.06620(26)	0.35973(22)	−0.33915(34)	5.00(21)
C8	−0.11362(23)	0.37884(20)	−0.22537(33)	4.28(19)
C9	−0.06934(20)	0.35781(18)	−0.10897(31)	3.42(15)
C10	0.17093(19)	0.40893(15)	0.02265(28)	2.75(13)
C11	0.21872(21)	0.40802(19)	0.14368(32)	3.60(17)
C12	0.30244(22)	0.43831(21)	0.12889(36)	4.56(20)
C13	0.29747(26)	0.50734(23)	0.07956(41)	5.63(24)
C14	0.24820(25)	0.51049(20)	−0.03743(37)	4.84(21)
C15	0.16422(22)	0.47927(17)	−0.02384(33)	3.67(17)
C16	0.13747(29)	0.250	0.37877(41)	2.63(20)
C17	0.21762(31)	0.250	0.34215(45)	3.34(23)
C18	0.28157(32)	0.250	0.42520(51)	4.22(27)
C19	0.26362(33)	0.250	0.55005(50)	4.09(25)
C20	0.18360(34)	0.250	0.58982(44)	3.89(26)
C21	0.12075(30)	0.250	0.50415(43)	3.37(23)
N	0.19298(28)	0.250	−0.01368(44)	4.13(22)
O	0.25529(31)	0.250	−0.06930(59)	9.85(37)
H	−0.0009(32)	0.250	0.0310(47)	6.2(14)
H1C9	−0.1002	0.3733	−0.0378	4.3
H2C9	−0.0663	0.3100	−0.1070	4.3

is −0.32 e/Å³. Scattering factors are from the usual sources and include terms for anomalous scattering.[21] The crystallographic mirror plane contains the ruthenium, hydride, and P(2) atoms along with the phenyl ring and the N-O group.

Results and Discussion

Crystal Structure of RuH(NO)(Cyttp). Figure 1 shows the ORTEP view of the final structure of RuH(NO)(Cyttp) and crystallographic details and final positional parameters are summarized in Table 1 and 2, respectively. The structure of RuH(NO)(Cyttp) is highly distorted from the ideal TBP (Trigonal Bipyramidal), with the central phosphine, nitrosyl and hydride ligands comprising the equtorial plane and two wing phosphine ligands occupying the axial positions. It is best described as intermediate between TBP and SP (Square Pyramidal). The ruthenium atom is slightly displaced from the plane which triphosphine comprises toward the NO ligand (0.39 Å). This type of displacement is common in the TBP structure where two axial ligands from the plane which three monophosphines comprise show different coordinating abilities. (0.55 Å, RuH(NO)(PPh₃)₃;[11] 0.030 Å, CoH(N₂)(PPh₃)₃;[22] 0.36 Å, RhH(CO)(PPh₃)₃;[22] 0.51 Å, [IrH(NO)(PPh₃)₃]ClO₄(black isomer)[12]) This displacement is partly

Table 3. Selected Bond Lengths and Angles of RuH(NO)(Cyttp)

Atoms	Distances, Å	Atoms	Angle, deg
Ru-P$_1$	2.326(1)	P$_1$-Ru-P$_2$	93.61(2)
Ru-P$_2$	2.295(1)	P$_1$-Ru-N	94.96(3)
Ru-N	1.783(4)	P$_1$-Ru-P$_1$	157.81(3)
Ru-H	1.62 (5)	P$_1$-Ru-H	79.9(18)
N-O	1.186(5)	P$_2$-Ru-N	134.2(2)
		P$_2$-Ru-H	84.8(18)
		N-Ru-H	141.0(18)
		Ru-N -O	176.5(5)

*standard deviation is shown in the parenthesis. *more information is available on request.

