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Crystal and Molecular Structure of Trichloronitrosylbis(methyldiphenylphosphine)ruthenium(II), $RuCl_3(NO)(PMePh_2)_2$

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Received June 25, 1973

The crystal and molecular structure of trichloronitrosylbis(methyldiphenylphosphine)ruthenium(II), $RuCl_3(NO)(PMePh_2)_2$, has been determined from three-dimensional X-ray data collected by counter methods using the θ–2θ scan technique. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 12.308$ (4), $b = 16.579$ (6), $c = 14.700$ (4) Å, $\beta = 114.82$ (2)°, and $V = 2728$ Å^3. An experimental density of 1.56 (2) g/cm^3 agrees with a calculated value of 1.55 g/cm^3 for $Z = 4$. The structure was solved by standard heavy-atom methods and has been refined by least squares to a conventional R factor of 0.044. The coordination geometry about the Ru atom is essentially octahedral with the phosphine ligands in trans positions. The nitrosyl is linearly coordinated with an Ru–N distance of 1.744 (6) Å and an Ru–N–O bond angle of 176.4 (6)°. These parameters agree with those reported for other ruthenium(II) nitrosyl complexes and confirm the notion that complexes of the type $RuCl_3(NO)L_2$ where L = tertiary phosphine are best described as NO^+ complexes of Ru(II). The Ru–Cl distance trans to the nitrosyl is shorter than the other Ru–Cl distances in the structure (2.357 (2) Å *vs.* 2.398 (7) Å) and the N–Ru–P bond angles average 94.1 (6)°, thus giving further structural evidence of the strong metal–nitrosyl π interaction in this system. The bonding in $RuCl_3(NO)(PMePh_2)_2$ is compared with that of the isoelectronic complex $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ whose structure has recently been determined.

Introduction

Ruthenium forms more nitrosyl complexes than any other element, and of these complexes the ruthenium nitrosyl phosphines form a most interesting subset.[2] The first members of this class of complexes were reported in 1966 by Fairy and Irving[3] and by Chatt and Shaw[4] and have the general formula $RuCl_3(NO)L_2$ where L is a tertiary phosphine, arsine, or stibine. These complexes exhibit nitrosyl stretching frequencies in the range 1829–1899 cm^{-1} and are viewed formally as NO^+ complexes of Ru(II). A linear mode of nitrosyl coordination is thus assumed for these systems and resonance structures I and II are used to explain the metal–nitrosyl bonding.

$$\ddot{M}\leftarrow N\equiv\overset{+}{O}: \longleftrightarrow M=\overset{+}{N}=\ddot{O}$$
$$\text{I} \qquad\qquad \text{II}$$

During the last few years interest in nitrosyl complexes has been stimulated by the knowledge that NO can coordinate to transition-metal ions in either a linear or a bent manner[5-24] and that certain nitrosyl complexes have been found to be catalytically active.[25-28] In our laboratory we have been investigating the structures of ruthenium nitrosyl phosphines, and in particular low valent systems which contain metal–nitrosyl units formally assigned as Ru^0–NO^+ [19,23] and Ru^{II}–NO^-.[18] In order to compare the structural parameters obtained in these studies with those of one of the parent Ru^{II}–

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NO^+ systems, we have undertaken the structure determination of the complex $RuCl_3(NO)(PMePh_2)_2$.[4]

An additional motivating reason for investigating the structure of $RuCl_3(NO)(PMePh_2)_2$ is that we have recently determined the structure of the corresponding arylazo complex $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$.[29] This structure shows an essentially linear Ru–N–N grouping with an Ru–N–N bond angle of 171.2 (9)° and an Ru–N distance of 1.796 (9) Å. These observed structural parameters are interpreted in terms of a synergic bonding interaction between the metal and arylazo group as embodied in resonance structures III and IV. Since the N–N–C bond angle in $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ is only 135.9 (11)°, structure IV and the π back bonding it portrays are clearly dominant in describing the metal–arylazo bonding. Since ArN_2^+ and NO^+ are formally isoelectronic ligands, their bonding may be viewed as analogous. The structure of a corresponding nitrosyl complex thus seemed desirable. In this paper we present the complete structure determination of $RuCl_3(NO)(PMePh_2)_2$ which is such a complex.

