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Crystal and Molecular Structure of Dinitrosylbis(triphenylphosphine)ruthenium-Hemibenzene, $Ru(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$

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The structure of dinitrosylbis(triphenylphosphine)ruthenium-hemibenzene, $Ru(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$ has been determined from three-dimensional X-ray data collected by counter techniques. The material crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with four molecules of the complex and two molecules of solvent (C_6H_6) in the unit cell. Crystal data are $a = 17.031$ (2) Å, $b = 18.792$ (2) Å, $c = 10.800$ (1) Å, $\beta = 97.03$ (1)°, $V = 3430.6$ Å^3, $\rho_{\text{measd}} = 1.43$ (2) g/cm^3, and $\rho_{\text{calcd}} = 1.401$ g/cm^3. The structure has been refined by a full-matrix least-squares procedure to a conventional R index (on F) of 0.043 for 2985 observations having $F_o^2 > 3\sigma(F_o^2)$. The coordination geometry about the ruthenium atom may be described as distorted tetrahedral. Bond distances of interest are Ru-P, 2.337 (2) and 2.353 (2) Å, and Ru-N, 1.762 (6) and 1.776 (6) Å. The N-Ru-N angle, 139.2 (3)°, is significantly different from the tetrahedral value and the Ru-N-O angles are 177.7 (6) and 170.6 (5)°. The structural results support the formulation of $Ru(NO)_2(P(C_6H_5)_3)_2$ as a d^{10} complex of Ru(–II) with the nitrosyl groups coordinated as NO$^+$. A novel nitrosyl-transfer reaction of this complex with $RuCl_2(P(C_6H_5)_3)_3$ to yield the Ru(0) complex $Ru(NO)Cl(P(C_6H_5)_3)_2$ is described and some of its implications are discussed.

Introduction

The four-coordinate dinitrosyl complexes of the group VIII metals and their isoelectronic analogs form an interesting series of pseudo d^{10} complexes. These systems exhibit low *formal* oxidation states of the metal and in theory are capable of undergoing two successive oxidative addition reactions. The molecular structures of a number of these complexes have been determined and the results[2] show that the coordination geometries are basically tetrahedral and that the nitrosyl groups are approximately linear with M-N-O angles in the range 170-180°. The structural data thus provide the basis for the formalistic view of these complexes as d^{10} systems having nitrosyl coordinated as NO$^+$.

The first dinitrosyl complex in this series to be studied structurally, $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$,[3] was found to exhibit large distortions from tetrahedral geometry. The N-Ir-N bond angle was determined to be 154°, and the nitrosyl ligands were found to coordinate in an intermediate manner with an Ir-N-O bond angle of 163.5 (1)°. While these results precluded an unequivocal assignment of the metal oxidation state, the Ir-N distance and the coordination geometry were most consistent with a d^{10} formulation of this complex. The 154° bond angle between the two nitrosyl groups in $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$ is significantly greater than the C-Pt-C angle of 117° in $Pt(CO)_2(P(C_2H_5)(C_6H_5)_2)_2$[4] and the N-Ir-C bond angle of 128.7° in $Ir(NO)(CO)(P(C_6H_5)_3)_2$.[2] The results on these isoelectronic complexes have led to the suggestion[2] that the angle between the two strong π-acceptor ligands is determined in part by the repulsions between the bonding electrons in the metal-π-acceptor bonds, assuming NO$^+$ to be a stronger π acid than CO. In order to test this hypothesis and to determine the effect of varying the metal atom in these systems, a study of the complex $Ru(NO)_2(P(C_6H_5)_3)_2$ was carried out. The results are reported here.

Experimental Section

The complex $Ru(NO)_2(P(C_6H_5)_3)_2$ was first reported by Grundy, *et al.*,[5] who observed that it reacts with O_2 to give $Ru(O_2)(NO_3)(NO)(P(C_6H_5)_3)_2$ and with X_2 (X = halogen) to yield $RuX_3(NO)(P(C_6H_5)_3)_2$. However, unlike its Os analog, it does not react with strong acids to give hydride cations. In our investigations of low-valent ruthenium-nitrosyl systems we have found that $Ru(NO)_2(P(C_6H_5)_3)_2$ is readily formed in a number of reactions and does not undergo oxidative addition reactions with as wide a variety of substrates as does $Os(NO)_2(P(C_6H_5)_3)_2$ and the mononitrosyl systems $M(NO)(P(C_6H_5)_3)_3$ (M = Rh, Ir).[6] However, $Ru(NO)_2(P(C_6H_5)_3)_2$ does undergo a novel nitrosyl-transfer reaction with $RuCl_2(P(C_6H_5)_3)_3$ to yield the Ru(0) complex $Ru(NO)Cl(P(C_6H_5)_3)_2$ originally reported by Stiddard and Townsend.[7]

$$Ru(NO)_2(P(C_6H_5)_3)_2 + RuCl_2(P(C_6H_5)_3)_3 \xrightarrow{\text{Zn dust}} 2Ru(NO)Cl(P(C_6H_5)_3)_2 + P(C_6H_5)_3$$

$Ru(NO)_2(P(C_6H_5)_3)_2$ was prepared by a modification of the Levison-Robinson[8] procedure in which the intermediate product, $RuH_2(P(C_6H_5)_3)_4$, is first isolated before reaction with Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide). In a typical preparation 0.5 g of $RuH_2(P(C_6H_5)_3)_4$ and 0.5 g of Diazald were introduced into a Schlenk tube and the system was degassed. Thirty milliliters of methanol (or ethanol) was added and the suspension brought to reflux. After approximately 10 min, the suspension of deep red crystals was cooled, filtered, and washed with ethanol and hexane. *Anal.* Calcd for $C_{36}H_{30}N_2O_2P_2Ru$: C, 63.06; H, 4.38; N, 4.08; P, 9.05. Found: C, 62.74; H, 4.29; N, 3.94; P, 8.89. The material shows ν_{NO} at 1605, 1655 cm^{-1} (Nujol mull) and melts at 150°. $Ru(NO)_2(P(C_6H_5)_3)_2$ can be recrystallized from either methylene chloride–ethanol or benzene-hexane.

