reveals a difference in the number of bonds in the π-pentadienyl system which will overlap in the two cases. In the observed conformation there are three bonds which overlap, while in the centrosymmetric case, only two bonds are overlapped. If the bonding in these systems involves appreciable inter-ring overlap, then the observed conformation is preferred. Therefore, the present structure gives the first indication that an interaction between two π systems may be important and may control the observed configuration. However, the effect of packing forces cannot be ascertained although the centrosymmetric structure would have been predicted *a priori*. Nevertheless, the Fe–ring distance of 1.57 Å is slightly shorter than the predicted value of 1.60 Å,[2] in support of an inter-ring interaction. Clearly, the nature of the bonding in bis(cyclohexadienyl)metal and ferrocene systems is not well understood and additional studies must be carried out.

A second important point is the question of whether substituent groups on π systems should bend inward or outward. Inspection of the deviations in Table IV indicates that the substituents on the planar four-membered system C(1), C(2), C(4), and C(5) are all bent toward the iron atom. Similar displacements of the hydrogen atoms are found in *N*-formylaminomethylferrocene;[16] in diacetylferrocene,[6] one methyl group and one oxygen atom on the opposite rings are displaced toward the metal atom, and in $C_6H_7Mn(CO)_3$,[1] two of the three hydrogen atoms are displaced toward the metal atom. In contrast, the chlorine atoms in decachlororuthenocene[17] are all displaced away from the center of the rings so that the Cl···Cl distances are larger than anticipated for van der Waals contacts. These observations together with a consideration of the orientation of the rings, *vide supra*, suggest that interligand interactions may be important and will influence both the orientation of the rings as well as the planarity of groups on the π system.

The three cyclohexadienyl complexes whose structures have been determined[1-3] all have a broad C–H stretch in the region of 2730–2830 cm^{-1}. This band has been assigned to the exo hydrogen atom on the tetrahedral carbon atom in the cyclohexadienyl ring. The present compound does not have a C–H stretch in this region; therefore, the *tert*-butyl group was assumed to be exo, with the hydrogen atom in the endo position.[18] This suggestion has been verified in the present study. Therefore, the presence of this absorption band is indeed a useful diagnostic tool for the conformation at the saturated carbon atom. Furthermore, the exo orientation of the *tert*-butyl group is easily rationalized on the basis of steric repulsions between groups on the two rings. The shortest intermolecular forces were surveyed and did not indicate any unusual interactions. With the lack of hydrogen bonding or other similar attractive force, the molecular packing is governed by van der Waals forces.

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[16] L. H. Hall and G. M. Brown, *Acta Crystallogr., Sect. B*, **27**, 81 (1971).

[17] G. M. Brown, F. L. Hedberg, and H. Rosenberg, *Chem. Commun.*, 5 (1972).

[18] J. F. Helling and D. M. Braitsch, *J. Amer. Chem.*, **92**, 7209 (1970).

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The Crystal and Molecular Structure of Nitrosylcarbonylbis(triphenylphosphine)iridium, $Ir(NO)(CO)(P(C_6H_5)_3)_2$

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The structure of nitrosylcarbonylbis(triphenylphosphine)iridium, $Ir(NO)(CO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 11.271$ (3) Å, $b = 18.036$ (6) Å, $c = 18.240$ (6) Å, and $\beta = 119.23$ (2)°. The observed and calculated densities are 1.55 (±0.02) and 1.59 g cm^{-3}, respectively. Least-squares refinement has led to a final value of the conventional R factor (on F) of 0.030 for the 2946 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well-separated molecules, and the coordination around the iridium atom is distorted tetrahedral. Structural parameters describing this geometry are the P–Ir–P angle of 103.9 (1)°, the N–Ir–C angle of 128.8 (2)°, and the dihedral angle between the P–Ir–P and N–Ir–C planes of 84.3 (2)°. The nitrosyl ligand is coordinated to the metal in a nearly linear fashion, with an Ir–N bond length of 1.787 (8) Å and an Ir–N–O bond angle of 174.1 (7)°. The compound is therefore formulated as an NO^+ complex of iridium(−I). Other important bond distances in the molecule are as follows (Å): Ir–P, 2.323 (2), 2.324 (2); Ir–C, 1.873 (11); C–O, 1.144 (11); and N–O, 1.180 (9).

Introduction

In recent years, five- and six-coordinate nitrosyl complexes of the transition metals have been well described.[1] Two distinct modes of coordination of the nitrosyl ligand have been identified. In the first, the nitrosyl is formally coordinated as NO^+, while in the second it may be described as NO^-. A structural difference is associated with these two types of coordination. The NO^+ species has a formal triple bond with sp hybridization; it is therefore linearly coordinated to the metal. The NO^- ligand, however,

[1] For a recent review of monomeric transition metal nitrosyl complexes see B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci. Inorg. Chem., Ser. One, 1972.*

has a formal double bond with sp^2 hybridization, and an angle of close to 120° is found for the metal–N–O grouping. It has been observed that the metal–nitrogen bond distance in a typical NO^+ complex is 0.1–0.2 Å shorter than that found in a typical NO^- complex, implying a higher degree of multiple bond formation arising from the overlap of the filled d orbitals on the metal with the π^*-antibonding orbitals of the nitrosyl. On the basis of molecular orbital arguments, it has been suggested[2] that metals in low or high oxidation states will tend to coordinate nitric oxide as NO^+, while those in intermediate oxidation states will show NO^- coordination.

