

Fig. 1. Bond distances (Å) and angles ($^{\circ}$) in the oxalate fragment. The standard deviations are 0.2° for all angles, 0.003 Å for both C—O bonds, and 0.004 Å for the C—C bond. Thermal ellipsoids are scaled to enclose 50% probability.

interchanged. The oxalate ion is planar within the experimental limits. The equation of the least-squares plane through the six atoms is given by: $-x + 0.4649y + 1.4720z = 0.0000$. Displacements of the individual atoms from this plane are (in Å): C, 0.0005 ; O(1), -0.0001 ; O(2), -0.0001 ; with a standard deviation of 0.0004 Å.

The dimensions of the oxalate moiety are in excellent agreement with those proposed by Hahn (1957) for a completely ionized structure. The abnormally long C—C bond length found for $\text{Na}_2\text{C}_2\text{O}_4$ parallels a similar result in other oxalates (Beagley & Small, 1964; Hodgson & Ibers, 1969; Robertson, 1965), binoxalates (Küppers, 1973), and oxalic acids (Delaplane & Ibers, 1969). The 1.568 Å bond length found in the present work agrees with the average for other ionic oxalates and is longer than the average for binoxalates or oxalic acid (Küppers, 1973). A theoretical explanation by Brown & Harcourt (1963) based on delocalization of the oxygen non-bonding electrons into the C—C bond seems to account for the observations (Küppers, 1973).

The O atoms form a distorted octahedron around the Na^+ ion. The $\text{Na}\cdots\text{O}$ distances are listed in Table 2.* Comparison of these distances indicates that O(1) is slightly closer to the Na^+ ions than O(2), in contrast to

* See deposition footnote.

the results of Jeffrey & Parry (1954). Also, the difference in length to the nearest Na^+ ion from O(1) and O(2) is smaller. The minor differences in the bond lengths and angles between C—O bonds probably reflect the small difference in the electrostatic perturbation of the surrounding Na^+ ions.

The principal axes of the thermal ellipsoids and orthonormal reference vectors are listed in Table 3.* Calculations of bond lengths and bond angles using isotropic thermal parameters for all atoms showed no differences outside of the standard deviations from those using anisotropic thermal parameters. No corrections to the bond lengths and angles for thermal motion were applied.

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* See deposition footnote.

References

- BEAGLEY, B. & SMALL, R. W. H. (1964). *Acta Cryst.* **17**, 783–788.
 BROWN, R. D. & HARCOURT, R. D. (1963). *Aust. J. Chem.* **16**, 737–758.
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press.
 DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423–2437.
 HAHN, T. (1957). *Z. Kristallogr.* **109**, 438–466.
 HODGSON, D. L. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 469–476.
 JEFFREY, G. A. & PARRY, G. S. (1954). *J. Am. Chem. Soc.* **76**, 5283–5286.
 KÜPPERS, H. (1973). *Acta Cryst.* **B29**, 318–327.
 ROBERTSON, J. H. (1965). *Acta Cryst.* **18**, 410–417.

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Nitrosyltris(triphenylphosphine)iridium Cyclopropane Solvate

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Abstract. $[\text{Ir}(\text{NO})(\text{PPh}_3)_3] \cdot \text{C}_3\text{H}_6$, hexagonal, $P6_3$, $a = 12.625$ (5), $c = 17.382$ (5) Å, $D_m = 1.49$ (5), $D_c = 1.45$ Mg m^{-3} for $Z = 2$; $R = 0.036$, $R_w = 0.028$ for

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2797 observed reflexions. $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ molecules with C_3 symmetry pack along the threefold axes, surrounding channels of cyclopropane molecules which

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lie along, and are crystallographically generated by, the 6_3 axes. This is the first reported occurrence of unsubstituted cyclopropane in a crystal structure determined with X-rays.

Introduction. In an attempt to prepare an iridium metalocycle by direct reaction between coordinatively unsaturated $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ (Reed & Roper, 1969) and cyclopropane (313 K, 48 h) the title compound was isolated as orange-red crystals. While infrared spectroscopy indicated that $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ had been recovered unchanged, elemental analysis (C, H and N) suggested otherwise. A check on the cell parameters and crystal symmetry confirmed that the crystals were different from those of $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ [Albano, Bellon & Sansoni (henceforward ABS) (1971)]. The full X-ray analysis was therefore undertaken. Preliminary photography established hexagonal symmetry with the absences $000l, l = 2n + 1$. A crystal $0.3 \times 0.3 \times 0.2$ mm was used for data collection. Intensities were measured on a four-circle Philips PW 1100 diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) and the ω - 2θ scan mode. 3230 reflexions were measured, of which 2797 unique observed [$I > \sigma(I)$] reflexions were employed in the analysis. No crystal decomposition was observed. Lorentz-polarization but no absorption corrections were applied.

