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The Crystal and Molecular Structure of Chlorocarbonylnitrosylbis(triphenylphosphine)iridium Tetrafluoroborate, $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$

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The crystal and molecular structure of chlorocarbonylnitrosylbis(triphenylphosphine)iridium tetrafluoroborate, $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system with four molecules in a cell of dimensions $a = 19.417$ (7), $b = 9.965$ (3), $c = 20.886$ (8) Å, $\beta = 117.70$ (2)°. The observed and calculated densities are 1.67 and 1.677 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.037 for the 2410 independent reflections having $F^2 > 3\sigma(F^2)$. The nitrosyl group has been distinguished from the carbonyl group and has been shown to be bonded to the metal through the nitrogen, by examination of the root-mean-square amplitudes of vibration of the various atoms. The crystal structure consists of well-separated monomeric ions. The coordination geometry around the Ir is that of a tetragonal pyramid, with CO, Cl, and *trans*-P atoms in the basal plane and the N of the nitrosyl group at the apex; the Cl and CO lie slightly below the plane perpendicular to the Ir–N bond and passing through the Ir atom, the N–Ir–Cl and N–Ir–C angles being 101.3 (3) and 97.4 (5)°, respectively. The basal interatomic distances are normal, but the Ir–N bond length of 1.97 (1) Å is long. The nitrosyl group is bonded to the metal in an unusual way, the Ir–N–O angle being 124.1 (9)°. This is the first accurately documented example of a distinctly bent M–N–O linkage in a metal–nitrosyl complex. The basic geometry of the complex is similar to that of the analogous SO_2 complex, $IrCl(CO)(SO_2)(P(C_6H_5)_3)_2$, and markedly different from that of the O_2 complex, $IrCl(CO)(O_2)(P(C_6H_5)_3)_2$.

Introduction

The bonding of the NO group in metal nitrosyls has been of considerable interest for many years, and this interest has led to several structural studies. In most of the structures reported the M–N–O bond has been found to be approximately linear, but in at least one study[1] it was felt that this angle deviated greatly from linearity.

The preparations of several addition compounds of $IrCl(CO)(P(C_6H_5)_3)_2$ have been reported, including compounds involving the addition of molecular oxygen,[2] sulfur dioxide,[3] tetracyanoethylene,[4] and nitrosonium ion.[5] A structure determination of the O_2 complex, $IrCl(CO)(O_2)(P(C_6H_5)_3)_2$, showed that the O_2 group, the CO group, Ir, and Cl are coplanar, with *trans*-P atoms lying above and below this plane.[6] The coordination around the Ir can be considered as either a distorted octahedron or a trigonal bipyramid. The SO_2 complex, however, was found to have a very different structure; in $IrCl(CO)(SO_2)(P(C_6H_5)_3)_2$ the coordination around the Ir atom is a tetragonal pyramid, with *trans* P, Cl, and CO in the basal plane and the S of SO_2 at the apex.[7] The tetracyanoethylene (TCNE) complex, $IrBr(CO)(P(C_6H_5)_3)_2(C_2(CN)_4)$, was found to have the trigonal-bipyramidal structure found for the O_2 adduct, but in this case the phosphorus atoms are *cis* in the equatorial plane along with the TCNE molecule with *trans* Cl and CO lying above and below this plane.[8] Thus three different geometries around Ir have been found for these addition compounds. A complete structural determination of the nitrosyl complex, $IrCl(CO)(NO)(P(C_6H_5)_3)_2{}^+$, was undertaken because of our interest in the mode of attachment of the nitrosyl moiety to the metal and because of our continued interest in the geometries of closely related five-coordinated transition metal complexes.

Collection and Reduction of the X-Ray Data

Violet, well-formed crystals of $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$ were prepared by the method previously described.[5] On the basis of optical goniometry and precession photography of the 0*kl*, *h*0*l*, *h*1*l*, 1*kl*, and 2*kl* zones using Cu Kα radiation, we established that these crystals belong to the monoclinic system. The observed extinctions are 0*k*0 for *k* odd and *h*0*l* for *l* odd, which strongly suggest that the space group is $C_{2h}{}^5$-$P2_1/c$. The lattice constants, obtained by the least-squares procedure described below, are $a = 19.417$ (7), $b = 9.965$ (3), $c = 20.886$ (8) Å, $\beta = 117.70$ (2)°. The observations were made at 23° with the wavelength assumed as λ (Mo Kα_1) = 0.70930 Å. A density of 1.677 g cm^{-3} calculated for four molecules in the unit cell agrees well with that of 1.67 (1) g cm^{-3} measured by flotation in diiodomethane–bromoethane solution. Hence, no crystallographic symmetry conditions need be imposed on the ions.

Diffraction data were collected from a hexagonal-prismatic crystal; the hexagonal faces were (100) and $(\bar{1}00)$ and the six rectangular faces were $(11\bar{1})$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}01)$, and $(10\bar{1})$. One parallel pair of the hexagonal edges was 0.017 cm in length, the other pairs being 0.010 cm; the separation of the two hexagonal faces was 0.024 cm. The crystal was mounted on a glass fiber normal to the (001) planes and in this orientation intensity data were collected at room temperature on a Picker four-circle automatic diffractometer using Mo Kα radiation. 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 0.08°, which is acceptably low.[9] Twelve reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 0.5°. These observations formed the basis for the least-squares refinement of cell parameters and orientation; the refinement was effected in our program PICK as previously described.[10]

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(1) (a) P. R. H. Alderman and P. G. Owston, *Nature*, **178**, 1071 (1956); (b) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(2) L. Vaska, *Science*, **140**, 809 (1963).

(3) L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).

(4) W. H. Baddley, *ibid.*, **88**, 4545 (1966).

(5) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *ibid.*, **90**, 4486 (1968).

(6) J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964); S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(7) S. J. La Placa and J. A. Ibers, *Inorg. Chem.* **5**, 405 (1966).

(8) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

Intensity data were collected at a takeoff angle of 1.0°; at this angle the peak intensity of a typical strong reflection is approximately 80% of the maximum value as a function of takeoff angle. The receiving aperture size selected to minimize extraneous background was 4.0 mm high by 4.0 mm wide and was positioned 29 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1.0°/min. The scan range for all reflections was 1.5° in 2θ, from -0.60 to $+0.90°$ from the calculated 2θ value for reflections with $2\theta \leq 30°$, and from -0.5 to $+1.0°$ for reflections with $2\theta > 30°$. Stationary counter–stationary crystal background counts of 10 sec were taken at each end of the scan. The Mo Kα beam was filtered through 3.0-mil Zr foil after diffraction from the crystal. Attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils, their thicknesses being chosen to give attenuator factors of approximately 2.3. These attenuator factors were determined as previously described.[11] The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

A unique data set having $2\theta < 40°$ was gathered; a total of 3073 independent intensities were recorded. The intensities of four standard reflections, measured after every 200 reflections, remained essentially constant throughout the run, showing only the deviations from the mean predicted from counting statistics. There were very few reflections above background at values of $2\theta > 40°$.

All data processing was carried out as previously described.[10] The value of p in the expression $\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ was selected as 0.05. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption. The absorption coefficient μ of this compound for Mo Kα radiation is 41.9 cm^{-1}, and for the sample chosen transmission coefficients were found to range from 0.40 to 0.59.[12] Of the 3073 independent reflections, 558 were less than their estimated standard deviations.

