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The Crystal and Molecular Structure of Nitrosylbis[1,2-bis(diphenylphosphino)ethane]ruthenium Tetraphenylborate-Acetone, $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$

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Received July 11, 1972

The crystal and molecular structure of the complex $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$ (diphos = 1,2-bis(diphenylphosphino)ethane) 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 $P2_1/n$ in a cell of dimensions $a = 19.06$ (1) Å, $b = 23.09$ (1) Å, $c = 15.39$ (1) Å, $\beta = 93.3$ (1)°, and $V = 6766$ Å^3. There are four formula weights corresponding to $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$ per unit cell ($\rho_{\text{exptl}} = 1.29$ (2) g/cm^3; $\rho_{\text{calcd}} = 1.280$ 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 0.074 for 3195 reflections with $F_o^2 \geqslant 2\sigma(F_o^2)$. The cationic ruthenium complex possesses an approximately trigonal-bipyramidal geometry with the bidentate diphos ligands bridging axial and equatorial positions and the nitrosyl occupying the remaining equatorial position. The nitrosyl group coordinates in an essentially linear manner with a Ru-N distance of 1.74 (1) Å and a Ru-N-O bond angle of 174 (1)°. The average Ru-P distance in the structure is 2.39 (1) Å. The complex $[Ru(NO)(diphos)_2]^+$ is thus formulated as a formally d^8 Ru(0) complex of NO$^+$. Its bonding is discussed.

Introduction

X-Ray structural studies[2-12] have shown that five-coordinate group VIII nitrosyl complexes can possess either the trigonal-bipyramidal or square-pyramidal coordination geometries and that the nitrosyl groups contained therein coordinate in either a linear[2,10-12] or bent manner[3-9] depending upon the particular geometry. For example, in the NO$^+$ adducts of the d^8 complexes $IrCl(CO)(P(C_6H_5)_3)_2$ [3] and $RuCl(NO)(P(C_6H_5)_3)_2$,[7] the nitrosyl group coordinates in the apical position of a square pyramid with an M-N-O bond angle approaching 120°. The formation of these adducts may be described as an oxidative addition process whereby the nitrosyl group bonds as formally NO$^-$ and the metal d electron configuration changes from d^8 to d^6. An alternative to this molecular geometry and the bent mode of NO bonding occurs in the complexes $RuH(NO)(P(C_6H_5)_3)_3$ [10] and $[IrH(NO)(P(C_6H_5)_3)_3]^+$ [11] which have been found to possess the trigonal-bipyramidal structure with linearly coordinated nitrosyl groups in the axial position. Despite the low values for ν(N-O) in these two complexes (1640 and 1780 cm^{-1}, respectively), the linear mode of nitrosyl bonding permits their formulation as *formally* NO$^+$ complexes of d^8 metal ions. As yet, the factors resulting in the stabilization of a particular molecular geometry and nitrosyl bonding mode have not been fully delineated for the five-coordinate systems although recently we have correlated the two possible NO bonding configurations in complexes of approximately tetragonal symmetry.[13]

As part of our continuing study to define the structure-determining factors in group VIII nitrosyl complexes, we have investigated the structure of the cationic complex $[Ru(NO)(diphos)_2]^+$ (diphos = 1,2-bis(diphenylphosphino)ethane) which was synthesized by Townsend.[14] In his synthetic studies, Townsend found that the reaction of $RuCl(NO)(P(C_6H_5)_3)_2$ with diphos yields the product complex $[Ru(NO)(diphos)_2]Cl$ which is a 1:1 electrolyte and has a value for ν(N-O) of 1673 cm^{-1}.[14] This low ν(N-O) value together with the square-planar geometry of the related d^8 system $[Rh(diphos)_2]^+$ [15] suggested that the Townsend complex might have a tetragonal-pyramidal arrangement with a bent apical NO group. However, in view of the fact that ν(N-O) is not a good structural diagnostic for the mode of nitrosyl coordination in these complexes and also the observation that the isoelectronic complex $Ir(CO)(diphos)_2^+$ possesses a trigonal-bipyramidal structure,[16] we could not rule out such an arrangement as a structural alternative. In order to unambiguously establish the molecular structure of $[Ru(NO)(diphos)_2]^+$ and thus hopefully shed further light on the various stabilizing factors in these five-coordinate group VIII systems, we have determined its solid-state structure as the tetraphenylborate salt. A preliminary report of this structure determination has been communicated previously.[10] Since that time, the structure of another bis-chelated five-coordinate nitrosyl complex has been determined by Enemark and Feltham.[17] These investigators find that $[Co(NO)(diars)_2]^{2+}$ (diars =

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o-phenylenebis(dimethylarsine)) possesses a trigonal-bipyramidal geometry with a linearly coordinated nitrosyl in the equatorial plane.[17] This is essentially the same arrangement reported for $[Ru(NO)(diphos)_2]^+$ which is described in detail below.

Collection and Reduction of the X-Ray Data

Crystals of $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$ were kindly provided by Dr. R. E. Townsend. On the basis of Weissenberg and precession photographs of primary and upper level zones, it was established that the complex crystallizes in the monoclinic system. The observed extinctions of $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ uniquely determine the space group as $P2_1/n$, a special setting of $P2_1/c$ (C_{2h}^5, No. 14).[18] The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 25 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are found to be a = 19.06 (1) Å, b = 23.09 (1) Å, c = 15.39 (1) Å, β = 93.3 (1)°, and V = 6766 Å^3. This refinement was performed using our local PICKLST program.[19] An experimental density of 1.29 (2) g/cm^3 obtained by the flotation method agrees with a calculated value of 1.280 g/cm^3 for four formula weights corresponding to $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$ per unit cell.

A crystal of approximate dimensions 0.20 × 0.22 × 0.41 mm was mounted along the b axis. The mosaic spread of the crystal was determined using the narrow-source, open-counter, ω-scan technique.[20] The average width at half-height was found to be 0.09°. 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 scan range in 2θ was used from −0.5 to +0.6° of the Mo Kα peak with allowances made for the Kα_1–Kα_2 separation. Intensity data were gathered within the angular range $5° \leqslant 2\theta \leqslant 45°$. 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 of thickness chosen to given an approximate attenuation factor of 3.0. During data collection, the intensities of five 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 6% during the time required to collect data. The data were processed in the usual way and the values of I and $\sigma(I)$ (*vide infra*) were corrected for Lorentz and polarization effects. The intensities of a total of 9393 reflections were measured of which only 3195 were observed to be greater than 2σ. No correction was made for absorption effects due to the small value for the linear absorption coefficient (μ = 3.71 cm^{-1}).