III IV

Experimental Section

Preparation of $RuCl_3(NO)(PMePh_2)_2$. The complex was prepared according to a modification of the previously published procedure.[4] $Ru(NO)Cl_3 \cdot 2H_2O$ (3.25 g), which had been prepared by bubbling NO through an aqueous solution of $RuCl_3 \cdot xH_2O$ (Matthey Bishop), was dissolved in 50 ml of ethanol and 20 ml of 2,2-dimethoxypropane. Methyldiphenylphosphine (4.0 ml) (Strem Chemical) was then added to the solution using a syringe and the reaction solution was refluxed for 5 min. The crystalline product separated over a period of several days upon cooling. The product is recrystallized from a methylene chloride–ethanol solution.

Collection and Reduction of the X-Ray Data. From precession and Weissenberg photographs, it was determined that the orange crystals belonged to the monoclinic system. Extinctions for $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, were observed, which uniquely determine the space group as $P2_1/c\text{-}C_{2h}^5$.[30] The unit cell constants at ambient room temperature (23°) were determined from a least-squares refinement[31] of the angular settings of 12 strong reflections centered on a Picker FACS-I diffractometer equipped with a monochromator. Mo Kα radiation (λ 0.7107 Å) was employed. The reflections were centered in the counter aperture using the Picker centering routine which is based on locating the angular settings for the half-heights of the peak profile. Since the 2θ values for the reflections used in the centering procedure were less than 30°, separation of the Mo Kα_1–Kα_2 components of the reflections was not possible *by this method*, and the angular settings obtained were based on the weighted average of the Kα_1–Kα_2 doublet. The cell constants thus obtained were $a = 12.308$ (4), $b = 16.579$ (6), $c = 14.700$ (4) Å, $\beta = 114.82$ (2)°, $V = 2728$ Å^3. An experimental density of 1.56 (2) gm/cm^3 obtained by the flotation method is in good agreement with the calculated density of 1.55 g/cm^3 for four molecules per unit cell.

After many attempts, a crystal of dimensions 0.46 × 0.44 × 0.08 mm was found which did not exhibit any evidence of twinning. An average mosaic spread of 0.08° was measured from narrow source–open counter ω scans[32] of several strong reflections with the crystal mounted along the b^* direction. Data were collected with the θ–2θ scan technique using a symmetric scan range of 1.50° plus the Mo Kα_1–Mo Kα_2 separation at a scan rate of 1°/min and with background counts of 10 sec at each end of the scan. A take-off angle of 2.5° was employed in the data collection as was pulse height analysis designed to accept 90% of the Mo Kα radiation. Three reflections in different regions of reciprocal space were measured at intervals of every 100 reflections and were found to deviate less than 3% from their mean values. Attenuation was necessary for 22 reflections when the count rate exceeded approximately 9000 counts/sec during the scan. A total of 5232 reflections having $5° \leq 2\theta \leq 50°$ were thus measured. The data were then processed in the usual way for Lorentz and polarization effects and reduced to a set of structure factor amplitudes F_o. Of those measured, 3120 independent reflections were observed to have $F_o^2 > 2\sigma(F_o^2)$. The standard deviations $\sigma(F_o^2)$ were estimated from counting statistics according to the formula

$$\sigma(F_o^2) = (\mathrm{Lp})^{-1}[C + 0.825 + 0.25(t_c/t_b)^2(B_1 + B_2 + 1.65) + q^2(C^2 + (B_1 + B_2)^2)]^{1/2}$$

where Lp is the Lorentz-polarization factor, C is the *estimated* total count obtained in time t_c, B_1 and B_2 are the *estimated* background counts each obtained in time t_b, and q is the uncertainty parameter[33] with a value of 0.03 for this structure. Because the Picker instrument truncates the least significant figure from the scaler without proper round-off, the estimated total count C is the recorded total count $C' + 0.45$, and the estimated background count B_i is the recorded background count $B_i' + 0.45$ where $i = 1$ or 2. The constants 0.825 and 1.65 appear in the equation for $\sigma(F_o^2)$ as estimates of the errors associated with the 0.45 term which is added to each raw count in calculating F_o^2 as a means of eliminating the systematic error resulting from the truncation. It should be noted that the 0.45 term is not a constant but only a best estimate of the truncated number. The linear absorption coefficient μ equals 4.72 cm^{-1} and the data were not corrected for absorption.