The nitrosyl-transfer reaction was carried out as follows. A 0.5-g amount of $Ru(NO)_2(P(C_6H_5)_3)_2$, 0.7 g of $RuCl_2(P(C_6H_5)_3)_3$, and 2.0 g of Zn dust were placed in a Schlenk tube and the system was degassed. Dried benzene (20 ml) was added and the system brought to reflux. An emerald green solution developed after approximately 3 min. After 30 min the reaction mixture was filtered to remove excess Zn dust, hexane was added, and the solution was cooled at 0° overnight. The resulting green precipitate was shown to be $Ru(NO)Cl(P(C_6H_5)_3)_2$ by its solid-state reaction with O_2 to yield the tan dioxygen adduct which exhibits characteristic ir bands at 1765 cm^{-1}

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[2] C. P. Brock and J. A. Ibers, *Inorg. Chem.*, 11, 2812 (1972). See Table VI therein for a tabulation of structural parameters for a series of isoelectronic tetrahedral complexes.

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(ν_{NO}) and 875 cm^{-1} (ν_{O_2}).^{9} This method of preparing $Ru(NO)Cl(P(C_6H_5)_3)_2$, which employs $Ru(NO)_2(P(C_6H_5)_3)_2$ as the nitrosyl source, is superior to the method first suggested by Stiddard and Townsend^7 because that preparation is very sensitive to the quality of the Zn dust used.

Collection and Reduction of the X-Ray Data. Deep red crystals of $Ru(NO)_2(P(C_6H_5)_3)_2$ suitable for X-ray analysis were obtained by slow recrystallization from cold benzene–hexane. Based on preliminary precession photographs and optical goniometry, they were assigned to the monoclinic system. The systematic absences, $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, strongly suggest that the space group is $C_{2h}{}^5$-$P2_1/n$.^{10} The crystal chosen for data collection shows 14 of the faces belonging to the forms {010}, {210}, {101}, {$\bar{1}$01}, and {$\bar{1}$11}. It was carefully measured in anticipation of an absorption correction ($\mu = 49.5$ cm^{-1}, Cu Kα). Its dimensions were 0.42 × 0.20 × 0.20 mm along the principal crystallographic directions and it had a calculated volume of 0.0137 mm^3. Cell constants at 22° were determined from a least-squares refinement^{11} of the setting angles of 12 reflections which had been centered on a Picker four-circle diffractometer using nickel-filtered Cu Kα radiation (λ 1.54056 Å) at a takeoff angle of 1.5°. They are $a = 17.031$ (2) Å, $b = 18.792$ (2) Å, $c = 10.800$ (1) Å, and $\beta = 97.03$ (1)°. Comparison of the observed density (1.43 (2) g/cm^3), determined by flotation in a carbon tetrachloride–hexane mixture, with that calculated on the basis of four molecules of the complex in the unit cell ($\rho_{calcd} = 1.326$ g/cm^3) suggests the presence of two molecules of solvent (C_6H_6) in the lattice ($\rho_{calcd} = 1.401$ g/cm^3). No crystallographic symmetry is imposed on the complex although the solvent of crystallization (unless disordered) is constrained to lie on symmetry centers. The presence of the solvent of crystallization was ultimately confirmed by the structural results.

The mosaic spread of the crystal was examined by means of open-counter, narrow-source ω scans^{12} of several strong reflections. The average width at half-height was 0.06°, which is acceptably low. Intensity data were collected by the θ-2θ scan technique^{12} on a computer-controlled Picker FACS-1 automatic diffractometer with the a^* axis of the crystal approximately coincident with the diffractometer spindle axis. Cu Kα radiation, prefiltered through a 1-mil nickel foil, was employed with pulse height analysis set to accept approximately 90% of the Cu Kα line. The takeoff angle was 2.5° at which the intensity is about 85% of the maximum available as a function of takeoff angle. A 6 mm × 6 mm counter aperture was positioned 31 cm from the crystal. An asymmetric scan range in 2θ was employed from 0.95° below the Kα_1 peak position to 0.75° above the Kα_2 peak position. The scan rate was 2°/min with stationary-crystal, stationary-counter background counts taken at the limits of the scan for each reflection. In order to improve the signal to noise ratio, the duration of the background counts varied from 10 sec ($3° \leqslant 2\theta \leqslant 50°$) to 20 sec ($50° < 2\theta \leqslant 75°$) to 40 sec ($75° < 2\theta \leqslant 100°$). Cu foil attenuators (ratio ~2.3) were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec.

A total of 3827 reflections ($h \geqslant 0, k \geqslant 0, \pm l$) were recorded in the range $3° \leqslant 2\theta \leqslant 100°$. The intensities of six reflections in diverse regions of reciprocal space were monitored after every 100 reflections and no significant trends were noted. The variations in individual measurements of a given standard were less than expected from counting statistics.

All data processing was carried out as previously described.^{13} The value of p was 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects thereby yielding 3120 statistically significant ($F_o{}^2 > 3\sigma(F_o{}^2)$) reflections. The transmission coefficients varied from 0.33 to 0.47. Of the 3120 observations, 132 were symmetrically equivalent. Four reflections which are required from space group considerations to be extinguished were judged to be observed. One of these (050) showed $F_o{}^2 > 24\sigma(F_o{}^2)$ which we attribute to multiple reflection since the ($\bar{2}$10) and (240) reflections are the strongest in the data set. None of these four space group extinguished reflections was observed on precession photographs using either Cu Kα or Mo Kα radiation. The space group extinct reflections and the symmetry-related spectra were eliminated to yield 2984 reflections which were used as the basis for subsequent refinement of the structure.

