Structure of a Binuclear Rhodium(I) Complex: Tris[μ-(2,5-dimethyl-2,5-hexanediyl diisocyanide)-C,C']-μ-3,3,6,6-tetramethylaza-1-cyclohexen-2-ido-(N,C²)-dirhodium(I)(Rh–Rh) Trifluoromethanesulfonate, $[Rh_2(C_9H_{16}N)(C_{10}H_{16}N_2)_3]CF_3SO_3$*

By J. S. Najdzionek and B. D. Santarsiero†

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

Abstract. $M_r = 985.86$, monoclinic, $P2_1/c$, $a = 17.515$ (7), $b = 8.597$ (4), $c = 32.294$ (15) Å, $\beta = 91.51$ (3)°, $V = 4861$ (4) Å³, $Z = 4$, $D_x = 1.35$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 7.6$ cm⁻¹, $F(000) = 2040$, $T = 160 \pm 5$ K. The structure was refined to a goodness-of-fit of 1.46 with all 4281 reflections and 475 parameters ($R = 0.060$ from sums including only the 3903 reflections with $F_o^2 > 0$, $R = 0.037$ from sums including only the 2896 reflections with $F_o^2 > 3\sigma_{F2}$). The Rh–Rh distance of 2.970 (1) Å is relatively short for binuclear rhodium(I) complexes with bridging isocyanide ligands. The average Rh–C(≡N) bond length to the isocyanide ligands is 1.95 (2) Å. The Rh–C units are staggered and tilted with respect to each other, presumably to accommodate the small 'bite' of the aza-1-cyclohexen-2-ide ligand.

Introduction. Electrochemical studies of binuclear complexes provide useful information on the energetics of metal–metal bonding. During such an investigation, the two-electron reduced species $[Rh_2(tmh)_3(tmi)]CF_3SO_3$ (tmh = 2,5-dimethyl-2,5-hexanediyl diisocyanide, tmi = 3,3,6,6-tetramethylaza-1-cyclohexen-2-ide) was isolated from the bulk electrolysis or reaction of 3% Na/Hg amalgam with $Rh_2(tmh)_4(CF_3SO_3)_2$ in acetonitrile (Najdzionek, 1982). Characterization of the binuclear product by single-crystal X-ray diffraction indicated that one of the tmh ligands was reduced, and this results in a cation with some unusual structural features.

Experimental. Dark-blue prisms coated with epoxy (moderately air-sensitive), 0.3 mm on edge, locally modified Syntex $P\bar{1}$ diffractometer (Samson, Goldish & Dick, 1980) with graphite monochromator, Mo $K\alpha$, 15 reflections ($14 < 2\theta < 24°$) used to refine orientation matrix, systematic absences: $0k0$ for k odd, $h0l$ for l

odd, 4407 ($\pm h,k,l$) with $2\theta < 40°$, 126 deleted,‡ Lp correction, no absorption correction, three check reflections (20$\bar{8}$, $\bar{6}$0$\bar{2}$, 02$\bar{5}$) showed no unusual variation (all within $\pm 3\sigma$); heavy-atom methods, full-matrix least-squares refinement on F^2 using all reflections and weights w, $w^{-1} = \sigma_{F2}^2 + (0.02 \times \text{scan counts})^2$, anisotropic Gaussian amplitudes, partial population of CN(1) and CN(6),§ H atom fixed (from ΔF maps) with $B = 5$ Å², *CRYM* program library (Duchamp, 1964); final $S = 1.46$ (4281 reflections, 475 parameters), $R = 0.060$ (3903 reflections with $F_o^2 > 0$ in sums), $R_w = 0.082$, maximum peak 0.6 e Å⁻³ in final ΔF map, mean and max. ratio of shift to error in final cycle: 0.1 and 0.5, H-atom from factors from Stewart, Davidson & Simpson (1965), all other form factors from *International Tables for X-ray Crystallography* (1974).¶

