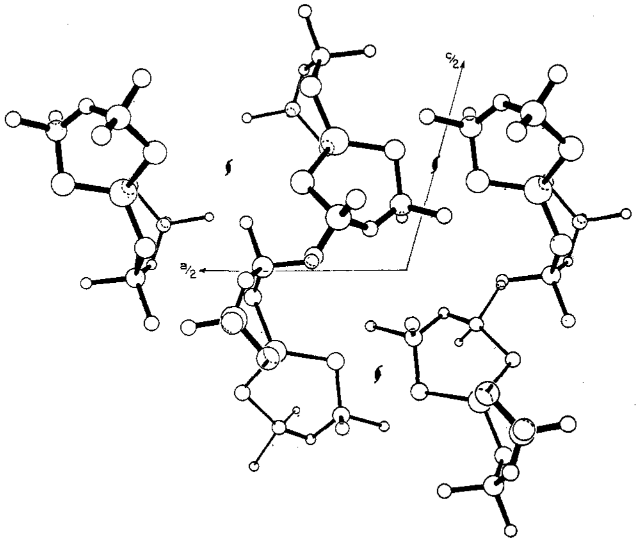

Figure 2.—Packing of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ molecules within the unit cell, viewed down "*b*."

atoms P(1), N(1), and P(2) lie −0.422, +0.527, and +1.081 Å (respectively) from plane A [defined by Ni, S(1), S(2); see Table VI], whereas atoms P(3), N(2), and P(4) are displaced by −1.414, −1.433, and −0.356 Å from plane B.

The Crystal Structure

Intermolecular contacts less than 3.5 Å all involve hydrogen atoms (which were not located in this crystallographic analysis). However, it is clear that the crystal contains independent units of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$, separated by normal van der Waa's distances. Packing of molecules within the unit cell is shown in Figure 2.

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The Crystal and Molecular Structure of Dichloronitrosylbis(triphenylphosphine)iridium, $IrCl_2(NO)(P(C_6H_5)_3)_2$

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The structure of dichloronitrosylbis(triphenylphosphine)iridium, $IrCl_2(NO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group C_{2h}^6-$I2/a$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 15.851$ (4), $b = 9.624$ (3), $c = 22.050$ (6) Å, $\beta = 104.6$ (3)°. The observed and calculated densities are 1.66 (±0.02) and 1.67 g/cm³. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.032 for the 1338 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well-separated discrete molecules. There is a crystallographically imposed twofold axis on the molecule and the geometry around the iridium atom is approximately square-pyramidal with the nitrogen atom of the nitrosyl group occupying the apical position. Despite the fact that the oxygen and nitrogen atoms are disordered about the twofold axis an iridium–nitrogen–oxygen bond angle of 123 (2)° may be derived from the data. Important bond lengths in the molecule are as follows: Ir–Cl, 2.348 (2); Ir–P, 2.367 (2); Ir–N, 1.94 (2); N–O, 1.03 (2) Å. This complex provides another example of the nitrosyl ligand coordinated to iridium in a nonlinear fashion. The bonding in this complex is rationalized in terms of a qualitative molecular orbital scheme, and the complex is described formally as an NO^- complex of iridium(III).

Introduction

X-Ray structural studies of $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or I)[1,2] showed that in each compound the metal–nitrosyl geometry was very different from that previously observed in reliable structural determinations of transition metal–nitrosyl complexes. The metal–nitrogen–oxygen bond angles are approximately 120° in the iridium complexes in contrast to the approximately 180° bond angle usually observed for nitrosyl complexes. The complexes with linear metal–nitrogen–oxygen bond angles have been formulated as complexes of NO^+, because they show properties and geometries similar to those of analogous carbonyl complexes. Hodgson, *et al.*,[1] suggested that in the complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$, which were prepared from the reaction of $NO^+BF_4^-$ with $IrX(CO)(P(C_6H_5)_3)_2$, the NO^+ ion was acting as a Lewis acid accepting two electrons from the metal d_{z^2} orbital into an empty sp^2 hybrid orbital on the nitrogen atom. However, the complex $[CoCl(NO)(en)_2][ClO_4]$ (en = ethylenediamine), which was prepared from nitric oxide[3] and which also has the nitrosyl ligand coordinated in a nonlinear fashion,[4] has been formulated as a complex of NO^-. These formulations (Figure 1) are equivalent and represent two of the canonical forms which may be used to describe the bonding in these ions.

The structural determinations of the complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or Br)[1,2] prompted us to study other iridium complexes which might have the nitrosyl ligand coordinated in a bent

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(1) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968); D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

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

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(4) D. A. Snyder and D. L. Weaver, *Chem. Commun.*, 1425 (1969).

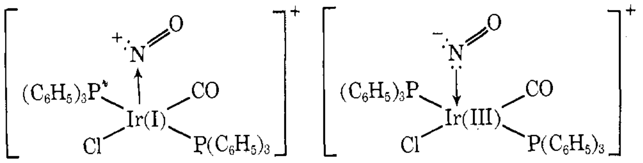

Figure 1.—Canonical forms representing the bonding in the $IrCl(NO)(CO)(P(C_6H_5)_3)_2^+$ ion: left, NO^+ acting as a Lewis acid, accepting electrons from an Ir(I) filled orbital; right, NO^- acting as a Lewis base, donating electrons to an Ir(III) empty orbital.

fashion (hereafter referred to as NO^-). Reed and Roper[5] have recently reported the preparations of a wide variety of five-coordinate nitrosyl complexes from oxidative addition reactions of the complex $Ir(NO)(P(C_6H_5)_3)_3$. We have determined the structures of three of these complexes: $IrCl_2(NO)(P(C_6H_5)_3)_2$, which is discussed in this paper, and $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ and $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$, which will be discussed in subsequent papers. The complex $IrCl_2(NO)(P(C_6H_5)_3)_2$ had also been prepared earlier by Angoletta and Caglio[6] by a different route. These complexes are isoelectronic with the previously studied complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or I) and we were interested in examining the effects of such widely different ligands on the metal–nitrosyl geometry, the metal–nitrogen bond length, and the geometry of the ligands around the metal. Thus it was of interest to see if the square-pyramidal geometry observed for the complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ is retained for these complexes despite the wide differences in bonding characteristics of the nonnitrosyl ligands.