Solution and Refinement of the Structure

The structure was solved with difficulty. Initially, trial positions for the ruthenium and the two phosphorus atoms were derived from an analysis of a three-dimensional origin-removed Patterson function.^{14}

Expansion of the model to include the light atoms was complicated by the considerable scrambling of their positions caused by a pseudomirror operation present in the subsequent difference synthesis. The pseudomirror operation results from the location of the ruthenium atom on the glide plane (x, $^1/_4$, z). An attempt was made to overcome this difficulty by direct methods using Sayre's equation^{15} as implemented in a local version of the LSAM system of computer programs.^{14} Normalized structure factors were computed and the distribution of the 200 reflections having $E \geqslant 1.98$ with respect to the eight parity classes was examined. An abnormal distribution was found, with only two reflections in the parity class (ooe) and none in the classes (eeo), (eoo), and (oee). Expansion of the set to include 300 reflections with $E \geqslant 1.82$ did not materially alter the distribution in the parity classes. As a result of this peculiarity,^{16} it was impossible to select three linearly independent reflections that simultaneously fixed the origin and entered into a significant number of interactions for the phase determining process. The difference synthesis was therefore reexamined and the remaining light atoms (excluding hydrogen) were ultimately located on a succession of difference syntheses based on previously located atoms.

The trial structure was refined (on F) by a full-matrix least-squares procedure.^{14} The function minimized is $\Sigma w(|F_o| - |F_c|)^2$ where the weights, w, are taken as $4F_o{}^2/\sigma^2(F_o{}^2)$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The discrepancy indices, R_1 and R_2, are defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively. The scattering factors for neutral Ru, P, O, N, and C were obtained from the tabulation of Cromer and Waber^{17a} while those for H were taken from Stewart, *et al.*^{17b} The anomalous terms for Ru, P, O, and N were those reported by Cromer and Liberman^{18} and were included in F_c.^{19} During the refinement, the phenyl rings and the benzene of crystallization were treated as rigid groups possessing D_{6h} symmetry (C–C bond length 1.392 Å). A refinement of the complete trial structure with individual isotropic thermal parameters for each atom resulted in values of 0.085 and 0.115 for R_1 and R_2, respectively. Two additional cycles of refinement based on 2984 observations and 143 variables including anistropic thermal parameters for the nongroup atoms resulted in final values of 0.043 for R_1 and 0.063 for R_2.^{20} Between the last two cycles, the contributions to the calculated structure factors from the hydrogen atoms of the phenyl and benzene groups were computed^{21} and included in the final cycle of refinement as fixed contributions. A correction for isotropic extinction was made, but this resulted in no improvement in the discrepancy indices. The value of the isotropic extinction parameter is 5 (2) × 10^{-7} e^{-2}. The largest parameter shifts in the last cycle were less than 0.1 of their estimated standard deviations. The standard deviation of an observation of unit weight is 2.24 e. A final difference Fourier map shows no peak higher than 0.7 e/Å^3, whereas the average electron density of a carbon atom in this structure is 3.3 e/Å^3. Of the 707 reflections omitted from the

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(9) K. R. Laing and W. R. Roper, *Chem. Commun.*, 1556 (1968).

(10) Nonstandard setting of $C_{2h}{}^5$-$P2_1/c$ with equipoints: $\pm(x, y, z)$, $\pm({}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

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

(12) T. C. Furnas, "Single Crystal Orienter Instruction Manual," The General Electric Co., Milwaukee, Wis., 1967.

(13) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 204 (1967).

(14) In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE error function program, Johnson's ORTEP thermal ellipsoid plotting program, Dewar's FAME normalized structure factor program, and the Main, Woolfson, and Germain direct-methods programs LSAM. Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. The absorption program, AGNOST, incorporates the Coppens–Leiserowitz–Rabinovich logic for gaussian integration.

(15) D. Sayre, *Acta Crystallogr.*, 5, 60 (1952).

(16) Atoms whose y coordinates are $^1/_4$ do not contribute to the intensity of reflections with $h + l$ odd. The reflections with $h + l$ odd belong to the parity classes (eeo), (eoo), (oee), and (ooe).

(17) (a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(18) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(19) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(20) See paragraph at end of paper regarding supplementary material.

(21) The phenyl hydrogen atoms and those of the benzene solvate were treated as rigid groups whose positional and orientational parameters were those of the carbon skeleton and whose thermal parameters were estimated as 1 Å^2 greater than the carbon atom to which they are bonded. The assumed C–H distance is 0.95 Å.

Table I. Positional, Thermal, and Group Parameters for $Ru(NO)_2(P(C_6H_5)_3)_2\cdot{}^1/_2C_6H_6$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.19377 (3)	0.24752 (2)	0.02793 (4)	30.4 (3)	23.0 (2)	75.8 (6)	2.1 (1)	−1.6 (3)	−7.2 (2)
P(1)	0.14191 (9)	0.17448 (8)	−0.13722 (14)	28.4 (7)	22.3 (5)	73.0 (16)	−1.0 (5)	8.3 (7)	−4.0 (7)
P(2)	0.10910 (9)	0.34690 (8)	0.01199 (14)	29.4 (7)	23.1 (5)	69.1 (15)	−0.5 (5)	4.6 (8)	−3.3 (7)
N(1)	0.2837 (4)	0.2830 (3)	−0.0096 (6)	35 (3)	41 (2)	167 (8)	−8 (2)	17 (4)	−35 (4)
O(1)	0.3438 (4)	0.3061 (4)	−0.0391 (7)	61 (3)	101 (4)	340 (14)	−43 (3)	76 (6)	−84 (6)
N(2)	0.1587 (3)	0.1930 (3)	0.1438 (5)	55 (3)	31 (2)	76 (6)	6 (2)	4 (3)	2 (3)
O(2)	0.1276 (4)	0.1528 (3)	0.2082 (5)	89 (4)	48 (2)	99 (6)	1 (2)	19 (4)	19 (3)

