Contribution from the Chemistry Department,
University of Auckland, Auckland, New Zealand

Crystal and Molecular Structure of a Second Isomer of Hydridonitrosyltris(triphenylphosphine)iridium(I) Perchlorate

G. R. CLARK, J. M. WATERS,* and K. R. WHITTLE

Received July 23, 1973

AIC30551X

The crystal structure of a second isomer of hydridonitrosyltris(triphenylphosphine)iridium(I) perchlorate, [IrH(NO)(P-$(C_6H_5)_3)_3]ClO_4$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group *Pbca* of the orthorhombic system with eight molecules in a unit cell of dimensions $a = 23.245$ (2), $b = 21.308$ (2), and $c = 19.441$ (5) Å. Least-squares refinement has given a final R of 0.089 for the 2654 reflections having $I > 3\sigma(I)$. The cation adopts a distorted trigonal-bipyramidal arrangement with two triphenylphosphine ligands in the apical positions. The trigonal plane contains the remaining triphenylphosphine group, a linear nitrosyl, and presumably the hydrido ligand, but this last group was not located. The linear nitrosyl group suggests that the complex is best formulated as an NO^+ complex of Ir(I). The structures of the two isomers differ in the relative arrangement of ligands about the central metal atom.

Two common modes of coordination to transition metals have been established for the nitrosyl group. When bound in the "bent" mode with a metal–nitrogen–oxygen angle close to 120°, this ligand is formulated as NO^- whereas it is best regarded as NO^+ when the link is a linear one. Further, in five-coordinate iridium complexes the manner of binding of the nitrosyl ligand and the configuration about the central metal atom are closely interrelated. In, for example, the complexes $[IrX(NO)(CO)(PPh_3)_2][BF_4]$ (X = Cl, I)[1,2] and $[IrXY(NO)(PPh_3)_2]$ (X = Y = Cl;[3] X = I, Y = CH_3[4]) the nitrosyl group is bent and is associated with the tetragonal-pyramidal configuration for the metal consistent with the d^6 formulation, Ir^{III}-NO^-. In contrast the formulation Ir^I-NO^+ is consistent with the presence of a linear nitrosyl ligand and trigonal-bipyramidal geometry about the metal. That the metal configuration and nitrosyl geometry is sensitive to the electronegativity and steric requirements of other ligands present is shown by the change in geometry which occurs on replacement of groups X and Y by groups of differing electronegativity.[5] Three isomers of the complex $[IrH(NO)(PPh_3)_3]ClO_4$ have been isolated (green, brown, and black) and all show variations in the position of the ir band attributed to the stretching vibration of the nitrosyl group (1715, 1720, and 1780 cm^{-1}, respectively).[6] A structural analysis of the black isomer[5] (also referred to as dark brown) reveals a distorted trigonal-bipyramidal arrangement about the central iridium atom and a linear nitrosyl group. Thus this complex must be formulated as Ir^I-NO^+ despite its apparent similarity with the previously cited tetragonal-pyramidal complexes. For the remaining green and brown isomers the ir data allow no conclusions concerning the nature of the nitrosyl ligand or the precise configuration about the iridium atom. We report here the results of an X-ray structural analysis on the brown isomer of $[IrH(NO)(PPh_3)_3]^+$.

Collection and Reduction of Intensity Data

Brown tabular crystals of a second form of $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$ were kindly supplied by Dr. W. R. Roper. Preliminary Weissenberg photography established that the crystals belong to the orthorhombic system and the systematic absences observed (*hk*0, *h* odd; 0*kl*, *k* odd; *h*0*l*, *l* odd) are consistent with the space group *Pbca*. On the basis of optical goniometry the faces of the crystal chosen for data collection were identified as (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), and (00$\bar{1}$). Lattice constants were determined from a least-squares refinement of the setting angles of 12 reflections[7] centered on a Hilger and Watts automatic four-circle diffractometer using Cu Kα radiation (λ 1.5418 Å). They are $a = 23.245$ (2), $b = 21.308$ (2), and $c = 19.441$ (5) Å. The density calculated for eight formula weights per unit cell is 1.53 g/cm^3 in agreement with that (1.52 g/cm^3) measured by flotation in a carbon tetrachloride–ethanol mixture.

