Figure 3.—The cyclooctatetraene dianion ring carbon atoms in $Th(C_8H_8)_2$ viewed perpendicular to the plane of the ring are shown on the right. The left view is rotated 65°. The numbering sequence increases sequentially in a clockwise direction from the upper right carbon atom, C_1, in both rings.

Comparison of the $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ structures demonstrates the ability to use ionic radii in predicting bond distances in an isostructrual actinide (or lanthanide) series of organometallic π complexes. The following comparisons are made using ionic radii calculated for a coordination number (CN) of IX (CN of VIII gives the same results; values for CN of X are not available). The thorium–carbon bond lengths can be estimated from the ionic radii of uranium (IV), 1.05 Å,[19] and thorium (IV), 1.09 Å.[19] The difference in these radii, when added to the average U–C bond length, predicts a Th–C bond length of 2.69 Å. This compares well with the observed value of 2.70 Å. An estimation can also be made for a lanthanide with a similar π-sandwich structure, $K(diglyme)Ce(C_8H_8)_2$.[20] The difference between the ionic radii of uranium(IV)

(19) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969); **26**, 1046 (1970).

(20) K. O. Hodgson and K. N. Raymond, to be submitted for publication.

and cerium(III), 1.15 Å,[19] predicts a Ce–C bond length of 2.75 Å. Preliminary structural results, before final refinement, give an experimental average Ce–C bond distance of 2.74 Å.[20] It is thus apparently possible to predict M–C bond lengths to within about 0.01 Å for these actinide and lanthanide $C_8H_8{}^{2-}$ complexes.

The general features of the bonding in $Th(C_8H_8)_2$ and $U(C_8H_8)_2$, as established by this study, are substantially identical. Questions regarding the relative importance of f-orbital involvement in the bonding of these compounds and how this may affect the relative reactivities of compounds such as $Th(C_8H_8)_2$ and $U(C_8H_8)_2$ cannot be directly answered by structural studies alone. It was observed by Streitwieser and Yoshida that $Th(C_8H_8)_2$, in contrast to $U(C_8H_8)_2$, is easily solvolyzed in solvents which can act as Lewis bases.[2] The degree to which f-orbital back-bonding explains the chemical differences in this series remains to be established by the magnetic resonance and spectroscopic studies which are in progress.

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The Molecular Structure of Chlorodinitrosylbis(triphenylphosphine)ruthenium Hexafluorophosphate–Benzene. A Complex Having Linear and Bent Nitrosyl Groups

BY CORTLANDT G. PIERPONT[1] AND RICHARD EISENBERG*

The crystal and molecular structure of the dinitrosyl complex $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6] \cdot C_6H_6$ has been determined from three-dimensional single-crystal X-ray data collected by the θ–2θ counter technique. The complex crystallizes in the monoclinic space group $P2_1/c$ in a cell of dimensions $a = 12.51$ (1), $b = 14.67$ (1), $c = 23.00$ (1) Å, $\beta = 91.8$ (2)°, and $V = 4219$ Å^3. There are four molecules per unit cell ($\rho_{exptl} = 1.49 \pm 0.01$ g/cm^3; $\rho_{calcd} = 1.484$ 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 0.065 for 1522 reflections with $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$. The structure of the ruthenium dinitrosyl cation is a distorted square pyramid in which an apical nitrosyl group coordinates in a bent manner (Ru–N, 1.85 (2) Å; Ru–N–O, 138 (2)°) while a basal nitrosyl coordinates in a linear manner (Ru–N, 1.74 (2) Å; Ru–N–O, 178 (2)°). As such, this Ru(II) complex represents a striking illustration of the two different modes of coordination for nitrosyl. The average Ru–P and Ru–Cl distances are 2.426 (6) and 2.362 (6) Å, respectively. The bonding of the apical nitrosyl group in this and other closely related systems is discussed in terms of a simple orbital correlation diagram.

Introduction

In 1967, Hodgson, *et al.*, reported the reaction between $IrCl(CO)(P(C_6H_5)_3)_2$ and NO^+ and showed that it yields a nitrosyl complex with a metal–nitrogen–oxygen bond angle of 124 (1)°.[2,3] Since the initial

(1) National Institutes of Health Predoctoral Fellow, 1969–1971.

(2) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

(3) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

report of this system, other examples of nitrosyl coordination to group VIII metal ions exhibiting M–N–O angles approaching 120° have appeared.[4–8] From

(4) D. J. Hodgson and J. A. Ibers, *ibid.*, **8**, 1282 (1969).

(5) D. A. Snyder and D. L. Weaver, *ibid.*, **9**, 2760 (1970).

(6) D. M. P. Mingos and J. A. Ibers, *ibid.*, **10**, 1035 (1971).

(7) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, **10**, 1043 (1971).

(8) C. S. Pratt, B. A. Coyle, and J. A. Ibers, as quoted in ref 6.

bonding formalisms, the bent nitrosyl groups are considered as NO$^-$ while linearly coordinated nitrosyls are viewed as NO$^+$. The bonding of NO$^+$ to transition metal ions is analogous to that of carbonyl with a strong π-acceptor interaction between filled metal d_π orbitals and empty doubly degenerate π^*(NO) levels, while the bonding of NO$^-$ may be viewed as primarily the σ donation of an electron pair of the nitrogen atom to the metal. The sp^2 hybridization of the nitrogen atom in coordinated NO$^-$ results in an approximately 120° angle with the metal.

In 1969 Stiddard and Townsend reported the preparation of the ruthenium complex RuCl(NO)(P(C$_6$H$_5$)$_3$)$_2$[9] which is isoelectronic with the well-known Vaska's complex IrCl(CO)(PC$_6$H$_5$)$_3$)$_2$.[10] In order to illustrate the two modes of nitrosyl bonding within the same system, we have synthesized the nitrosyl adduct of Stiddard's complex and determined its molecular structure as the PF$_6$$^-$ salt. The details of this single-crystal X-ray structure determination are reported herein. A communication of this work has appeared previously.[11] The two different nitrosyl groups of the cationic RuCl(NO)$_2$(P(C$_6$H$_5$)$_3$)$_2$$^+$ complex make possible a direct comparison of the different bonding modes of the nitrosyl ligand within the same molecule.