Solution and Refinement of the Structure

The position of the ruthenium atom was determined from a three-dimensional Patterson function. One cycle of least-squares refinement of the positional and isotropic thermal parameters of the ruthenium atom and a single scale factor reduced the discrepancy factors $R = \Sigma\| F_o| - |F_c\|/\Sigma|F_o|$ and $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ to 0.457 and 0.478, respectively. From a difference Fourier map over the region around the ruthenium atom, the positions of the four phosphorus atoms and the nitrosyl group were determined. Two additional cycles of least-squares refinement including these seven atoms further reduced the discrepancy factors to R = 0.332 and R' = 0.441. The positions of all other nonhydrogen atoms in the structure were then determined from a series of difference syntheses which were based on phases obtained from the refined parameters of the previously located atoms.

The complete trial structure was refined by a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights w were assigned as $4F_o^2/\sigma^2(F_o^2)$ where the standard deviations $\sigma(F_o^2)$ were estimated from counting statistics according to the formula given by Corfield, *et al.*,[21] with a value of 0.03 for the uncertainty parameter p. The phenyl rings of the cation and anion were treated as a rigid group with assumed D_{6h} symmetry and a C–C distance of 1.392 Å.[22,23] In all refinements, only the 3195 reflections for which $F_o^2 \geqslant 2\sigma(F_o^2)$ were used. The atomic scattering factors of the nonhydrogen atoms were taken from Cromer and Waber's tabulation while that of hydrogen was taken from the report by Stewart, *et al.*[24] The effects of anomalous dispersion were included in the calculated structure factors with the values of $\Delta f'$ and $\Delta f''$ for Ru and P taken from Cromer's report.[25] Two cycles of least-squares refinement including all nonhydrogen atoms with isotropic thermal parameters and group temperature factors for the phenyl groups reduced the discrepancy indices to R = 0.093 and R' = 0.101. Two cycles of refinement with anisotropic thermal parameters for the nongroup atoms and individual isotropic temperature factors for the members of the phenyl ring groups reduced the discrepancy factors to R = 0.082 and R' = 0.090.

At this point, it was noted that the temperature factors of C(2), C(3), C(5), and C(6) of ring 2 were unusually high, while the temperature factors of C(1) and C(4) were approximately normal (*ca.* 7 Å^2). A difference Fourier map was calculated including all atoms of the structure excluding ring 2. The electron density distributions for the atoms of this ring indicated a torsional disorder about an axis including P(1) and ring carbon atoms C(1) and C(4). An attempt was made to refine the atoms of this ring individually with anisotropic thermal parameters. However, the resulting positions for the atoms deviated significantly from planarity. It was therefore decided that the refinement including ring 2 as a rigid group represented the more reasonable model despite the high temperature factors of the ring atoms and this procedure was followed in the final refinements. Two final cycles of least squares were then performed. On the first cycle only the 145 positional and thermal parameters for the 12 groups and the single scale factor were refined. On the second cycle only the 145 positional and thermal parameters for the 16 atoms and the scale factor were refined. Also, on these cycles of refinement, the contributions from the hydrogen atoms associated with the phenyl rings, assuming a C–H distance of 1.08 Å, were included. The final discrepancy indices were R = 0.074 and R' = 0.083 with no parameter changing on these cycles by more than 15% of its standard deviation. The estimated standard deviation of an observation of unit weight is 1.43. A final difference Fourier map showed residual electron density equivalent to about 15% of the height of a carbon atom in the region of the tetraphenylborate anion. A table of the final F_o and $|F_c|$ values (in electrons × 10) for the 3195 reflections used in the refinements has been deposited and is available upon order.[26] The final positional and thermal parameters for the individually refined atoms and the positional parameters for the groups are given in Table I. The derived positional parameters for the atoms of the groups with their thermal parameters are given in Table II, and in Table III the root-mean-square amplitudes of vibration of the anisotropically refined atoms are presented.

Description of the Structure

The crystal structure consists of the packing of discrete $[Ru(NO)(diphos)_2]^+$ cations, tetraphenylborate anions, and acetone molecules of crystallization. The intermolecular

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(18) "International Tables of X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, p 99.

(19) The programs used in this study were our PICKLST refinement and setting program and local versions of the Busing-Levy ORFLS least-squares program, the Ibers-Doedens group refinement least-squares program, the Zalkin FORDAP Fourier program, the Busing-Martin-Levy ORFFE functions and error program, and C. K. Johnson's ORTEP plotting program. All computing was performed on Brown University's IBM 360/67 computer.

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(26) 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. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number 73-199.

Table I. Final Structural Parameters for $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$

Atomic Positional and Anisotropic Thermal Parameters

Atom	x^a	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.42045 (8)	0.17760 (7)	0.16992 (9)	0.00256 (5)	0.00186 (3)	0.00310 (7)	−0.00009 (5)	−0.00042 (5)	−0.00007 (6)
P(1)	0.4815 (3)	0.2528 (2)	0.2520 (3)	0.0032 (2)	0.0023 (1)	0.0047 (3)	−0.0002 (1)	−0.0004 (2)	0.0000 (2)
P(2)	0.4273 (2)	0.1318 (2)	0.3069 (3)	0.0030 (2)	0.0023 (1)	0.0039 (3)	−0.0002 (1)	−0.0005 (2)	0.0000 (2)
P(3)	0.3590 (3)	0.0996 (2)	0.0994 (3)	0.0034 (2)	0.0018 (1)	0.0037 (3)	−0.0002 (1)	−0.0003 (2)	−0.0001 (2)
P(4)	0.3026 (3)	0.2152 (2)	0.1704 (3)	0.0031 (2)	0.0023 (1)	0.0044 (3)	0.0002 (1)	−0.0004 (2)	−0.0004 (2)
N	0.4853 (6)	0.1781 (6)	0.0954 (8)	0.0024 (5)	0.0010 (3)	0.0037 (7)	−0.0008 (4)	0.0000 (5)	−0.0007 (5)
O	0.5338 (7)	0.1759 (7)	0.0494 (8)	0.0045 (6)	0.0039 (4)	0.0077 (9)	−0.0012 (9)	0.0028 (6)	−0.0013 (6)
C(1)	0.4906 (11)	0.2317 (8)	0.3679 (11)	0.0071 (11)	0.0025 (6)	0.0038 (11)	−0.0022 (7)	−0.0035 (9)	0.0015 (7)
C(2)	0.4335 (11)	0.1899 (8)	0.3918 (10)	0.0067 (10)	0.0022 (6)	0.0028 (10)	0.0004 (6)	−0.0012 (8)	−0.0009 (6)
C(3)	0.2696 (8)	0.0978 (7)	0.1393 (10)	0.0022 (7)	0.0009 (4)	0.0054 (11)	−0.0003 (4)	0.0003 (7)	−0.0007 (5)
C(4)	0.2388 (8)	0.1576 (7)	0.1261 (10)	0.0019 (6)	0.0012 (5)	0.0051 (11)	−0.0001 (4)	−0.0010 (6)	−0.0005 (5)
B	−0.0249 (9)	0.1677 (9)	0.1648 (12)	0.0024 (8)	0.0021 (6)	0.0051 (12)	−0.0002 (6)	0.0000 (8)	0.0002 (8)
AO	−0.1888 (11)	−0.0296 (9)	0.3570 (12)	0.0086 (10)	0.0062 (7)	0.0112 (14)	−0.0013 (7)	0.0016 (11)	−0.0016 (8)
AC(1)	−0.1287 (16)	−0.0105 (14)	0.3457 (26)	0.0044 (14)	0.0052 (12)	0.0186 (37)	−0.0016 (10)	−0.0024 (20)	0.0018 (16)
AC(2)	−0.0971 (17)	0.0241 (14)	0.4157 (18)	0.0121 (19)	0.0077 (13)	0.0089 (20)	−0.0034 (13)	−0.0033 (15)	−0.0010 (13)
AC(3)	−0.0956 (15)	−0.0248 (16)	0.2648 (17)	0.0075 (15)	0.0132 (18)	0.0082 (19)	0.0038 (13)	0.0030 (13)	−0.0047 (15)

