

References

- DÀO, C. N. (1987). PhD Dissertation, Univ. of Wrocław, Poland.
 DREW, M. G. B. (1977). *Coord. Chem. Rev.* **24**, 179–275.
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 JONES, P. G. (1986). *Acta Cryst.* **A42**, 57.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Germany.
 SINHA, S. P. (1976). *Struct. Bonding (Berlin)*, **25**, 69–154.
 STARYNOWICZ, P. (1991). *Acta Cryst.* **C47**, 32–35.
 UGOZZOLI, F. (1987). *Comput. Chem.* **11**(2), 109–120.

Acta Cryst. (1991). **C47**, 297–300

Structure of 1,1,1,2,2-Pentacarbonyl- μ -hydrido- μ -2 η -[(*Z,s-cis,Z*)-*N*-isopropyl-cinnamylideneamino- μ -*N*, μ -C η]-diruthenium(*Ru*–*Ru*), HRu₂(CO)₅(C₁₂H₁₄N)

BY ANTHONY L. SPEK* AND ALBERT J. M. DUSENBERG

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, Universiteit te Utrecht, Padualaan 8, 3548 CH Utrecht, The Netherlands

AND WILHELMUS P. MUL, OLAF C. P. BEERS AND CORNELIS J. ELSEVIER*

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

(Received 12 May 1990; accepted 20 July 1990)

Abstract. C₁₇H₁₅NO₅Ru₂, $M_r = 515.45$, orthorhombic, *Pcab*, $a = 12.828$ (1), $b = 16.813$ (1), $c = 34.324$ (2) Å, $V = 7402.9$ (8) Å³, $Z = 16$, $D_x = 1.85$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 16.3$ cm⁻¹, $F(000) = 4032$, $T = 295$ K, $R = 0.038$ for 5117 reflections with $I > 2.5\sigma(I)$. The two crystallographically independent molecules are essentially identical except for one torsion angle. The Ru–Ru bond is bridged asymmetrically by both a hydride atom and an *N*-isopropyl cinnamaldimin-4-yl ligand.

Introduction. Transition metal hydrido complexes are believed to be the key intermediates in important catalytic processes like hydrogenation, hydroformylation, hydrocyanation, and double-bond migration of olefins (see *e.g.* Crabtree, 1988). The presence of hydrides in combination with unsaturated ligands on transition metal carbonyl moieties affords an opportunity to study the chemical and structural properties of such crucial species in detail.

In the course of our study on the coordination and reactivity of monoazadienes ($R^1\text{CH}=\text{CHCH}=\text{NR}^2$) on transition metal carbonyls we recently reported the preparation of a series of linear tetranuclear clusters, Ru₄(CO)₁₀[$R^1\text{C}=\text{CHCH}=\text{NR}^2$]₂ (1a: $R^1 = \text{Me}$, $R^2 = i\text{-Pr}$; 1b: $R^1 = \text{Me}$, $R^2 = c\text{-Hex}$; 1c: $R^1 = \text{Me}$, $R^2 = t\text{-Bu}$; 1d: $R^1 = \text{Ph}$, $R^2 = i\text{-Pr}$; 1e: $R^1 = \text{Ph}$, $R^2 = t\text{-Bu}$) (Polm, Mul, Elsevier, Vrieze, Christophersen & Stam, 1988; Mul, Elsevier, Polm, Vrieze,

Zoutberg, Heijdenrijk & Stam, 1990). These clusters are formed in high yield by thermolysis of Ru₂(CO)₆[$R^1\text{C}=\text{CHCH}_2\text{NR}^2$]. In one case an intermediate, a dinuclear hydrido complex, HRu₂(CO)₅[Ph–C=CHCH=N-*i*-Pr] (2d), could be isolated. We now report the crystal structure of this dinuclear hydrido complex.