For the data collection a crystal with dimensions 0.25 × 0.20 × 0.03 mm was chosen and mounted approximately along [*c*]. Intensities were measured by the ω-2θ scan technique, a symmetric scan range of 1.20° being used. No attenuators were required. The pulse height analyzer was set for approximately a 90% window centered on the Cu Kα peak.

The intensities of three standard reflections were measured every 100 reflections and they showed deviations less than ±3%. Intensity data were collected up to θ(Cu Kα) = 49° and were processed according to the procedure described by Ibers.[8] An initial p value of 0.04 was chosen. A total of 2654 independent reflections were observed with $I > 3\sigma(I)$. The linear absorption coefficient for the compound for Cu Kα radiation is 71.4 cm^{-1} and hence absorption corrections were applied to the data[9] the factors ranging from 1.26 to 1.75.

Solution and Refinement of the Structure

A "sharpened" Patterson synthesis revealed the site of the iridium atom and the subsequent structure factor calculation returned the conventional residual, R_1, as 0.32. From the "heavy atom" electron density map all nonhydrogen atoms other than those of the perchlorate group were located ($R_1 = 0.19$); sites of the remaining atoms were determined from a second electron density map ($R_1 = 0.17$). The atomic scattering factors used for the iridium atom were those of Cromer and Waber[10] and for all other atoms those listed in ref 11. The effects of anomalous dispersion were included in the calculation of F_c,[12] the values of Δf^{I} and Δf^{II} for iridium, phosphorus, and chlorine being those given by Cromer.[13] Four cycles of block-diagonal least-squares refinement assuming isotropic thermal motion lowered the discrepancy factors R_1 and $R_2 = (\Sigma w\cdot(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ to 0.118 and 0.134, respectively, where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$.[14] The function mini-

---

(1) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 7, 2345 (1968).

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

(3) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1035 (1971).

(4) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, 10, 1043 (1971).

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

(6) C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).

(7) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967).

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

(9) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957).

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

(11) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

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

(13) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(14) R. C. G. Killean, *Acta Crystallogr.*, 23, 54 (1967).

Table I. Atomic Coordinates and Isotropic Thermal Parameters[a]

Atom	x/a	y/b	z/c	B, Å^2
Ir	0.08146 (4)	0.20268 (4)	0.22230 (5)	
Cl	0.1971 (5)	0.0050 (4)	0.4545 (5)	
P(1)	0.0194 (3)	0.1166 (3)	0.2059 (3)	
P(2)	0.0288 (3)	0.2687 (3)	0.2959 (3)	
P(3)	0.1767 (3)	0.2268 (3)	0.2470 (4)	
O(1)	0.0940 (11)	0.2243 (12)	0.0738 (11)	
N(1)	0.0864 (10)	0.2171 (9)	0.1312 (9)	
O(11)	0.2499 (20)	0.0186 (19)	0.4823 (20)	15.1 (1.2)
O(12)	0.1601 (23)	0.0511 (27)	0.4438 (27)	21.2 (1.9)
O(13)	0.1702 (23)	−0.0502 (26)	0.4742 (28)	20.6 (1.9)
O(14)	0.2034 (22)	−0.0069 (24)	0.3832 (26)	19.9 (1.8)

[a] In all tables standard deviations are in parentheses.