Group	$x_c{}^c$	y_c	z_c	δ	ϵ	η
P(1)R(1)	−0.0423 (2)	0.1445 (1)	−0.1158 (3)	0.358 (3)	2.482 (3)	−0.318 (3)
P(1)R(2)	0.1700 (2)	0.2231 (1)	−0.4137 (3)	1.920 (3)	2.859 (2)	1.783 (3)
P(1)R(3)	0.2225 (2)	0.0188 (2)	−0.1235 (3)	−1.141 (4)	−2.144 (3)	3.133 (4)
P(2)R(1)	−0.0005 (1)	0.3785 (1)	−0.2455 (3)	1.436 (3)	−2.522 (2)	1.665 (3)
P(2)R(2)	0.2094 (2)	0.4911 (1)	0.0666 (3)	0.829 (4)	2.253 (3)	−2.947 (4)
P(2)R(3)	−0.0151 (2)	0.3430 (2)	0.2140 (3)	2.947 (3)	2.919 (2)	−2.267 (3)
$C_6H_6{}^d$	$^1/_2$	$^1/_2$	0	2.541 (5)	3.145 (5)	1.145 (6)

[a] Estimated standard deviations of the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers. The angles δ, ϵ, and η (radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 793 (1965). [d] The rigid-group center of the benzene solvate is constrained to a crystallographic center of symmetry.

Table II. Derived Parameters of Ring Carbon and Hydrogen Atoms for $Ru(NO)_2(P(C_6H_5)_3)_2\cdot{}^1/_2C_6H_6$

Atom[a]	x	y	z	B, Å^2	Atom[a]	x	y	z	B, Å^2
P(1)R(1)C(1)	0.0365 (2)	0.1559 (2)	−0.1324 (4)	3.2 (1)	P(1)R(1)H(2)[c]	−0.0095	0.2335	−0.2518	5.0[d]
P(1)R(1)C(2)	−0.0227 (2)	0.1977 (2)	−0.1963 (3)	4.0 (1)	P(1)R(1)H(3)	−0.1425	0.2145	−0.2234	5.7
P(1)R(1)C(3)	−0.1014 (2)	0.1863 (2)	−0.1796 (4)	4.7 (1)	P(1)R(1)H(4)	−0.1753	0.1253	−0.0879	6.2
P(1)R(1)C(4)	−0.1211 (2)	0.1331 (2)	−0.0991 (4)	5.2 (2)	P(1)R(1)H(5)	−0.0761	0.0551	0.0194	6.0
P(1)R(1)C(5)	−0.0619 (2)	0.0914 (2)	−0.0353 (4)	5.0 (2)	P(1)R(1)H(6)	0.0569	0.0741	−0.0090	5.4
P(1)R(1)C(6)	0.0169 (2)	0.1028 (2)	−0.0519 (4)	4.4 (1)	P(1)R(2)H(2)	0.0491	0.1692	−0.3875	6.0
P(1)R(2)C(1)	0.1549 (2)	0.2015 (2)	−0.2957 (3)	3.3 (1)	P(1)R(2)H(3)	0.0744	0.2061	−0.5867	6.8
P(1)R(2)C(2)	0.0981 (2)	0.1913 (2)	−0.3983 (4)	5.0 (1)	P(1)R(2)H(4)	0.1950	0.2600	−0.6125	6.4
P(1)R(2)C(3)	0.1133 (2)	0.2129 (3)	−0.5163 (3)	5.8 (2)	P(1)R(2)H(5)	0.2905	0.2772	−0.4405	6.4
P(1)R(2)C(4)	0.1852 (3)	0.2448 (2)	−0.5318 (3)	5.4 (2)	P(1)R(2)H(6)	0.2652	0.2403	−0.2413	5.1
P(1)R(2)C(5)	0.2420 (2)	0.2550 (2)	−0.4292 (4)	5.4 (2)	P(1)R(3)H(2)	0.2518	0.0996	0.0406	5.6
P(1)R(2)C(6)	0.2268 (2)	0.2334 (2)	−0.3111 (3)	4.1 (1)	P(1)R(3)H(3)	0.3105	−0.0137	0.0514	6.7
P(1)R(3)C(1)	0.1876 (2)	0.0859 (2)	−0.1296 (4)	3.2 (1)	P(1)R(3)H(4)	0.2810	−0.0944	−0.1124	6.7
P(1)R(3)C(2)	0.2402 (3)	0.0669 (2)	−0.0261 (3)	4.6 (1)	P(1)R(3)H(5)	0.1932	−0.0624	−0.2870	6.8
P(1)R(3)C(3)	0.2751 (3)	−0.0002 (2)	−0.0199 (4)	5.7 (2)	P(1)R(3)H(6)	0.1345	0.0509	−0.2978	5.9
P(1)R(3)C(4)	0.2574 (3)	−0.0483 (2)	−0.1174 (4)	5.7 (2)	P(2)R(1)H(2)	−0.0584	0.3792	−0.0601	5.3
P(1)R(3)C(5)	0.2048 (3)	−0.0293 (2)	−0.2210 (4)	5.8 (2)	P(2)R(1)H(3)	−0.1362	0.4006	−0.2516	6.5
P(1)R(3)C(6)	0.1699 (2)	0.0379 (2)	−0.2271 (3)	4.9 (1)	P(2)R(1)H(4)	−0.0780	0.3997	−0.4367	6.8
P(2)R(1)C(1)	0.0456 (2)	0.3658 (2)	−0.1322 (3)	3.3 (1)	P(2)R(1)H(5)	0.0574	0.3776	−0.4317	5.9
P(2)R(1)C(2)	−0.0350 (2)	0.3792 (2)	−0.1352 (3)	4.3 (1)	P(2)R(1)H(6)	0.1352	0.3562	−0.2402	5.0
P(2)R(1)C(3)	−0.0811 (2)	0.3918 (3)	−0.2486 (4)	5.5 (2)	P(2)R(2)H(2)	0.1152	0.4857	−0.1103	5.4
P(2)R(1)C(4)	−0.0467 (2)	0.3911 (3)	−0.3589 (3)	5.8 (2)	P(2)R(2)H(3)	0.1919	0.5888	−0.0689	6.2
P(2)R(1)C(5)	0.0339 (2)	0.3778 (2)	−0.3559 (3)	4.9 (1)	P(2)R(2)H(4)	0.2857	0.5941	0.1080	6.3
P(2)R(1)C(6)	0.0800 (2)	0.3651 (2)	−0.2425 (4)	4.0 (1)	P(2)R(2)H(5)	0.3032	0.4969	0.2437	6.4
P(2)R(2)C(1)	0.1639 (2)	0.4300 (2)	0.0421 (4)	3.4 (1)	P(2)R(2)H(6)	0.2265	0.3938	0.2023	5.6
P(2)R(2)C(2)	0.1535 (2)	0.4879 (2)	−0.0386 (3)	4.4 (1)	P(2)R(3)H(2)	0.0087	0.2423	0.0968	5.1
P(2)R(2)C(3)	0.1989 (3)	0.5490 (2)	−0.0141 (4)	5.2 (2)	P(2)R(3)H(3)	−0.0831	0.2371	0.2423	6.2
P(2)R(2)C(4)	0.2548 (3)	0.5522 (2)	0.0911 (4)	5.3 (2)	P(2)R(3)H(4)	−0.1065	0.3378	0.3594	6.6
P(2)R(2)C(5)	0.2652 (2)	0.4944 (2)	0.1719 (4)	5.4 (2)	P(2)R(3)H(5)	−0.0387	0.4437	0.3320	6.7
P(2)R(2)C(6)	0.2198 (3)	0.4333 (2)	0.1474 (3)	4.6 (1)	P(2)R(3)H(6)	0.0531	0.4489	0.1865	5.7
P(2)R(3)C(1)	0.0394 (2)	0.3461 (2)	0.1281 (3)	3.3 (1)	H(1)[e]	0.4077	0.4257	0.0792	9.2
P(2)R(3)C(2)	−0.0013 (2)	0.2832 (2)	0.1439 (4)	4.1 (1)	H(2)[e]	0.4562	0.3970	−0.1092	9.3
P(2)R(3)C(3)	−0.0558 (2)	0.2801 (2)	0.2298 (4)	5.2 (2)	H(3)[e]	0.5483	0.4714	−0.1877	9.5
P(2)R(3)C(4)	−0.0696 (2)	0.3399 (2)	0.3000 (4)	5.6 (2)					
P(2)R(3)C(5)	−0.0289 (3)	0.4028 (2)	0.2842 (4)	5.7 (2)					
P(2)R(3)C(6)	0.0257 (3)	0.4059 (2)	0.1982 (4)	4.7 (1)					
C(1)[b]	0.4457 (3)	0.4559 (3)	0.0486 (7)	8.2 (2)					
C(2)[b]	0.4737 (4)	0.4384 (2)	−0.0634 (6)	8.3 (2)					
C(3)[b]	0.5279 (4)	0.4825 (4)	−0.1120 (4)	8.5 (2)					