Collection and Reduction of Intensity Data

Small, yellow-brown crystals of $IrCl_2(NO)(P(C_6H_5)_3)_2$ were prepared by the method of Angoletta and Caglio[6] and were characterized by their elemental analysis and infrared spectrum. On the basis of Weissenberg and precession photography of the $0kl$, $1kl$, $2kl$, $hk0$, $hk1$, $hk2$, and $h0l$ nets we established that the crystals belong to the monoclinic system. The observed extinctions $h + k + l = 2n + 1$ for hkl and $h = 2n + 1$ for $h0l$ are consistent with the space groups C_{2h}^6-$I2/a$ and C_s^4-Ia. On the basis of optical goniometry the six faces of that crystal chosen for data collection were identified as belonging to the forms $\{110\}$ and $\{001\}$. The lattice constants at 21.5°, which were determined from a least-squares refinement of the setting angles of 14 strong X-ray reflections that had been centered on a Picker four-circle automatic diffractometer[7] using Cu $K\alpha_1$ radiation (λ 1.54056 Å), are a = 15.851 (4), b = 9.624 (6), c = 22.050 (6) Å, β = 104.6 (3)°. The density calculated for four molecules per unit cell is 1.67 g/cm³, which agrees well with that of 1.66 (±0.02) g/cm³ measured by suspending crystals in a mixture of iodomethane and methylene chloride. With four molecules in the unit cell either a twofold axis or a center of symmetry is imposed on the molecule in $I2/a$, but no symmetry is imposed on the molecule if the material crystalizes in the noncentric space group Ia.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique. The width at half-height for a typical strong reflection was found to be approximately 0.05°, which is acceptably low.[8] The intensity data were collected as previously described[7] using a crystal with approximate dimensions 0.091 × 0.048 × 0.062 mm. The crystal was mounted on the diffractometer with the spindle axis approximately along the long dimension of the crystal, the a^* reciprocal lattice vector.

For data collection Cu $K\alpha$ radiation was used and the diffracted beams were filtered through 0.5 mil of nickel foil. The intensities were measured by the θ–2θ scan technique at a takeoff angle of 1.5°. At this angle the intensity of a reflection was about 80% of the maximum value as a function of takeoff angle. A receiving aperture 4 × 4 mm was used and was positioned 31 cm from the crystal. A nonsymmetric scan range in 2θ was used, from −0.4 to +0.6° from the $K\alpha_1$ peak for reflections with $\theta < 40°$ and −0.5 to +1.0° for the reflections with $40° < \theta < 51°$. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils whose thickness had been chosen to give attenuator factors of approximately 2.3. The pulse height analyzer was set for approximately a 90% window, centered on the Cu $K\alpha$ peak.

Intensity data were collected for all reflections of this monoclinic crystal up to $\theta(\text{Cu } K\alpha_1) \leqslant 35°$ and only independent reflections were collected in the region $35° \leqslant \theta(\text{Cu } K\alpha_1) \leqslant 51°$. Past this point very few intensities were above background under the conditions of data collection just detailed. The intensities of four standard reflections measured every 100 observations remained essentially constant throughout the run showing only the deviations ±1%. The data were processed as previously described.[6] The value of p was selected as 0.05. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Of the 1963 reflections examined, 1722 were independent. Of the independent reflections, 180 had intensities which were less than their standard deviations. The linear absorption coefficient for the compound for Cu $K\bar{\alpha}$ radiation is 104.3 cm⁻¹. The data were corrected for absorption; the transmission coefficients ranged from 0.560 to 0.685. The resultant values of F_o^2 were examined for systematic variations among reflections that would be nonequivalent in Ia. No systematic variations were detected, suggesting that $I2/a$ is the correct space group.

Solution and Refinement of the Structure

The coordinates of the iridium atom were found from a three-dimensional Patterson function.[9] The iridium atom occupies one of the fourfold positions of $I2/a$; $(0, 0, 0;\ ^1/_2, ^1/_2, ^1/_2) \pm (^1/_4, y, 0)$. The general eightfold positions for this space group are $(0, 0, 0;\ ^1/_2, ^1/_2, ^1/_2) \pm (x, y, z;\ ^1/_2 - x, y, \bar{z})$. After one cycle of refinement of scale factor and iridium coordinates the discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ were 0.33 and 0.40, respectively, where the weights, w, are taken as $4F^2/\sigma^2(F^2)$. In this and subsequent calculations

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(5) C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).

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

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

(9) In addition to various local programs, those used in this work include local modifications of Hamilton's GONO9 absorption program, Johnson's ORTEP thermal ellipsoid plotting program, and Zalkin's FORDAP Fourier program. Our local least-squares program NUCLS in its nongroup form closely resembles the Busing–Levy ORFLS program.

only the 1338 reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used. In all calculations of $|F_c|$ the usual tabulation of atomic scattering factors[10] was used for P, Cl, O, N, and C, those for hydrogen were from Stewart, Davidson, and Simpson,[11] and those of Cromer and Waber[12] were used for Ir. The effects of anomalous dispersion were included in the calculation of $|F_c|$;[13] the values of $\Delta f'$ and $\Delta f''$ for Ir, Cl, and P were those given by Cromer.[14]

Based on a subsequent structure factor calculation, a difference Fourier synthesis was computed which revealed the positions of the nitrogen atom (which occupies one of the special fourfold positions) and the phosphorus, chlorine, and ring carbon atoms (which occupy general positions). In the subsequent least-squares refinement the phenyl rings were treated as rigid groups of D_{6h} symmetry, $d(\text{C–C}) = 1.390$ Å,[15,16] and the nongroup atoms were assigned isotropic thermal parameters. Two cycles of least-squares refinement gave the discrepancy factors $R_1 = 0.066$ and $R_2 = 0.094$. A subsequent difference Fourier synthesis revealed that the oxygen atom was disordered and occupied the general eightfold position. A cycle of least-squares refinement including trial coordinates of the oxygen atom gave discrepancy factors of $R_1 = 0.057$ and $R_2 = 0.081$. The nongroup atoms were then assigned anisotropic temperature factors and the group atoms were assigned individual isotropic temperature factors. Two cycles of least-squares refinement lowered the discrepancy factors to $R_1 = 0.037$ and $R_2 = 0.051$. A further difference Fourier synthesis revealed the positions of all the phenyl hydrogen atoms. The positions of the hydrogen atoms were idealized ($d(\text{C–H}) = 1.08$ Å) and each hydrogen atom was assigned an isotropic temperature factor of 3.0 Å^2. In subsequent structure factor calculations the contributions of these hydrogen atoms were taken into account. The fact that the hydrogen atoms were located and no systematic deviations were observed for the intensities of Friedel pairs led us to discard the possibility that the true space group is C_s^4-*Ia*.

An examination of the values of $|F_o|$ and $|F_c|$ showed that a correction for secondary extinction was necessary and during the last cycles of refinement an extinction parameter of the type suggested by Zachariasen[17] was varied. The final cycle yielded the discrepancy factors $R_1 = 0.03180$ and $R_2 = 0.04223$.