responsible for the slight deviation of the angles between ligands from the ideal values (Table 3). A slightly wider bite angle of Cyttp (93.61°) than ttp (approximate 90°; 90.73(2)°, RhCl(ttp); 90.34(8)°, [Rh(ttp)(NO)Cl]$^+$ [23]) is observed and this is rationalized by the fact that cyclohexyl groups demand more steric bulkiness than phenyl groups. The position of the hydride ligand is not ideal (P$_1$-Ru-H, 79.9(18)°; P$_2$-Ru-H, 84.8(18)°) and it appears that the hydrogens of C$_9$ and C$_9$' prevent hydride ligand from occupying the ideal position. This type of deviation was also found in RuHCl(PPh$_3$)$_3$(89°)[24] and RhHCl(PPh$_3$)$_2$(SiCl$_3$)·xSiHCl$_3$(69°)[25] and this is ascribed to the proximity of bulky central groups. The NO ligand is essentially linear (176.5(5)°) and this result is rater surprising because ν_{NO} in the IR spectrum is rater low (1580 cm^{-1}) and increased π-back bonding might favor a bending of {MNO} group[26] (Triphosphine is more basic than the monophosphine analogues and π-back bonding in this complex is more favorable than that in the isoelectronic complex of [RhCl(NO)(ttp)]$^+$ where NO is bent). However, recalling that increased electron density on the metal atom may lead to the bending of the NO group or to the structural change to the TBP,[27] the structural change process seems to be energetically favorable in this case. Ru-N distance (1.783(4) Å) (equatorial position) is comparable with that (1.792(11) Å) in RuH(NO)(PPh$_3$)$_3$ (axial position) but it must be pointed out that Ru-N distance is sensitive to the position of NO group in TBP structure as found in the isoelectronic iridium complexes; distance of axial NO (1.68(3) Å) (black isomer) is shorter than that of the equatorial NO (1.80(3) Å) (brown isomer)[13] in [IrH(NO)(PPh$_3$)$_3$]$^+$. Therefore, it is reasonable to say that a change of monophosphine to chelating phosphine leads to a shortening of the Ru-N distance as expected from the fact that increased electron density on the metal results in increased π-back bonding. However, the N-O distance does not show any significant elongation (RuH(NO)(Cyttp), 1.186(5) Å; RuH(NO)(PPh$_3$)$_3$, 1.183(11) Å) and this type of insensitivity of N-O distance to the degree of π-bonding can be easily recognized by the brief review of known crystal structures of nitrosyl complexes ([Os(NO)(CO)$_2$(PPh$_3$)$_2$]$^+$, TBP, angle of Os-N-O, 177(1)°, distance of N-O, 1.12(1) Å;[28] [IrCl(NO)(CO)(PPh$_3$)$_2$]$^+$, SP, angle of Ir-N-O, 124.1(9)°, distance of N-O, 1.16(1) Å;[29] [RhCl(NO)(ttp)]$^+$, SP, angle of Rh-N-O, 131.0(1.4)°, distance of N-O, 1.081(16) Å) The observed M-N distance lies in the middle of the range reported for linear NO complexes (1.68-1.89 Å). The Ru-P distances

Table 4. Comparison of Selected Bond Distances and Angles of Triphosphine Complexes

Atoms	Rh(ttp)Cl	[Rh(ttp)Cl(NO)]PF$_6$	RuH(NO)(Cyttp)
M-P$_1$	2.288(1) Å	2.374(3) Å	2.326(1) Å
M-P$_2$	2.201(2)	2.282(4)	2.295(1)
P$_2$-C$_3$	1.827(4)	1.829(11)	1.833(3)
P$_2$-C$_{16}$	1.836(6)	1.797(9)	1.849(5)
M-P$_2$-C$_3$	118.1(1)°	116.7(4)°	117.9(1)°
M-P$_2$-C$_{16}$	112.5(2)	111.9(4)	116.5(2)
C$_3$-P$_2$-C$_3$'	98.6(3)	98.7(5)	98.4(2)

1. Standard deviation is shown in the parenthesis. 2. P$_1$ and P$_2$ represent central and wing phosphine, respectively. 3. C$_3$, C$_3$' and C$_{16}$ represent ipso carbons of phenyl or cyclohexyl ring of phosphine and nearest carbon of propyl back-bone to the wing phosphine, respectively.

