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Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines II-Structures of $[\text{RuH}_2(\text{NO})\text{P}_3]^+$ (P_3 : Chelating Triphosphines)

Ik-Mo Lee*, Devon W. Meek^{†,‡}, and Judith Gallucci[†]

Department of Chemistry, Inha University, Incheon 402-751

[†]*Department of Chemistry, The Ohio State University, 140 West 18th Avenue,*

Columbus, Ohio 43210, U.S.A., [‡]deceased on December 7, 1988. Received March 18, 1992

The protonation of $\text{RuH}(\text{NO})(\text{Cytpt})$ resulted in the formation of $[\text{RuH}_2(\text{NO})(\text{Cytpt})]^+$ 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 $[\text{RuH}_2(\text{NO})(\text{etp})]^+$ probably due to instability of the complex but the crystal structure of $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{etp})]^+$ formed by the protonation of $\text{RuH}(\text{NO})(\text{etp})$ followed by the addition of PMe_3 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 $F_o^2 > 3 \sigma(F_o^2)$ 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 H_2 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 articles⁶ 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 electrochemical redox me-

thod⁷ 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 complexes⁸⁻¹¹ 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 manipulations were performed under an argon atmosphere using standard Schlenk techniques unless stated other-

wise. Solvents were all reagents 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 $\text{RuH}(\text{NO})(\text{Cytp})$, $\text{RuH}(\text{NO})(\text{etp})$, $\text{RuD}(\text{NO})(\text{etp})$ and $\text{RuD}(\text{NO})(\text{Cytp})$ was prepared by the literature method.¹³ The $^{31}\text{P}\{^1\text{H}\}$, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded by using 5 mm tubes 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. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Az., U.S.A.

$[\text{RuH}_2(\text{NO})(\text{Cytp})]\text{BF}_4$. $\text{RuH}(\text{NO})(\text{Cytp})$ (350 mg, 0.49 mmole) was suspended in 10 ml of ether under hydrogen atmosphere and the solution was freeze-dried by liquid nitrogen and excess $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was added. The solution was warmed up slowly while stirring. The color changed from dark brown to light brown. After stirring the solution for 15 min, the sticky solid was collected by filtration and dried by passing hydrogen gas through the frit for 2 days. Yield: 230 mg (43% based on the following formula of the product; $[\text{RuH}_2(\text{NO})(\text{Cytp})]\text{BF}_4 \cdot 1.8\text{HBF}_4 \cdot \text{Et}_2\text{O}$) $^{31}\text{P}\{^1\text{H}\}$ NMR(CD_2Cl_2) δ 8.35 (t), δ 38.65 (d), $J_{\text{pp}} = 25.0$ Hz ^1H -NMR(CD_2Cl_2 , 303K) δ -6.73 (broad) IR(CH_2Cl_2) $\nu_{\text{Ru-H}}$: 1940, 1850 cm^{-1} , ν_{NO} : 1760 cm^{-1} . Anal. Calcd. for $\text{C}_{43.2}\text{H}_{82.8}\text{B}_{2.8}\text{F}_{11.2}\text{NO}_{2.8}\text{P}_3\text{Ru}$: C, 47.25; H, 7.60; N, 1.28. Found: C, 47.15; H, 7.12; N, 1.49.

$[\text{RuD}_2(\text{NO})(\text{Cytp})]\text{BF}_4$. This reaction was monitored by the ^{31}P , ^1H and ^2H -NMR spectra. The sample was prepared by dissolving 20 mg of $[\text{RuH}_2(\text{NO})(\text{Cytp})]\text{BF}_4$ in 0.5 ml of CD_2Cl_2 and then bubbling of D_2 through the solution for 3 min.