The four-coordinate nitrosyl complexes are less well understood. A summary of the structural analyses[1] of these complexes shows that all four-coordinate nitrosyls studied so far have approximately linear metal–nitrosyl linkages, although the deviations from linearity are generally larger than those observed for five- and six-coordinate species. The geometries of the four-coordinate complexes tend to be severely distorted. The coordination in $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ is basically tetrahedral,[3] but the angle N–Ni–N is 129°. The $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$ cation, prepared by Angoletta,[4,5] was formulated as an Ir^{-I}–$(NO^+)_2$ species. The coordination of this d^{10} cation would be expected to be tetrahedral, while if the correct formulation were Ir^{I}–$(NO^+)(NO^-)$, a d^8 square-planar geometry should result. The X-ray structure determination[6] of this complex shows such large distortions from tetrahedral coordination, including a N–Ir–N angle of 154°, that an unambiguous determination of the oxidation state of the metal is not possible. This large angle is especially surprising since the C–Pt–C bond angle in the structure of the isoelectronic molecule $Pt(CO)_2(P(C_2H_5)(C_6H_5)_2)_2$[7] is 117°. In this paper we report the structure of a third complex in this series, $Ir(NO)(CO)(P(C_6H_5)_3)_2$. This complex is isoelectronic with the iridium dinitrosyl and the platinum dicarbonyl complexes. By comparing the structures of these three complexes, we hoped to assess the significance of the very large N–Ir–N angle in the iridium cation, and to understand more about the effect of the nitrosyl ligand on the coordination geometry of four-coordinate complexes.

Collection and Reduction of Intensity Data

Orange, well-formed crystals of $Ir(NO)(CO)(P(C_6H_5)_3)_2$ were kindly supplied by Dr. W. Roper. Preliminary precession photographs using Cu Kα radiation showed Laue symmetry $2/m$, indicating that the crystals belong to the monoclinic system. The extinctions observed, $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, are uniquely consistent with the space group C_{2h}^5-$P2_1/c$.

The eight faces of the crystal selected for data collection were identified by optical goniometry as belonging to the {010}, {10$\bar{2}$}, and {110} forms, the distance between centrosymmetrically related faces being *ca.* 0.2 mm. In order to minimize multiple diffraction effects,[8] the crystal was mounted with no symmetry axis coincident with the spindle axis.

All measurements were made using a Picker FACS-I computer-controlled four-circle X-ray diffractometer equipped with scintillation counter, pulse-height analyzer, and graphite monochromator. Cell constants and their standard deviations were derived[9] from a least-squares refinement of the setting angles of ten reflections with 2θ values of 19–27° which had been centered on the Mo Kα_1 peak, λ 0.70930 Å. The unit cell parameters at 21° are a = 11.271 (3) Å, b = 18.036 (6) Å, c = 18.240 (6) Å, and β = 119.23 (2)°. The density calculated for four molecules per unit cell is 1.59 g/cm³, which agrees with the experimental value of 1.55 (±0.02) g/cm³ measured by flotation in an aqueous solution of $ZnCl_2$. The mosaicity of the crystal was measured by means of the narrow-source, open-counter, ω-scan technique. At a takeoff angle of 1.1° the three reflections surveyed all had peak widths at half-height of 0.075° or less.

Intensity data were collected as previously described.[9,10] Molybdenum radiation was reflected from the (002) face of a graphite crystal, resulting in an incident beam of monochromatized Mo Kα radiation. The intensities were measured by the θ–2θ scan technique at a takeoff angle of 1.84°. At this angle the intensity of a reflection is about 80% of the maximum value as a function of the takeoff angle. A nonsymmetric scan range in 2θ was used, the scan ranging from 0.7° below the Mo Kα_1 peak center to 0.8° above the Mo Kα_2 peak center; the background was measured at each end of the scan. The data were collected in two shells. For those reflections $0° < 2\theta$ (Mo Kα_1) $\leq 25°$, the scan rate was 1.0°/min with 20 sec background counts; while for the data $25° \leq 2\theta$ (Mo Kα_1) $\leq 42°$, a scan rate of 0.5°/min with 40 sec background counts was used. 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 Mo Kα peak. Five standard reflections from diverse parts of reciprocal space were measured after every 50 reflections to test for crystal decomposition and electronic stability; these varied throughout the data collection by less than 5%.

The intensities of 3644 reflections were measured for the unique quadrant of reciprocal space with $2\theta \leq 42°$; of these, 884 had $I < 3\sigma(I)$ and were omitted from the refinement. Beyond this point, there were very few reflections of significant intensity. All data were processed as previously described;[10] the value of p in the formula for the standard deviations of the corrected intensities was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. The dimensions of the crystal were determined with the use of a micrometer eyepiece attached to a polarizing microscope in preparation for an absorption correction.