Table II. Anisotropic Thermal Parameters (×10^4)[a]

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ir	16.0 (2)	11.3 (2)	19.7 (2)	−2.2 (5)	1.8 (5)	−4.2 (5)
Cl	51 (3)	27 (2)	46 (3)	−1 (5)	−36 (5)	−2 (5)
P(1)	18 (1)	13 (1)	22 (2)	1 (3)	−7 (3)	1 (3)
P(2)	19 (2)	13 (1)	20 (2)	1 (3)	−1 (3)	−2 (3)
P(3)	16 (2)	15 (1)	25 (2)	−10 (3)	0 (3)	3 (3)
O(1)	55 (7)	62 (8)	25 (6)	−64 (12)	15 (12)	−22 (13)
N(1)	30 (5)	27 (6)	6 (5)	−35 (10)	4 (10)	5 (9)

[a] The scattering factor is in the form $f = f_o \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Table III. Rigid-Group Parameters[a]

Phenyl ring	x_c	y_c	z_c	δ	ϵ	η
11	0.0774 (5)	0.0146 (5)	0.1022 (6)	1.593 (11)	−2.956 (10)	−2.440 (11)
12	−0.0115 (6)	0.0274 (7)	0.3344 (8)	1.302 (19)	2.377 (14)	2.412 (19)
13	−0.0908 (6)	0.1627 (6)	0.1204 (8)	−1.825 (15)	2.690 (12)	−1.748 (15)
21	−0.0489 (7)	0.1943 (6)	0.4076 (7)	0.663 (17)	2.383 (13)	2.628 (17)
22	−0.0657 (5)	0.3534 (6)	0.2159 (6)	−2.653 (14)	2.627 (11)	−1.111 (14)
23	0.1015 (5)	0.3765 (5)	0.3736 (6)	2.511 (12)	2.704 (10)	−1.482 (13)
31	0.2332 (5)	0.3364 (6)	0.1544 (6)	1.656 (11)	−3.073 (11)	−0.716 (11)
32	0.2120 (6)	0.2541 (7)	0.4047 (7)	−0.428 (18)	2.369 (11)	1.361 (18)
33	0.2490 (6)	0.1058 (7)	0.1999 (7)	0.264 (18)	2.434 (12)	−1.284 (19)

[a] x_c, y_c, z_c are the fractional coordinates of the phenyl ring center; δ, ϵ, η are in radians.

mized was $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic thermal motion was then assumed for all nonhydrogen atoms other than those of the phenyl groups and perchlorate oxygens. The phenyl rings were refined as rigid groups ($d_{C-C} = 1.393$ Å),[15-17] and after several cycles of full-matrix least-squares refinement $R_1 = 0.095$ and $R_2 = 0.116$. Analysis of the weighting scheme showed that $\langle w\Delta F^2 \rangle$ was dependent on $|F_o|$ and hence the p value was increased to 0.06 to further downweight reflections of high intensity. Further least-squares refinement converged with $R_1 = 0.089$ and $R_2 = 0.112$ and inspection of $\langle w\Delta F^2 \rangle$ now showed it to be approximately constant over the range of F_o values. The final difference map showed no peak which could be unambiguously assigned to the hydrogen atom attached to the metal. No attempt was made to locate the phenyl ring hydrogen atoms. The final atomic parameters with their standard deviations are listed in Tables I-IV. The numbering system of the molecule is given in Figure 1, and in Figure 2 is shown the inner coordination sphere of the $IrH(NO)(PPh_3)_3^+$ ion. Bond distances and angles other than those associated with the phenyl rings are given in Tables V and VI, with their standard deviations. Root-mean-square amplitudes of vibration have been calculated for those atoms where anistropic thermal motion has been assumed and are given in Table VII. A table of observed and calculated structure amplitudes is available.[18]

Results and Discussion

The crystal structure of the brown isomer of $[IrH(NO)(PPh_3)_3]ClO_4$ consists of monomeric ions. The iridium atom adopts a distorted trigonal-bipyramidal arrangement with two triphenylphosphine groups occupying apical positions. In the trigonal plane lie the remaining triphenylphosphine group, an essentially linear nitrosyl group, and presumably the hydrido ligand, but this last group was not located. The structure can be compared with the black isomer where the three triphenylphosphine ligands form the trigonal plane and the linear nitrosyl occupies one of the apical positions.[5] In this analysis also the hydrido ligand was not located but was assumed to occupy the remaining apical position.

