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Seven Dinuclear Rhodium(II) Complexes with *o*-Oxypyridine Anions as Ligands

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The structures of seven dirhodium(II) compounds with bridging ligands other than carboxylato anions are reported. The bridging ligands are either 2-oxy-6-methylpyridine (mhp) or 2-oxy-6-chloropyridine (chp). Each compound has been fully identified and characterized by X-ray crystallography. Compound **1**, $Rh_2(mhp)_4{\cdot}H_2O$, crystallizes in the space group $P\bar{1}$ with $a = 12.330$ (3) Å, $b = 19.360$ (4) Å, $c = 10.754$ (2) Å, $\alpha = 94.42$ (2)°, $\beta = 96.36$ (2)°, $\gamma = 81.89$ (2)°, and $Z = 4$. There are two independent molecules each devoid of axial ligands. Molecule A has an essentially eclipsed conformation with Rh–Rh = 2.370 (1) Å; molecule B has a twist of about 9.3° away from the eclipsed conformation and Rh–Rh = 2.365 (1) Å. The nitrogen atoms on each end are trans. Compound **2**, $Rh_2(mhp)_4(CH_3CN)$, crystallizes in the space group $P2_1/n$ with $a = 9.159$ (3) Å, $b = 20.185$ (2) Å, $c = 13.906$ (2) Å, $\beta = 92.69$ (2)°, and $Z = 4$. The formula unit comprises the crystallographic asymmetric unit. The mhp ligands are arranged so that three nitrogen atoms are coordinated to one Rh atom and the CH_3CN is coordinated to the other one with a relatively short (2.152 (7) Å) Rh–N distance. The Rh–Rh distance, 2.372 (1) Å, is as short as in **1**, however. The rotational conformation is twisted by 23° from eclipsed. Compound **3a**, $Rh_2(mhp)_2(O_2CCH_3)_2(C_3H_4N_2)$, crystallized in the space group $C2/c$ with $a = 10.702$ (2) Å, $b = 13.138$ (3) Å, $c = 15.369$ (2) Å, $\beta = 102.58$ (1)°, and $Z = 4$. The Rh–Rh bond (2.388 (2) Å) lies along a crystallographic twofold axis. This mixed-ligand complex has pairs of mhp and acetate bridging ligands in a trans configuration. The $C_3H_4N_2$ ligand is coordinated (Rh–N = 2.17 (1) Å) to the Rh atom to which the mhp oxygen atoms are bound. This ligand appears to be an imidazole molecule, but its chemical origin is as yet unknown. Compound **3b**, $Rh_2(mhp)_2(O_2CCH_3)_2(C_3H_4N_2){\cdot}2CH_2Cl_2$, is essentially identical with **3a** except for the solvent molecules in the lattice. The compound crystallizes in the space group $C2/c$ with four formula units in a cell of dimensions $a = 21.488$ (10) Å, $b = 12.603$ (2) Å, $c = 11.086$ (2) Å, and $\beta = 112.21$ (2)°. The cell constants and data of this compound were obtained at −111 °C. The Rh–Rh bond, coincident with a crystallographic twofold axis, has a length of 2.388 (1) Å with the single axial imidazole nitrogen atom coordinated to one of the Rh atoms at 2.133 (7) Å. Crystals of compound **4**, $Rh_2(mhp)_4(C_3H_4N_2){\cdot}0.5CH_3CN$, are monoclinic, space group $C2/c$, with eight formula units in a cell of dimensions $a = 11.827$ (3) Å, $b = 15.714$ (2) Å, $c = 31.228$ (5) Å, and $\beta = 95.95$ (2)°. Four mhp ligands are coordinated about the dirhodium(II) unit in a fashion analogous to that in compound **2** and have a mean twist angle of 19.5° away from the eclipsed conformation. An imidazole molecule is bound to one axial position with a Rh–N distance of 2.144 (4) Å; the other axial site is quite effectively blocked by the methyl groups of the mhp ligands. The Rh–Rh distance is 2.384 (1) Å. No crystallographic symmetry is imposed on the dinuclear molecule, but the acetonitrile molecules are located along twofold axes in the lattice. Compound **5**, $Rh_2(chp)_4$, crystallizes in the space group $Pbca$ with $a = 15.992$ (2) Å, $b = 18.740$ (3) Å, $c = 15.490$ (3) Å, and $Z = 8$. The molecule, which has no axial ligands, has symmetry approximating to D_{2d} and a Rh–Rh distance of 2.379 (1) Å. Compound **6**, $Rh_2(chp)_4(C_3H_4N_2){\cdot}3H_2O$, crystallizes in the tetragonal space group $P4_2/n$ with eight formula units in a cell of dimensions $a = 22.372$ (3) Å and $c = 12.457$ (3) Å. The structure closely resembles that of **4** with a Rh–Rh distance of 2.385 (1) Å, a single axially bound imidazole molecule with a Rh–N distance of 2.129 (9) Å, and an average twist angle in the chp ligands of 20.7° away from the eclipsed conformation. Four crystallographically distinct types of water molecule are found in the lattice although two of the positions are only 50% occupied.