Reflexion statistics and the restrictions inherent in the other possible groups indicated $P6_3$ as the correct space group, a choice confirmed by the successful solution and refinement of the structure. A difference map phased on the Ir atom at $(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ [Wyckoff position (b) with z held to fix the origin] revealed the non-hydrogen atoms of the independent triphenylphosphine group and the nitrosyl group. In further refinement non-hydrogen atoms were treated anisotropically [thermal parameters for the Ir, N and O

atoms were restricted thus: $U_{11} = U_{22} = 2U_{12}$, $U_{23} = U_{13} = 0$ (Peterse & Palm, 1966)] and H atoms were included in calculated positions. A region of electron density centred on the 6_3 axis was recognized as a cyclopropane molecule and its coordinates were refined. No attempt was made to locate and refine the cyclopropane H atoms. R converged to 0.036; R_w was 0.028 with weights $w = 0.44/\sigma^2(F)$. In a final difference map, a peak of 1.3 e \AA^{-3} coincided approximately with the centroid of the cyclopropane ring. Another peak with height 1.0 e \AA^{-3} was associated with the Ir atom. Other peaks had heights $< 1.0 \text{ e \AA}^{-3}$. The isotropic temperature factor of the cyclopropane C atom converged to $U = 0.18 (1) \text{ \AA}^2$ and that of the phenyl H atoms to $U = 0.07 (1) \text{ \AA}^2$. Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). Final positional parameters for the non-hydrogen atoms are given in Table 1.*

* Lists of structure factors, thermal parameters, H atom positions and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35817 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

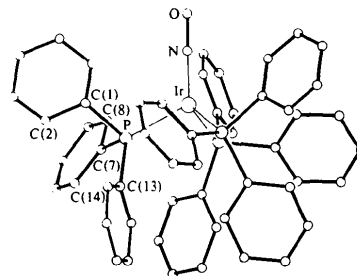


Fig. 1. Structure and atom numbering of the $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ moiety.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$) for the heavy atoms, with e.s.d.'s in parentheses

	x	y	z	U_{eq}^\dagger		x	y	z	U_{eq}^\dagger
Ir	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	17 (0)	C(8)	9889 (5)	5773 (5)	4846 (4)	22 (2)
N	$\frac{1}{3}$	$\frac{1}{3}$	6003 (5)	24 (2)	C(9)	11167 (5)	6353 (5)	4808 (4)	24 (2)
O	$\frac{1}{3}$	$\frac{1}{3}$	6705 (4)	22 (2)	C(10)	11774 (6)	7118 (6)	4195 (4)	24 (2)
Cy*	532 (16)	-136 (21)	2742 (5)		C(11)	11146 (6)	7353 (6)	3638 (4)	25 (2)
P	7561 (1)	5222 (1)	4401 (1)	18 (0)	C(12)	9880 (5)	6796 (5)	3687 (4)	22 (2)
C(1)	7526 (4)	6421 (4)	5018 (6)	19 (1)	C(13)	7031 (4)	5437 (4)	3460 (3)	18 (1)
C(2)	7958 (5)	7597 (5)	4710 (3)	23 (2)	C(14)	6156 (5)	5805 (5)	3396 (3)	20 (1)
C(3)	8005 (5)	8521 (5)	5149 (5)	24 (2)	C(15)	5705 (5)	5861 (5)	2682 (4)	23 (2)
C(4)	7594 (7)	8286 (7)	5891 (5)	25 (2)	C(16)	6132 (7)	5582 (6)	2028 (3)	24 (2)
C(5)	7140 (8)	7113 (8)	6198 (4)	27 (2)	C(17)	7015 (6)	5232 (6)	2088 (4)	24 (2)
C(6)	7126 (6)	6190 (6)	5746 (4)	24 (2)	C(18)	7437 (5)	5136 (5)	2798 (3)	21 (1)
C(7)	9239 (5)	5995 (5)	4271 (3)	19 (1)					

* Cy denotes the independent cyclopropane C atom.

† Defined as $U_{\text{eq}} = (U_1 U_2 U_3)^{1/3}$ where U_1 , U_2 and U_3 are the root-mean-square displacements along the axes of the thermal ellipsoid defined by the anisotropic temperature factor matrix of the atom, such that 50% of the electron density is enclosed by the surface of the ellipsoid (Johnson, 1976).

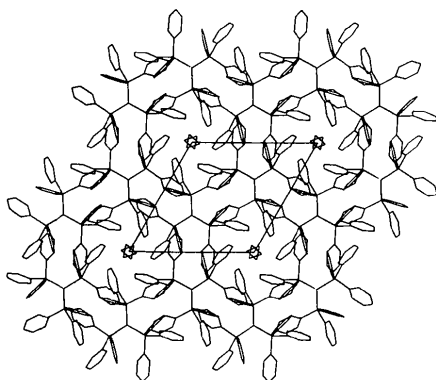


Fig. 2. Projection of the structure on to (0001).