However, an examination of the bond lengths at this point showed that the nitrogen–oxygen bond length (0.90 (2) Å) was unreasonably short for a nitrosyl complex (usually about 1.15 Å). The Ir–N–O bond angle was 138 (2)°. The plot of the thermal ellipsoids at this stage of refinement (see Figure 2) indicated that the nitrogen atom was vibrating excessively in the plane perpendicular to the twofold axis. This suggests that in addition to the oxygen atom the nitrogen atom might also be disordered about the twofold axis as shown in Figure 3. Because of their proximity the two disordered deminitrogen atoms cannot be refined as atoms with half-occupancy by least-squares methods. Therefore in order to obtain a chemically more reasonable model for the nitrosyl group the nitrogen and oxygen atoms were refined as a diatomic group with a variable interatomic distance. To accommodate this model certain changes had to be made in the least-squares refinement program, which will be discussed in more detail elsewhere.[18] Briefly, a diatomic group requires three positional coordinates and two orientation angles to define its position uniquely relative to a crystal-based axial system. The origin of the group was chosen midway between the oxygen and nitrogen atoms and inspection showed that of the three rigid-group orientation angles defined previously,[15,16] δ, ϵ, and η, the value of ϵ could be assigned arbitrarily. The internal-coordinate axis was made coincident with the nitrogen–oxygen vector, and therefore the internal positional coordinates of the nitrogen and oxygen atoms (in ångströms) are, respectively, $(-X, 0, 0)$ and $(X, 0, 0)$. The positional parameter X was varied directly in the least-squares refinement and the appropriate constraints on the parameters and their derivatives were made. The nitrogen and oxygen atoms were assigned isotropic temperature factors and three cycles of least-squares refinement yielded the discrepancy factors $R_1 = 0.03180$ and $R_2 = 0.04229$ and an N–O bond length of 1.00 (2) Å. (These agreement factors are given to more than the usual number of decimals to facilitate comparisons among the various refinement models.) The oxygen atom was then allowed to vibrate anisotropically and two cycles of least-squares refinement gave the discrepancy factors $R_1 = 0.03183$ and $R_2 = 0.04224$ and increased the N–O bond length to 1.03 Å. With these rigid-group models the nitrogen atom refined to a position 0.2 Å from the twofold axis. Predictably, attempts to refine the nitrogen atom anisotropically resulted in nonpositive definite thermal ellipsoids for this atom and large oscillations in the nitrosyl group parameters. The N–O bond length of 1.03 (2) Å is still somewhat shorter than that usually found for nitrosyl ligands, presumably because the rigid-group model does not take into account the anisotropic thermal motion of the nitrogen atom. The positional and

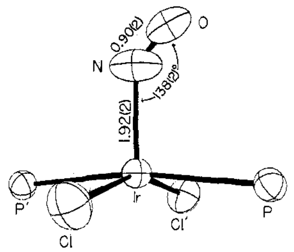

Figure 2.—Inner coordination around the iridium atom when the nitrogen atom is constrained to the twofold axis. This constraint leads to an unsatisfactory geometry. Atoms related by the twofold axis are represented by X and X'.

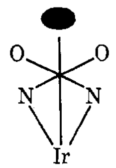

Figure 3.—Diagram showing the postulated disorder for the nitrosyl group about the twofold axis.

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TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $IrCl_2(NO)(P(C_6H_5)_3)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	1/4	0.20863 (6)[b]	0	0.00253 (3)	0.00618 (10)	0.00138 (2)	0	0.00046 (2)	0
Cl	0.1433 (2)	0.1608 (3)	0.0541 (1)	0.0037 (1)	0.0120 (4)	0.0019 (1)	−0.0013 (2)	0.0009 (1)	0.0003 (1)
P	0.3600 (2)	0.1877 (2)	0.0947 (1)	0.0025 (1)	0.0070 (3)	0.0014 (1)	0.0001 (2)	0.0004 (1)	−0.0004 (1)
Group	x_c[c]	y_c	z_c	δ	ϵ	η			
NO	0.2601 (18)	0.4428 (10)	0.0083 (12)	0.800 (29)	0	−0.500 (35)			
R1	0.3395 (3)	0.3577 (4)	0.2154 (2)	−1.933 (4)	−2.846 (3)	2.041 (4)			
R2	0.5502 (3)	0.2933 (4)	0.0875 (1)	0.380 (4)	−3.172 (4)	−0.283 (4)			
R3	0.3707 (2)	−0.1361 (4)	0.1302 (2)	3.069 (5)	−2.413 (3)	−1.790 (5)			

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Standard deviations of the least significant figures are given in parentheses here and in subsequent tables. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers. The angles δ, ϵ, and η (in radians) have been defined previously.[15,16]

TABLE IIa

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

	x	y	z	B, Å^2
		Ring 1		
R1C1	0.3471 (4)	0.2833 (6)	0.1630 (2)	3.0 (2)
R1C2	0.2731 (3)	0.3628 (6)	0.1605 (2)	3.0 (2)
R1C3	0.2655 (3)	0.4373 (6)	0.2129 (3)	3.3 (2)
R1C4	0.3320 (4)	0.4322 (6)	0.2678 (2)	3.7 (2)
R1C5	0.4060 (3)	0.3526 (6)	0.2703 (2)	4.9 (3)
R1C6	0.4135 (3)	0.2782 (6)	0.2179 (3)	4.3 (2)
		Ring 2		
R2C1	0.4691 (3)	0.2430 (6)	0.0904 (3)	2.8 (2)
R2C2	0.5387 (4)	0.1520 (4)	0.0959 (3)	3.3 (2)
R2C3	0.6198 (3)	0.2023 (6)	0.0931 (3)	4.0 (2)
R2C4	0.6313 (3)	0.3436 (7)	0.0847 (3)	4.2 (2)
R2C5	0.5616 (5)	0.4346 (4)	0.0791 (3)	5.0 (3)
R2C6	0.4805 (4)	0.3843 (6)	0.0820 (3)	4.8 (2)
		Ring 3		
R3C1	0.3673 (4)	0.0050 (5)	0.1161 (3)	2.6 (2)
R3C2	0.3827 (4)	−0.0910 (6)	0.0730 (2)	3.9 (2)
R3C3	0.3861 (4)	−0.2320 (6)	0.0871 (3)	4.7 (2)
R3C4	0.3742 (4)	−0.2771 (5)	0.1442 (3)	4.8 (2)
R3C5	0.3588 (4)	−0.1811 (6)	0.1873 (2)	4.7 (3)
R3C6	0.3554 (4)	−0.0401 (6)	0.1733 (2)	3.7 (2)

[a] Cl is attached to P; other carbon atoms are numbered in succession so that C4 is para to C1.

TABLE IIb

DERIVED PARAMETERS FOR NITROSYL GROUP ATOMS

Atom	x	y	z	B, Å^2
N	0.2395 (24)	0.4090 (15)	−0.0067 (17)	3.3 (6)
O	0.2807 (14)	0.4766 (11)	0.0232 (9)	*a*

[a] The oxygen anisotropic thermal parameters: β_{11}, 0.0048 (11); β_{22}, 0.0101 (24); β_{33}, 0.0025 (5); β_{12}, 0.0018 (13); β_{13}, 0.0011 (5); β_{23}, 0.0010 (9).

thermal parameters of the oxygen atom for the rigid-group model agree with those calculated for the independent atom model to within less than one standard deviation.