Introduction

Recently, dirhodium(II) compounds have been under active investigation with respect to their reactivity, electronic properties, and structures.[1–13] A prime consideration in all of these studies has been the role of the axial ligands and their effect on the metal–metal bond. The marked propensity for dirhodium(II) complexes to form stable adducts with a wide variety of axial ligands can be understood by examination of the pattern of orbitals in the ground-state configuration, as derived from SCF-Xα-SW calculations[13] which were recently substantiated by UV photoelectron spectroscopic data:[12] $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$. Ligands can donate electron density into unoccupied σ^* orbitals, and each rhodium atom may utilize its filled π^* orbital toward suitable π-acceptor ligands.

The structural data published to date[4b,5,7–12] on rhodium(II) dimers with bridging ligands reveal a qualitative relationship between axial donor strength and the Rh–Rh bond length similar to that found for the dichromium(II) carboxylates[14a] and amidates.[14b] The Rh–Rh bond length varies from 2.359 (1) Å in $Rh_2(mhp)_4$[12] to 2.936 (2) Å in $Rh_2(dmg)_4(PPh_3)_2{\cdot}H_2O{\cdot}C_3H_7OH$[15] (mhp = 2-oxy-6-methylpyridine, dmg = dimethylglyoximate anion) with the latter dimer having no bridging ligands between metal centers. Among dimers having four bridging ligands, the Rh–Rh bond distance has been found to be as long as 2.550 (3) Å in $Rh_2(OSCCH_3)_4(CH_3CSOH)_2$.[5a]

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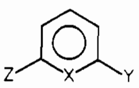
The rhodium(II) dimers which have been prepared and structurally characterized show that considerable lengthening of the Rh–Rh bond is possible. Ligands were sought which would specifically exclude axial interactions. Ligands of the general type



have been used successfully to obtain the first exceedingly short (<1.9 Å) quadruple bonds in dichromium(II) complexes (X = C, Y = X = OCH_3).[16] It was then found that congeneric complexes of the group 6 metal ions having the formula $M_2(mhp)_4$ (X = N, Y = O, Z = CH_3) could be readily prepared and that they are quite stable, with unusually short metal–metal distances.[17] We began several years ago to prepare rhodium(II) complexes which would incorporate mhp as a bridging ligand. As this paper was being written, Garner, Clegg, and co-workers[12] reported in preliminary fashion the preparation and structure of a yellow-brown material which is one of the reaction products between Na(mhp) and $Rh_2(OAc)_4$ (OAc = acetate anion) and has the composition $Rh_2(mhp)_4$. In this compound, which has approximately D_{2d} molecular symmetry and Rh–O and Rh–N bonds trans to their own kind, the structural type is one which has been encountered before in the group 6 $M_2(mhp)_4$ compounds.[17] Our investigations of the reaction products between Hmhp and $Rh_2(OAc)_4$ have revealed not only a solvated form of the structure described by Garner et al.[12] but also two completely new structural types which have not been found previously with the group 6 metals. In this paper we report the preparation and structures of seven compounds of which five are with mhp and two are with 2-oxy-6-chloropyridine which we shall designate chp.

Experimental Section

Materials. Rhodium(II) acetate was prepared by a literature method.[18] The ligands 2-hydroxy-6-methylpyridine (Hmhp) and 6-chloro-2-pyridinol (Hchp) were obtained from Aldrich Chemical Co. Some samples of Hmhp were also obtained via a literature procedure.[19] Both compounds were purified by sublimation prior to use.

Preparation of 1–4. Previous work[20] with α-pyridone ligands has shown that their relatively high acidity can be used to exchange with ligands such as Cl^- or RCO_2^- with use of a solid melt. Thus, in a typical reaction 0.05 g of $Rh_2(OAc)_4$ and 0.06 g of Hmhp (a slight excess) were heated in an argon atmosphere for 15 min at 160 °C. When the Hmhp melted, the mixture turned dark green. The excess Hmhp was removed by sublimation under vacuum at 110 °C. Many solvents were used in attempts to crystallize the product: acetonitrile, anisole, benzene, CH_2Cl_2, CH_2Cl_2–hexane, chlorobenzene, EtOH, MeOH, THF, THF–hexane, and toluene. Recrystallization from benzene yielded green hexagonal platelets which eventually lost crystallinity, apparently due to loss of benzene of crystallization. Only acetonitrile and methylene chloride yielded suitable crystals. When the cooled green melt was dissolved in acetonitrile, a blue-green solution formed from which small blue-red dichroic crystals (**3a**) were deposited after 1–2 weeks. The solution, now green in color, was slowly evaporated, yielding beautiful, large orange-brown prisms (**1**) and very irregular dark green crystals (**2**). Continued recrystallization from acetonitrile of one preparation gave after 4 weeks rather irregular pink prisms and plates (**4**) with well-developed faces and a small quantity of microcrystalline green material (**2**).