Solution and Refinement of the Structure. The position of the ruthenium atoms was determined from a three-dimensional Patterson function map. A least-squares refinement of the ruthenium positional and isotropic thermal parameters reduced the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ to 0.417 and 0.522, respectively. In the least-squares procedure, 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 positions of all nonhydrogen atoms in the structure were determined from a succession of difference Fourier maps and least-squares refinements. Throughout all refinements, the phenyl rings were treated as rigid groups of D_{6h} symmetry (d(C–C) = 1.392 Å, d(C–H) = 0.95 Å) in the manner described previously.[34] Atomic scattering factors for all nonhydrogen atoms were those reported by Cromer and Waber,[35] while the hydrogen scattering factor was taken from Stewart, *et al.*[36] Anomalous dispersion effects for the Ru, Cl, and P atoms were included using the $\Delta f'$ and $\Delta f''$ values reported by Cromer.[37]

In the final refinements, anisotropic thermal parameters were used for all the nongroup atoms except the methyl carbons. No attempt was made to locate or refine the methyl hydrogen atoms. On the final cycle of least-squares refinement, the discrepancy factors converged to values of 0.044 and 0.051 for R_1 and R_2, respectively. The estimated standard deviation of an observation of unit weight was 1.36 electrons and the highest peak on the final difference Fourier map was approximately 30% of the height of a ring carbon atom in this structure.

The parameters obtained from this final cycle of refinement are taken as the final parameters for the structure and are presented in Table I along with their estimated standard deviations as obtained from the inverse matrix. The derived positional and isotropic thermal parameters for the group carbon atoms are tabulated in Table II. In Table III, the root-mean-square amplitudes of thermal motion for the anisotropically refined atoms are presented. A table of the final values of F_o and $|F_c|$ for the 3120 reflections included in the refinement is available.[38]

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Table I

Final Positional and Thermal Parameters for $RuCl_3(NO)(PMePh_2)_2$

Atom	x^a	y^a	z^a	B^b
Ru	0.17926 (5)[c]	0.09289 (3)	0.24752 (4)	*d*
Cl(1)	0.2670 (2)	0.2222 (1)	0.2760 (1)	*d*
Cl(2)	0.2786 (2)	0.0694 (1)	0.4252 (1)	*d*
Cl(3)	0.0731 (2)	0.1177 (1)	0.0718 (1)	*d*
P(1)	0.0134 (2)	0.1515 (1)	0.2748 (1)	*d*
P(2)	0.3602 (2)	0.0529 (1)	0.2314 (1)	*d*
N	0.1194 (5)	−0.0043 (4)	0.2252 (4)	*d*
O	0.0794 (5)	−0.0668 (3)	0.2055 (4)	*d*
P1Me	0.0604 (7)	0.2046 (5)	0.3960 (5)	4.2 (2)
P2Me	0.4947 (6)	0.0700 (4)	0.3468 (5)	3.9 (2)

Anisotropic Thermal Parameters[e]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	61 (1)	23 (0)	36 (0)	−3 (0)	22 (0)	−2 (0)
Cl(1)	88 (2)	27 (1)	48 (1)	−12 (1)	28 (1)	−6 (1)
Cl(2)	106 (2)	37 (1)	40 (1)	0 (1)	27 (1)	5 (1)
Cl(3)	70 (2)	42 (1)	39 (1)	2 (1)	17 (1)	−1 (1)
P(1)	71 (2)	29 (1)	43 (1)	−4 (1)	30 (1)	−3 (1)
P(2)	56 (2)	31 (1)	38 (1)	1 (1)	17 (1)	3 (1)
N	78 (6)	30 (3)	48 (4)	−7 (3)	31 (4)	−5 (3)
O	124 (7)	28 (3)	90 (5)	−20 (3)	57 (5)	−11 (3)