[a] C(1) is attached to P and the atoms in the ring are numbered sequentially with C(4) para to P. [b] These are the three independent carbon atoms of the benzene solvate. [c] The numbering system for the hydrogen atoms is analogous to that used for the carbon atoms with H(2) attached to C(2). [d] The thermal parameters of the hydrogen atoms are taken as 1 Å^2 higher than the carbon atom to which they are bonded. [e] These are the independent hydrogen atoms of the benzene solvate.

refinement ($F_o{}^2 < 3\sigma(F_o{}^2)$), 13 had $|F_o{}^2 - F_c{}^2| > 3\sigma(F_o{}^2)$ and five had $|F_o{}^2 - F_c{}^2| > 5\sigma(F_o{}^2)$. The parameters obtained from the final cycle of refinement are given in Table I along with their estimated standard deviations as obtained from the inverse matrix. The derived parameters for the group atoms are reported in Table II. The root-mean-square amplitudes of vibration of the seven atoms refined anisotropically are given in Table III.

Description of the Structure

The crystal structure consists of discrete molecules of $Ru(NO)_2(P(C_6H_5)_3)_2$ occupying the four general positions of the space group with molecules of benzene situated about the symmetry centers at ($^1/_2$, $^1/_2$, 0) and (0, 0, $^1/_2$). The shortest Ru-Ru distance is 9.509 Å and the shortest inter-

Table III. Root-Mean-Square Amplitudes of Vibration along Principal Ellipsoid Axes (Å)

Atom	Min	Intermed	Max
Ru	0.1870 (9)	0.1993 (9)	0.2373 (8)
P(1)	0.192 (2)	0.198 (2)	0.216 (2)
P(2)	0.193 (2)	0.207 (2)	0.210 (2)
N(1)	0.208 (9)	0.228 (8)	0.352 (8)
O(1)	0.218 (9)	0.325 (8)	0.548 (10)
N(2)	0.208 (8)	0.230 (8)	0.289 (8)
O(2)	0.216 (8)	0.308 (7)	0.360 (7)

molecular contact is 2.44 Å between several phenyl hydrogen atoms. The molecular packing is dominated by the bulky triphenylphosphine groups with the benzene of crystallization filling voids in the structure. Although there are no specific intermolecular interactions, note that a given nitrosyl group is oriented in the direction of its nearest benzene of crystallization. The resulting arrangement is depicted in Figure 1.

