Crystal and Molecular Structure of Five-co-ordinate Fumaronitrile(8-methoxycyclo-oct-4-enyl)(1,10-phenanthroline)iridium(I)

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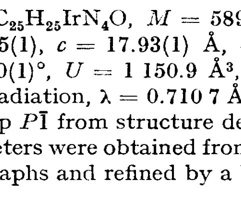
The crystal structure of the title compound was determined from three-dimensional *X*-ray data by conventional Fourier methods. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$, and cell parameters $a = 9.848(6)$, $b = 14.25(1)$, $c = 17.93(1)$ Å, $\alpha = 36.28(4)$, $\beta = 128.5(1)$, $\gamma = 125.0(1)$°. Least-squares refinement, based on 1 921 independent reflexions, reduced R to 0.078. Crystals consist of discrete molecules in which the iridium(I) atom has distorted trigonal-bipyramidal stereochemistry with the phenanthroline and cyclo-octenyl ligands both spanning axial and equatorial positions; the fumaronitrile molecule occupies the remaining equatorial position. The σ-bonded carbon atom of the cyclo-octenyl ligand is axial [Ir–C 2.13(3) Å] and the two olefinic linkages are equatorial with the C=C bonds practically coplanar with the metal atom.

RECENTLY cationic iridium(I) complexes with *cis,cis*-cyclo-octa-1,5-diene (cod) and bidentate ligands such as bipyridine or 1,10-phenanthroline (phen) have been prepared which are able to co-ordinate small molecules giving stable five-co-ordinate addition complexes.[1] It has been found that upon co-ordination of π-acceptor ligands, such as fumaronitrile, these complexes undergo nucleophilic attack at a double-bond of the co-ordinated diolefin in protic solvents and basic media. This conclusion was suggested on the basis of elemental analyses and i.r. and n.m.r. spectra.[1]

In order to confirm the aforementioned reaction we have carried out a crystal structure analysis of the reaction product obtained from $[Ir(phen)(cod)]^+$ and fumaronitrile in methanol for which structure (I) was suggested.[1] Furthermore, since it is to be expected that in the parent five-co-ordinate complex the diolefin spans an axial and an equatorial position of a trigonal bipyramid, it was of interest to ascertain the co-ordination environment of the metal atom, so as to establish the site of attack of the nucleophilic agent.



(I)

EXPERIMENTAL

Crystal Data.—$C_{25}H_{25}IrN_4O$, $M = 589.7$, Triclinic, $a = 9.848(6)$, $b = 14.25(1)$, $c = 17.93(1)$ Å, $\alpha = 36.28(4)$, $\beta = 128.5(1)$, $\gamma = 125.0(1)$°, $U = 1\,150.9$ Å^3, $Z = 2$, $D_c = 1.70$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) $= 61.6$ cm^{-1}. Space group $P\bar{1}$ from structure determination.

Unit-cell parameters were obtained from Weissenberg and precession photographs and refined by a least-squares fit of

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[1] G. Mestroni, G. Zassinovich, and A. Camus, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 359.

the diffractometer 2θ, χ, ϕ setting angles for 12 accurately centred reflexions in the 2θ range 36—44°.

Intensity Measurements.—A crystal of dimensions *ca.* 0.18 × 0.28 × 0.20 mm was mounted on an automated Siemens diffractometer and intensity data collected by the θ—2θ scan technique up to 2θ 54° by use of Mo-K_α radiation. Reflexions having $I_o < 3\sigma(I_o)$ were rejected, the remainder (1 921) being corrected for Lorentz-polarization factors and used in the subsequent calculations. No correction for absorption [$\mu(\rho)$ *ca.* 0.71] or anomalous dispersion of the iridium atom was applied.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods assuming the centrosymmetric space group $P\bar{1}$, the choice of which was confirmed by the subsequent successful refinement. After least-squares refinement, with anisotropic temperature factors assigned only to the iridium atom, R was reduced to 0.078. No attempt was made to locate hydrogen atoms. The final weighting scheme was of the form $w = 1/(A + B|F_o| + C|F_o|^2)$. Atomic parameters are listed in Table 1, with estimated standard deviations in parentheses, calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle.