Group Parameters

Group	x_c[f]	y_c	z_c	ϕ	θ	ρ	B, Å^2
P1R(1)	−0.1499 (3)	0.2906 (2)	0.1284 (2)	2.002 (3)	−2.664 (3)	2.720 (3)	0.0[g]
P1R(2)	−0.1617 (3)	0.0066 (2)	0.2695 (3)	2.487 (3)	−2.904 (3)	1.611 (3)	0.0
P2R(1)	0.3486 (3)	−0.1355 (2)	0.1773 (2)	−1.795 (3)	−2.594 (3)	2.866 (3)	0.0
P2R(2)	0.4337 (3)	0.1362 (2)	0.0665 (2)	0.756 (3)	−3.013 (3)	2.093 (3)	0.0

[a] *x*, *y*, and *z* are in fractional coordinates. [b] Isotropic thermal parameters in Å^2. [c] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure. [d] Atoms refined anisotropically. [e] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The anisotropic thermal parameters given are $\times 10^4$. [f] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers. The angles ϕ, θ, and ρ have been previously defined. See ref 34. [g] Group thermal parameters were not refined. See Table II for thermal parameters of the group atoms.

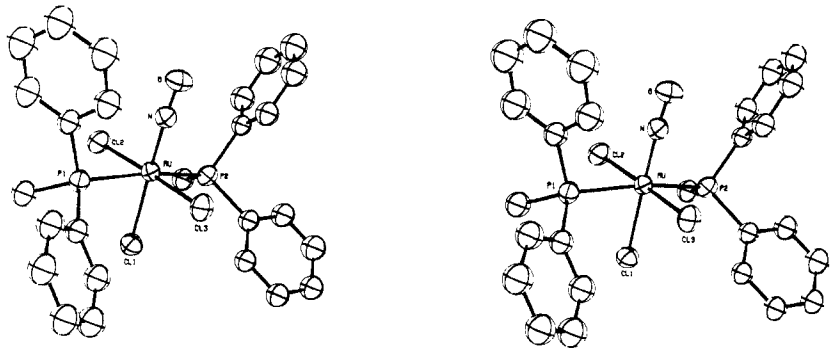

Figure 1. A stereoscopic view of the complex $RuCl_3(NO)(PMePh_2)_2$.

Description of the Structure and Discussion

The crystal structure described by the unit cell constants, the symmetry of the space group, and the parameters of Table I consist of the packing of discrete molecules of $RuCl_3(NO)(PMePh_2)_2$. The closest intermolecular contacts excluding hydrogens are between Cl(1)···P2R2C(5), O···P1R1C(3), and O···P1R1C(4) at distances of 3.425, 3.209, and 3.292 Å, respectively. Since all intermolecular contacts in the structure are normal, they are not tabulated.

The coordination geometry about the Ru atom is essentially octahedral with trans phosphine ligands. Figure 1 is a perspective drawing of a molecule of the complex while Figure 2 presents a view of the inner coordination geometry in which the phosphine substituents have been omitted for clarity. All important intramolecular distances and angles are tabulated in Table IV, and selected least-squares planes with deviations of the atoms from these planes are given in Table V. The deviations from the octahedral geometry in $RuCl_3(NO)(PMePh_2)_2$ are relatively small but significant. Of the three trans angles, P(1)-Ru-P(2) shows the greatest deivation from the ideal value of 180° at a value of 171.46 (6)°. The cis angles about Ru range in value from 83.98 (7) to 94.7 (2)°. One explanation of the observed deviations from the ideal octahedral angles is presented below.