Group Positional Parameters[c]

Group	X_c	Y_c	Z_c	ϕ	θ	ρ
R(1)	0.4219 (4)	0.3840 (4)	0.2443 (6)	2.091 (37)	1.815 (7)	2.988 (37)
R(2)	0.6411 (6)	0.2709 (5)	0.2019 (7)	−2.862 (17)	−2.606 (12)	0.323 (12)
R(3)	0.5677 (4)	0.0561 (3)	0.3511 (5)	2.036 (24)	−1.895 (7)	−0.522 (24)
R(4)	0.3150 (4)	0.0416 (4)	0.3801 (5)	−2.626 (11)	2.579 (8)	−2.670 (9)
R(5)	0.3324 (4)	0.1086 (3)	−0.1092 (5)	−0.613 (7)	−3.212 (8)	1.425 (7)
R(6)	0.4207 (5)	−0.0295 (4)	0.1171 (4)	1.958 (10)	−2.955 (7)	−0.050 (7)
R(7)	0.2392 (4)	0.2580 (4)	0.3484 (6)	2.547 (9)	3.216 (10)	−2.034 (7)
R(8)	0.2509 (4)	0.3109 (3)	0.0281 (5)	1.388 (10)	−2.582 (9)	2.168 (9)
RB(1)	−0.0366 (4)	0.2992 (4)	0.1478 (4)	1.658 (10)	2.755 (7)	−3.231 (8)
RB(2)	0.0704 (4)	0.1182 (4)	0.0262 (5)	−0.281 (8)	2.870 (8)	2.286 (7)
RB(3)	0.0284 (4)	0.1389 (4)	0.3540 (6)	0.621 (8)	−2.790 (10)	−1.670 (8)
RB(4)	−0.1697 (5)	0.1100 (3)	0.1364 (6)	−2.365 (43)	1.813 (8)	2.769 (42)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. x, y, and z are fractional coordinates. [b] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] X_c, Y_c, and Z_c are the fractional coordinates of the rigid-group centers. The angles ϕ, θ, and ρ are in radians and have been previously defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

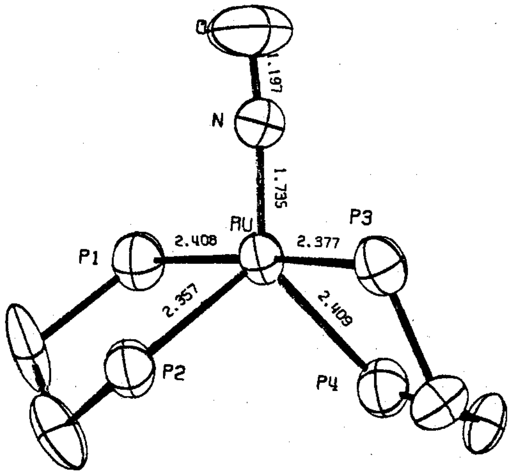

Figure 1. A perspective drawing of the inner coordination geometry of $[Ru(NO)(diphos)_2]^+$ with the phenyl rings omitted for clarity.

distances within the unit cell are normal with the closest contact (excluding hydrogens) between C(4) and RB2C(5) at a value of 3.31 Å. The intermolecular contacts are therefore not tabulated. Principal intramolecular distances and angles for the structure are given in Table IV.

The cationic ruthenium complex has an approximate trigonal-bipyramidal geometry in which the bidentate bis(diphenylphosphino)ethane ligands bridge axial and equatorial positions in the coordination polyhedron, and the nitrosyl group occupies the remaining equatorial position. A perspective drawing of the inner coordination geometry is given in Figure 1 and a stereoscopic view of the entire complex is presented in Figure 2. The nitrosyl group is coordinated in an essentially linear manner with a Ru-N-O bond angle of 174 (1)° and a Ru-N bond length of 1.74 (1) Å. Conventionally then, the complex is best formulated as a d^8 Ru(0) complex of NO^+. The observed Ru-N bond length compares favorably with values of 1.79 (1), 1.70 (1), 1.779 (8), 1.74 (2), 1.75, and 1.72 Å reported for $RuH(NO)(P(C_6H_5)_3)_3$,[10] $[Ru(NO)(\mu\text{-}P(C_6H_5)_2)(P(C_6H_5)_2(CH_3))]_2$,[12] $[Ru(NO)_2Cl(P(C_6H_5)_3)_2]^+$,[7] $[Ru(OH)(NO_2)_4(NO)]^{2-}$,[27] and $Ru(NO)(S_2CN(C_2H_5))_3$,[28] in which the nitrosyl groups are in essence linearly coordinated, and is significantly shorter than the 1.86 (2) Å value found for the "severely" bent apical nitrosyl group in $[Ru(NO)_2Cl(P(C_6H_5)_3)_2]^+$.[7]

While basically trigonal bipyramidal, the inner coordination geometry is somewhat distorted from the ideal configuration. The P(2)-Ru-N and P(4)-Ru-N angles of the trigonal plane have values of 126.1 (4) and 134.5 (4)° with a P(2)-Ru-P(4) angle of 99.3 (2)°. The angles formed by the chelating ligands (P(1)-Ru-P(2) = 81.6 (2)°, P(3)-Ru-P(4) = 80.8 (2)°) are significantly less than 90° and are comparable to similar values found in $[Ir(O_2)(diphos)_2]^+$,[29] $[Rh(O_2)(diphos)_2]^+$,[29] and $[Ir(CO)(diphos)_2]^+$,[16] where the diphos ligand also bridges axial and equatorial positions of a distorted trigonal-bipyramidal complex. This type of deviation obviously results from the relatively small bite of the diphos ligand when coupled with the metal-

