This was accomplished by preparing the isotopically labeled complex $[RuCl(^{14}NO)(^{15}NO)(P(C_6H_5)_3)_2]^+$ and monitoring the ν(NO) values in the infrared spectrum. Our structure determination of the related complex $[Ru(NO)(diphos)_2]^+$,[15] which possesses a linear nitrosyl in the equatorial position of a trigonal bipyramid, suggests a very simple and plausible pathway by which the interconversion of the two nitrosyl groups in the present structure is effected. This suggested mechanism is illustrated below. The scrambling of the labeled nitrosyl ligand occurs through a trigonal-bipyramidal intermediate with equivalent linear (or *slightly* bent) nitrosyl groups in the equatorial plane.

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The Crystal and Molecular Structure of the Catalytically Active Complex Hydridonitrosyltris(triphenylphosphine)ruthenium, $RuH(NO)(P(C_6H_5)_3)_3$

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The crystal and molecular structure of the catalytically active complex $RuH(NO)(P(C_6H_5)_3)_3$ has been determined from three-dimensional single-crystal X-ray data collected by the θ–2θ scan technique using a scintillation counter. The complex crystallizes in the monoclinic space group $P2_1/n$ (a special setting of $P2_1/c$-C_{2h}^5) in a cell of dimensions $a = 10.12$ (1), $b = 33.49$ (2), $c = 13.37$ (1) Å, $\beta = 90.3$ (1)°, and $V = 4533$ Å^3. There are four molecules per unit cell ($\rho_{\text{exptl}} = 1.34$ (1) g/cm^3; $\rho_{\text{calcd}} = 1.337$ g/cm^3). The structure was solved by Patterson and Fourier methods and has been refined by a least-squares procedure to a conventional R factor of 0.062 for 2773 reflections with $F_o^2 \geqslant 2\sigma(F_o^2)$. The coordination geometry about the ruthenium atom is a slightly distorted trigonal bipyramid with the hydride and nitrosyl ligands located in the axial positions. The nitrosyl group coordinates in a linear manner with a Ru–N distance of 1.79 (1) Å and a Ru–N–O bond angle of 176 (1)°. The three Ru–P distances average 2.339 (4) Å although significant differences between these distances arise as the result of steric interactions between the triphenylphosphine groups. These interactions lead to slight but significant deviations from C_{3v} symmetry within the coordination sphere. The Ru atom is displaced 0.55 Å from the trigonal plane of the phosphorus donor atoms toward the axial nitrosyl. Attempts to locate the hydride proved unsuccessful but its position may be inferred from the bond angles about the ruthenium. The bonding in this complex is discussed and a suggested energy-level ordering presented for trigonal-bipyramidal complexes with axial nitrosyl groups.

Introduction

Nitrosyl complexes of group VIII elements[2] represent an area of current chemical interest because of the unusual structural[3-13] and bonding[10-16] features of the metal–NO bond and the possible or actual use of these complexes as homogeneous catalysts.[17,18] Structural studies to data have established that nitrosyls can coordinate to transition metal ions either in a linear mode of attachment as formally NO^+ [9,12,19-22] or in a bent configuration as NO^- with a metal–N–O bond angle approaching 120°.[3-7,10,11,13] These two bonding modes illustrate the amphoteric nature of the nitrosyl ligand[5,17] which may be responsible in part for the catalytic activity of certain group VIII nitrosyl complexes. In many of these systems, however, the factors which serve to produce one bonding mode in preference over the other are unclear.

In a previous study,[6,13] we reported the synthesis and structure of the cationic complex $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$ which exhibits both types of nitrosyl coordination. This complex possesses an essentially square-pyramidal coordination geometry with a linear basal nitrosyl coordinating as NO^+ and a bent apical nitrosyl bonding as NO^-, and, hence, it may be viewed as a coordinatively unsaturated compound of Ru(II). Recently, Wilson and Osborn[18] synthesized the complex $RuH(NO)(P(C_6H_5)_3)_3$ and found it to be a catalytically active system, especially in the isomerization

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of terminal olefins. The low nitrosyl stretching frequency reported for $RuH(NO)(P(C_6H_5)_3)_3$ (1640 cm^{-1} *vs.* $\nu(NO)$ of 1687 cm^{-1} for the bent nitrosyl in $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$), together with its stoichiometric similarity to the Ru(II) system $RuHCl(P(C_6H_5)_3)_3$,[23,24] suggested the possibility of a bent nitrosyl complex having a distorted tetragonal-pyramidal geometry. However, other evidence reported by Wilson and Osborn,[18] such as the high-field quartet observed for the hydride resonance in the nmr spectrum of the complex and the significant coupling between $\nu(NO)$ and $\nu(M-H)$ as found through deuterium substitution, ruled against the tetragonal-pyramidal geometry and these authors proposed a trigonal-bipyramidal arrangement for the catalytically active complex. In order to establish unequivocally the molecular geometry and mode of nitrosyl coordination in $RuH(NO)(P(C_6H_5)_3)_3$, we have determined its molecular structure by single-crystal X-ray diffraction methods. This study, together with others on related systems,[13,25,26] will hopefully shed light on the factors favoring one type of nitrosyl coordination over the other and on the structure–function relationship of the nitrosyl group in certain catalytically active systems.