Crystalline products could also be obtained from CH_2Cl_2. In a minimum volume of CH_2Cl_2, the green melt was dissolved and cooled in a freezer for several days. Golden yellow prismatic crystals were obtained, examined on a CAD-4 diffractometer (vide infra), and found to have cell constants essentially identical with the values found for the group 6 $M_2(mhp)_4 \cdot CH_2Cl_2$ compounds. Blue-red prisms (**3b**) were also collected from the cold CH_2Cl_2 solution but found to lose crystallinity if not protected.

The elemental composition of each of these five compounds was shown by X-ray crystallography (vide infra) to be $Rh_2(mhp)_4 \cdot H_2O$ (**1**), $Rh_2(mhp)_4(CH_3CN)$ (**2**), $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)$ (**3a**), $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2) \cdot 2CH_2Cl_2$ (**3b**), and $Rh_2(mhp)_4(C_3H_4N_2) \cdot 0.5CH_3CN$ (**4**).

Preparation of 5 and 6. A mixture of 0.5 g of $Rh_2(OAc)_4$ and 0.09 g of Hchp (a slight excess) was heated to 140 °C under argon for 30 min. Excess Hchp was sublimed off and the fused mixture dissolved in 1:1 CH_2Cl_2–hexane. Evaporation of the solvent yielded small, golden, octahedral crystals (**5**) and a red-violet product (**6**). Crystals of **6** were obtained by slow evaporation of an acetonitrile solution. X-ray structure analysis showed the composition of **5** to be $Rh_2(chp)_4$ and **6** to be $Rh_2(chp)_4(C_3H_4N_2) \cdot 3H_2O$.

X-ray Crystallography. Collection of Data. Data for **1**, **3a**, and **5** were collected on a Syntex P$\bar{1}$ diffractometer using Mo Kα radiation with a graphite-crystal monochromator in the incident beam. Lattice constants were obtained from a least-squares fit of 15 strong reflections in the range $24° < 2\theta < 34°$. Data were collected at 22 ± 3 °C with use of the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min. Other procedures for data collection have been presented elsewhere.[21] Crystallographic data and other pertinent information are summarized in Table I. Lorentz and polarization corrections were applied to the intensity data, but, because of the small linear absorption coefficients, absorption corrections were not applied.

The diffraction data for **2**, **4**, and **6** were collected at 26 ± 1 °C on an Enraf-Nonius CAD-4F diffractometer using Mo Kα radiation with a graphite-crystal monochromator in the incident beam. The cell constants were determined from a least-squares fit of 23–25 reflections in the range $16° < 2\theta < 34°$. Further details concerning the procedures for data collection and reduction have been given elsewhere.[22] An absorption correction was applied to the data only for compound **6** with use of an empirical method based on ψ scans (ψ = 0–360° every 10°) for χ values near 90°. Nine sets of ψ scan curves were used with maximum, minimum, and average relative transmission values of 1.00, 0.85, and 0.92, respectively.

Crystals of **3b** were mounted in glass capillaries and examined on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation at Molecular Structure Corp., College Station, TX. The cell constants (Table I) and data were obtained at −111 ± 2 °C with use of a cryostat designed by Molecular Structure Corp. The width at half-height from ω scans was 0.5°. A takeoff angle of 2.8° was used with a counter aperature width of 2.0 mm. The incident-beam collimator diameter was 0.7 mm, and the crystal-to-detector distance was 21 cm. A variable-scan rate in ω of 2–20°/min was used with moving-crystal moving-counter background counts taken at the end of each scan range. The ratio of scan time to background counting time was 2.0. The scan width ($\Delta\omega$) was $0.6 + 0.35 \tan \theta$. The intensities and their standard deviations were derived as previously described.[22]

Solution and Refinement of the Structures.[23] **Compound 1.** The positions of the four independent Rh atoms in $Rh_2(mhp)_4 \cdot H_2O$ (**1**) were located with use of the direct-methods program MULTAN.

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Table I. Crystallographic Data for the Seven Compounds