Solution and Refinement

The position of the Ir atom could not be unambiguously determined from a three-dimensional, origin-removed, sharpened Patterson function; it was found to lie near $y = {}^1/_4$. Thus the Patterson function contains a false mirror plane since the Ir does not contribute to reflections for which l is odd. As a result, the Ir was known to be near either $({}^1/_4, {}^1/_4, {}^1/_4)$ or $({}^1/_4, {}^1/_4, 0)$. Two pairs of P atoms were also located in this Patterson function. On the basis of preliminary least-squares refinements of the two possible models, it seemed likely that the correct location of the Ir atom was near $({}^1/_4, {}^1/_4, {}^1/_4)$. This subsequently proved to be correct. All least-squares refinements were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factor for Ir was taken from Cromer and Waber,[13] and that for hydrogen was taken from Stewart, Davidson, and Simpson;[14] scattering factors for all other atoms were from the tabulation by Ibers.[15] The effects of anomalous dispersion were included in calculations of F_c,[16] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[17] Of the 3073 independent intensities gathered, 2410 were greater than three times their estimated standard deviations. Only these reflections were used in the refinement of the structure.

Initially, the Ir and P atoms were assigned fixed isotropic thermal parameters. After one cycle of least-squares refinement the usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ were 0.487 and 0.620, respectively. The values of the agreement factors were very high at this stage of the refinement because the Ir atom is located near $y = {}^1/_4$ and contributes only minimally to reflections for which l is odd. A difference Fourier synthesis revealed the remaining nonphenyl atoms and three rings, although solution of the Fourier map was greatly complicated by the continued presence of the false mirror. The parameters obtained from this map were refined by least-squares procedures. The nonphenyl atoms were refined with isotropic thermal parameters; the phenyl rings were treated as rigid groups and restricted to their known geometry (D_{6h} symmetry, C–C = 1.390 Å, C–H = 1.00 Å). The variable parameters for a ring included an over-all isotropic thermal parameter, the coordinates of the ring center, and three orientation angles which have been

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

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

(11) D. J. Hodgson and J. A. Ibers, *Acta Cryst.*, in press.

(12) In addition to various local programs, the programs used in the refinement of this structure were local modifications of Hamilton's GONO9 absorption correction program, Busing and Levy's ORFFE function and error program, Johnson's ORTEP thermal ellipsoid plotting program, and Zalkin's FORDAP Fourier program.

(13) D. T. Cromer and J. A. Waber, *Acta Cryst.*, **18**, 104 (1965).

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

(15) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, Table 3.3.1A.

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

(17) D. T. Cromer, *ibid.*, **18**, 17 (1965).

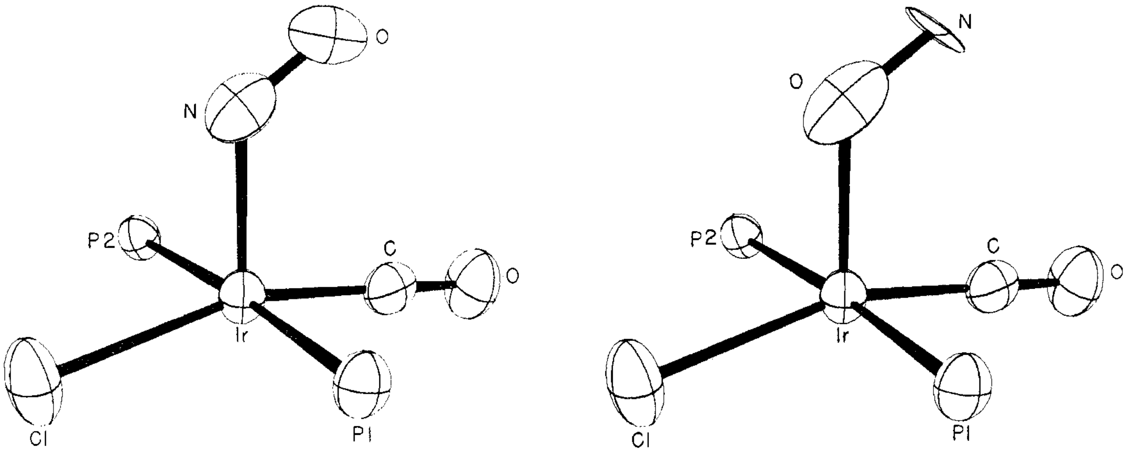

Figure 1.—View of the inner coordination sphere about Ir in the $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ cation after refinement with NO bonded through the N atom (left) and refinement with NO bonded through the O atom (right).

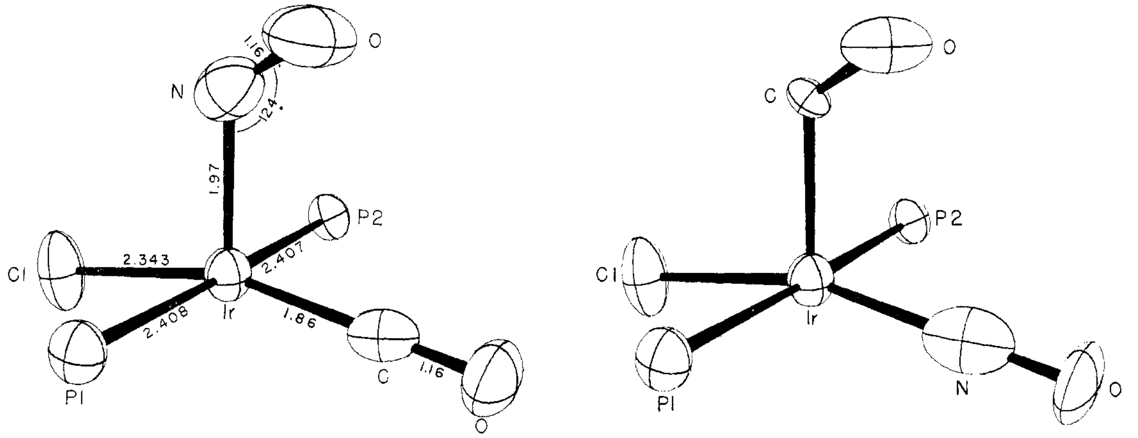

Figure 2.—View of the inner coordination sphere about Ir in the $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ cation after refinement with the bent group as NO (left) and refinement with the bent group as CO (right). The drawing at left depicts the final model.

defined previously.[6,7,18] This refinement converged to agreement factors $R_1 = 0.146$ and $R_2 = 0.231$. Examination of a Fourier synthesis at this point produced the location of the three missing phenyl rings and gave an indication of considerable anisotropy of thermal motion of the BF_4^- group. A further cycle of least-squares refinement was run in which the nonphenyl atoms (except for the BF_4^- group) were assigned variable anisotropic thermal parameters and the carbon atoms of the phenyl rings were assigned variable isotropic thermal parameters. This calculation yielded $R_1 = 0.040$ and $R_2 = 0.055$. A difference Fourier synthesis at this stage showed evidence of disorder in the BF_4^- region. The two separate F_4^- group positions which were observed were refined as rigid tetrahedral groups in a final cycle of least-squares calculation. The F–F separation was taken as 2.196 Å, the average of the six F–F distances obtained from the previous cycle. The two groups were given multiplicities of α and $(1 - \alpha)$, and the parameter α was varied with the appropriate constraints among the derivatives being taken into account. The least-squares calculation yielded final values of $R_1 = 0.037$ and $R_2 = 0.049$ and a value of $\alpha = 0.82$ (1); *i.e.*, we have an approximately 80–20% disorder in the BF_4^- group. The center of the 18% F_4^- group moved 0.5 (1) Å from the position of the B atom, which suggests that we might have more suitably refined the groups as two separate BF_4^- groups instead of keeping one B atom. Since B is a very light atom, however, this change would have made only little difference to the values of R_1 and R_2. The lowness of R_1 and R_2, the lack of correlation between the BF_4^- parameters and parameters in the cation, and the expense involved in performing further least-squares cycles led us to terminate the calculation at this stage. In this final cycle the largest shift in any other atomic or ring parameter was exhibited by phenyl group 6, whose center moved by one standard deviation. No other parameter showed any appreciable change. The estimated error in an observation of unit weight is 1.50.