Collection and Reduction of the X-Ray Data

The complex [RuCl(NO)$_2$(P(C$_6$H$_5$)$_3$)$_2$][PF$_6$] was prepared by the addition of 0.20 g of (NO)(PF$_6$) in 10 ml of methanol to 0.50 g of RuCl(NO)(P(C$_6$H$_5$)$_3$)$_2$ in 60 ml of benzene. The dark green RuCl(NO)(P(C$_6$H$_5$)$_3$)$_2$ was prepared under N$_2$ in the manner described by Stiddard and Townsend.[9] On the addition of (NO)(PF$_6$), the green solution turned red-orange. The volume of the solution was reduced with an aspirator to about 30 ml, and after several hours, orange-red crystals of [RuCl(NO)$_2$-(P(C$_6$H$_5$)$_3$)$_2$][PF$_6$]·C$_6$H$_6$ appeared. The complex shows two characteristic infrared bands for the nitrosyl groups at 1687 and 1845 cm^{-1}.

On the basis of Weissenberg and precession photographs of the $h0l$, $h1l$, $0kl$, $1kl$, $hk0$, and $hk1$ zones, it was determined that the crystals belong to the monoclinic system. The observed extinctions of l odd for $h0l$ and k odd for $0k0$ uniquely determine the space group as $P2_1/c$ ($C_{2h}{}^5$; no. 14).[12] The lattice constants at room temperature, which were determined from a least-squares refinement[13] of the angular settings of 21 reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å), are $a = 12.51$ (1), $b = 14.67$ (1), $c = 23.00$ (1) Å, $\beta = 91.8$ (2)°, and $V = 4219$ Å^3. An experimental density of 1.49 g/cm^3 for four formula weights corresponds to [RuCl(NO)$_2$(P(C$_6$H$_5$)$_3$)$_2$][PF$_6$]·C$_6$H$_6$ per unit cell. The presence of the benzene molecule was confirmed by chemical analysis.

A crystal of dimensions 0.13 × 0.14 × 0.20 mm was mounted along the b axis and prepared for data collection. The b axis of the crystal was aligned parallel to the ϕ axis of the diffractometer. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique.[14] The average width at half-height was found to be 0.15°. 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 4 × 5 mm was positioned 21 cm from the crystal and a scan range from −0.6 to +0.7° of the Kα peak

was used. The data set was collected within the angular range 5° ≤ 2θ ≤ 40°. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded approximately 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 with the values of I and $\sigma(I)$ being corrected for Lorentz and polarization effects. The intensities of a total of 4187 reflections were measured, of which 2293 were observed to be greater than 1.5σ and 1522 greater than 3σ. The data were not corrected for absorption effects due to the small value of the linear absorption coefficient ($\mu = 6.1$ cm^{-1}) and the approximate uniformity of crystal dimensions.

Solution and Refinement of the Structure

The positions of the ruthenium, chlorine, and two phosphorus atoms of the cation were determined from a three-dimensional Patterson function. After one cycle of refinement (*vide infra*) of the positional parameters of the four atoms, their isotropic temperature factors, and a single scale factor, the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$ were 0.310 and 0.423, respectively. From a difference Fourier map based on the phases of the four heavy atoms of the cation, the positions of all other atoms of the cation, the benzene of crystallization, and the phosphorus atom of the PF$_6$$^-$ group were determined. The fluorine atoms of the PF$_6$$^-$ anion were not located at this stage.

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 $4F_o{}^2/\sigma^2(F_o{}^2)$. The standard deviations $\sigma(F_o{}^2)$ were estimated from counting statistics according to the formula given by Corfield, *et al.*,[15] with a value of 0.03 for the uncertainty parameter p. In the initial refinements, all atoms were treated independently and the 2293 reflections for which $F_o{}^2 \geq 1.5\sigma(F_o{}^2)$ were used. In these calculations, the atomic scattering factors for the nonhydrogen atoms were taken from Cromer and Waber[16a] while that of hydrogen was taken from Stewart, *et al.*[16b] The effects of anomalous dispersion were included in these calculations with the values of $\Delta f'$ and $\Delta f''$ for Ru, P, and Cl taken from Cromer's tabulation.[17] This refinement of individual positional and isotropic thermal parameters converged to discrepancy factors of $R_1 = 0.163$ and $R_2 = 0.202$. A difference Fourier map based on this refinement over the region of the PF$_6$$^-$ anion revealed two possible orientations for the octahedral configuration of fluorine atoms with approximately equal peak heights. Several models for the disordered fluorine atoms were formulated and tried in subsequent cycles of refinement. In the first of these, the fluorine atoms were treated independently with fixed occupancy factors of 0.5. After several cycles of refinement, the fluorine atom positional parameters continued to change with large shifts and gave no indications of converging. The two F$_6$ octahedra were therefore treated as rigid groups constrained to O_h symmetry with a fluorine atom to center of gravity distance of 1.58 Å and an occupancy factor of 0.5. The phosphorus atom of the PF$_6$$^-$ group was treated as an independent atom in the refinement procedure. In all subsequent calculations, the phenyl rings were also treated as rigid groups constrained to D_{6h} symmetry with a C–C distance of 1.392 Å.

In the next round of calculations, the nongroup atoms were assigned anisotropic thermal parameters while the phenyl ring carbon atoms were assigned variable individual isotropic temperature factors. Three cycles of least-squares refinement of this model converged to $R_1 = 0.080$ and $R_2 = 0.084$. The positions of the hydrogen atoms of the phenyl rings were then assumed (d(C–H) = 1.08 Å) and fixed contributions from these atoms were included in subsequent structure factor calculations and refinements assuming individual isotropic temperature factors of 5.0 Å^2. The discrepancy factors after three more cycles of least

(9) M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc. D*, 1372 (1969).

