octahedral geometry, and the approximate coordination symmetry is C_s. The two Mo—O(phenolate) distances, Mo—O2 = 1·938 (3) and Mo—O3 = 1·929 (3) Å, are similar to those of the only other reported mononuclear molybdenum complex containing a unidentate alkoxide ligand (Chisholm, Folting, Huffman & Kirkpatrick, 1984) and suggest some *R*O-to-Mo π bonding (Chisholm, Heppert & Huffman, 1984). The Mo—O_t distance for *L*MoO$(OPh)_2$ is the same as the Mo—O_t distance observed for the analogous bis(thiophenolate) structure (Cleland *et al.*, 1987). The elongation of the Mo—N11 bond *trans* to the terminal oxygen atom is of the expected magnitude. Distances and angles in the polypyrazolylborate ligand are normal (Cleland *et al.*, 1987).

The phenyl group containing O2 projects into the pocket formed by the 3-methyl groups of *L*, while the phenyl ring containing O3 lies between two pyrazole rings of *L*. Despite the differing environments of the phenolate ligands, the O1—Mo—O2 and O1—Mo—O3 bond angles are not different, whereas in the analogous SPh complex these angles differ by 4·9° (97·8 *vs* 102·7°). The disparity in orientations of the two phenyl rings in the complex is characterized by differences in the O—Mo—O—C torsional angles. In *L*MoO$(OPh)_2$, the O—Mo—O—C torsional angles are −49° (O1—Mo—O2—C41) and −90° (O1—Mo—O3—C51), similar to those in the analogous SPh complex (−34 and −110°) (Cleland *et al.*, 1987). While the phenyl-ring orientations in these two structures are similar, they are quite different from those in the analogous nitrosyl complex *L*Mo(NO)$(SPh)_2$ (Roberts & Enemark, 1989) where the filled d_{xz} and d_{yz} orbitals on the molybdenum restrict the ON—Mo—S—C torsional angles to values near 0 and 180°.

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Structures of [(*R*)- and (*S*)-Prolinato](Optically Active Cyclen)cobalt(III) Complexes*

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Abstract. *cis*-(*SSSR*)-β_1-(*R*)-{[(*R*)-Prolinato](2*R*,5*R*,8*R*,11*R*-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane)}cobalt(III) bromide perchlorate monohydrate (2), $[Co(C_5H_8NO_2)(C_{16}H_{36}N_4)]Br(ClO_4).H_2O$, $M_r = 654{\cdot}91$, tetragonal, $P4_3$, $a = 14{\cdot}427$ (6), $c = 13{\cdot}678$ (2) Å, $U = 2846{\cdot}9$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}530$, $D_x = 1{\cdot}528$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ =

* Structural Studies on Metal Complexes of Chiral Cyclen. 10. Part 9: Tsuboyama, Tsuboyama & Sakurai (1989).

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2·13 mm^{-1}, $F(000) = 1368$, $T = 296$ K, final $R = 0·048$ for 2283 unique reflections with $|F_o| > 3\sigma(|F_o|)$. *cis*-(*SSSR*)-β_1-(*S*)-{[(*S*)-Prolinato](2*R*,5*R*,8*R*,11*R*-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane)}-cobalt(III) diperchlorate dihydrate (3), $[Co(C_5H_8NO_2)(C_{16}H_{36}N_4)](ClO_4)_2.2H_2O$, $M_r = 692·47$, orthorhombic, $P2_12_12_1$, $a = 12·575$ (3), $b = 25·192$ (5), $c = 9·757$ (7) Å, $U = 3091$ (2) Å^3, $Z = 4$, $D_m = 1·490$, $D_x = 1·488$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·79$ mm^{-1}, $F(000) = 1464$, $T = 296$ K, final $R = 0·056$ for 2332 unique reflections. In each molecule, the coordination around the Co^{III} ion is octahedral with the macrocycle ligand and the respective proline residue coordinated through N and O in β_1. The absolute configurations of the asymmetric N atoms in the cyclen for both complexes are *SSSR*, and that of the coordinated (*R*)-proline is *R* and for the (*S*)-proline *S*.