It is clear from the final values of R_2 that the various models of NO attachment are indistinguishable. Thus from the experimental data available in this instance there is no direct basis for choosing among those Ir–N–O geometries which are in the range Ir–N–O = 138 (2)°, N–O = 0.90 (2) Å to Ir–N–O = 123 (2)°, N–O = 1.03 (2) Å. On the basis of other considerations, mainly commonly accepted values for the N–O bond length, we favor the latter results of the rigid-group model with its off-axis disordered nitrogen atom, but, again, it should be emphasized that this is a *subjective* choice consistent with but not uniquely derived from the experimental observations.

Two other compounds that have been studied recently in this laboratory also show anomalously short N–O bond lengths and have been treated similarly. In each case the N–O bond length increased by approximately 0.2 Å and the final lengths are 1.22 (2) Å for $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ and 1.15 (2) Å for $[Co(NO)(NH_3)_5]Cl_2$.[19] A possible reason why the nitrogen atom does not lie on the twofold axis in $IrCl_2(NO)(P(C_6H_5)_3)_2$ will be discussed below. Fortunately the Ir–N bond length is insensitive to the model chosen to describe the nitrosyl ligand. When the nitrogen atom is placed on the twofold axis, the Ir–N bond length is 1.92 (2) Å; the two rigid-group models give bond lengths of 1.94 (2) Å.

The estimated standard deviation of an observation of unit weight is 0.73 electron, which indicates that the standard deviations of the intensity data were slightly overestimated. Values of $\Sigma w(F_o - F_c)^2$ obtained from the final cycle of least-squares refinement show no dependence on $|F_o|$ or on $\lambda^{-1} \sin \theta$; thus the choice of p of 0.05 is essentially correct. A difference Fourier map based on the final parameters contains no peaks higher than 0.82 (9) e$^-$/Å^3, approximately 12% of the height of a carbon atom peak in this study.

The positional, thermal, and group parameters obtained from the last cycle of least-squares refinement are presented in Table I, along with the associated standard deviations as estimated from the inverse matrix. The positional parameters of the nitrosyl group atoms and the ring carbon atoms, which may be derived from the data in Table I, are presented in Tables IIa and IIb together with their thermal parameters as obtained from the last cycle of least-squares refinement. The final values of $5|F_o|$ and $5|F_c|$ in electrons are given in Table III. Only the 1338 reflections which were used in the refinement are listed in this table. Of the 384 reflections omitted from the refinement, for which $|F_o^2| < 3\sigma(F_o^2)$, none had $|F_o^2 - F_c^2| > 2\sigma(F^2)$. The final value of the extinction parameter is 0.218×10^{-4} electron^{-2}.

Description of Structure

The crystal structure consists of well-separated monomeric units of $IrCl_2(NO)(P(C_6H_5)_3)_2$. In Figure 4 a stereoscopic view of the overall geometry is given and in Figure 5 only the inner coordination about the iridium atom is shown. Principal intermolecular distances and important angles are given in Table IV. The root-mean-square amplitudes along the principal axes of thermal motion for the atoms which were refined anisotropically are shown in Table V. The directions

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(19) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, **10**, 1043 (1971); C. S. Pratt, B. A. Coyle, and J. A. Ibers, submitted for publication.

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×5) IN ELECTRONS FOR $IrCl_2(NO)(P(C_6H_5)_3)_2$