$[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{Cytp})]\text{BF}_4$. $[\text{RuH}_2(\text{NO})(\text{Cytp})]\text{BF}_4 \cdot 1.8\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (150 mg, 0.14 mmole) was dissolved in 5 ml of CH_2Cl_2 and 0.15 ml of trimethyl phosphine solution (1.00 M in THF, 0.15 mmole) was added quickly. Bubbling was observed upon addition of PMe_3 and the solution was stirred for 5 min. No more bubbling was observed and after removing solvent under reduced pressure, 10 ml of ether was added to precipitate the pale yellow solid out. The solid was collected by filtration and washed with 3 ml of ether three times and dried under vacuum overnight. Yield: 110 mg (70% based on the following formula of the product; $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{Cytp})]\text{BF}_4 \cdot 1.5\text{HBF}_4 \cdot \text{Et}_2\text{O}$) $^{31}\text{P}\{^1\text{H}\}$ NMR (Acetone- d_6) δ 11.62 (dd, P_w) δ 1.50 (td, P_c) δ -14.79 (td, P_L) (P_w : wing phosphine of Cytp, P_c : central phosphine of Cytp, P_L : PMe_3), $J_{\text{pp}} = 51.8$, 28.9 and 23.5 Hz IR (Nujol Mull) ν_{NO} : 1650 cm^{-1} . Anal. Calcd. for $\text{C}_{45}\text{H}_{86.5}\text{B}_{2.5}\text{F}_{10}\text{NO}_{2.5}\text{P}_4\text{Ru}$: C, 48.10; H, 7.62; N, 1.25. Found: C, 47.22; H, 7.59; N, 1.17.

$[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{etp})]\text{BF}_4$. $\text{RuH}(\text{NO})(\text{etp})$ (140 mg, 0.21 mmole) was suspended in 10 ml of ether under hydrogen atmosphere and the solution was freeze-dried by liquid nitrogen and excess $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was added. The solution was warmed up slowly while stirring. When the color of the solution turns to purple, 0.50 ml of trimethyl phosphine solution (1.00 M in THF, 0.50 mmole) was added quickly. When the temperature of the solution goes up to room temperature, red brown solid was precipitated out. The solid was collected by filtration and washed with 3 ml of ether three times and dried

under vacuum overnight. Yield: 140 mg (80% based on the title formula) $^{31}\text{P}\{^1\text{H}\}$ NMR (Acetone- d_6) δ 97.34 (td, P_c) δ 71.85 (dd, P_w) δ -4.57 (td, P_L) (same notation as Cytp analogue), $J_{\text{pp}} = 185.5$, 33.4, 20.9 Hz.

Crystal Structure of $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{etp})]\text{Cl} \cdot \text{C}_6\text{H}_6 \cdot 2\text{H}_2\text{O}$. Crystals of this compound which is grown from the reaction mixture between $\text{RuH}(\text{NO})(\text{etp})$ and PMe_3 in benzene in the presence of trace HCl are dark brown and their clarity is poor. The crystal used for data collection was cut from a larger crystal and coated with epoxy as a precaution against possible decomposition in air. Preliminary examination of the diffraction pattern with a Rigaku AFC5 diffractometer indicated a monoclinic crystal system with systematic absences *oko*, $k=2n+1$ and *hol*, $h+l=2n+1$. So the space group is uniquely determined as $\text{P}2_1/\text{n}$. The cell constants, $a=14.130$ (2) Å, $b=21.026$ (3) Å, $c=14.760$ (1) Å and $\beta=97.88$ (1)°, were determined at room temperature by a least squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 29 to 30° and with MoK α radiation. Data was collected by ω scan method. Six standard reflections were measured after every 150 reflections and indicated that the crystal was stable during the course of data collection. The data were corrected for Lorentz and polarization effects but no absorption correction was applied because of the small value of the absorption coefficient. Structure solution and refinement was done with the TEXSAN package¹⁴ of crystallographic programs. The structure was solved by locating the ruthenium atom on a Patterson map. This atom was then used as a phasing model in the DIRDIF procedure¹⁵ and the remainder of the ruthenium complex was located on the electron density map. After several cycles of full-matrix least-squares refinement, it became evident that there were solvent molecules and ions present. One benzene molecule of solvation appeared in a difference electron density map along with one large peak (9 $e/\text{\AA}^3$) which was not bonded to any of the other atoms in the structure. This lone peak was assumed to be a Cl^- ion in order to balance the positively charged ruthenium complex. After a cycle of anisotropic refinement of the ruthenium complex, the hydrogen atoms were included in the model at their calculated positions with $\text{C-H}=0.98$ Å and were held fixed during least-squares refinement. The hydrogen atoms on the methyl carbon atoms were idealized to tetrahedral geometry based on their positions in a difference electron density map. At this point there was still some unaccounted for electron density appearing in the difference maps at 1.8 and 1.4 $e/\text{\AA}^3$ and neither of these were bonded to any other atoms in the model. These were assumed to be oxygen atoms of two water molecules. They were included in the model at the isotropic level and their occupancy factors were allowed to refine. The final refinement cycle (on F) resulted in agreement indices of $R=0.046$ and $R_w=0.056$ for the 4779 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 440 variables (The non-hydrogen atoms of the ruthenium complex are anisotropic as is the Cl ion, benzene carbon atoms and two water oxygen atoms are isotropic, all the hydrogen atoms are fixed). The occupancy factors for the two water oxygen atoms refined to final values of 0.80 (2) for O2 and 0.48 (2) for O3. The largest peak in the final difference electron density map is 0.88 $e/\text{\AA}^3$ and is located in the vicinity of the benzene ring. Scattering factors for neutral atoms were used and are from

