

N(2)—Mn—N(4)	170.22 (7)	C(b3)—C(b4)—C(a4)	106.9 (2)
N(3)—Mn—N(4)	89.28 (7)	C(b6)—C(b5)—C(a5)	106.9 (2)
N(1)—Mn—O(1)	95.30 (6)	C(b5)—C(b6)—C(a6)	106.8 (2)
N(2)—Mn—O(1)	94.44 (6)	C(b8)—C(b7)—C(a7)	106.6 (2)
N(3)—Mn—O(1)	94.26 (6)	C(b7)—C(b8)—C(a8)	106.8 (2)
N(4)—Mn—O(1)	95.34 (6)	C(a1)—C(m1)—C(a8)	125.7 (2)
C(a1)—N(1)—Mn	126.73 (13)	C(a2)—C(m2)—C(a3)	125.0 (2)
C(a2)—N(1)—Mn	127.32 (12)	C(a4)—C(m3)—C(a5)	125.5 (2)
C(a3)—N(2)—Mn	127.44 (13)	C(a6)—C(m4)—C(a7)	125.2 (2)
C(a4)—N(2)—Mn	127.09 (13)	C(a1)—C(b1)—C(11)	125.0 (2)
C(a5)—N(3)—Mn	127.00 (14)	C(a2)—C(b2)—C(21)	124.8 (2)
C(a6)—N(3)—Mn	127.46 (13)	C(a3)—C(b3)—C(31)	125.5 (2)
C(a7)—N(4)—Mn	127.45 (13)	C(a4)—C(b4)—C(41)	124.7 (2)
C(a8)—N(4)—Mn	126.66 (13)	C(a5)—C(b5)—C(51)	124.8 (2)
C(a1)—N(1)—C(a2)	105.56 (15)	C(a6)—C(b6)—C(61)	125.3 (2)
C(a3)—N(2)—C(a4)	105.4 (2)	C(a7)—C(b7)—C(71)	125.6 (2)
C(a5)—N(3)—C(a6)	105.4 (2)	C(a8)—C(b8)—C(81)	125.0 (2)
C(a7)—N(4)—C(a8)	105.3 (2)	C(b2)—C(b1)—C(11)	127.9 (2)
N(1)—C(a1)—C(b1)	110.2 (2)	C(b1)—C(b2)—C(21)	128.4 (2)
N(1)—C(a2)—C(b2)	110.4 (2)	C(b4)—C(b3)—C(31)	127.9 (2)
N(2)—C(a3)—C(b3)	110.6 (2)	C(b3)—C(b4)—C(41)	128.4 (2)
N(2)—C(a4)—C(b4)	110.5 (2)	C(b6)—C(b5)—C(51)	128.2 (2)
N(3)—C(a5)—C(b5)	110.4 (2)	C(b5)—C(b6)—C(61)	127.9 (2)
N(3)—C(a6)—C(b6)	110.4 (2)	C(b8)—C(b7)—C(71)	127.7 (2)
N(4)—C(a7)—C(b7)	110.7 (2)	C(b7)—C(b8)—C(81)	128.2 (2)
N(4)—C(a8)—C(b8)	110.7 (2)	C(b1)—C(11)—C(12)	113.6 (2)
N(1)—C(a1)—C(m1)	124.9 (2)	C(b2)—C(21)—C(22)	111.7 (2)
N(1)—C(a2)—C(m2)	125.1 (2)	C(b3)—C(31)—C(32)	112.9 (2)
N(2)—C(a3)—C(m2)	125.0 (2)	C(b4)—C(41)—C(42)	113.2 (2)
N(2)—C(a4)—C(m3)	125.2 (2)	C(b5)—C(51)—C(52)	112.9 (2)
N(3)—C(a5)—C(m3)	125.0 (2)	C(b6)—C(61)—C(62)	114.1 (2)
N(3)—C(a6)—C(m4)	125.0 (2)	C(b7)—C(71)—C(72)	112.9 (2)
N(4)—C(a7)—C(m4)	124.9 (2)	C(b8)—C(81)—C(82)	113.6 (2)
N(4)—C(a8)—C(m1)	125.0 (2)	O(1)—Cl—O(2)	106.93 (9)
C(m1)—C(a1)—C(b1)	124.9 (2)	O(1)—Cl—O(3)	109.49 (11)
C(m2)—C(a2)—C(b2)	124.4 (2)	O(1)—Cl—O(4)	107.67 (10)
C(m2)—C(a3)—C(b3)	124.5 (2)	O(2)—Cl—O(3)	111.10 (11)
C(m3)—C(a4)—C(b4)	124.3 (2)	O(2)—Cl—O(4)	110.83 (11)
C(m3)—C(a5)—C(b5)	124.5 (2)	O(3)—Cl—O(4)	110.68 (12)
C(m4)—C(a6)—C(b6)	124.6 (2)	Cl—O(1)—Mn	127.13 (8)
C(m4)—C(a7)—C(b7)	124.4 (2)		