Experimental. The air-sensitive title compound was prepared by thermolysis of Ru₂(CO)₆[Ph–C=CHCH₂N-*i*-Pr] in refluxing heptane and purified by chromatography on silica employing hexane/dichloromethane (9/1) as the eluent (Mul *et al.*, 1990). Crystals suitable for X-ray diffraction work were grown by cooling a concentrated hexane solution at 243 K. X-ray data for a light-brown crystal (0.12 × 0.25 × 0.63 mm), sealed in a Lindemann-glass capillary, were collected on an Enraf–Nonius CAD-4F diffractometer using Zr-filtered Mo $K\alpha$ radiation. Lattice parameters and their e.s.d.'s were derived from the setting angles of 25 SET4 reflections ($14 < \theta < 18^\circ$). The space group was determined from the observed systematic absences. A total of 9711 reflections [$\theta < 27.5^\circ$; $\omega/2\theta$ scan; $\Delta\omega = 0.60 + 0.35\tan(\theta)^\circ$; $0 < h < 16$, $0 < k < 21$, $0 < l < 44$] were scanned. Three reference reflections (204, 220, 012) showed a small linear decay of 1% during the 132 h of X-ray exposure time. The intensities were corrected for Lp for the small decay and for absorption (Gaussian integration; grid 8 × 8 × 8; corrections 1.22 to 1.49), resulting in a set of 5117 unique

* Authors to whom correspondence should be addressed.

reflections with $I > 2.5\sigma(I)$. Variance $\sigma^2(I)$ calculated based on counting statistics plus a term $(PI)^2$, where $P (= 0.04)$ is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). The structure was solved by Patterson methods (*SHELXS86*; Sheldrick, 1986). Refinement was carried out by full-matrix least-squares techniques on F with *SHELX76* (Sheldrick, 1976) on a MicroVAX cluster. All non-H atoms were refined with anisotropic thermal parameters. The two hydride H atoms were located from a difference density map and their positions refined with one common isotropic thermal parameter. All other H atoms were introduced on calculated positions ($C-H = 0.95 \text{ \AA}$) and their positions refined with fixed geometry with respect to their carrier atoms with two separate isotropic thermal parameters. Convergence was reached at $R = 0.038$ [$wR = 0.044$, $w^{-1} = \sigma^2(F)$], 5117 reflections, 472 parameters, $S = 3.51$; $(\Delta/\sigma)_{\max} = 0.3$, $-0.40 < \Delta\rho < 0.76 e \text{ \AA}^{-3}$, the highest peaks being within 1 \AA from Ru and interpreted as residual absorption artifacts. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Scattering factors of Cromer & Mann (1968), corrected for anomalous dispersion (Cromer & Liberman, 1970) were used. Geometrical calculations and illustrations were performed with the programs *PLATON* and *PLUTON* of the *EUCLID* package (Spek, 1982).

Discussion. The orthorhombic unit cell contains sixteen discrete molecules of the title compound. Fig. 1 shows one of the two crystallographically independent molecules with adopted numbering. Selected data on the geometry have been assembled in Table 2. The differences in the geometry of the molecules are minor (except for one dihedral angle, see below), and therefore only the data pertaining to molecule (1) will be discussed with those for molecule (2) in square brackets where appropriate.

The molecule consists of a $(CO)_2Ru-Ru(CO)_3$ core in which the Ru(11)—Ru(12) bond is asymmetrically bridged by hydride H(1): Ru(11)—H(1) $1.99(5)$ [$1.94(5)$] \AA , Ru(12)—H(1) $1.68(5)$ [$1.60(5)$] \AA , Ru(11)—H(1)—Ru(12) $96(2)$ [$100(3)$] $^\circ$. The latter bond length represents a 'normal' metal-hydride distance of $(r_M + 0.3) \text{ \AA}$. (r_M is the covalent radius of the metal: $r_{Ru} = 1.40 \text{ \AA}$). Based on valence electron count for Ru(11) and Ru(12) a terminal position of H(1) might be expected, but as in many