Introduction. Recently we described amino acid (AA) complexation to a Co^{III} complex containing an optically active cyclen: *cis*-(*SSSR*)-[(aquabromo)-(2*R*,5*R*,8*R*,11*R*-2,5,8,11-tetraethyl-1,4,7,10-tetraaza-cyclododecane)]cobalt(III) dibromide (1) (Tsuboyama, Sakurai & Tsuboyama, 1987). The structure determinations of the (*R*)- and (*S*)-alanine (Ala) coordinated complexes, (4) and (5), were also carried out by X-ray analysis. In the neutral amino acidato complexes prepared, the patterns of the circular-dichroism spectra for the (*R*)- and (*S*)-prolinato complexes (2) and (3) were different from those of the other respective enantiomeric series. This is because proline (Pro) is a unique amino acid which produces a new additional chiral center by coordination with a metal ion, and imposes a certain restriction on the conformation of the complex. In order to obtain definitive information, we have undertaken the X-ray analyses of these complexes.

Experimental. The compounds were prepared as described previously (Tsuboyama *et al.*, 1987). The density was measured by floatation in CCl_4–benzene. Orange–red crystals, Rigaku AFC four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, cell parameters from 16 reflections with $20 < 2\theta < 30°$. For data collection ω ($2\theta < 30°$) and ω–2θ ($2\theta > 30°$) scans, scan rate 4·0° min^{-1} for $2\theta < 55°$. Three standard reflections after every 150, no significant variation in intensities. The data were corrected for Lorentz and polarization factors, but not for absorption. Additional experimental details are given in Table 1. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Calculations performed using the program system *UNICS*III (Sakurai & Kobayashi, 1979) on a FACOM M-780. The H-atom coordinates were calculated assuming ideal geometry. Refinement was carried out using a block-diagonal least-squares procedure. Unit weight was given for all reflections, and anisotropic thermal factors were used for all non-H atoms. All H atoms were included in the final refinement with isotropic temperature factors. The absolute configurations of the complex cations were assigned from the known configurations of the ligand as an internal reference (Sakurai, Tsuboyama & Tsuboyama, 1980). Scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974).

Table 1. *Experimental details* [*upper:* (2); *lower:* (3)]

Crystal (mm)	Prismatic, 0·30 × 0·30 × 0·50
	Rectangular, 0·30 × 0·25 × 0·65
Scan ranges of *h, k, l*	0→18, 0→18, 0→17
	0→16, 0→32, 0→12
Reflections observed	2548
	2416
No. of unobserved reflections	1387
[criterion: $|F_o| < 3\sigma(|F_o|)$]	1697
No. of variables	502
	547
R	0·048
	0·056
wR	0·051
	0·057
Maximum shift/e.s.d.	0·21
	0·22
Max. height in final map (e Å^{-3})	0·5
	0·7
S	2·25
	2·34

Discussion. The atomic parameters for the structures are given in Table 2,* selected bond lengths, angles and torsion angles in Table 3. The molecular structures are shown in Fig. 1. The geometries of both complexes are similar; they have a slightly distorted octahedral geometry and are six-coordinate; the absolute configurations of the asymmetric N atoms in the cyclen part (*SSSR*) are the same as those of the starting complex (1) (Sakurai *et al.*, 1980). Thus four N atoms of the tetraaza macrocycle, and the N and O atoms of Pro are coordinated to the Co ion in *cis* β_1 form [N(13) *trans* to N(10)]. The configurations at N(13) in Pro are assigned as *R* for (2) and *S* for (3) by analogy with other (*S*)-prolinato metal complexes (Freeman & Maxwell. 1970; Freeman, Marzilli & Maxwell, 1970; Mathieson & Welsh, 1952; Oki & Yoneda, 1981). The bond parameters of (2) and (3) are similar to each other and to those of (1), except for the flexible terminal ethyl groups.