Distortion of the trigonal bipyramid can be seen in the trans phosphorus angle of 141.6 (2)° (180° if no distortion)—see Figure 2b—and compares with 153.1 (2)° found in the similar hydrido complex, $RuHCl(PPh_3)_3$.[19] The P(2)-Ir-N(1) angle shows little deviation from the ideal value (122.1 (7)°) but for P(1)-Ir-P(2) (103.3 (2)°), P(1)-Ir-N(1) (92.2 (7)°), P(2)-Ir-P(3) (103.8 (3)°) and P(3)-Ir-N(1) (96.0 (7)°) there is considerable distortion from the ideal values, this presumably arising from repulsions between the three bulky triphenylphosphine groups.

The coordinated nitrosyl makes an angle of 174.5 (2.1)° at the nitrogen suggesting that this group is linear or very nearly so. The root-mean-square amplitudes of vibration determined for the oxygen atom are greater than those for the other atoms, an effect which has been observed elsewhere.[5,20] The iridium-nitrogen bond length of 1.80 (2) Å is slightly longer than the range of 1.57-1.77 Å found so far for $Ir-NO^+$ but it is clearly shorter than the range (1.89-1.97 Å) observed for $Ir-NO^-$.[5] A thermal motion correction for the Ir-N(1) bond has been calculated[21] (0.02 Å) and the bond length is increased slightly but still does not differ significantly from the range already observed for the NO^+ group. The nitrogen-oxygen bond length of 1.14 (3) Å is a normal value.

Although the hydride ligand was not located, the overall geometry of the brown isomer is very similar to that found in the compounds $RuHCl(PPh_3)_3$[19] and $RhHCl(SiCl_3)(PPh_3)_2 \cdot xSiHCl_3$[22] which adopt distorted trigonal-bipyramidal structures with apical triphenylphosphine groups and the hydride ligand in the trigonal plane. In both these compounds an α hydrogen of a phenyl ring comes within 2.85 and 2.79 Å of the central metal and blocks the sixth coordination site. This α hydrogen is believed to stabilize[23,24] the five-coordinate geometry. In the present analysis, an α hydrogen (H(112)) is estimated to lie 3.0 Å away from the iridium atom

---

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

(16) S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965).

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

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

(19) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 1230 (1968).

(20) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1094 (1972).

(21) D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 757 (1956).

(22) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970).

(23) J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 2088 (1963).