Table 1. *Final coordinates and equivalent isotropic thermal parameters (\AA^2) of the non-H atoms and their e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Ru(11)	0.04640 (4)	0.10520 (3)	0.11645 (1)	0.0414 (2)
Ru(12)	-0.00649 (4)	0.00498 (3)	0.17599 (1)	0.0431 (2)
O(11)	0.2476 (4)	0.1700 (3)	0.0832 (2)	0.085 (2)
O(12)	-0.0607 (4)	0.0872 (3)	0.0364 (2)	0.085 (2)
O(13)	-0.0544 (4)	0.2684 (3)	0.1198 (2)	0.082 (2)
O(14)	-0.1351 (4)	-0.1450 (3)	0.1750 (2)	0.092 (2)
O(15)	-0.1134 (5)	0.0399 (4)	0.2518 (2)	0.101 (3)
N(1)	0.1003 (4)	-0.0116 (3)	0.1277 (1)	0.046 (2)
C(101)	0.1011 (5)	0.1835 (3)	0.1983 (2)	0.048 (2)
C(102)	0.0104 (5)	0.2241 (4)	0.2086 (2)	0.056 (2)
C(103)	0.0146 (6)	0.2927 (4)	0.2302 (2)	0.067 (3)
C(104)	0.1081 (7)	0.3237 (4)	0.2422 (2)	0.072 (3)
C(105)	0.1977 (6)	0.2850 (5)	0.2331 (2)	0.076 (3)
C(106)	0.1954 (5)	0.2163 (4)	0.2111 (2)	0.061 (3)
C(107)	0.1011 (4)	0.1112 (3)	0.1740 (2)	0.044 (2)
C(108)	0.1601 (4)	0.0452 (4)	0.1861 (2)	0.048 (2)
C(109)	0.1570 (5)	-0.0210 (4)	0.1612 (2)	0.051 (2)
C(110)	0.1073 (5)	-0.0801 (4)	0.0998 (2)	0.058 (2)
C(111)	0.1971 (7)	-0.0639 (5)	0.0719 (2)	0.085 (3)
C(112)	0.0056 (7)	-0.0978 (5)	0.0791 (3)	0.088 (4)
C(113)	0.1724 (6)	0.1466 (4)	0.0951 (2)	0.053 (2)
C(114)	-0.0219 (6)	0.0885 (4)	0.0658 (2)	0.059 (2)
C(115)	-0.0171 (5)	0.2070 (4)	0.1182 (2)	0.055 (2)
C(116)	-0.0844 (5)	-0.0883 (4)	0.1747 (2)	0.058 (2)
C(117)	-0.0740 (5)	0.0278 (4)	0.2224 (2)	0.061 (2)
Ru(21)	0.59212 (4)	0.00535 (3)	0.13331 (1)	0.0391 (2)
Ru(22)	0.65478 (4)	-0.09626 (3)	0.07596 (1)	0.0405 (2)
O(21)	0.3888 (4)	0.0776 (3)	0.1600 (2)	0.082 (2)
O(22)	0.6797 (4)	-0.0248 (3)	0.2158 (1)	0.085 (2)
O(23)	0.7084 (4)	0.1625 (3)	0.1341 (1)	0.076 (2)
O(24)	0.7777 (5)	-0.2479 (3)	0.0844 (2)	0.092 (2)
O(25)	0.7908 (4)	-0.0692 (3)	0.0062 (2)	0.084 (2)
N(2)	0.5313 (4)	-0.1087 (3)	0.1189 (1)	0.044 (2)
C(201)	0.5679 (5)	0.0882 (3)	0.0508 (2)	0.042 (2)
C(202)	0.6645 (6)	0.1185 (4)	0.0410 (2)	0.060 (2)
C(203)	0.6745 (6)	0.1887 (4)	0.0194 (2)	0.069 (3)
C(204)	0.5857 (7)	0.2286 (4)	0.0082 (2)	0.074 (3)
C(205)	0.4908 (6)	0.2001 (4)	0.0177 (2)	0.068 (3)
C(206)	0.4808 (5)	0.1298 (4)	0.0382 (2)	0.052 (2)
C(207)	0.5547 (4)	0.0151 (3)	0.0745 (2)	0.038 (2)
C(208)	0.4947 (4)	-0.0475 (3)	0.0591 (2)	0.046 (2)
C(209)	0.4853 (5)	-0.1144 (3)	0.0829 (2)	0.046 (2)
C(210)	0.5099 (5)	-0.1780 (3)	0.1447 (2)	0.056 (2)
C(211)	0.4113 (7)	-0.1598 (5)	0.1680 (2)	0.086 (3)
C(212)	0.5991 (7)	-0.2009 (5)	0.1701 (3)	0.091 (3)
C(213)	0.4655 (5)	0.0516 (3)	0.1506 (2)	0.051 (2)
C(214)	0.6477 (5)	-0.0168 (4)	0.1857 (2)	0.056 (2)
C(215)	0.6659 (5)	0.1039 (4)	0.1345 (2)	0.051 (2)
C(216)	0.7286 (5)	-0.1922 (4)	0.0814 (2)	0.060 (3)
C(217)	0.7392 (5)	-0.0780 (4)	0.0329 (2)	0.056 (2)

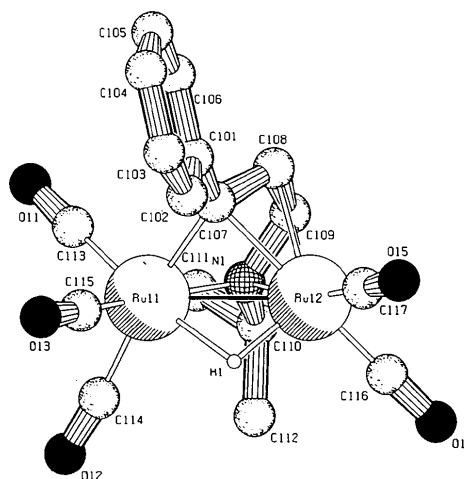


Fig. 1. View of the molecule with adopted numbering.