Solution and Refinement of Structure

Refinement of the structure was carried out by full-matrix least-squares technique.[11] Throughout the refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where weight w is $4F_o^2/\sigma^2(F_o^2)$. The agreement factors R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The scattering factors for P, O, N, and C were taken from the usual tabulation,[12] while those for Ir were calculated by Cromer and Waber.[13] The hydrogen scattering factors were those of Stewart, *et al.*[14] The effects of anomalous dispersion were taken into account in the structure factor calculations,[15] the values of $\Delta f'$ and $\Delta f''$ for Ir and P being those given by Cromer and Liberman.[16]

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[2] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).

[3] J. H. Enemark, *ibid.*, **10**, 1952 (1971).

[4] M. Angoletta, *Gazz. Chim. Ital.*, **93**, 1591 (1963).

[5] M. Angoletta and G. Caglio, *ibid.*, **93**, 1584 (1963); L. Malatesta, M. Angoletta, and G. Caglio, *Angew. Chem.*, **75**, 1103 (1963).

[6] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).

[7] V. G. Albano, P. L. Bellon, and M. Manassero, *J. Organometal. Chem.*, **35**, 423 (1972).

[8] W. H. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).

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

[10] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[11] In addition to various local programs for the CDC 6400 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, the Busing–Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program. Our local least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program, and Cahen's program AGNOST for absorption corrections includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration.

[12] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, Table 3.3.1.A.

[13] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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

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

TABLE I

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

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.21537 (3)[b]	0.22761 (2)	0.18316 (2)	0.01199 (4)	0.00244 (1)	0.00344 (2)	0.00089 (2)	0.00415 (2)	0.00049 (1)
P(1)	0.29008 (19)	0.15729 (11)	0.10684 (12)	0.00784 (23)	0.00233 (7)	0.00276 (9)	0.00003 (10)	0.00224 (12)	0.00005 (6)
P(2)	0.13294 (20)	0.33548 (11)	0.10469 (12)	0.00865 (23)	0.00206 (7)	0.00326 (7)	0.00000 (10)	0.00284 (13)	0.00002 (6)
N	0.3355 (8)	0.2539 (4)	0.2881 (5)	0.0123 (9)	0.0038 (3)	0.0040 (4)	0.0010 (4)	0.0025 (5)	−0.0002 (3)
O(NO)	0.4110 (8)	0.2776 (4)	0.3554 (5)	0.0182 (10)	0.0065 (4)	0.0046 (4)	0.0011 (5)	0.0008 (5)	−0.0004 (3)
C	0.0549 (11)	0.1727 (5)	0.1453 (6)	0.0163 (14)	0.0034 (4)	0.0063 (5)	0.0023 (6)	0.0065 (8)	0.0007 (4)
O(CO)	−0.0411 (8)	0.1380 (4)	0.1247 (6)	0.0173 (11)	0.0055 (4)	0.0131 (7)	−0.0022 (5)	0.0096 (7)	−0.0002 (4)

Group	x_c	y_c	z_c	δ[c]	ϵ	η
R(11)	0.5751 (3)	0.2103 (2)	0.1235 (2)	−0.722 (8)	−1.980 (3)	−1.080 (8)
R(12)	0.0583 (3)	0.1406 (2)	−0.0862 (2)	−0.391 (3)	2.642 (3)	−2.314 (4)
R(13)	0.3836 (3)	−0.0090 (2)	0.1760 (2)	−2.773 (15)	1.806 (3)	1.543 (15)
R(21)	−0.1928 (3)	0.3422 (2)	−0.0105 (2)	0.042 (3)	−2.630 (3)	−3.009 (4)
R(22)	0.2072 (3)	0.4778 (2)	0.2261 (2)	2.823 (6)	−2.185 (3)	1.531 (6)
R(23)	0.2411 (3)	0.3813 (2)	−0.0237 (2)	−1.751 (3)	−2.810 (3)	−1.868 (3)

[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] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the group with a fixed external coordinate system are those previously described.[17,18]

The coordinates of the iridium atom were found from a three-dimensional Patterson function, the iridium atom occupying a general fourfold position in $P2_1/c$. After one cycle of refinement of the scale factor and the iridium coordinates and temperature factor, the discrepancy factors R_1 and R_2 were 0.29 and 0.37, respectively. Based on a subsequent structure factor calculation, a difference Fourier synthesis was computed which revealed the positions of the phosphorus atoms and four of the phenyl rings. These rings were treated as rigid groups of D_{6h} symmetry, d(C–C) = 1.397 Å,[17,18] in subsequent least-squares cycles. They were assigned group temperature factors, while the nongroup atoms were refined with individual isotropic thermal parameters. On a second difference Fourier synthesis all other atoms except the carbon of the carbonyl group were located; refinement of these positions led to R_1 and R_2 values of 0.066 and 0.089. In the next least-squares cycle the iridium atom was allowed to vibrate anisotropically, while the missing carbon atom was given coordinates corresponding to a chemically reasonable position. Convergence was reached after two more cycles of isotropic refinement to give agreement factors of 0.038 and 0.051.

At this point the data were corrected for absorption and decomposition. The linear absorption coefficient of the compound for Mo Kα radiation is 45.1 cm^{-1} based on the μ/ρ values given by Cromer and Liberman;[16] the resultant transmission factors ranged from 0.443 to 0.540. A plot of the intensities of the standard reflections showed loss of intensity with time in the second shell. A linear correction corresponding to overall decomposition of 1.64% was applied to the data.