Cell-constants determination and intensity-data collection were performed on an Enraf-Nonius FAST area-detector diffractometer with an Mo rotating anode source. Our detailed methods and procedures for small molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). All H atoms were idealized with the standard methods in *SHELXL93* (Sheldrick, 1993) and included in the least-square process as fixed contributors (for methyl H atoms, the methyl group orientations were refined) using a riding model for CH (C—H = 0.95 Å), CH₂ (C—H = 0.99 Å) and CH₃ (C—H = 0.98 Å).

Data collection: *MADNES* (Messerschmitt & Pflugrath, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[(R)-1,2-Diethoxycarbonyl]bis(dimethylglyoximato)(methyldiphenylphosphine)cobalt(III)

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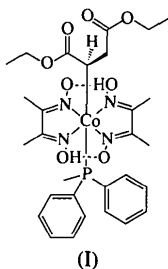
Abstract

The crystal structure of the title compound, [Co(C₄H₇N₂O₂)₂(C₈H₁₃O₄)(C₁₃H₁₃P)], has been determined in order to examine whether or not the chiral 1,2-diethoxycarbonyl group is racemized on exposure to either visible light or X-rays with retention of the single-crystal form. Although the reaction cavity of the chiral group is considerably large, the chiral group is isolated from the other chiral groups in the structure. The cooperative motion between the chiral groups necessary for the racemization of bulky groups may be impossible in such an isolated environment.

Comment

In the study of crystalline-state racemization of bis(dimethylglyoximato)cobalt(III) complexes, three kinds of chiral group bonded to the Co atom,

namely, 1-cyanoethyl (ce) (Ohashi, 1988), 1-methoxycarbonylethyl (mce) (Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984) and 1,2-dimethoxycarbonylethyl (dmce) (Sekine *et al.*, 1990; Sakai, Ohashi, Arai & Ohgo, 1992), have been found to be racemized on exposure to X-rays or visible light without degradation of crystallinity. In order to examine a complex having a bulkier chiral group, the cobaloxime complex (I), with 1,2-diethoxycarbonylethyl (dece) and methylphenylphosphine groups as axial ligands, has been prepared.



The molecular structure and atom-numbering scheme are shown in Fig. 1. The crystal structure viewed along the *c* axis is shown in Fig. 2. The L-type conformation of the dece group, in which one of the ester groups is parallel and the other ester group is perpendicular to the dimethylglyoxime plane, is essentially the same

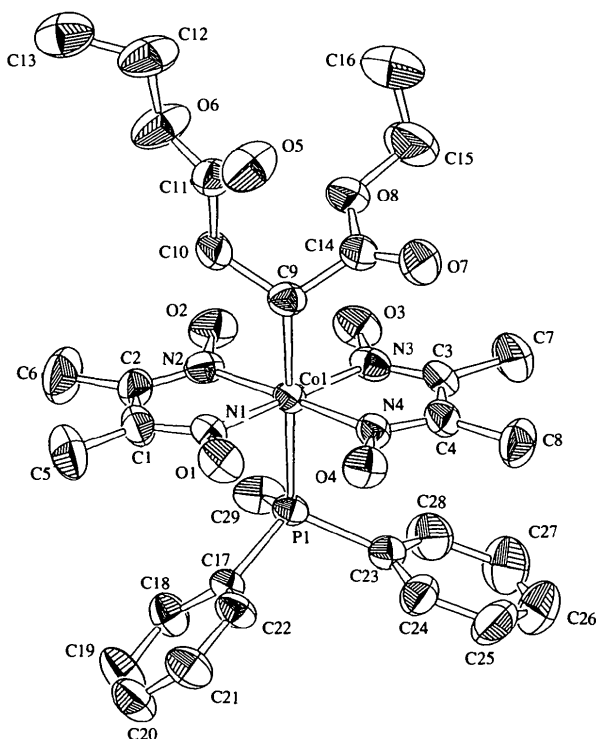


Fig. 1. The molecular structure and atomic numbering scheme for the title compound. Displacement ellipsoids are plotted at the 50% probability level.