* Lists of structure factors, anisotropic thermal parameters complete bond distances and bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53446 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and bond angles (°) ($n = 1, 2$)

The hydrido metal carbonyl part				
	(1)	(2)	(1)	(2)
Ru(n1)—Ru(n2)	2.7342 (6)	2.7276 (6)	C(n13)—O(n1)	1.119 (9) 1.123 (8)
Ru(n1)—C(n13)	1.907 (7)	1.897 (6)	C(n14)—O(n2)	1.124 (9) 1.120 (8)
Ru(n1)—C(n14)	1.967 (7)	1.970 (7)	C(n15)—O(n3)	1.139 (8) 1.126 (8)
Ru(n1)—C(n15)	1.897 (7)	1.909 (7)	C(n16)—O(n4)	1.154 (8) 1.133 (9)
Ru(n2)—C(n16)	1.860 (7)	1.880 (7)	C(n17)—O(n5)	1.147 (9) 1.140 (8)
Ru(n2)—C(n17)	1.853 (7)	1.858 (7)		
The metal ligand part				
Ru(n1)—N(n)	2.117 (5)	2.129 (5)	Ru(n2)—C(n07)	2.258 (5) 2.271 (5)
Ru(n1)—C(n07)	2.098 (6)	2.083 (5)	Ru(n2)—C(n08)	2.268 (5) 2.286 (5)
Ru(n2)—N(n)	2.168 (5)	2.173 (5)	Ru(n2)—C(n09)	2.202 (6) 2.208 (6)
The ligand part				
C(n01)—C(n07)	1.474 (8)	1.483 (7)	N(n)—C(n09)	1.369 (8) 1.373 (8)
C(n07)—C(n08)	1.406 (8)	1.407 (7)	N(n)—C(n10)	1.501 (8) 1.490 (8)
C(n08)—C(n09)	1.405 (9)	1.395 (8)		

	(1)	(2)
Ru(n1)—C(n13)—O(n1)	178.4 (6)	177.7 (6)
Ru(n1)—C(n14)—O(n2)	172.9 (6)	176.0 (6)
Ru(n1)—C(n15)—O(n3)	179.1 (6)	178.0 (6)
Ru(n2)—C(n16)—O(n4)	177.4 (6)	176.4 (6)
Ru(n2)—C(n17)—O(n5)	177.4 (6)	177.9 (6)
Ru(n1)—N(n)—Ru(n2)	79.28 (17)	78.70 (17)
Ru(n1)—C(n07)—Ru(n2)	77.67 (18)	77.45 (17)
Ru(n1)—N(n)—C(n09)	115.7 (4)	115.5 (4)
Ru(n1)—C(n07)—C(n08)	114.9 (4)	115.5 (4)
Ru(n2)—N(n)—C(n09)	73.1 (3)	73.2 (3)
Ru(n2)—C(n07)—C(n08)	72.3 (3)	72.6 (3)
C(n01)—C(n07)—C(n08)	118.9 (5)	118.5 (5)
C(n07)—C(n08)—C(n09)	115.4 (5)	115.5 (5)
C(n08)—C(n09)—N(n)	115.8 (6)	115.7 (5)
C(n09)—N(n)—C(n10)	114.5 (5)	113.7 (5)
C(n07)—Ru(n1)—C(n14)	171.0 (3)	169.6 (3)
N(n)—Ru(n1)—C(n15)	166.2 (2)	165.6 (2)
C(n07)—Ru(n2)—C(n16)	173.9 (2)	174.0 (2)
N(n)—Ru(n2)—C(n17)	168.2 (2)	168.5 (2)

other di- and polynuclear transition metal carbonyl complexes an (asymmetrically) bridging position is preferred (Bau, Teller, Kirtley & Koetzle, 1979). The bridging position of the hydride was confirmed chemically, since no H/Cl exchange was observed in a reaction with tetrachloromethane. Rapid H/Cl exchange would be expected if a terminal hydride was present in (2*d*).