parameter	1	2	3a	3b	4	5	6
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$C2/c$	$C2/c$	$Pbca$	$P4_2/n$
a, Å	12.330 (3)	9.159 (3)	10.702 (2)	21.488 (10)	11.827 (3)	15.992 (2)	22.372 (3)
b, Å	19.360 (4)	20.185 (2)	13.138 (3)	12.603 (2)	15.714 (2)	18.740 (3)	22.372 (3)
c, Å	10.754 (2)	13.906 (2)	15.369 (2)	11.086 (2)	31.228 (5)	15.490 (3)	12.457 (3)
α, deg	94.42 (2)	90.0	90.0	90.0	90.0	90.0	90.0
β, deg	96.36 (2)	92.69 (2)	102.58 (1)	112.21 (2)	95.95 (2)	90.0	90.0
γ, deg	81.89 (2)	90.0	90.0	90.0	90.0	90.0	90.0
V, Å^3	2520.7 (9)	2568 (1)	2109.0 (7)	2778 (3)	5772 (3)	4642 (1)	6235 (3)
d_{calcd}, g/cm^3	1.76	1.76	1.91	1.86	1.67	2.06	1.79
Z	4	4	4	4	8	8	8
fw	656.31	679.35	608.22	778.09	726.90	719.97	842.09
cryst size, mm	0.2 × 0.2 × 0.4	0.1 × 0.3 × 0.4	0.05 × 0.10 × 0.20	0.1 × 0.2 × 0.2	0.2 × 0.3 × 0.4	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.6
μ(Mo Kα), cm^{-1}	13.164	12.941	15.678	15.804	11.596	18.761	14.214
range 2θ, deg	3–45	4–45	4–45	4–60	3–48	4–45	3–45
no. of data collected	5977	3341	749	4221	3926	1964	4303
no. data, $F_o^2 > 3\sigma(F_o^2)$	5096	2650	732	2099	3709	1624	2348
no. variables	381	334	92	178	358	207	248
R_1	0.050	0.048	0.037	0.058	0.043	0.038	0.057
R_2	0.074	0.065	0.050	0.069	0.067	0.053	0.070
esd	1.678	1.503	1.114	1.805	1.872	1.107	1.541
largest peak, e/Å^3 [a]	0.67	0.53	0.30	0.49	1.46	0.31	0.60