(10) L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, **83**, 2784 (1961).

(11) C. G. Pierpont, D. G. VanDerveer, W. Durland, and R. Eisenberg, *ibid.*, **92**, 4760 (1970).

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

(13) 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 function and error program, and C. K. Johnson's ORTEP plotting program. All computing was performed on Brown University's IBM 360/67 computer.

(14) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

(15) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(16) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(17) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

TABLE I

FINAL POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6] \cdot C_6H_6$

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	−0.0911 (2)[b]	0.2330 (1)	0.11889 (9)	0.0059 (2)	0.0027 (1)	0.00143 (4)	0.0006 (2)	−0.00012 (6)	0.00006 (8)
P(1)	−0.1022 (4)	0.2358 (4)	0.0132 (2)	0.0066 (6)	0.0025 (4)	0.0014 (1)	−0.0002 (4)	0.0003 (2)	−0.0001 (2)
P(2)	−0.1145 (5)	0.1808 (5)	0.2174 (3)	0.0051 (6)	0.0030 (4)	0.0019 (2)	−0.0002 (4)	0.0000 (3)	−0.0003 (2)
Cl	−0.0120 (5)	0.0887 (4)	0.1050 (3)	0.0118 (7)	0.0035 (4)	0.0020 (2)	0.0022 (4)	0.0001 (3)	−0.0001 (2)
N(1)	0.0270 (15)	0.3062 (15)	0.1345 (7)	0.0079 (19)	0.0083 (19)	0.0003 (4)	−0.0035 (15)	−0.0001 (7)	0.0004 (7)
O(1)	0.0443 (15)	0.3818 (12)	0.1473 (8)	0.0137 (21)	0.0051 (14)	0.0034 (6)	−0.0033 (14)	−0.0007 (8)	−0.0017 (7)
N(2)	−0.1962 (15)	0.3101 (15)	0.1248 (9)	0.0062 (20)	0.0084 (18)	0.0020 (6)	0.0037 (15)	0.0006 (9)	0.0002 (8)
O(2)	−0.2667 (16)	0.3609 (13)	0.1275 (9)	0.0139 (24)	0.0068 (15)	0.0044 (7)	0.0072 (14)	−0.0001 (10)	0.0012 (8)
P(3)	0.4095 (6)	0.2328 (6)	0.1355 (3)	0.0132 (8)	0.0070 (5)	0.0036 (3)	0.0003 (6)	−0.0014 (4)	0.0003 (3)

Group	$x_0{}^c$	y_c	z_c	ϕ	θ	ρ	B, Å²
P1R(1)	0.1142 (8)	0.1965 (6)	−0.0526 (4)	−1.011 (15)	−2.257 (10)	2.192 (15)	e
P1R(2)	−0.1901 (7)	0.4244 (7)	−0.0409 (4)	−0.747 (14)	−2.308 (9)	0.573 (13)	e
P1R(3)	−0.2825 (8)	0.0862 (7)	−0.0187 (4)	−2.329 (11)	2.876 (9)	2.934 (9)	e
P2R(1)	0.0940 (8)	0.1312 (6)	0.2964 (5)	1.810 (15)	−2.238 (10)	−1.153 (15)	e
P2R(2)	−0.2232 (9)	0.3463 (8)	0.2841 (4)	2.023 (10)	3.085 (9)	−2.686 (9)	e
P2R(3)	−0.2705 (8)	0.0054 (7)	0.2134 (4)	0.894 (15)	2.445 (9)	−0.004 (13)	e
BZ	0.4654 (7)	0.0989 (8)	0.3791 (6)	3.080 (10)	−3.022 (14)	−1.692 (10)	e
PF(1)	0.4057 (16)[d]	0.2277 (15)	0.1348 (9)	1.888 (23)	−3.187 (16)	−2.223 (21)	16.5 (8)
PF(2)	0.4137 (15)	0.2393 (14)	0.1314 (8)	1.383 (19)	−2.989 (15)	−1.772 (18)	14.0 (7)

[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_0, y_c, z_c are the fractional coordinates of the rigid-group centers. The angles ϕ, θ, ρ (in radians) have been previously defined: S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965). [d] Fractional occupancy factors were set at 0.5 for each of the disordered groups. [e] Individual atoms assigned variable isotropic thermal parameters.

squares including the 2293 reflections with $F_o{}^2 \geqslant 1.5\sigma(F_o{}^2)$ converged to $R_1 = 0.075$ and $R_2 = 0.075$.

Because of the use of the group refinement procedure for the phenyl rings and the F₆ octahedra, the total number of refined parameters for the structure amounted to only 180. Further cycles of refinement were therefore carried out in which only the more precisely measured reflections with $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ were included. With 1522 reflections and 180 variables, the ratio of observations to parameters remained relatively high at approximately 8.5. After several cycles of refinement, the discrepancy factors converged to final values of $R_1 = 0.065$ and $R_2 = 0.70$. The parameters obtained from this refinement are considered as the final parameters of the structure determination. No parameter changed by more than 30% of its standard deviation during the final cycle of refinement with the largest changes occurring for the F₆ groups. Within the cation, the largest parameter shifts were less than 10% of their respective estimated standard deviations. The estimated standard deviation of an observation of unit weight is 1.34 electrons and the final difference Fourier map shows peaks of about 25% of the height of a half fluorine atom in the region of the PF₆⁻ anion. The parameters obtained from this final cycle of refinement are presented in Table I along with their estimated standard deviations as derived from the
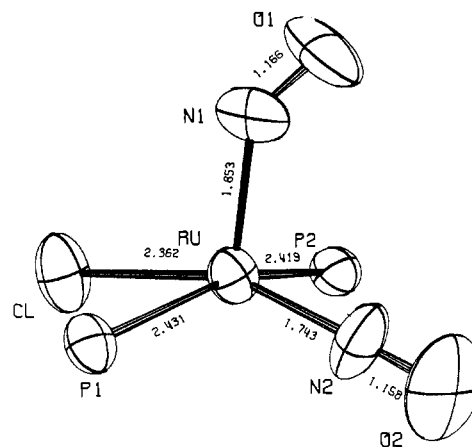