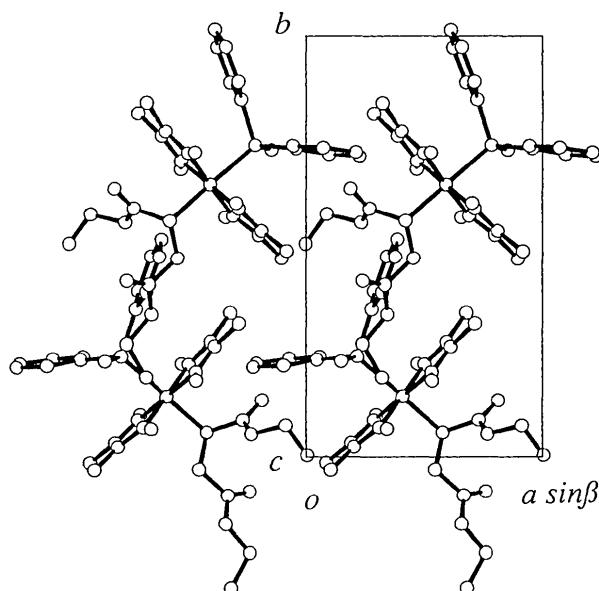


Fig. 2. The crystal structure of the title compound viewed along the *c* axis.

as that of the dmce group except for the two terminal methyl groups. The Co—C bond is slightly longer [2.088 (6) Å] than the corresponding ones in the dmce complexes [2.062 (5)–2.069 (7) Å] (Sakai *et al.*, 1991, 1993). The three angles around the C9 atom, Co—C9—C10, Co—C9—C14 and C10—C9—C14, are in good agreement with the corresponding angles of the dmce complexes, the average values being 114.0, 110.5 and 110.6°, respectively (Sakai *et al.*, 1991, 1993).

The complex was not racemized by X-rays or visible light with retention of the single-crystal form, although the powdered sample was racemized on exposure to a xenon lamp at low reaction rate. The reaction cavity was calculated in the same way as reported previously (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981). The volume of the cavity is 75.8 Å³, which is significantly larger than those of the reactive dmce groups (34–55 Å³), even if the terminal methyl groups are taken into account (Sakai *et al.*, 1993).

There is only one molecule in the asymmetric unit of the *P*2₁ cell. The dece group is surrounded by the phosphine and dimethylglyoxime ligands. Cooperative motion between the reactive groups observed in the mce and dmce complexes seems to be impossible in such an isolated environment. This must be a reason why crystalline-state racemization is not seen in the present crystal.

Experimental

Crystal data

[Co(C₄H₇N₂O₂)₂(C₈H₁₃O₄)-(C₁₃H₁₃P)]

Mo K α radiation
 $\lambda = 0.71073$ Å

$M_r = 662.55$
 Monoclinic
 $P2_1$
 $a = 9.593 (3) \text{ \AA}$
 $b = 15.915 (2) \text{ \AA}$
 $c = 11.427 (2) \text{ \AA}$
 $\beta = 113.890 (13)^\circ$
 $V = 1595.1 (5) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.380 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections
 $\theta = 12.5\text{--}15.0^\circ$
 $\mu = 0.645 \text{ mm}^{-1}$
 $T = 296 (2) \text{ K}$
 Prism
 $0.55 \times 0.30 \times 0.30 \text{ mm}$
 Dark red

C27	0.6225 (11)	0.9731 (5)	0.6698 (9)	0.101
C26	0.6137 (11)	1.0147 (5)	0.7700 (10)	0.098
C25	0.6583 (9)	0.9744 (5)	0.8861 (9)	0.078
C11	0.3333 (6)	0.4077 (4)	0.7437 (6)	0.048
C12	0.2399 (9)	0.2708 (5)	0.6724 (9)	0.082
C13	0.3209 (10)	0.1910 (5)	0.6806 (7)	0.079
C14	0.2698 (6)	0.5890 (4)	0.6842 (6)	0.050
C17	0.9548 (5)	0.7336 (4)	0.9595 (5)	0.038
C22	0.9437 (6)	0.7404 (4)	1.0763 (5)	0.047
C21	1.0721 (7)	0.7358 (5)	1.1892 (5)	0.058
C20	1.2118 (7)	0.7250 (5)	1.1880 (6)	0.066
C19	1.2255 (7)	0.7157 (5)	1.0734 (6)	0.072
C18	1.0964 (6)	0.7193 (4)	0.9588 (6)	0.054
C29	0.8528 (7)	0.7300 (5)	0.6856 (5)	0.055
C16	-0.0034 (11)	0.5045 (7)	0.4203 (10)	0.149
C15	0.0877 (9)	0.5755 (6)	0.4671 (9)	0.106