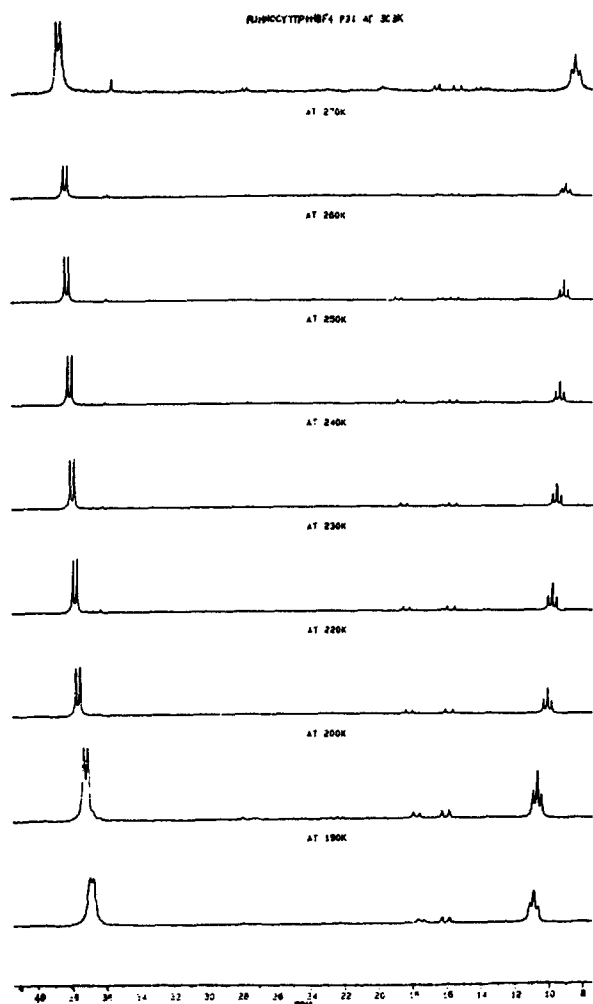


Figure 1. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{RuH}_2(\text{NO})(\text{Cyttp})]\text{BF}_4$ in CD_2Cl_2 at 101.252 MHz.

the usual sources.¹⁶ Terms for anomalous scattering were included.

Results and Discussion

For $[\text{RuH}_2(\text{NO})(\text{Cyttp})]\text{BF}_4$ (Cyttp: Bis(dicyclohexylphosphinopropyl)phenylphosphine), T_1 measurement by the inversion recovery method and attempts to measure the J_{HD} in the $[\text{Ru}(\text{HD})(\text{NO})(\text{Cyttp})]\text{BF}_4$ were made to clarify the nature of H_2 ligand but in the etp complexes (etp: Bis(diphenylphosphinoethyl)phenylphosphine), several attempts to isolate and even confirm the existence of the title complex in situ by NMR have failed, presumably owing to the extremely unstable nature of this compound. $T_{1,\text{min}}$ of $[\text{RuH}_2(\text{NO})(\text{Cyttp})]^+$ was recorded as 147 msec at 220 K. This value is relatively high for a molecular hydrogen complex (in most cases, T_1 values are less than 80 msec for a molecular hydrogen complex), but as Kubas¹⁷ pointed out, this value might be in the "gray area". An attempt to measure J_{HD} in the complex of $[\text{Ru}(\text{HD})(\text{NO})(\text{Cyttp})]^+$ was failed due to fast exchange between two hydride ligands. Selective decoupling of resonance frequencies of the phosphorus peaks does not help identify this value. Hydride peaks which are broad at room temperature begin to resolve into two peaks as the