Both pyrrolidine rings are nonplanar. The deviations of the C_γ atom, C(18), from the mean plane formed by N(13), C(14), C(17) and C(19) are 0·52 (2) and −0·54 (2) Å, respectively. As found in other prolinato

* Lists of H-atom coordinates, anisotropic thermal parameters, least-squares planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51695 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic parameters*

Positional parameters are multiplied by 10^4. The equivalent isotropic temperature factor is defined as $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

Compound (2)	x	y	z	B_{eq}(Å^2)
Co	1520 (1)	2975 (1)	0*	2·2
N(1)	1546 (6)	3854 (5)	−1091 (6)	3·1
C(2)	2405 (8)	4459 (7)	−1089 (9)	3·8
C(3)	2831 (7)	4398 (6)	−52 (9)	3·6
N(4)	2745 (5)	3432 (5)	316 (6)	2·8
C(5)	2940 (7)	3333 (7)	1398 (8)	3·0
C(6)	2507 (6)	2401 (6)	1663 (7)	2·6
N(7)	1534 (5)	2365 (5)	1300 (5)	2·4
C(8)	859 (6)	2848 (6)	1986 (7)	2·6
C(9)	249 (7)	3499 (7)	1400 (8)	3·3
N(10)	882 (5)	3967 (5)	698 (6)	2·8
C(11)	465 (7)	4703 (7)	5 (8)	3·3
C(12)	652 (8)	4379 (7)	−1032 (8)	3·4
C(2)1	3071 (9)	4151 (9)	−1894 (10)	5·1
C(2)2	3782 (12)	4804 (11)	−2135 (13)	8·0
C(5)1	3953 (7)	3432 (9)	1638 (9)	4·3
C(5)2	4163 (9)	3452 (12)	2717 (12)	6·9
C(8)1	266 (7)	2134 (8)	2566 (9)	4·0
C(8)2	795 (9)	1597 (9)	3330 (9)	4·7
C(11)1	−546 (8)	4892 (7)	165 (9)	4·2
C(11)2	−882 (10)	5671 (9)	−489 (10)	5·6
N(13)	1965 (5)	1854 (5)	−718 (6)	2·4
C(14)	1196 (7)	1167 (7)	−734 (7)	3·2
C(15)	307 (6)	1701 (7)	−763 (7)	2·8
O(15)	−401 (5)	1354 (6)	−1098 (6)	4·6
O(16)	332 (4)	2530 (4)	−382 (5)	3·0
C(17)	1350 (8)	506 (9)	−1594 (10)	4·7
C(18)	2206 (9)	886 (7)	−2109 (8)	4·0
C(19)	2261 (8)	1879 (7)	−1775 (7)	3·4
Br	4281 (1)	1586 (1)	−351 (1)	4·1
Cl	2777 (2)	2382 (2)	5439 (3)	4·9
O(1)	2933 (11)	2178 (16)	4494 (12)	16·5
O(2)	1839 (6)	2168 (7)	5666 (8)	6·1
O(3)	3354 (8)	1784 (11)	5909 (15)	13·6
O(4)	2969 (10)	3267 (9)	5583 (19)	16·6
O(*W*)	723 (8)	3300 (8)	−2981 (7)	7·6

