at present no explanation can be offered for the high molecular weight observed in $CHCl_3$ solution. An X-ray diffraction study on the PF_6 salt is currently under way.

Reactions with Excess Triphenylphosphine. The reaction of the complex $[Ir(NO)PPh_3]_2O$ with PPh_3 seems to involve the removal of the oxygen atom from the bridge and the addition of 2 mol of phosphine to each of the fragments $[Ir(NO)PPh_3]$. The final product contains only iridium(−1).

We suggest that the reactions of the complexes $[IrX(NO)PPh_3]_2O$ (where X = Cl or Br) with PPh_3 follow initially a similar pattern, with removal of the oxygen atom to leave the two fragments $[IrX(NO)PPh_3]^+$ and $[IrX(NO)PPh_3]^-$. Addition of 1 mol of phosphine to the former fragment would result in the formation of the cation $[IrX(NO)(PPh_3)_2]^+$ which is known[13] to accept halide ion readily, to form the complex $IrX_2(NO)(PPh_3)_2$, one of our observed products. This halide ion might be transferred from the other fragment $[IrX(NO)PPh_3]^-$ which on subsequent addition of 2 mol of phosphine would lead to the formation of our second observed product, $Ir(NO)(PPh_3)_3$.

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Registry No. $[Ir(NO)PPh_3]_2O$, 26317-79-3; $[IrCl(NO)PPh_3]_2O$, 53260-38-1; $[IrBr(NO)PPh_3]_2O$, 53260-39-2; $[IrI(NO)PPh_3]_2O$, 53260-40-5; $[IrCl(NO)PPh_3]_2O{\cdot}HgCl_2$, 53260-35-8; $[IrBr(NO)PPh_3]_2O{\cdot}HgBr_2$, 53260-36-9; $[IrI(NO)PPh_3]_2O{\cdot}HgI_2$, 53260-37-0; $[Ir(NO)PPh_3]_2O{\cdot}C_2(CN)_4$, 53260-33-6; $\{[Ir(NO)PPh_3]_2O{\cdot}p\text{-}FC_6H_4N_2\}BF_4$, 53449-42-6; $\{[Ir(NO)PPh_3]_2O{\cdot}p\text{-}FC_6H_4N_2\}PF_6$, 53352-74-2; *trans*-$[IrCl(CO)(PPh_3)_2]$, 15318-31-7; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; $(p\text{-}FC_6H_4N_2)BF_4$, 19578-37-1; $(p\text{-}FC_6H_4N_2)PF_6$, 53260-51-8; PPh_3, 603-35-0.

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Crystal and Molecular Structure of the Bridged Oxygen Complex μ-Oxido-bis[chlorotriphenylphosphinenitrosyliridium(I)]

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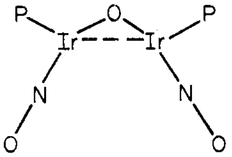
An X-ray crystal structure analysis has been carried out on μ-oxido-bis[chlorotriphenylphosphinenitrosyliridium(I)]. Crystals belong to the triclinic system, space group $P\bar{1}$, a = 16.828 (8) Å, b = 11.515 (6) Å, c = 10.667 (5) Å, α = 66.05 (1)°, β = 107.37 (1)°, and γ = 100.41 (1)°, with two molecules per cell. The complex, which is prepared by treating μ-oxido-bis[triphenylphosphinenitrosyliridium(0)] with $HgCl_2$, has the Ir–O–Ir bridge intact (but with a more obtuse angle) and square-planar coordination about the iridium atoms.

Introduction

It has been shown[1] that treatment of I with 1 equiv of $HgCl_2$ yields $[IrCl(NO)PPh_3]_2O$. We report here a crystal structure analysis of this product confirming that the Ir–O–Ir bridge is left intact but that the Ir–Ir bond has undergone oxidative cleavage.



I

Experimental Section

Crystals of known elemental analysis were supplied by Professor A. Walker.[1]

Crystal data for $Ir_2C_{36}H_{30}N_2O_3Cl_2P_2$, of formula weight 1055.5, are as follows: triclinic, $P1$ or $P\bar{1}$ (latter confirmed); a = 16.828 (8), b = 11.515 (6), c = 10.667 (5) Å; α = 66.05 (1), β = 107.37 (1), γ = 100.41 (1)°; V = 1798.4 (7) Å^3; ρ_o = 1.94 (1), ρ_c = 1.95 g cm^{-3} for Z = 2. No molecular symmetry required.