Table 2. Relevant bond lengths (Å) (with *e.s.d.*'s)

Ir—P	2.314 (1)	Cy—Cy	1.34 (5)
Ir—N	1.743 (9)	C—C: R1 (range)	1.34 (1)–1.41 (1)
N—O	1.22 (1)	R2	1.37 (1)–1.41 (1)
P—C(1)	1.872 (8)	R3	1.37 (1)–1.40 (1)
P—C(7)	1.851 (5)		
P—C(13)	1.838 (6)		

Table 3. Relevant bond angles (°) (with *e.s.d.*'s)

N—Ir—P	116.7 (2)	C(13)—P—Ir	121.8 (1)
P—Ir—P	101.3 (2)	C(1)—P—C(7)	97.3 (2)
C(1)—P—Ir	112.2 (3)	C(1)—P—C(13)	103.5 (3)
C(7)—P—Ir	116.0 (2)	C(7)—P—C(13)	102.7 (2)

Choice of the correct enantiomer was indicated by a significance test (Hamilton, 1965): $R_G = 0.0289$ for the published and 0.0724 for the inverted coordinates. Fig. 1 shows the atom labelling and Fig. 2 the packing projected on to (0001). Tables 2 and 3 list some bond lengths and angles.

Discussion. A search through the Cambridge Data File revealed no other instances where free unsubstituted cyclopropane has been found in a compound as a molecule of solvation. In fact, there were *no* reported structures containing solvate molecules which would exist as a gas under ambient conditions. This probably reflects the difficulty of carrying out reactions under the conditions needed to render such gases liquid. Further work is in progress in this laboratory investigating the possibility of co-crystallizing $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ with other small molecules, such as carbon monoxide and low-molecular-weight alkanes and alkenes. Unfortunately the thermal motion of the cyclopropane molecule in the present study introduces rather a large uncertainty into the C—C length of 1.34 Å and when it is compared with reported values of between 1.48 and 1.55 Å (Pascard, Prangé, de Meijere, Weber, Barnier & Conia, 1979, and references therein) it is clear that

little reliance can be placed in this value. A low-temperature study of this crystal is indicated.

Comparisons of the $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ molecule may be drawn between this structure and those reported by ABS (1971), and that of trigonal $[\text{Pt}(\text{CO})(\text{PPh}_3)_3]$ (ABS, 1969). The most arresting is the similarity of these molecules. If torsion angles round the M—P and P—C (phenyl ring) bonds are considered,* the variation among like-handed molecules in the two structures containing $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ molecules is no more than a few degrees {trigonal $[\text{Pt}(\text{CO})(\text{PPh}_3)_3]$, being isomorphous with $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$, will not be further discussed}. This conformation is not exhibited by the other monoclinic polymorph of $[\text{Pt}(\text{CO})(\text{PPh}_3)_3]$ (Albano, Basso Ricci & Bellon, 1969) and clearly must be related to the similar packing patterns in the compounds.

The $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ moieties stack along threefold axes in the same sense, with a repeat distance of *c* separating Ir atoms. This means that in $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ itself the non-bonded O—Ir distance is 7.9 Å while in $[\text{Ir}(\text{NO})(\text{PPh}_3)_3] \cdot \text{C}_3\text{H}_6$ the corresponding distance is 14.4 Å. However, the perpendicular distance between threefold axes is 7.3 Å in the latter, compared with 11.5 Å in $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$, so that the stacks of $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ molecules are more intermeshed. Two important differences in the packing patterns are that in $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ three independent molecules are found, one being an approximate mirror image of the other two (however, it is unlikely that this unbalanced stereoisomerism would give rise to optical activity in solution, as ABS suggest, as the phenyl groups in PPh_3 are free to rotate). In the title complex there is only one independent molecule and all Ir—N—O vectors in the crystal are oriented in the same direction whereas in $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ one stack of molecules is oriented oppositely to the other two stacks.

Bond lengths and angles within the $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$ moiety are unremarkable. Unfortunately no comparison may be made of the Ir—N and N—O lengths with those reported by ABS since the latter authors refined an averaged model for their Ir—N—O system, on the grounds that the complex displayed a unique sharp $\nu(\text{N—O})$ band at 1615 cm^{-1} in the infrared spectrum. In fact the band is quite broad (width at half height = 20 cm^{-1}) and centred on 1600 cm^{-1} {Reed & Roper (1969) and the author's measurements on pure recrystallized (benzene) $[\text{Ir}(\text{NO})(\text{PPh}_3)_3]$. There is a sharp side band at 1580 cm^{-1} and a shoulder at 1570 cm^{-1} . Moreover, this infrared pattern is also shown by the title complex, which has only *one* unique Ir—N—O system. In the author's view it is advisable to tread with great caution when correlating crystallographic evidence with spectroscopic behaviour.