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Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms[a]

Atom	x	y	z	B, Å²	Atom	x	y	z	B, Å²
		Ring R1					Ring R2		
R1C1	0.4484 (38)	0.3279 (12)	0.2496 (8)	4.0 (4)	R2C1	0.5712 (6)	0.2645 (11)	0.2216 (10)	5.7 (5)
R1C2	0.4485 (18)	0.3622 (11)	0.3239 (6)	6.1 (5)	R2C2	0.5911 (10)	0.3108 (9)	0.1708 (10)	12.6 (9)
R1C3	0.4220 (22)	0.4184 (6)	0.3186 (8)	7.2 (6)	R2C3	0.6610 (11)	0.3173 (7)	0.1511 (10)	14.4 (9)
R1C4	0.3955 (38)	0.4402 (12)	0.2391 (10)	7.1 (6)	R2C4	0.7110 (6)	0.2773 (12)	0.1823 (12)	9.4 (7)
R1C5	0.3954 (18)	0.4058 (11)	0.1648 (7)	7.5 (6)	R2C5	0.6911 (10)	0.2310 (9)	0.2331 (12)	22.5 (15)
R1C6	0.4219 (22)	0.3497 (6)	0.1700 (7)	5.6 (5)	R2C6	0.6212 (11)	0.2246 (7)	0.2528 (10)	17.4 (12)
		Ring R3					Ring R4		
R3C1	0.5084 (15)	0.0900 (18)	0.3325 (9)	3.5 (4)	R4C1	0.3630 (8)	0.0808 (6)	0.3488 (8)	4.4 (4)
R3C2	0.5560 (11)	0.0805 (8)	0.2689 (6)	4.9 (5)	R4C2	0.3126 (9)	0.0996 (5)	0.4043 (9)	6.7 (5)
R3C3	0.6153 (8)	0.0466 (12)	0.2875 (8)	6.2 (5)	R4C3	0.2647 (6)	0.0605 (7)	0.4357 (8)	7.6 (6)
R3C4	0.6270 (15)	0.0222 (18)	0.3698 (10)	5.7 (5)	R4C4	0.2671 (8)	0.0025 (7)	0.4115 (9)	6.9 (5)
R3C5	0.5793 (11)	0.0317 (7)	0.4334 (7)	5.1 (5)	R4C5	0.3174 (10)	−0.0163 (4)	0.3559 (9)	7.1 (6)
R3C6	0.5200 (8)	0.0656 (12)	0.4147 (7)	5.6 (5)	R4C6	0.3654 (6)	0.0228 (7)	0.3246 (8)	5.6 (5)
		Ring R5					Ring R6		
R5C1	0.3441 (7)	0.1070 (6)	−0.0191 (6)	4.4 (4)	R6C1	0.3925 (8)	0.0260 (5)	0.1106 (8)	4.3 (4)
R5C2	0.3019 (6)	0.0653 (5)	−0.0613 (9)	5.1 (5)	R6C2	0.4642 (7)	0.0176 (5)	0.1035 (8)	5.6 (5)
R5C3	0.2903 (6)	0.0669 (5)	−0.1514 (9)	5.2 (5)	R6C3	0.4924 (5)	−0.0379 (7)	0.1099 (8)	6.9 (6)
R5C4	0.3208 (7)	0.1103 (6)	−0.1993 (6)	5.8 (6)	R6C4	0.4489 (9)	−0.0850 (5)	0.1235 (8)	7.0 (6)
R5C5	0.3629 (6)	0.1520 (5)	−0.1571 (9)	5.9 (6)	R6C5	0.3772 (8)	−0.0766 (6)	0.1306 (9)	8.3 (7)
R5C6	0.3746 (6)	0.1504 (5)	−0.0670 (9)	5.7 (6)	R6C6	0.3490 (7)	−0.0211 (8)	0.1242 (8)	7.0 (7)
		Ring R7					Ring R8		
R7C1	0.2636 (7)	0.2396 (7)	0.2695 (7)	4.2 (4)	R8C1	0.2751 (8)	0.2728 (6)	0.0932 (8)	4.4 (4)
R7C2	0.2868 (6)	0.2920 (6)	0.3057 (10)	6.6 (5)	R8C2	0.3158 (6)	0.2838 (7)	0.0228 (10)	5.6 (5)
R7C3	0.2624 (8)	0.3104 (5)	0.3846 (10)	8.3 (6)	R8C3	0.2916 (8)	0.3220 (6)	−0.0423 (8)	8.1 (6)
R7C4	0.2149 (8)	0.2764 (8)	0.4273 (7)	8.3 (6)	R8C4	0.2268 (9)	0.3491 (6)	−0.0370 (8)	8.4 (6)
R7C5	0.1917 (7)	0.2241 (7)	0.3912 (11)	10.1 (7)	R8C5	0.1861 (6)	0.3380 (7)	0.0333 (11)	7.6 (6)
R7C6	0.2161 (8)	0.2057 (5)	0.3122 (11)	9.0 (7)	R8C6	0.2103 (7)	0.2999 (5)	0.0984 (8)	6.3 (5)
		Ring RB1					Ring RB2		
RB1C1	−0.0327 (9)	0.2392 (4)	0.1556 (8)	5.0 (5)	RB2C1	0.0284 (6)	0.1409 (6)	0.0889 (7)	4.4 (4)
RB1C2	0.0238 (6)	0.2734 (7)	0.1854 (8)	6.5 (5)	RB2C2	0.0325 (6)	0.0812 (6)	0.0773 (8)	6.0 (5)
RB1C3	0.0199 (7)	0.3334 (6)	0.1776 (8)	7.0 (5)	RB2C3	0.0745 (7)	0.0586 (4)	0.0146 (9)	6.7 (5)
RB1C4	−0.0405 (10)	0.3592 (4)	0.1400 (8)	6.3 (5)	RB2C4	0.1125 (6)	0.0955 (6)	−0.0366 (7)	5.6 (5)
RB1C5	−0.0970 (6)	0.3250 (7)	0.1102 (8)	6.8 (5)	RB2C5	0.1084 (6)	0.1552 (6)	−0.0250 (8)	5.5 (5)
RB1C6	−0.0931 (6)	0.2650 (6)	0.1180 (8)	5.3 (5)	RB2C6	0.0663 (7)	0.1778 (4)	0.0378 (9)	5.8 (5)
		Ring RB3					Ring RB4		
RB3C1	0.0080 (8)	0.1523 (7)	0.2681 (6)	4.9 (5)	RB4C1	−0.1030 (19)	0.1341 (35)	0.1491 (12)	5.4 (5)
RB3C2	0.0528 (7)	0.1057 (6)	0.2865 (9)	6.6 (5)	RB4C2	−0.1470 (15)	0.1310 (15)	0.2180 (8)	8.7 (6)
RB3C3	0.0733 (7)	0.0924 (5)	0.3725 (12)	8.3 (6)	RB4C3	−0.2137 (9)	0.1068 (21)	0.2052 (9)	11.2 (8)
RB3C4	0.0489 (8)	0.1255 (7)	0.4400 (7)	8.2 (6)	RB4C4	−0.2364 (19)	0.0858 (35)	0.1237 (13)	7.7 (6)
RB3C5	0.0041 (7)	0.1720 (6)	0.4215 (9)	7.8 (6)	RB4C5	−0.1924 (14)	0.0890 (15)	0.0548 (9)	6.5 (5)
RB3C6	−0.0164 (7)	0.1854 (5)	0.3355 (11)	6.9 (5)	RB4C6	−0.1257 (9)	0.1131 (21)	0.0675 (9)	6.6 (5)