[a] Largest peak in the final difference Fourier map.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(mhp)_4 \cdot H_2O$ (1)[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.20354 (6)	0.44805 (3)	0.16196 (6)	2.61 (3)	2.15 (3)	2.21 (3)	−0.23 (2)	0.06 (2)	0.22 (2)
Rh(2)	0.26222 (6)	0.35561 (4)	0.29631 (6)	2.64 (3)	2.65 (3)	2.27 (3)	−0.02 (2)	−0.04 (2)	0.51 (2)
Rh(3)	0.32933 (6)	0.86697 (3)	0.08400 (6)	2.79 (3)	2.35 (3)	2.01 (3)	−0.30 (2)	0.20 (2)	0.19 (2)
Rh(4)	0.27783 (6)	0.86133 (4)	0.28800 (6)	3.39 (3)	2.62 (3)	1.91 (3)	−0.33 (3)	0.22 (2)	0.15 (2)
O(1)	0.2059 (5)	0.4161 (3)	0.4432 (5)	3.9 (3)	4.2 (3)	2.0 (2)	−0.1 (3)	0.4 (2)	0.0 (2)
O(2)	0.3505 (5)	0.4833 (3)	0.2040 (6)	3.7 (3)	2.7 (3)	4.2 (3)	−0.8 (2)	0.3 (2)	−0.0 (2)
O(3)	0.0569 (5)	0.4126 (3)	0.1200 (6)	3.8 (3)	2.8 (2)	3.0 (3)	−0.8 (2)	−0.6 (2)	0.8 (2)
O(4)	0.3172 (5)	0.2934 (3)	0.1495 (6)	3.7 (3)	2.5 (2)	3.2 (3)	0.2 (2)	0.5 (2)	0.2 (2)
O(5)	0.3323 (5)	0.7580 (3)	0.2828 (6)	4.6 (3)	2.8 (3)	3.0 (3)	−0.1 (2)	0.1 (2)	0.7 (2)
O(6)	0.1714 (5)	0.8627 (4)	0.0144 (6)	3.7 (3)	4.7 (3)	2.5 (3)	−0.7 (3)	−0.4 (2)	0.6 (2)
O(7)	0.2221 (5)	0.9651 (3)	0.2903 (6)	4.9 (3)	2.5 (3)	2.9 (3)	0.2 (2)	0.5 (2)	0.1 (2)
O(8)	0.4861 (5)	0.8713 (3)	0.1567 (6)	3.6 (3)	3.6 (3)	3.2 (3)	−0.8 (2)	0.2 (2)	0.1 (2)
N(1)	0.1476 (6)	0.5068 (4)	0.3131 (7)	2.1 (3)	3.3 (3)	2.6 (3)	−0.1 (3)	0.1 (3)	−0.1 (3)
N(2)	0.4096 (6)	0.3947 (4)	0.3325 (7)	2.7 (3)	4.3 (4)	2.6 (3)	0.1 (3)	−0.5 (3)	0.4 (3)
N(3)	0.1103 (6)	0.3248 (4)	0.2545 (7)	3.8 (3)	2.7 (3)	2.6 (3)	−0.6 (3)	0.3 (3)	0.1 (3)
N(4)	0.2642 (6)	0.3836 (4)	0.0179 (7)	2.5 (3)	3.0 (3)	2.3 (3)	−0.1 (3)	0.0 (2)	0.1 (3)
N(5)	0.3602 (6)	0.7605 (4)	0.0723 (6)	3.2 (3)	2.3 (3)	2.4 (3)	−0.4 (3)	0.5 (3)	−0.3 (3)
N(6)	0.1287 (6)	0.8394 (4)	0.2076 (7)	3.2 (3)	3.6 (3)	2.8 (3)	−0.9 (3)	0.4 (3)	0.8 (3)
N(7)	0.2976 (6)	0.9732 (4)	0.1085 (7)	3.9 (3)	2.2 (3)	2.4 (3)	−0.1 (3)	0.1 (3)	0.4 (3)
N(8)	0.4309 (7)	0.8826 (4)	0.3573 (7)	5.1 (4)	2.6 (3)	2.3 (3)	−0.5 (3)	−1.4 (3)	−0.1 (3)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(9)	0.049 (1)	0.0405 (9)	0.416 (2)	14.1 (5)	C(46)	0.2088 (9)	0.4845 (6)	−0.1103 (10)	4.3 (2)
O(10)	0.867 (2)	0.0895 (11)	0.237 (2)	19.9 (7)	C(51)	0.3562 (7)	0.7246 (5)	0.1757 (8)	2.7 (2)
C(11)	0.1596 (7)	0.4798 (5)	0.4289 (8)	2.9 (2)	C(52)	0.3778 (8)	0.6504 (5)	0.1684 (10)	3.7 (2)
C(12)	0.1206 (8)	0.5228 (5)	0.5325 (10)	3.8 (2)	C(53)	0.4047 (9)	0.6151 (6)	0.0580 (11)	4.7 (2)
C(13)	0.0722 (9)	0.5882 (6)	0.5209 (10)	4.5 (2)	C(54)	0.4089 (9)	0.6527 (6)	−0.0466 (10)	4.4 (2)
C(14)	0.0580 (9)	0.6160 (6)	0.3991 (11)	4.7 (2)	C(55)	0.3858 (7)	0.7262 (5)	−0.0367 (9)	3.0 (2)
C(15)	0.0969 (8)	0.5745 (5)	0.2993 (9)	3.6 (2)	C(56)	0.3932 (8)	0.7694 (5)	−0.1473 (10)	4.0 (2)
C(16)	0.0886 (9)	0.5990 (6)	0.1676 (11)	4.7 (2)	C(61)	0.1010 (7)	0.8460 (5)	0.0847 (9)	3.1 (2)
C(21)	0.4256 (7)	0.4530 (5)	0.2813 (9)	3.0 (2)	C(62)	−0.0058 (9)	0.8336 (6)	0.0297 (10)	4.4 (2)
C(22)	0.5265 (9)	0.4820 (6)	0.3128 (11)	4.6 (2)	C(63)	−0.0787 (11)	0.8111 (7)	0.1052 (12)	5.7 (3)
C(23)	0.6072 (11)	0.4475 (7)	0.3949 (12)	5.7 (3)	C(64)	−0.0450 (10)	0.8036 (6)	0.2330 (11)	5.1 (3)
C(24)	0.5895 (10)	0.3875 (7)	0.4465 (12)	5.5 (3)	C(65)	0.0584 (9)	0.8190 (6)	0.2816 (10)	4.4 (2)
C(25)	0.4892 (9)	0.3619 (6)	0.4176 (10)	4.3 (2)	C(66)	0.0972 (11)	0.8130 (7)	0.4168 (13)	5.9 (3)
C(26)	0.4629 (10)	0.2970 (6)	0.4706 (12)	5.5 (3)	C(71)	0.2508 (7)	1.0040 (5)	0.2075 (8)	2.9 (2)
C(31)	0.0337 (7)	0.3588 (5)	0.1718 (8)	2.8 (2)	C(72)	0.2275 (8)	1.0781 (5)	0.2234 (9)	3.5 (2)
C(32)	−0.0704 (8)	0.3361 (5)	0.1414 (10)	3.8 (2)	C(73)	0.2647 (9)	1.1180 (6)	0.1376 (10)	4.2 (2)
C(33)	−0.0953 (9)	0.2794 (6)	0.1988 (11)	4.5 (2)	C(74)	0.3175 (9)	1.0864 (6)	0.0395 (10)	4.3 (2)
C(34)	−0.0154 (9)	0.2461 (6)	0.2857 (10)	4.3 (2)	C(75)	0.3317 (8)	1.0130 (5)	0.0210 (9)	3.5 (2)
C(35)	0.0820 (8)	0.2703 (5)	0.3133 (9)	3.2 (2)	C(76)	0.3812 (9)	0.9726 (6)	−0.0898 (10)	4.4 (2)
C(36)	0.1713 (9)	0.2403 (6)	0.4129 (10)	4.3 (2)	C(81)	0.5087 (8)	0.8822 (5)	0.2774 (9)	3.1 (2)
C(41)	0.3091 (7)	0.3170 (4)	0.0367 (8)	2.6 (2)	C(82)	0.6181 (9)	0.8938 (6)	0.3257 (10)	4.4 (2)
C(42)	0.3467 (8)	0.2723 (5)	−0.0624 (9)	3.2 (2)	C(83)	0.6413 (10)	0.9095 (6)	0.4531 (11)	5.0 (2)
C(43)	0.3372 (9)	0.2956 (6)	−0.1812 (11)	4.6 (2)	C(84)	0.5598 (10)	0.9095 (7)	0.5319 (12)	5.3 (3)
C(44)	0.2894 (9)	0.3675 (6)	−0.1990 (11)	4.6 (2)	C(85)	0.4544 (9)	0.8960 (6)	0.4827 (10)	4.4 (2)