TABLE 1

Fractional co-ordinates (× 10⁴) and thermal factors * with estimated standard deviations in parentheses

	x	*y*	*z*	*B*
Ir	4 705(1)	717(1)	1 738(1)	*
O	8 883(24)	3 050(18)	3 194(14)	6.3(6)
N(1)	3 280(24)	−1 129(18)	1 656(15)	4.2(5)
N(2)	4 755(24)	−1 468(18)	3 785(15)	4.0(5)
N(3)	998(34)	2 388(25)	−1 815(20)	7.6(8)
N(4)	2 691(35(	1 459(26)	2 631(21)	7.8(9)
C(1)	2 681(32)	−918(24)	635(20)	4.6(6)
C(2)	1 877(36)	−2 217(27)	695(22)	5.8(8)
C(3)	1 790(37)	−3 800(28)	2 002(22)	5.9(8)
C(4)	2 465(32)	−3 991(24)	3 095(20)	4.7(6)
C(5)	3 252(30)	−2 639(23)	2 929(19)	4.1(6)
C(6)	3 928(32)	−2 833(24)	4 039(20)	4.6(6)
C(7)	3 791(30)	−4 372(23)	5 280(19)	4.2(6)
C(8)	4 427(36)	−4 492(28)	6 338(23)	5.7(8)
C(9)	5 214(38)	−3 093(29)	6 105(23)	6.5(8)
C(10)	5 281(29)	−1 592(22)	4 708(18)	4.1(6)
C(11)	2 428(33)	−5 516(25)	4 404(20)	4.9(7)
C(12)	3 020(33)	−5 710(25)	5 469(20)	5.0(7)
C(13)	1 785(37)	2 408(27)	−990(22)	5.8(8)
C(14)	2 792(32)	2 262(24)	146(20)	4.7(7)
C(15)	2 351(31)	1 023(24)	1 381(19)	4.4(6)
C(16)	2 528(35)	1 342(27)	1 992(22)	5.7(7)
C(17)	6 217(30)	1 909(23)	618(19)	4.2(6)
C(18)	6 944(34)	524(26)	1 950(21)	5.2(7)
C(19)	8 793(34)	505(26)	3 005(21)	5.4(7)
C(20)	9 350(34)	1 757(26)	2 986(21)	5.3(7)
C(21)	8 010(32)	1 905(24)	3 046(20)	4.6(6)
C(22)	6 326(32)	2 476(24)	1 811(20)	4.5(6)
C(23)	6 832(37)	4 003(28)	452(23)	5.9(8)
C(24)	7 084(36)	3 646(27)	−35(22)	5.8(8)
C(25)	7 931(45)	2 954(33)	3 647(26)	8.0(11)

* Anisotropic temperature factors (× 10⁵) in the form: $\exp-(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)$, with parameters

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Ir	1 316(12)	204(16)	519(14)	819(8)	−863(11)	989(7)

Bond lengths and angles are listed in Table 2, and equations of some least-squares planes in Table 3, together with displacements of relevant atoms from them. The atom numbering scheme is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21612 (7 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 2.

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bond distances

Ir–N(1)	2.25(3)	C(4)–C(5)	1.43(5)
Ir–N(2)	2.17(1)	C(4)–C(11)	1.42(3)
Ir–A	2.02(3)	C(5)–C(6)	1.47(6)
Ir–B	2.05(4)	C(6)–C(7)	1.40(2)
Ir–C(14)	2.11(3)	C(7)–C(8)	1.46(6)
Ir–C(15)	2.20(4)	C(7)–C(12)	1.40(5)
Ir–C(17)	2.11(4)	C(8)–C(9)	1.43(6)
Ir–C(18)	2.14(4)	C(9)–C(10)	1.50(3)
Ir–C(22)	2.13(3)	C(11)–C(12)	1.42(6)
O–C(21)	1.51(5)	C(13)–C(14)	1.49(5)
O–C(25)	1.48(8)	C(15)–C(16)	1.38(7)
N(1)–C(1)	1.33(5)	C(17)–C(18)	1.42(2)
N(1)–C(5)	1.39(2)	C(17)–C(24)	1.54(4)
N(2)–C(6)	1.37(4)	C(18)–C(19)	1.60(4)
N(2)–C(10)	1.27(5)	C(19)–C(20)	1.51(6)
N(3)–C(13)	1.18(6)	C(20)–C(21)	1.53(7)
N(4)–C(16)	1.19(7)	C(21)–C(22)	1.54(3)
C(1)–C(2)	1.47(6)	C(22)–C(23)	1.62(4)
C(2)–C(3)	1.45(3)	C(23)–C(24)	1.49(8)
C(3)–C(4)	1.44(6)		