[a] R1 and R2 are bonded to P(1); R3 and R4 are bonded to P(2); R5 and R6 are bonded to P(3); R7 and R8 are bonded to P(4); RB1, RB2, RB3, and RB4 are bonded to the boron atom of the anion.

Table III. Root-Mean-Square Amplitudes of Vibration (Å) of Anisotropically Refined Atoms[a]

Atom	Min	Intermed	Max	Atom	Min	Intermed	Max
Ru	0.180 (2)	0.224 (3)	0.230 (3)	C(2)	0.16 (4)	0.25 (3)	0.36 (3)
P(1)	0.218 (8)	0.248 (9)	0.261 (8)	C(3)	0.14 (4)	0.20 (3)	0.26 (3)
P(2)	0.200 (8)	0.241 (8)	0.256 (8)	C(4)	0.15 (3)	0.19 (3)	0.27 (2)
P(3)	0.200 (8)	0.225 (9)	0.259 (8)	B	0.21 (3)	0.24 (3)	0.25 (3)
P(4)	0.212 (8)	0.237 (8)	0.270 (8)	AO	0.34 (2)	0.37 (2)	0.45 (2)
N	0.11 (4)	0.22 (2)	0.24 (2)	AC(1)	0.25 (5)	0.37 (4)	0.51 (5)
O	0.22 (2)	0.28 (2)	0.39 (2)	AC(2)	0.26 (4)	0.42 (4)	0.55 (4)
C(1)	0.14 (4)	0.21 (3)	0.43 (3)	AC(3)	0.17 (5)	0.39 (4)	0.64 (4)

[a] Calculated along principal axes of thermal motion.

phosphorus distances in these systems. However, in contrast to the aforementioned deviation from the ideal trigonal-bipyramidal geometry, the angle formed by the trans axial phosphine atoms with the metal is nearly linear (P(1)-Ru-P(3) = 175.2 (2)°) and the angles of these phosphorus atoms with the nitrosyl nitrogen atom are close to 90° (P(1)-Ru-N = 90.1 (4), P(3)-Ru-N = 93.1 (4)°). While some of the angular distortions in the coordination geometry can be rationalized in terms of the restrictive bite of the diphos ligand, others cannot. One in particular involves the angles in the trigonal plane. If the large values for the P-Ru-N bond angles are rationalized in terms of repulsions between the bonding electrons of the nitrosyl and the equatorial phosphines, one might also expect such repulsions to be operative between the nitrosyl and the axial phosphines yielding P_{ax}-Ru-N bond angles significantly greater than 90°. Such is clearly not the case in the present study. An explanation which rationalizes the observed

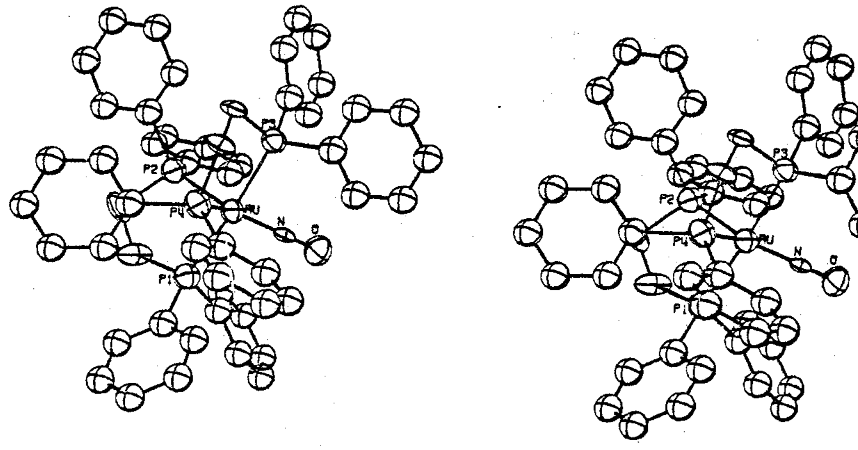

Figure 2. A stereoscopic view of the entire $[Ru(NO)(diphos)_2]^+$ complex. The drawings constitute a stereopair and should be viewed with the aid of a stereoviewer.

Table IV. Principal Intramolecular Distances and Angles for $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$