A preliminary report of this investigation has been communicated previously.[9]

Collection and Reduction of the X-Ray Data

A sample of the complex $RuH(NO)(P(C_6H_5)_3)_3$ was kindly supplied by Dr. John Osborn, and crystals suitable for single-crystal structural studies were grown from a methylene chloride–methanol solution. On the basis of Weissenberg and precession photographs of primary and upper level zones it was determined that the crystals belong to the monoclinic system. The observed extinctions $h + l$ odd for $h0l$ and k odd for $0k0$ uniquely determine the space group to be $P2_1/n$, a special setting of $P2_1/c$ (C_{2h}^5, no. 14).[27] The general positions in $P2_1/n$ are x, y, z; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$. The lattice constants at ambient room temperature were determined from a least-squares refinement[28] of the angular settings of 17 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are found to be a = 10.12 (1) Å, b = 33.49 (2) Å, c = 13.37 (1) Å, β = 90.3 (1)°, and V = 4533 Å^3. An experimental density of 1.34 (1) g/cm^3 obtained by the flotation method agrees with a calculated value of 1.337 g/cm^3 for four $RuH(NO)(P(C_6H_5)_3)_3$ molecules per unit cell.

A crystal of dimensions 0.24 × 0.10 × 0.42 mm was mounted along the a^* axis and prepared for data collection. The mosaic spread of the crystal was determined using the narrow-source, open-counter ω-scan technique.[29] The average width at half-height was found to be 0.08°. An independent set of intensity data was collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation at a takeoff angle of 1.5°. A receiving aperture of dimensions 3 × 3 mm was positioned 21 cm from the crystal. An unsymmetrical 2θ scan range from -0.5 to $+0.6°$ of the Mo Kα peak was employed. Intensity data were gathered within the angular range $5° \leqslant 2\theta \leqslant 40°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded about 9000 counts/sec during the scan. The attenuators used were brass foil whose thickness had been chosen to give an approximate attenuation factor of 3.0. During data collection, the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 2% during the time required to collect the data. The data were processed in the usual way, and the values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects to yield a set of structure factor amplitudes F_o and standard deviations $\sigma(F_o^2)$. The standard deviations were estimated from counting statistics according to the formula given by Corfield, *et al.*,[30] with a value of 0.03 for the uncertainty parameter p. The intensities of a total of 4519 reflections were measured, of which 2773 were observed to have $F_o^2 \geqslant 2\sigma(F_o^2)$. The data were not corrected for absorption effects due to the small value of the linear absorption coefficient (μ = 4.81 cm^{-1}).

Solution and Refinement of the Structure

The positional parameters of the ruthenium and three phosphorus atoms were determined from a three-dimensional Patterson function. One cycle of least-squares refinement (*vide infra*) of the positional parameters of these atoms, together with variable isotropic temperature factors assigned to each of them and a single variable scale factor, reduced the discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ to 0.357 and 0.455, respectively. From a difference Fourier map based on the phases obtained from these four atoms, the positions of all other nonhydrogen atoms in the molecule were determined.

The trial structure was refined by a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations, the atomic scattering factors for the nonhydrogen atoms were those of Cromer and Waber,[31a] while the hydrogen scattering factor table was taken from Stewart, *et al.*[31b] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Ru and P atoms taken from the report by Cromer.[32] Throughout all of the refinements, the phenyl rings were treated as rigid groups of D_{6h} symmetry (d(C–C) = 1.392 Å) in the manner described previously.[33,34]

Three cycles of least-squares refinement with individual isotropic temperature factors assigned to the nongroup atoms and single-group thermal parameters assigned to the phenyl rings converged to discrepancy factors R_1 and R_2 of 0.082 and 0.089, respectively. Three more cycles of refinement with anisotropic thermal parameters for the nongroup atoms and individual isotropic temperature factors for the ring carbon atoms further reduced the discrepancy factors to R_1 = 0.069 and R_2 = 0.078. The positions of the hydrogen atoms of the phenyl rings were then idealized (d(C–H) = 1.08 Å) and included in subsequent calculations as fixed contributions. An additional cycle of refinement led to final convergence at R_1 = 0.062 and R_2 = 0.067 for the 2773 reflections with $F_o^2 \geqslant 2\sigma(F_o^2)$.