In further refinements, the nongroup atoms were allowed to vibrate anisotropically and the group atoms were given individual isotropic thermal parameters. The hydrogen atom positions around the phenyl rings were idealized (d(C–H) = 1.00 Å) and each hydrogen atom was assigned an isotropic temperature factor 1 Å^2 larger than that of the attached carbon atom. In subsequent structure factor calculations the contributions of these hydrogen atoms were taken into account. The refinement converged to give final agreement factors of 0.030 and 0.036 for the 2760 independent reflections having $I > 3\sigma(I)$.

Inspection of the data showed that no correction for extinction is necessary and a comparison of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based on $|F_o|$, Miller indices, and the scattering angle shows only a slight dependence on the scattering angle. However, the weighted agreement factor did decrease significantly as a function of increasing $|F_o|$ indicating that the value of p in the expression for the standard deviation of the intensity was too high. A new weighting function was derived which removed the dependence of the quantity $\Sigma w \cdot (|F_o| - |F_c|)^2$ on the observed intensity. Subsequent refinement using this new weighting function led to no significant shifts in the atomic parameters, and left the agreement factors unchanged. The error in a reflection of unit weight is 1.2 e. Of the reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, none had $|F_o^2 - F_c^2| > 3.2\sigma(F_o^2)$. The largest peak in the final difference Fourier synthesis has a height of 1.04 e/Å^3, about one-fifth of a carbon peak, and appears to be associated with the iridium anisotropy.

The final least-squares parameters are given in Table I, with the standard deviations of these parameters as derived from the inverse matrix. The parameters of the ring carbon atoms which may be derived from the data in Table I are presented in Table II, together with the thermal parameters as obtained from the last cycle of least-squares refinement. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III; only the re-

TABLE II

DERIVED PARAMETERS FOR RING CARBON ATOMS[a]

Atom	x	y	z	B, A^2
R(11)C(1)	0.4489 (4)	0.1874 (3)	0.1123 (3)	2.8 (1)
R(11)C(2)	0.4796 (4)	0.1788 (3)	0.0472 (2)	3.8 (2)
R(11)C(3)	0.6058 (5)	0.2017 (3)	0.0584 (3)	4.5 (2)
R(11)C(4)	0.7013 (4)	0.2332 (3)	0.1346 (3)	4.7 (2)
R(11)C(5)	0.6705 (4)	0.2418 (3)	0.1997 (2)	4.6 (2)
R(11)C(6)	0.5444 (5)	0.2189 (3)	0.1885 (2)	3.8 (2)
R(12)C(1)	0.1662 (4)	0.1459 (3)	−0.0041 (2)	3.2 (1)
R(12)C(2)	0.0710 (5)	0.0888 (2)	−0.0258 (3)	4.7 (2)
R(12)C(3)	−0.0369 (5)	0.0836 (3)	−0.1079 (3)	5.3 (2)
R(12)C(4)	−0.0496 (4)	0.1354 (3)	−0.1683 (2)	4.6 (2)
R(12)C(5)	0.0455 (5)	0.1924 (3)	−0.1466 (3)	4.3 (2)
R(12)C(6)	0.1534 (4)	0.1977 (2)	−0.0645 (3)	3.5 (2)
R(13)C(1)	0.3375 (5)	0.0620 (2)	0.1443 (3)	3.1 (1)
R(13)C(2)	0.3502 (6)	0.0410 (3)	0.2215 (3)	4.1 (2)
R(13)C(3)	0.3964 (6)	−0.0300 (3)	0.2533 (3)	5.3 (2)
R(13)C(4)	0.4298 (6)	−0.0800 (2)	0.2077 (4)	5.3 (2)
R(13)C(5)	0.4170 (6)	−0.0591 (3)	0.1305 (3)	5.8 (2)
R(13)C(6)	0.3709 (6)	0.0119 (3)	0.0987 (3)	4.5 (2)
R(21)C(1)	−0.0518 (3)	0.3404 (3)	0.0409 (3)	3.2 (1)
R(21)C(2)	−0.1178 (5)	0.2828 (2)	−0.0159 (3)	4.1 (2)
R(21)C(3)	−0.2589 (5)	0.2846 (3)	−0.0674 (3)	4.6 (2)
R(21)C(4)	−0.3339 (3)	0.3440 (3)	−0.0619 (3)	5.2 (2)
R(21)C(5)	−0.2678 (5)	0.4015 (3)	−0.0051 (3)	5.0 (2)
R(21)C(6)	−0.1268 (5)	0.3997 (2)	0.0463 (3)	4.1 (2)
R(22)C(1)	0.1762 (5)	0.4168 (2)	0.1726 (3)	3.3 (2)
R(22)C(2)	0.2140 (5)	0.4840 (3)	0.1519 (3)	3.8 (2)
R(22)C(3)	0.2450 (6)	0.5450 (2)	0.2054 (3)	4.8 (2)
R(22)C(4)	0.2382 (6)	0.5388 (3)	0.2796 (3)	5.3 (2)
R(22)C(5)	0.2005 (6)	0.4716 (3)	0.3003 (3)	6.0 (2)
R(22)C(6)	0.1695 (6)	0.4105 (2)	0.2468 (3)	4.6 (2)
R(23)C(1)	0.1902 (4)	0.3632 (3)	0.0302 (3)	3.0 (1)
R(23)C(2)	0.1012 (3)	0.3836 (3)	−0.0528 (3)	4.0 (2)
R(23)C(3)	0.1521 (5)	0.4016 (3)	−0.1067 (2)	5.1 (2)
R(23)C(4)	0.2920 (5)	0.3993 (3)	−0.0776 (3)	5.4 (2)
R(23)C(5)	0.3810 (4)	0.3789 (3)	0.0055 (3)	4.6 (2)
R(23)C(6)	0.3302 (4)	0.3609 (3)	0.0594 (2)	3.8 (2)