Because of an interest in the mode of bonding of the nitrosyl group to Ir, two further least-squares calculations were performed. In the first, the O and N atoms of the nitrosyl group were reversed; in the second, the nitrosyl and carbonyl groups were interchanged. These changes had little effect on R_1 and R_2, although both R_1 and R_2 were slightly smaller for the original model. The thermal parameters of the atoms were significantly altered, as expected. X-Rays are scat-

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

Table I

Positional, Thermal, and Group Parameters for $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.25675 (2)	0.24638 (5)	0.24424 (2)	0.00225 (2)	0.00841 (7)	0.00209 (2)	−0.00047 (3)	0.00111 (1)	−0.00055 (3)
P_1	0.1508 (2)	0.1457 (3)	0.1404 (1)	0.0023 (1)	0.0093 (4)	0.0021 (1)	−0.0007 (1)	0.0009 (1)	−0.0005 (1)
P_2	0.3692 (2)	0.3401 (3)	0.3450 (1)	0.0021 (1)	0.0075 (4)	0.0020 (1)	0.0000 (2)	0.0009 (1)	−0.0006 (2)
Cl	0.3408 (2)	0.1822 (4)	0.1977 (2)	0.0033 (1)	0.0201 (5)	0.0035 (1)	−0.0014 (2)	0.0020 (1)	−0.0036 (2)
C	0.1997 (6)	0.2427 (11)	0.2951 (6)	0.0022 (4)	0.0076 (14)	0.0024 (4)	−0.0006 (8)	0.0002 (4)	0.0005 (7)
O (of CO)	0.1661 (5)	0.2398 (9)	0.3286 (4)	0.0045 (4)	0.0159 (13)	0.0037 (3)	−0.0015 (6)	0.0029 (3)	−0.0008 (5)
N	0.2235 (6)	0.4255 (11)	0.2005 (5)	0.0044 (5)	0.0119 (15)	0.0029 (4)	−0.0018 (8)	0.0013 (4)	0.0001 (6)
O (of NO)	0.1771 (7)	0.4903 (9)	0.2060 (5)	0.0059 (5)	0.0100 (12)	0.0064 (5)	0.0020 (6)	0.0031 (4)	0.0022 (6)
B	0.774 (1)	0.379 (2)	0.1421 (9)	0.010 (1)	0.026 (3)	0.0031 (7)	0.011 (1)	0.0034 (8)	0.001 (1)

Group	x_c[b]	y_c	z_c	δ	ϵ	η	B, Å^2	α[c]
R_1[d]	0.0988 (3)	0.3225 (5)	0.9970 (3)	1.690 (5)	−2.890 (5)	−0.979 (5)		
R_2	0.0011 (3)	0.1082 (6)	0.1652 (2)	0.020 (5)	−2.992 (5)	2.479 (5)		
R_3	0.1883 (3)	0.8561 (5)	0.0996 (3)	1.226 (7)	2.201 (5)	−2.492 (8)		
R_4	0.3331 (3)	0.4172 (4)	0.4757 (2)	−2.222 (5)	−2.819 (4)	1.634 (5)		
R_5	0.5196 (3)	0.1548 (5)	0.4191 (2)	−0.626 (4)	3.094 (5)	0.109 (5)		
R_6	0.4179 (3)	0.6111 (5)	0.2935 (3)	2.501 (8)	−2.166 (4)	0.896 (8)		
F_4 (1)	0.7787 (4)	0.3827 (6)	0.1461 (3)	−2.136 (5)	−3.163 (5)	−1.455 (5)	8.6 (2)	0.82 (1)
F_4 (2)	0.759 (2)	0.407 (3)	0.132 (2)	−0.82 (4)	2.37 (3)	1.03 (4)	7.8 (13)	0.18 (1)

[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] 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.[5,6,17] [c] α is the multiplicity of the two disordered F_4^- groups; *i.e.*, we have here an 82–18% disorder. [d] Phenyl rings R_1, R_2, and R_3 are attached to phosphorus P_1; rings R_4, R_5, and R_6 are attached to P_2.

tered by the atomic electrons, and so, if too much electron density (*i.e.*, an atom whose atomic number is too high) is assumed for a particular scatterer, the thermal motion of that scatterer will be found to increase in order that the electron density be dispersed over a larger volume. Conversely, if too little electron density is assumed for a particular scatterer, the thermal motion will be decreased. Figures 1 and 2 show the thermal ellipsoids, all at the 40% probability level, before and after the rearrangements. The views have been chosen to emphasize the differences between the models. It is clear from Figure 1 that reversal of the N and O atoms causes the new O atom to become unusually dispersed while the new N atom has become extremely condensed. It is evident that we have placed too many electrons at the site bonded to the metal and too few at the terminal position. The original model (left) is clearly much more reasonable. Figure 2 shows the result of reversing the N and C atoms; the new C atom has been condensed so that it is now the atom which has the smallest thermal motion, despite the fact that it is much less tightly bound and much lighter than the Ir atom. The new N atom, however, has become so dispersed that its thermal motion is greater than that of its own terminal O atom, despite its being much more tightly bound. Again we feel that the original model is much more reasonable. We conclude, therefore, that the bent group is the nitrosyl rather than the carbonyl and that the nitrosyl group is bonded to the Ir through N rather than through O.

The value of R_2 obtained from the final cycle of least-squares refinement shows no dependence on $|F_o|$ or on $\sin \theta$, which indicates that our choice of $p = 0.05$ is essentially correct. Comparison of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary. A final difference Fourier map shows no peak higher than 0.8 e Å^{-3}; $\sigma(\Delta\rho)$ for this difference synthesis is 0.11 e Å^{-3}. All peaks greater than 0.5 e Å^{-3} are in the regions of the BF_4^- group and the phenyl rings and are presumably due to anisotropy of thermal motion of these groups.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement are presented in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. The positional parameters of the ring carbon atoms which may be derived from the data in Table I are presented in Table II, along with the thermal parameters for the phenyl carbon atoms 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 2410 reflections which were used in the refinement are listed in Table III. The reflections for which $F_o^2 < 3\sigma(F_o^2)$ all have $|F_c| < 2|F_o|$.

Description of the Structure

The structure consists of discrete, monomeric ions. The inner coordination geometry of the cation is shown in Figure 2, and a stereoscopic view of the cation is shown in Figure 3. The coordination polyhedron about the Ir is a distorted tetragonal pyramid, with *trans* P, Cl, and CO in the base and the N of NO at the apex. The chlorine atom and carbonyl group are slightly below the plane perpendicular to the Ir–N bond and passing through the Ir atom, the N–Ir–Cl and N–Ir–C angles being 101.3 (3) and 97.4 (5)°, respectively.[5] The BF_4^- group occupies roughly the sixth coordination site, the Ir–B distance being 4.54 Å and the closest Ir–F contact being 3.63 Å.