Data collection

Rigaku AFC-7 diffractometer
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 27.56^\circ$
 $\omega/2\theta$ scans
 $h = 0 \rightarrow 12$
 Absorption correction: none
 $k = 0 \rightarrow 20$
 $l = -14 \rightarrow 13$
 4009 measured reflections
 3794 independent reflections
 2878 observed reflections
 $[I > 2\sigma(I)]$
 3 standard reflections monitored every 100 reflections
 intensity decay: 1.7%

Refinement

Refinement on F^2
 $R(F) = 0.044$
 $wR(F^2) = 0.098$
 $S = 1.063$
 3794 reflections
 388 parameters
 H atoms riding on associated atoms
 $w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.105$
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: χ parameter = 0.01 (2) (Flack, 1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
Co1	0.59135 (7)	0.64604 (4)	0.79090 (6)	0.033
P1	0.7834 (2)	0.7416 (1)	0.8119 (1)	0.034
O1	0.7030 (4)	0.6017 (3)	1.0541 (3)	0.054
O2	0.6576 (5)	0.5676 (3)	0.5958 (4)	0.058
O4	0.5277 (4)	0.7241 (3)	0.9864 (3)	0.053
O3	0.4681 (5)	0.6835 (3)	0.5241 (3)	0.060
O5	0.2409 (6)	0.4169 (3)	0.7868 (5)	0.081
O6	0.3434 (6)	0.3391 (3)	0.6815 (5)	0.080
O8	0.2335 (5)	0.5553 (3)	0.5675 (4)	0.064
O7	0.1873 (5)	0.6365 (4)	0.7072 (5)	0.075
N1	0.7127 (5)	0.5890 (3)	0.9417 (4)	0.039
N2	0.6903 (5)	0.5713 (3)	0.7218 (4)	0.043
N3	0.4692 (5)	0.7035 (3)	0.6397 (4)	0.044
N4	0.4987 (5)	0.7224 (3)	0.8613 (4)	0.039
C1	0.8102 (6)	0.5346 (4)	0.9335 (6)	0.048
C2	0.7979 (7)	0.5245 (4)	0.8028 (7)	0.051
C5	0.9160 (8)	0.4866 (5)	1.0438 (7)	0.075
C6	0.8964 (9)	0.4692 (5)	0.7646 (8)	0.085
C4	0.4049 (6)	0.7757 (4)	0.7827 (6)	0.046
C3	0.3876 (6)	0.7647 (4)	0.6507 (6)	0.049
C8	0.3228 (7)	0.8430 (4)	0.8238 (8)	0.067
C7	0.2864 (8)	0.8180 (5)	0.5411 (7)	0.085
C9	0.4222 (6)	0.5593 (4)	0.7776 (6)	0.043
C10	0.4547 (6)	0.4700 (4)	0.7506 (6)	0.052
C24	0.7117 (7)	0.8928 (4)	0.9011 (6)	0.054
C23	0.7225 (6)	0.8513 (3)	0.7989 (5)	0.044
C28	0.6773 (8)	0.8908 (5)	0.6822 (7)	0.072

Table 2. Selected geometric parameters (\AA , $^\circ$)

Co1—N4	1.870 (4)	P1—C23	1.829 (6)
Co1—N1	1.877 (4)	O5—C11	1.185 (7)
Co1—N2	1.883 (4)	O6—C11	1.328 (7)
Co1—N3	1.885 (4)	O8—C14	1.346 (7)
Co1—C9	2.088 (6)	O7—C14	1.198 (7)
Co1—P1	2.325 (2)	C9—C14	1.495 (8)
P1—C17	1.822 (5)	C9—C10	1.513 (9)
P1—C29	1.827 (5)	C10—C11	1.507 (8)
N1—Co1—N2	81.3 (2)	C10—C9—Co1	114.7 (4)
N1—Co1—C9	85.5 (2)	C11—C10—C9	114.2 (5)
C14—C9—C10	112.0 (5)	O7—C14—C9	125.8 (6)
C14—C9—Co1	110.4 (4)	O8—C14—C9	111.5 (5)
N2—Co1—P1—C29	32.4 (3)	C14—C9—C10—C11	-54.2 (7)
N3—Co1—C9—C10	-15.7 (4)	Co1—C9—C10—C11	178.9 (4)
N2—Co1—C9—C10	12.8 (5)		