The crystal used for data collection was of approximate dimensions 0.12 × 0.12 × 0.03 mm mounted perpendicular to the plate. Intensities were collected on a computer-controlled Picker four-circle diffractometer equipped with pulse height analyzer using filtered Cu Kα radiation. Scanning was in θ–2θ mode at 2° min^{-1}. Background was determined for 30 sec at each end of the scan range of 2.2° adjusted for α splitting. The takeoff angle was 3.0°. Throughout the course of data collection there was no significant deviation in the standard reflections recorded after every 50 reflections. Counting statistics

Table II. Atomic Coordinates and Thermal Parameters ($\times 10^4$)[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir(1)	2681 (0.2)	911 (0.4)	2448 (0.4)	18 (0.2)	67 (0.5)	75 (0.6)	5 (0.2)	5 (0.2)	−23 (0.4)
Ir(2)	2338 (0.2)	4146 (0.4)	522 (0.4)	18 (0.2)	67 (0.5)	73 (0.6)	4 (0.2)	4 (0.2)	−26 (0.4)
Cl(1)	1666 (2)	1330 (3)	3321 (3)	40 (1)	122 (3)	118 (3)	20 (2)	29 (2)	−29 (3)
Cl(2)	3412 (2)	3946 (3)	2598 (3)	31 (1)	112 (3)	86 (3)	5 (1)	−7 (1)	−45 (2)
P(1)	3600 (1)	577 (2)	1420 (3)	15 (1)	66 (2)	76 (3)	3 (1)	3 (1)	−25 (2)
P(2)	1371 (1)	4302 (2)	−1577 (3)	17 (1)	66 (2)	73 (3)	4 (1)	4 (1)	−22 (2)
O(1)	3116 (8)	−1290 (10)	5008 (10)	90 (7)	182 (13)	127 (12)	70 (8)	41 (7)	57 (10)
O(2)	2288 (8)	6723 (9)	222 (12)	84 (7)	113 (10)	244 (18)	31 (6)	−11 (9)	−103 (11)
O(3)	2432 (4)	2423 (6)	819 (7)	25 (3)	68 (6)	87 (8)	12 (3)	−4 (4)	−31 (6)
N(1)	2926 (6)	−406 (10)	3940 (10)	33 (4)	123 (11)	110 (12)	23 (5)	14 (5)	−28 (10)
N(2)	2273 (6)	5708 (9)	284 (10)	31 (4)	92 (9)	136 (12)	7 (5)	3 (5)	−65 (9)
C(1)R(1)	4162 (6)	−869 (10)	2592 (11)	22 (4)	75 (9)	96 (12)	6 (5)	−4 (5)	−36 (9)
C(2)R(1)	4997 (7)	−787 (12)	3261 (13)	23 (4)	121 (13)	133 (16)	15 (6)	−7 (6)	−46 (12)
C(3)R(1)	5391 (8)	−1905 (12)	4229 (15)	32 (5)	113 (13)	165 (19)	24 (7)	−15 (8)	−43 (13)
C(4)R(1)	4935 (8)	−3090 (12)	4412 (14)	47 (6)	107 (12)	157 (18)	34 (7)	−6 (9)	−58 (13)
C(5)R(1)	4097 (9)	−3141 (12)	3692 (15)	49 (6)	93 (12)	152 (18)	18 (7)	1 (8)	−47 (12)
C(6)R(1)	3704 (7)	−2033 (11)	2775 (13)	35 (5)	86 (11)	128 (15)	15 (6)	6 (7)	−33 (11)
C(1)R(2)	3107 (7)	275 (9)	−189 (10)	31 (4)	69 (9)	67 (11)	−4 (5)	11 (6)	−24 (8)
C(2)R(2)	3553 (7)	−350 (12)	−641 (13)	32 (5)	125 (13)	126 (15)	7 (6)	16 (7)	−49 (12)
C(3)R(2)	3174 (9)	−606 (13)	−1861 (14)	51 (7)	129 (15)	140 (17)	−5 (8)	22 (9)	−83 (14)