The Ru(11)—Ru(12) bond is further bridged by a formally seven-electron-donating σ -N, σ -C, η^2 -C=N, η^2 -C=C bonded *N*-isopropyl cinnamaldimin-4-yl ligand. The interatomic distances within the N=C—C=C skeleton of this unsaturated organic fragment are comparable to those found in the seven-electron-donating *N*-isopropyl crotonaldimin-4-yl ligands present in Ru₄(CO)₁₀[MeC=CHCH=N-*i*-Pr]₂ (1*a*) and Ru₃(CO)₆[Me—C=CHCH=N-*i*-Pr]₂ (3*a*) (see Table 3), and indicate extensive electron delocalization in the cinnamaldimin-4-yl backbone (Polm *et al.*, 1988; Mul, Elsevier, Vrieze, Smeets & Spek, 1988). The N(1), C(109), C(108) and C(107) atoms define a plane (deviations < 0.01 Å) with C(101), C(110) and Ru(11) deviating by 0.03, 0.12 and 0.33 Å, respectively. The dihedral angle between this plane N(1)C(109)C(108)C(107) and the N(1)Ru(11)C(107)

Table 3. Comparison of some pertinent bond distances in (1*a*), (2*d*) and (3*a*)

	Suffixes to the atoms refer to the general N=C _{im} —C _α =C _β moiety.		
	(1 <i>a</i>)	(2 <i>d</i>)	(3 <i>a</i>)
Ru(11)—Ru(12)	2.7084 (4)	2.7342 (6)	2.704 (1)
Ru(11)—C _β	2.048 (3)	2.098 (6)	2.049 (5)
Ru(11)—N	2.123 (2)	2.117 (5)	2.093 (4)
N=C _{im}	1.358 (3)	1.369 (8)	1.386 (7)
C _{im} —C _α	1.405 (5)	1.405 (9)	1.40 (1)
C _α =C _β	1.417 (4)	1.406 (8)	1.401 (8)
Ru(12)—N	2.311 (3)	2.168 (5)	2.123 (4)
Ru(12)—C _{im}	2.300 (4)	2.202 (6)	2.128 (5)
Ru(12)—C _α	2.311 (3)	2.268 (5)	2.189 (5)
Ru(12)—C _β	2.362 (3)	2.258 (5)	2.217 (4)

plane is 11.5 (4)°. Corresponding angles in (1*a*) and (3*a*) are 4.4 and 11.0°. The dihedral angle between the N(1)C(109)C(108)C(107) plane and the phenyl plane of 50.3 (3) [58.3 (3)]° and the C(101)—C(107) distance of 1.474 (8) Å, which corresponds to a standard C(sp²)—C(sp²) single bond (Burke-Laing & Laing, 1976), indicate that there is little or no conjugation between these two π systems.

The Ru(11)—C(107) bond length of 2.098 (6) Å is somewhat longer compared to its counterparts in (1*a*) and (3*a*). This might be ascribed to the presence of the phenyl group on C(107) instead of a methyl group as in (1*a*) and (3*a*). This phenyl group might (when compared to the methyl group) decrease the effective π overlap between the relevant Ru(11) *d* orbital and the π* orbital located on C(107) to some extent. However, one would then expect a certain amount of π interaction between C(101) and C(107), which is not observed. Other effects, *e.g.* steric repulsion between the phenyl group and C(115)=O(13) or the presence of the bridging hydride, might also be responsible for the observed lengthened Ru(11)—C(107) bond. The bond distances of the cinnamaldimin-4-yl ligand in (2*d*) to Ru(12) are intermediate compared to the relevant bond lengths in (1*a*) and (3*a*) and can be ascribed to increasing π back bonding from Ru(12) to the monoazadienyl ligand in the series (1*a*) < (2*d*) < (3*a*) (Table 3).

In general, bridging hydride ligands cause an increase of the metal–metal distance in ruthenium complexes by *ca* 0.2 Å. This effect, however, strongly depends on other bridging ligands present (Bruce, 1982). The Ru(11)—Ru(12) distance in (2*d*) of 2.7342 (6) Å is only slightly longer than those found in (1*a*) and (3*a*) [2.7084 (4) and 2.704 (1) Å, respectively], indicating that the bridging hydride only marginally influences the intermetallic distance in (2*d*).

The ruthenium–carbon distances in the Ru(11) (CO)₃ unit of (2*d*) are similar to those in (1*a*) and (3*a*). Thus, the Ru(11)—C(114) distance of 1.967 (7) Å is significantly longer than the Ru(11)—C(113) and the Ru(11)—C(115) distances, which

amount to 1.907 (7) and 1.897 (7) Å, respectively. This can be ascribed to the large *trans* influence exerted by C(107).