C(45)	0.2549 (8)	0.4089 (5)	−0.1005 (9)	3.2 (2)	C(86)	0.3606 (10)	0.8955 (7)	0.5634 (12)	5.6 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(mhp)_4(CH_3CN)$ (**2**)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.49040 (7)	0.10120 (3)	0.29474 (5)	1.83 (2)	2.21 (2)	2.90 (3)	0.01 (2)	0.43 (2)	0.12 (2)
Rh(2)	0.32446 (7)	0.18977 (3)	0.26437 (5)	1.83 (2)	2.19 (2)	3.11 (3)	0.08 (2)	0.46 (2)	−0.13 (2)
O(1)	0.5775 (6)	0.1568 (3)	0.4032 (4)	3.2 (3)	2.7 (2)	3.7 (3)	−0.4 (2)	−0.6 (2)	−0.0 (2)
O(2)	0.4136 (6)	0.2016 (3)	0.1358 (4)	2.3 (2)	3.6 (3)	2.8 (2)	0.3 (2)	−0.1 (2)	0.1 (2)
O(3)	0.2423 (6)	0.1713 (3)	0.3938 (4)	2.8 (2)	3.0 (2)	3.6 (2)	−0.0 (2)	1.1 (2)	−0.2 (2)
O(4)	0.1904 (6)	0.1196 (3)	0.2047 (4)	1.9 (2)	2.3 (2)	4.1 (3)	−0.2 (2)	0.1 (2)	−0.7 (2)
N(1)	0.4804 (7)	0.2513 (3)	0.3313 (5)	2.6 (3)	2.4 (3)	3.2 (3)	0.1 (2)	0.4 (2)	−0.3 (2)
N(2)	0.6199 (7)	0.1470 (3)	0.1967 (5)	2.0 (3)	2.5 (3)	3.7 (3)	−0.1 (2)	0.1 (2)	0.5 (3)
N(3)	0.3437 (7)	0.0666 (3)	0.3921 (5)	2.7 (3)	2.5 (3)	3.3 (3)	−0.4 (3)	0.6 (2)	0.0 (3)
N(4)	0.3845 (7)	0.0490 (3)	0.1879 (5)	2.7 (3)	2.0 (3)	3.7 (3)	−0.0 (2)	1.1 (2)	−0.4 (2)
N(5)	0.1435 (8)	0.2565 (4)	0.2389 (6)	3.3 (3)	2.8 (3)	5.4 (4)	0.1 (3)	0.9 (3)	−0.4 (3)
C(1)	0.0322 (14)	0.2801 (6)	0.2332 (12)	5.0 (6)	4.2 (5)	15 (1)	−0.5 (5)	−1.7 (7)	−2.6 (7)
C(2)	−0.1054 (14)	0.3085 (6)	0.2293 (15)	3.6 (5)	3.9 (5)	22 (1)	1.4 (4)	−2.1 (8)	−3.7 (7)
C(11)	0.5711 (9)	0.2198 (5)	0.3969 (6)	2.2 (3)	4.3 (4)	3.3 (4)	−0.6 (3)	0.3 (3)	−0.8 (4)
C(12)	0.6649 (12)	0.2579 (5)	0.4617 (7)	4.2 (5)	4.7 (5)	4.9 (5)	−0.7 (4)	0.1 (4)	−1.6 (4)
C(13)	0.6708 (12)	0.3267 (5)	0.4513 (8)	3.8 (5)	3.8 (4)	6.8 (6)	−0.1 (4)	0.0 (4)	−0.9 (4)
C(14)	0.5846 (10)	0.3564 (5)	0.3752 (7)	3.3 (4)	4.1 (4)	5.9 (5)	−0.8 (4)	0.9 (4)	−1.1 (4)
C(15)	0.4927 (9)	0.3181 (4)	0.3166 (6)	2.5 (4)	3.1 (4)	4.2 (4)	−0.3 (3)	0.7 (3)	−0.4 (3)
C(16)	0.4055 (12)	0.3502 (5)	0.2367 (8)	5.7 (6)	2.7 (4)	5.6 (5)	−0.4 (4)	−0.5 (5)	0.6 (4)
C(21)	0.5506 (9)	0.1855 (4)	0.1293 (6)	2.9 (3)	2.0 (3)	3.3 (3)	−0.2 (3)	1.1 (3)	−0.2 (3)
C(22)	0.6251 (10)	0.2106 (4)	0.0482 (7)	3.9 (4)	2.7 (4)	4.0 (4)	0.4 (3)	0.7 (3)	0.0 (3)
C(23)	0.7745 (10)	0.1969 (4)	0.0450 (7)	3.6 (4)	3.4 (4)	4.5 (4)	−0.2 (3)	1.6 (3)	−0.4 (4)
C(24)	0.8462 (10)	0.1605 (4)	0.1198 (6)	3.2 (4)	3.3 (4)	3.5 (4)	−0.4 (3)	1.2 (3)	−0.4 (3)
C(25)	0.7675 (9)	0.1369 (4)	0.1935 (6)	2.1 (3)	2.5 (3)	3.4 (4)	0.1 (3)	0.2 (3)	−0.3 (3)
C(26)	0.8419 (10)	0.1009 (5)	0.2777 (8)	2.7 (4)	5.8 (5)	6.1 (5)	1.1 (4)	0.5 (4)	2.4 (4)
C(31)	0.2492 (9)	0.1121 (4)	0.4270 (6)	2.4 (3)	3.3 (4)	3.9 (4)	−0.8 (3)	0.6 (3)	−0.2 (3)
C(32)	0.1592 (12)	0.0955 (5)	0.5035 (7)	4.3 (5)	4.8 (5)	4.3 (4)	−0.6 (4)	1.3 (4)	0.4 (4)
C(33)	0.1600 (12)	0.0329 (6)	0.5375 (8)	4.9 (5)	6.0 (5)	5.5 (5)	−1.2 (4)	1.5 (4)	1.4 (5)
C(34)	0.2493 (11)	−0.0163 (6)	0.4986 (7)	3.6 (4)	6.0 (5)	5.2 (5)	0.2 (4)	1.5 (4)	1.5 (4)
C(35)	0.3383 (10)	0.0030 (4)	0.4252 (7)	3.4 (4)	3.4 (4)	4.0 (4)	−0.1 (3)	0.0 (4)	0.4 (3)
C(36)	0.4387 (11)	−0.0478 (5)	0.3812 (8)	4.4 (5)	3.7 (4)	5.6 (5)	0.4 (4)	1.0 (4)	−0.2 (4)
C(41)	0.2423 (9)	0.0667 (4)	0.1681 (6)	2.3 (3)	2.6 (3)	3.6 (4)	−0.1 (3)	0.2 (3)	0.9 (3)
C(42)	0.1504 (10)	0.0252 (4)	0.1083 (7)	3.6 (4)	3.1 (4)	4.1 (4)	−1.0 (3)	−0.1 (4)	−0.6 (4)
C(43)	0.2082 (12)	−0.0295 (5)	0.0672 (7)	4.9 (5)	4.8 (5)	3.8 (4)	−0.9 (4)	−0.3 (4)	−0.7 (4)
C(44)	0.3576 (11)	−0.0442 (5)	0.0813 (7)	4.4 (5)	3.4 (4)	3.6 (4)	−0.3 (4)	0.2 (4)	−0.9 (3)
C(45)	0.4413 (9)	−0.0051 (4)	0.1416 (6)	3.5 (4)	2.9 (4)	3.5 (4)	−0.1 (3)	1.4 (3)	0.2 (3)
C(46)	0.6036 (10)	−0.0181 (5)	0.1578 (8)	3.3 (4)	3.0 (4)	7.1 (6)	1.2 (4)	1.3 (4)	0.1 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Subsequent least-squares cycles and difference Fourier maps in the space group $P\bar{1}$ located the remaining 66 atoms. Anisotropic thermal parameters were assigned to the four Rh atoms and to the 16 O and N atoms in the coordination spheres of the rhodium atoms. Several more least-squares cycles led to convergence with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ having the values listed in Table I. The weighting factor w in R_2 is defined by $4F_o^2/\sigma(F_o^2)^2$. The error in an observation of unit weight (esd), also recorded in Table I, is given by $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of variables. The largest peak in the final difference map was located in the vicinity of O(10).