At this stage, attempts were made to locate the hydride ligand assuming it to be trans to the nitrosyl group. These attempts involved calculating difference Fourier summations over the region of interest while successively limiting the angular range of terms included in the summations.[33] These efforts, however, did not meet with success and the hydride was not located in the present study. The most prominent feature of the final difference Fourier map were peaks of electron density equivalent to about 25% of the height of a carbon atom in the region of phosphorus atom P(2).

In the final cycle of refinement, no parameter changed by more than 10% of its estimated standard deviation. The final positional and thermal parameters for the individual atoms and the groups are presented in Table I along with their estimated standard deviations as derived from the inverse matrix. The derived positional and isotropic thermal parameters for the group carbon atoms are tabulated in Table II. The estimated standard devia-

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TABLE I

FINAL POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $RuH(NO)(P(C_6H_5)_3)_3$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.2876 (1)[b]	0.11067 (3)	0.22583 (7)	0.0055 (1)	0.00065 (1)	0.00379 (7)	0.00001 (4)	0.00106 (6)	0.00005 (3)
P(1)	0.2171 (3)	0.1124 (1)	0.0588 (2)	0.0072 (4)	0.00075 (4)	0.0041 (2)	0.0000 (1)	0.0006 (2)	0.0001 (1)
P(2)	0.1870 (3)	0.0656 (1)	0.3361 (2)	0.0061 (4)	0.00077 (4)	0.0045 (2)	−0.0002 (1)	0.0003 (2)	0.0002 (1)
P(3)	0.3095 (3)	0.1747 (1)	0.2917 (2)	0.0068 (4)	0.00073 (4)	0.0045 (2)	0.0001 (1)	0.0012 (2)	0.0000 (1)
N	0.4443 (12)	0.0866 (3)	0.2102 (7)	0.0140 (17)	0.0006 (1)	0.0052 (8)	0.0008 (4)	−0.0012 (9)	0.0004 (2)
O	0.5443 (10)	0.0692 (3)	0.1964 (8)	0.0107 (15)	0.0019 (2)	0.0140 (11)	0.0030 (4)	0.0001 (9)	−0.0012 (3)

Group[c,d]	x_c	y_c	z_c	ϕ	θ	ρ
P1R1	0.2305 (6)	0.0279 (2)	−0.0611 (4)	1.548 (5)	2.963 (5)	0.526 (5)
P1R2	0.4041 (5)	0.1675 (2)	−0.0814 (4)	0.091 (7)	−2.364 (5)	2.272 (7)
P1R3	−0.0816 (6)	0.1380 (2)	0.0067 (4)	−0.506 (9)	2.253 (5)	0.356 (8)
P2R1	−0.1170 (6)	0.0862 (2)	0.3828 (3)	2.829 (5)	2.839 (5)	−2.978 (5)
P2R2	0.1984 (5)	−0.0276 (2)	0.2718 (4)	2.266 (11)	−2.019 (5)	0.695 (11)
P2R3	0.3283 (6)	0.0540 (1)	0.5540 (4)	1.488 (6)	−2.642 (5)	1.661 (6)
P3R1	0.1632 (5)	0.2475 (2)	0.1758 (4)	2.171 (5)	3.081 (5)	2.613 (5)
P3R2	0.6077 (6)	0.2086 (2)	0.3015 (4)	−2.755 (8)	2.271 (5)	−0.029 (8)
P3R3	0.2276 (6)	0.1853 (2)	0.5239 (5)	−2.472 (6)	−2.928 (6)	−1.720 (5)

[a] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. [c] x_c, y_c, and z_c are the fractional coordinates of the ring centers. The angles ϕ, θ, and ρ in radians have been defined previously.[33] [d] Individual atoms assigned variable isotropic thermal parameters.

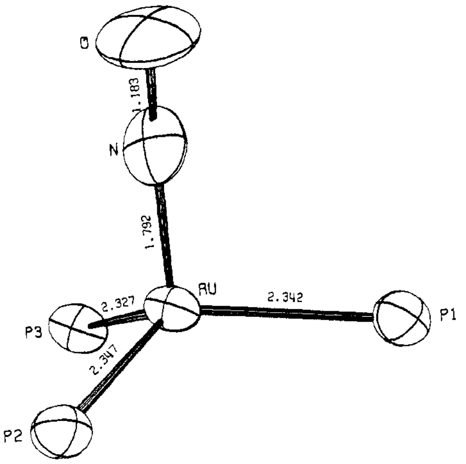

Figure 1.—A perspective drawing of the inner coordination geometry of $RuH(NO)(P(C_6H_5)_3)_3$. The hydride ligand, which was not located in the determination, is not shown.