Figure 1.—A perspective drawing of the inner coordination sphere of the $RuCl(NO)_2(P(C_6H_5)_3)_2{}^+$ cation. The thermal ellipsoids have been scaled to approximately 50% probability distributions.
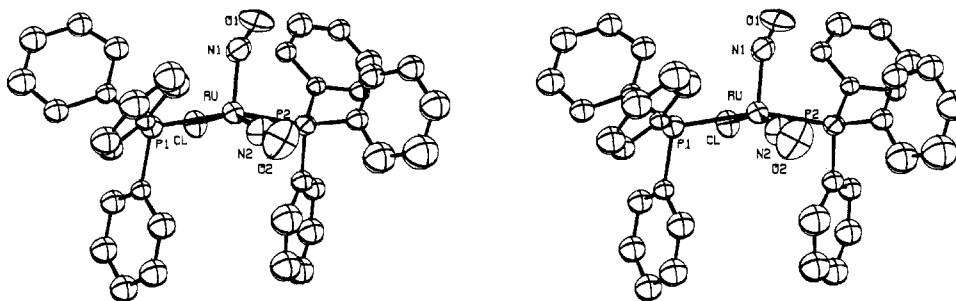

Figure 2.—A stereoscopic view of the complete cationic complex $RuCl(NO)_2(P(C_6H_5)_3)_2{}^+$.

inverse matrix. The derived parameters for the group atoms are given in Table II. A table of the final values of F_o and $|F_o|$ (in electrons × 10) for the 1522 reflections included in the last cycle of refinement is available.[18] The root-mean-square amplitudes of thermal motion of the anisotropically refined atoms are given in Table III.

(18) 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 INOR-72-1088. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Description of the Structure

The crystal structure consists of well-separated complex cations, octahedral anions, and solvent molecules of crystallization. A view of the inner coordination geometry of the cationic ruthenium complex is shown in Figure 1, and a stereoscopic view of the complete cation is shown in Figure 2. In Table IV are presented principal intramolecular distances and angles of the cation.

The cationic complex may be described as a distorted

TABLE II
DERIVED POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR GROUP ATOMS

Group atom	x	y	z	B, Å^2
P1R1C(1)	0.0204 (9)	0.2115 (18)	−0.0230 (6)	3.1 (5)
P1R1C(2)	0.0156 (10)	0.1764 (15)	−0.0793 (7)	4.2 (6)
P1R1C(3)	0.1094 (14)	0.1614 (10)	−0.1088 (5)	5.1 (6)
P1R1C(4)	0.2080 (10)	0.1815 (19)	−0.0821 (7)	5.5 (7)
P1R1C(5)	0.2128 (9)	0.2166 (15)	−0.0259 (7)	5.4 (6)
P1R1C(6)	0.1190 (12)	0.2317 (10)	0.0037 (5)	3.3 (5)
P1R2C(1)	−0.1518 (20)	0.3423 (9)	−0.0182 (6)	2.6 (5)
P1R2C(2)	−0.2150 (17)	0.3428 (9)	−0.0692 (6)	4.3 (6)
P1R2C(3)	−0.2533 (11)	0.4250 (12)	−0.0918 (5)	5.3 (7)
P1R2C(4)	−0.2284 (20)	0.5065 (9)	−0.0637 (7)	5.4 (7)
P1R2C(5)	−0.1652 (17)	0.5060 (8)	−0.0128 (7)	6.1 (7)
P1R2C(6)	−0.1269 (11)	0.4239 (12)	0.0100 (5)	4.8 (6)
P1R3C(1)	−0.2032 (12)	0.1501 (10)	−0.0053 (6)	3.2 (5)
P1R3C(2)	−0.3103 (14)	0.1726 (8)	0.0006 (6)	4.4 (6)
P1R3C(3)	−0.3896 (9)	0.1087 (13)	−0.0128 (7)	5.9 (7)
P1R3C(4)	−0.3618 (12)	0.0223 (11)	−0.0321 (7)	5.7 (7)
P1R3C(5)	−0.2546 (14)	−0.0003 (8)	−0.0380 (6)	4.9 (6)
P1R3C(6)	−0.1753 (9)	0.0636 (12)	−0.0246 (6)	3.9 (6)
P2R1C(1)	0.0056 (11)	0.1526 (18)	0.2606 (6)	2.7 (5)
P2R1C(2)	0.1077 (14)	0.1539 (9)	0.2383 (7)	3.6 (6)
P2R1C(3)	0.1960 (9)	0.1326 (16)	0.2741 (8)	5.3 (6)
P2R1C(4)	0.1822 (11)	0.1099 (19)	0.3321 (7)	4.9 (6)
P2R1C(5)	0.0800 (14)	0.1085 (10)	0.3544 (5)	5.1 (6)
P2R1C(6)	−0.0083 (9)	0.1299 (16)	0.3186 (7)	4.0 (6)
P2R2C(1)	−0.1771 (13)	0.2707 (9)	0.2583 (6)	3.6 (5)
P2R2C(2)	−0.1136 (9)	0.3444 (11)	0.2756 (6)	3.6 (5)
P2R2C(3)	−0.1598 (13)	0.4200 (9)	0.3014 (6)	4.8 (6)
P2R2C(4)	−0.2694 (14)	0.4219 (10)	0.3099 (7)	5.9 (7)
P2R2C(5)	−0.3329 (9)	0.3483 (14)	0.2925 (7)	8.1 (8)
P2R2C(6)	−0.2867 (12)	0.2727 (11)	0.2667 (7)	6.6 (7)
P2R3C(1)	−0.2006 (16)	0.0793 (12)	0.2145 (7)	3.6 (5)
P2R3C(2)	−0.1779 (10)	0.0029 (14)	0.2486 (6)	4.4 (6)
P2R3C(3)	−0.2478 (17)	−0.0710 (9)	0.2476 (6)	6.5 (7)
P2R3C(4)	−0.3404 (17)	−0.0684 (13)	0.2124 (7)	5.4 (7)
P2R3C(5)	−0.3631 (10)	0.0079 (15)	0.1783 (7)	6.6 (7)
P2R3C(6)	−0.2932 (16)	0.0818 (9)	0.1793 (6)	6.1 (7)
BZC(1)	0.4780 (13)	0.0870 (16)	0.3197 (6)	7.0 (8)
BZC(2)	0.4776 (12)	0.1744 (12)	0.3433 (9)	6.7 (7)
BZC(3)	0.4650 (14)	0.1863 (10)	0.4027 (10)	7.2 (8)
BZC(4)	0.4528 (13)	0.1108 (16)	0.4386 (6)	8.9 (9)
BZC(5)	0.4531 (12)	0.0235 (12)	0.4150 (9)	6.8 (7)
BZC(6)	0.4658 (13)	0.0116 (10)	0.3555 (10)	6.4 (7)
PF1F(1)	0.4340 (28)	0.1668 (25)	0.0808 (13)	a
PF1F(2)	0.5257 (18)	0.2612 (25)	0.1400 (14)	a
PF1F(3)	0.4337 (30)	0.1454 (18)	0.1769 (15)	a
PF1F(4)	0.3775 (28)	0.2886 (22)	0.1888 (12)	a
PF1F(5)	0.2858 (18)	0.1941 (29)	0.1296 (14)	a
PF1F(6)	0.3778 (31)	0.3100 (22)	0.0927 (14)	a
PF2F(1)	0.3905 (25)	0.2211 (26)	0.0645 (9)	a
PF2F(2)	0.5364 (16)	0.2194 (22)	0.1232 (14)	a
PF2F(3)	0.3943 (28)	0.1350 (16)	0.1447 (15)	a
PF2F(4)	0.4368 (24)	0.2574 (28)	0.1984 (9)	a
PF2F(5)	0.2910 (16)	0.2591 (27)	0.1397 (13)	a
PF2F(6)	0.4330 (29)	0.3435 (15)	0.1182 (15)	a