Distances, Å			
Ru-P(1)	2.408 (5)	P(2)-N	3.66 (1)
Ru-P(2)	2.357 (5)	P(3)-N	3.02 (1)
Ru-P(3)	2.377 (5)	P(4)-N	3.83 (1)
Ru-P(4)	2.409 (5)	P(1)-R1C(1)	1.85 (2)[a]
Ru-N	1.74 (1)	P(1)-R2C(1)	1.82 (2)[a]
N-O	1.20 (1)	P(2)-R3C(1)	1.84 (2)[a]
P(1)-C(1)	1.85 (2)	P(2)-R4C(1)	1.84 (2)[a]
P(2)-C(2)	1.87 (2)	P(3)-R5C(1)	1.84 (2)[a]
P(3)-C(3)	1.85 (2)	P(3)-R6C(1)	1.82 (2)[a]
P(4)-C(4)	1.90 (1)	P(4)-R7C(1)	1.83 (2)[a]
C(1)-C(2)	1.52 (2)	P(4)-R8C(1)	1.84 (2)[a]
C(3)-C(4)	1.51 (2)	B-RB1C(1)	1.66 (2)[a]
P(1)-P(2)	3.113 (7)	B-RB2C(1)	1.71 (2)[a]
P(3)-P(4)	3.102 (7)	B-RB3C(1)	1.71 (2)[a]
P(2)-P(4)	3.633 (7)	B-RB4C(1)	1.68 (2)[a]
P(1)-P(4)	3.670 (7)	AO-AC(1)	1.25 (3)
P(2)-P(3)	3.460 (6)	AC(1)-AC(2)	1.44 (4)
P(1)-N	2.97 (1)	AC(1)-AC(3)	1.47 (4)
Angles, Deg			
Ru-N-O	174 (1)	Ru-P(1)-C(1)	109.4 (6)
P(1)-Ru-P(2)	81.6 (2)	P(1)-C(1)-C(2)	112 (1)
P(3)-Ru-P(4)	80.8 (2)	Ru-P(2)-C(2)	107.5 (6)
P(1)-Ru-P(3)	175.5 (2)	P(2)-C(2)-C(1)	108 (1)
P(2)-Ru-P(4)	99.3 (2)	Ru-P(3)-C(3)	107.8 (5)
P(1)-Ru-P(4)	99.3 (2)	P(3)-C(3)-C(4)	107 (1)
P(2)-Ru-P(3)	93.9 (2)	Ru-P(4)-C(4)	108.9 (5)
P(1)-Ru-N	90.1 (4)	P(4)-C(4)-C(3)	111 (1)
P(3)-Ru-N	93.1 (4)	AO-AC(1)-AC(2)	116 (4)
P(2)-Ru-N	126.1 (4)	AO-AC(1)-AC(3)	119 (3)
P(4)-Ru-N	134.5 (4)	AC(2)-AC(1)-AC(3)	125 (3)

Dihedral Angles between Planes, Deg	
[Ru, P(1), P(2)] and [Ru, P(3), P(4)]	81.1 (2)
[Ru, P(1), C(1)] and [Ru, P(2), C(2)]	26.7 (7)
[Ru, P(3), C(3)] and [Ru, P(4), C(4)]	30.0 (6)

[a] Estimated standard deviation obtained using estimated standard deviations for the derived positional parameters of the group atom.

angles and which is consistent with other structural parameters is not readily apparent at this time.

The axial and equatorial Ru-P distances in the structure range from 2.357 (5) to 2.409 (5) Å in no apparent order and yield an average Ru-P distance of 2.388 (12) Å. McGinnety, *et al.*,[29] also found an unexpectedly broad range for metal-phosphorus distances in the diphos complex $[Ir(O_2)(diphos)_2]^+$ where the values range from 2.283 (7) to 2.452 (9) Å with the shortest and longest distances in the equatorial positions as is found here. A somewhat less pronounced variation is also observed in the $[Rh(O)_2(diphos)_2]^+$ complex.[29] The average Ru-P distance of 2.388 (12) Å is significantly longer than those found in most ruthenium-phosphine complexes (2.30 Å in $RuH(C_{10}H_7)((CH_3)_2PCH_2CH_2P(CH_3)_2)_2$,[30] 2.34 Å in $RuCl_2((CH_3)(C_6H_5)PCH_2P(CH_3)(C_6H_5))_2$,[31] 2.339 (4) Å in $RuH(NO)(P(C_6H_5)_3)_3$[10] and 2.315 (4) Å in $[Ru(NO)(\mu\text{-}P(C_6H_5)_2)(P(CH_3)(C_6H_5))]_2$[12]) although it is in approximate agreement with Ru-P distances in the basal plane of some Ru(II) tetragonal complexes (2.393 (6) Å in $RuCl_2(P(C_6H_5)_3)_3$,[32] 2.359 (6) Å in $RuH(CH_3CO_2)(P(C_6H_5)_3)_3$,[33] and 2.426 (6) Å in $[Ru(NO)_2Cl(P(C_6H_5)_3)_2]^+$ [7]).

Table V. Torsion Angles about Bonds in the Chelate Rings (deg)

Ring	τ(Ru-P)	τ(P-C)	τ(C-C)	τ(C-P)	τ(P-Ru)
[Ru, P(1), P(2), C(1), C(2)]	3.6 (7)	26 (1)	−48 (1)	49 (1)	−26.0 (7)
[Ru, P(3), P(4), C(3), C(4)]	−28.8 (6)	53 (1)	−49 (1)	25 (1)	5.2 (6)

As expected, the chelate rings are distinctly nonplanar. During the last 10 years, conformational analysis of metal-chelate rings has been a fertile and active area of study. Theoretical calculations of the conformational energies of saturated, five-membered diamine chelate rings have indicated that there are a number of energetically equivalent symmetrical (C_2) and unsymmetrical minimum energy conformations.[34] Hall, *et al.*,[15] have compiled data on a number of structural studies of bidentate diphosphine complexes and have found that examples of the unsymmetrically bridged ligands greatly outnumber the symmetrically bridged variety. In the chelate rings of $[Ru(NO)(diphos)_2]^+$, the ethylene bridges are also of the unsymmetrically bridged type. This is indicated by the torsion angles about each bond in the chelate ring as presented in Table V (see also Table VI of ref 15). The planes defined by the ruthenium and two phosphorus atoms of each chelate ring are given in Table VI along with the deviations of atoms from these planes. Both bridging carbon atoms for each ring are on the *same* side of their respective plane as might be expected for an unsymmetrically bridged conformation. This can be contrasted with the conformations recently found by Bonds and Ibers[35] in the $[Ir(S_2)(diphos)_2]^+$

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(30) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971).

(31) I. Kawada, *Tetrahedron Lett.*, 10, 793 (1969).

(32) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 4, 778 (1965).

(33) A. C. Skapski and F. A. Stephens, *Chem. Commun.*, 1008 (1969).

(34) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 8, 1168 (1969).

Table VI. Equations of Planes and Deviations of Atoms from Their Respective Planes (in Monoclinic Coordinates)

Plane through Ru, P(1), P(2)
$16.95x - 9.41y - 4.00z = 4.78$

Atom	Dist, Å	Atom	Dist, Å
C(1)	−0.11	P(3)	−0.03
C(2)	−0.78	P(4)	−2.35

Plane through Ru, P(3), P(4)
$-3.12x - 9.98y + 13.78z = -0.75$

Atom	Dist, Å	Atom	Dist, Å
C(3)	0.85	P(1)	0.19
C(4)	0.16	P(2)	2.32

Plane through P(2), P(4), N
$6.45x + 19.53y + 6.04z = 7.18$

Atom	Dist, Å	Atom	Dist, Å
Ru	0.02	C(1)	2.73
P(1)	2.38	C(2)	1.69
P(3)	−2.32	C(3)	−2.70
O	0.00	C(4)	−1.80

Plane through AO, AC(1), AC(2), AC(3)[a]
$-7.14x + 19.01y - 6.22z = -1.43$

Atom	Dist, Å	Atom	Dist, Å
AO	−0.001 (21)	AC(2)	−0.002 (32)
AC(1)	0.004 (31)	AC(3)	−0.002 (34)

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961).

complex in which the bridging carbon atoms are on opposite sides of the best least-squares plane through each chelate ring. Other important planes in the structure are also included in Table VI.