trans to each other (Ru-P$_1$ or Ru-P$_1$') are longer than that which does not have *trans* phosphine (Ru-P$_2$) are longer (2.326(1) Å *vs.* 2.295(1) Å) due to *trans* influence of phosphine. This phenomenon is also observed in other phosphine complexes (RhCl(PPh$_3$)$_3$, 2.320 Å and 2.331 Å *vs.* 2.210 Å;[30] [RhCl(NO)(ttp)]$^-$, 2.374(3) Å *vs.* 2.282(4) Å) Also, Ru-P distances are shorter than those in other Ru(0) complexes, which represents stronger donating abilities of chelating triphosphines than those of monophosphines (RuH(NO(PPh$_3$)$_3$, 2.345(3) and 2.328(3) Å; RuI(NO)(CO)(PPh$_3$)$_2$, 2.391(8) Å;[31] Ru(NO)$_2$(PPh$_3$)$_2$ ·1/2C$_6$H$_6$, 2.337(2) and 2.353(2) Å[32]). Moreover, distortions[33] which are the consequences of shortening the Ru-P distances, such as longer P-C bonds to the phenyl ring, cyclohexyl rings and propyl chain, an opening of the Ru-P-C angles and a closing of the C-P-C angles, are found as in [Rh(NO)Cl (ttp)]$^+$ and Rh(ttp)Cl but in this complex the distortion is more severe (Table 4). The phenyl ring of the central phosphine lies *trans* to the hydride ligand which is contrary to the result of the NOE (Nuclear Overshauser Effect) experiment (vide infra). However, as Hoffmann[27] pointed out, if there are many possible structures of similar energy, solid state structures may be different from solution structures. This statement is also appliable to RuHCl(PPh$_3$)$_3$,[24] which has identical phosphines in solution but two different sets of phosphines in the solid state.

Spectroscopic Data of RuH(NO)P$_3$. Typical NMR spectra of RuH(NO)P$_3$ are shown in Figure 2 and 3 spectral data are summarized in Table 5 and 6. In contrast to the monophosphine analogues, these complexes do not show any fluxionality from 210 K to 342 K except fac-RuH(NO)(ttp) (proposed structures and a mechanism are shown in Figure 4 based on the spectroscopic data and the details of the mechanism of fluxionality are discussed separately.[34]) as expected from the properties of chelating triphosphines (vide supra). The fluxional process of fac-RuH(NO)(ttp) is reversible in these temperature ranges but there was no exchange between mer-RuH(NO)(ttp) and fac-RuH(NO)(ttp). Several attempts to prepare pure one isomer by changing solvents and reaction temperatures (including refluxing in benzene) have failed. Therefore, the assignments of the spectroscopic data of RuH(NO)(ttp) were based on variable temperature NMR experiments and the assumption that Cyttp and ttp
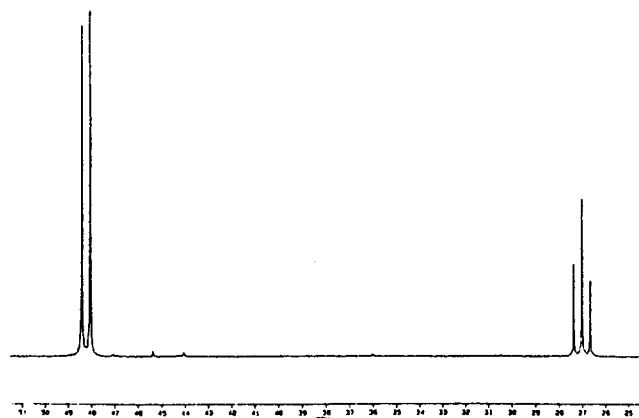
Structures of RuH(NO)P₃

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Figure 2. ³¹P{¹H} NMR Spectrum of RuH(NO)(Cyttp) in C₆D₆ at 101.252 MHz.
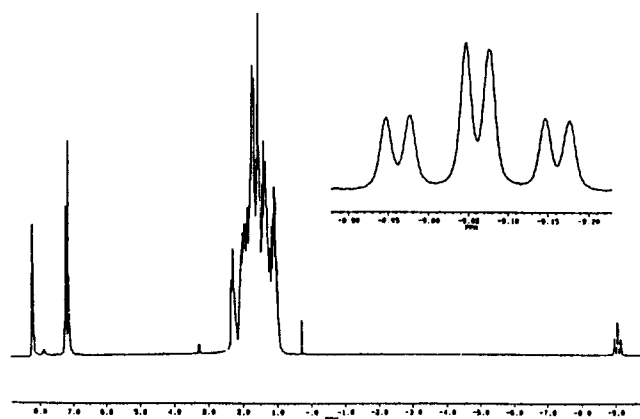
Figure 3. ¹H-NMR Spectrum of RuH(NO)(Cyttp) in C₆D₆ at 250.133 MHz.