(*b*) Bond angles

N(1)–Ir–N(2)	79(1)	C(5)–C(6)–C(7)	119(3)
N(1)–Ir–A	97(1)	C(7)–C(6)–N(2)	125(3)
N(1)–Ir–B	88(1)	C(6)–C(7)–C(8)	117(3)
N(1)–Ir–C(22)	173(1)	C(6)–C(7)–C(12)	121(3)
N(2)–Ir–C(22)	103(1)	C(8)–C(7)–C(12)	122(2)
A–Ir–C(22)	89(1)	C(7)–C(8)–C(9)	121(2)
A–Ir–B	138(1)	C(8)–C(9)–C(10)	112(4)
A–Ir–N(2)	107(1)	C(9)–C(10)–N(2)	128(3)
B–Ir–N(2)	115(1)	C(4)–C(11)–C(12)	123(3)
B–Ir–C(22)	85(2)	C(7)–C(12)–C(11)	120(2)
C(21)–O–C(25)	114(2)	N(3)–C(13)–C(14)	174(3)
Ir–N(1)–C(5)	109(2)	C(13)–C(14)–C(15)	126(2)
Ir–N(1)–C(1)	128(1)	C(14)–C(15)–C(16)	124(3)
C(1)–N(1)–C(5)	123(3)	C(15)–C(16)–N(4)	173(2)
Ir–N(2)–C(6)	115(2)	C(18)–C(17)–C(24)	125(2)
Ir–N(2)–C(10)	127(2)	C(17)–C(18)–C(19)	126(2)
C(6)–N(2)–C(10)	117(2)	C(18)–C(19)–C(20)	118(3)
N(1)–C(1)–C(2)	125(2)	C(19)–C(20)–C(21)	116(2)
C(1)–C(2)–C(3)	113(4)	C(20)–C(21)–O	108(2)
C(2)–C(3)–C(4)	120(3)	C(20)–C(21)–C(22)	113(3)
C(3)–C(4)–C(5)	122(2)	Ir–C(22)–C(21)	114(2)
C(3)–C(4)–C(11)	123(3)	Ir–C(22)–C(23)	105(3)
C(5)–C(4)–C(11)	116(3)	C(21)–C(22)–C(23)	110(2)
C(4)–C(5)–C(6)	122(2)	C(22)–C(23)–C(24)	117(3)
N(1)–C(5)–C(4)	117(3)	C(17)–C(24)–C(23)	109(3)
N(1)–C(5)–C(6)	121(3)		
C(5)–C(6)–N(2)	116(2)		

TABLE 3

Equation of least-squares planes and, in square brackets, distances (Å) of atoms from the planes. The equations are referred to the crystal axes and x, y, z are fractional co-ordinates

Plane (1): Ir, N(2), A, B

$$-0.357x + 11.653y + 12.261z = 2.768$$

[Ir 0.030, C(14) −0.053, C(15) 0.033, C(17) −0.008, C(18) −0.015, A −0.011, B −0.012]

Plane (2): N(1), N(2), C(1)—12

$$9.439x - 6.366y - 6.912z = 2.714$$

[N(1) −0.044, N(2) 0.092, C(1) −0.038, C(2) −0.012, C(3) 0.010, C(4) 0.014, C(5) 0.011, C(6) 0.005, C(7) −0.002, C(8) −0.057, C(9) −0.044, C(10) 0.030, C(11) 0.045, C(12) −0.009]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[2] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 3. A local program was used to obtain best molecular planes, whose equations were calculated according to ref. 4.

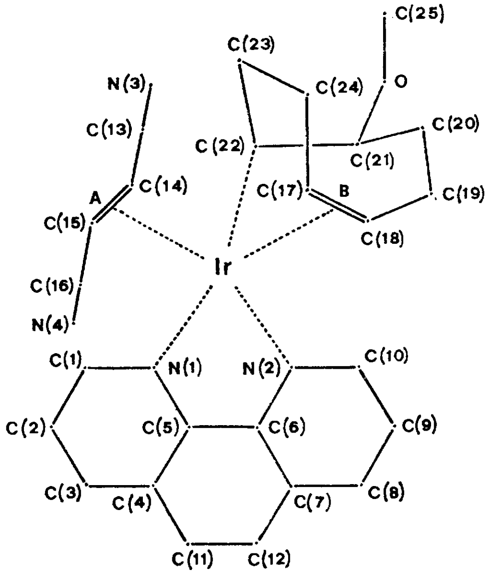

FIGURE 1 Numbering scheme of the atoms. A and B represent the midpoints of the two olefinic bonds

RESULTS AND DISCUSSION

Figure 2 shows a perspective view of the molecule. The results confirm the nucleophilic attack at one double-bond of the cyclo-octadiene ligand and show that this attack has occurred in an axial position of the five-co-ordinate parent compound.

The co-ordination polyhedron around the iridium atom can be described as a distorted trigonal bipyramid if the olefinic ligands are considered unidentate. Axial sites are occupied by the σ-bonded carbon atom of the methoxycyclo-octenyl ligand (meocot) and one nitrogen atom of the phenanthroline molecule, while equatorial sites are occupied by the other nitrogen atom of phenanthroline, and by the olefinic linkages of the cyclo-octenyl and fumaronitrile ligands. Bond angles within the iridium co-ordination sphere deviate from expected values for an idealized trigonal-bipyramid. Thus angles involving axial and equatorial ligands range from 79(1) to 103(1)°, while those in the ' trigonal ' plane range from 107(1) to 138(1)°. Such a distortion is probably due to some close intermolecular contacts involving mainly the fumaronitrile and the meocot ligand [C(14) · · · C(17) 3.17, C(14) · · · C(22) 2.90, C(15) · · · C(22) 3.12 Å].