The coordination of the nitrosyl ligand is essentially linear as expected. The Ru-N distance is 1.744 (6) Å and the Ru-N-O bond angle is 176.4 (6)°. The Ru-N distance is in agreement with the corresponding values found in a number of Ru^{II}-NO^+ complexes such as 1.738 (2) Å in $[Ru(NO)Cl_5]^{2-}$,[20] 1.74 (2) Å in $[RuCl(NO)_2(PPh_3)_2]^+$,[18] 1.72 Å in $Ru(NO)(S_2CN(C_2H_5)_2)_3$,[7] and 1.75 Å in $[Ru(OH)(NO_2)_4(NO)]^{2-}$.[6] It also agrees with the Ru-N distances of linearly coordinated nitrosyl groups in low valent ruthenium nitrosyl complexes such as 1.74 (1) Å in $[Ru(NO)(diphos)_2]^+$,[23] 1.70 (1) Å in $[Ru(\mu\text{-}PPh_2)(NO)(PMePh_2)]_2$,[22] and 1.79 (1) Å in $RuH(NO)(PPh_3)_3$.[19] This value is significantly shorter, however, than the Ru-N distance of 1.85 (2) Å for the bent

Table II. Derived Positional and Isotropic Thermal Parameters for Group Atoms

Group atom	x	y	z	B, Å^2
P1R1C(1)	−0.0811 (4)	0.2276 (3)	0.1870 (4)	3.3 (1)[a]
P1R1C(2)	−0.0285 (3)	0.2861 (3)	0.1506 (4)	4.3 (2)
P1R1C(3)	−0.0973 (5)	0.3491 (2)	0.0921 (4)	4.8 (2)
P1R1C(4)	−0.2188 (5)	0.3536 (3)	0.0698 (4)	4.8 (2)
P1R1C(5)	−0.2714 (3)	0.2951 (3)	0.1062 (4)	4.9 (2)
P1R1C(6)	−0.2026 (4)	0.2321 (2)	0.1648 (4)	4.3 (2)
P1R1H(2)	0.0544 (3)	0.2828 (5)	0.1660 (5)	6.0
P1R1H(3)	−0.0618 (7)	0.3891 (3)	0.0671 (6)	6.0
P1R1H(4)	−0.2657 (6)	0.3966 (4)	0.0299 (6)	6.0
P1R1H(5)	−0.3543 (3)	0.2984 (5)	0.0909 (5)	6.0
P1R1H(6)	−0.2381 (6)	0.1920 (3)	0.1898 (5)	6.0
P1R2C(1)	−0.0879 (4)	0.0713 (3)	0.2731 (4)	3.4 (1)
P1R2C(2)	−0.1059 (5)	0.0507 (3)	0.3575 (3)	5.4 (2)
P1R2C(3)	−0.1796 (5)	−0.0140 (3)	0.3539 (3)	6.3 (2)
P1R2C(4)	−0.2354 (4)	−0.0582 (3)	0.2659 (4)	6.1 (2)
P1R2C(5)	−0.2174 (5)	−0.0376 (3)	0.1815 (3)	5.8 (2)
P1R2C(6)	−0.1437 (4)	0.0271 (3)	0.1850 (3)	4.7 (2)
P1R2H(2)	−0.0677 (7)	0.0810 (5)	0.4174 (4)	6.0
P1R2H(3)	−0.1921 (7)	−0.0282 (5)	0.4114 (4)	6.0
P1R2H(4)	−0.2857 (6)	−0.1024 (4)	0.2635 (6)	6.0
P1R2H(5)	−0.2557 (7)	−0.0679 (4)	0.1215 (4)	6.0
P1R2H(6)	−0.1312 (6)	0.0414 (4)	0.1276 (4)	6.0
P2R1C(1)	0.3580 (5)	−0.0541 (2)	0.2026 (3)	2.9 (1)
P2R1C(2)	0.2635 (4)	−0.0810 (3)	0.1157 (3)	3.8 (2)
P2R1C(3)	0.2541 (4)	−0.1624 (3)	0.0904 (3)	4.7 (2)
P2R1C(4)	0.3391 (6)	−0.2169 (2)	0.1520 (4)	5.4 (2)
P2R1C(5)	0.4336 (4)	−0.1900 (3)	0.2389 (4)	5.6 (2)
P2R1C(6)	0.4431 (4)	−0.1086 (3)	0.2642 (3)	4.7 (2)
P2R1H(2)	0.2057 (6)	−0.0436 (4)	0.0738 (4)	6.0
P2R1H(3)	0.1898 (5)	−0.1811 (4)	0.0311 (4)	6.0
P2R1H(4)	0.3327 (8)	−0.2725 (2)	0.1347 (5)	6.0
P2R1H(5)	0.4915 (6)	−0.2274 (4)	0.2807 (5)	6.0
P2R1H(6)	0.5074 (5)	−0.0899 (4)	0.3234 (3)	6.0
P2R2C(1)	0.3980 (4)	0.1007 (3)	0.1354 (3)	3.3 (1)
P2R2C(2)	0.4893 (4)	0.0660 (2)	0.1162 (3)	4.3 (2)
P2R2C(3)	0.5249 (4)	0.1015 (3)	0.0473 (4)	4.9 (2)
P2R2C(4)	0.4694 (4)	0.1717 (3)	−0.0024 (3)	4.1 (2)
P2R2C(5)	0.3782 (4)	0.2064 (2)	0.0168 (3)	3.8 (2)
P2R2C(6)	0.3425 (3)	0.1709 (3)	0.0857 (3)	3.4 (1)
P2R2H(2)	0.5269 (6)	0.0181 (3)	0.1503 (5)	6.0
P2R2H(3)	0.5872 (5)	0.0781 (4)	0.0340 (5)	6.0
P2R2H(4)	0.4938 (6)	0.1960 (4)	−0.0494 (4)	6.0
P2R2H(5)	0.3405 (6)	0.2543 (3)	−0.0173 (5)	6.0
P2R2H(6)	0.2803 (4)	0.1944 (4)	0.0990 (5)	6.0