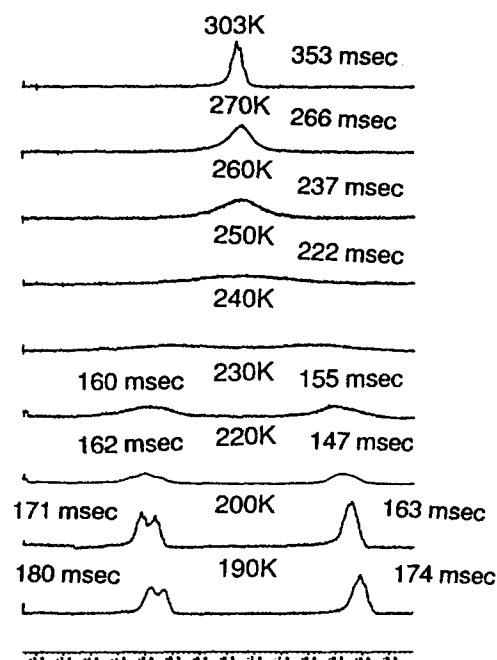
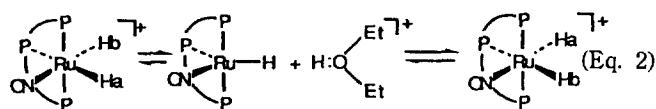
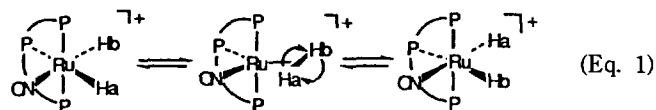


Figure 2. Variable temperature ^1H -NMR spectra and T_1 of $[\text{RuH}_2(\text{NO})(\text{Cyttp})]\text{BF}_4$ in CD_2Cl_2 at 250.133 MHz.

temperature is lowered. However, limiting, well-resolved spectra could not be obtained. Therefore, it is concluded that this complex has two classical hydride ligands, not a molecular hydride ligand. However, there is a recent report that a classical hydride complex $[\text{ReH}_6(\text{PPh}_3)_3]^+$ ¹⁸ determined by the conventional NMR method shows nonclassical behavior by other criteria⁷ and the exact nature of this complex remains uncertain. In the variable temperature NMR experiments, ^{31}P -NMR spectra do not change throughout the whole temperature range (190–303 K) (Figure 1) but ^1H -NMR spectra (Figure 2) show that the hydride at -5.37 ppm is *trans* to central phosphine ($J_{\text{PH}} = 62$ Hz) and the hydride at -8.95 ppm is *trans* to NO and these hydride ligands exchange their positions each other. The classical hydridic character is also confirmed by the IR spectrum where $\nu_{\text{Ru-H}}$ appears at 1950 and 1850 cm^{-1} . NO seems to be linear because ν_{NO} appears at 1750 cm^{-1} . Based on these data, the following two mechanisms are proposed to explain the fluxional behavior of this complex (Eq. 1 and 2). The intensity of the



hydride peak of $\text{Ru}(\text{HD})(\text{NO})(\text{Cyttp})$ was monitored in the presence of a large excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ for a fairly long time by NMR to see whether this fluxional process is intramolecular (Eq. 1) or not. Since the intensity of the hydride peak did not change, intramolecular process is more favored. In this mechanism, an equilibrium between hydrides and

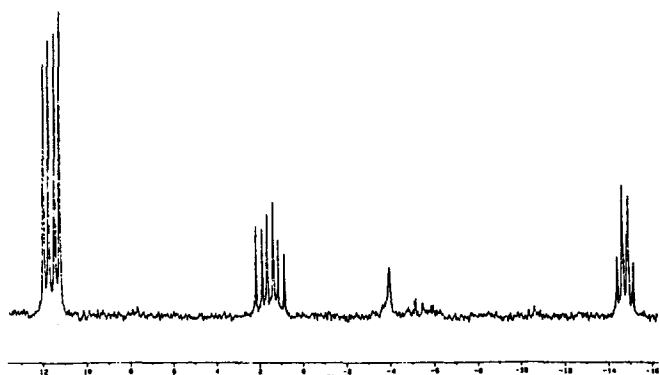


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{Cyttp})]\text{BF}_4$ in acetone- d_6 at 101.252 MHz.