The geometry of the tetraphenylborate anion is essentially the same as found in previous structure determinations. The average boron-ring carbon distance is 1.69 (2) Å, and the average (ring carbon)-B-(ring carbon)′ angle around the boron atom is 111 (1)°. The molecular structure of the acetone is also similar to previously reported dimensions.

Discussion

The cationic complex $[Ru(NO)(diphos)_2]^+$ is a second example of zerovalent ruthenium stabilized by the strong π-back-bonding interaction with linearly coordinated nitrosyl, or formally NO^+. This compound and the related complex $RuH(NO)(P(C_6H_5)_3)_3$ are the only examples of discrete Ru(0) complexes which do not contain carbonyl groups. As has been mentioned previously,[10] the relatively low value for ν_{NO} in the present complex (1673 cm^{-1}) is in the region of overlap for linear and bent nitrosyl groups and illustrates the danger associated with the assignment of nitrosyl bonding configuration as a function of the nitrosyl stretching frequency.

A molecular orbital view of the bonding in $[Ru(NO)(diphos)_2]^+$ is of considerable interest, especially in trying to correlate the present results with structures found for related "isoelectronic" systems. For example, $RuH(NO)(P(C_6H_5)_3)_3$[10] and $[IrH(NO)(P(C_6H_5)_3)_3]^+$[11] exhibit trigonal-bipyramidal structures with axial nitrosyl groups bonded in the linear manner whereas $[Ru(NO)_2Cl(P(C_6H_5)_3)_2]^+$,[7] $[IrX(NO)(CO)(P(C_6H_5)_3)_2]^+$ (X = Cl, I)[2,3] and related systems[8,9] possess square-pyramidal geometries with bent apical nitrosyl groups. In discussing the bonding in these complexes previously,[7,10,13] we have considered them as 22-electron systems derived *initially* from a d^8 metal ion, 6 electrons in the nitrosyl bonding functions (*i.e.*, $(\pi_{2px,2py})^4(\sigma_{2pz})^2$), and 8 electrons in the remaining ligand σ^b orbitals. $[Ru(NO)(diphos)_2]^+$ is also a 22-electron system, and its bonding scheme should offer an electronically stable alternative to others which have been presented. It is important to realize that while the constraint of the bidentate diphos ligand eliminates the structural possibility adopted by $RuH(NO)(P(C_6H_5)_3)_3$, the formation of a square-pyramidal complex with a bent apical nitrosyl is a viable structural possibility for $[Ru(NO)(diphos)_2]^+$. Therefore, its observed structure represents a relative energetic minimum.

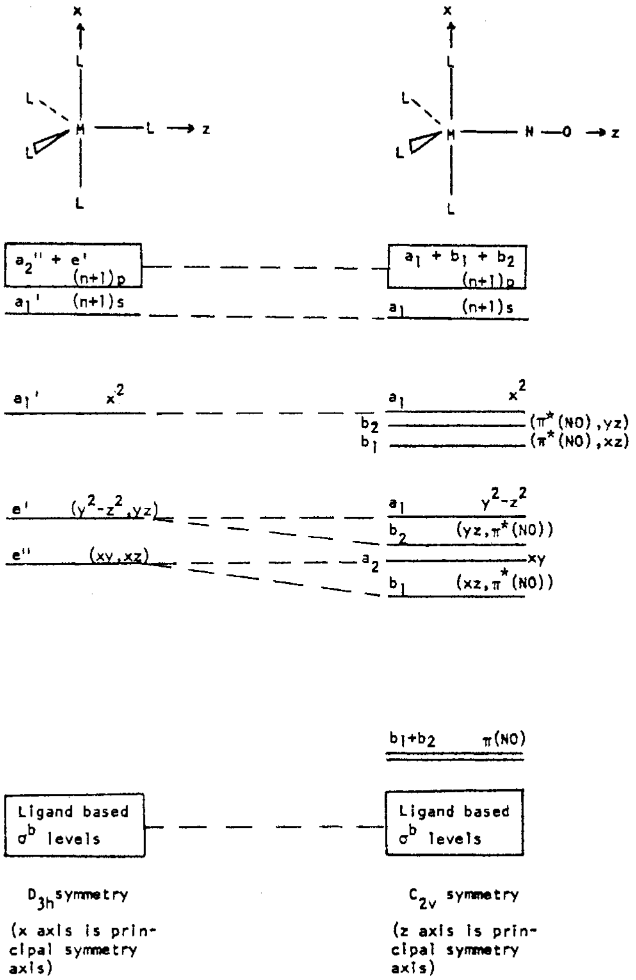

Figure 3. Proposed energy level orderings for trigonal-bipyramidal complexes ML_5 and $M(NO)L_4$. In the latter the nitrosyl is linearly coordinated in the equatorial plane.

The molecular orbitals for $[Ru(NO)(diphos)_2]^+$ are most easily visualized as being derived from a trigonal bipyramid in which the threefold symmetry of the coordination geometry and the degeneracy of certain levels are lost. For ease of correlating the resultant molecular orbitals with energy level orderings put forth previously,[7,13] we choose as the principal axis of the trigonal bipyramid the x axis with the z axis in the trigonal plane oriented along the Ru-N vector as shown in Figure 3. In the undistorted trigonal bipyramid, the ordering of the "d" levels is thus simply $x^2 > (yz, y^2 - z^2) > (xy, xz)$. (The orbitals x^2 and $y^2 - z^2$ are linear combinations of the more conventionally used z^2 and $x^2 - y^2$.) Upon introducing the nitrosyl group into the trigonal plane, the symmetry of the complex is

(35) W. D. Bonds, Jr., and J. A. Ibers, *J. Amer. Chem. Soc.*, 94, 3413 (1972).

