

[Co(daes)<sub>2</sub>]Cl<sub>3</sub>·2H<sub>2</sub>O structure (Hammershoi *et al.*, 1978). A similar result has been observed for the analogous Ni complexes, [Ni(daes)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (Hart, Boeyens & Hancock, 1983) and [Ni(tasn)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (Hart, Boeyens, Michael & Hancock, 1983), which adopt *cis* and *trans* S geometries respectively. The <sup>13</sup>C NMR spectrum of [Co(tasn)<sub>2</sub>]<sup>3+</sup> has eight resonances, and is inconsistent with the presence of only the *trans* isomer for which only three resonances are expected. Thus, we must conclude that the chromatographic methods have failed in this case to achieve a separation of the isomers. This result must cast a slight doubt on the report that only one isomer of [Co(daes)<sub>2</sub>]<sup>3+</sup> exists, although the <sup>13</sup>C NMR spectrum in that case does support that assertion (Searle & Larsen, 1976).

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**[(+)-(R)-2,2'-Bis(diphenylphosphino)-6,6'-dimethylbiphenyl](8,9,10-trinorborna-2,5-diene)rhodium(I) Tetrafluoroborate**

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**Abstract.** [Rh(C<sub>7</sub>H<sub>8</sub>)(C<sub>38</sub>H<sub>32</sub>P<sub>2</sub>)]BF<sub>4</sub>, *M<sub>r</sub>* = 832·48, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12·292 (2), *b* = 16·766 (6), *c* = 18·167 (7) Å, *V* = 3744 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1·476 (1) Mg m<sup>-3</sup>, λ(Mo *K*α) = 0·71069 Å, μ = 0·587 mm<sup>-1</sup>, *F*(000) = 1704, *T* = 210 K, final *R* = 0·036 for 2247 reflections. The rhodium atom has a distorted square-planar coordination involving the two phosphorus atoms and the two double bonds in norbornadiene. The norbornadiene molecule is tilted 13·7 (1)° compared with the P(1)–Rh–P(2) plane. The diphosphine ligand coordinates to the Rh<sup>I</sup> and forms a seven-membered chelate ring with a λ skew(*v*) conformation. The helical chirality of both phosphorus atoms is assigned as *P* (right-handed). The coordination of the diphosphine ligand causes the dihedral angle between the least-squares planes through the two phenyl rings in the biphenyl unit to be 71·8 (3)°. The absolute conformation of the diphosphine ligand has been assigned as *R*.

**Introduction.** Optical yields approaching 100% have been obtained by the use of chiral rhodium(I) diphosphine complexes (Knowles, Vineyard, Sabacky & Stults, 1979; Chan, Pluth & Halpern, 1979*a*). An interesting new type of chiral diphosphine ligand, (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, subsequently abbreviated binap, was recently published (Miyashita, Yasuda, Toriumi, Ito, Souchi & Noyori, 1980) and the structure of its rhodium(I) norbornadiene complex was determined by X-ray crystallography (Toriumi, Ito, Takaya, Souchi & Noyori, 1982). In order to obtain a catalyst system which would be easier to modify, both enantiomers of the ligand bis(diphenylphosphino)-6,6'-dimethylbiphenyl have been prepared (Hansen & Schmid, 1984; Frejd, 1986). The ligand is abbreviated dimep below. Here we report an X-ray study of the tetrafluoroborate salt of the Rh<sup>I</sup> complex with ligands dimep and norbornadiene.

**Experimental.** Dark red crystals of [Rh(norbornadiene)-{(+)dimep}]BF<sub>4</sub> were grown from a (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O/CHCl<sub>3</sub> solution; approximate dimensions 0·10 ×

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0.15 × 0.15 mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo K $\alpha$  radiation,  $\omega/2\theta$  scan ( $\Delta\omega = 0.60^\circ + 0.50^\circ \tan\theta$ ); systematic absences  $h00, 0k0$  and  $00l$  ( $h, k, l = 2n$ ) consistent with  $P2_12_12_1$ . Cell constants from setting angles of 39 reflections with  $10 < \theta < 25^\circ$ . Data corrected for Lorentz, polarization and absorption effects, transmission factor 0.88–0.92. Three standard reflections measured every hour showed no significant variation. 3979 reflections measured, 3661 unique,  $R_{\text{int}} = 0.031$ , 2247 with  $I > 3.0\sigma(I)$  used in refinement, index range  $h - 14 \rightarrow 0, k - 19 \rightarrow 0, l - 21 \rightarrow 0$ ;  $2\theta_{\text{max}} = 50^\circ$ .