H	K	FO	FC
***** L = 0 *****			
0	0		7965
0	2	1903	2045
0	4	456	440
0	6	310	335
0	8	486	505
1	1	1900	2071
1	3	581	578
1	7	429	409
1	9	418	403
2	0	1687	1648
2	2	688	684
2	4	482	467
2	8	401	405
3	1	1488	1463
3	3	286	289
3	9	312	331
4	0	660	622
4	2	130	145
4	4	298	339
4	6	440	455
5	1	1109	1075
5	3	661	649
5	5	610	609
5	7	192	170
6	0	712	713
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11	3	514	482
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4	9	405	416
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5	4	234	268
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6	7	552	579
7	2	504	463
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7	8	427	401
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9	6	604	576
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9	3	654	671
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3	4	850	855
3	6	461	411
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4	5	801	845
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5	4	888	910
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8	7	627	626
9	2	521	572
9	4	634	589
9	6	484	528
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6	8	362	330
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7	5	352	359
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8	4	316	316
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9	3	251	236
9	5	242	269
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3	8	352	365
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5	4	1060	1114
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5	8	324	313
6	3	610	618
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7	6	840	819
7	8	587	572
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8	5	547	565
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7	3	552	548
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9	3	426	424
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-9	5	209	224
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6	4	361	355
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7	3	410	440
7	5	337	368
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8	2	397	370
8	4	485	510
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9	3	453	461
9	5	309	327
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-8	0	1238	1186
-8	2	701	707
-8	4	601	631
-7	1	942	958
-7	3	580	583
-6	0	1207	1188
-6	2	632	655
-6	4	412	394
-6	8	354	351
-5	1	1031	1012
-5	3	546	549
-4	0	988	1028
-4	2	663	688
-4	4	252	222
-3	1	1026	1047
-3	3	317	315
-3	5	239	217
-2	0	584	645
-2	2	531	560
-2	8	265	275
-1	1	634	631
-1	3	731	732
-1	5	502	508
0	0	1437	1467
0	2	951	928
0	4	636	623
0	8	382	366
1	1	920	950
1	3	630	615
1	5	338	361
2	0	919	904
2	2	707	682
2	4	388	387
2	8	382	398
3	1	925	931
3	3	556	570
4	0	1031	1041
4	2	647	643
4	4	264	275
5	1	982	984
5	3	473	471
5	5	210	227
6	0	728	709
6	2	630	635
6	4	271	289
7	1	596	618
7	3	238	225
8	0	635	630
8	2	523	563
9	1	576	554
9	3	478	481
10	0	625	624
10	2	551	550
10	4	230	234
11	1	520	503
11	3	438	439
12	0	279	283
***** L = 11 *****			
-14	3	427	447
-13	4	492	506
-12	3	479	497
-12	5	526	521
-11	2	513	509
-11	4	756	720
-11	6	553	513
-10	3	594	603
-10	5	701	716
-9	4	667	652
-9	6	488	486
-8	3	457	440
-8	5	608	628
-8	7	639	621
-7	4	471	460
-7	6	370	410
-6	3	553	552
-6	5	358	363
-6	7	472	511
-5	2	507	513
-5	4	609	590
-5	6	617	613
-5	8	398	405
-4	1	362	346
-4	3	735	708
-4	5	515	536
-4	7	310	286
-3	2	915	878
-3	4	879	910
-3	6	663	635
-2	1	364	366
-2	3	732	754
-2	5	893	911
-2	7	470	478
-1	2	551	563
-1	4	742	766
-1	6	694	707
-1	8	424	418
0	3	685	699
0	5	1063	1082
0	7	792	781
1	4	667	667
1	6	700	688
1	8	487	497
2	3	286	279
2	5	441	457
2	7	648	612
3	2	309	302
3	4	488	494
3	6	495	501
4	3	294	280
4	5	343	365
5	2	431	436
5	4	378	383
5	6	543	606
6	1	328	323
6	3	488	485
6	5	621	638
7	2	500	528
7	4	547	530
7	6	513	534
8	1	334	321
8	3	473	489
8	5	664	668
9	4	444	454
10	3	295	304
***** L = 12 *****			
-15	1	266	236
-14	0	522	548
-14	2	411	411
-13	1	580	561
-12	0	785	786
-12	2	461	447
-11	1	893	938
-11	3	631	619
-10	0	909	896
-10	2	703	727
-10	4	458	481
-9	1	761	785
-9	3	667	694
-9	5	259	297
-8	0	596	594
-8	2	676	689
-8	4	348	355
-7	1	198	187
-7	3	344	357
-6	0	346	375
-6	2	480	467
-6	4	380	415
-6	6	299	277
-5	1	773	759
-5	3	451	426
-5	5	219	201
-4	0	1083	1101
-4	2	657	674
-4	4	193	197
-3	1	1466	1463
-3	3	470	464
-3	7	271	268
-2	0	1323	1263
-2	2	875	861
-2	4	258	256
-2	6	325	345
-2	8	398	383
-1	1	1186	1211
-1	3	699	716
0	0	1440	1488
0	2	1034	1009
0	4	352	321
0	8	260	283
1	1	403	400
1	3	705	693
1	5	288	294
2	0	248	257
2	2	717	726
2	4	437	429
3	1	620	608
3	3	481	473
3	5	240	225
4	0	414	403
4	2	523	517
4	4	241	245
5	1	826	843
5	3	361	370
6	0	845	853
6	2	572	577
6	6	263	277
7	1	768	781
7	3	382	384
8	0	926	943
8	2	720	738
8	4	231	218
9	1	597	597
9	3	434	440
10	0	493	507
10	2	406	410
***** L = 13 *****			
-13	2	318	311
-13	4	442	460
-12	1	447	411
-12	3	618	631
-12	5	585	587
-11	2	562	574
-11	4	629	622
-10	3	471	471
-10	5	596	588
-9	4	527	497
-9	6	648	650
-8	5	377	355
-8	7	567	605
-7	4	350	339
-7	6	501	478
-6	5	430	429
-6	7	478	479
-5	4	469	470
-5	6	549	554
-4	1	303	312
-4	3	700	722
-4	5	831	879
-4	7	338	354
-3	2	535	563
-3	4	902	912
-3	6	597	630
-2	1	482	499
-2	3	928	886
-2	5	914	886
-2	7	522	544
-1	2	630	624
-1	4	906	914
-1	6	654	661
0	3	438	423
0	5	559	542
0	7	565	580
1	4	277	291
1	6	574	561
2	5	313	308
2	7	453	494
3	6	540	526
4	3	283	273
4	5	695	672
5	2	373	358
5	4	603	587
5	6	522	521
6	1	397	381
6	3	773	786
6	5	689	704
7	2	452	461
7	4	743	764
8	3	488	473
***** L = 14 *****			
-14	0	708	679
-14	2	377	391
-13	1	726	757
-13	3	339	328
-12	0	1032	980
-12	2	639	613
-11	1	1061	1069
-11	3	347	375
-10	0	741	777
-10	2	502	542
-9	1	494	489
-8	0	386	398
-8	2	280	305
-8	4	262	239
-8	6	243	220
-7	1	219	211
-7	3	314	296
-7	5	510	497
-6	0	868	865
-6	2	443	429
-6	4	437	445
-5	1	962	963
-5	3	447	458
-4	0	1227	1223
-4	2	658	646
-4	4	228	233
-4	6	272	269
-3	1	1198	1210
-3	3	531	549
-3	7	334	349
-2	0	1227	1178
-2	2	1002	992
-2	4	296	314
-1	1	1182	1212
-1	3	560	525
-1	7	263	238
0	0	819	835
0	2	634	623
0	4	238	264
1	1	278	235
1	3	307	305
1	5	368	381
2	0	316	350
2	2	232	259
2	4	264	266
3	1	400	407
3	3	241	254
3	5	450	454
4	0	588	601
4	2	428	421
4	4	414	398
5	1	735	760
5	3	443	451
6	0	924	955
6	2	681	640
6	4	246	223
7	1	829	825
7	3	482	484
8	0	696	660
8	2	579	603
9	1	405	416
***** L = 15 *****			
-12	3	659	653
-11	2	437	420
-11	4	650	650
-10	3	554	557
-10	5	471	486
-9	4	439	418
-7	4	290	307
-7	6	413	410
-6	5	562	577
-5	2	405	375
-5	4	571	599
-5	6	493	499
-4	3	743	738
-4	5	754	765
-4	7	428	409
-3	2	629	631
-3	4	810	808
-3	6	512	520
-2	1	306	289
-2	3	834	847
-2	5	576	583
-2	7	317	319
-1	2	367	365
-1	4	710	763
-1	6	523	526
0	3	357	360
0	5	408	424
1	4	327	333
1	6	412	411
2	3	283	251
2	5	560	533
3	4	397	368
3	6	392	389
4	3	332	334
4	5	565	570
5	2	440	436
5	4	542	534
6	3	566	567
7	2	382	403
***** L = 16 *****			
-13	1	521	537
-12	0	569	541
-12	2	515	543
-11	1	530	501
-11	3	249	236
-10	0	596	647
-10	2	468	475
-9	1	448	447
-9	3	341	352
-8	0	497	507
-8	2	319	324
-8	4	359	347
-7	1	516	573
-7	3	523	598
-7	5	366	385
-6	0	564	594
-6	2	515	490
-6	4	418	420
-5	1	678	710
-5	3	454	466
-4	0	725	740
-4	2	742	747
-4	4	353	363
-3	1	801	750
-3	3	446	440
-2	0	915	913
-2	2	768	806
-1	1	616	652
-1	3	301	292
0	0	240	250
0	2	270	263
1	1	386	404
1	3	470	504
2	0	502	528
2	2	499	504
2	4	453	394
3	1	548	565
3	3	577	580
4	0	637	598
4	2	733	728
4	4	340	348
5	1	571	548
5	3	400	414
6	0	534	512
6	2	534	551
7	1	527	509
***** L = 17 *****			
-10	3	316	358
-9	2	275	280
-9	4	350	378
-8	3	377	383
-8	5	434	430
-7	2	307	326
-7	4	557	568
-6	3	419	379
-6	5	554	553
-5	2	394	370
-5	4	509	518
-5	6	554	559
-4	3	420	430
-4	5	526	483
-3	2	334	326
-3	4	371	376
-3	6	477	487
-2	1	349	346
-2	3	524	518
-2	5	471	465
-1	2	330	260
-1	4	424	412
-1	6	360	375
0	1	409	412
0	3	359	334
0	5	454	405
1	2	369	433
1	4	413	415
2	3	305	258
2	5	536	522
3	4	420	423
4	3	297	331
***** L = 18 *****			
-12	0	473	478
-11	1	370	360
-11	3	245	226
-10	0	693	680
-10	2	307	293
-9	1	640	635
-9	3	342	356
-8	0	644	636
-8	2	458	420
-8	4	267	284
-7	1	839	857
-7	3	478	453
-6	0	564	562
-6	2	649	655
-6	4	237	228
-5	1	396	410
-5	3	351	331
-4	0	444	437
-4	2	535	532
-4	4	327	321
-3	1	291	273
-3	3	352	357
-2	0	589	651
-2	2	361	334
-1	1	618	590
-1	3	343	316
0	0	758	691
0	2	461	433
1	1	1003	1026
1	3	361	375
2	0	824	834
2	2	634	620
3	1	563	545
3	3	274	277
4	0	462	468
4	2	413	464
5	1	281	272
***** L = 19 *****			
-9	2	387	405
-8	3	564	562
-7	2	345	361
-7	4	559	533
-6	3	424	414
-5	4	384	373
-4	5	380	356
-1	4	394	397
0	3	488	471
1	2	458	448
1	4	606	633
2	3	577	546
***** L = 20 *****			
-10	0	624	602
-9	1	739	716
-8	0	832	840
-8	2	665	649
-7	1	682	666
-7	3	237	227
-6	0	493	471
-6	2	412	406
-5	1	287	260
-5	3	269	275
-4	0	397	374
-4	4	344	310
-3	1	403	438
-3	3	373	357
-2	0	529	537
-2	2	305	299
-1	1	589	550
-1	3	295	311
0	0	660	650
0	2	626	672
1	1	689	697
1	3	322	283
2	0	553	531
2	2	521	550
***** L = 21 *****			
-7	2	306	325
-1	2	465	463
0	1	307	281
***** L = 22 *****			
-6	0	368	333
-5	1	337	358
-3	1	296	274