[a] C(1) is attached to P; other C atoms are numbered in succession so that C(4) is para to C(1).

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(17) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(18) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

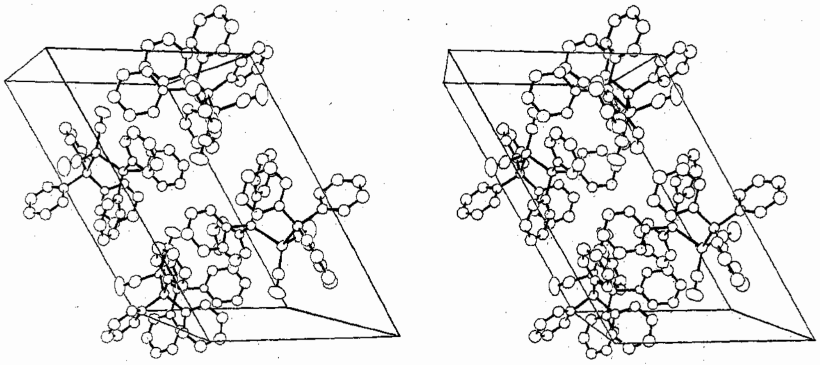

Figure 1.—A stereoscopic view of the unit cell of $Ir(NO)(CO)(P(C_6H_5)_3)_2$. The *a* axis is horizontal, the *c* axis is vertical, and the *b* axis points into the paper. The shapes of the atoms in this and the following drawings represent 50% probability contours of thermal motion. H atoms are omitted for the sake of clarity.

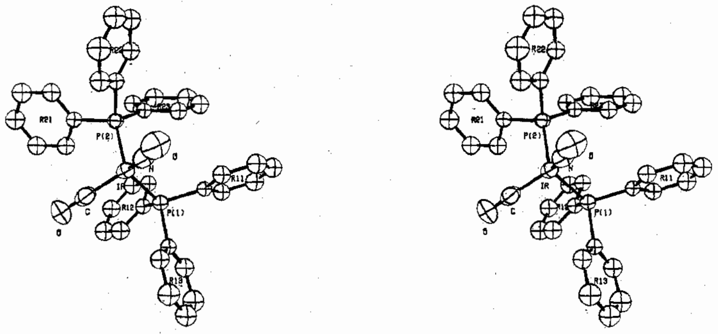

Figure 2.—A stereoscopic view of the molecule $Ir(NO)(CO)(P(C_6H_5)_3)_2$.

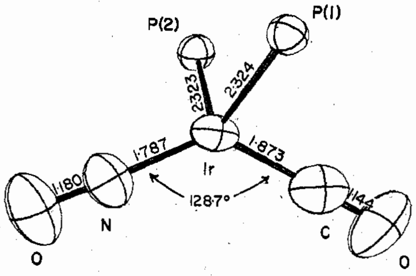

Figure 3.—The inner coordination sphere of the molecule.

flections which were used in the refinement are listed in this table.[19]

Description of the Structure

The crystal structure consists of discrete, well-separated units of $Ir(NO)(CO)(P(C_6H_5)_3)_2$. The shortest iridium–iridium contact is 9.156 (3) Å, and there are no hydrogen–hydrogen contacts less than 2.4 Å. The molecular packing is dominated by the bulky triphenylphosphine groups, and is illustrated in Figure 1.

The overall geometry of the individual molecule is shown in Figure 2, while the inner coordination sphere is given in Figure 3. Principal distances and angles and their standard deviations are given in Table IV. These bond distances may be corrected for thermal motion using the "riding" and "independent" models of Busing and Levy;[20] however, differences between bond lengths remain essentially the same when either of these corrections is applied. The root-mean-square amplitudes of vibration along the principal

