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Structure of *ab*-Bis(benzonitrile)-*df*-dicarbonyl-*ce*-dichlororuthenium, $RuCl_2(CO)_2(C_6H_5CN)_2$

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Abstract. $M_r = 434{\cdot}2$, monoclinic, $C2/c$, $a = 18{\cdot}18$ (2), $b = 9{\cdot}95$ (1), $c = 12{\cdot}22$ (2) Å, $\beta = 129{\cdot}4$ (1)°, $U = 1709$ Å^3, $Z = 4$, $D_x = 1{\cdot}69$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 1{\cdot}22$ mm^{-1}, $F(000) = 1470$, $T = 298$ K. Final $R = 0{\cdot}066$ for 998 observed diffractometer data. Carbonyl groups and N atoms of the benzonitrile ligands are each arranged *cis*; Cl atoms are *trans* to each other. The phenyl rings are coplanar with the plane defined by the CO groups and N atoms.

Introduction. The π-coordination chemistry of ligands containing CN triple bonds is limited, primarily owing to the preferential formation of σ-bonded adducts. In order to enhance the π-coordination of the CN function, the use of electron-withdrawing substituents such as CF_3CN or CCl_3CN might be considered; indeed side-on coordination for CF_3CN has been described (Thomas, 1975; Dawoodi, Mays & Raithby, 1981; Adams, Katahira & Yang, 1981). As part of our interest in the reactions between unsaturated organic molecules and carbonyl clusters, the reaction of CF_3CN and CCl_3CN with $Ru_3(CO)_{12}$ has been studied. The title compound appeared as a by-product during a series of reactions with CCl_3CN. An X-ray structure determination has been undertaken to define the structure of the molecule.

Experimental. Excess CCl_3CN (3 mmol) added to a solution of 0·2 g $Ru_3(CO)_{12}$ (0·312 mmol) in 100 ml toluene, mixture refluxed under dry N_2 for 8 h; after removing toluene and treating residue with benzonitrile, yellow crystals suitable for X-ray analysis obtained by cooling solution to 273 K. Prismatic crystal, 0·10 × 0·10 × 0·16 mm, set up about [100] on a laboratory-made automatic three-circle diffractometer. Cell dimensions and e.s.d.'s derived from least-squares analysis of setting angles of nine well separated reflections. θ–2θ scans, scan speed 1·04° min^{-1} (θ), scan range $(1{\cdot}10 + 0{\cdot}345\tan\theta)°$ (θ), background measurements at extremes, each for one quarter of the time taken for the scan, $3 < 2\theta < 50°$, Mo $K\alpha$ radiation, graphite-crystal monochromator set in front of the counter. 1632 unique reflections excluding standards (two every 100 data, no significant fluctuations). Data corrected for Lorentz and polarization but not for absorption. 998 reflections used in analysis $[F_o > 3\sigma(F_o)]$; index range h 0/21, k 0/11, $l \pm 11$. Scattering factors, including f' and f'' for Ru and Cl, from *International Tables for X-ray Crystallography* (1974). Structure solved using heavy-atom technique. H atoms included as a fixed contribution at their calculated idealized positions (C—H = 1·0 Å). Full-matrix least-squares refinements, anisotropic thermal parameters for Ru,Cl,C and O, fixed isotropic thermal parameters, 1·0 Å^2 higher than those of the C atoms to which they are attached, for H. $R = 0{\cdot}066$, $R_w = 0{\cdot}069$, $w = 2F/\sigma(I)$, $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2} = 1{\cdot}27$, $m = 998$, $n = 105$. $(\Delta/\sigma)_{\max} = 0{\cdot}002$. Final difference Fourier showed max. electron density 0·39 e Å^{-3}. Computations utilized A. Zalkin's *FORDAP* Fourier summation program (Ibers, Hamilton & Muir, 1973), Y. Jeannin and J.-J. Bonnet's *MDRCR* modification of the Busing, Martin & Levy (1962) least-squares program *ORFLS* and J. A. Ibers's *ORFEC* modification of the Busing, Martin & Levy (1964) *ORFFE* program.