* See deposition footnote.

All calculations were performed on the University of South Africa's Burroughs B6800 computer with *SHELX* (Sheldrick, 1978). I thank Dr G. Gafner of the CSIR, Pretoria, for the diffractometer data collection.

References

- ALBANO, V. G., BASSO RICCI, G. M. & BELLON, P. L. (1969). *Inorg. Chem.* **8**, 2109–2115.
- ALBANO, V. G., BELLON, P. L. & SANSONI, M. (1969). *J. Chem. Soc. Chem. Commun.* pp. 899–901.
- ALBANO, V. G., BELLON, P. & SANSONI, M. (1971). *J. Chem. Soc. A*, pp. 2420–2425.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- PASCARD, C., PRANGÉ, T., DE MEJERE, A., WEBER, W., BARNIER, J.-P. & CONIA, J.-M. (1979). *J. Chem. Soc. Chem. Commun.* pp. 425–426.
- PETERSE, W. J. A. M. & PALM, J. H. (1966). *Acta Cryst.* **20**, 147–150.
- REED, C. A. & ROPER, W. R. (1969). *J. Chem. Soc. Chem. Commun.* p. 155.
- SHELDRICK, G. M. (1978). *Computing in Crystallography*. Delft Univ. Press.

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Di- μ -methoxy-bis{[2,3-dimethylbutane-2,3-diolato(1-)]-*cis*-dioxomolybdenum(VI)}-Methanol (1/2)

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Abstract. $[\text{Mo}(\text{CH}_3\text{O})(\text{C}_6\text{H}_{13}\text{O}_2)\text{O}_2]_2 \cdot 2\text{CH}_3\text{OH}$, $\text{C}_{14}\text{H}_{32}\text{Mo}_2\text{O}_{10} \cdot 2\text{CH}_4\text{O}$, monoclinic, $P2_1/c$, $a = 7.167$ (2), $b = 11.499$ (4), $c = 15.789$ (4) Å, $\beta = 101.65$ (2)°, $V = 1274.42$ Å³, $M_r = 552.3$, $D_c = 1.44$ Mg m⁻³, $Z = 2$, $\mu(\text{Mo } K\alpha) = 0.916$ mm⁻¹, $R = 0.046$ for 838 reflections. In this colourless dimeric complex the Mo atoms are linked by a double methoxy bridge. The coordination about each Mo is completed by two O atoms from a bidentate singly deprotonated pinacol ligand and two terminal oxo ligands. Intermolecular hydrogen bonds link pinacol O atoms through methanol molecules.

Introduction. Crystals of the title compound were prepared (Knobler, Penfold, Robinson, Wilkins & Yong, 1980) as colourless parallelepipeds. Crystals are stable in their mother liquor but when dry they slowly become opaque dark blue. The space group $P2_1/c$ was established uniquely from systematic absences. The crystal used for intensity measurements was 1.2 mm long with a cross-section of 0.14 mm and was sealed in a capillary tube. Intensities were recorded on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and the θ - 2θ scan technique. 1077 reflections were recorded (before decomposition) at room temperatures (298 K) in the

range $0 < 2\theta < 42^\circ$. Of these, 838 had $I > 3\sigma(I)$ and were used in the analysis. The detailed procedures for data collection and assignment of errors were as described by Countryman & Penfold (1972). Corrections for absorption were not applied.

Coordinates of the Mo atom were ascertained from the Patterson function and the remaining 14 non-hydrogen atoms were located from electron-density maps. Positions of all these atoms were refined by full-matrix least squares until R had fallen to 0.047 for a completely isotropic model. H atoms of methyl groups were then introduced as members of rigid groups constrained to $\text{C}-\text{H} = 1.0$ Å and $\text{H}-\text{C}-\text{H} = 109.5^\circ$. From a difference map, one of the remaining H atoms was located (as the highest peak > 1.5 Å from Mo) 1.0 Å from a diol O atom and 1.8 Å from the O atom of the methanol solvate. The hydroxy H atom of the methanol solvate was not located and was not included in the model. Refinement converged at $R = 0.046$, based on 84 parameters and 838 reflections. The function minimized was $\sum w|F_o| - |F_c|^2$ and the weights w were $2.568/[\sigma^2(F) + 0.000034 F^2]$. Scattering factors for Mo, C, and O were from Cromer & Mann (1968), those of H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections f' and f'' were from Cromer & Liberman (1970). Positional and thermal parameters are listed in Table 1,