C(4)R(2)	2372 (8)	−212 (14)	−2649 (13)	42 (6)	150 (16)	122 (16)	−9 (8)	10 (8)	−80 (14)
C(5)R(2)	1961 (8)	401 (12)	−2198 (14)	43 (6)	110 (13)	118 (16)	−8 (7)	−17 (8)	−35 (12)
C(6)R(2)	2320 (7)	647 (9)	−945 (11)	28 (4)	66 (9)	82 (12)	5 (5)	−9 (6)	−18 (8)
C(1)R(3)	4389 (5)	1878 (9)	1010 (10)	13 (3)	76 (9)	102 (12)	5 (4)	10 (5)	−29 (8)
C(2)R(3)	4609 (6)	2325 (11)	−262 (12)	23 (4)	89 (11)	134 (15)	3 (5)	14 (6)	−24 (10)
C(3)R(3)	5262 (8)	3332 (12)	−499 (14)	37 (5)	101 (12)	173 (18)	−14 (6)	47 (8)	−42 (12)
C(4)R(3)	5645 (7)	3776 (11)	586 (15)	34 (5)	87 (12)	213 (21)	−16 (6)	31 (8)	−60 (13)
C(5)R(3)	5409 (7)	3332 (12)	1823 (16)	32 (5)	104 (12)	233 (22)	−19 (6)	35 (8)	−93 (14)
C(6)R(3)	4782 (8)	2375 (11)	2059 (14)	38 (5)	91 (12)	158 (18)	−1 (6)	16 (8)	−55 (12)
C(1)R(4)	380 (6)	3369 (10)	−1441 (10)	21 (4)	98 (11)	74 (11)	3 (5)	8 (5)	−28 (9)
C(2)R(4)	385 (8)	2205 (12)	−358 (14)	33 (5)	104 (12)	142 (17)	−5 (7)	4 (8)	−23 (12)
C(3)R(4)	−384 (8)	1474 (13)	−214 (16)	28 (5)	121 (15)	199 (22)	−10 (7)	27 (8)	−34 (14)
C(4)R(4)	−1101 (8)	1908 (14)	−1255 (16)	34 (5)	149 (17)	186 (21)	−34 (7)	22 (8)	−60 (15)
C(5)R(4)	−1101 (8)	3034 (15)	−2366 (15)	33 (5)	154 (17)	161 (19)	−19 (8)	10 (8)	−8 (15)
C(6)R(4)	−350 (7)	3794 (14)	−2481 (13)	25 (5)	160 (16)	123 (16)	−15 (7)	3 (7)	−23 (13)
C(1)R(5)	1798 (6)	3931 (9)	−2733 (11)	23 (4)	67 (9)	98 (12)	7 (5)	5 (5)	−34 (8)
C(2)R(5)	1253 (7)	3579 (12)	−3842 (12)	29 (5)	112 (12)	106 (14)	7 (6)	4 (6)	−46 (11)
C(3)R(5)	1595 (9)	3408 (15)	−4764 (13)	58 (7)	167 (17)	108 (15)	30 (9)	−8 (8)	−78 (14)
C(4)R(5)	2454 (9)	3584 (16)	−4642 (13)	53 (7)	207 (20)	95 (14)	26 (9)	20 (8)	−64 (14)
C(5)R(5)	3019 (10)	3847 (15)	−3486 (15)	61 (8)	148 (17)	142 (18)	1 (9)	38 (10)	−57 (15)
C(6)R(5)	2653 (7)	4032 (12)	−2557 (12)	25 (4)	122 (13)	121 (15)	1 (6)	23 (6)	−52 (11)
C(1)R(6)	1052 (6)	5929 (10)	−2615 (11)	24 (4)	81 (10)	106 (13)	13 (5)	−12 (5)	−34 (9)
C(2)R(6)	1251 (8)	6625 (10)	−3932 (13)	41 (5)	67 (10)	122 (15)	2 (6)	5 (7)	−8 (10)
C(3)R(6)	956 (10)	7840 (14)	−4733 (15)	59 (7)	124 (16)	152 (19)	26 (9)	−10 (9)	−48 (14)
C(4)R(6)	546 (11)	8332 (15)	−4229 (19)	65 (8)	126 (17)	207 (25)	24 (9)	−20 (11)	−45 (17)
C(5)R(6)	335 (8)	7698 (16)	−2923 (21)	33 (5)	179 (19)	338 (32)	40 (8)	−22 (10)	−156 (22)
C(6)R(6)	590 (7)	6454 (13)	−2102 (14)	26 (4)	161 (16)	161 (18)	31 (7)	3 (7)	−63 (14)