Table 5. ³¹P-NMR Parameters of Ruthenium Hydridonitrosyl Complexes

Complex	δP_{center}, ppm	δP_{wing}, ppm	$^2J_{pp}$, Hz	Δ^a, ppm	ΔR^b, ppm	Solvent
RuH(NO)(Cyttp)	26.99	48.25	35.8	55.1	−12.8	benzene-d_6
mer-RuH(NO)(ttp)	7.90	34.52	39.8	36.1	−31.8	CD₂Cl₂
fac-RuH(NO)(ttp)^c	22.52	−	−	−	−	CD₂Cl₂
RuH(NO)(etp)	106.42	83.09	18.8	123.0	55.1	benzene-d_6
RuH(NO)(PPh₃)₃	61.88			69.7		benzene-d_6

$^a\Delta$: $\delta P_{center, complex}-\delta P_{free\ ligand}$. $^b\Delta_R$: $\Delta_{complex}-\Delta_{monophosphine\ complex}$. ^{c}at 303 K.

Table 6. ¹H-NMR and IR spectral Data of Ruthenium Hydridonitrosyl complexes

Complex	δH(or δD), ppm	$^2P_{PH}$, Hz	Solvent	v(Ru-H)	v(NO)	medium
RuH(NO)(Cyttp)	−9.05(dt)	24.9, 7.3	C₆D₆	1800	1580	Nujol Mull
RuD(NO)(Cyttp)	−9.19(broad s)		CH₂Cl₂	1290(1293)^b	1590	Nujol Mull
mer-RuH(NO)(ttp)	−4.37(td)	48.1, 26.5	CD₂Cl₂	1885	1608	Nujol Mull
fac-RuH(NO)(ttp)^c	−4.72(dt, broad)	18.0, 8.1	CD₂Cl₂	1830	1585	Nujol Mull
RuH(NO)(etp)	−3.19(td)	54.4, 23.4	C₆D₆	1840	1600	Nujol Mull
RuD(NO)(etp)	−3.70(broad, d)	5.44	CH₂Cl₂	1305(1307)^b	1615	Nujol Mull
RuH(NO)(PPh₃)₃^c	−6.35(q)	30.0	C₆D₆	1965	1640	Nujol Mull
RuD(NO)(PPh₃)₃^c				−(1396)^b	1660	Nujol Mull

^{a}at 303 K. ^{b}theoretical value. ^{c}reference 17. *IR stretching frequencies are measured in unit of cm⁻¹

do not cause large differences of the structure between mer-RuH(NO)(ttp) and RuH(NO)(Cyttp) which is true so far in most Cyttp and ttp complexes (vide infra). For Cyttp and mer-ttp compounds, the peak of the central phosphine appears upfield from that of the wing phosphines in ³¹P-NMR spectra while reverse pattern is observed for the etp case (Table 5). The chemical shift of the chelating phosphine is influenced by the ring effect[35] (In the 4- or 6-member ring-forming chelating posphine complexes, the δ³¹P shifts upfield than that in the monophosphine complexes and reverse trend appears in the 5-member ring-forming chelating phosphine complexes) and *trans* ligand effect[10]. (Strong *trans*-influence ligands *trans* to phosphine ligands tend to shift upfield of the δ³¹P). In the 6-member ring system (Cyttp and ttp complexes) with strong *trans* ligands such as H and NO, these two effects are exerted in the same direction but in the