[a] The overall group temperature factors are 0.0. Individual hydrogen atom temperature factors were not refined.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Ru	0.173 (3)	0.179 (4)	0.200 (2)
Cl(1)	0.179 (3)	0.211 (3)	0.247 (3)
Cl(2)	0.183 (3)	0.231 (3)	0.263 (3)
Cl(3)	0.186 (3)	0.221 (3)	0.242 (3)
P(1)	0.180 (3)	0.195 (3)	0.220 (3)
P(2)	0.181 (4)	0.195 (4)	0.210 (3)
N	0.192 (11)	0.196 (10)	0.234 (8)
O	0.179 (9)	0.254 (8)	0.305 (7)

nitrosyl group in $[RuCl(NO)_2(PPh_3)_2]^+$,[18] which is formally an Ru^{II}-NO^- bond, and observed Ru-N single bond distances in the range of 2.08-2.12 Å reported for a number of Ru(II) amine complexes. The linearity of the nitrosyl coordination together with the relatively short Ru-N distance found in the present structure confirms the notion of NO^+ coordination as described in terms of a strong π back-bonding interaction embodied in resonance structure II.

Other structural parameters also confirm this view of the nitrosyl coordination. For example, the Ru-Cl distance for Cl(1) which is trans to the nitrosyl is significantly shorter than the other Ru-Cl distances in the structure (2.357 (2) Å *vs.* 2.398 (7) Å). Shortening of the bond between a metal atom and a purely σ donor ligand when the latter is trans to a strong π acceptor has been observed previously in the Ru(II) nitrosyl structures $[Ru(NO)Cl_5]^{2-}$ [20] and $[Ru(OH)(NO_2)_4(NO)]^{2-}$.[6] In $[Ru(NO)Cl_5]^{2-}$ [20] the complex has approximately C_{4v} symmetry with the equatorial Ru-Cl distances averaging 2.376 (2) Å while the axial Ru-Cl distance is significantly shorter at 2.357 (1) Å. In $[Ru(OH)(NO_2)_4(NO)]^{2-}$ [6] the equatorial ligands are different from the axial ligand but covalent radii arguments may be used to show the shortening of the Ru-OH bond which is trans to the nitrosyl.[20]