[a] The temperature factor is of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

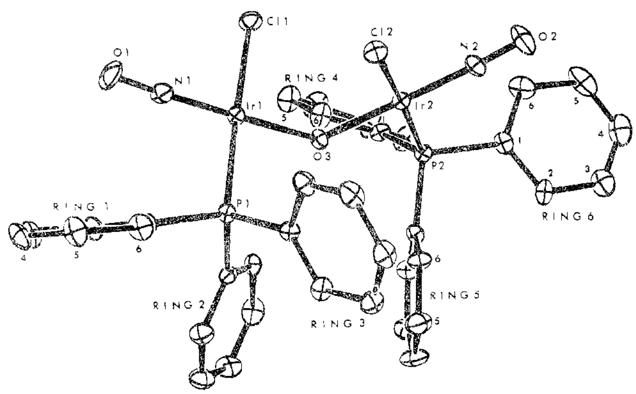


Figure 1. Atomic numbering scheme and thermal ellipsoid plot (30% probability).

and an Abrahams factor[2] of 0.02 were used to calculate $\sigma(I)$. Of the 5992 independent reflections measured, 5639 were considered significant on the criterion $|F_o| > \sigma(F_o)$. Absorption corrections were originally applied, but since, after refinement, these corrections were found to increase R slightly, they were omitted.

Table III

	Bond Lengths, Å		
Ir(1)-O(3)	1.897 (7)	N(2)-O(2)	1.14 (2)
Ir(2)-O(3)	1.906 (8)	P(1)-C(1)R(1)[a]	1.84 (1)
Ir(1)-Cl(1)	2.372 (3)	P(1)-C(1)R(2)	1.81 (1)
Ir(2)-Cl(2)	2.359 (3)	P(1)-C(1)R(3)	1.82 (1)
Ir(1)-P(1)	2.306 (3)	P(2)-C(1)R(4)	1.82 (1)
Ir(2)-P(2)	2.301 (3)	P(2)-C(1)R(5)	1.81 (1)
Ir(1)-N(1)	1.70 (1)	P(2)-C(1)R(6)	1.83 (1)
Ir(2)-N(2)	1.73 (1)	C-C(mean)	1.39 (2)
N(1)-O(1)	1.18 (2)		
	Nonbonded Distances, Å		
Ir(1)· · ·Ir(2)	3.505 (2)	Cl(1)· · ·H(5)R(6) (at $\bar{x}, \bar{y}, \bar{z}$)	2.82
Cl(1)· · ·Cl(2)	3.817 (5)	O(3)· · ·H(2)R(4)	2.43

[a] R(n) means Ring n.

The Patterson function showed only four strong independent peaks indicative of $P\bar{1}$ rather than $P1$ (six peaks expected). The space group $P\bar{1}$ was confirmed by complete structure analysis. Application of the heavy-atom method was routine. Refinement was by the XFLS-3 program[3] using weights from counting statistics[2] and Hartree–Fock scattering factors[4] with appropriate corrections for anomalous dispersion applied for Ir, Cl, and P. Hydrogen atomic positions could not be determined from the Fourier difference map using phases from full anisotropic refinement and were not included in the F_c listed in Table I. (See paragraph at end of paper regarding supplementary material.) Their positions were however calculated and used to check for any unusual interatomic distances. The final conventional unweighted R was 0.062; the weighted R, 0.083. The final difference Fourier map showed a few spurious peaks at *ca.* 2 e Å^{-3} in the neighborhood of the Ir atoms. Atomic coordinates and thermal parameters are given in Table II.