(24) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

Table IV. Derived Parameters for the Phenyl Ring Carbon Atoms

Atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
		Phenyl Ring 11		
C(111)	0.0533 (8)	0.0572 (7)	0.1482 (8)	2.6 (5)
C(112)	0.1121 (7)	0.0586 (7)	0.1350 (9)	3.8 (6)
C(113)	0.1363 (5)	0.0160 (9)	0.0890 (10)	4.3 (6)
C(114)	0.1015 (8)	−0.0281 (7)	0.0563 (8)	4.0 (6)
C(115)	0.0427 (7)	−0.0295 (7)	0.0695 (9)	4.6 (7)
C(116)	0.0186 (5)	0.0132 (8)	0.1154 (9)	3.7 (6)
		Phenyl Ring 12		
C(121)	0.0011 (11)	0.0674 (11)	0.2793 (9)	4.4 (6)
C(122)	0.0427 (8)	0.0549 (2)	0.3293 (11)	5.1 (7)
C(123)	0.0302 (9)	0.0149 (10)	0.3839 (10)	5.1 (7)
C(124)	−0.0240 (12)	−0.0126 (11)	0.3890 (11)	7.0 (9)
C(125)	−0.0657 (9)	0.0000 (16)	0.3394 (14)	8.6 (1.1)
C(126)	−0.0531 (8)	0.0400 (11)	0.2848 (12)	8.0 (1.0)
		Phenyl Ring 13		
C(131)	−0.0454 (8)	0.1395 (11)	0.1597 (9)	3.7 (6)
C(132)	−0.0975 (9)	0.1543 (10)	0.1910 (8)	5.4 (7)
C(133)	−0.1429 (7)	0.1774 (11)	0.1517 (12)	7.4 (9)
C(134)	−0.1361 (9)	0.1858 (14)	0.0811 (12)	8.8 (1.2)
C(135)	−0.0840 (11)	0.1710 (11)	0.0498 (8)	6.2 (8)
C(136)	−0.0386 (8)	0.1479 (10)	0.0891 (10)	4.6 (7)
		Phenyl Ring 21		
C(211)	−0.0159 (8)	0.2283 (12)	0.3608 (9)	3.4 (5)
C(212)	0.0109 (7)	0.1909 (14)	0.4101 (10)	4.6 (6)
C(213)	−0.0222 (10)	0.1569 (10)	0.4568 (10)	6.8 (1.0)
C(214)	−0.0819 (10)	0.1603 (13)	0.4543 (11)	6.6 (8)
C(215)	−0.1087 (6)	0.1977 (16)	0.4051 (12)	8.5 (1.0)
C(216)	−0.0757 (8)	0.2317 (9)	0.3583 (10)	4.7 (6)
		Phenyl Ring 22		
C(221)	−0.0223 (8)	0.3181 (9)	0.2467 (9)	2.2 (4)
C(222)	−0.0468 (8)	0.3683 (9)	0.2819 (7)	4.8 (6)
C(223)	−0.0901 (9)	0.4036 (8)	0.2512 (10)	5.3 (7)
C(224)	−0.1090 (9)	0.3887 (11)	0.1851 (11)	6.0 (8)
C(225)	−0.0845 (8)	0.3385 (11)	0.1499 (8)	6.1 (7)
C(226)	−0.0412 (8)	0.3032 (7)	0.1807 (8)	4.7 (6)
		Phenyl Ring 23		
C(231)	0.0695 (7)	0.3287 (7)	0.3433 (8)	3.1 (5)
C(232)	0.0763 (9)	0.3304 (8)	0.4144 (8)	4.2 (6)
C(233)	0.1083 (9)	0.3782 (9)	0.4447 (6)	5.7 (8)
C(234)	0.1335 (8)	0.4243 (8)	0.4039 (9)	4.8 (7)
C(235)	0.1267 (9)	0.4227 (8)	0.3328 (9)	4.9 (7)
C(236)	0.0947 (8)	0.3749 (8)	0.3024 (6)	3.7 (6)
		Phenyl Ring 31		
C(311)	0.2091 (8)	0.2914 (7)	0.1975 (8)	3.6 (5)
C(312)	0.2686 (7)	0.2969 (9)	0.1926 (9)	4.9 (6)
C(313)	0.2927 (6)	0.3420 (10)	0.1495 (11)	6.0 (8)
C(314)	0.2573 (9)	0.3815 (8)	0.1113 (10)	5.6 (7)
C(315)	0.1978 (8)	0.3760 (8)	0.1162 (9)	4.4 (6)
C(316)	0.1737 (5)	0.3309 (8)	0.1593 (9)	3.0 (5)
		Phenyl Ring 32		
C(321)	0.1964 (9)	0.2451 (10)	0.3362 (7)	3.6 (6)
C(322)	0.1786 (13)	0.2025 (11)	0.3862 (10)	4.6 (6)
C(323)	0.1943 (10)	0.2115 (9)	0.4546 (9)	6.7 (9)
C(324)	0.2277 (11)	0.2631 (12)	0.4731 (8)	6.3 (9)
C(325)	0.2454 (13)	0.3056 (11)	0.4231 (11)	6.7 (8)
C(326)	0.2298 (9)	0.2967 (8)	0.3547 (10)	5.9 (7)
		Phenyl Ring 33		
C(331)	0.2205 (13)	0.1597 (10)	0.2218 (10)	3.2 (5)
C(332)	0.2323 (10)	0.1117 (11)	0.2684 (8)	5.6 (7)
C(333)	0.2609 (10)	0.0579 (8)	0.2465 (11)	7.1 (9)
C(334)	0.2775 (14)	0.0519 (11)	0.1780 (12)	6.8 (9)
C(335)	0.2657 (11)	0.0998 (12)	0.1314 (8)	7.2 (9)
C(336)	0.2371 (10)	0.1537 (9)	0.1533 (9)	6.2 (8)