Structure solved by Patterson methods which gave the position of the Rh atom. Subsequent electron density maps gave the position of the rest of the structure. Least-squares refinement of all non-H atoms treated anisotropically, H atoms with a fixed isotropic temperature factor,  $U = 0.08 \text{ \AA}^2$ , coordinates for H atoms were not refined. Function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w = [\sigma^2(F_o) + (0.025F_o)^2]^{-1}$ , final  $R = 0.036$ ,  $wR = 0.040$ ,  $S = 0.917$ ,  $(\Delta/\sigma)_{\text{max}} = 0.16$ .  $\Delta\rho$  in final electron density map between +0.42 and -0.35 e  $\text{\AA}^{-3}$ , no extinction effects were detected. Data and final model were compared by probability plotting (Abrahams & Keve, 1971) of ordered values of  $\delta R_i = \Delta F_i / \sigma(|F_o|_i)$  vs those expected for ordered normal deviates  $\sigma(|F_o|_i) = w^{-1/2}$ ; the result was a slope of 0.9134 (8), intercept of 0.0361 (8) and a correlation coefficient of 0.9991. The slope and intercept of the curve indicate that the systematic errors are small and that  $\sigma(|F_o|_i)$  is on average rather well estimated.

As a confirmation of the absolute configuration chosen the enantiomeric structure was refined under identical conditions to  $R = 0.039$  and  $wR = 0.044$ . When the  $R$ -factor test (Hamilton, 1965) was applied to  $wR$  this alternative configuration could be rejected at the less than 0.005 significance level, assuming no systematic errors in the data [ $wR(2)/wR(1) = 1.100$ ;  $\mathcal{R}_{1.1764, 0.005} \approx 1.002$ ]. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The system of computer programs used in this study is described by Lundgren (1982).

**Discussion.** The final atomic parameters for the non-H atoms are listed in Table 1 and selected bond lengths and angles in Table 2.\* A perspective view of the molecule with the atom-numbering scheme is shown in Fig. 1 and a stereographic view of the molecular packing is shown in Fig. 2.

The bond lengths and bond angles for the phenyl

rings are unexceptional. Their ranges are 1.350–1.422 Å and 117.2–121.5°, respectively. The Rh–P(1,2) distances, 2.353 (2) and 2.276 (2) Å respectively, are within the range of distances found in other Rh–phosphine complexes (Nappier, Meek, Kirchner & Ibers, 1973; Ball & Payne, 1977; Chan, Pluth & Halpern, 1979*a,b*). The Rh<sup>I</sup> atom is coordinated in a distorted square-planar geometry by the two P atoms in dimep and the two double bonds in norbornadiene, C(73)–C(74) and C(76)–C(77). The average Rh–C distance for the coordinated double bonds is 2.20 (4) Å. The angle between the P(1)–Rh–P(2) plane and the plane defined by the Rh atom and the midpoints of the two double bonds in norbornadiene is 13.7 (1)°. The atoms C(74) and C(76) are located above the P(1)–Rh–P(2) plane and C(73) and C(77) below it, at distances 0.897 (13), 0.331 (13),