Discussion

The crystal structure consists of discrete molecules one of which is shown in Figure 1. Bond lengths and angles are listed in Tables III and IV. The coordination around each iridium atom is square planar, the maximum deviation from the best least-squares planes being 0.09 (0) Å (Table V). Although the molecule might be expected to have a diad axis through the bridging oxygen atom, in the crystal at least, it departs significantly from this symmetry. This can be traced to the different degrees of twist of the square planes about the Ir–O bonds. Plane O(3)–Ir(1)–Cl(1) makes a dihedral angle of 49.8 (4)° with Ir(1)–O(3)–Ir(1) whereas O(3)–Ir(2)–Cl(2) makes 34.5 (4)° with it. The contrast with I[5] is of interest for this latter molecule has a strict diad axis through the oxygen atom; the Ir–Ir bond prevents any distortion from twofold symmetry.

Bonding to chlorine leaves the iridium atoms with an even number of valence electrons and hence an Ir···Ir bond is no longer formed. The Ir–O–Ir angle opens up to 134.4 (4)° from the 82.3° found in I. This is accompanied by shortening of the Ir–O bonds from 1.94 (1) to 1.903 (8) Å caused possibly by increased positive charge on Ir.

There is a substantial difference between the N–Ir–P angles found in I and in the present molecule, 104.50° as against 93.6 (4)°. (This angle appears to be subject to wide variations in the known crystal structures of iridium nitrosyl complexes.) The atoms Ir–N–O are virtually collinear, the nitrosyl group therefore presumably behaving as NO^+ with iridium in its first oxidation state. The Ir–N bond lengths are somewhat shorter (1.70 (1), 1.73 (1) Å) and the N–O lengths somewhat longer (1.18 (2), 1.14 (2) Å) than those found in I (1.763 (15) and 1.12 (2) Å, respectively) suggestive of increased bonding between nitrogen and iridium brought about by the chlorine atoms. The geometry of Ir–N–O in fact matches that[6] in $(IrH(NO)(PPh_3)_3ClO_4$ more closely than in I, above, and supports the assignment as Ir(I).

Ir–P and Ir–Cl lengths are in accord with those normally found. The Ir···Ir and Cl···Cl contact distances together with shortest contacts involving hydrogen are given in Table III.

Table IV. Bond Angles (deg)

Ir(1)–O(3)–Ir(2)	134.3 (4)	P(1)–Ir(1)–N(1)	93.6 (4)
Cl(1)–Ir(1)–O(3)	89.3 (2)	P(2)–Ir(2)–N(2)	93.6 (3)
Cl(2)–Ir(2)–O(3)	89.9 (2)	Ir(1)–N(1)–O(1)	177.2 (10)
Cl(1)–Ir(1)–N(1)	90.3 (4)	Ir(2)–N(2)–O(2)	174.2 (10)
Cl(2)–Ir(2)–N(2)	88.8 (3)	Ir–P–C(mean)	113.6
P(1)–Ir(1)–O(3)	86.9 (2)	C–P–C(mean)	105.6
P(2)–Ir(2)–O(3)	87.7 (2)		

Table V. Best Least-Squares Planes[a] of Square-Planar Systems

Plane 1

$$-0.4960X - 0.7490Y - 0.4393Z + 4.2419 = 0$$

Deviations, Å

Ir(1)	−0.002 (0)	O(3)	−0.038 (7)
Cl(1)	0.060 (3)	N(1)	−0.034 (11)
P(1)	0.037 (3)		

Plane 2

$$0.8236X + 0.1274Y - 0.5051Z - 2.8594 = 0$$

Deviations, Å

Ir(2)	−0.004 (0)	O(3)	−0.020 (7)
Cl(2)	0.091 (3)	N(2)	0.017 (10)
P(2)	0.071 (3)		

Angle between Planes 1 and 2: 72.7 (4)°

[a] In real orthogonal coordinates: X along x and Z along z^*.

Registry No. μ-Oxido-bis[chlorotriphenylphosphinenitrosyl-iridium(I)], 53260-38-1.

Supplementary Material Available. Table I, 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 AIC40211R.

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