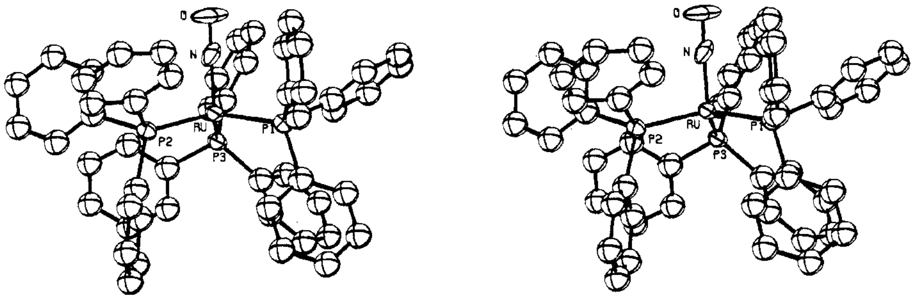

Figure 2.—A stereoscopic drawing of $RuH(NO)(P(C_6H_5)_3)_3$ showing the orientation of the phenyl rings in the complex.

tion of an observation of unit weight is 1.45 electrons. In Table III the root-mean-square amplitudes of thermal motion for the anisotropically refined atoms are presented. A tabulation of the final values of F_o and $|F_c|$ (in electrons × 10) for the 2773 reflections included in the refinements is available.[35]

Description of the Structure

The crystal structure consists of the packing of discrete molecules of $RuH(NO)(P(C_6H_5)_3)_3$ according to the symmetry of space group $P2_1/n$, the unit cell constants, and the parameters of Table I. The closest intermolecular contact excluding hydrogens is between the nitrosyl oxygen and a phenyl ring carbon atom at a distance of 3.20 Å. The packing of the $RuH(NO)(P(C_6H_5)_3)_3$ molecules appears to be reasonably efficient with a volume of 378 Å^3 per triphenylphosphine group *vs.* a value of 364 Å^3 in triphenylphosphine itself.[36] Ibers and coworkers have compiled values for the volume per triphenylphosphine group in a number of related complexes.[10,37] Since all intermolecular contacts appear normal, they are not tabulated.

The molecular geometry of the $RuH(NO)(P(C_6H_5)_3)_3$ complex is best described as a slightly distorted trigonal bipyramid with the phosphine ligands comprising the equatorial plane and the nitrosyl and hydride ligands occupying the axial positions. Figure 1 is a view of the inner coordination geometry about the ruthenium atom, while Figure 2 is a stereoscopic view of the complete molecule. The principal bond distances and angles for the structure are given in Table IV. Although the hydride was not located directly in this structure, it is reasonable to assume, on the basis of the bond angles about the ruthenium, that it occupies the axial position trans to NO in analogy with the isoelectronic complexes $CoH(N_2)(P(C_6H_5)_3)_3$,[38] $RhH(CO)(P(C_6H_5)_3)_3$,[33] and $IrH(CO)_2(P(C_6H_5)_3)_2$[39] for which

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(35) The table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1094. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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TABLE II
DERIVED POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR GROUP CARBON ATOMS