^{a} Individual isotropic thermal parameters not employed.

TABLE III
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Ru	0.167 (4)	0.195 (3)	0.222 (3)
P(1)	0.164 (12)	0.192 (10)	0.231 (9)
P(2)	0.177 (11)	0.202 (11)	0.230 (10)
Cl	0.175 (11)	0.231 (10)	0.316 (9)
N(1)	0.09 (6)	0.20 (4)	0.34 (3)
O(1)	0.16 (4)	0.33 (3)	0.35 (3)
N(2)	0.17 (5)	0.23 (3)	0.34 (3)
O(2)	0.14 (4)	0.35 (3)	0.40 (3)
P(3)	0.267 (12)	0.287 (12)	0.353 (11)

tetragonal pyramid containing two nitrosyl groups in quite different modes of coordination. The nitrosyl group in the basal plane is bonded to the ruthenium atom in an essentially linear manner (Ru–N(2)–O(2) = 178 (2)°) as formally NO$^+$. The second nitrosyl group is bonded in the apical position of the tetragonal complex with a Ru–N(1)–O(1) angle of 138 (2)°, and hence it may be viewed as NO$^-$. The linear mode

of nitrosyl coordination in Ru(II) complexes has been characterized previously in $[Ru(OH)(NO_2)_4(NO)]^{2-}$ [19] and $Ru(S_2CN(C_2H_5)_2)_3(NO)$ [20] which have Ru–N distances of 1.75 and 1.72 Å and N–O distances of 1.13 and 1.17 Å, respectively. These values compare well with the corresponding distances of 1.74 (2) and 1.16 (2) Å found for the basal nitrosyl group in the present structure. The bent mode of coordination for nitrosyl groups has not been observed before in ruthenium complexes but it has been well characterized in other complexes,[2–8] particularly by Ibers and coworkers. Table V contains a summary of compounds which have been found to have bent nitrosyl groups. The M–N–O bond angles in these systems approach 120° and the M–N distances are considerably longer than has been found in complexes having NO$^+$ coordination. In the present case, this is also observed with the apical Ru–N distance of 1.85 (2) Å being significantly longer than the corresponding basal distance. When corrected for riding, these distances increase *insignificantly* to 1.87 (2) and 1.77 (2) Å, respectively. The apical distance in the present study is relatively short, however, when compared with the M–N bond lengths in other structures of bent nitrosyl complexes (*cf.* Table V) and the Ru–N(1)–O(1) angle of 138° is quite large. These values suggest that a significant interaction between a filled metal d_π orbital and the remaining π^* function of the apical nitrosyl still exists in [RuCl(NO)$_2$(P(C$_6$H$_5$)$_3$)$_2$]$^+$. It seems probable that in these bent nitrosyl complexes, Ru(II) is capable of functioning as a better π donor than Ir(III) or Co(III), at least on the basis of charge considerations. We note that in contrast with the recent structures of IrCl$_2$(NO)(P(C$_6$H$_5$)$_3$)$_2$ and IrI(CH$_3$)(NO)(P(C$_6$H$_5$)$_3$)$_2$ by Mingos, Robinson, and Ibers,[6,7] where an initial Ir–N–O bond angle of approximately 138° and a short N–O bond distance indicated the presence of disorder, there is no disorder of the apical nitrosyl group in the present study, nor is any crystallographic symmetry imposed on the molecule. The apical N–O bond length of 1.17 (2) Å in the present study agrees well with the corresponding values found in the closely analogous complexes [IrX(NO)(CO)(P(C$_6$H$_5$)$_3$)$_2$]$^+$ (X = Cl, I)[3,4] and is not anomalously short as observed initially in the disordered structures.[6,7]

Although a lengthening of the N–O bond distance might be expected in going from the NO$^+$ linear mode of coordination to the NO$^-$ bent mode, no significant difference between the two N–O bond lengths exists in our study. Weaver and Snyder[5] have noted that, at present, no real correlation can be drawn between the mode of nitrosyl coordination and N–O bond length because of difficulties in accurately determining the N–O bond length by X-ray methods and the possible insensitivity of bond length to bond order change in these systems.