A selection of intramolecular distances and angles is given in Table IV. The root-mean-square amplitudes of vibration of the atoms in the inner coordination sphere are listed in Table V. The directions of vibration of these atoms are shown in Figure 2. The bond distances shown in Table IV can be "corrected" for thermal motion using the "riding" and "independent" models of Busing and Levy.[19] The differences between

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(19) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

TABLE II

DERIVED PARAMETERS FOR RING CARBON ATOMS[a]

Ring atom	*x*	*y*	*z*	*B*, Å^2
R_1C_1	0.1207 (4)	0.2486 (7)	0.0600 (3)	3.4 (2)
R_1C_2	0.1771 (3)	0.2995 (8)	0.0433 (4)	4.3 (3)
R_1C_3	0.1551 (5)	0.3734 (8)	0.9803 (5)	6.0 (3)
R_1C_4	0.0768 (5)	0.3963 (9)	0.9340 (4)	6.1 (3)
R_1C_5	0.0204 (4)	0.3454 (9)	0.9507 (4)	7.3 (4)
R_1C_6	0.0424 (4)	0.2716 (8)	0.0137 (4)	5.4 (3)
R_2C_1	0.0646 (4)	0.1231 (8)	0.1522 (4)	3.4 (2)
R_2C_2	0.0342 (4)	0.9962 (6)	0.1507 (4)	4.4 (3)
R_2C_3	0.9706 (5)	0.9812 (7)	0.1637 (4)	6.2 (3)
R_2C_4	0.9375 (4)	0.0932 (9)	0.1782 (4)	6.4 (3)
R_2C_5	0.9679 (4)	0.2201 (7)	0.1797 (4)	6.0 (3)
R_2C_6	0.0315 (5)	0.2351 (6)	0.1667 (4)	4.7 (3)
R_3C_1	0.1729 (8)	0.9837 (6)	0.1167 (4)	3.0 (2)
R_3C_2	0.2194 (5)	0.8959 (7)	0.1715 (3)	4.1 (3)
R_3C_3	0.2348 (6)	0.7683 (8)	0.1545 (4)	5.6 (3)
R_3C_4	0.2037 (8)	0.7285 (7)	0.0826 (4)	5.9 (3)
R_3C_5	0.1572 (5)	0.8164 (7)	0.0277 (3)	4.7 (3)
R_3C_6	0.1417 (5)	0.9440 (8)	0.0448 (3)	3.6 (2)
R_4C_1	0.3504 (4)	0.3834 (7)	0.4201 (3)	2.5 (2)
R_4C_2	0.2889 (3)	0.4698 (6)	0.4068 (3)	3.3 (2)
R_4C_3	0.2717 (4)	0.5036 (7)	0.4624 (4)	4.2 (3)
R_4C_4	0.3159 (5)	0.4510 (8)	0.5312 (3)	4.3 (3)
R_4C_5	0.3774 (4)	0.3647 (7)	0.5446 (3)	4.6 (3)
R_4C_6	0.3946 (4)	0.3309 (7)	0.4890 (4)	3.9 (2)
R_5C_1	0.4542 (3)	0.2355 (7)	0.3837 (4)	2.9 (2)
R_5C_2	0.4459 (3)	0.0974 (7)	0.3864 (4)	4.4 (3)
R_5C_3	0.5113 (5)	0.0167 (5)	0.4219 (4)	6.0 (3)
R_5C_4	0.5849 (4)	0.0741 (8)	0.4546 (4)	5.6 (3)
R_5C_5	0.5933 (3)	0.2122 (8)	0.4518 (4)	5.6 (3)
R_5C_6	0.5279 (4)	0.2929 (5)	0.4164 (4)	4.7 (3)
R_6C_1	0.3991 (7)	0.4945 (6)	0.3186 (5)	2.7 (2)
R_6C_2	0.4272 (9)	0.4867 (6)	0.2684 (6)	5.2 (3)
R_6C_3	0.4460 (5)	0.6032 (9)	0.2434 (4)	6.2 (3)
R_6C_4	0.4367 (7)	0.7276 (7)	0.2685 (5)	6.0 (3)
R_6C_5	0.4087 (9)	0.7354 (5)	0.3187 (6)	5.7 (3)
R_6C_6	0.3898 (4)	0.6189 (7)	0.3437 (4)	4.2 (3)

[a] C_1 is attached to P; other C atoms are numbered in succession so that C_4 is *para* to C_1.

the various bond lengths remain essentially the same when either of these "corrections" is applied.

The Ir–P distances of 2.407 (3) and 2.408 (3) Å are significantly longer than both of the values of 2.359 (9) and 2.328 (8) Å found in the SO_2 complex[7] and the values of 2.38 (1) and 2.36 (1) Å found in the O_2 complex.[6] The Ir–Cl distance of 2.343 (3) Å is slightly shorter than the value of 2.37 (1) Å found in the SO_2 complex[7] and the values of the disordered Ir–Cl distances of 2.38 (2) and 2.42 (2) Å in the O_2 complex.[6] The C–O distance of 1.16 (1) Å is similar to the values typically found for carbonyl derivatives of transition metals.[20] There is no evidence of disorder between CO and Cl as there is in the analogous O_2 adduct.[6] The geometry of the triphenylphosphine groups is similar to that found in previous studies.[6,7]

The bonding of the nitrosyl group to the metal atom in this complex is clearly unusual. The Ir–N–O bond angle and the Ir–N and N–O bond lengths are compared in Table VI with the results obtained in previous three-dimensional X-ray and neutron studies of metal–nitrosyl complexes. While no direct comparisons can be made, the Ir–N bond length of 1.97 (1) Å is clearly long. Moreover, the Ir–N–O bond angle of 124 (1)° is quite different from the near linearity reported for almost all metal–nitrosyl complexes. The bonding here is evidently very different from that in $Ru(NO)(NO_2)_4(OH)^{2-}$, for example, in which the Ru–N–O fragment is strictly linear and the Ru–N distance is approximately 1.75 Å.[21]

It is our belief that these differences between $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ and other metal–nitrosyl complexes result from the amphoteric nature of NO^+. In most metal–nitrosyl complexes NO^+ donates a pair of σ electrons to the metal and acts as a Lewis base. The bond between the metal and the ligand uses an sp hybrid on the nitrogen; consequently, the M–N–O linkage is similar to the M–C–O linkage in metal carbonyls. The M–N and M–C bonds in these systems are relatively short because there is considerable π bonding from the metal to the NO and CO groups. In the case of $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ there is no readily available empty metal orbital to which the NO^+ group can donate a pair of electrons; consequently NO^+ acts as a σ acceptor, or Lewis acid, and accepts an electron pair from the metal. The metal–ligand bond, therefore, uses an sp^2 hybrid on the nitrogen, with a lone pair occupying another hybrid orbital. The Ir—N—O angle would be expected to have a value of 120°, which is in good agreement with the observed value of 124.1 (9)°. Furthermore, the N—O stretch in the infrared spectrum ($1680\ cm^{-1}$) falls in the range found for sp^2 hybridized compounds of the general formula RN=O, where R is a halogen or an alkoxy, alkyl, or aryl group.[22]

As can be seen from Table VI, there is one other metal–nitrosyl complex which has been shown to have an M–N–O angle which probably deviates greatly from linearity, namely, $Co(NO)(S_2CN(CH_3)_2)_2$.[1] The corresponding iron complexes, $Fe(NO)(S_2CN(CH_3)_2)_2$[23] and $Fe(NO)(S_2CN(C_2H_5)_2)_2$,[24] have recently been shown to have linear M–N–O linkages, and this has caused some doubt that the earlier cobalt structure determination is correct. We believe, however, that NO^+ could act as a Lewis acid in the cobalt complex, since this is electronically and structurally similar to the iridium complex, and consequently the original structure determination may be correct.