Compound (3)	x	y	z	B_{eq}(Å^2)
Co	15 (1)	1651 (0·4)	4598 (1)	2·4
N(1)	241 (6)	1521 (3)	6561 (8)	3·2
C(2)	1240 (8)	1191 (4)	6803 (10)	3·3
C(3)	1602 (7)	949 (3)	5421 (11)	3·3
N(4)	1388 (6)	1326 (3)	4304 (8)	2·8
C(5)	1424 (7)	1090 (4)	2898 (10)	3·2
C(6)	828 (8)	1459 (4)	1956 (11)	4·0
N(7)	−216 (5)	1601 (3)	2609 (8)	3·1
C(8)	−1059 (8)	1187 (4)	2300 (11)	4·0
C(9)	−1596 (8)	1012 (4)	3627 (12)	3·8
N(10)	−732 (6)	967 (3)	4648 (9)	3·2
C(11)	−996 (7)	790 (4)	6066 (11)	3·3
C(12)	−754 (8)	1256 (4)	7028 (11)	3·6
C(2)1	2077 (8)	1535 (4)	7499 (11)	4·1
C(2)2	3053 (10)	1217 (6)	7925 (15)	6·5
C(5)1	2587 (9)	986 (4)	2418 (13)	4·8
C(5)2	2639 (12)	541 (8)	1444 (18)	9·8
C(8)1	−1842 (10)	1362 (5)	1193 (13)	5·7
C(8)2	−2596 (11)	1790 (7)	1626 (17)	8·4
C(11)1	−2138 (8)	583 (4)	6219 (14)	4·7
C(11)2	−2437 (11)	431 (7)	7598 (18)	9·1
N(13)	614 (5)	2377 (3)	4645 (9)	2·9
C(14)	−142 (7)	2723 (3)	5435 (11)	3·6
C(15)	−1244 (7)	2503 (3)	5179 (11)	3·2
O(15)	−2046 (5)	2795 (2)	5281 (9)	4·1
O(16)	−1305 (4)	2011 (2)	4876 (7)	2·9
C(17)	5 (10)	3300 (4)	5001 (15)	6·5
C(18)	860 (9)	3262 (4)	3920 (14)	5·1
C(19)	825 (9)	2700 (4)	3367 (11)	4·6
Cl(1)	9309 (3)	2647 (1)	9341 (3)	5·7
O(1)	10030 (12)	2261 (4)	8921 (13)	11·9
O(2)	8345 (11)	2528 (7)	8765 (15)	15·9
O(3)	9648 (9)	3143 (4)	8889 (13)	10·0
O(4)	9271 (11)	2621 (4)	10756 (10)	10·3
Cl(2)	−77 (3)	4869 (1)	5328 (3)	5·0
O(5)	−566 (14)	4619 (5)	4369 (15)	15·5
O(6)	568 (10)	4540 (4)	6156 (13)	10·2
O(7)	334 (14)	5315 (5)	5055 (18)	19·4
O(8)	−765 (18)	5062 (9)	6204 (23)	24·6
O(*W*)1	−108 (8)	4921 (3)	1230 (9)	6·1
O(*W*)2	5443 (9)	776 (4)	863 (12)	9·3

* This parameter was used to define the unit-cell origin along z and is listed without e.s.d.

complexes, the position of the C_γ atom is *trans* to the carboxyl C atom. The displacements are moderate compared with those (0·70–0·48 Å) found in other Pro metal complexes. The orientations of the pyrrolidine ring differ between the diastereoisomers. For (2) the ring is directed toward N(1) in the macrocycle ligand, and toward N(7) for (3). The resulting nonbonded interactions between Pro and the 12-membered rings are partially relieved by an increase of the bond angles: N(13)—Co—N(1) for (2) [98·3 (3)°], and N(13)—Co—N(7) for (3) [98·0 (3)°]. Some ring strain within the pyrrolidine ring is shown by the mean internal angle. Both have the same value: 104·8 (8)°. This value closely resembles the average angles (104–104·5°) obtained in the references cited above.

Some puckerings are observed in five-membered chelate rings formed by Pro and the metal ion. The maximum deviations from the respective mean planes for the chelate rings are found for C(14) [−0·294 (8) Å for (2), 0·296 (9) Å for (3)]. An analogous situation is found in the Ala complexes [−0·154 (6) Å for (4), 0·243 (6) Å for (5)]. These values are larger than those generally obtained in other metal complexes containing AA (Freeman, 1967). In fact, a small deviation (maximum 0·09 Å) is found in (*RRS*)- or (*SSS*)-$\{Co[(S)\text{-}Pro](trien)\}^{2+}$ (trien = triethylenetetramine) (Freeman & Maxwell, 1970; Freeman *et al.*, 1970). This result is probably responsible for the strain introduced by the ring closure together with the steric effect of the chiral ethyl groups in the 12-membered ring (Curtis, 1979). The abnormal bond angles for Co—N(13)—C(19) are 122·8 (6)° for (2) and 123·0 (6)° for (3). Larger and comparable distortions occur in the corresponding angles for the trien complexes: 125·3 (7)° for (*RRS*) and 122·2 (17)° for (*SSS*). It seems that an open-chain complex is more labile, and has more room to be spread out compared with a complex macrocyclic ligand.