	x	y	z	B, Å²
		P1R1		
C(1)	0.2210 (8)	0.0640 (2)	−0.0097 (5)	3.2 (3)
C(2)	0.3429 (7)	0.0452 (2)	−0.0189 (6)	4.0 (3)
C(3)	0.3525 (7)	0.0091 (2)	−0.0703 (6)	4.2 (3)
C(4)	0.2401 (9)	−0.0081 (2)	−0.1125 (6)	4.1 (3)
C(5)	0.1182 (7)	0.0107 (2)	−0.1032 (6)	4.6 (3)
C(6)	0.1086 (6)	0.0468 (2)	−0.0518 (6)	3.6 (3)
		P1R2		
C(1)	0.3223 (11)	0.1429 (3)	−0.0251 (6)	3.6 (3)
C(2)	0.3709 (11)	0.1296 (2)	−0.1164 (7)	5.6 (4)
C(3)	0.4526 (8)	0.1542 (3)	−0.1728 (5)	6.0 (4)
C(4)	0.4858 (11)	0.1921 (3)	−0.1378 (6)	4.4 (3)
C(5)	0.4372 (11)	0.2053 (2)	−0.0465 (7)	5.3 (3)
C(6)	0.3555 (7)	0.1807 (3)	0.0099 (5)	4.8 (3)
		P1R3		
C(1)	0.0492 (6)	0.1290 (5)	0.0301 (6)	3.2 (3)
C(2)	−0.0526 (9)	0.1137 (3)	0.0882 (5)	4.5 (3)
C(3)	−0.1834 (7)	0.1227 (4)	0.0648 (7)	5.8 (4)
C(4)	−0.2124 (7)	0.1471 (5)	−0.0167 (7)	5.9 (4)
C(5)	−0.1106 (10)	0.1624 (3)	−0.0748 (6)	6.2 (4)
C(6)	0.0202 (8)	0.1534 (4)	−0.0514 (6)	5.1 (3)
		P2R1		
C(1)	0.0142 (6)	0.0755 (3)	0.3671 (6)	2.9 (3)
C(2)	−0.0165 (7)	0.1136 (2)	0.4019 (6)	4.0 (3)
C(3)	−0.1477 (9)	0.1242 (2)	0.4176 (6)	5.1 (3)
C(4)	−0.2482 (6)	0.0969 (3)	0.3985 (6)	5.0 (3)
C(5)	−0.2176 (7)	0.0589 (2)	0.3637 (6)	5.2 (3)
C(6)	−0.0864 (8)	0.0482 (2)	0.3480 (6)	3.8 (3)
		P2R2		
C(1)	0.1916 (22)	0.0123 (2)	0.3006 (6)	2.7 (3)
C(2)	0.2346 (15)	0.0024 (2)	0.2052 (5)	3.9 (3)
C(3)	0.2414 (11)	−0.0375 (3)	0.1764 (5)	5.5 (4)
C(4)	0.2052 (22)	−0.0675 (2)	0.2430 (7)	5.5 (4)
C(5)	0.1623 (15)	−0.0575 (2)	0.3385 (6)	5.2 (3)
C(6)	0.1554 (11)	−0.0176 (3)	0.3673 (4)	3.9 (3)
		P2R3		
C(1)	0.3928 (9)	0.0487 (3)	0.6452 (5)	5.6 (4)
C(2)	0.4647 (6)	0.0487 (3)	0.5568 (7)	5.7 (4)
C(3)	0.4003 (8)	0.0541 (2)	0.4656 (5)	3.8 (3)
C(4)	0.2639 (8)	0.0594 (3)	0.4628 (5)	2.9 (3)
C(5)	0.1920 (6)	0.0593 (3)	0.5512 (6)	4.0 (3)
C(6)	0.2564 (9)	0.0539 (2)	0.6424 (5)	5.0 (3)
		P3R1		
C(1)	0.2269 (8)	0.2171 (2)	0.2284 (5)	3.0 (3)
C(2)	0.2931 (6)	0.2526 (3)	0.2080 (6)	3.7 (3)
C(3)	0.2295 (8)	0.2829 (2)	0.1554 (6)	4.9 (3)
C(4)	0.0996 (8)	0.2778 (2)	0.1233 (6)	4.6 (3)
C(5)	0.0334 (6)	0.2423 (3)	0.1437 (6)	4.4 (3)
C(6)	0.0970 (8)	0.2120 (2)	0.1963 (6)	3.5 (3)
		P3R2		
C(1)	0.4793 (7)	0.1937 (4)	0.2991 (6)	3.1 (3)
C(2)	0.5145 (7)	0.2226 (3)	0.3691 (5)	4.1 (3)
C(3)	0.6430 (9)	0.2374 (3)	0.3715 (6)	4.5 (3)
C(4)	0.7362 (7)	0.2234 (4)	0.3039 (7)	5.2 (4)
C(5)	0.7009 (7)	0.1945 (3)	0.2339 (6)	5.6 (4)
C(6)	0.5724 (9)	0.1797 (3)	0.2315 (5)	4.2 (3)
		P3R3		
C(1)	0.2615 (9)	0.1823 (3)	0.4235 (5)	3.3 (3)
C(2)	0.1723 (9)	0.2114 (3)	0.4544 (7)	6.7 (4)
C(3)	0.1383 (9)	0.2144 (3)	0.5548 (8)	8.3 (5)
C(4)	0.1936 (10)	0.1883 (3)	0.6244 (5)	6.9 (4)
C(5)	0.2828 (9)	0.1592 (3)	0.5935 (6)	5.2 (3)
C(6)	0.3168 (8)	0.1563 (2)	0.4931 (7)	4.1 (3)