Similarly, in SO_2 complexes we believe that SO_2 can act as either a Lewis acid or a Lewis base. In the complex $[Ru(NH_3)_4Cl(SO_2)]Cl$ the Ru–SO_2 fragment is planar and the Ru–S bond is 2.072 (3) Å;[25] this, we feel, is an example of SO_2 acting as a Lewis base. If the SO_2 were to act as a Lewis acid one would expect, by the

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TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) IN ELECTRONS

H	L	FO	FC
***** K = 0 *****			
0	0		18233
-18	6	891	825
-18	8	629	591
-18	10	712	724
-18	12	500	493
-17	2	725	645
-17	4	511	477
-17	6	692	690
-17	8	1302	1310
-17	10	1215	1251
-17	12	683	858
-17	14	1083	1070
-16	2	773	739
-16	4	814	801
-16	6	1165	1165
-16	8	1085	1086
-16	10	1096	1131
-16	12	399	379
-16	14	298	258
-16	16	281	272
-15	2	497	536
-15	4	890	854
-15	6	1461	1476
-15	8	962	963
-15	10	650	662
-15	12	814	808
-15	14	1347	1324
-15	16	1525	1549
-15	18	1262	1278
-14	2	716	693
-14	4	1206	1225
-14	6	797	796
-14	8	794	855
-14	10	930	966
-14	12	684	684
-14	14	883	891
-14	16	650	610
-13	2	1428	1421
-13	4	1376	1430
-13	6	1309	1376
-13	8	991	1065
-13	10	1006	1029
-13	12	1150	1186
-13	14	1310	1315
-13	16	1135	1174
-13	18	739	750
-12	2	1836	1682
-12	4	1499	1508
-12	6	1061	1111
-12	8	643	621
-12	10	1092	1096
-12	12	866	996
-12	14	991	1046
-12	16	798	854
-12	18	378	406
-11	2	1384	1416
-11	4	1557	1695
-11	6	1472	1519
-11	8	1216	1261
-11	10	1541	1517
-11	12	1022	1111
-11	14	1009	1006
-11	16	631	646
-11	18	521	532
-10	2	2563	2665
-10	4	1830	1846
-10	6	1195	1229
-10	8	1154	1176
-10	10	1254	1216
-10	12	950	988
-10	14	871	875
-10	16	603	628
-10	18	567	561
-10	20	370	346
-9	2	645	610
-9	4	664	926
-9	6	209	244
-9	8	1776	1780
-9	10	1961	2032
-9	12	1372	1463
-9	14	1049	1118
-9	16	541	565
-9	18	1019	1103
-9	20	1067	1067
-8	2	1739	1676
-8	4	2707	2724
-8	6	2332	2357
-8	8	1797	1848
-8	10	1524	1483
-8	12	753	802
-8	14	684	723
-8	16	731	668
-8	18	723	805
-8	20	622	650
-7	2	474	452
-7	4	1321	1287
-7	6	1403	1384
-7	8	2756	2639
-7	10	1579	1685
-7	12	596	604
-7	14	1271	1315
-7	16	1576	1679
-7	18	1098	1014
-7	20	600	605
-6	2	2207	2185
-6	4	2304	2301
-6	6	2452	2515
-6	8	2784	2873
-6	10	2717	2671
-6	12	1455	1422
-6	14	1011	1081
-6	16	1136	1162
-6	18	376	393
-5	2	1091	1005
-5	4	1268	1320
-5	6	1706	1665
-5	8	1376	1295
-5	12	961	1056
-5	14	1769	1728
-5	16	1029	1013
-5	18	982	984
-4	2	3237	3247
-4	4	367	367
-4	6	2994	3156
-4	8	2167	[illegible]
-4	10	1334	1328
-4	12	2238	2375
-4	14	1162	1215
-4	16	964	924
-4	18	554	544
-3	2	654	653
-3	4	2400	2487
-3	6	944	979
-3	10	640	669
-3	12	1009	957
-3	14	1159	1124
-3	16	805	815
-3	18	905	916
-2	2	4215	4658
-2	4	2549	2570
-2	6	539	481
-2	8	1027	1067
-2	10	1860	1961
-2	12	1731	1666
-2	14	1503	1541
-2	16	737	756
-2	18	946	944
-1	2	134	119
-1	4	341	312
-1	6	2829	2933
-1	8	1155	1203
-1	10	1042	1071
-1	12	852	864
-1	14	289	303
-1	16	494	531
-1	18	575	548
0	2	3343	3315
0	4	1522	1470
0	6	502	616
0	8	634	844
0	10	2367	2365
0	12	1509	1592
0	14	1111	1137
0	16	780	760
1	0	172	184
1	2	666	606
1	4	716	712
1	8	200	256
1	10	1366	1287
1	12	567	566
1	16	544	474
2	0	3602	3606
2	2	1474	1418
2	4	2150	2103
2	6	3267	3253
2	8	2180	2200
2	10	1086	1140
2	12	557	501
2	14	657	666
2	16	878	873
3	4	1426	1419
3	6	901	917
3	8	674	697
3	14	564	541
3	16	716	690
4	0	2005	1929
4	2	2404	2409
4	4	3052	3071
4	6	2965	2944
4	8	1960	1920
4	10	1329	1261
4	12	1195	1155
4	14	1175	1177
5	0	1828	1824
5	2	372	393
5	4	273	248
5	6	1024	1002
5	8	352	323
5	12	438	454
5	14	818	810
6	0	1836	1838
6	2	2513	2546
6	4	2248	2243
6	6	2013	2074
6	8	1412	1360
6	10	1214	1201
6	12	1641	1594
7	0	708	683
7	2	664	727
7	4	771	809
7	8	315	347
7	10	245	188
7	12	426	385
8	0	1758	1799
8	2	1322	1396
8	4	802	815
8	6	788	779
8	8	997	1006
8	10	1850	1758
8	12	1502	1427
9	0	1349	1302
9	6	369	382
9	10	286	256
10	0	2467	2524
10	2	1510	1502
10	4	624	[illegible]
10	6	934	989
10	8	1652	1634
10	10	1220	1221
11	0	469	519
11	2	291	307
11	6	614	605
11	8	562	526
12	0	1176	1222
12	2	991	970
12	4	1622	1530
12	6	1267	1257
13	0	564	517
13	2	358	399
13	4	748	738
13	6	526	[illegible]
14	0	869	846
14	2	1176	1133
14	4	1066	1091
15	0	522	527
15	2	665	690
16	0	415	460
***** K = 1 *****			
-18	6	509	460
-18	8	1063	1074
-18	10	1378	1353
-18	12	979	965
-17	2	611	643
-17	4	629	604
-17	6	787	823
-17	8	720	700
-17	10	957	928
-17	11	360	345
-17	12	530	492
-16	2	577	586
-16	4	323	360
-16	6	1125	1140
-16	8	1220	1197
-16	10	1011	1011
-16	12	826	872
-16	14	1139	1132
-16	16	1405	1406
-15	1	211	148
-15	2	609	565
-15	4	683	665
-15	6	1062	1013
-15	8	1021	1048
-15	10	922	939
-15	12	662	661
-15	13	334	370
-15	14	624	688
-15	16	304	369
-14	2	969	980
-14	3	276	271
-14	4	1261	1206
-14	6	1418	1432
-14	8	898	894
-14	10	654	657
-14	12	993	1059
-14	14	1204	1201
-14	16	1422	1377
-14	18	1069	1096
-13	2	1228	1194
-13	4	1322	1394
-13	6	914	921
-13	7	233	165
-13	8	954	969
-13	10	867	848
-13	11	221	212
-13	12	1241	1186
-13	14	891	877
-13	16	549	556
-13	18	313	307
-12	1	251	324
-12	2	1170	1164
-12	3	244	252
-12	4	1222	1302
-12	5	980	959
-12	8	927	947
-12	10	1262	1274
-12	12	1313	1309
-12	14	1220	1271
-12	16	815	792
-12	18	731	730
-11	1	349	356
-11	2	2414	2449
-11	4	1456	1472
-11	6	1011	1045
-11	7	395	345
-11	8	1013	1042
-11	10	636	662
-11	12	1093	1101
-11	14	917	896
-11	16	624	600
-11	17	221	216
-11	18	619	630
-10	2	1088	1107
-10	3	446	415
-10	4	1102	1079
-10	6	1188	1182
-10	7	303	301
-10	8	1389	1438
-10	10	1817	1941
-10	11	389	420
-10	12	1617	1659
-10	14	999	1017
-10	16	498	535
-10	18	911	824
-9	2	1843	1978
-9	4	1648	1617
-9	5	619	643
-9	6	2011	2039
-9	7	363	390
-9	8	1746	1747
-9	9	209	146
-9	10	1453	1546
-9	11	267	359
-9	12	978	971
-9	14	848	851
-9	16	606	668
-9	18	665	615
-9	19	243	232
-9	20	521	489
-8	1	267	252
-8	2	473	500
-8	4	293	317
-8	5	164	106
-8	6	992	982
-8	7	191	110
-8	8	2154	2224
-8	9	311	264
-8	10	1650	1710
-8	11	259	283
-8	12	1772	1820
-8	13	271	279
-8	14	751	722
-8	16	990	949
-8	18	1106	1091
-8	20	770	728
-7	1	529	505
-7	2	1820	1784
-7	3	1001	906
-7	4	2431	2341
-7	5	823	831
-7	6	3450	3435
-7	8	2196	2181
-7	9	608	596
-7	10	1593	1651
-7	12	877	925
-7	14	716	655
-7	16	1017	1049
-7	18	731	717
-7	19	236	197
-6	2	745	721
-6	6	1270	1211
-6	7	335	287
-6	8	1051	1094
-6	9	176	132
-6	10	650	723
-6	11	[illegible]	405
-6	12	1166	1163
-6	14	1670	1733
-6	16	1461	1420
-6	17	223	210
-6	18	970	956
-5	1	604	551
-5	2	1459	1381
-5	3	335	290
-5	4	3062	2934
-5	5	900	866
-5	6	2623	2517
-5	7	154	76
-5	8	2940	3006
-5	9	364	297
-5	10	1181	1179
-5	11	567	514
-5	12	1091	1066
-5	13	396	440
-5	14	1376	1475
-5	16	1061	1085
-5	18	[illegible]	[illegible]
-4	1	550	532
-4	2	504	467
-4	3	264	263
-4	4	1163	1096
-4	5	958	979
-4	6	1287	1263
-4	7	154	165
-4	9	238	179
-4	10	980	1030
-4	12	1257	1317
-4	13	413	459
-4	14	1438	1439
-4	16	877	888
-4	18	940	882
-3	1	217	219
-3	2	3161	2956
-3	3	266	284
-3	4	3125	3006
-3	5	1256	1221
-3	6	2274	2264
-3	7	768	765
-3	8	1717	1605
-3	9	390	426
-3	10	1564	1621
-3	11	934	933
-3	12	2005	1990
-3	13	264	261
-3	14	1598	1566
-3	16	953	966
-3	17	297	237
-3	18	730	692
-2	1	875	818
-2	2	962	860
-2	3	566	521
-2	4	395	400
-2	5	567	531
-2	6	522	508
-2	7	503	517
-2	8	1089	1027
-2	9	490	475
-2	10	481	434
-2	11	343	365
-2	12	1011	1026
-2	13	334	314
-2	14	591	565
-2	15	287	269
-2	16	573	568
-2	18	715	683
-1	1	487	438
-1	2	3933	3973
-1	3	272	284
-1	4	2662	2762
-1	5	1072	1054
-1	6	1469	1466
-1	7	678	642
-1	8	1708	1680
-1	9	358	331
-1	10	1752	1694
-1	12	1382	1361
-1	14	1226	1156
-1	16	946	914
-1	18	873	824
0	1	664	842
0	2	632	578
0	3	965	915
0	4	2004	1958
0	5	406	396
0	6	956	932
0	7	959	932
0	8	562	505
0	9	415	464
0	10	630	618
0	12	628	661
0	14	293	274
0	15	250	263
0	16	467	456
1	0	3641	3625
1	1	345	317
1	2	1903	1863
1	3	1048	1023
1	4	2926	2933
1	5	139	126
1	6	2399	2499
1	7	603	633
1	8	2310	2369
1	9	485	490
1	10	1644	1659
1	11	236	280
1	12	979	1001
1	14	778	778
1	16	966	970
2	0	169	134
2	1	1461	1432
2	2	150	173
2	3	1897	1856
2	4	603	567
2	5	766	746
2	6	352	336
2	8	855	823
2	9	467	484
2	10	1091	1093
2	11	469	451
2	12	489	473
2	16	515	499
3	0	1588	1539
3	1	1675	1654
3	2	3625	3593
3	3	1141	1135
3	4	3743	3804
3	5	463	459
3	6	3023	3086
3	7	380	400
3	8	1798	1922
3	10	1268	1309
3	12	597	597
3	13	240	270
3	14	1179	1181
3	16	990	966
4	0	1631	1590
4	1	1132	1148
4	2	385	412
4	3	1096	1123
4	4	422	378
4	5	347	345
4	7	206	227
4	8	286	274
4	14	702	644
5	0	696	690
5	1	231	227
5	2	1802	1773
5	3	617	642
5	4	2468	2512
5	5	241	257
5	6	2306	2349
5	7	721	721
5	8	1758	1842
5	10	1200	1225
5	11	367	350
5	12	1146	1144
5	14	1136	1152
6	0	341	332
6	1	735	738
6	2	328	313
6	5	822	808
6	6	315	283
6	7	357	364
6	12	285	247
7	0	1395	1350
7	1	246	193
7	2	2092	2065
7	4	2123	2135
7	6	1541	1605
7	7	383	407
7	8	1359	1400
7	10	1195	1220
7	11	226	219
7	12	1433	1494
8	0	762	815
8	2	201	213
8	4	371	386
8	5	249	289
8	7	245	234
8	9	293	385
9	0	2416	2432
9	1	520	523
9	2	1750	1831
9	3	212	284
9	4	1196	1173
9	6	803	830
9	7	287	252
9	8	1180	1194
9	10	1348	1324
10	0	1063	1163
10	1	283	290
10	2	438	496
10	7	262	241
11	0	1772	1810
11	1	348	338
11	2	1010	1035
11	3	207	213
11	4	758	757
11	5	336	332
11	6	1343	1265
11	8	1076	1054
12	0	1104	1087
12	2	339	357
12	6	419	397
13	0	1035	1052
13	2	1234	1167
13	4	1392	1327
13	6	1142	1152
14	0	583	615
14	2	764	696
14	3	268	282
14	4	728	734
15	0	953	942
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2	9	217	226
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2	12	1202	1226
2	14	1245	1225
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3	2	166	91
3	4	223	209
3	5	322	286
3	6	383	387
3	7	264	265
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4	7	307	295
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5	1	210	212
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5	6	335	347
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6	11	257	272
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7	9	375	393
7	11	297	260
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8	2	931	985
8	3	230	225
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8	6	1521	1530
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8	10	1111	1092
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9	2	342	345
9	3	234	272
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9	6	223	282
9	7	413	406
9	9	226	257
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10	1	263	242
10	2	1173	1228
10	3	203	153
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10	8	1082	1035
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11	2	640	626
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11	5	248	243
11	6	219	196
12	0	1137	1110
12	1	220	199
12	2	1344	1390
12	4	1029	1097
13	0	1137	1115
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14	0	1299	1294
14	2	933	888
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-14	2	718	703
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-14	8	961	967
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-14	12	925	935
-14	14	739	701
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-13	4	813	813
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-11	12	509	470
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-9	12	1095	1140
-9	14	814	866
-9	16	953	910
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-8	6	715	701
-8	7	249	196
-8	8	623	666
-8	9	256	226
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-8	11	353	312
-8	12	1374	1354
-8	14	1059	1047
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-8	17	214	217
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-7	10	1070	1036
-7	11	239	200
-7	12	1052	1053
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-7	16	821	819
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-6	6	663	648
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-6	8	679	617
-6	9	194	200
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-6	16	555	525
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-5	14	740	741
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TABLE III (*Continued*)