The distances C15—C16, C26—C27 and C27—C28 were constrained in the refinement.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: AS1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Redetermination of the Crystal Structure of Bis(cyclopentadienyldicarbonylruthenium)

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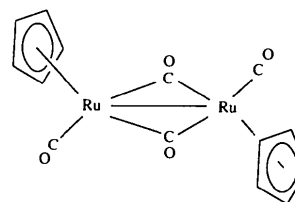
Abstract

The structure of *trans*-di- μ -carbonyl-bis[carbonyl-(η^5 -cyclopentadienyl)ruthenium], $[\{\text{Ru}(\text{C}_5\text{H}_5)\text{CO}\}_2(\mu\text{-CO})_2]$, has been redetermined from diffractometer data leading to considerably more accurate geometric parameters than those obtained in the original determination from film data.

Comment

Recently we have been investigating the use of the 'metalloligand' (η^5 -C₅H₅)RuCl{ η^1 -MeN(PF₂)₂}₂ (Mague & Lin, 1994) for the directed synthesis of ligand-bridged heterobimetallic complexes. On reacting this species [prepared from CpRuCl(CO)₂ (Eisenstadt, Tannenbaum & Efrati, 1981)] with RhCl(CO)(PMe₂Ph)₂, a small quantity of orange crystals was obtained, although little of the desired heterobimetallic complex appeared to have formed according to ³¹P NMR data for the crude reaction mixture. Presuming this to be the product, a structural study was initiated. From the unit cell obtained it was clear that this was not the case and a search of the Cambridge Structural Database showed that the crystals were in fact [Cp₂Ru₂(CO)₄], (1), which is a possible side product in the synthesis of CpRuCl(CO)₂, and was evidently present as a contaminant in the sample of the dicarbonyl used to prepare the 'metalloligand'. Noting that the original structure determination for (1) (Mills & Nice, 1967) was of low

quality (film data, $R = 0.097$), it was decided to continue with the structure determination in order to obtain more accurate structural parameters.



(1)

The quality of the present data set allowed for the refinement of anisotropic displacement parameters for all non-H atoms, as well as the location and refinement of all H atoms. While no substantial differences in the geometric parameters between the two structure determinations were found, an improvement in the e.s.d.'s by a factor of about four was realized, as was a greater uniformity in bond distances between comparable atoms. As a result of the improved accuracy, the apparent differences in the Ru—C(cyclopentadienyl) distances seen in the original determination now appear real, with Ru—C(5) and Ru—C(6) significantly shorter ($\Delta/\sigma = 11$ and 6, respectively) than the average of the other three Ru—C(cyclopentadienyl) bonds. At first sight, this could be taken to indicate a distortion of the bonding of the cyclopentadienyl group towards the 'allyl-ene' mode, but this is not supported by the C—C distances in the ring, which are equal within experimental error. Presumably it reflects more subtle electronic factors resulting from the low symmetry of the remainder of the coordination sphere. The Ru—Ru distance compares well with those found in a variety of related species, e.g.

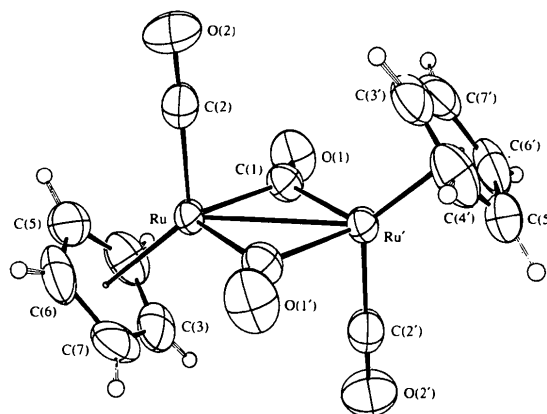


Fig. 1. A perspective view of *trans*-[Cp₂Ru₂(CO)₄], (1). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms while H atoms are represented by circles of arbitrary size. The primed atoms are related to the unprimed atoms by the crystallographic center of symmetry.