A stereoscopic view of an individual molecule is presented in Figure 2 and a perspective view of the inner coordination sphere is depicted in Figure 3. Interatomic distances and angles together with their estimated standard deviations are given in Table IV. As can be seen from the figures, the ruthenium atom is in a four-coordinate environment surrounded by two nitrogen and two phosphorus atoms. The two Ru-P bond lengths of 2.337 (2) and 2.353 (2) Å are within the range found in other complexes of ruthenium containing coordinated triphenylphosphine.[22-24] The Ru-N distances, 1.762 (6) and 1.776 (6) Å, are equal within experimental error and are in the upper limits of the range found in other structures[23-26] with formally NO^+ coordinated to ruthenium. The Ru-N(1)-O(1) angle, 177.7 (6)°, is essentially linear and therefore consistent with an NO^+ formulation, while the Ru-N(2)-O(2) angle, 170.6 (5)°, shows a small but significant deviation from linearity. The magnitude of the distortion is not, however, sufficient to preclude an assignment as NO^+.[27] The P-Ru-N angles range from 94.1 (2) to 107.8 (2)° and the pattern of angles is similar to that found in $Ir(NO)(CO)(P(C_6H_5)_3)_2$.[2] The coordination geometry about the ruthenium atom is irregular. The relevant structural parameters needed to distinguish between the alternative forms of four-coordination (tetrahedral, square planar, or trigonal pyramidal) are given in Table V. From these we conclude that the geometry about the ruthenium atom can best be described as distorted tetrahedral.

The most striking feature of the complex is the large N-Ru-N angle of 139.2 (3)°. This value is intermediate between those observed in two isoelectronic complexes, 154.2 (7)° in $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$ [3] and 128.7 (2)° in $Ir(NO)(CO)(P(C_6H_5)_3)_2$.[2] This result is consistent with the suggestion[2] that this angle is increased in order to alleviate nonbonded repulsions between the two π-acceptor ligands. The P-Ru-P angle of 103.85 (6)° is slightly less than the tetrahedral value and agrees within experimental error with that observed in $Ir(NO)(CO)(P(C_6H_5)_3)_2$.[2] This value is significantly different from the P-Ir-P angle of 116.3 (2)° found in $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$ [3] and from those found in other tetrahedral bis(triphenylphosphine) complexes.[28,29] In those complexes exhibiting large (relative to the tetrahedral value) P-M-P angles, the increase apparently results from the minimization of nonbonded repulsions between phenyl rings on adjacent triphenylphosphine groups. In $Ru(NO)_2(P(C_6H_5)_3)_2$, however, the P-Ru-P angle is less than the tetrahedral value and this lowering may be related to the unusual conformation of the phenyl rings associated with P(1) (see Figure 2). Generally, the phenyl rings of coordinated triphenylphosphine adopt a propeller conformation when viewed down the pseudo-threefold axis. In the triphenylphosphine group associated with P(1), however, the rings are oriented such that the triphenylphosphine group possesses approximate mirror symmetry relating the rings designated R(2) and R(3) as well as the ortho and meta carbon atoms of R(1). A consequence of the conformation of the phenyl groups about P(1) is that the plane defined by the phenyl ring designated R(3) is almost perpendicular to the plane defined by N(1), Ru, N(2) (dihedral angle 83.1°) and approximately bisects the N(1)-Ru-N(2) angle. However, because of the relatively small P-Ru-P angle and the large N-Ru-N angle, no abnormally short contacts involving the two nitrosyl groups and the R(3) hydrogen atoms result. The shortest contact is 2.7 Å between N(2) and the hydrogen bound to P(1)R(3)C(2). In the present structure, then, nonbonded repulsions between phenyl rings on adjacent phosphorus atoms are minimized *via* a change in the conformation of the phenyl rings about P(1) rather than by an increase in the P-Ru-P angle. The triphenylphosphine group associated with P(2) exhibits the usual propeller conformation. The shortest intramolecular hydrogen contact between phenyl rings on the two phosphorus atoms is 2.23 Å. Except for the peculiarities noted above, all angles and distances associated with the phenyl rings are in the range of those observed for other triphenylphosphine complexes. A similar arrangement of the triphenylphosphine ligands is found in the structure of $Ir(NO)(CO)(P(C_6H_5)_3)_2$.[2]

Discussion

The complex $Ru(NO)_2(P(C_6H_5)_3)_2$ is another member of the series of four-coordinate, isoelectronic complexes whose structures have been determined by X-ray diffraction. Based on the structural results presented above, we formulate the title compound as a d^{10} system in which the nitrosyl groups are coordinated as NO^+ and the Ru atom has a formal oxidation state of −II. In all of these four-coordinate, formally d^{10} complexes at least one strong π-acceptor ligand (CO or NO) is present which helps to stabilize the low oxidation state of the metal *via* a π-backbonding interaction. This stabilization is obviously of great importance in $Ru(NO)_2(P(C_6H_5)_3)_2$ and explains in part its relative lack of reactivity with oxidative addition substrates as compared with $M(NO)(P(C_6H_5)_3)_3$ (M = Rh, Ir).[6] $Ru(NO)_2(P(C_6H_5)_3)_2$ does, however, undergo a nitrosyl-transfer reaction with $RuCl_2(P(C_6H_5)_3)_3$ in the presence of Zn to yield the highly reactive complex $Ru(NO)Cl(P(C_6H_5)_3)_2$. This reaction represents a novel equilibration between a Ru(II) complex on one hand and a Ru(−II) system on the other. Recently, Caulton[30] has published a report on nitrosyl-transfer reactions in Co complexes and has viewed reactions of the type reported here in