5-member ring system (etp complexes), these two effects go to the opposite directions and ring effect appears to be predominant from the spectroscopic data. Meanwhile, it is well recognized that in the 5-coordinate complexes, the d^6 complex prefers SP structure while d^8 one favors TBP.[36,37] Since X-ray crystal structure of RuH(NO)(Cyttp) is proved to have TBP structure and a linear NO group and v$_{NO}$'s in the RuH (NO)P₃ complexes are similar (Table 6), the structures of these complexes can be assigned to have TBP structure and a linear NO group (d^8 complexes) even though IR stretching frequency of NO does not represent the bonding modes of NO unequivocally. IR stretching frequencies of NO in these complexes are rather low (*ca.* 1600 cm⁻¹) but viewed from the fact that v$_{NO}$ of a well-characterized linear NO complex goes as low as 1427 cm⁻¹ in a recent paper[38] these values are still acceptable for the linear NO stretching frequency.
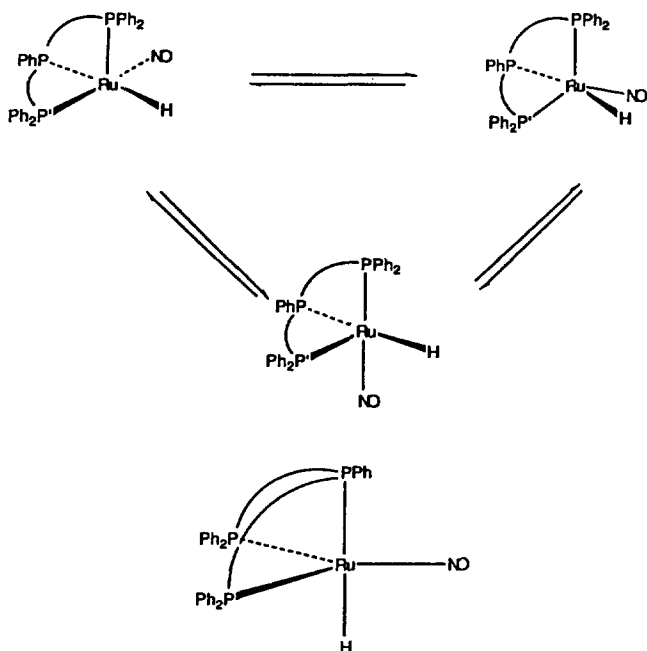
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Figure 4. Proposed structures of fac-RuH(NO)(ttp) (top) and RuH(NO)(etp)(bottom).

Figure 5. $^{13}C\{^{1}H\}$ NMR Spectrum of RuH(NO)(Cyttp) in C_6D_6 at 62.896 MHz (Two left-side triplets are assigned as cyclohexyl ipso carbon peaks) (top) and NOE Spectrum (Irradiated at hydride peaks) in C_6D_6 at 250.133 MHz (bottom).