Discussion. Atom nomenclature is defined in Fig. 1 and the corresponding coordinates are listed in Table 1.* Bond distances and angles are in Table 2. The Ru^{II} atom is at the centre of an octahedron. The carbonyl groups are arranged *cis* as are the N atoms of the benzonitrile ligands; these four ligands occupy the vertices of one of the equatorial planes; the two vertices *trans* to this plane are occupied by Cl atoms.

The Ru—CO distance may be compared to 1·864 Å found in $RuCl_2(CO)_2(PBzPh_2)_2$ (Bz = benzyl) (Wilkes *et al.*, 1982) or 1·831 Å in $RuCl_2(\eta\text{-}C_2H_4)(PMe_2Ph)_2$ (Brown, Barnard, Daniels, Mawby & Ibers, 1978), where CO groups are *trans* to Cl which is known to be a weak π-donor; however, in the title compound the CO groups are each *trans* to N of the benzonitrile which is known to be a π-acceptor with metals in a low-spin d^6 configuration (Ford, 1970).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38936 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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For a metal rich in d electrons as Ru^{II} is, the $d\pi - p\pi$ interaction between the weak π-donating Cl atom and Ru should be destabilizing. The *trans* configuration is preferred over the *cis* because the Cl ligands will share two d orbitals (d_{xz}, d_{yz}) and leave one non-bonding (d_{xy}), whereas for the *cis* form they would use three, one d orbital each [d_{xz} for Cl(1), d_{yz} for Cl(2)] and share a third (d_{xy}). In the same way, for the π-acceptor ligands such as CO and nitrile, the *cis* configuration is preferred because of a better overlap between the π^* orbitals of the ligands and Ru d orbitals. The reason for the *trans* position of CO with respect to nitrile might be the fact that, CO being a stronger π-acceptor than CN, such an arrangement leads to a better balance than two *trans* CO groups.

However, in the phosphine complexes $RuCl_2(CO)_2(PBzPh_2)_2$ and $RuCl_2(CO)_2(PBz_3)_2$ (Wilkes *et al.*, 1982), the *cis* Cl isomer is thermodynamically more stable than the *trans*. The reason might be found in the bulky phosphine ligands which would only occupy *trans* positions, thus forcing Cl and CO to be in the same octahedral equatorial plane.

Although a direct comparison of the Ru—N(nitrile) bond length with those in other complexes containing Ru in such an octahedral geometry is precluded by the lack of structural data, it appears that the Ru—N distance of 2·119 Å is somewhat shorter than would be expected from comparison either with Fe—N(nitrile), *e.g.* 2·183 Å in $[Fe(NCCH_3)_6]^{2+}$ (Constant, Daran & Jeannin, 1972) or with W—N(nitrile), 2·218 Å in $WCl(CO)_2(\eta\text{-}C_3H_5)P(C_6H_5)_3(NCCH_3).NCCH_3$ (Boyer, Daran, Dromzee & Jeannin, 1980). This shortening might be accounted for by the fact that the nitrile behaves as a π-acceptor.

The two phenyl rings are coplanar with the equatorial plane defined by N and CO. The dihedral angle between the rings is 177 (1)°. A similar arrangement has also been observed in $VOCl_3(NCC_6H_5)_2$, with a dihedral angle of 178° (Daran, Gourdon & Jeannin, 1980). The ring coplanarity with the octahedral basal plane may be related to the overlap between π-ring and π-CN orbitals, and π^*-CN and Ru d orbitals; this demonstrates the electron-accepting ability of CN with respect to Ru d electrons.

The crystal structure consists of planes as shown in Fig. 2 containing the phenyl rings. An interesting feature is that the Cl—Ru—Cl line is just sandwiched between two rings belonging to two different planes. Such an arrangement might suggest a 'charge transfer' between Cl and phenyl rings. However, it would be very weak since:

(*a*) The C···Cl distances range from 3·69 to 4·20 Å, which is long compared to 3·36 Å found in the benzene–Br compound in which such an interaction takes place (Hassel & Strømme, 1958).

(*b*) The Ru—Cl line does not pass through the central point of the ring; the deviation is 1·04 Å.

(*c*) It is well known that such 'charge transfer' lowers the X_2 stretching frequency (Pearson, Erickson & Buckles, 1957); then by comparison a decrease of (Ru—Cl) should occur; this is not the case; the 345 cm^{-1} observed value is similar to 334 cm^{-1} in $RuCl_2(CO)_2(PBzPh_2)_2$, or 355 cm^{-1} for $RuCl_2(CO)_2(PBz_3)_2$ (Wilkes *et al.*, 1982).