and in such a position that the hydrido ligand must be considerably distorted from its ideal position in the trigonal plane. In the ruthenium and rhodium compounds the metal–hydrido ion bond length is 1.7 (2) Å in the former and 1.48 Å in the latter, although in $RhHCl(SiCl_3)(PPh_3)_2 \cdot xSiHCl_3$ there is some doubt concerning its location. In both these analyses also the hydrido ion is considerably distorted from its ideal position.

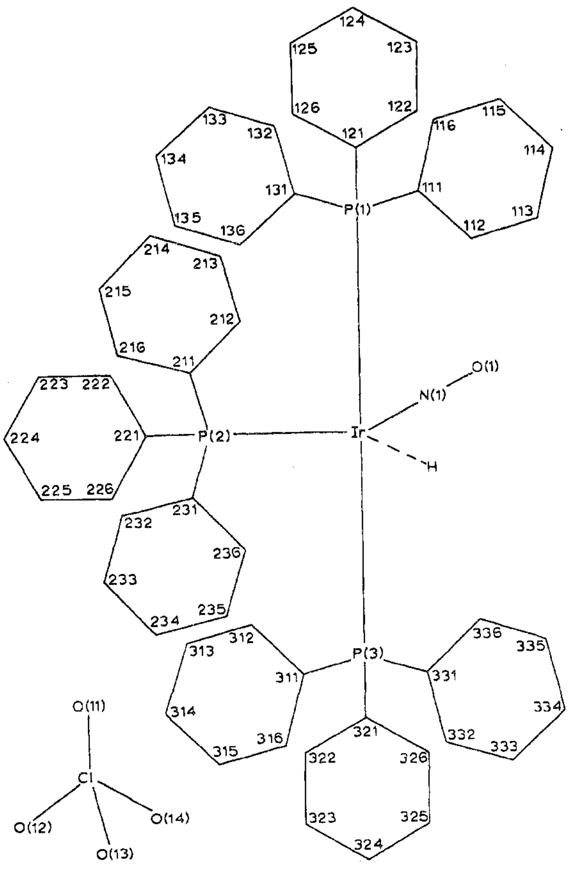

Figure 1. Diagram showing the numbering system.

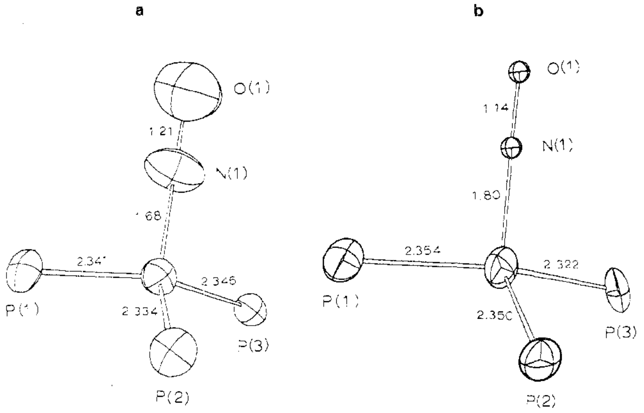

Figure 2. The inner coordination sphere of the $IrH(NO)(PPh_3)_3{}^+$ ion: (a) black isomer;[5] (b) brown isomer (ORTEP diagrams, 50% probability contours for atomic vibration ellipsoids).