TABLE III
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION, Å

Atom	Min	Intermed	Max
Ru	0.154 (2)	0.191 (2)	0.199 (2)
P(1)	0.182 (5)	0.203 (8)	0.209 (5)
P(2)	0.173 (6)	0.200 (5)	0.215 (5)
P(3)	0.171 (6)	0.204 (6)	0.216 (5)
N	0.156 (21)	0.230 (17)	0.279 (16)
O	0.148 (22)	0.333 (14)	0.396 (15)

the hydrides were located. The nitrosyl group is linearly coordinated with a Ru–N distance of 1.792 (11) Å and a Ru–N–O bond angle of 176 (1)°. The nitrosyl thus coordinates as *formally* NO^+, and the complex can be viewed as a d^8 coordinatively saturated system of Ru(0). The 1.79-Å Ru–N distance is intermediate between the values of 1.74 (2) and 1.85 (2) Å involving the linear and bent nitrosyl groups, respectively, in the complex $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$[6,13] and is slightly longer than the Ru–linear nitrosyl distances of 1.75 and 1.72 Å reported for the Ru(II) complexes $[Ru(OH)(NO_2)_4(NO)]^{2-}$[21] and $Ru(NO)(S_2CN(C_2H_5)_2)_3$.[21] The present Ru–N distance is also considerably longer than the 1.68 (3) Å value found for the Ir–N distance in the closely analogous complex $[IrH(NO)(P(C_6H_5)_3)_3]^+$.[12]

The equation of the equatorial plane defined by the three phosphorus atoms is $9.54x - 11.04y - 0.83z = 0.78$ (in monoclinic coordinates) with the Ru atom displaced 0.55 Å from this plane toward the axial nitrosyl group. Similar displacements of the metal ion from the equatorial plane have been found in other trigonal-bipyramidal structures in which the two axial ligands are of different coordinating abilities. These displacements have been particularly great for group VIII metal complexes containing hydride and a strong π-acceptor ligand in the axial positions (*e.g.*, 0.030 Å in $CoH(N_2)(P(C_6H_5)_3)_3$,[38] 0.36 Å in $RhH(CO)(P(C_6H_5)_3)_3$,[38] and 0.51 Å in $[IrH(NO)(P(C_6H_5)_3)_3]^+$ [12]). Mingos and Ibers have proposed that these displacements result from electron pair repulsions between the M–P and M–X bonds where X represents the strong π-acceptor ligand in the axial position.[12]

We find in the present study that, as a consequence of the metal displacement from the trigonal plane, the N–Ru–P bond angles are all significantly greater than 90° but that this increase is not uniform for the three angles. The N–Ru–P(1) and N–Ru–P(2) angles are 99.5 (3) and 99.9 (3)°, respectively, while the N–Ru–P(3) angle is considerably larger at 112.1 (3)°. The Ru–P distances and the P–Ru–P bond angles also show corresponding variations. For example, the Ru–P(1) and Ru–P(2) bond lengths do not differ significantly and average 2.345 (3) Å, while Ru–P(3) is shorter at 2.328 (3) Å. Similarly, P(1)–Ru–P(3) and P(2)–Ru–P(3) average 112 (1)° whereas P(1)–Ru–P(2) is significantly larger at a value of 119.0 (1)°. These variations in bond distances and angles appear to result from steric interactions between the three equatorial triphenylphosphine groups as illustrated in Figure 2. The phenyl rings associated with P(1) and P(2) have similar orientations with two rings of each phosphine located above the trigonal plane (*i.e.*, on the side of the trigonal plane toward the nitrosyl) and one below. On the other hand, the rings associated with P(3) are in an opposite orientation with one above and two below the trigonal plane. These interactions reduce the symmetry of the inner coordination geometry of the complex from C_{3v} for a perfect trigonal bipyramid with differing axial ligands

TABLE IV

PRINCIPAL BOND DISTANCES AND ANGLES

Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Angle, deg
Ru-P(1)	2.342 (3)	P(3)-N	3.429 (11)	Ru-N-O	176 (1)
Ru-P(2)	2.347 (3)	P(1)-P(2)	4.040 (4)	P(1)-Ru-P(2)	119.0 (1)
Ru-P(3)	2.328 (3)	P(1)-P(3)	3.860 (5)	P(1)-Ru-P(3)	111.5 (1)
Ru-N	1.792 (11)	P(2)-P(3)	3.905 (4)	P(2)-Ru-P(3)	113.3 (1)
N-O	1.183 (11)	P(1)-RC(1)$_{av}$	1.85 (1)	N-Ru-P(1)	99.5 (3)
P(1)-N	3.175 (11)	P(2)-RC(1)$_{av}$	1.85 (1)	N-Ru-P(2)	99.9 (3)
P(2)-N	3.188 (12)	P(3)-RC(1)$_{av}$	1.84 (1)	N-Ru-P(3)	112.0 (3)

to C_s or m symmetry. In addition, Figure 2 reveals that an ortho proton of the ring bonded to P(3) above the trigonal plane is directed toward the nitrogen of the NO group. The approximate N···H internuclear distance is 2.62 Å, and this nonbonding contact may help explain the unusual shape of the nitrogen atom's anisotropic thermal ellipsoid.