(*d*) The 'charge transfer' should lengthen the Ru—Cl distance; however, the 2·380 Å which is observed can be compared to the range 2·39–2·43 Å found in several other Ru^{II} complexes, all of them with two *trans* Cl atoms and no such arrangement of Cl with respect to phenyl rings: $RuCl_2(PPh_3)_3$ 2·388 (7) (La Placa & Ibers, 1965), $RuCl_2(CO)_2(PBz_3)_2$ 2·418 (1) and $RuCl_2(CO)_2(PBzPh_2)_2$ 2·429 (2) Å (Wilkes *et al.*, 1982).

Thus, it seems that the arrangement of the molecules in the crystal is governed more by steric factors.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Ru	0·0000	0·0474 (1)	0·2500	2·47 (5)
Cl	0·1425 (2)	0·0561 (4)	0·2794 (3)	4·52 (14)
C(2)	0·0510 (10)	−0·0894 (11)	0·3862 (13)	4·17 (61)
O(2)	0·0770 (9)	−0·1764 (11)	0·4581 (11)	6·54 (61)
N(1)	0·0564 (8)	0·1980 (10)	0·4073 (12)	4·05 (51)
C(1)	0·0866 (8)	0·2727 (12)	0·4971 (14)	3·75 (55)
C(11)	0·1219 (8)	0·3642 (12)	0·6121 (12)	3·42 (52)
C(12)	0·1574 (10)	0·3137 (12)	0·7424 (15)	4·63 (66)
C(13)	0·1885 (12)	0·4049 (14)	0·8516 (14)	5·66 (68)
C(14)	0·1853 (9)	0·5406 (17)	0·8278 (13)	4·72 (58)
C(15)	0·1496 (11)	0·5897 (13)	0·6981 (16)	4·81 (69)
C(16)	0·1185 (9)	0·5033 (11)	0·5888 (14)	4·21 (56)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ru—Cl	2·380 (4)	C(11)—C(12)	1·379 (22)
Ru—C(2)	1·877 (13)	C(12)—C(13)	1·402 (22)
Ru—N(1)	2·119 (12)	C(13)—C(14)	1·374 (22)
N(1)—C(1)	1·138 (18)	C(14)—C(15)	1·367 (24)
C(2)—O(2)	1·104 (17)	C(15)—C(16)	1·373 (22)
C(1)—C(11)	1·439 (19)	C(16)—C(11)	1·406 (17)
Cl—Ru—N(1)	89·0 (5)	N(1)—C(1)—C(11)	177·1 (20)
Cl—Ru—C(2)	90·8 (6)	C(1)—C(11)—C(12)	119·3 (11)
Cl—Ru—N(1)′	88·0 (5)	C(11)—C(12)—C(13)	118·3 (12)
Cl—Ru—C(2)′	92·2 (6)	C(12)—C(13)—C(14)	119·8 (15)
Cl—Ru—Cl′	175·8 (2)	C(13)—C(14)—C(15)	121·4 (14)
N(1)—Ru—C(2)	91·5 (5)	C(14)—C(15)—C(16)	120·3 (13)
N(1)—Ru—C(2)′	178·1 (7)	C(15)—C(16)—C(11)	118·8 (14)
N(1)—Ru—N(1)′	90·0 (6)	C(16)—C(11)—C(1)	119·3 (13)
C(2)—Ru—C(2)′	87·1 (8)	C(16)—C(11)—C(12)	121·4 (11)
Ru—N(1)—C(1)	175·5 (13)	Ru—C(2)—O(2)	174·7 (11)

Primed atoms are related to those listed in Table 1 by the symmetry transformation $-x, y, \frac{1}{2}-z$.

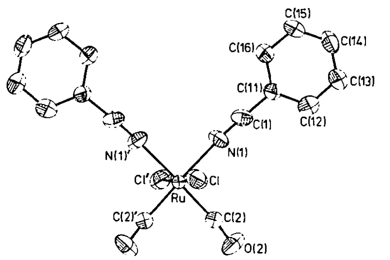

Fig. 1. Perspective view drawn with *ORTEP* (Johnson, 1965) of the molecular structure with the atom numbering. Ellipsoids represent the 50% probability level.