Although the displacements from the respective mean planes involving the pyrrolidine and chelate rings are approximately equal in magnitude for (2) and (3), the directions are exactly opposite as shown in Table 3(*c*). There are several hydrogen bonds whose lengths are presented in Table 3(*d*).

Table 3. *Selected bond lengths* (Å), *bond angles* (°), *and torsion angles* (°)

(*a*) Bond parameters around the cobalt ions

	(2)	(3)
Co–N1	1·959 (8)	1·963 (8)
Co–N4	1·935 (8)	1·932 (7)
Co–N7	1·984 (7)	1·967 (8)
Co–N10	1·951 (8)	1·963 (7)
Co–N13	1·999 (7)	1·979 (7)
Co–O16	1·903 (6)	1·911 (6)
N1–Co–N4	86·1 (3)	86·8 (3)
N1–Co–N7	165·9 (3)	166·7 (3)
N1–Co–N10	84·7 (3)	84·2 (3)
N1–Co–N13	98·3 (3)	94·4 (3)
N1–Co–O16	91·5 (3)	93·8 (3)
N4–Co–N7	86·7 (3)	87·6 (3)
N4–Co–N10	94·1 (3)	93·4 (3)
N4–Co–N13	95·3 (3)	93·2 (3)
N4–Co–O16	177·0 (3)	176·8 (3)
N7–Co–N10	83·8 (3)	84·1 (3)
N7–Co–N13	94·5 (3)	98·0 (3)
N7–Co–O16	96·1 (3)	92·4 (3)
N10–Co–N13	170·3 (3)	173·2 (3)
N10–Co–O16	87·5 (3)	89·8 (3)
N13–Co–O16	83·2 (3)	83·6 (3)

(*b*) 12-Membered rings

	(2)	(3)
N(1)–C(2)	1·51 (1)	1·52 (1)
N(1)–C(12)	1·50 (1)	1·49 (1)
C(2)–C(3)	1·55 (2)	1·55 (1)
C(3)–N(4)	1·49 (1)	1·47 (1)
N(4)–C(5)	1·51 (1)	1·50 (1)
C(5)–C(6)	1·53 (1)	1·51 (1)
C(6)–N(7)	1·49 (1)	1·50 (1)
N(7)–C(8)	1·52 (1)	1·52 (1)
C(8)–C(9)	1·52 (1)	1·53 (2)
C(9)–N(10)	1·49 (1)	1·48 (1)
N(10)–C(11)	1·55 (1)	1·49 (1)
C(11)–C(12)	1·52 (1)	1·53 (1)
C(2)–N(1)–C(12)	114·4 (7)	113·6 (7)
N(1)–C(2)–C(3)	107·1 (8)	108·8 (8)
C(2)–C(3)–N(4)	109·3 (8)	109·7 (7)
C(3)–N(4)–C(5)	113·9 (8)	114·7 (7)
N(4)–C(5)–C(6)	103·9 (8)	107·4 (7)
C(5)–C(6)–N(7)	109·7 (7)	108·8 (8)
C(6)–N(7)–C(8)	112·5 (7)	111·3 (7)
N(7)–C(8)–C(9)	109·3 (8)	109·8 (8)
C(8)–C(9)–N(10)	105·4 (8)	105·6 (8)
C(9)–N(10)–C(11)	118·0 (7)	119·0 (7)
N(10)–C(11)–C(12)	107·0 (8)	107·1 (7)
N(1)–C(12)–C(11)	111·1 (8)	108·9 (8)
C(12)–N(1)–C(2)–C(3)	103·3 (9)	103·8 (8)
C(2)–N(1)–C(12)–C(11)	−77·6 (10)	−70·6 (9)
N(1)–C(2)–C(3)–N(4)	38·7 (11)	35·5 (10)
C(2)–C(3)–N(4)–C(5)	−167·1 (8)	−164·3 (7)
C(3)–N(4)–C(5)–C(6)	161·8 (8)	160·4 (8)
N(4)–C(5)–C(6)–N(7)	−50·8 (9)	−47·8 (10)
C(5)–C(6)–N(7)–C(8)	81·7 (9)	−85·3 (9)
C(6)–N(7)–C(8)–C(9)	131·3 (8)	129·3 (9)
N(7)–C(8)–C(9)–N(10)	−42·5 (9)	−40·8 (10)
C(8)–C(9)–N(10)–C(11)	−178·4 (7)	−178·7 (8)
C(9)–N(10)–C(11)–C(12)	−121·1 (9)	−115·3 (9)
N(10)–C(11)–C(12)–N(1)	−32·3 (10)	−39·3 (10)