For the RuH(NO)(ttp), since a meridional isomer was assumed to have a TBP structure with linear NO(d^8 complex) as RuH(NO)(Cyttp) and a facial one has larger contribution of square pyramidal structures with higher possibility of a bent NO group (d^6 complex), the higher NO stretching frequency was assigned to the meridional isomer. $^2J_{pp}$ of the etp complex is smaller than those of Cyttp and ttp complexes. This phenomenon is typical for the 5-member ring system and has been attributed to the different sign of the coupling constants of through-metal and through-backbone.[39] One of the $^2J_{PH}$'s($^2J_{P2-H}$) of RuH(NO)(Cyttp)is abnormally low (7.3 Hz) while those of mer-RuH(NO)(ttp) fall in the normal range for cis coupling (Table 6). This might be due to distortion from the ideal position of the hydride ligand (84.8°, vide supra) but in the complexes with the similar distortions, the coupling constants are in the normal range (RuHCl(PPh₃)₃, 26 Hz;[40] RhHCl(PPh₃)₂(SiCl₃), 16 Hz[41]). One possible explanation is that $|^2J_{PH,\ trans}| > |^2J_{PH,cis}|$ and these coupling constants have the opposite sign which is trun in most cases.[42] Therefore, if the angle of H-Ru-P₂ is in the turning point where the sign of $^2J_{PH}$ changes, a small value of $^2J_{PH}$ is possible. This point of view is supported by the fact that $^2J_{P1-H}$ is in the normal range (24.9 Hz) in spite of more severe distortion from the ideal value (79.9°). From this standpoint, the geometries of RuH(NO)(Cyttp) and mer-RuH(NO)(ttp) are expected to be different, especially in angle of H-Ru-P₂ even though the basic structure (TBP) might be same. This situation can be easily expected by considering the fact that cyclohexyl group is bulkier than phenyl group even though electronic factor might play some role. For the RuH(NO)(etp), it is difficult to determine the meaning of $^2J_{PH}$ (54.4 Hz) because this value falls on the border line between the value ranges of *trans* (usually more than 80 Hz) and *cis* (20-50 Hz) coupling constants. In other words, *cis* and *trans* isomers are all possible from this value only. Therefore, in assigning
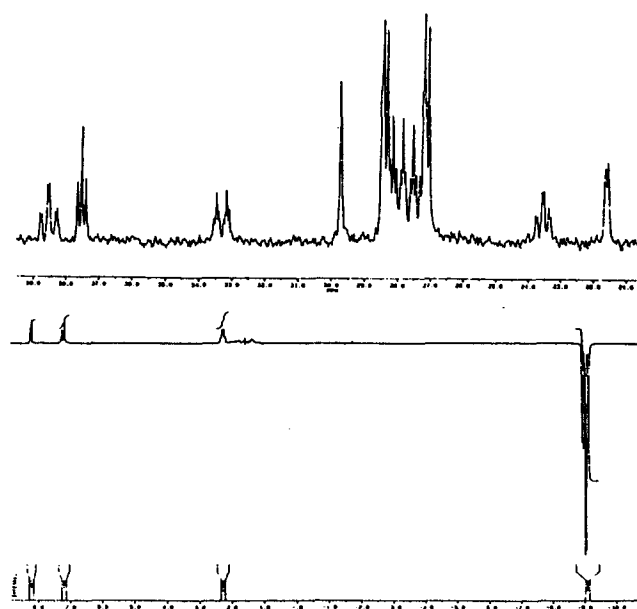
the geometry of RuH(NO)(etp) following properties should be satisfied as many as possible.

1. etp ligand favors facial geometry due to smaller bite angle (*ca.* 83°)[43] than Cyttp and ttp.

2. v_{NO}'s are similar in these complexes, which indicates linear NO and formal oxidation state of Ru is O(d^8)-favors TBP.

3. In the TBP structure, π-acceptor ligand favors the equatorial position for maximum overlap[27], and placement of the hydride ligand on the axial position can lead to minimum nonbonding repulsions by allowing the central metal to move out of the equatorial plane away from the hydrogen atom.[44]

Therefore, a TBP structure with two wing phosphines and nitrosyl ligands comprising the equatorial plane and the central phosphine and hydride ligands occupying the axial positions (*trans* to each other) is proposed for the geometry of RuH(NO)(etp) (Figure 4). The crystal structure of [Ru(PMe₃)(NO)(etp)]Cl which is formed by the substitution reaction between [RuH₂(NO)(etp)]⁺ (a protonation product of RuH (NO)(etp)) and PMe₃ supports this assignment. This complex has a TBP structure with two wing phosphines and nitrosyl lignds comprising equatorial plane and the cental phosphine and PMe₃ occupying the axial positions (*trans* to each other) (Further detail of structure and reactions of dihydride complexes are presented elsewhere[45]). Deuterium analogues of RuH(NO)(Cyttp) and RuH(NO)(etp) help determine the v_{Ru-H} in the IR spectra. Despite the assignment of v_{Ru-D}, their assignment is suspicious because these peakes are not distinctive. For the RuH(NO)(Cyttp), meridional geometry of Cyttp was confirmed by the $^{13}C\{^{1}H\}$ NMR spectrum where resonance peaks of the ipso carbons of the cyclohexyl rings are triplets (two triplets of far left in Figure 5). From the recent research, it is found that ipso carbon of the cyclohexyl ring appears as a triplet when Cyttp has a meridional geo-