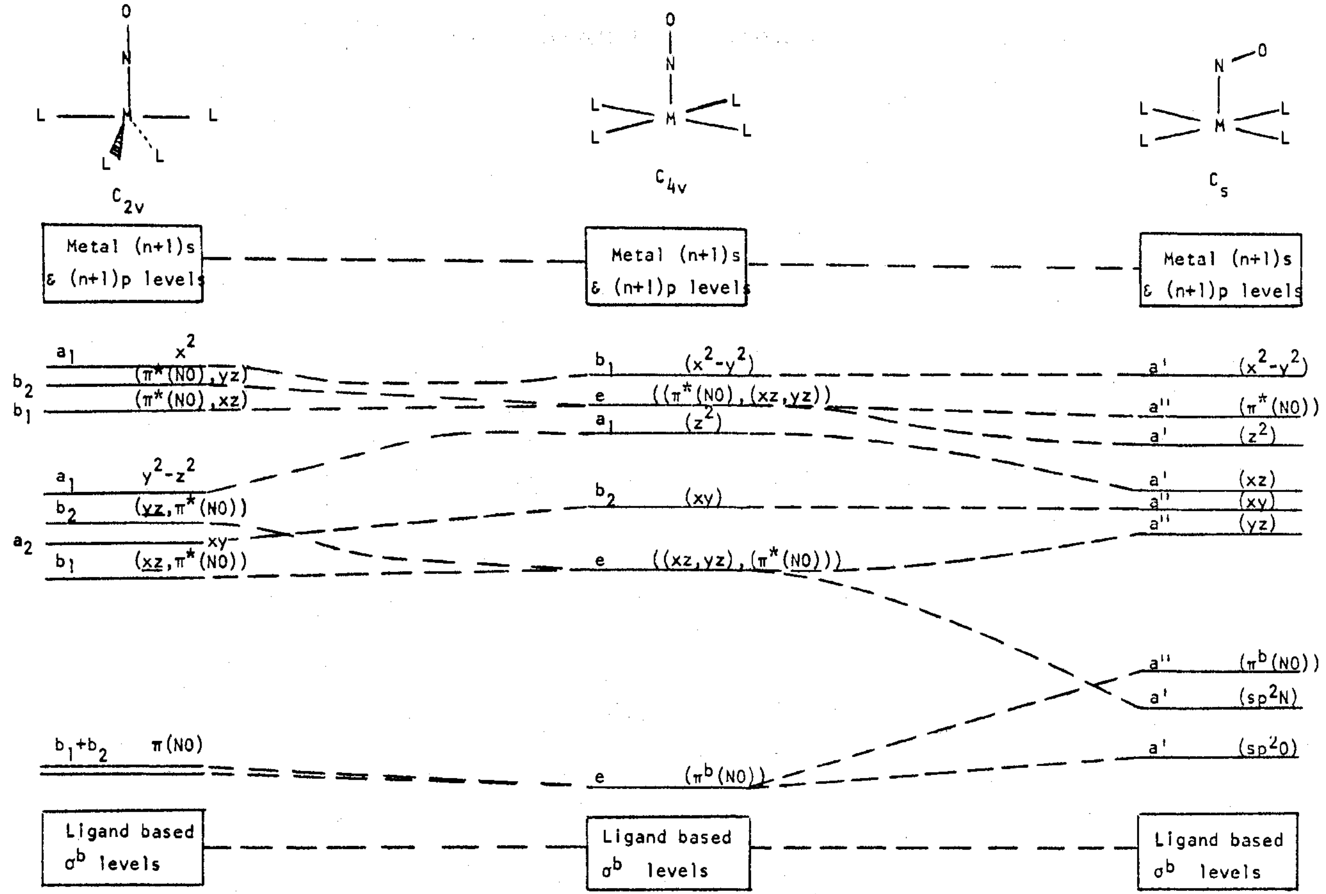

Figure 4. A correlation of the proposed level orderings in five-coordinate nitrosyl complexes of C_{2v}, C_{4v}, and C_s symmetries. The level orderings for C_{4v} and C_s symmetries are those which have been presented previously in ref 13.

reduced to C_{2v}, if one neglects the phosphine substituents, with the z axis emerging as the principal symmetry axis. When the nitrosyl π^* functions are included in the energy level scheme, the following changes in level ordering occur: (1) the metal xz orbital and a π^*(NO) function interact yielding a more stable (and somewhat delocalized) xz level and a destabilized primarily π^*(NO) level; (2) the metal yz orbital, which is σ^* in the trigonal plane, interacts with the remaining π^*(NO) function leading to relative stabilization of yz and destabilization of π^*(NO); (3) the metal $d_{y^2-z^2}$ is slightly destabilized because of the strong metal-nitrosyl σ interaction; (4) the metal x^2 and xy levels remain essentially unchanged. The ordering thus proposed for $[Ru(NO)(diphos)_2]^+$ is shown in Figure 3 and the ground-state configuration is . . . $(yz)^2(y^2-z^2)^2$. These levels can be correlated with the energy levels proposed for a tetragonal-pyramidal system with a linear apical nitrosyl in C_{4v} symmetry and a bent nitrosyl in C_s symmetry as illustrated in Figure 4. The correlation shows that by changing the ligand field geometry about the metal while preserving the strong metal-nitrosyl π interaction, the complex can achieve a relative energetic minimum when compared with the C_{4v} case. However, the correlation also indicates that the square-pyramidal-bent NO geometry should be of similar stability and thus accessible in the thermodynamic sense. Recently, Enemark and Feltham[36] have suggested a level ordering for trigonal-bipyramidal complexes containing a linearly bonded nitrosyl in the equatorial position, and their ordering appears to be similar to that proposed here although differences in the correlations of Figure 4 exist.

Stereochemical interconversions have been proposed for a number of metal-nitrosyl complexes. Fluxional behavior has been reported for the $CoCl_2(NO)L_2$ and $MH(NO)L_3$ systems (L = tertiary phosphine; M = Ru, Os) by Collman, *et al.*,[37] and by Wilson and Osborn,[38] respectively, and Collman has investigated the interconversion of apical and basal nitrosyls in the $[Ru(NO)_2Cl(P(C_6H_5)_3)_2]^+$ complex using ^{15}N-labeled nitric oxide. For $[Ru(NO)_2Cl(P(C_6H_5)_3)_2]^+$, a trigonal-bipyramidal intermediate containing equivalent equatorial nitrosyl groups has been proposed[7] based on the molecular structure of $[Ru(NO)(diphos)_2]^+$ which demonstrates the feasibility of such coordination. Moreover the recent structural results for $CoCl_2(NO)L_2$[39] and for $[Co(NO)(diars)_2]^{2+}$[17] indicate the viability of this geometry in stereochemical interconversions in nitrosyl complexes.

Registry No. $[Ru(NO)(diphos)_2][B(C_6H_5)_4]\cdot(CH_3)_2CO$, 36182-30-6.

Acknowledgments. We wish to thank the National Science Foundation (Grant GP-23139) and the Advanced Research Projects Agency for support of this work. We especially want to thank Dr. Robert E. Townsend for the sample of the complex.

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