Discussion. The atomic parameters are listed in Table 1 and bond lengths and angles are in Table 2. The structure is composed of discrete binuclear cations (Fig. 1) and $CF_3SO_3^-$ anions, and no crystallographic symmetry is imposed on either ionic unit (see Fig. 2). The two Rh atoms are bridged by one tmi and three tmh units, resulting in a relatively short Rh–Rh distance of 2.970 (1) Å, compared to the parent Rh^I-bridged complex $Rh_2(tmh)_4(PF_6)_2.2CH_3CN$

---

‡ During one period of data collection, an intermittent pulse of electronic noise was introduced into the detector chain. Reflections with unusual scans or backgrounds (either due to overlap or noise) were deleted.

§ The use of C-atom form factors for both CN(1) and CN(6) led to unreasonably small B's; likewise, the use of N-atom form factors was also unsatisfactory. Refinement of the population p assuming C/N disorder at those two positions gave $p = 0.50$ (5), and thus indicated a 1:1 occupancy of C and N atoms at CN(1) and CN(6). An elemental analysis of the solid is ·consistent with this formulation.

¶ Fractional atomic coordinates of H atoms, anisotropic Gaussian amplitudes for non-hydrogen atoms, and a listing of structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38345 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[3·262 (1) Å (Mann, Thich, Bell, Coyle & Gray, 1980)], the (*unbridged*) dimeric cation $Rh_2(CNPh)_8^{2+}$ [3·193 (1) Å (Mann, Lewis, Williams, Gray & Gordon, 1978)], or chloro-bridged complexes such as $[Rh(CO)_2Cl]_2$ [3·12 Å (Dahl, Martell & Wampler 1961)]. The present Rh—Rh distance is considerably longer than that found in Rh^0 or Rh^{II} compounds where there is a conventional single bond, *e.g.* $[Rh(CO)(PPh_3)_2]_2$ [2·630 (1) Å (Singh, Dammann & Hodgson, 1973)], $Rh_2(C_8H_8NO)_4$ [2·359 (1) Å (Berry, Garner, Hillier, & MacDowell, 1980)], or $Rh_2(OAc)_4(CO)_2$ [2·4196 (4) Å (Christoph & Koh, 1979)]. Thus, the Rh—Rh distance reported here

suggests a relatively weak metal—metal bond, consistent with the interaction observed for the oligomerization of $Rh(CNR)_4^+$ units in solution (Mann *et al.*, 1978).

Table 1. *Atomic coordinates ($\times 10^4$) and isotropic Gaussian amplitudes ($\times 10^3$) for all non-hydrogen atoms*