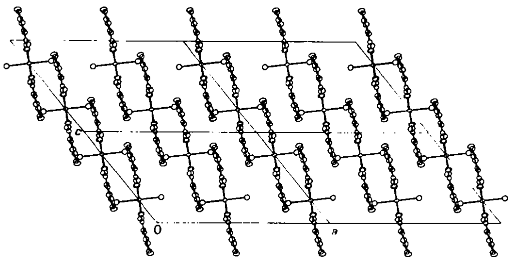

Fig. 2. View of four unit cells projected onto the *xz* plane.

References

Adams, R. D., Katahira, D. A. & Li-wu Yang (1981). *J. Organomet. Chem.* **219**, 85–101.

Boyer, M., Daran, J. C., Dromzee, Y. & Jeannin, Y. (1980). Proc. XXI Int. Conf. Coord. Chem. Toulouse, France, p. 124.

Brown, L. D., Barnard, C. F. G., Daniels, J. A., Mawby, R. J. & Ibers, J. A. (1978). *Inorg. Chem.* **17**, 2932–2935.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Constant, G., Daran, J. C. & Jeannin, Y. (1972). *J. Organomet. Chem.* **44**, 353–363.

Daran, J. C., Gourdon, A. & Jeannin, Y. (1980). *Acta Cryst.* B**36**, 309–312.

Dawoodi, Z., Mays, M. J. & Raithby, P. R. (1981). *J. Organomet. Chem.* **219**, 103–113.

Ford, P. C. (1970). *Coord. Chem. Rev.* **5**, 75–99.

Hassel, O. & Strømme, K. O. (1958). *Acta Chem. Scand.* **12**, 1146–1147.

Ibers, J. A., Hamilton, W. C. & Muir, K. (1973). *FORDAP*. Northwestern Univ., Evanston, Illinois.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

La Placa, S. J. & Ibers, J. A. (1965). *Inorg. Chem.* **4**, 778–783.

Pearson, W. B., Erickson, R. E. & Buckles, R. E. (1957). *J. Chem. Phys.* **27**, 1211–1212.

Thomas, J. L. (1975). *J. Am. Chem. Soc.* **97**, 5943–5944.

Wilkes, L. M., Nelson, J. H., Mitchener, J. P., Babich, M. W., Riley, W. C., Helland, B. J., Jacobson, R. A., Meng Yu Cheng, Seff, K. & Mc Cusker, L. B. (1982). *Inorg. Chem.* **21**, 1376–1382.

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Tricarbonyl[2–5-η-(methyl 1α-phenyl-2,4-cyclohexadiene-1β-carboxylate)]iron(0), [$Fe(C_{14}H_{14}O_2)(CO)_3$]

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Abstract. $M_r = 354{\cdot}15$, monoclinic, $P2_1/c$, $a = 17{\cdot}499$ (3), $b = 7{\cdot}546$ (1), $c = 13{\cdot}243$ (2) Å, $\beta = 114{\cdot}87$ (2)°, $U = 1586{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}482$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}54051$ Å, $\mu = 7{\cdot}96$ mm^{-1}, $F(000) = 724$, $T = 293$ (2) K. Final $R = 0{\cdot}044$ for 1437 unique diffractometer data. The carboxylate group is characteristically slightly aplanar due to the presence of a proximal, short, intramolecular nonbonding interaction to a neighbouring carbonyl group.

Introduction. The use of >$Fe(CO)_3$ as a protective and/or directing group in regio- and stereospecific organic syntheses has been studied extensively by A. J. Birch and co-workers (*e.g.* Birch *et al.*, 1981). The organic precursors are commonly 1,4-cyclohexadienes (from Birch reduction of aromatics) and their reaction products with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ are commonly mixtures of isomeric 1,3-diene–$Fe(CO)_3$ complexes. Detailed characterization of both the reaction products and their isomeric distributions is an obvious prerequisite to the use of those products as synthetic intermediates. The present complex is the sole isomer obtained from the reaction of methyl 1-phenyl-2,5-cyclohexadiene-1-carboxylate with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ (Bandara, 1981). The stereochemistry could only be assigned with certainty by recourse to crystal-structure analysis.

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