The average iridium–phosphorus bond length of 2.342 (17) Å can be compared with that found in the black isomer (average 2.340 (6) Å)[5] and in $IrCl(CO)_2(PPh_3)_2$ (average 2.332 (13) Å)[25] where the phosphorus atoms lie in trans positions to one another. Within the triphenylphosphine groups all bond distances and angles are normal. The average phosphorus–carbon bond length and iridium–phosphorus–carbon, carbon–phosphorus–carbon, and phosphorous-carbon–carbon angles are 1.84 (2) Å, 114 (4)°, 104 (3)°, and 120 (3)°, respectively, and these compare well with the mean phosphorus–carbon bond length of 1.81 (1) Å and carbon–phosphorus–carbon angle of 104 (1)° found in $IrCl(CO)_2(PPh_3)_2$.[25]

The high isotropic thermal parameters of the perchlorate

---

(25) N. C. Payne and J. A. Ibers, *Inorg. Chem.*, **8**, 2714 (1969).

Table V. Bond Lengths (Å)

Ir-P(1)	2.354 (7)	P(1)-C(131)	1.82 (2)	P(3)-C(331)	1.82 (2)
Ir-P(2)	2.350 (7)	P(2)-C(211)	1.85 (2)	O(1)-N(1)	1.14 (3)
Ir-P(3)	2.322 (8)	P(2)-C(221)	1.85 (2)	Cl-O(11)	1.37 (5)
Ir-N(1)	1.80 (2)	P(2)-C(231)	1.84 (2)	Cl-O(12)	1.32 (6)
P(1)-C(111)	1.87 (2)	P(3)-C(311)	1.84 (2)	Cl-O(13)	1.39 (6)
P(1)-C(121)	1.83 (2)	P(3)-C(321)	1.84 (2)	Cl-O(14)	1.42 (5)

Table VI. Bond Angles (deg)

P(1)-Ir-P(2)	103.3 (2)	P(1)-C(111)-C(112)	121 (2)
P(1)-Ir-P(3)	141.6 (2)	P(1)-C(111)-C(116)	119 (2)
P(1)-Ir-N(1)	92.2 (7)	P(1)-C(121)-C(122)	119 (2)
P(2)-Ir-P(3)	103.8 (3)	P(1)-C(121)-C(126)	121 (2)
P(2)-Ir-N(1)	122.1 (7)	P(1)-C(131)-C(132)	124 (2)
P(3)-Ir-N(1)	96.0 (7)	P(1)-C(131)-C(136)	115 (2)
Ir-N(1)-O(1)	174.5 (2.1)	P(2)-C(211)-C(212)	119 (2)
Ir-P(1)-C(111)	110.6 (7)	P(2)-C(211)-C(216)	121 (2)
Ir-P(1)-C(121)	118.9 (9)	P(2)-C(221)-C(222)	116 (2)
Ir-P(1)-C(131)	111.4 (8)	P(2)-C(221)-C(226)	123 (2)
Ir-P(2)-C(211)	115.5 (9)	P(2)-C(231)-C(232)	125 (2)
Ir-P(2)-C(221)	111.1 (8)	P(2)-C(231)-C(236)	115 (2)
Ir-P(2)-C(231)	117.0 (7)	P(3)-C(311)-C(312)	120 (2)
Ir-P(3)-C(311)	116.6 (7)	P(3)-C(311)-C(316)	119 (2)
Ir-P(3)-C(321)	118.7 (8)	P(3)-C(321)-C(322)	117 (2)
Ir-P(3)-C(331)	107.6 (9)	P(3)-C(321)-C(326)	123 (2)
C(111)-P(1)-C(121)	100 (1)	P(3)-C(331)-C(332)	121 (2)
C(111)-P(1)-C(131)	104 (1)	P(3)-C(331)-C(336)	119 (2)
C(121)-P(1)-C(131)	110 (1)	O(11)-Cl-O(12)	119 (3)
C(211)-P(2)-C(221)	105 (1)	O(11)-Cl-O(13)	118 (3)
C(211)-P(2)-C(231)	106 (1)	O(11)-Cl-O(14)	109 (3)
C(221)-P(2)-C(231)	101 (1)	O(12)-Cl-O(13)	112 (3)
C(311)-P(3)-C(321)	103 (1)	O(12)-Cl-O(14)	93 (3)
C(311)-P(3)-C(331)	103 (1)	O(13)-Cl-O(14)	99 (3)
C(321)-P(3)-C(331)	106 (1)		