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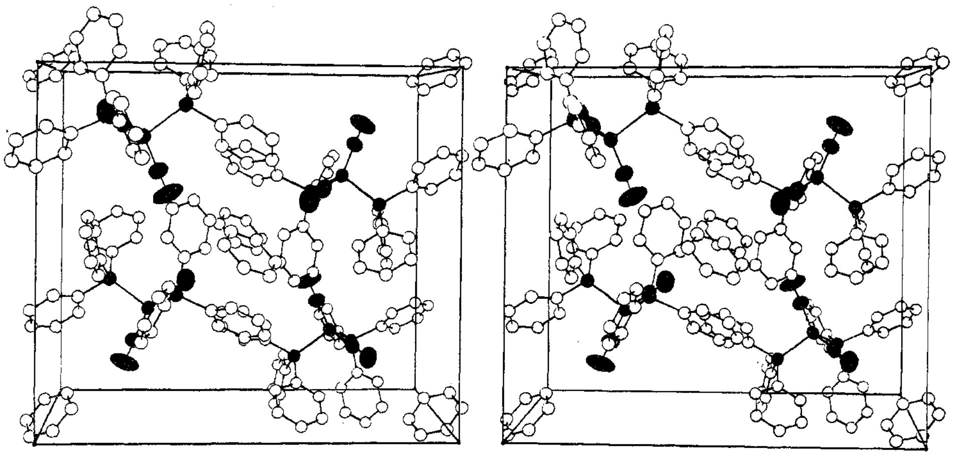

Figure 1. Stereoscopic view of the unit cell of $Ru(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$. The *x* axis is horizontal, the *y* axis is vertical, and the *z* axis points out from the paper. The shapes of the atoms in this and the following drawings represent 50% probability contours of thermal motion. The atoms of the coordination sphere have been darkened and the H atoms omitted for the sake of clarity.

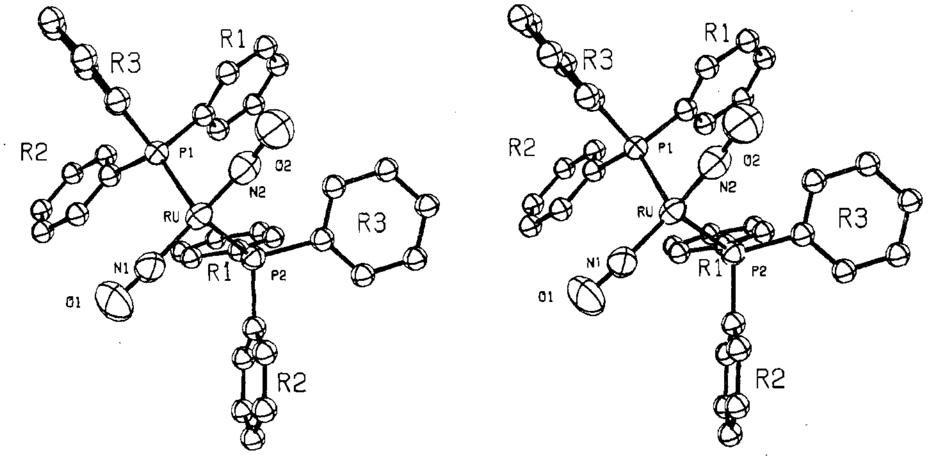

Figure 2. A stereoscopic view of the molecule $Ru(NO)_2(P(C_6H_5)_3)_2$.

Table IV. Interatomic Distances (Å) and Angles (deg) in $Ru(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$

		Distances	
Ru-P(1)	2.337 (2)	P(2)-N(2)	3.288 (6)
Ru-P(2)	2.353 (2)	P(1)-P(2)	3.692 (2)
Ru-N(1)	1.762 (6)	P(1)-O(1)	4.262 (6)
Ru-N(2)	1.776 (6)	P(1)-O(2)	3.791 (5)
Ru-O(1)	2.952 (6)	P(2)-O(1)	4.172 (7)
Ru-O(2)	2.961 (6)	P(2)-O(2)	4.211 (6)
N(1)-O(1)	1.190 (7)	P(1)-P(1)R(1)C(1)	1.836 (3)
N(2)-O(2)	1.194 (7)	P(1)-P(1)R(2)C(1)	1.824 (4)
N(1)-N(2)	3.316 (9)	P(1)-P(1)R(3)C(1)	1.835 (4)
P(1)-N(1)	3.328 (6)	P(2)-P(2)R(1)C(1)	1.819 (3)
P(1)-N(2)	3.034 (6)	P(2)-P(2)R(2)C(1)	1.828 (4)
P(2)-N(1)	3.241 (6)	P(2)-P(2)R(3)C(1)	1.829 (4)
		Angles	
O(1)-Ru-O(2)	142.7 (2)	P(1)R(3)C(1)-P(1)-Ru	112.3 (1)
P(1)-Ru-P(2)	103.85 (6)	P(1)R(1)C(1)-P(1)-P(1)R(2)C(1)	108.1 (2)
N(1)-Ru-N(2)	139.2 (3)	P(1)R(1)C(1)-P(1)-P(1)R(3)C(1)	103.7 (2)
N(1)-Ru-P(1)	107.8 (2)	P(1)R(2)C(1)-P(1)-P(1)R(3)C(1)	101.3 (2)
N(1)-Ru-P(2)	103.0 (2)	P(2)R(1)C(1)-P(2)-Ru	120.9 (1)
N(2)-Ru-P(1)	94.1 (2)	P(2)R(2)C(1)-P(2)-Ru	111.7 (1)
N(2)-Ru-P(2)	104.7 (2)	P(2)R(3)C(1)-P(2)-Ru	112.7 (1)
Ru-N(1)-O(1)	177.7 (6)	P(2)R(1)C(1)-P(2)-P(2)R(2)C(1)	102.9 (2)
Ru-N(2)-O(2)	170.6 (5)	P(2)R(1)C(1)-P(2)-P(2)R(3)C(1)	102.7 (2)
P(1)R(1)C(1)-P(1)-Ru	111.7 (1)	P(2)R(2)C(1)-P(2)-P(2)R(3)C(1)	104.2 (2)
P(1)R(2)C(1)-P(1)-Ru	118.3 (1)		

terms of an NO-Cl interchange. It is not clear at this time, however, that a bimolecular interchange of ligands is indeed occurring in the present reaction.