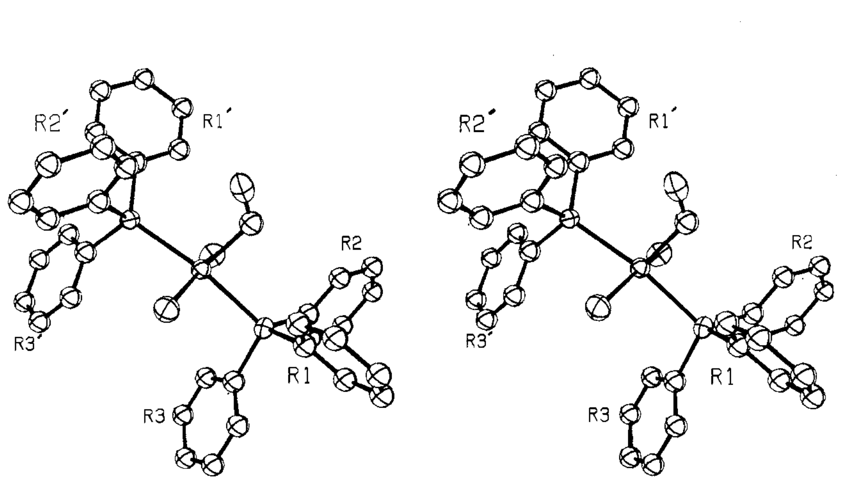

Figure 4.—A stereoscopic view of the molecule $IrCl_2(NO)(P(C_6H_5)_3)_2$. The nitrogen and oxygen atoms related by the twofold axis have been omitted for clarity. The isotropic thermal parameters of the carbon atoms have all been set to 3.0 Å^2. For all other atoms 50% probability ellipsoids are shown.

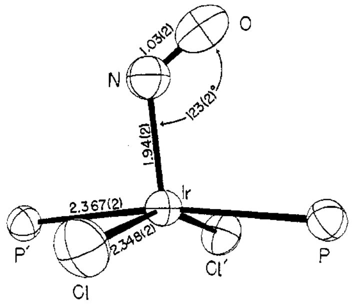

Figure 5.—Inner coordination around the iridium atom when the nitrogen and oxygen atoms are refined as a group and the nitrogen atom is not constrained to the twofold axis. This is the preferred model.

TABLE IV

SELECTED DISTANCES AND ANGLES[a]

Intramolecular distances, Å		Angles, deg	
Ir–Cl	2.348 (2)	N–Ir–P	100.5 (10)
Ir–P	2.367 (2)	N–Ir–P′	89.3 (10)
Ir–N	1.94 (2)	N–Ir–Cl	100.1 (10)
Ir–O	2.65 (1)	N–Ir–Cl′	102.5 (10)
N–O	1.03 (2)	P–Ir–P′	170.2 (1)
N–P	3.32 (3)	P–Ir–Cl	90.0 (1)
N–P′	3.04 (3)	P–Ir–Cl′	88.1 (1)
N–Cl	3.30 (3)	Cl–Ir–Cl′	157.4 (1)
N–Cl′	3.35 (3)	Ir–N–O	123.4 (20)
P–P′	4.717 (5)	Ir-P–R1C1	118.4 (2)
P–Cl	3.334 (4)	Ir–P–R2C1	115.0 (2)
P–Cl′	3.278 (3)	Ir–P–R3C1	107.2 (2)
Cl–Cl′	4.605 (5)	R1C1–P–R2C1	101.6 (3)
P–RC1 (av of 3)	1.824 (7)	R1C1–P–R3C1	106.7 (3)
Ir–R1H2	3.2[b]	R2C1–P–R3C1	107.2 (3)
Ir–R3H2	3.4		
O–R2H6	2.3[b]	Intermolecular distances, Å	
O–R1H2	2.7	O–R2H4	2.5[b]
		R1H3–R3H6	2.2[b]

[a] X and X′ represent atoms related by the twofold axis of symmetry. [b] These distances represent the closest contacts.

TABLE V

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a]

Atom	Min	Intermed	Max
Ir	0.170 (1)	0.173 (1)	0.178 (1)
Cl	0.184 (4)	0.215 (4)	0.249 (4)
P	0.167 (4)	0.171 (4)	0.195 (4)
O	0.19 (4)	0.23 (3)	0.27 (3)

[a] Measured along the principal axes of the thermal ellipsoids.

of the principal axes can be discerned at least approximately from the figures. Corrections of the bond lengths for the approximate effects of thermal motion affect very little the differences among these bond lengths.[20]

The packing is largely dictated by the intermolecular contacts among the bulky triphenylphosphine ligands. This may be emphasized by comparing this structure with those of $ReNCl_2(P(C_6H_5)_3)_2$[21] and $OsCl_3(NH_3)(P(C_6H_5)_3)_2$,[22] which crystallize in the same space group in cells of very similar dimensions (Table VI). In these structures the orientations of the phenyl rings are only slightly different and the volumes occupied per triphenylphosphine group are very similar (and only about 15% larger than that of triphenylphosphine itself[23]).