	x	y	z	$U_{eq}\dagger(Å^2)$
Rh(1)	2123·3 (3)	864·0 (7)	1360·2 (2)	19·6
Rh(2)	2273·3 (3)	3975·7 (7)	971·3 (2)	19·3
C(1*A*)	1705 (4)	1584 (9)	1883 (2)	32
N(2*A*)	1471 (3)	2001 (7)	2202 (2)	29
C(3*A*)	1189 (5)	2753 (9)	2577 (2)	35
C(31*A*)	330 (5)	2483 (11)	2569 (3)	59
C(32*A*)	1565 (5)	1928 (11)	2951 (3)	55
C(4*A*)	1382 (4)	4462 (9)	2554 (2)	30
C(5*A*)	2236 (4)	4828 (9)	2540 (2)	29
C(6*A*)	2439 (4)	6146 (9)	2248 (2)	29
C(61*A*)	3302 (5)	6405 (11)	2248 (3)	45
C(62*A*)	2025 (5)	7662 (10)	2332 (2)	40
N(7*A*)	2218 (3)	5606 (7)	1827 (2)	27
C(8*A*)	2179 (4)	4969 (9)	1506 (2)	27
C(1*B*)	2510 (4)	−124 (9)	871 (2)	30
N(2*B*)	2783 (4)	−764 (8)	591 (2)	35
C(3*B*)	3242 (4)	−1376 (9)	241 (2)	30
C(31*B*)	4029 (5)	−1777 (11)	421 (3)	51
C(32*B*)	2835 (5)	−2811 (10)	75 (3)	52
C(4*B*)	3278 (4)	−68 (9)	−71 (2)	31
C(5*B*)	2510 (5)	441 (9)	−278 (2)	29
C(6*B*)	2432 (4)	2167 (9)	−362 (2)	29
C(61*B*)	1666 (5)	2523 (10)	−579 (2)	45
C(62*B*)	3091 (5)	2841 (10)	−607 (2)	39
N(7*B*)	2429 (3)	2929 (7)	49 (2)	28
C(8*B*)	2370 (4)	3266 (9)	394 (2)	26
C(1*C*)	3108 (4)	487 (9)	1630 (2)	27
N(2*C*)	3719 (3)	392 (7)	1772 (2)	31
C(3*C*)	4490 (4)	789 (10)	1930 (2)	32
C(31*C*)	4445 (5)	918 (12)	2400 (2)	53
C(32*C*)	5022 (5)	−523 (10)	1809 (3)	47
C(4*C*)	4707 (4)	2362 (9)	1738 (2)	32
C(5*C*)	4829 (4)	2330 (9)	1265 (2)	33
C(6*C*)	4809 (4)	3889 (10)	1054 (2)	35
C(61*C*)	5043 (5)	3746 (11)	601 (2)	46
C(62*C*)	5312 (5)	5125 (10)	1273 (3)	45
N(7*C*)	4014 (3)	4463 (7)	1045 (2)	30
C(8*C*)	3359 (4)	4396 (9)	1011 (2)	30
CN(1)	1119 (4)	1676 (8)	1063 (2)	20 (2)‡
C(2)	409 (4)	644 (9)	1005 (2)	28 (2)‡
C(21)	562 (5)	−451 (10)	640 (3)	49
C(22)	294 (5)	−360 (9)	1389 (3)	46
C(3)	−311 (4)	1606 (9)	912 (2)	35 (2)‡
C(4)	−157 (4)	2937 (9)	614 (2)	34 (2)‡
C(5)	475 (4)	4020 (9)	789 (2)	23 (2)‡
C(51)	719 (4)	5131 (9)	449 (3)	35
C(52)	205 (5)	4978 (10)	1155 (3)	42
CN(6)	1157 (3)	3065 (7)	947 (2)	17 (2)‡
S	7100·8 (13)	1666·1 (28)	1348·3 (6)	36·8
O(1)	6646 (3)	1881 (8)	975 (2)	54
O(2)	6700 (3)	1924 (7)	1729 (2)	46
O(3)	7601 (3)	339 (6)	1348 (2)	54
C	7755 (5)	3291 (11)	1341 (3)	48
F(1)	8316 (3)	3168 (6)	1624 (1)	54
F(2)	8103 (3)	3399 (7)	972 (1)	68
F(3)	7405 (3)	4633 (6)	1396 (2)	72

† $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

‡ Atom refined using isotropic $U(Å^2)$.