We wish to thank Professor Dr K. Vrieze for his stimulating interest. The investigations were supported in part (ALS, WPM) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References

- BAU, R., TELLER, R. G., KIRTLEY, S. W. & KOETZLE, T. F. (1979). *Acc. Chem. Res.* **12**, 176–183.
 BRUCE, M. I. (1982). *Comprehensive Organometallic Chemistry*, Vol. 4, edited by G. WILKINSON, F. G. A. STONE & E. W. ABEL, p. 846. Oxford: Pergamon Press.
 BURKE-LAING, M. & LAING, M. (1976). *Acta Cryst.* **B32**, 3216–3224.

- CRABTREE, R. H. (1988). *The Organometallic Chemistry of the Transition Metals*, Chapter 9. New York: Wiley-Interscience.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
 MUL, W. P., ELSEVIER, C. J., POLM, L. H., VRIEZE, K., ZOUTBERG, M. C., HEIJDENRIJK, D. & STAM, C. H. (1990). *Organometallics*. Submitted.
 MUL, W. P., ELSEVIER, C. J., VRIEZE, K., SMEETS, W. J. J. & SPEK, A. L. (1988). *Recl Trav. Chim. Pays-Bas*, **107**, 297–298.
 POLM, L. H., MUL, W. P., ELSEVIER, C. J., VRIEZE, K., CHRISTOPHERSEN, M. J. N. & STAM, C. H. (1988). *Organometallics*, **7**, 423–429.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE. Oxford: Clarendon Press.

Acta Cryst. (1991). **C47**, 300–303

Structure of Bis(2,3-butanedione dioximato)[(*S*)-1-cyanoethyl]- (dimethylphenylphosphine)cobalt(III) at 298 and 223 K

BY YUKO KOJIMA, SEIKO IWASAKI AND YUJI OHASHI

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

AND SHOE BABA AND YOSHIAKI OHGO

Niigata College of Pharmacy, Kamishinei-cho, Niigata 950-21, Japan

(Received 28 May 1990; accepted 18 July 1990)

Abstract. [Co(C₄H₇N₂O₂)₂(C₃H₄N){P(CH₃)₂(C₆H₅)}], *M*_r = 481.37, monoclinic, *P*2₁; *T* = 298 K, *a* = 9.5074 (9), *b* = 14.265 (1), *c* = 8.5947 (8) Å, β = 101.71 (1)°, *V* = 1141.37 (2) Å³, *Z* = 2, *D*_x = 1.40 g cm⁻³, *F*(000) = 574, μ(Mo *K*α) = 9.02 cm⁻¹, λ = 0.71069 Å, *R* = 0.053 for 2570 observed reflections; *T* = 223 K, *a* = 9.486 (4), *b* = 14.068 (3), *c* = 8.808 (3) Å, β = 101.27 (3)°, *V* = 1126.5 (6) Å³, *Z* = 2, *D*_x = 1.42 g cm⁻³, μ(Mo *K*α) = 9.08 cm⁻¹, *R* = 0.027 for 1987 observed reflections. The crystal shows crystalline-state racemization at 298 K. During the early stages of data collection, about 30% of the chiral cyanoethyl group was inverted. The initial structure was obtained at 223 K, since the rate of the racemization became sufficiently low.

Introduction. It has been reported that the chiral 1-cyanoethyl (cn) group in some crystals of the bis(dimethylglyoximato)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato) (cobaloxime)

complex is racemized by X-ray exposure keeping the single-crystal form (Ohashi, 1988). The process of racemization has been found to be divided into three modes (Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1985), of which the first mode is the simplest, since the crystal has only one molecule in its asymmetric unit so that the reactive cn group is separated from the other cn groups in the crystalline lattice. Three crystals have been observed to proceed *via* the first mode: [(*R*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]cobaloxime, *R*-cn-*S*-mba (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), [(*S*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]cobaloxime, *S*-cn-*S*-mba (Ohashi, Sasada & Ohgo, 1978) and [(*R*)-1-cyanoethyl](pyrrolidine)cobaloxime, *R*-cn-pyrr (Tamura, 1986). The present crystal, *S*-cn-dmp, also belongs to the first mode. The racemization rate was so high that the chiral cn group was racemized during data collection. Therefore, the initial structure was obtained at 223 K. The present paper reports the