An additional piece of supporting evidence for the strong π interaction between the Ru and the nitrosyl is found in the P-Ru-N bond angles which average 94.1 (7)°. These are clearly the largest cis angles and they can be rationalized in terms of nonbonded repulsions between electron density in the metal-nitrosyl and metal-phosphine bonds.[39] The range of 91.0 to 94.2° for the *cis*-N-Ru-Cl angles in [Ru(NO)-

Table IV. Principal Intramolecular Distances and Angles for $RuCl_3(NO)(PMePh_2)_2$

Distances, Å		Angles, deg	
Ru-N	1.744 (6)	Ru-N-O	176.4 (6)
N-O	1.132 (6)	Cl(1)-Ru-Cl(2)	88.15 (6)
Ru-Cl(1)	2.357 (2)	Cl(1)-Ru-Cl(3)	92.16 (6)
Ru-Cl(2)	2.405 (2)	Cl(1)-Ru-P(1)	87.76 (7)
Ru-Cl(3)	2.391 (2)	Cl(1)-Ru-P(2)	83.98 (7)
Ru-P(1)	2.441 (2)	Cl(1)-Ru-N	177.5 (2)
Ru-P(2)	2.429 (2)	Cl(2)-Ru-Cl(3)	177.6 (1)
P(1)-P1Me	1.849 (7)	Cl(2)-Ru-P(1)	88.00 (7)
P(1)-P1R1C(1)	1.830 (8)	Cl(2)-Ru-P(2)	89.57 (7)
P(1)-R1R2C(1)	1.816 (5)	Cl(2)-Ru-N	92.1 (2)
P(2)-P2Me	1.827 (7)	Cl(3)-Ru-P(1)	89.63 (6)
P(2)-P2R1C(1)	1.822 (4)	Cl(3)-Ru-P(2)	92.84 (7)
P(2)-P2R2C(1)	1.841 (4)	Cl(3)-Ru-N	87.7 (2)
		P(1)-Ru-P(2)	171.46 (6)
		P(1)-Ru-N	94.7 (2)
		P(2)-Ru-N	93.5 (2)
		P1Me-P(1)-Ru	113.8 (2)
		P2Me-P(2)-Ru	112.2 (2)

Table V. Weighted Least-Squares Planes (in Monoclinic Coordinates) and the Atoms from their Respective Planes[a]

Plane Through Ru, Cl(1), Cl(2), Cl(3), and N $11.35x - 6.04y - 7.44z = -0.38$	
Atom	Distance, Å
Ru	0.007 (1)
Cl(1)	0.008 (2)
Cl(2)	−0.046 (2)
Cl(3)	−0.041 (2)
N	0.081 (6)
Plane Through Ru, Cl(2), Cl(3), P(1), and P(2) $4.32x + 15.37y - 0.43z = 2.12$	
Atom	Distance, Å
Ru	−0.022 (1)
Cl(2)	−0.029 (2)
Cl(3)	−0.024 (2)
P(1)	0.152 (2)
P(2)	0.153 (2)
Plane Through Ru, Cl(1), P(1), P(2), and N $0.67x - 3.27y + 12.73z = 2.97$	
Atom	Distance, Å
Ru	−0.007 (1)
Cl(1)	−0.008 (2)
P(1)	0.039 (2)
P(2)	0.040 (2)
N	−0.014 (6)