Table 2. *Important bond distances (Å) and angles (°)*

tmh arms	Arm *A*	Arm *B*	Arm *C*	Average*
Rh(1)—C(1)	1·959 (7)	1·932 (8)	1·939 (7)	
Rh(2)—C(8)	1·937 (8)	1·973 (7)	1·937 (7)	1·946 (16)
C(1)—N(2)	1·175 (9)	1·171 (10)	1·156 (9)	
C(8)—N(7)	1·173 (9)	1·158 (9)	1·151 (9)	1·164 (10)
N(2)—C(3)	1·470 (10)	1·500 (10)	1·471 (10)	
N(7)—C(6)	1·479 (9)	1·481 (9)	1·477 (10)	1·480 (11)
C(3)—C(4)	1·510 (11)	1·512 (10)	1·540 (11)	
C(4)—C(5)	1·530 (10)	1·549 (10)	1·548 (11)	
C(5)—C(6)	1·522 (10)	1·514 (10)	1·504 (11)	1·525 (17)
Rh(1)—C(1)—N(2)'	178·2 (6)	175·5 (7)	173·4 (6)	
Rh(2)—C(8)—N(7)	171·6 (7)	176·5 (6)	171·9 (6)	175 (3)
C(1)—N(2)—C(3)	171·6 (7)	170·0 (7)	162·3 (7)	
C(8)—N(7)—C(6)	165·2 (7)	167·4 (7)	157·2 (7)	166 (5)
N(2)—C(3)—C(4)	107·9 (6)	105·9 (6)	107·3 (6)	
N(7)—C(6)—C(5)	106·1 (6)	105·9 (6)	108·4 (6)	106·9 (11)
C(3)—C(4)—C(5)	115·0 (6)	116·5 (6)	115·1 (6)	
C(4)—C(5)—C(6)	114·6 (6)	115·3 (6)	115·5 (6)	115·3 (7)

tmi (arm *D*)				Average
Rh(1)—CN(1)	2·102 (6)	Rh(2)—CN(6)	2·107 (6)	2·105
CN(1)—C(2)	1·535 (10)	CN(6)—C(5)	1·526 (9)	1·53
C(2)—C(3)	1·531 (11)	C(4)—C(5)	1·542 (10)	1·54
CN(1)—CN(6)	1·254 (9)	C(3)—C(4)	1·524 (11)	

$CF_3SO_3^-$ anion

C—F(1)	1·328 (10)	C—F(2)	1·356 (10)	C—F(3)	1·321 (10)
S—O(1)	1·439 (6)	S—O(2)	1·449 (6)	S—O(3)	1·439 (6)
		S—C	1·807 (9)			

* Average over chemically equivalent distances and angles. The standard deviation of the average is estimated as $[\sum_{n=1}^n (d_i - \bar{d})^2 / (n-1)]^{1/2}$.
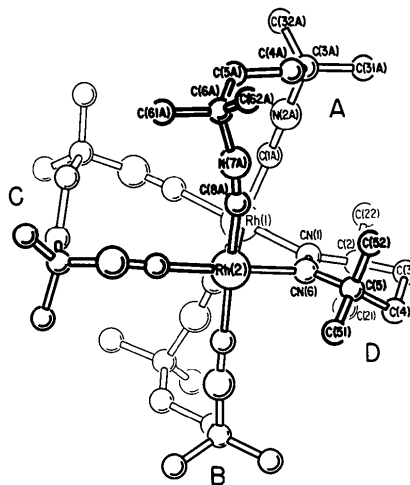

Fig. 1. View of the $[Rh_2(tmh)_3(tmi)]^+$ cation (labeling scheme is shown for arms *A* and *D*).
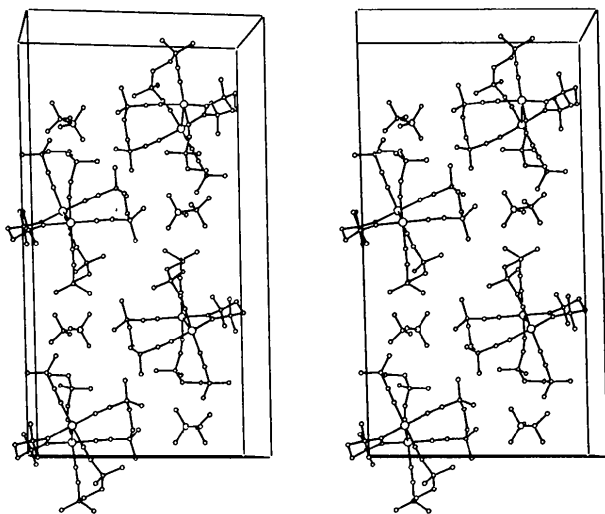
Fig. 2. Stereoscopic drawing of the unit cell. The *a* axis runs across, the *b* axis into, the *c* axis up the page.