The axial Ir–C(22) distance [2.13(3) Å] is the same as for Ir(I)–CH_3 bonds in a series of (cod)methyliridium(I) complexes [2.133(16)—2.202(22) Å].[5] The distances between iridium and the midpoints A and B of the C(14)–C(15) and C(17)–C(18) double bonds are 2.02(4) and 2.05(4) Å respectively and compare well with the previously found values for equatorial iridium–olefin bonds.[5,6] Similarly the olefinic C–C bond lengths [C(14)–C(15) 1.49(4), C(17)–C(18) 1.42(2) Å] are in the range found in transition-metal–olefin complexes, in agreement with the usual Chatt–Dewar metal–olefin bonding scheme.[6]

The C=C bonds lie practically in the equatorial plane (±0.04 Å), as is usual in trigonal bipyramids,[6] in contrast to the situation in square-planar complexes where the double-bonds are normal to the co-ordination plane.[6,7]

The fumaronitrile molecule maintains its *trans*-configuration, but the cyanide groups are markedly bent away from the metal atom, as is found in other compounds containing fumaronitrile or tetracyanoethylene.[6] The mean dihedral angle between the Ir,C(14),C(15) plane and the C(13)—(15) and C(14)—(16) planes is 110°, whereas that between the two last-mentioned planes is 140°.

The Ir–N distances appear slightly different, the axial bond length being longer [2.246(28) Å] than the equatorial [2.167(15) Å], a difference (0.079 Å) significant at the 3σ level. However, it seems likely that if such a difference is truly significant, it is due not to steric factors, but rather to the *trans*-influence of the $C(sp^3)$ atom. In fact, the N · · · N distance [2.80(4) Å] is close to that found in various phenanthroline complexes [2.63—2.78 Å],[8] and

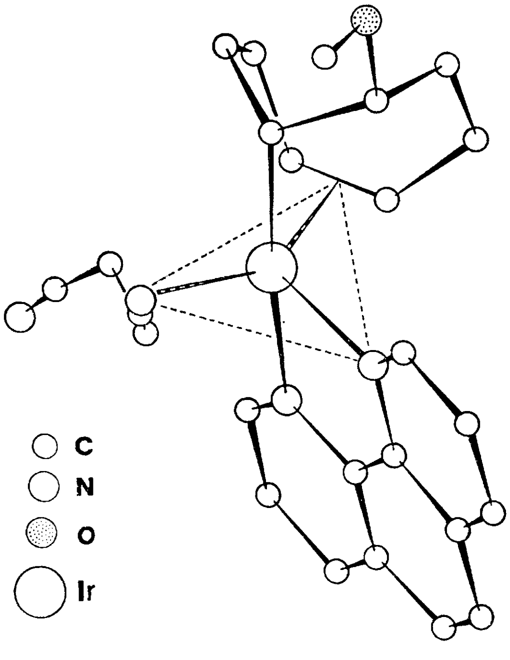

FIGURE 2 A perspective view of the molecule projected along the *c* axis

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[3] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[4] V. Schomaker, J. Waser, R. F. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

[5] M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1972, **11**, 2243; 1973, **12**, 260, 531.

[6] L. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 1969, **47**, 84.

[7] G. Bombieri, E. Forsellini, and R. Graziani, *J.C.S. Dalton*, 1972, 525.

[8] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109.

the molecule appears quite normal, being planar to within ±0.05 Å. In this respect it is interesting that there is a similar difference, between equatorial and axial distances, in iridium(I)–cyclo-octadienyl complexes in which a methyl group occupies an axial position.[5] This trend is the opposite to that expected for a low-spin d^8 metal atom, on the basis of the one-electron splitting scheme of d orbitals in a field of C_{3v} symmetry,[9] and may in fact be due to the *trans*-influence of the organic ligand.

TABLE 4

Relevant torsion angles (°) around the bonds of the meocot ligand

C(17)–C(18)	1	C(21)–C(22)	47
C(18)–C(19)	37	C(22)–C(23)	88
C(19)–C(20)	52	C(23)–C(24)	18
C(20)–C(21)	64	C(17)–C(24)	77

The overall conformation of the 8-methoxycyclo-oct-4-enyl ligand is similar to that found in the platinum(II) complex [Pt(meocot)(py)Cl].[7] Torsion angles of interest are reported in Table 4. Bond lengths and angles are also similar in the two compounds and also for *trans*-cyclo-octene,[10] except for effects resulting from co-ordination on the double bond.

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[9] P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285.

[10] O. Ermer, *Angew. Chem. Internat. Edn.*, 1974, **13**, 604.