TABLE IV
SELECTED DISTANCES (Å) AND ANGLES (DEG) IN $Ir(NO)(CO)(P(C_6H_5)_3)_2$

Ir–Ir	9.156 (3)	P(1)–Ir–P(2)	103.9 (1)
Ir–P(1)	2.324 (2)	P(1)–Ir–N	118.7 (2)
Ir–P(2)	2.323 (2)	P(2)–Ir–N	107.7 (2)
Ir–N	1.787 (8)	Ir–N–O	174.1 (7)
Ir–O(NO)	2.963 (7)	P(1)–Ir–C	93.3 (3)
N–O	1.180 (9)	P(2)–Ir–C	101.1 (3)
Ir–C	1.873 (11)	Ir–C–O	177.8 (9)
Ir–O(CO)	3.016 (8)	N–Ir–C	128.7 (4)
C–O	1.144 (11)	P(1)–Ir–O(NO)	120.1 (2)
P(1)–R(11)C(1)	1.826 (6)	P(2)–Ir–O(NO)	105.4 (2)
P(1)–R(12)C(1)	1.824 (9)	P(1)–Ir–O(CO)	93.5 (2)
P(1)–R(13)C(1)	1.830 (6)	P(2)–Ir–O(CO)	101.8 (2)
P(2)–R(21)C(1)	1.825 (9)	O(NO)–Ir–O(CO)	128.8 (2)
P(2)–R(22)C(1)	1.826 (7)	Ir–P(1)–R(11)C(1)	116.0 (2)
P(2)–R(23)C(1)	1.836 (4)	Ir–P(1)–R(12)C(1)	114.9 (2)
P(1)–N	3.547 (8)	Ir–P(1)–R(13)C(1)	114.5 (2)
P(1)–C	3.067 (10)	R(11)C(1)–P(1)–R(12)C(1)	107.0 (2)
P(2)–N	3.333 (8)	R(11)C(1)–P(1)–R(13)C(1)	99.1 (3)
P(2)–C	3.253 (10)	R(12)C(1)–P(1)–R(13)C(1)	103.5 (3)
P(1)–P(2)	3.661 (3)	Ir–P(2)–R(21)C(1)	115.0 (2)
P(1)–O(NO)	4.592 (8)	Ir–P(2)–R(22)C(1)	111.1 (2)
P(1)–O(CO)	3.918 (8)	Ir–P(2)–R(23)C(1)	120.3 (2)
P(2)–O(NO)	4.221 (8)	R(21)C(1)–P(2)–R(22)C(1)	103.7 (3)
P(2)–O(CO)	4.168 (8)	R(21)C(1)–P(2)–R(23)C(1)	102.6 (3)
C–N	3.300 (14)	R(22)C(1)–P(2)–R(23)C(1)	102.1 (3)
C–O(NO)	4.399 (14)		
N–O(CO)	4.350 (11)		

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

Atom	Min	Intermediate	Max
Ir	0.1796 (6)	0.1945 (6)	0.2509 (5)
P(1)	0.188 (3)	0.196 (3)	0.197 (3)
P(2)	0.184 (3)	0.196 (3)	0.208 (3)
N	0.222 (10)	0.233 (10)	0.283 (10)
O(NO)	0.225 (10)	0.316 (9)	0.379 (10)
C	0.206 (14)	0.248 (13)	0.311
O(CO)	0.230 (10)	0.321 (10)	0.411 (10)

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[19] A listing of structure factor amplitudes (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2812. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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

TABLE VI

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) FOR SOME ISOELECTRONIC FOUR-COORDINATE TETRAHEDRAL COMPLEXES

	M–P	M–N, M–C	M–N–O	N(C)–M–N(C)	P–M–P	P–M–N(C)
$Fe(NO)_2(F_6\text{-fos})$[a]	2.240 (2), 2.248 (2)	1.661 (7), 1.645 (7)	177.8 (7), 176.9 (7)	125.4 (4)	86.8 (1)	104.5 (3), 114.7 (3) 112.9 (3), 105.8 (3)
$Co(NO)(CO)(P(C_6H_5)_3)_2$[b]	2.233 (av)	1.71[c]	175	121	114	104, 108
$Co(NO)(CO)_2(P(C_6H_5)_3)$[b]	2.244	1.71, 1.76, 1.73[d]	178, 179, 179	113, 116, 111		105, 106, 104
$Ni(N_3)(NO)(P(C_6H_5)_3)_2$[e]	2.257 (2), 2.306 (2)	1.686 (7)	152.7 (7)	128.8 (3)	120.5 (1)	101.1 (2), 110.4 (2)
$Ni(NO)(tep)$[f]	2.208	1.579	180		93.5	122.8
$[Ir(NO)_2(P(C_6H_5)_3)_2]^+$[g]	2.339 (3)	1.771 (12)	163.5 (10)	154.2 (7)	116.3 (2)	100.4 (3), 93.2 (3)
$Ir(NO)(CO)(P(C_6H_5)_3)_2$[h]	2.323 (2), 2.324 (2)	1.787 (8), 1.873 (11)	174.1 (7)	128.7 (4)	103.9 (1)	N: 118.7 (2), 107.7 (2) C: 93.3 (3), 101.1 (3)
$Ir(NO)(P(C_6H_5)_3)_3$[i]	2.31 (1)[j]	1.67 (2)	180		101.3 (6)	116.8 (5)
$Pt(CO)_2(P(C_2H_5)(C_6H_5)_2)_2$[k]	2.360 (4)	1.92 (2)	174 (3)	117 (1)	97.9 (2)	105.0 (6), 115.1 (8)
$Pt(CO)(P(C_6H_5)_3)_3$						
Monoclinic form[l]	2.352 (8), 2.333 (8), 2.335 (8)	1.86 (3)	171 (3)		113.7 (3), 110.9 (3), 109.6 (2)	105 (1), 109 (1), 108 (1)
Trigonal form[m]	2.36 (1)[j]	1.84 (2)	180		105.7 (7)	113.0 (1.0)