(*c*) Pyrrolidine rings

	(2)	(3)
N(13)–C(14)	1·49 (1)	1·50 (1)
N(13)–C(19)	1·51 (1)	1·51 (1)
C(14)–C(15)	1·50 (1)	1·51 (1)
C(14)–C(17)	1·53 (2)	1·53 (1)
C(15)–O(15)	1·23 (1)	1·25 (1)
C(15)–O(16)	1·31 (1)	1·28 (1)
C(17)–C(18)	1·52 (2)	1·51 (2)
C(18)–C(19)	1·51 (1)	1·52 (1)
C(14)–N(13)–C(19)	102·3 (7)	102·8 (7)
N(13)–C(14)–C(17)	108·5 (8)	109·5 (9)
C(14)–C(17)–C(18)	104·4 (9)	102·7 (8)
C(17)–C(18)–C(19)	104·2 (9)	106·7 (9)
N(13)–C(19)–C(18)	104·7 (8)	102·3 (9)

Table 3 (*cont.*)

	(2)	(3)
Co–N(13)–C(14)	107·8 (6)	107·9 (5)
Co–N(13)–C(19)	122·8 (6)	123·0 (6)
N(13)–C(14)–C(15)	107·3 (8)	106·4 (7)
C(14)–C(15)–O(16)	116·0 (8)	116·7 (7)
Co–O(16)–C(15)	116·3 (6)	116·2 (5)
C(14)–C(15)–O(15)	120·9 (9)	120·6 (8)
O(16)–C(15)–O(15)	123·1 (9)	122·7 (8)
O(16)–Co–N(13)–C(14)	−23·9 (6)	24·1 (5)
Co–N(13)–C(14)–C(15)	32·1 (8)	−31·6 (8)
N(13)–C(14)–C(15)–O(16)	26·8 (11)	25·9 (11)
C(14)–C(15)–O(16)–Co	7·3 (10)	6·6 (10)
N(13)–Co–O(16)–C(15)	10·0 (6)	10·6 (6)
C(19)–N(13)–C(14)–C(17)	26·3 (10)	−24·5 (10)
C(14)–N(13)–C(19)–C(18)	−39·3 (9)	37·8 (9)
N(13)–C(14)–C(17)–C(18)	−3·7 (11)	1·0 (11)
C(14)–C(17)–C(18)–C(19)	−20·5 (11)	23·3 (12)
C(17)–C(18)–C(19)–N(13)	37·6 (10)	38·9 (11)

(*d*) Hydrogen bonds

	(2)	(3)
N(1)···O(*W*)^{i}	2·96 (1)	
N(7)···O(15)^{ii}	2·85 (1)	
N(10)···Br^{iii}	3·371 (8)	
N(13)···Br^{i}	3·400 (7)	
O(2)···O(*W*)^{iv}	2·95 (1)	
N(1)···O(1)^{v}		2·98 (1)
N(4)···O(15)^{vi}		2·991 (9)
N(10)···O(*W*)^{vii}		2·97 (1)
N(13)···O(15)^{ii}		2·976 (9)
O(3)···O(*W*)2^{vi}		2·91 (1)
O(6)···O(*W*)2^{viii}		3·02 (2)
O(*W*)1···O(*W*)2^{ix}		2·78 (1)