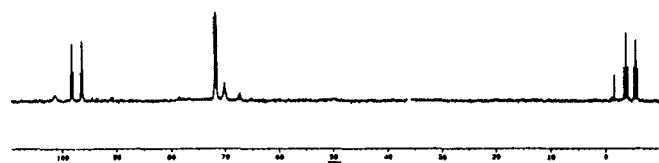


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{etp})]\text{BF}_4$ in acetone- d_6 at 101.252 MHz.

molecular hydrogen^{4,9} and rotation about M-H₂ bond are assumed and these phenomena have been reported recently.^{19,20} Even though there is no spectroscopic evidence except a very weak peak at 2650 cm^{-1} in the IR spectrum for the presence of molecular hydrogen complexes, reactivity of this complex toward neutral ligands strongly indicates the presence of molecular hydrogen ligand. Generally, neutral ligands such as PMe_3 , D_2 , CO and CH_3CN replace the H_2 easily. For the D_2 exchange, it is worth mentioning that molecular hydrogen complexes can be utilized to catalyze H^+/D_2 exchange reactions in the recent paper.²¹ In the PMe_3 and CH_3CN cases, H_2 bubbling was observed. Reactions with acetylenes will be discussed elsewhere. Moreover, application of vacuum appears to induce loss of H_2 followed by the solvent activation by the reactive 16-electron, 4-coordinate complex probably formed in situ; when the reaction was run in CH_2Cl_2 , evaporation of the solvent followed by addition of diethyl ether produced $\text{RuCl}(\text{NO})(\text{Cyttp})$ in high yield. The reaction in ether under the argon atmosphere yielded a uncharacterized complex, presumably $[\text{Ru}(\text{NO})(\text{Cyttp})]\text{BF}_4$ or $[\text{Ru}(\text{NO})(\text{Cyttp})(\text{Et}_2\text{O})]\text{BF}_4$. Even though some hydride complexes containing *cis*-dihydride ligands undergo elimination of molecular hydrogen easily, these reactions usually require some external assistance such as heating, irradiation or application of vacuum^{1b} but, to date, it is very hard to find examples where ether eliminates these hydrides and some molecular hydrogen complexes such as $[\text{CpRu}(\text{CO})(\text{PPh}_3)(\text{H}_2)]\text{X}$ ²² are unstable even in the presence of ether to decompose into free H_2 and bridging-hydride dimers of the type $\{[\text{CpRu}(\text{CO})(\text{PPh}_3)]_2(\mu\text{-H})\}\text{X}$. However, under the N_2 atmosphere, the expected dinitrogen complexes could not be detected. Instead, very complicated products were obtained with no title complexes left. This might be due to further reactions of unstable dinitrogen complexes and activation of solvents by the reactive 16-electron, 4-coordinate complexes. Replacement of H_2

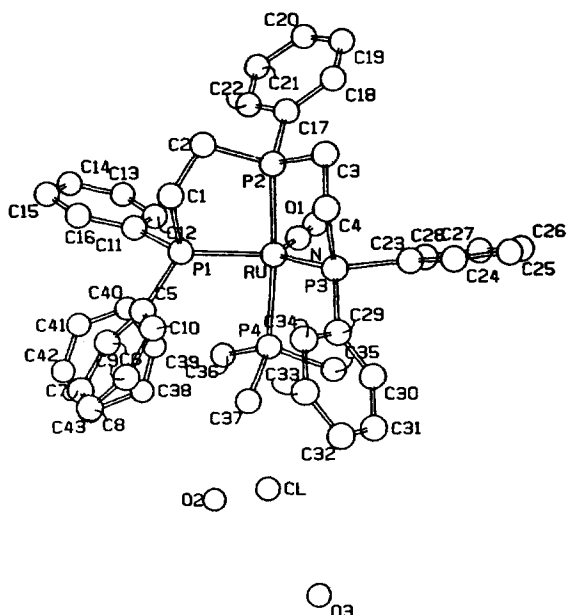


Figure 5. X-ray crystal structure of $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{etp})]\text{Cl} \cdot \text{C}_6\text{H}_6 \cdot 2\text{H}_2\text{O}$.