Table 1. Final atomic parameters with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Rh	0.24000 (6)	0.52547 (4)	0.27287 (4)	0.0286 (3)
P(1)	0.1476 (2)	0.6393 (1)	0.2300 (1)	0.0276 (7)
P(2)	0.3472 (2)	0.6030 (1)	0.3458 (1)	0.0247 (7)
B	-0.0346 (11)	0.4863 (8)	0.4990 (8)	0.046 (5)
F(1)	0.0455 (5)	0.4955 (4)	0.5508 (4)	0.073 (3)
F(2)	0.0002 (6)	0.4385 (4)	0.4414 (4)	0.078 (3)
F(3)	-0.1244 (5)	0.4511 (4)	0.5326 (4)	0.063 (3)
F(4)	-0.0672 (5)	0.5595 (4)	0.4721 (4)	0.062 (3)
C(11)	0.1577 (7)	0.7323 (5)	0.2831 (5)	0.029 (3)
C(12)	0.2577 (7)	0.7706 (4)	0.2925 (4)	0.022 (2)
C(13)	0.2654 (8)	0.8393 (5)	0.3358 (5)	0.036 (3)
C(14)	0.1725 (9)	0.8668 (6)	0.3712 (5)	0.040 (4)
C(15)	0.0750 (8)	0.8283 (6)	0.3640 (5)	0.040 (4)
C(16)	0.0662 (8)	0.7619 (6)	0.3207 (5)	0.040 (3)
C(17)	0.3749 (9)	0.8792 (7)	0.3484 (6)	0.051 (4)
C(21)	0.0014 (7)	0.6137 (6)	0.2305 (6)	0.034 (3)
C(22)	-0.0354 (7)	0.5732 (7)	0.2917 (5)	0.047 (4)
C(23)	-0.1426 (10)	0.5464 (7)	0.2958 (7)	0.061 (5)
C(24)	-0.2133 (8)	0.5620 (7)	0.2380 (7)	0.058 (4)
C(25)	-0.1764 (8)	0.6015 (8)	0.1773 (7)	0.056 (4)
C(26)	-0.0680 (8)	0.6307 (7)	0.1724 (5)	0.042 (4)
C(31)	0.1800 (7)	0.6717 (6)	0.1369 (5)	0.028 (3)
C(32)	0.1304 (8)	0.7396 (6)	0.1079 (5)	0.041 (4)
C(33)	0.1537 (10)	0.7643 (6)	0.0353 (6)	0.047 (4)
C(34)	0.2317 (10)	0.7231 (6)	-0.0045 (6)	0.050 (4)
C(35)	0.2841 (9)	0.6575 (6)	0.0245 (5)	0.044 (4)
C(36)	0.2586 (8)	0.6324 (5)	0.0957 (5)	0.033 (3)
C(41)	0.4071 (6)	0.6675 (5)	0.2749 (5)	0.024 (2)
C(42)	0.3572 (7)	0.7404 (5)	0.2537 (4)	0.029 (3)
C(43)	0.3988 (8)	0.7798 (6)	0.1904 (6)	0.038 (3)
C(44)	0.4821 (8)	0.7491 (7)	0.1512 (5)	0.044 (4)
C(45)	0.5273 (7)	0.6760 (7)	0.1706 (5)	0.043 (4)
C(46)	0.4895 (7)	0.6350 (6)	0.2325 (6)	0.031 (3)
C(47)	0.3504 (9)	0.8586 (7)	0.1641 (6)	0.052 (4)
C(51)	0.4580 (8)	0.5551 (5)	0.3968 (5)	0.033 (3)
C(52)	0.5672 (7)	0.5763 (6)	0.3936 (5)	0.033 (3)
C(53)	0.6419 (8)	0.5429 (7)	0.4410 (5)	0.041 (4)
C(54)	0.6103 (9)	0.4826 (7)	0.4893 (5)	0.044 (4)
C(55)	0.5030 (10)	0.4611 (7)	0.4937 (6)	0.051 (4)
C(56)	0.4272 (8)	0.4969 (6)	0.4469 (5)	0.036 (3)
C(61)	0.2928 (7)	0.6614 (6)	0.4231 (5)	0.025 (3)
C(62)	0.3596 (9)	0.7159 (6)	0.4595 (5)	0.038 (3)
C(63)	0.3208 (10)	0.7540 (7)	0.5215 (6)	0.047 (4)
C(64)	0.2183 (10)	0.7379 (7)	0.5467 (5)	0.045 (4)
C(65)	0.1524 (9)	0.6821 (7)	0.5123 (6)	0.049 (4)
C(66)	0.1896 (7)	0.6434 (6)	0.4497 (5)	0.034 (3)
C(71)	0.2239 (8)	0.3127 (5)	0.2342 (7)	0.052 (4)
C(72)	0.3017 (9)	0.3790 (7)	0.2114 (7)	0.063 (5)
C(73)	0.3314 (8)	0.4157 (6)	0.2849 (7)	0.056 (4)
C(74)	0.2403 (14)	0.4110 (6)	0.3266 (6)	0.062 (5)
C(75)	0.1538 (9)	0.3707 (6)	0.2797 (7)	0.057 (4)
C(76)	0.1332 (9)	0.4330 (6)	0.2230 (9)	0.063 (5)
C(77)	0.2246 (13)	0.4379 (7)	0.1806 (6)	0.063 (5)

\* Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43098 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Rh—P(1)	2.353 (2)	C(43)—C(47)	1.524 (15)
Rh—P(2)	2.276 (2)	C(71)—C(72)	1.523 (15)
Rh—C(73)	2.167 (10)	C(71)—C(75)	1.539 (15)
Rh—C(74)	2.154 (10)	C(72)—C(73)	1.513 (18)
Rh—C(76)	2.225 (12)	C(72)—C(77)	1.478 (18)
Rh—C(77)	2.237 (11)	C(73)—C(74)	1.355 (19)
P(1)—C(11)	1.838 (9)	C(74)—C(75)	1.522 (18)
P(1)—C(21)	1.847 (8)	C(75)—C(76)	1.489 (18)
P(1)—C(31)	1.821 (9)	C(76)—C(77)	1.366 (19)
P(2)—C(41)	1.836 (9)	B—F(1)	1.371 (16)
P(2)—C(51)	1.833 (10)	B—F(2)	1.386 (16)
P(2)—C(61)	1.839 (9)	B—F(3)	1.392 (15)
C(12)—C(42)	1.500 (12)	B—F(4)	1.380 (15)
C(13)—C(17)	1.521 (15)		
P(1)—Rh—P(2)	90.5 (1)	C(12)—C(42)—C(43)	121.1 (8)
Rh—P(1)—C(11)	118.8 (3)	C(72)—C(71)—C(75)	92.1 (8)
Rh—P(1)—C(21)	106.3 (3)	C(71)—C(72)—C(73)	102.1 (10)
Rh—P(1)—C(31)	116.3 (3)	C(71)—C(72)—C(77)	100.8 (9)
C(11)—P(1)—C(21)	105.1 (4)	C(73)—C(72)—C(77)	102.6 (9)
C(11)—P(1)—C(31)	102.7 (4)	C(72)—C(73)—C(74)	105.7 (9)
C(21)—P(1)—C(31)	106.6 (4)	C(73)—C(74)—C(75)	106.8 (9)
Rh—P(2)—C(41)	99.3 (3)	C(71)—C(75)—C(74)	101.0 (9)
Rh—P(2)—C(51)	118.3 (3)	C(71)—C(75)—C(76)	99.6 (10)
Rh—P(2)—C(61)	122.5 (4)	C(74)—C(75)—C(76)	101.2 (9)
C(41)—P(2)—C(51)	108.3 (4)	C(75)—C(76)—C(77)	107.0 (10)
C(41)—P(2)—C(61)	111.6 (4)	C(72)—C(77)—C(76)	105.9 (10)
C(51)—P(2)—C(61)	96.7 (4)	F(1)—B—F(2)	111.1 (10)
C(11)—C(12)—C(42)	120.3 (7)	F(1)—B—F(3)	108.4 (10)
C(13)—C(12)—C(42)	119.2 (8)	F(1)—B—F(4)	110.5 (10)
C(63)—C(64)—C(65)	121.3 (10)	F(2)—B—F(3)	109.3 (10)
C(12)—C(13)—C(17)	120.5 (9)	F(2)—B—F(4)	109.7 (10)
C(14)—C(13)—C(17)	120.8 (8)	F(3)—B—F(4)	107.7 (10)
C(12)—C(42)—C(41)	121.1 (7)		

Table 3. Selected torsion angles for the title compound (I) and for Rh(norbornadiene)-{(+)binap} (II) (Toriumi, Ito, Takaya, Souchi &amp; Noyori, 1982)