Although the Ru-P distances differ significantly from a statistical point of view, they may be averaged for purposes of comparison. The average Ru-P distance of 2.339 Å is shorter than the Ru(II)-basal phosphine distances of 2.426 (6), 2.393 (6), and 2.359 (5) Å found in the square-pyramidal complexes $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$,[6,13] $RuCl_2(P(C_6H_5)_3)_3$,[37] and $RuH(CH_3COO)(P(C_6H_5)_3)_3$,[40] respectively, but is considerably longer than the Ru(II)-apical phosphine distances of 2.230 (8) and 2.229 (4) Å found in the latter two complexes. The average Ru-P distance of 2.339 Å does, however, agree closely with the average value of 2.340 (6) Å reported for the average Ir-P distance in the isoelectronic complex $[IrH(NO)(P(C_6H_5)_3)_3]^+$ [12] and with the average Os-P distance of 2.36 (4) Å found in the trigonal-bipyramidal Os(0) complex $Os(CO)_3(P(C_6H_5)_3)_2$.[41] Unfortunately, a more direct comparison of the value obtained in the present study with other Ru(0)-P distances is not possible because of a lack of structural data.

Discussion

The structure of $RuH(NO)(P(C_6H_5)_3)_3$ and its isoelectronic iridium analog, $[IrH(NO)(P(C_6H_5)_3)_3]^+$,[12] poses an interesting problem in the bonding of nitrosyl complexes and the factors influencing each type of nitrosyl coordination. Previously, we have discussed the bonding of nitrosyl to transition metal ions in tetragonal complexes[16] and have concluded that, for a five-coordinate 22-electron system composed of eight electrons in the ligand σ^b levels of the basal plane, six electrons in the nitrosyl functions (*i.e.*, $(\pi_{2p_x,2p_y})^4(\sigma_{2p_z})^2$), and a d^8 metal ion, the bent mode of coordination for an axial NO group is preferred. In this tetragonal situation, the coordinated nitrosyl bends at the energetic expense of very significant metal→nitrosyl π bonding in order to avoid the placement of electrons into a more strongly antibonding level. It may be noted, however, that the square-pyramidal arrangement of donor atoms is preserved in these five-coordinate systems and that this arrangement leads to more effective σ bonding between the metal and the other ligands in the complex than does the other five-coordinate geometry, the trigonal bipyramid.[42] The structure of $RuH(NO)(P(C_6H_5)_3)_3$ illustrates that a stable alternative to the tetragonal pyramid-bent nitrosyl structure is indeed open to 22-electron nitrosyl complexes whereby the placement of electrons into a strongly antibonding level is avoided through a change in the ligand field geometry about the metal ion. In the trigonal-bipyramidal geometry of essentially C_{3v} symmetry, the significant metal-nitrosyl π interaction is preserved, but the effectiveness of the metal-ligand σ bonding in the rest of the structure is somewhat diminished. This point is more clearly illustrated by considering the suggested molecular orbital energy level ordering for $RuH(NO)(P(C_6H_5)_3)_3$ and related trigonal-bipyramidal nitrosyl systems presented in Figure 3. For a 22-electron system, the electronic configuration is $\ldots((xz, yz),(\pi^*(NO)))^4(x^2 - y^2, xy)^4$ yielding a $^1A_1$ ground state, and since the highest filled doubly degenerate level has some σ^* character,[42] the σ structure in the trigonal plane is somewhat weakened.