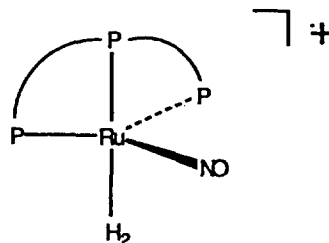


Figure 6. Proposed structure of $[\text{RuH}_2(\text{NO})(\text{etp})]^+$.

by PMe_3 shows that the incoming PMe_3 ligand occupies the position where the molecular hydrogen left, the equatorial site in the TBP structure. The ^{31}P -NMR spectrum of this product (Figure 3) supports this assignment (Only *cis* coupling constants are recorded). However, more bulky PPh_3 cannot coordinate to the metal center probably due to steric hindrance imposed by the Cyttp rings and 4-coordinate (or solvent adduct) complexes are produced. Meanwhile, successive addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and PMe_3 to $\text{RuM}(\text{NO})(\text{etp})$ produced the PMe_3 adduct where PMe_3 occupies the apical site *trans* to the central phosphine. The ^{31}P -NMR spectrum of this complex is shown in Figure 4 and the existence of a *trans* coupling constant is clearly shown. The structure of this product was determined by X-ray crystallography (Figure 5). These data indicate that a molecular hydrogen (or *cis*-dihydride) ligand, if present in $[\text{Ru}(\text{H}_2)(\text{NO})(\text{etp})]\text{BF}_4$, occupies the apical site in the TBP structure (Figure 6). In the $[\text{Ru}(\text{PMe}_3)(\text{NO})(\text{etp})]^+$ complex, NO is linear ($175.1(6)^\circ$) and Ru-N distance ($1.771(5) \text{ \AA}$) is comparable with that of $\text{RuH}(\text{NO})(\text{Cyttp})$ ($1.783(4) \text{ \AA}$) or $\text{RuH}(\text{NO})(\text{PPh}_3)_3$ ($1.792(11) \text{ \AA}$) but NO distance ($1.160(6) \text{ \AA}$) is considerably shorter than those of $\text{RuH}(\text{NO})(\text{Cyttp})$ ($1.186(5) \text{ \AA}$) and $\text{RuH}(\text{NO})(\text{PPh}_3)_3$ ($1.183(11) \text{ \AA}$) which indicates less π -back bonding to the NO group as expected from the positive charge of this complex. In Table 1, selected bond lengths and bond angles are listed and crystallographic details are summarized in Table

Table 1. Selected Bond Distances and Angles of [Ru(PMe₃)(NO)(etp)]Cl

Atoms	Distances, Å	Atoms	Angle, deg
Ru-N	1.771 (5)	N-Ru-P ₁	127.0 (2)
Ru-P ₁	2.333 (2)	N-Ru-P ₃	123.2 (2)
Ru-P ₃	2.335 (2)	N-Ru-P ₂	95.8 (2)
Ru-P ₂	2.341 (2)	N-Ru-P ₄	90.6 (2)
Ru-P ₄	2.375 (2)	P ₁ -Ru-P ₃	108.79 (6)
N-O	1.160 (6)	P ₁ -Ru-P ₂	81.59 (6)
		P ₁ -Ru-P ₄	93.77 (6)
		P ₃ -Ru-P ₂	81.35 (5)
		P ₃ -Ru-P ₄	96.00 (5)
		P ₂ -Ru-P ₄	173.53 (7)
		O-N-Ru	175.1 (6)

¹Standard deviation is shown in the parenthesis. ²P₁, P₂, P₃ and P₄ represent wing, central and wing phosphines of etp and PMe₃, respectively. ³More information is available on request.