Compound 2. The space group $P2_1/n$ was determined uniquely from the systematic absences in the reflection data: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. A three-dimensional Patterson function was used to determine the position of one of the two independent rhodium atoms in $Rh_2(mhp)_4(CH_3CN)$ (**2**). The positions of the remaining 36 atoms were obtained with use of difference Fourier maps followed by least-squares refinement. All 37 atoms were given anisotropic thermal parameters, and the structure was smoothly refined to convergence with variation of all 334 parameters during the final three cycles. No peaks of structural significance were found in the final difference Fourier map.

Compound 3a. Systematic absences of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, were consistent with the space groups Cc or $C2/c$. The acentric space group was initially used but without success. In the space group $C2/c$ the positions of the two independent Rh atoms were located on a twofold rotation axis by using direct methods. Several difference Fourier maps followed by least-squares cycles were necessary to locate all of the atoms of the mhp and acetate groups.

The identity of the ligand in the axial position of Rh(2) was the last structural feature to be elucidated. The ligand was found to be situated along the twofold axis with the coordinating atom (assigned as N(2)) colinear with the Rh(1)–Rh(2) vector, which coincides with the C_2 axis. Two additional atoms, which were assigned to C(9) and C(10), comprise the rest of ligand which forms a five-membered heterocyclic ring. What appears to be the same ring was also identified in compounds **4** and **6** (vide infra), and after a careful consideration of the possible identities, the molecule was assigned as imidazole and coordination to rhodium through the imine nitrogen. Consequently, the secondary amine nitrogen of the imidazole, N(3), in **3a** is disordered about the twofold axis with C(10). Anisotropic temperature factors were given to the Rh atoms and the O and N atoms within the coordination spheres of the Rh atoms. The structure was refined to convergence with no prominent features in the final difference Fourier map.