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

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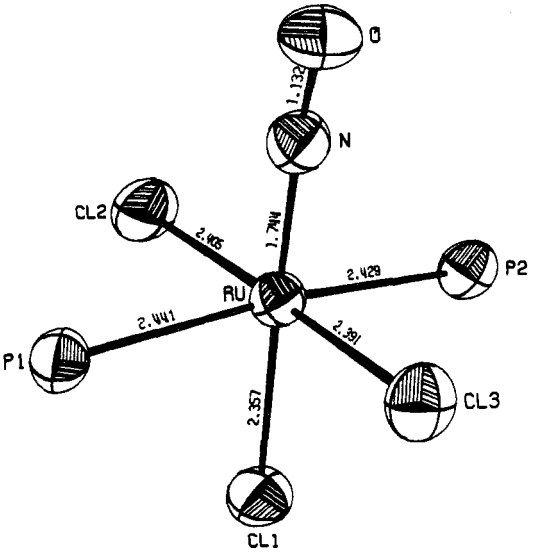

Figure 2. A perspective drawing of the inner coordination geometry of $RuCl_3(NO)(PMePh_2)_2$ with the phosphine substituents omitted for clarity.

$Cl_5]^{2-}$ [20] and an average *cis*-N-Fe-C angle of 96° in $[Fe(CN)_5(NO)]^{2-}$ [5] may also be due to these repulsions. An alternative explanation is based on repulsions between the donor atoms themselves such as that used by Bright and Ibers[40] to account for distortions in rhenium and osmium nitrido and arylimino complexes.[40-44]

The average Ru-P bond length of 2.435 (6) Å is in the upper range of the Ru(II)-phosphine distances reported in the literature in which the trans ligand is another phosphine. These values include 2.420 (6) and 2.431 (6) Å in $RuCl(NO)_2L_2^+$,[18] 2.374 (6) and 2.412 (6) Å in $RuCl_2L_3$,[45] 2.361 (4) and 2.329 (4) Å in $RuHClL_3$,[46] and 2.429 (4) and 2.438 (4) Å in $RuCl_3(p\text{-}N_2C_6H_4Me)L_2$,[29] where L = PPh_3.

Finally a comparison of the ruthenium-nitrosyl bond parameters in the present structure with those of the ruthenium-arylazo bond in the isoelectronic complex $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$[29] seems instructive. These parameters are summarized in Table VI. Both the nitrosyl and arylazo groups coordinate in an essentially linear manner in these complexes. The dominance of resonance structure IV for the arylazo complex has been noted by the N-N-C bond angle of 135.9 (11)°. However, the Ru-N distance in the arylazo complex is significantly longer than in the nitrosyl system, and no significant difference is found between the Ru-Cl distances cis and trans to the arylazo group as is found in the nitrosyl structure. These structural parameters can be interpreted as indicative of the fact that NO^+ is a stronger π acid than ArN_2^+. Differences in these parameters arising from differences in the basicity and steric requirements of the phosphine ligands $PMePh_2$ and PPh_3 can only be assessed once the structures of $RuCl_3(NO)(PPh_3)_2$ and $RuCl_3(p\text{-}N_2C_6H_4Me)(PMePh_2)_2$ are known. However, we believe that the effects of the phosphines on the nitrosyl and arylazo structural parameters will be minimal and that these other structures will also confirm the intuitively obvious notion that NO^+ is a stronger π acid than ArN_2^+.

Table VI. Comparison of $RuCl_3(NO)(PMePh_2)_2$ and $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ Bond Parameters

	$RuCl_3(NO)(PMePh_2)_2$	$RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$[a]
Ru-N-X[b]	176.4 (6)°	171.2 (9)°
Ru-N	1.744 (6) Å	1.796 (9) Å
N-X	1.132 (6) Å	1.144 (10) Å
Ru-P (av)	2.435 (6) Å	2.434 (4) Å
Ru-Cl (trans to N)	2.357 (2) Å	2.385 (3) Å
Ru-Cl (trans to Cl, av)	2.398 (7) Å	2.390 (3) Å
N-Ru-P (av)	94.1 (6)°	90.4 (3)°

[a] Reference 29. [b] X = O or N.

Acknowledgments. We wish to thank the National Science Foundation (Grant GP-35667X) and the Materials Research Program of the National Science Foundation for support of this work.

Registry No. $RuCl_3(NO)(PMePh_2)_2$, 29857-61-2.

Supplementary Material Available. The table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th 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 INORG-74-732.

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