[a] $F_6\text{-fos} = (C_6H_5)_2PC{=}CP(C_6H_5)(CF_2)_2CF_2$; W. Harrison and J. Trotter, *J. Chem. Soc. A*, 1542 (1971). [b] V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, Abstracts of the 5th Meeting of the Italian Crystallographic Association, Bari, Oct 1971, p 127. [c] Nitrosyl and carbonyl are disordered and indistinguishable. [d] Disordered about a twofold axis. [e] Reference 3. [f] tep = $CH_3C(CH_2P(C_2H_5)_2)_3$; P. G. Eller and P. W. R. Corfield, personal communication. [g] Reference 6. [h] This paper. [i] Reference 23. [j] Average of three independent molecules each with a threefold axis of symmetry. [k] Reference 7. [l] V. G. Albano, P. L. Bellon, and G. H. Basso Ricci, *Inorg. Chem.*, **8**, 2109 (1969). [m] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc. D*, 899 (1969).

axes of thermal motion for the atoms which were refined anisotropically are given in Table V. The directions of the principal axes can be discerned at least approximately from the figures.

As can be seen from the figures, the complex is a distorted tetrahedron. While the P–Ir–P angle of 103.9 (1)° is only slightly smaller than the ideal tetrahedral value of 109.5°, the C–Ir–N angle of 128.7 (4)° is much larger. Presumably this angle is increased in order to alleviate nonbonded repulsions between the carbonyl and nitrosyl groups. An examination of the distances between the phosphorus atoms and the carbon and nitrogen atoms shows that the two phosphorus atoms are 3.33 and 3.55 Å away from the nitrogen atom, while they are only 3.07 and 3.25 Å away from the carbon atom. This asymmetry is reflected in P–Ir–N and P–Ir–C bond angles; the former have values of 118.7 (2) and 107.7 (2)°, while the latter are significantly smaller at 93.3 (3) and 101.1 (3)°. The angle between the nitrogen–carbon vector and the plane defined by the two phosphorus atoms and the iridium atom is 165.3 (2)°, showing that the plane including the phosphorus atoms is effectively tipped 15° toward the carbon from the tetrahedral position. The dihedral angle between the phosphorus–iridium plane and the nitrogen–carbon–iridium plane is 84.3 (2)°, close to the ideal value of 90°.

Although the distortions from the ideal geometry are large, it is nevertheless clear that this complex exhibits tetrahedral rather than square-planar coordination. This conclusion is supported by the observation[6] that distortions in d^{10} tetrahedral complexes are considerably larger than those in d^8 square-planar systems. The compound may therefore be described as an NO^+ complex of Ir(−I), a d^{10} system, rather than as an NO^- complex of Ir(I), which would have a d^8 configuration. This formulation is confirmed by the nearly linear geometry of the Ir–N–O grouping.

The individual bond distances are all normal. The iridium–phosphorus distances of 2.324 (2) and 2.323 (2) Å do not differ significantly and are similar to those found in other four-coordinate complexes of third-row transition metals (see Table VI). Similarly, the iridium–nitrogen and iridium–carbon bond distances of 1.787 (8) and 1.873 (11) Å are in the range of those expected for coordinated nitrosyls and carbonyls. Specifically, metal–nitrogen distances in complexes of NO^+ have been observed in the range 1.56–1.80 Å, while the distances vary from 1.70 to 1.98 Å in NO^- complexes.[1] As expected, the iridium–nitrogen distance is about 0.1 Å shorter than the iridium–carbon distance, reflecting the greater σ–π synergetic interaction of the nitrosyl ligand with the metal. The observation of the expected difference between the two bond distances, together with the reasonable shapes of the thermal ellipsoids of the atoms, suggests that the probability of any disorder between the carbonyl and nitrosyl groups is very small.

The Ir–C–O bond angle is linear to within experimental error, while the Ir–N–O angle of 174.1 (7)° shows a small, but statistically significant, deviation from linearity. Distortions of this magnitude have been observed for other complexes of NO^+.[1]

All angles and distances associated with the rings are in the range of those observed for other triphenylphosphine complexes; there are no unusual interactions between ring carbons or hydrogens and other atoms. The shortest hydrogen–hydrogen contact is 2.396 Å and is between the R(11)H(2) and R(12)H(6) atoms belonging to the same molecule.

Discussion

The complex $Ir(NO)(CO)(P(C_6H_5)_3)_2$ is a member of a series of isoelectronic complexes for which the structures have been determined by X-ray diffraction. These compounds, together with a similar series of isoelectronic complexes of first row transition metals, are listed in Table VI. All of the molecules are tetrahedral complexes of π-bonding ligands which stabilize low oxidation states. The nitrosyl complexes listed show essentially linear coordination of the NO ligand; they may therefore be classified as NO^+ d^{10} systems. This formulation is in agreement with the prediction[2] that metals in low oxidation states will coordinate nitrosyl as NO^+. Since coordination numbers of four are generally associated with such states, all four-coordinate complexes of the nitrosyl ligand studied so far show approximate tetrahedral geometry and linear M–N–O groupings.