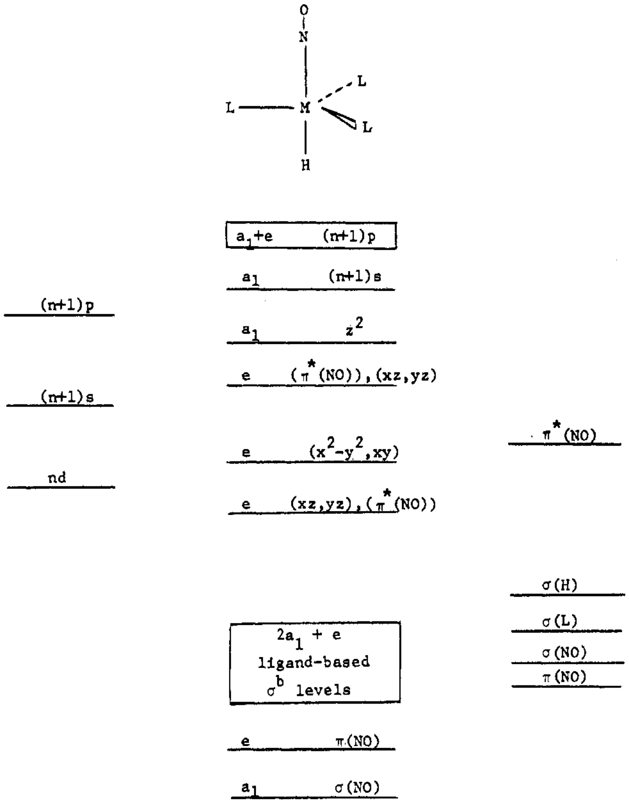

Figure 3.—A suggested molecular orbital energy level ordering for $RuH(NO)(P(C_6H_5)_3)_3$ and related trigonal-bipyramidal nitrosyl complexes. The orbital energies are not drawn to scale and the suggested ordering is based in part on orderings given in ref 14 and 42.

The factors which serve to produce one mode of nitrosyl coordination over the other are thus intertwined with the factors governing the preferred ligand

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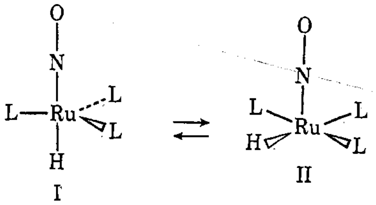
field geometry about the metal ion in a given 22-electron system. The present study shows that the trigonal-bipyramidal geometry is the most stable configuration for the title compound, and this structure is maintained in solution as determined by the high-field quartet observed for the hydride resonance in its ^1H nmr spectrum.[18] Further studies by Wilson and Osborn,[18] however, reveal that the trigonal-bipyramidal geometry reported herein is *not* maintained by other closely related members of the series $MH(NO)L_3$ where M = Ru or Os and L is a tertiary phosphine. In particular, these authors find that the methyldiphenylphosphine derivatives possess an entirely different molecular structure in solution while the isopropyldiphenylphosphine member of the Ru series exists in solution at ambient temperatures as two interconverting isomers, one of which is analogus to the trigonal-bipyramidal structure of $RuH(NO)(P(C_6H_5)_3)_3$.[18] Differences were also found in the catalytic properties of the ruthenium complexes with the triphenylphosphine derivative considerably more active than the methyldiphenylphosphine complex. On the basis of their studies, Wilson and Osborn[18] proposed several possible structures for the complex $RuH(NO)(P(CH_3)(C_6H_5)_2)_3$, including a square-pyramidal structure with an axial nitrosyl group. This structure, which has several points of support, should possess a bent nitrosyl group bonding as NO^-, and if so, the complex can be viewed as a coordinatively unsaturated system of Ru(II). The unexpected and striking differences in the molecular geometry and properties of the $RuH(NO)L_3$ complexes for L = $P(C_6H_5)_3$ and $P(CH_3)(C_6H_5)_2$ are most plausibly explained on the basis of the different steric requirements of the tertiary phosphine ligands and serve to indicate how closely balanced the various structure-determining factors are in these systems.[43] Further support for the importance of steric factors in these systems may be obtained from the isopropyldiphenylphosphine derivative in which the thermodynamic minima for the two structures are more closely comparable ($\Delta H = -4.6$ kcal mol^{-1}) and interconversion at ambient room temperatures is observed between the two significantly populated forms.[18] Wilson and Osborn[18] have suggested that a reasonable way of viewing this equilibrium is



where L = $P(i\text{-}C_3H_7)(C_6H_5)_2$. Since II should possess a *bent* nitrosyl group as a 22-electron system with a tetragonal-pyramidal geometry, we believe that the ruthenium atom may be undergoing an internal redox reaction with the coordinated nitrosyl as has been reported by Collman, *et al.*,[44] for the cobalt nitrosyl complexes $CoCl_2(NO)L_2$ where L is a tertiary phosphine.

Finally, it is interesting to speculate that the difference in the catalytic activity of the triphenylphosphine and methyldiphenylphosphine derivatives of $RuH(NO)L_3$ arises from the greater driving force of the former to assume the coordinatively saturated structure reported herein once the catalyzed reaction step is completed. This suggestion assumes that the stability of the final adduct relative to that of the original complex plus free product is a key factor, albeit only one of several, in determining the catalytic behavior of such systems.

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(43) One may observe that a greater crowding of the triphenylphosphine groups in $RuH(NO)(P(C_6H_5)_3)_3$ is possible such as has been found in $RuCl_2(P(C_6H_5)_3)_3$, but the trigonal-bipyramidal structure which we find for the former represents its most stable geometry as determined by a combination of σ- and π-bonding effects and the steric requirements of the different ligands in this system.

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