metry, while it gives a doublet of doublet when Cyttp has a facial geometry. For the ttp and etp complexes this pattern cannot be recognized due to overlap of many aromatic peaks. This phenomenon resembles the virtual coupling of PMe_2Ph in the ¹H-NMR spectra, which is useful in determining the geometry of the complexes.[46] However, general application of this phenomenon requires caution because an exceptional case[47] was reported. In the NOE experiment (Figure 5), relatively large intensity change of ortho hydrogen of phenyl ring (a triplet located far left) shows that there is an interaction between the ortho hydrogen of phenyl ring of central phosphine and a hydride ligand. This indicates phenyl ring of central phosphine appears to be in the same side of the hydride ligand which is contrary to the crystal structure of RuH(NO)(Cyttp). Therefore, it is concluded that a solution structure is different from that of solid state. One of the possible interconversion routes between these two forms (one is that the phenyl ring of the central phosphine and a hydride locate in the same side and the other is that they locate in the opposite sides.) is three-step one; dissociation of the central phosphine followed by the partial rotation of back bone and then coordination to metal again. This can be supported by the common observation of rapid dissociation-coordination behaviors of monophosphines in the corresponding complexes and free rotation of single-bond chain.

Conclusions

Chelating triphosphines are proved to be useful to freeze the fluxionality and to minimize the number of isomers found in the monophosphine analogues and increased electron density on the metal imposed by the introduction of chelating triphosphines was not enough to change the bonding modes of NO. TBP structures as found in the monophosphine analogues are retained with linear NO groups but Cyttp prefers meridional geometry while etp prefers facial one and ttp complexes are found as a mixture of two isomers.

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Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines II-Structures of $[RuH_2(NO)P_3]^+$ (P_3 : Chelating Triphosphines)

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The protonation of RuH(NO)(Cyttp) resulted in the formation of [RuH₂(NO)(Cyttp)]⁺ which is characterized as a classical *cis*-dihydried complex. This complex is fluxional and the intramolecular process involving a molecular hydrogen complex is proposed. This mechanism was further supported by the reactivity of this complex toward neutral 2-electron ligands. On the other hand, it failed to detect the existence of [RuH₂(NO)(etp)]⁺ probably due to instability of the complex but the crystal structure of [Ru(PMe₃)(NO)(etp)]⁺ formed by the protonation of RuH(NO)(etp) followed by the addition of PMe₃ was determined to have a trigonal bipyramidal structure with a linear NO in the equatorial plane and a facial etp ligand. The crystals are monoclinic, space group $P2_1/n$, with unit cell dimensions $a = 14.130$ (2), $b = 21.026$ (3), $c = 14.760$ (1) Å, $\beta = 97.88$ (1)° $V = 4344$ Å³, $Z = 4$, $R = 0.046$ and $R_w = 0.056$ for the 4779 intensities with $F_o^2 > 3$ σ (F_o^2) and the 440 variables.

Introduction

Introduction of hydride ligands by protonation has been recognized as one of the important preparation methods of hydride complexes.[1] From the electron counting view point, proton does not contribute the electron to the metal center and this method can be used to introduce hydride ligand to the coordinatively saturated complexes as well as coordinatively unsaturated ones. A classical example of this reaction can be found in the Vaska complexes.[2] Recently, molecular hydrogen complexes have attracted much interest as a model of H₂ activation which, in turn, is important in the various hydrogenation processes catalyzed by the various metal complexes. Since the first discovery of this kind of complex by Kubas,[3] two recent reviews[4,5] have been published and many articles[6] have been followed. Up to date, various characterization methods of the molecular hydrogen complexes such as NMR (T_1 and J_{HD} measurement), IR, neutron or X-ray diffraction[4,5] and electroochemical redox me-

thod[7] have been established. However, NMR techniques, especially T_1 measurement in the various temperature developed by mainly Crabtree and Morris, have been widely used because of their convenience and clarity. Since many reported molecular hydrogen complexes are prepared by protonation of the hydride complexes[8-11] and cationic d^6 complexes containing strong *trans* influence ligands such as H and CO[5,12] favor molecular hydrogen complexes, the possibilities of molecular hydrogen complexes of the title complexes were investigated in this paper. Moreover, bonding modes of NO ligands and structures of these complexes were examined to find the clue of the relationship between bonding modes of NO ligands and structures of complexes, especially in the 5-coordinated nitrosyl complexes.

Experimental Section

All manupulations were performed under an argon atmosphere using standard Schlenk techniques unless stated other-