The coordination geometry around each Rh atom is essentially square planar with a slight tetrahedral distortion. The two 'RhC$_4$' (least-squares) planes are tipped by 40·2 (2)° (where 0° would be parallel), presumably due to the small 'bite' of the tmi ligand. The torsional blade angles, C(1)—Rh(1)—Rh(2)—C(8), are equal for the two tmh groups opposite each other: 16·6 (3)° for arm *A* and 16·4 (3)° for arm *B*; the corresponding angles for arms *C* and *D* are smaller, 12·0 (3) and 5·3 (3)°. The average Rh—C bond length of 1·95 (2) Å and the Rh—C≡N angle of 175 (3)° are consistent with the structural data of other Rh-bridge complexes (Mann *et al.*, 1980). The C—C and C—N

bond lengths, and associated angles, within the tmh rings are normal. The CN(1)—CN(6) bond length of 1·25 (1) Å implies a formal C—N double bond, and leads to the formulation of this arm as an aza-1-cyclohexen-2-ide ring. The bond distances and angles within the anion are normal.

References

BERRY, M., GARNER, C. D., HILLIER, I. H. & MACDOWELL, A. A. (1980). *J. Chem. Soc. Chem. Commun.* pp. 494–495.
CHRISTOPH, G. C. & KOH, Y. B. (1979). *J. Am. Chem. Soc.* **101**, 1422–1434.
DAHL, L. F., MARTELL, C. & WAMPLER, D. J. (1961). *J. Am. Chem. Soc.* **83**, 1761–1762.
DUCHAMP, D. J. (1964). *CRYM Crystallographic Computing System.* California Institute of Technology, Pasadena, California, USA.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98. Birmingham: Kynoch Press.
MANN, K. R., LEWIS, N. S., WILLIAMS, R. M., GRAY, H. B. & GORDON, J. G. (1978). *Inorg. Chem.* **17**, 828–834.
MANN, K. R., THICH, J. A., BELL, R. A., COYLE, C. L. & GRAY, H. B. (1980). *Inorg. Chem.* **19**, 2462–2468.
NAJDZIONEK, J. S. (1982). PhD thesis, California Institute of Technology, Pasadena, California, USA.
SAMSON, S., GOLDISH, E. & DICK, C. J. (1980). *J. Appl. Cryst.* **13**, 425–432.
SINGH, P., DAMMANN, C. B. & HODGSON, D. J. (1973). *Inorg. Chem.* **12**, 1335–1339.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1983). C**39**, 579–582

Structure of a Complex between *rel*-(6*R*,11*S*,17*R*,22*S*)-6,7,8,9,10,11,17,18,19,20,21,22-Dodecahydro-1,5,12,16,23,26,29-heptaoxa[7³,¹⁴][5.5]orthocyclophane and Magnesium Bis(perchlorate) Monohydrate, C$_{22}$H$_{38}$O$_7$·Mg(ClO$_4$)$_2$·H$_2$O

BY JOHN D. OWEN

Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Hertfordshire AL5 2JQ, England

Abstract. $M_r = 655·8$, monoclinic, $P2_1/c$, $a = 17·145$ (4), $b = 20·848$ (4), $c = 16·628$ (5) Å, $\beta = 92·31$ (2)°, $U = 5938$ Å^3, $Z = 8$, $D_m = 1·45$, $D_x = 1·47$ g cm^{-3}, Mo *K*α, $\lambda = 0·71069$ Å, $\mu = 3·07$ cm^{-1}, $F(000) = 2768$, m.p. > 520 K (decomp.), $R = 0·083$ for 2724 observations $[I > 2\sigma(I)]$. There are two molecules in the asymmetric unit, each containing one Mg coordinated to the seven O atoms of the macrobicycle, and to the O of a water molecule. Two perchlorates are H-bonded in different ways to the waters in the two molecules which are otherwise almost identical.