Symmetry code: (i) x, y, z; (ii) $y, -x, z+\frac{1}{4}$; (iii) $y, 1-x, z+\frac{1}{4}$; (iv) $x, y, z+1$; (v) $x-1, y, z$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, 1-z$; (vii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x-\frac{1}{2}, -y+\frac{1}{2}, 1-z$; (ix) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

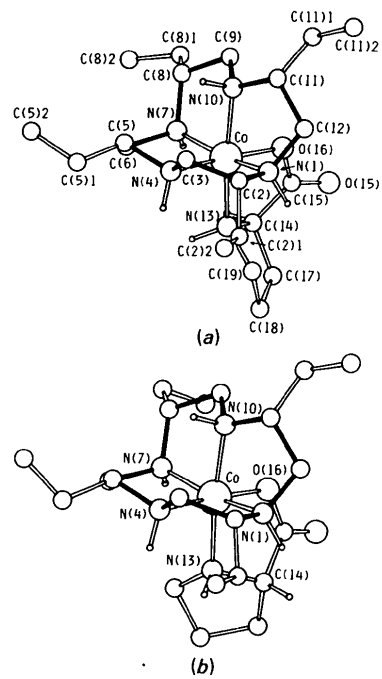

Fig. 1. Perspective drawings of (*a*) the cation of (2) with atom numbering, and (*b*) the cation of (3). Only the H atoms at the asymmetric N atoms and at the chiral center in proline are shown for clarity.

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(8,9,10-Trinorbornadiene)[1,2,3-tris(diphenylphosphino)propane]rhodium Hexafluorophosphate

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Abstract. $[Rh(C_7H_8)((C_6H_5)_2PCH\{CH_2P(C_6H_5)_2\}_2)]$-$[PF_6]$, $C_{46}H_{43}F_6P_4Rh$, $M_r = 936{\cdot}6$, monoclinic, $P2_1/n$, $a = 18{\cdot}241\,(7)$, $b = 10{\cdot}512\,(5)$, $c = 21{\cdot}995\,(7)$ Å, $\beta = 104{\cdot}43\,(6)°$, $V = 4085\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}523$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 6{\cdot}2$ cm^{-1}, $F(000) = 1909$, $T = 293$ K, $R = 0{\cdot}056$ for 4512 observed reflections. The Rh atom is pentacoordinated by the P atoms of the triphosphine ligand 1,2,3-tris(diphenylphosphino)propane, C_3triphos, and by the midpoints of the coordinated double bonds of the 8,9,10-trinorbornadiene ligand, nbd. The metal coordination sphere is essentially a trigonal bipyramid with one olefinic residue in axial position and the other in equatorial position.

Introduction. In the course of an investigation on rhodium complexes with the tripod-like tridentate ligand $H_3CC(CH_2PPh_2)_3$, triphos, the new tripod-like ligand $Ph_2PCH(CH_2PPh_2)_2$, C_3triphos, was synthesized in order to study whether changes in the triphos geometry could affect the properties of triphos complexes (Ott, 1986).

The main difference between the two ligands is in the lack of a methylene group in C_3triphos, so that, on coordination to a metal centre, C_3triphos forms a rigid backbone consisting of two five- and one six-membered rings.

triphos = $H_3CC(CH_2PPh_2)_3$ $\quad$ C_3triphos = $Ph_2PCH(CH_2PPh_2)_2$

As in triphos, the structure of this ligand only allows small variations of the P—*M*—P angles from the ideal values of 90°, so that some facial coordination geometries can be obtained only with strong distortions.

The present work deals with the first structure of a complex containing the C_3triphos ligand.

Experimental. Crystals were obtained from CH_3CN/CH_3CH_2OH solution; Nicolet *R*3 four-circle diffractometer; graphite-monochromatized Mo $K\alpha$ radiation;

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