	(I)	(II)
Rh—P(1)—C(11)—C(12)	63.1 (8)	70.8 (4)
P(1)—C(11)—C(12)—C(42)	5.5 (11)	11.1 (7)
C(11)—C(12)—C(42)—C(41)	-70.9 (11)	-74.4 (6)
C(12)—C(42)—C(41)—P(2)	4.7 (13)	10.4 (7)
C(42)—C(41)—P(2)—Rh	89.9 (7)	67.2 (4)
C(41)—P(2)—Rh—P(1)	-58.4 (3)	-35.0 (2)
P(2)—Rh—P(1)—C(11)	-18.0 (3)	-40.6 (2)
Rh—P(1)—C(11)—C(12)	63.1 (8)	67.2 (4)
Rh—P(1)—C(21)—C(22)	43.2 (9)	54.1 (6)
Rh—P(1)—C(31)—C(32)	-171.1 (6)	-169.8 (6)
Rh—P(2)—C(41)—C(42)	89.9 (7)	70.8 (4)
Rh—P(2)—C(51)—C(52)	124.5 (8)	54.8 (5)
Rh—P(2)—C(61)—C(62)	-171.4 (6)	-171.1 (4)

0.415 (11) and 0.994 (13) Å, respectively. This tilted coordination is often observed for coordinated double bonds as shown, for example, by Ball & Payne (1977). Dimep coordinates to the Rh atom and a seven-membered chelate ring, Rh—P(1)—C(11)—C(12)—C(41)—C(42)—P(2), is formed (see Fig. 1). The endocyclic torsion angles for this ring are listed in Table 3. This seven-membered chelate ring has a skew(*v*) conformation and its absolute configuration is designated as  $\lambda$  (Kashiwabara, Hanaki & Fujita, 1980) [the *v* in skew(*v*) implies the vertical direction of the central C(12)—C(42) bond in the chelate ring; see Fig. 1]. This coordination of dimep to the Rh<sup>I</sup> causes the dihedral angle between the least-squares planes through the two phenyl rings in biphenyl to be fixed. The angle is 71.8 (3)° in dimep and 74.4 (2)° in binap (Toriumi, Ito, Takaya, Souchi & Noyori, 1982). The absolute conformation for dimep has been assigned as *R* by the *R*-factor test (see above).

The orientations of the phenyl groups *A*–*F* (see Fig. 1) can be described by the torsion angles Rh—P(1,2)—C(*X*1)—C(*X*2), *X* = 1, 2, ..., 6. These angles are listed in Table 3. The phenyl groups on P(1), *B* and *C*, are arranged in an edge-face manner with *C* approximately parallel to *D* in the biphenyl unit. On P(2) the arrangement of the phenyl groups *E* and *F* is more like face-face with *F* approximately parallel to *A* in biphenyl. The angle between the least-squares planes through *C* and *D* is 13.4 (7)° while it is 18.1 (7)° between the *F* and *A* planes. The helical chirality caused by the two phenyl groups on each phosphorus atom is assigned as *P* (right-handed) for both P(1) and P(2) (Cahn, Ingold & Prelog, 1966). The phenyl rings are essentially planar with a maximum deviation of 0.024 (10) Å for C(53) and C(32). The two methyl carbons C(17) and C(47) on the biphenyl deviate from the least-squares planes by 0.076 (11) and 0.033 (11) Å, respectively.

The crystal is built up from discrete Rh<sup>I</sup> complexes and BF<sub>4</sub><sup>-</sup> anions as shown in Fig. 2. The geometry of the tetrafluoroborate anion is unexceptional with an average B—F bond length of 1.38 (1) Å. The shortest Rh—F distance is 4.493 (7) Å. An examination of

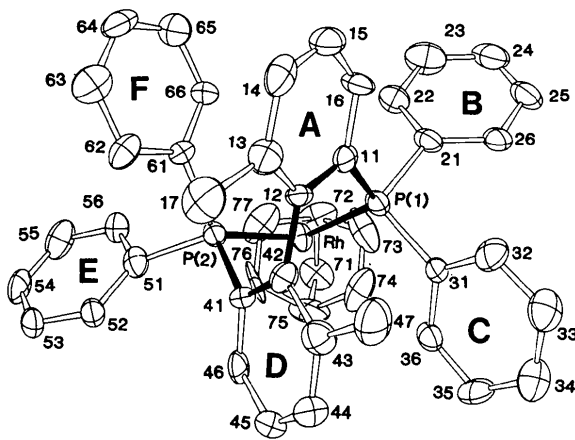


Fig. 1. A perspective view of Rh(norbornadiene){(+)-dimep} with the atom-numbering scheme. The seven-membered chelate ring is indicated with black bonding lines and the phenyl groups are named *A*–*F*.