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

Atom	Min	Intermed	Max
Ir	0.155	0.194	0.212
Cl	0.247	0.258	0.401
P(1)	0.174	0.191	0.232
P(2)	0.170	0.197	0.225
P(3)	0.158	0.218	0.231
O(1)	0.208	0.258	0.481
N(1)	0.092	0.175	0.342

Table VIII. Some Nonbonded Intramolecular Distances (Å)

P(1)· · ·P(2)	3.69	P(2)· · ·N(1)	3.64
P(1)· · ·N(1)	3.02	P(3)· · ·N(1)	3.08
P(2)· · ·P(3)	3.68		

anion (15.1-21.2 Å^2) presumably indicate some disorder, an effect which is also reflected in the wide variation of chlorine-oxygen bond lengths (1.32 (6)-1.42 (5) Å) and bond angles (93 (3)-119 (3)°). For this reason the atomic sites of the perchlorate anion will only be approximate. No other model was sought for this group.

Examination of the nonbonded intramolecular distances shows that no significant interactions occur except for the blocking of the sixth coordination site by hydrogen atom H(112) of phenyl ring 11. In Table VIII nonbonded intramolecular distances of adjacent ligand donor atoms in the cation are listed and these all represent normal approaches. Few intermolecular distances ≤3.50 Å are found (see Table IX) which indicates that the molecules cannot be tightly packed.

Table IX. Intermolecular Distances ≤3.50 Å

Atom 1	Atom 2	Symmetry position of atom 2	Translation	Distance, Å
O(1)	C(232)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	0, 0, −1	3.34
O(1)	C(233)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	0, 0, −1	3.34
O(11)	C(113)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	0, 0, 0	3.44
O(11)	C(314)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	0, 0, 0	3.29
O(13)	C(214)	$\bar{x}, \bar{y}, \bar{z}$	0, 0, 1	3.41
O(14)	C(224)	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	0, −1, 0	3.40

Table X. Selected Bond Angles (deg) for the Two Isomers of $[IrH(NO)(PPh_3)_3]^+$

	Brown	Black		Brown	Black
P(1)-Ir-P(2)	103.3	110.4	P(1)-Ir-N(1)	92	99
P(1)-Ir-P(3)	141.6	118.4	P(2)-Ir-N(1)	122	103
P(2)-Ir-P(3)	103.8	117.6	P(3)-Ir-N(1)	96	106

The coordination spheres for the black[5] and brown isomers are shown in Figure 2; bond angles subtended at the iridium atom for the two forms are given for comparison in Table X. These figures demonstrate the two different geometries. Whereas in the black isomer[5] the three triphenylphosphine groups are best described as lying in the trigonal plane, two of these groups in the brown form occupy apical positions. As a result of the latter arrangement considerable distortion from the ideal geometry is necessary to accommodate the bulky groups. In the brown form further distortion results from the approach of the α hydrogen to within 3.0 Å of the iridium, no such weak interaction being observed for the black form. In both complexes the nitrosyl group is bound in a linear manner but for the brown isomer a longer Ir-N distance is observed (Ir-N(brown), 1.80 Å; *cf.* Ir-N(black), 1.68 (3) Å). It has already been noted that the mode of bonding of the nitrosyl group is particularly sensitive to changes in the π-donor capacity of the iridium atom caused by differences in electronegativity and steric requirements of other ligands present.[5] Such changes have been sufficient to produce different geometries for a five-coordinate iridium atom as well as the alternative bonding mode for the nitrosyl group.

Acknowledgment. We are indebted to the University of Canterbury for the ORTEP diagram.

Registry No. $[IrH(NO)(PPh_3)_3]ClO_4$, 51371-94-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1628.