An additional feature of the bent nitrosyl coordination is that the oxygen atom of the bent nitrosyl group is oriented toward the basal NO function. We have suggested previously[11] that a direct, although weak, interaction between one of the π^* orbitals of the basal nitrosyl and one of the oxygen lone pairs of the apical

(19) S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, **27**, 307 (1965).

(20) A. Dominicano, A. Vaciago, L. Zambonelli, R. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).

TABLE IV
PRINCIPAL INTRAMOLECULAR DISTANCES AND ANGLES FOR $RuCl(NO)_2(P(C_6H_5)_3)_2^+$

Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Angle, deg
Ru–P(1)	2.431 (6)[a]	P(2)···N(2)	3.006 (21)	Ru–N(1)–O(1)	138 (2)
Ru–P(2)	2.419 (6)	Cl···N(1)	3.296 (23)	Ru–N(2)–O(2)	178 (2)
Ru–Cl	2.362 (6)	N(1)···N(2)	2.795 (26)	P(1)–Ru–P(2)	159.6 (2)
Ru–N(1)	1.853 (19)	N(1)···O(2)	3.759 (28)	P(1)–Ru–Cl	83.7 (2)
Ru–N(2)	1.743 (20)	O(1)···N(2)	3.215 (27)	P(1)–Ru–N(1)	101.7 (5)
N(1)–O(1)	1.166 (20)	O(1)···O(2)	3.915 (28)	P(1)–Ru–N(2)	92.8 (7)
N(2)–O(2)	1.158 (19)	P(1)–P1R1C(1)	1.81 (2)	P(2)–Ru–Cl	84.7 (2)
P(1)···Cl	3.199 (8)	P(1)–P1R2C(1)	1.82 (2)	P(2)–Ru–N(1)	97.0 (5)
P(1)···N(1)	3.343 (19)	P(1)–P1R3C(1)	1.82 (2)	P(2)–Ru–N(2)	91.0 (7)
P(1)···N(2)	3.059 (21)	P(2)–P2R1C(1)	1.82 (2)	Cl–Ru–N(1)	102.2 (7)
P(2)···Cl	3.220 (9)	P(2)–P2R2C(1)	1.81 (2)	Cl–Ru–N(2)	155.8 (7)
P(2)···N(1)	3.222 (19)	P(2)–P2R3C(1)	1.83 (2)	N(1)–Ru–N(2)	102 (1)

[a] Estimated standard deviations have been calculated with the inclusion of cell constant errors.

TABLE V
TETRAGONAL COMPLEXES WITH BENT AXIAL
NITROSYL GROUPS (L = $P(C_6H_5)_3$)

	M–N–O, deg	M–N, Å	$\nu(NO)$, cm^{-1}
$RuCl(NO)_2L_2^+$	138 (2)[a]	1.85 (2)	1687
$Os(OH)(NO)_2L_2^+$	128 (2)[b]	1.98 (5)	1632
$IrCl(NO)(CO)L_2^+$	124 (1)[c]	1.97 (1)	1680
$IrI(NO)(CO)L_2^+$	125 (3)[d]	1.89 (3)	1720
$IrCl_2(NO)L_2$	123 (2)[e]	1.94 (2)	1560
$Ir(CH_3)I(NO)L_2$	120 (2)[f]	1.91 (2)	1525
$CoCl(NO)(en)_2^+$	121 (2)[g]	1.82 (1)	1611
$Co(NO)(NH_3)_5^{2+}$	119 (1)[h]	1.87 (1)	1610

[a] This work. [b] J. M. Waters and K. R. Whittle, *J. Chem. Soc. D*, 518 (1971). [c] Reference 3. [d] Reference 4. [e] Reference 6. [f] Reference 7. [g] Reference 7. [h] Reference 5.

TABLE VI
SELECTED INTRAMOLECULAR DISTANCES AND ANGLES
IN Ru(II)–PHOSPHINE COMPLEXES (L = $P(C_6H_5)_3$)

	Distances, Å		Angles, deg	
	Ru–P[a,b]	Ru–Cl[b]	P–Ru–P[a,b]	Cl–Ru–X[b]
$RuCl(NO)_2L_2^+$[c]	2.420, 2.431	2.362	159.6	155.8 (X = N)
$RuCl_2L_3$[d]	2.374, 2.412	2.387, 2.388	156.4	157.2 (X = Cl)
$RuHClL_3$[e]	2.361, 2.329	2.421	153.1	
$RuH(CH_3CO_2)L_3$[f]	2.354, 2.363		154.9	

[a] Ru–P bond distances are given only for bonds in which the trans ligand is another phosphine. The P–Ru–P bond angles given are only the trans angles. [b] Estimated standard deviations are approximately 0.006 Å for all distances quoted and less than 0.7° for all bond angles. [c] This work. [d] Reference 22. [e] Reference 23. [f] A. C. Skapski and F. A. Stephens, *J. Chem. Soc. D*, 1008 (1969).

ligand is possible. A similar orientation of the apical nitrosyl toward the basal carbonyl is also found in each of the $[IrX(NO)(CO)(P(C_6H_5)_3)_2]^+$ (X = Cl, I) systems,[3,4] possibly implying a similar interaction with one of the carbonyl π^* functions. It is interesting to note that in the complexes $IrCl_2(NO)(P(C_6H_5)_3)_2$ and $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$,[6,7] the orientation of the bent nitrosyl is toward one of the basal phosphines. Since the vacant phosphorus 3d orbitals are available as π-acceptor functions and since the other basal ligands in these two complexes are not π acceptors, we conclude that a weak donor–acceptor interaction does indeed exist in these systems between a filled lone pair of the apical nitrosyl oxygen and a π-acceptor function such as $\pi^*(NO)$, $\pi^*(CO)$, or a phosphorus 3d orbital in the basal plane of the tetragonal pyramid. Very recently, the structure of an analogous dinitrosylosmium complex, $Os(OH)(NO)_2(P(C_6H_5)_3)_2^+$, has been reported by Waters and Whittle,[21] and the stereochemistry is very similar to that we observe in the present case.