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-3	10	1301	1331
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-3	12	765	769
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-2	2	154	83
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-2	6	639	607
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-2	8	860	873
-2	10	757	734
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-2	13	214	247
-2	14	635	635
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-1	4	1794	1790
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-1	12	887	875
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0	2	180	180
0	3	173	222
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0	10	261	264
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0	14	721	735
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1	2	1838	1842
1	3	668	682
1	4	2383	2380
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1	6	1643	1651
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1	8	1047	1070
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1	14	1209	1212
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5	4	1027	1020
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5	7	310	338
5	8	1381	1445
5	9	241	250
5	10	1165	1177
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6	0	688	672
7	0	1334	1309
7	1	188	210
7	2	1249	1266
7	4	1231	1190
7	6	1710	1790
7	8	1213	1311
7	9	217	197
7	10	896	894
8	0	260	305
8	1	187	212
8	2	198	299
8	4	215	176
8	5	210	174
8	6	240	238
8	7	371	349
8	9	360	343
9	0	849	861
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9	2	1096	1046
9	4	1406	1399
9	6	1255	1272
9	8	983	971
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10	2	576	618
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11	0	775	815
11	1	238	208
11	2	1099	1098
11	4	1139	1128
12	0	669	652
12	2	592	602
12	4	335	420
13	0	1029	1058
13	1	224	120
13	2	1093	1095
14	0	604	632
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-13	4	506	506
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-13	8	995	942
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-12	2	806	799
-12	4	820	851
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-12	7	229	211
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-11	4	537	513
-11	6	924	911
-11	7	321	323
-11	8	[illegible]	[illegible]
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-10	14	656	690
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-9	2	692	715
-9	3	379	379
-9	4	1009	963
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-9	6	919	871
-9	7	292	288
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-5	6	908	913
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6	9	332	324
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7	3	228	215
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9	4	295	288
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-10	12	796	768
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-9	13	322	302
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-8	3	225	182
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-8	10	718	737
-8	12	759	692
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-6	12	532	560
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-5	7	481	500
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-4	3	193	157
-4	4	426	421
-4	6	571	632
-4	7	217	132
-4	8	785	858
-4	10	712	718
-4	11	225	188
-4	12	609	615
-4	13	265	204
-3	1	215	207
-3	2	1420	1418
-3	4	1176	1154
-3	5	346	377
-3	6	1223	1187
-3	7	202	177
-3	8	1367	1388
-3	9	275	311
-3	10	1043	1031
-3	12	775	782
-3	13	261	276
-2	1	292	315
-2	3	252	292
-2	5	420	441
-2	6	449	432
-2	8	662	705
-2	9	217	278
-2	10	537	504
-2	12	414	440
-1	1	382	409
-1	2	1160	1214
-1	3	266	325
-1	4	1322	1317
-1	5	222	254
-1	6	1377	1416
-1	8	1188	1195
-1	10	1038	1030
-1	11	283	255
-1	12	698	630
0	1	437	452
0	3	398	429
0	7	399	349
0	10	331	305
0	11	229	277
0	12	550	550
1	0	1116	1159
1	1	198	220
1	2	1150	1097
1	3	419	428
1	4	1475	1455
1	6	1390	1367
1	8	1032	1067
1	10	856	872
1	11	245	225
2	0	452	462
2	1	409	434
2	5	411	417
2	6	352	305
2	8	251	290
2	9	286	206
2	10	438	428
3	0	1232	1292
3	2	1673	1739
3	3	323	373
3	4	1547	1598
3	5	249	231
3	6	824	829
3	8	865	900
3	9	387	374
3	10	827	863
4	0	209	162
4	1	227	239
4	2	230	204
4	3	379	421
4	7	200	230
4	8	356	343
4	9	362	331
5	0	1327	1309
5	1	325	353
5	2	1185	1203
5	4	898	888
5	5	184	205
5	6	986	941
5	7	396	349
5	8	1150	1160
6	0	668	640
6	3	311	267
6	4	274	267
6	5	545	568
6	6	332	366
6	7	307	299
7	0	872	931
7	2	1044	1035
7	4	1111	1052
7	6	1328	1301
8	0	469	470
8	3	472	449
8	4	227	227
8	5	349	378
9	0	995	1020
9	2	1022	1000
9	3	221	106
9	4	1032	1052
10	0	495	488
10	1	334	319
10	2	502	453
11	0	908	920
***** K = 8 *****			
-10	4	549	562
-10	6	690	707
-9	2	614	582
-9	4	538	522
-9	6	408	366
-9	8	443	375
-8	2	657	601
-8	3	243	210
-8	4	749	753
-8	6	953	953
-8	7	268	200
-8	8	517	469
-8	9	304	280
-8	10	800	739
-7	1	224	121
-7	2	460	467
-7	4	320	291
-7	5	226	262
-7	6	535	534
-7	7	232	228
-7	8	682	631
-7	10	552	540
-6	1	282	257
-6	2	1042	1027
-6	4	919	947
-6	6	793	814
-6	7	310	306
-6	8	639	582
-6	9	419	443
-6	10	928	921
-5	3	263	206
-5	4	437	468
-5	5	216	177
-5	6	696	694
-5	8	485	458
-5	10	385	465
-4	2	982	968
-4	4	1010	1080
-4	5	252	258
-4	6	845	883
-4	7	506	478
-4	8	988	1010
-4	10	769	776
-3	1	364	384
-3	4	398	409
-3	5	296	321
-3	6	456	405
-3	8	659	427
-3	9	222	183
-3	10	507	493
-2	2	1368	1357
-2	3	224	220
-2	4	1205	1253
-2	5	319	359
-2	6	980	1050
-2	7	262	275
-2	8	966	986
-2	10	804	700
-1	3	325	360
-1	4	268	333
-1	5	247	216
-1	7	215	232
-1	8	280	295
-1	9	396	346
-1	10	329	338
0	0	1666	1668
0	1	422	507
0	2	1262	1274
0	3	225	214
0	4	820	818
0	6	931	959
0	7	214	146
0	8	980	940
1	1	450	460
1	3	342	318
1	6	240	284
1	8	249	216
1	9	205	202
2	0	1137	1081
2	2	805	786
2	4	833	864
2	5	239	299
2	6	991	1075
2	7	240	307
2	8	822	808
3	3	234	198
3	5	227	326
4	0	1136	1139
4	1	183	73
4	2	1081	1095
4	3	342	298
4	4	1050	1073
4	5	215	184
4	6	865	876
6	0	1080	1080
6	2	1063	995
6	4	1092	1081
6	5	522	502
7	0	268	294
7	2	359	366
7	3	248	245
8	0	844	853
8	1	213	62
8	2	831	847
9	0	455	432
***** K = 9 *****			
-6	2	330	259
-6	3	232	211
-6	4	278	237
-6	5	366	409
-5	1	297	207
-5	2	846	835
-5	4	917	871
-5	6	906	853
-4	1	283	275
-4	3	244	261
-4	4	363	329
-4	6	410	388
-3	2	1054	1060
-3	3	328	323
-3	4	991	1006
-3	5	276	296
-3	6	823	817
-2	4	265	266
-2	6	322	379
-1	1	214	220
-1	2	956	1011
-1	3	291	350
-1	4	918	904
-1	6	747	684
1	0	1053	1150
1	2	729	824
1	4	766	757
3	0	686	665
3	1	297	343
3	2	759	757
3	3	284	323
3	4	790	799
5	0	647	708
5	1	281	256