TABLE VI

CELL CONSTANTS AND VOLUMES PER TRIPHENYLPHOSPHINE GROUP

	a, Å	*b*, Å	*c*, Å	*β*	Vol/ $P(C_6H_5)_3$, $Å^3$
$OsCl_3(NH_3)$-$(P(C_6H_5)_3)_2$	15.85	9.52	22.43	102° 51′	412
$ReNCl_2$-$(P(C_6H_5)_3)_2$	15.71	9.53	22.17	103° 26′	404
$IrCl_2(NO)$-$(P(C_6H_5)_3)_2$	15.85	9.62	22.05	104° 36′	407

The molecule lies on a twofold axis of symmetry which results in the nitrosyl group being disordered. The immediate coordination around the iridium atom is perhaps best described as distorted square pyramidal, with symmetry-related chlorine and phosphorus atoms lying in the basal plane and the nitrogen atom occupying the apical position. The metal–nitrogen–oxygen bond angle is 123 (2)°. (Refer to the discussion in the previous section.) Therefore the geometry is very similar to that found for the related iridium complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$[1,2] (X = Cl or I). Perhaps the most striking difference between the two classes of compounds is the fact that in the carbonyl–nitrosyl complexes and in the ruthenium complex $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]$[24] the nitrosyl moiety lies approximately in the X–metal–carbonyl (or nitrosyl for the ruthenium complex) plane (X = Cl or I). However, for $IrCl_2(NO)(P(C_6H_5)_3)_2$ the nitrosyl group lies approximately in the P–Ir–P plane. This difference does not appear to be steric in origin, because the orientations of the phenyl rings in all compounds are approximately the same. It is possible that in the nitrosyl–carbonyl and dinitrosyl complexes the observed orientation of the nitrosyl group results from a weak bonding interaction between the two oxygen atoms, as suggested by Pierpont, *et al.*[24] It may also be significant that in these four complexes the NO^- group lies in the plane containing the ligands of strongest π-bonding ability. In $IrCl_2(NO)(P(C_6H_5)_3)_2$ the N atom lies 0.2 Å from the twofold axis, which may be the result of nonbonded interactions between the oxygen atom and hydrogen atoms of the triphenylphosphine groups. One such contact is only 2.3 Å, considerably shorter than the sum of the van der Waals radii (2.7 Å).[25] Presumably nonbonded repulsions are decreased more effectively by displacing the nitrogen atom from the twofold axis than by keeping the nitrogen atom on axis and increasing the iridium–nitrogen–oxygen bond angle.

Table VII compares important bond lengths and angles for a closely related series of square-pyramidal triphenylphosphine complexes. As the metal–axial nitrogen bond length decreases the Cl–M–B (B = Cl, CO, or NO) bond angle shows larger distortions from the 180° expected for an ideal square pyramid. We believe that this distortion minimizes the nonbonded repulsions between the axial nitrogen atom and the basal ligands Cl and B. Similar arguments have been presented[26] to rationalize the distortions observed for a series of rhenium- and osmium–nitrido, –ammine, –imino complexes. Table VII also indicates that the metal–chlorine bond length increases with increased distortion. The P–

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[20] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

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

[22] D. Bright and J. A. Ibers, *ibid.*, **8**, 1078 (1969).

[23] J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

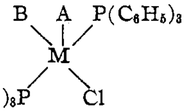
[24] C. G. Pierpont, D. G. van der Veer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4760 (1970).

[25] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

[26] D. Bright and J. A. Ibers, *Inorg. Chem.*, **8**, 709 (1969).

TABLE VII

IMPORTANT BOND LENGTHS AND ANGLES FOR SOME SQUARE-PYRAMIDAL TRIPHENYLPHOSPHINE COMPLEXES $MBClA(P(C_6H_5)_3)_2$ (M = Re, Ru, OR Ir; B = BASAL LIGAND = CO, Cl, OR NO; A = AXIAL LIGAND = N OR NO)



	$ReNCl_2$-$(P(C_6H_5)_3)_2$[a]	$[RuCl(NO)_2$-$(P(C_6H_5)_3)_2][PF_6]$[b]	$IrCl_2(NO)$-$(P(C_6H_5)_3)_2$[c]	$[IrCl(NO)(CO)$-$(P(C_6H_5)_3)_2][BF_4]$[d]
M	Re	Ru	Ir	Ir
A	N	NO	NO	NO
B	Cl	NO	Cl	CO
M–N, Å	1.60 (1)	1.82 (2)[e]	1.94 (2)	1.97 (1)
M–Cl, Å	2.377 (2)	2.366 (5)	2.348 (2)	2.343 (3)
M–P, Å	2.448 (2)	2.430 (5)	2.367 (2)	2.408 (3)
P–M–P, deg	163.1 (1)	159.3 (2)	170.2 (1)	175.7 (1)
B–M–Cl, deg	140.6 (1)	154.3 (6)	157.4 (1)	161.3 (3)
M–N–O, deg		135 (2)[f]	123 (2)	124 (1)
N–P, Å	3.12 (1)	3.35, 3.23	3.32 (3), 3.04 (3)	3.11 (1), 3.15 (1)
N–Cl, Å	3.28 (1)	3.29	3.30 (3), 3.35 (3)	3.35 (1)

[a] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). [b] Reference 24. [c] Present work. [d] Reference 1. [e] This is the Ru–N(axial) distance. [f] This is the Ru–N(axial)–O angle.

M–P bond angles, which are always closer to 180° than the corresponding Cl–M–B angles, do not appear to be influenced by nonbonded repulsions to the same extent. The P–M–P bond angles do not follow exactly the same trend as the Cl–M–B angles and the M–P bond lengths do not bear any relation to the P–M–P bond angles. We suggest that the M–P bond lengths depend markedly in this series of compounds on the π-accepting capabilities of the other ligands attached to the metal. For these ligands the following order of π-accepting ability seems reasonable: $N \gg NO^+ > CO > NO^- > Cl$. Because the phosphines are competing with these ligands for the filled metal orbitals of π symmetry, one would expect the following order of M–P bond lengths: $ReNCl_2(P(C_6H_5)_3)_2 > [RuCl(NO^+)(NO^-)(P(C_6H_5)_3)_2][PF_6] > [IrCl(NO^-)(CO)(P(C_6H_5)_3)_2][BF_4] > IrCl_2(NO^-)(P(C_6H_5)_3)_2$, which is the observed order.