The complexes in Table VI show differences in bond lengths and angles which vary systematically with the coordinated ligands; these differences may be explained in terms of the variation in the basicity and π-acceptor strengths of the individual ligands. Specifically, both carbonyl and nitrosyl are much better π acids than the phosphines, which participate in $d\pi$–$d\pi$ bonding only in the absence of good π-accepting ligands.

It has been noted[21] that in the platinum complexes, the platinum–phosphorus distance increases as one of the phosphines is replaced by a carbonyl. This lengthening is attributed to the decrease in $d\pi$–$d\pi$ bonding between the metal and the phosphorus with the introduction of a second strong π-acceptor ligand. A similar trend may be noted in the three iridium compounds, although the magnitude of the iridium–phosphorus bond lengthening, *ca.* 0.01 Å for each carbonyl or nitrosyl exchanged for a phosphine, is barely significant. It is not clear whether this effect is followed in complexes of first row transition metals.

A significant change in the iridium–nitrogen and platinum–carbon bond lengths can be seen with changing number of strong π acceptors. In both cases, these bond distances are lengthened by about 0.1 Å when a second nitrosyl or a carbonyl is substituted for one of the phosphines. Presumably the increase in bond length reflects the decreased d–π^* bonding per ligand when there are two π acids present. There is, however, no significant difference in the iridium–nitrogen bond length between $Ir(NO)(CO)(P(C_6H_5)_3)_2$ and $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$, indicating that substitution of either nitrosyl or carbonyl for phosphine has a similar effect on the previously coordinated NO. The shorter metal–NO bond as contrasted with the metal–CO bond has been observed previously[22] and ascribed to differences in covalent radii. Again, the trend among the first-row elements is not clear. The metal–nitrogen and metal–carbon bond distances in the cobalt complexes are not of high accuracy, however, because of problems of disorder between nitrosyl and carbonyl groups.

Albano, *et al.*, have also suggested[23] in comparing $Pt(CO)(P(C_6H_5)_3)_3$ and $Ir(NO)(P(C_6H_5)_3)_3$ that the metal–phosphorus distance decreases from platinum to iridium as the formal oxidation state of the metal changes from 0 to -1. They propose that the decrease in oxidation state would result in more extensive back-donation from the metal to the ligands, and thus should shorten the metal–phosphorus bond distances. More extensive crystallographic data seem to confirm this observation, although the differences are small, about 0.02 Å, and are not highly significant.

There is no apparent order in the deviations of the phosphorus–metal–phosphorus angle from the ideal tetrahedral value. Albano, *et al.*, proposed[21] that an increase in the size of this angle might parallel the electron density on the phosphorus atoms, and therefore the amount of metal–phosphorus $d\pi$–$d\pi$ bonding. The more extensive results of Table VI, however, do not confirm this suggestion. Since the molecular packing is largely dictated by the bulky triphenylphosphine groups, it may be that the variations in this angle are a result of steric interactions. It is possible, however, to interpret the angle between the two π-acceptor ligands, carbonyl and nitrosyl, as a measure of the electron density on the atoms bonded to the metal. Since nitrogen is more electronegative than carbon, and since nitrosyl is thought to be a better π acceptor than carbonyl, it might be expected that the electron density on the nitrogen would be greater than on the carbon. In this case, the nonbonded radius of the former should be larger than that of the latter, and bond angles would be expected to increase in the order OC–M–CO < ON–M–CO < ON–M–NO. Such a trend is indeed observed in the iridium and platinum complexes, with the angle ON–M–CO determined in this study intermediate between those of $Pt(CO)_2(P(C_2H_5)(C_6H_5)_2)_2$ and $[Ir(NO)_2(P(C_6H_5)_3)_2]^+$. A larger radius for the nitrogen than for the carbon atom is also supported by the observation that in $Ir(NO)(CO)(P(C_6H_5)_3)_2$ the phosphorus–nitrogen nonbonded contacts are *ca.* 0.25 Å longer than the phosphorus–carbon (carbonyl) contacts. We have no explanation for the fact that the nickel, cobalt, and iron complexes do not show this trend. In fact, all complexes studied but one have ON(OC)–M–NO(CO) angles between 120 and 130°; the exception is the iridium dinitrosyl cation with an ON–Ir–NO angle of 154.2 (7)°. This complex is also unusual in that the Ir–N–O angle of 163.5 (10)° is distinctly bent away from linearity, and is one of the few examples of a metal–nitrosyl linkage intermediate between 180 and 120°. Although there is no evidence of abnormal thermal ellipsoids in the nitrosyl ligands, it is possible that the observed structure is the result of disorder between bent and linear nitrosyls. It is also possible that this complex actually is an example of an intermediate form of nitrosyl coordination. In order to clarify this problem, the crystal structures of the dinitrosylbis(triphenylphosphine)ruthenium and -osmium complexes are being studied in this laboratory.

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[21] V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, Abstracts of the 5th Meeting of the Italian Crystallographic Association, Bari, Oct 1971, p 127.

[22] B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).

[23] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc. A*, 2420 (1971).