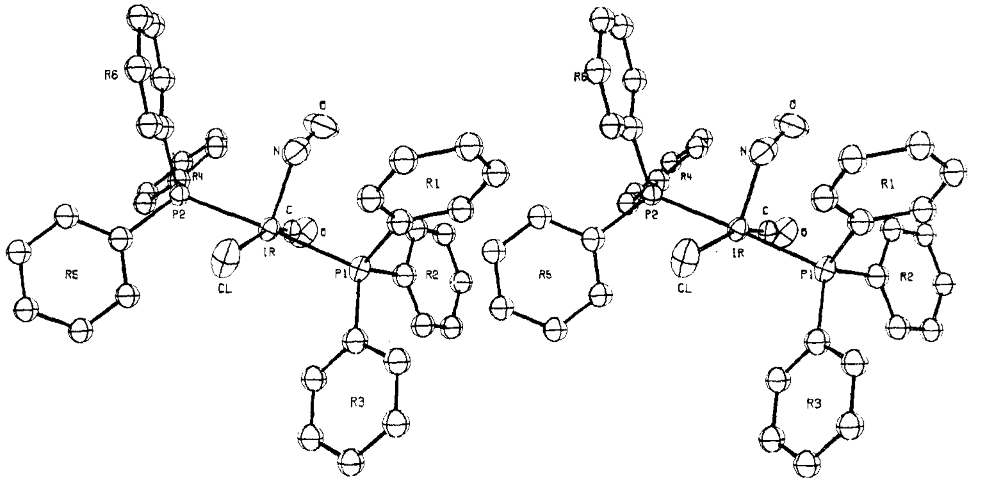

Figure 3.—Stereoscopic view of the $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ cation. Phenyl hydrogen atoms are not shown. Phenyl carbon atoms are shown with $B = 3.5$ Å^2.