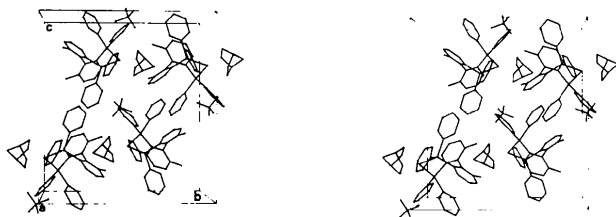


Fig. 2. A stereographic drawing of the molecular packing along the *a* axis.

intramolecular distances between non-H atoms shows that the crystal is stabilized by van der Waals interactions only; shortest distance is C(47)—C(54) ( $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ) = 3.511 (15) Å.

Comparison of the title compound with [Rh-(norbornadiene)-{(+)binap}](ClO<sub>4</sub>) (Toriumi, Ito, Takaya, Souchi & Noyori, 1982) reveals considerable differences in the orientation of the phenyl groups and in the conformation of the seven-membered chelate ring. Table 3 compares some torsion angles for both compounds. The main difference is the orientation of phenyl group *E*. The torsion angles Rh—P(2)—C(51)—C(52) are 124.5 (8) and 54.8 (5)°, respectively. Since the orientation of the phenyl groups provides the chiral environment at the olefin coordination site this difference has effects on the optical yields when the ligands binap and dimep are used as catalysts for asymmetric synthesis (Frejd, 1986).

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## On the Structure of Zn(C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>)

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**Abstract.** The crystal structure of this compound, originally formulated as bis(formamide)formatozinc(II) formate, was described in space group *Pnn2* and refined to  $R = 0.036$ ,  $S = 1.292$ . It is correctly described in *Pnna* [orthorhombic;  $a = 8.717$  (3),  $b = 11.617$  (10),  $c = 8.289$  (2) Å,  $Z = 4$ ]. Refinement in *Pnna*, to  $R = 0.032$  and  $S = 1.12$ , shows that the compound contains formamidine rather than formamide, the correct formulation being formamidinium tris(formato)zinc(II), [HC(NH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>[Zn(HCO<sub>2</sub>)<sub>3</sub>]<sup>-</sup>. The Zn<sup>II</sup> atom is surrounded by six O atoms in approximately octahedral coordination, with Zn—O distances from 2.066 (1) to 2.115 (1) Å. The formamidinium ion forms H bonds to the formate groups, with N...O distances of 2.866 (3) and 2.941 (3) Å.

**Introduction.** Recently, Fortier & Creber (1985; FC) reported on the preparation and crystal structure of a

compound they thought to be [Zn(CHO<sub>2</sub>)-(CH<sub>3</sub>NO)<sub>2</sub>]<sup>+</sup>.CHO<sub>2</sub><sup>-</sup> — bis(formamide)formatozinc(II) formate. The structure was described in space group *Pnn2* and refined to an  $R$  of 0.036 for 1914 reflections. Upon reinterpreting FC's data, I find that the structure is properly described in space group *Pnna* and that the correct formulation of the compound is [Zn(CHO<sub>2</sub>)<sub>3</sub>]<sup>-</sup>.[CH(NH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> — formamidinium tris(formato)zinc(II).

**Experimental.** The starting model in *Pnna* was obtained by transforming the coordinates in Table 1 of FC to  $x' = y + 0.25$ ,  $y' = x$ ,  $z' = z + 0.25$  and, where necessary, averaging equivalent atoms. The  $F_o$  and  $\sigma(F)$  values for 1914 reflections 'observed at  $3\sigma(I)$  level' were obtained from SUP 42448. Included in these 1914 reflections was only one, 110, which violates the extinction condition for the *a*-glide plane of *Pnna*; it had, at 2.5 e<sup>-</sup>, the smallest  $F_o$  value in the entire table. Refinement was by full-matrix minimization of

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