The best least-squares plane through the four atoms coordinated in the basal positions has the equation $10.27x + 8.09y + 2.80z = 0.89$ (in monoclinic coordinates). The distances of the P(1), P(2), Cl, and N(2) atoms from this plane are 0.004, 0.003, −0.004, and −0.048 Å, respectively, with estimated standard deviations of 0.01 Å for each. The ruthenium atom lies 0.39 Å above this plane toward the apical nitrosyl. The greatest deviation of the trans ligand angles from 180° occurs for the Cl–Ru–N(2) angle which has a value of 155.8 (2)°. In Table VI, information regarding metal–chlorine and metal–phosphorus bond parameters in a series of related Ru(II) complexes is presented. The Ru–Cl distance of 2.362 (6) Å in [RuCl-

(21) J. M. Waters and K. R. Whittle, *J. Chem. Soc. D*, 518 (1971).

$(NO)_2(P(C_6H_5)_3)_2]^+$ is slightly shorter than the average Ru–Cl distance of 2.387 (7) Å found in $RuCl_2(P(C_6H_5)_3)_3$[22] and significantly shorter than the 2.421 (5) Å value found in the distorted complex $RuHCl(P(C_6H_5)_3)_3$.[23] In $RuCl_2(P(C_6H_5)_3)_3$,[22] the trans Cl–Ru–Cl angle is 157.2 (2)° which compares favorably with the Cl–Ru–N(2) angle in the present structure.

The trans P(1)–Ru–P(2) angle of 159.6 (2)° found in $[RuCl(NO)_2(P(C_6H_5)_3)_2]^+$ is also significantly less than 180°. Moreover, this angle is less than the trans phosphine angles found in the iridium nitrosyl structures (*cf.* Table VII of ref 6). However, the trans phosphine angles found in the other Ru(II) systems of Table VI range from 153.1 to 156.4° and are in close agreement with the present structure. The large deviation of this angle from linearity for the tris phosphine structures of Table VI has been rationalized as the result of steric interactions between cis phosphine groups, but such steric interactions are absent in the present case. Finally, the Ru–P distances in [RuCl-$(NO)_2(P(C_6H_5)_3)_2]^+$ are longer than the basal phosphine–metal distances in the other Ru(II) complexes of Table VI. This lengthening may result from the presence of the strongly π-accepting nitrosyl ligand in the basal plane of this structure as suggested by Mingos and Ibers.[6]

The geometry of the benzene molecule has been idealized by use of the group refinement to have D_{6h} symmetry with a C–C distance of 1.392 Å and a C–H distance of 1.08 Å. The PF_6^- molecule has been assumed to have O_h symmetry with an approximate P–F distance of 1.58 Å. The use of the group refinement procedure to treat disorder in the PF_6^- anion has

(22) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).
(23) A. C. Skapski and P. G. H. Groughton, *Chem. Commun.*, 1230 (1968).

been done previously.[24] As noted above, attempts to refine the fluorine atoms independently proved unsuccessful. We interpret the large group temperature factors for the two half fluorine groups as suggestive of considerable anisotropic thermal motion. The two centers of mass for the F_6 fluorine groups have refined independently to positions close to the central phosphorus atom of the PF_6^- anion.

All intermolecular contacts in the structure appear normal with the only intermolecular contact (exluding hydrogens) less than 3.0 Å being between PF2F(6) and BZC(6) at a value of 2.83 Å.

Discussion

The structure of $[\text{RuCl(NO)}_2(\text{P(C}_6\text{H}_5)_3)_2]^+$ provides a striking illustration of the two different modes of nitrosyl coordination within the same molecule. Conceptually, we can visualize the complex as being formed by the oxidative addition of NO^+ to the d^8 ruthenium(0) complex $\text{RuCl(NO)(P(C}_6\text{H}_5)_3)_2$. In this view, the axial nitrosyl group functions as a Lewis acid in the addition process thus producing a five-coordinate, coordinatively unsaturated complex of Ru(II). The structure of $[\text{RuCl(NO)}_2(\text{P(C}_6\text{H}_5)_3)_2]^+$ thus contrasts with the structures of two other five-coordinate ruthenium nitrosyl complexes in which the coordination geometries are trigonal bipyramids and the nitrosyl groups are coordinated in the linear manner.[25] In $\text{RuH(NO)(P(C}_6\text{H}_5)_3)_3$, the linear nitrosyl occupies an axial position while in $[\text{Ru(NO)(diphos)}_2]^+$, it occupies an equatorial site.