In four-coordinate, formally d^{10} complexes such as $Ru(NO)_2(P(C_6H_5)_3)_2$ in which two strong π-acceptor ligands are present, the magnitude of the distortions from tetrahedral geometry may be considerable, especially in the angle between the two metal-π-acceptor bonds. The value of 139.2 (3)° for the N(1)-Ru-N(2) angle in the present structure clearly illustrates this fact. Since we believe NO^+ to be a stronger π acid than CO, the trend in this particular structure parameter in the series $Pt(CO)_2(P(C_2H_5)(C_6H_5)_2)_2$,[4] 117 (1)°, Ir(NO)-

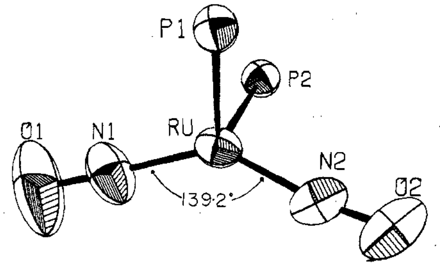

Figure 3. The inner coordination sphere of $Ru(NO)_2(P(C_6H_5)_3)_2$.

Table V

Dihedral Angle between Planes of Three Atoms about Ruthenium

Plane 1	Plane 2	Angle, deg
Ru, N(1), N(2)	Ru, P(1), P(2)	84.5 (1)
Ru, N(1), P(1)	Ru, N(2), P(2)	79.7 (1)
Ru, N(1), P(2)	Ru, N(2), P(1)	83.9 (1)

Distance of Ruthenium Atom from Bounding Faces of the Coordination Polyhedron

Plane	Dist, Å	Plane	Dist, Å
P(1), P(2), N(1)	0.846 (3)	N(1), N(2), P(1)	0.444 (4)
P(1), P(2), N(2)	0.961 (3)	N(1), N(2), P(2)	0.376 (3)

Distance of Ruthenium Atom from Bounding Faces of an Idealized Coordination Polyhedron[a]

Plane	Dist, Å	Plane	Dist, Å
P, P′, N	0.706	N, N′, P	0.645

[a] Ru-N = 1.78 Å; Ru-P = 2.35 Å; all bond angles 109.5°.

$(CO)(P(C_6H_5)_3)_2$,[2] 128.7 (4)°, $Ru(NO)_2(P(C_6H_5)_3)_2$, 139.2 (3)°, and $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$,[3] 154.2 (7)°, is rationalized by the degree of metal-ligand π back-bonding and the consequent repulsion between electrons in the metal-π-acceptor bonds.

$Ru(NO)_2(P(C_6H_5)_3)_2$ is only the third four-coordinate dinitrosyl complex to be studied structurally, and in it the nitrosyl groups are found to coordinate linearly as NO^+ (average Ru-N-O angle of 174.1°). In the other systems, the mode of nitrosyl coordination is either linear as in $Fe(NO)_2(F_6fos)$[31] ($F_6fos = (C_6H_5)_2PC{=}C(P(C_6H_5)_2(CF_2)_2CF_2)$) (average Fe-N-O bond angle of 177.3°) or slightly bent as in $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$ [3] (Ir-N-O angle of 163.5 (10)°). The difference between the nitrosyl bonding modes in these systems and the variation in the N-M-N bond angles are deserving of further study in order to establish clear structural correlations. The complexes $Fe(NO)_2(P(C_6H_5)_3)_2$[32] and $Os(NO)_2(P(C_6H_5)_3)_2$[33] are of particular interest in this regard because of the change in orbital energies in going from Fe to Ru and Os as well as to Ir in the cation $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$.[3] The structures of other four-coordinate d^{10} complexes in which different strong π-acceptor ligands are present should also help in developing the structural correlations.

Finally, one should consider any effects of crystal-packing forces. In compounds of the type under consideration here the packing in the solid state is dominated by interactions between the bulky triphenylphosphine groups. Thus the crystal structures of $Ru(NO)_2(P(C_6H_5)_3)_2$ and $Ir(NO)(CO)(P(C_6H_5)_3)_2$[2] are remarkably similar. However, neither bears any perceptible relation to the crystal structure of $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$,[3] probably because of the ionic forces that are also involved in the last structure. We have noted above that the conformation of one of the triphenylphosphine ligands in $Ru(NO)_2(P(C_6H_5)_3)_2$ differs from that normally found and that one of the phenyl rings of this triphenylphosphine group bears an unusual relationship to the N(1)-Ru-N(2) plane. In $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$,[3] however, the triphenylphosphine groups exhibit the usual conformation and bear no specific relationship to the N-Ir-N plane or to the nitrosyl groups. It is therefore difficult to rationalize the differences in the M-N-O and N-M-N angles in these complexes in terms of specific steric interactions since the largest distortions (from the ideal values) are found in $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$ [3] where no steric interactions are apparent.

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Registry No. $Ru(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$, 50442-23-4; $RuH_2(P(C_6H_5)_3)_4$, 19529-00-1; $CH_3C_6H_4SO_2N(Me)NO$, 80-11-5; $Ru(NO)_2(P(C_6H_5)_3)_2$, 50442-24-5; $RuCl_2(P(C_6H_5)_3)_3$, 15529-49-4; $Ru(NO)Cl(P(C_6H_5)_3)_2$, 38856-98-3.

Supplementary Material Available. A listing of 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-786.

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(32) The structure determination of $Fe(NO)_2(P(C_6H_5)_3)_2$ reveals an Fe-N-O angle of 178.2° and an N-Fe-N angle of 123.8°: V. G. Albano, A. Araneo, P. L. Bellon, G. Ciani, and M. Manassero, submitted for publication. We wish to thank Professor Bellon for a preprint of his paper.

(33) Unit cell and space group determination of $Os(NO)_2(P(C_6H_5)_3)_2$ indicate that the complex is isomorphous with $Ru(NO)_2(P(C_6H_5)_3)_2$. The results of the structure determination will be reported later.