The metal–nitrogen bond length in $IrCl_2(NO)(P(C_6H_5)_3)_2$, 1.94 (2) Å, lies between those found for $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl, Ir–N = 1.97 (2) Å;[1] X = I, Ir–N = 1.89 (3) Å).[2] The iridium–nitrogen bond length is clearly in the range found for $Ir–NO^-$ complexes but is much longer than that found for the $Ir–NO^+$ complexes $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ (Ir–N = 1.77 (1) Å)[27] and $Ir(NO)(P(C_6H_5)_3)_3$ (Ir–N = 1.67 (2) Å)[28] and for other second- and third-row transition metal–NO^+ complexes (see Table VI of ref 1).

Discussion

Most transition metal–nitrosyl complexes studied show properties similar to those of analogous carbonyl complexes. For example, $Fe(CO)_5$[29] and $Mn(NO)(CO)_4$[30] both have trigonal-bipyramidal geometries and the metal–carbon–oxygen and metal–nitrogen–oxygen bond angles are approximately 180°. These similarities have been rationalized by the suggestion that the nitrosyl ligand is coordinated as NO^+, which is isoelectronic with carbon monoxide.[31] More precisely one could say that the isoelectronic series of ligands CO, NO^+, N_2, and CN^- coordinate in a similar manner because they have the same electronic configuration, *i.e.*, $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p_x,2p_y})^4(\sigma_{2p_z})^2$.[32-34] The bonding orbital of highest energy has σ symmetry, and metal–ligand bond formation using this orbital is energetically preferred.

This structural determination and others which have reported previously[1-4,24] show that nitric oxide may also coordinate as NO^-, which is isoelectronic with O_2. However the mode of coordination of the NO^- ligand is quite different from that of the oxygen molecule which, in iridium– and rhodium–tertiary phosphine complexes, has been shown to coordinate in a π-bonded manner.[15,35]

Griffith[36] has argued that the oxygen molecule coordinates to transition metals in a π-bonded manner because the bonding π orbitals ($\pi_{2p_x,2p_y}$) are of higher energy than the σ_{2p_z} bonding orbital; *i.e.*, the electronic configuration of the oxygen molecule is $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2ps}{}^*)^2(\sigma_{2p_z})^2(\pi_{2p_x,2p_y})^4(\pi^*{}_{2p_x,2p_y})^2$. However, for the NO^- ligand a σ-bonding orbital is of higher energy than the π-bonding orbitals; *i.e.*, the electronic configuration is $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p_x,2p_y})^4(\sigma_{2pz})^2(\pi^*{}_{2p_x,2p_y})^2$ and therefore the NO^- ligand is expected to utilize its σ orbitals in coordinating to a metal. Griffith[36] has also shown that the σ orbitals for the oxygen molecule in its valence state (and presumably also for NO^-) have the same form as filled sp^2 hybrid orbitals on the oxygen atom. Valence-bond theory (see Introduction) also predicts that the NO^- ligand will coordinate through an sp^2 hybrid orbital and give a metal–nitrogen–oxygen bond angle of 120°, which of course is that found experimentally.

Molecular orbital theory also helps us understand why nitric oxide and oxygen are able to form complexes with electrons localized mainly in ligand antibonding orbitals (*e.g.*, NO^-, O_2,[15,35] O_2^-,[37] and O_2^{2-} [38]) whereas CO, N_2, and CN^- do not form coordinated reduced species with transition metals. The formation of

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NO^-, O_2^-, and O_2^{2-} complexes results because the $\pi^*_{2p_x,2p_y}$ orbital is of much lower energy for NO and O_2 than for CO, CN^-, and N_2.[32,33,34] For CO, CN^-, and N_2 these orbitals are of higher energy than metal d orbitals. (See ref 39–41 for molecular orbital calculations which support this suggestion.) However for NO and O_2 the $\pi^*_{2p_x,2p_y}$ orbitals are of approximately the same energies as metal d orbitals and in some cases are preferentially occupied with respect to the higher energy metal d orbitals. For example the molecular orbital energy level diagram for $Fe(CN)_5(NO)^{2-}$ shows the following energy level order: $d_{xz},d_{yz} < d_{xy} < \pi^*(NO) < d_{x^2-y^2} < d_{z^2} < \pi^*(CN^-)$.[41]

By analogy with the molecular orbital scheme for $Fe(CN)_5(NO)^{2-}$ we suggest than in the complexes $MX(NO)(CO)(P(C_6H_5)_3)_2^+$ (M = Ir, X = Cl or I; M = Ru, X = Cl) and $IrCl_2(NO)(P(C_6H_5)_3)_2$ the electronic configuration is $(d_{xz})^2(d_{yz})^2(d_{xy})^2(\pi^*(NO))^2$. Therefore as two electrons are localized mainly in $\pi^*(NO)$ orbitals, the complex is formally one of NO^- with iridium(III). This formulation is identical with that given previously in terms of valence-bond theory.[1]

Both approaches to the bonding in these complexes lead to the suggestion that the geometries of the nitrosyl complexes ought to bear a closer relationship to other d^6 complexes rather than to d^8 complexes. The crystal structures of four other five-coordinate d^6 triphenylphosphine complexes have been reported. Two of these, $RuCl_2(P(C_6H_5)_3)_3$[42] and $RhI_2(CH_3)(P(C_6H_5)_3)_2$,[43] have square-pyramidal geometries and the other two, $RuHCl(P(C_6H_5)_3)_3$[44] and $RhHCl(SiCl_3)(P(C_6H_5)_3)_2$,[45] are so distorted, presumably because of the minimal steric requirements of the hydrido ligands, that it is impossible to characterize their geometries as either square pyramidal or trigonal bipyramidal. In contrast, five-coordinate d^8 complexes of the second- and third-row transition elements have trigonal-bipyramidal geometries, *e.g.*, $IrCl(CO)_2(P(C_6H_5)_3)_2$[46] (which is isoelectronic with $IrCl(NO)(CO)(P(C_6H_5)_3)_2^+$), $Os(CO)_3(P(C_6H_5)_3)_2$,[47] $IrCl(CO)(O_2)(P(C_6H_5)_3)_2$,[15] and $IrBr(CO)(TCNE)(P(C_6H_5)_3)_2$[48] (TCNE = tetracyanoethylene). Therefore the square-pyramidal geometries of the nitrosyl complexes are consistent with their formulation as d^6 complexes. It is of interest to note that Pearson[49] has predicted on the basis of second-order Jahn–Teller arguments that the square-pyramidal geometry ought to be more stable than the trigonal-bipyramidal geometry for low-spin d^6 complexes of the type ML_5. Of course the d^6 phosphine complexes discussed above have lower symmetry than those considered by Pearson and therefore the symmetry arguments are no longer strictly valid.

Recent X-ray structural studies, including this one, have shown that the coordination of nitric oxide as NO^- is more common than previously thought. Further structural studies of iridium–nitrosyl complexes are in progress with the view of gaining a clearer understanding of the conditions which favor the coordination as NO^- as opposed to NO^+.

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