TABLE IV

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Intramolecular distance, Å		Angle, deg	
Ir–N	1.972 (11)	N–Ir–P_1	90.1 (3)
Ir–O (of NO)	2.791 (9)	N–Ir–P_2	91.3 (3)
Ir–Cl	2.343 (3)	N–Ir–Cl	101.3 (3)
Ir–P_1	2.408 (3)	N–Ir–C	97.4 (5)
Ir–P_2	2.407 (3)	P_1–Ir–P_2	175.70 (9)
Ir–C	1.858 (14)	P_1–Ir–Cl	88.9 (1)
Ir–O (of CO)	3.016 (9)	P_1–Ir–C	91.2 (3)
N–O	1.16 (1)	P_2–Ir–Cl	86.8 (1)
N–P_1	3.11 (1)	P_2–Ir–C	92.7 (3)
N–P_2	3.15 (1)	Cl–Ir–C	161.3 (3)
N–Cl	3.35 (1)	Ir–C–O	178.1 (9)
N–C (of CO)	2.88 (2)	Ir–N–O	124.1 (9)
P–C (av of 6)	1.81	C–P–C (av of 6)	105.9
P_1–P_2	4.811 (4)		
P_1–Cl	3.328 (4)		
P_2–Cl	3.265 (4)		
P_1–C (of CO)	3.07 (1)		
P_2–C (of CO)	3.11 (1)		
Cl–C (of CO)	4.15 (1)		

TABLE V

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

Atom	Minimum	Intermediate	Maximum
Ir	0.1773 (9)	0.1825 (9)	0.2136 (8)
P_1	0.175 (5)	0.198 (5)	0.223 (5)
P_2	0.176 (5)	0.178 (5)	0.207 (5)
Cl	0.184 (5)	0.219 (5)	0.346 (4)
C	0.163 (20)	0.190 (20)	0.263 (19)
O (of CO)	0.188 (15)	0.258 (12)	0.301 (12)
N	0.216 (15)	0.224 (15)	0.294 (15)
O (of NO)	0.205 (15)	0.293 (13)	0.342 (13)

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

same reasoning as given for the NO^+ case, that the metal–sulfur bond would be long and that the geometry at the S atom would be essentially tetrahedral. The Ir–S bond of 2.49 (1) Å and Ir–S–O angles of 104.2 (1.5) and 107.6 (1.5)° found in the SO_2 analog, $IrCl(CO)(SO_2)(P(C_6H_5)_3)_2$,[7] strongly support such a model.

There is other evidence that the SO_2 is σ bonded to

TABLE VI

THREE-DIMENSIONAL CRYSTALLOGRAPHIC DATA ON METAL-NITROSYL COMPLEXES

Complex	M–N, Å	N–O, Å	M–N–O, deg
$Cs[Fe_4(NO)_7S_3]\cdot H_2O$[a]	1.57,[b] 1.71, 1.63, 1.73 1.66, 1.70, 1.61	1.25,[c] 1.13, 1.17, 1.21 1.26, 1.17, 1.21	166,[d] 169, 160, 166, 175, 173, 165
$[Fe(NO)_2SC_2H_5]_2$[e]	1.66 (1)	1.18 (2)	167.2 (3.5)
	1.67 (1)	1.16 (2)	167.7 (3.5)
$Co(NO)(S_2CN(CH_3)_2)_2$[f]	1.70	1.1	127
$Fe(NO)(S_2CN(CH_3)_2)_2$[g]	1.71 (2)	1.1	160
$Fe(NO)(S_2CN(C_2H_5)_2)_2$[h]	1.69 (4)	1.16 (5)	174 (4)
$Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$[i]	1.63 (2)	1.13 (2)	178.3 (1.3)
$[Co(NH_3)_5NO]Cl_2$	1.99[j]	1.26[j]	180
	2.03[k]	1.41[k]	180
$Na_2[Ru(NO)(NO_2)_4OH]\cdot 2H_2O$[l]	1.748 (4)	1.127 (7)	179.98 (55)
π-$(C_5H_5)CrCl(NO)_2$[m]	1.72 (1)	1.13 (2)	166.4 (1.3)
	1.70 (1)	1.15 (2)	170.8 (1.3)
$Mn(CO)_2(NO)(P(C_6H_5)_3)_2$[n]	1.73 (1)	1.18 (1)	178.0 (1.3)
$Mn(CO)_3(NO)(P(C_6H_5)_3)$[o]	1.78 (2)	1.15 (1)	177.9 (1.4)
$[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$[p]	1.972 (11)	1.16 (1)	124.1 (9)

[a] G. Johansson and W. N. Lipscomb, *Acta Cryst.*, **11**, 594 (1958). [b] Estimated standard deviation on Fe–N lengths is 0.04 Å. [c] Estimated standard deviation on N–O lengths is 0.06 Å. [d] Values calculated from the atomic coordinates reported. [e] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, **11**, 599 (1958). [f] Reference 1. [g] G. R. Davies, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 81 (1968). [h] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *ibid.*, 583 (1967). [i] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963). [j] D. A. Hall and A. A. Taggart, *J. Chem. Soc.*, 1359 (1965). [k] D. Dale and D. C. Hodgkin, *ibid.*, 1364 (1965). [l] S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, **27**, 309 (1965) [m] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc., A*, 1095 (1966). [n] Reference 20. [o] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2339 (1968). [p] This work.

the metal in $IrCl(CO)(SO_2)(P(C_6H_5)_3)_2$ and related complexes. In π-bonded complexes the bonding changes markedly with chemical substitution. Thus, in the molecular oxygen complexes the replacement of Cl by I causes the O–O bond length to increase from 1.30[6] to 1.51 Å.[26] This change is ascribed to the greater electron density at the metal in the iodo complex; the more strongly the O_2 group is bound to the metal, the longer is the O–O bond.[26] Conversely, replacement of Ir by Rh, which reduces the electron density at the metal, causes a reduction in the O–O length. Thus in $[Ir(O_2)(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2][PF_6]$, the O–O bond length is 1.66 Å,[8] whereas in the corresponding Rh complex the O–O bond length is only 1.42 Å.[27] In the SO_2 complexes, however, no such changes are observed; in $RhCl(CO)(SO_2)(P(C_6H_5)_3)_2$ the Rh–S bond is 2.450 Å,[28] very similar to the Ir–S length of 2.49 Å in the analogous Ir complex.[7] Furthermore, the geometry around the S atom in the Rh complex compares very well with that found in the Ir complex.[7,28] In view of the large changes observed for π-bonded complexes, this absence of any real change in the bonding on change of the electron density at the metal strongly suggests that the M–S bond is largely σ in character.

We believe that similar results will be obtained for the nitrosyl complexes. In order to test this hypothesis, we are undertaking structural studies of the analogous iodo complex, $[IrI(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$, and of several other related complexes, including $IrCl(CO)_2(P(C_6H_5)_3)_2$.

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(28) K. W. Muir and J. A. Ibers, to be submitted for publication.