An examination of Table V reveals that all bent nitrosyl complexes have either a tetragonal pyramidal or a tetragonally distorted octahedral coordination geometry. Recently, we have discussed the bonding (and bending) of nitrosyls in tetragonal-pyramidal complexes and have suggested that a significant re-ordering of the energy levels occurs upon the formation of a bent nitrosyl.[26] These principal changes in level orderings are shown in Figure 3 which correlates the primary levels of interest for a linear nitrosyl complex of C_{4v} symmetry with the energy levels for a bent nitrosyl complex of C_s symmetry. It is shown, first, that the low-energy doubly degenerate $\pi^b(\text{NO})$ set in C_{4v} symmetry splits as the M–N–O angle deviates from 180° giving a nondegenerate $\pi^b(\text{NO})$ level of decreased stability and an essentially nonbonding orbital of a' symmetry localized on the nitrosyl oxygen. Second, the π-bonding e level delocalized over the metal d_{xz}, d_{yz} orbitals and the $\pi^*(\text{NO})$ functions splits in reduced symmetry correlating with the metal $d_{yz}(a'')$ level and a nonbonding orbital of a' symmetry localized on the bent nitrosyl nitrogen atom. This latter correlation is of particular importance since it is the change in orbital character from a primarily metal-based π function (or at least one that is traditionally assigned to the metal) to one localized on the nitrosyl group which explains the oxidative addition process in the coordination of NO^+ to nucleophilic d^8 complexes. A third correlation is that of the d_{z^2} level in C_{4v} symmetry, which is σ^* with respect to the metal–nitrosyl bond,

(24) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(25) C. G. Pierpont, A. Pucci, and R. Eisenberg, *ibid.*, **93**, 3050 (1971); C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1094 (1972).

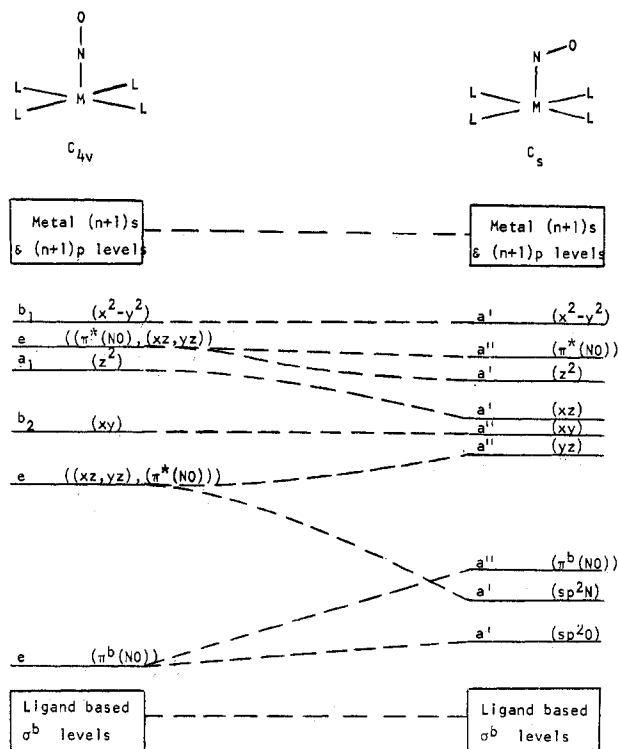(26) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971).

Figure 3.—An orbital correlation diagram which shows the principal levels of interest in the bending of nitrosyls in five-coordinate tetragonal systems.

correlating with the largely nonbonding $d_{zz}(a')$ level in C_s symmetry. Last, the higher energy π^* e level splits and correlates with a single $\pi^*(\text{NO})$ level and a metal a' level denoted as d_{z^2}. For the purposes of this diagram, the five-coordinate complexes of Table V may be viewed as 22-electron systems originating with eight electrons in the σ^b functions of the tetragonal plane, six electrons from the coordinating NO^+ (*i.e.*, $\ldots(\pi^b)^4(\sigma^b)^2$), and eight electrons in the metal d functions. Placement for these electrons into the orderings given in Figure 3 shows that the C_{4v} configuration of $\ldots(xz, yz)^4(xy)^2(z^2)^2$ is unstable relative to the bent nitrosyl configuration of $\ldots(yz)^2(xy)^2(xz)^2$ in C_s symmetry where the metal has undergone a formal two-electron oxidation. The more antibonding levels of higher energy are thus left vacant.

Recently, Collman, *et al.*,[27] have demonstrated that
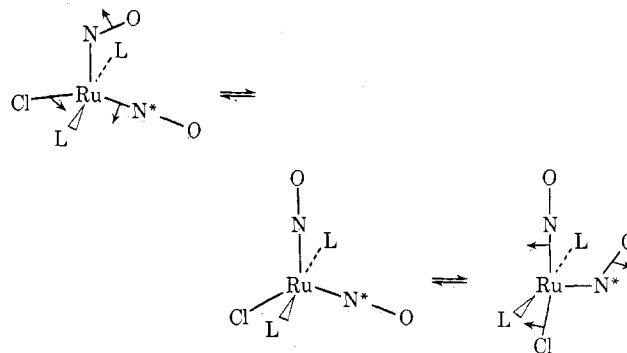
the complex $[\text{RuCl(NO)}_2(\text{P(C}_6\text{H}_5)_3)_2]^+$ undergoes intramolecular rearrangements in solution whereby the apical and basal nitrosyl groups are interchanged.

(27) J. P. Collman, P. Farnham, and G. Dolcetti, *ibid.*, **93**, 1788 (1971).

This was accomplished by preparing the isotopically labeled complex [RuCl(^{14}NO)(^{15}NO)(P(C$_6$H$_5$)$_3$)$_2$]$^+$ 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.

The Crystal and Molecular Structure of the Catalytically Active Complex Hydridonitrosyltris(triphenylphosphine)ruthenium, RuH(NO)(P(C$_6$H$_5$)$_3$)$_3$

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The crystal and molecular structure of the catalytically active complex RuH(NO)(P(C$_6$H$_5$)$_3$)$_3$ 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 ($\rho_{exptl} = 1.34$ (1) g/cm^3; $\rho_{calcd} = 1.337$ 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$_6$H$_5$)$_3$)$_2$]$^+$ 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$_6$H$_5$)$_3$)$_3$ and found it to be a catalytically active system, especially in the isomerization

(1) National Institutes of Health Predoctoral Fellow, 1969–1971.
(2) For a review of nitrosyl complexes through 1965, see B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).
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