Table 2. Crystallographic Details for [Ru(PMe₃)(NO)(etp)]Cl·C₆H₆·2H₂O

Formula	[RuNOP ₄ C ₃₇ H ₄₂]Cl·C ₆ H ₆ ·2H ₂ O
Formula wt., amu	891.32
Space Group	P2 ₁ /n
a, Å	14.130 (2)
b, Å	21.026 (3)
c, Å	14.760 (1)
β, deg	97.88 (1)
Volume, Å ³	4344
Z	4
Density (Calc.), g/cm ³	1.36
Crystal size	0.31 mm×0.35 mm×0.54 mm
Radiation	MoKα with graphite monochromator, λ=0.70926 Å
Linear abs. coeff., cm ⁻¹	6.00
Temperature	ambient
2θ limits	4° ≤ 2θ ≤ 50°
Scan speed	8 deg/min in ω with a total of 8 scans/reflection
Background time/scan time	0.5
Scan range	[1.50+(0.35) tan θ]° in ω
Data Collected	+h, +k, ±l
Unique data	5835
Unique data, with F _o ² <3σ (F _o ²)	4779
Final number of variables	440
R (F) ^a	0.046
R _w (F) _b	0.056
Error in observation of unit weight, e	1.69

^aR (F) = Σ |F_o - |F_c|| Σ |F_o|. ^bR_w (F) = [Σ_w(|F_o - |F_c||²/Σ_w|F_o|²)]^{1/2} with w = 1/σ²(F_o).

Table 3. Positional Parameters and B (eq) for [Ru(PMe₃)(NO)(etp)]Cl·C₆H₆·2H₂O

Atom	x	y	z	B (eq)
RU	0.34061 (3)	0.40597 (2)	0.27900 (3)	3.44 (2)
CL	0.3750 (2)	0.1222 (1)	0.4849 (2)	10.5 (2)
P1	0.3301 (1)	0.37022 (8)	0.1283 (1)	4.13 (7)
P2	0.3387 (1)	0.50499 (7)	0.2062 (1)	4.04 (7)
P3	0.1899 (1)	0.44038 (7)	0.3060 (1)	3.86 (6)
P4	0.3283 (1)	0.30220 (7)	0.3398 (1)	4.11 (7)
O1	0.5142 (4)	0.4337 (4)	0.4052 (5)	12.1 (4)
N	0.4463 (4)	0.4199 (3)	0.3558 (4)	5.3 (3)
C1	0.2812 (5)	0.4341 (3)	0.0503 (4)	5.0 (3)
C2	0.3288 (5)	0.4965 (3)	0.0812 (4)	5.2 (3)
C3	0.2341 (5)	0.5510 (3)	0.2263 (4)	5.2 (3)
C4	0.1502 (4)	0.5058 (3)	0.2277 (5)	5.0 (3)
C5	0.2630 (5)	0.3010 (3)	0.0852 (4)	4.8 (3)
C6	0.3058 (6)	0.2426 (3)	0.0740 (5)	6.2 (4)
C7	0.2498 (8)	0.1888 (4)	0.0467 (6)	8.1 (5)
C8	0.1514 (9)	0.1947 (5)	0.0302 (6)	8.7 (6)
C9	0.1085 (7)	0.2520 (5)	0.0407 (5)	7.9 (5)
C10	0.1634 (5)	0.3052 (4)	0.0679 (4)	5.9 (4)
C11	0.4469 (5)	0.3576 (3)	0.0895 (5)	5.0 (3)
C12	0.5299 (5)	0.3664 (4)	0.1485 (5)	6.3 (4)
C13	0.6188 (6)	0.3632 (4)	0.1181 (7)	8.2 (5)
C14	0.6224 (7)	0.3508 (4)	0.0274 (8)	8.8 (6)
C15	0.5415 (8)	0.3415 (4)	-0.0316 (6)	7.9 (5)
C16	0.4535 (6)	0.3453 (3)	-0.0023 (5)	6.4 (4)
C17	0.4410 (4)	0.5566 (3)	0.2338 (4)	4.6 (3)
C18	0.4373 (5)	0.6136 (3)	0.2779 (5)	5.6 (3)
C19	0.5182 (7)	0.6503 (4)	0.2998 (5)	7.5 (5)
C20	0.6018 (7)	0.6305 (5)	0.2753 (6)	8.3 (5)
C21	0.6087 (5)	0.5741 (5)	0.2293 (6)	7.7 (5)
C22	0.5278 (5)	0.5366 (3)	0.2096 (5)	6.2 (4)
C23	0.1932 (4)	0.4805 (3)	0.4164 (4)	4.3 (3)
C24	0.1129 (5)	0.5120 (3)	0.4379 (5)	6.1 (4)
C25	0.1145 (6)	0.5438 (4)	0.5193 (7)	8.1 (5)
C26	0.1942 (7)	0.5427 (4)	0.5821 (6)	7.8 (5)
C27	0.2743 (6)	0.5108 (4)	0.5641 (5)	7.3 (4)
C28	0.2726 (5)	0.4799 (3)	0.4810 (5)	5.6 (3)
C29	0.0846 (4)	0.3902 (3)	0.3056 (4)	4.0 (3)
C30	0.0687 (4)	0.3593 (3)	0.3841 (4)	4.9 (3)
C31	-0.0075 (5)	0.3180 (3)	0.3850 (5)	5.8 (4)
C32	-0.0701 (5)	0.3094 (4)	0.3075 (7)	6.9 (4)
C33	-0.0572 (5)	0.3405 (4)	0.2289 (6)	7.4 (4)
C34	0.0206 (5)	0.3812 (3)	0.2277 (5)	5.8 (3)
C35	0.3334 (5)	0.3027 (3)	0.4632 (4)	5.7 (3)
C36	0.4299 (5)	0.2534 (3)	0.3234 (5)	5.9 (3)
C37	0.2295 (5)	0.2501 (3)	0.3024 (4)	5.0 (3)

phines and NO ligands comprising the equatorial plane and the central phosphine and PMe₃ ligands occupying the axial positions. The products of the reactions between RuH(NO)(etp) and HBF₄·Et₂O were monitored in situ by ³¹P-NMR in various solvents. The results are shown in Table 4 and these data clearly show that 16-electron, 4-coordinate [Ru(NO)(etp)]BF₄ formed with the loss of molecular hydrogen might

2. In Table 3, positional parameters and B(eq) for [Ru(PMe₃)(NO)(etp)]Cl are listed. In this complex, etp adopts facial geometry and overall geometry is TBP, with two wing phos-

Table 4. $^{31}P\{^1H\}$ NMR Parameters for the Products of Reactions between $RuH(NO)(etp)$ and HBF_4 in Different Solvents

Solvents	δP_{center}	δP_{wing}	$^2P_{pp}$	NMR Solvent	Comment
CH_3CN	96.65	59.79	17.9	CD_3CN	
Ether	109.97	62.69	9.7	CD_2Cl_2	
CH_2Cl_2	110.72	62.65	9.6	CD_2Cl_2	
	107.47 (b)	75.17 (b)	24.3	CD_2Cl_2	
Acetone	101.24 (b)	70.06 (b)	21.7	Acetone- d_6	initial
	100.34	73.54	18.2	Acetone- d_6	initial
	101.24 (b)	70.06 (b)	21.7	Acetone- d_6	after 30 min

¹Chemical shift is shown in ppm relative to 85% H_3PO_4 . Positive value represents downfield shift from external standard. ²b means broad. ³Coupling constants are given in Hz

react further with various solvents. Further study is under-going to identify these complexes but difficulty in purification prevents from complete characterization.

Conclusions

$[RuH_2(NO)(Cyttp)]BF_4$ was obtained by protonation of $RuH(NO)(Cyttp)$ and characterized as a classical *cis*-dihydride complex by NMR techniques. This complex is fluxional and the process where two hydride ligands exchange their positions *via* a molecular hydrogen complex intermediate is proposed. Reactivity of this complex toward neutral 2-electron donor ligands reflects this property. However, the existence of $[RuH_2(NO)(etp)]BF_4$ was not confirmed maybe due to instability of this complex. The structure of this complex is proposed on the basis of the crystal structure of $[Ru(PMe_3)(NO)(etp)]^+$ which is TBP overall.

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