Compound 3b. Systematic absences of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, suggested the space groups as Cc or $C2/c$. A Patterson map revealed a distribution of Rh–Rh vectors and their corresponding intensities which were quite analogous to those encountered in **3a**. Two Rh atoms were located on the crystallographic twofold axis 0, y, $^1/_4$. Four cycles of least-squares refinement with these two atoms produced $R_1 = 0.31$ and $R_2 = 0.40$. Subsequent difference Fourier maps followed by least-squares refinement located all 17 atoms in the dinuclear $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)$. In the imidazole ring the amine nitrogen, N(3), was assigned average scattering factors for C and N. At this point, a difference Fourier map revealed the presence of a methylene chloride molecule located on general positions in the lattice. One of the chlorine atoms, Cl(2), was refined with two different positions having unequal occupancies. Refinement of the occupancy factors suggested reasonable values for Cl(2A) and Cl(2B) of 0.7 and 0.3, respectively. With these occupancy factors held fixed, the entire structure was refined with anisotropic temperature factors for all atoms including the major and minor sites for Cl(2). Final residuals are given in Table I. The largest peak in the final difference Fourier map (Table I) was associated with the CH_2Cl_2 molecule.

Compound 4. Here again, it was necessary to resolve the space group ambiguity of Cc or $C2/c$. The statistical tests failed to differentiate clearly between the centric and acentric space groups. The positions of the two independent Rh atoms were obtained with use

Table IV

A. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)$ (3a)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.5000 (0)	0.3089 (1)	0.2500 (0)	2.63 (5)	2.40 (5)	2.46 (5)	0[b]	0.39 (4)	0[b]
Rh(2)	0.5000 (0)	0.4907 (1)	0.2500 (0)	2.87 (5)	2.31 (5)	2.70 (5)	0[b]	0.36 (4)	0[b]
O(1)	0.4134 (6)	0.3108 (6)	0.3549 (5)	3.0 (3)	3.0 (3)	2.8 (3)	−0.2 (3)	0.7 (2)	0.0 (3)
O(2)	0.5727 (7)	0.4819 (6)	0.1371 (5)	4.0 (3)	3.0 (4)	3.1 (3)	−0.5 (3)	1.3 (3)	−0.0 (3)
O(3)	0.6780 (7)	0.4905 (6)	0.3276 (5)	2.6 (3)	3.0 (4)	3.6 (4)	−0.2 (3)	−0.2 (3)	−0.4 (3)
N(1)	0.3239 (8)	0.3161 (7)	0.1641 (6)	3.3 (4)	2.9 (4)	2.6 (4)	−0.7 (4)	0.5 (3)	−0.3 (4)
N(2)	0.5000 (0)	0.6560 (9)	0.2500 (0)	2.1 (5)	2.3 (5)	3.1 (6)	0[b]	0.3 (4)	0[b]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
N(3)[c]	0.4365 (0)	0.8156 (0)	0.2257 (0)		C(6)	0.1478 (12)	0.2234 (10)	0.0743 (9)	4.1 (3)
C(1)	0.6040 (9)	0.3964 (10)	0.1112 (7)	2.9 (2)	C(7)	0.2661 (11)	0.2257 (9)	0.1322 (8)	3.4 (3)
C(2)	0.6687 (11)	0.3979 (11)	0.0306 (8)	4.2 (3)	C(8)	0.3381 (11)	0.1285 (9)	0.1649 (8)	4.0 (3)
C(3)	0.2655 (9)	0.4077 (9)	0.1415 (7)	2.9 (2)	C(9)	0.4007 (12)	0.7161 (10)	0.2095 (9)	4.1 (3)
C(4)	0.1447 (11)	0.4113 (10)	0.0802 (8)	3.6 (2)	C(10)	0.4365 (22)	0.8156 (20)	0.2257 (17)	3.9 (5)
C(5)	0.0894 (11)	0.3178 (10)	0.0491 (8)	3.8 (3)					

B. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)\cdot 2CH_2Cl_2$ (3b)[a,d]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.0000 (0)	0.32330 (7)	0.2500 (0)	1.75 (2)	2.36 (3)	4.14 (4)	0[b]	0.59 (2)	0[b]
Rh(2)	0.0000 (0)	0.13388 (7)	0.2500 (0)	1.85 (2)	2.39 (3)	2.78 (3)	0[b]	0.15 (2)	0[b]
Cl(1)	0.7300 (2)	0.4287 (3)	0.4240 (4)	8.2 (2)	8.6 (2)	13.1 (2)	−1.9 (2)	5.3 (1)	−5.0 (2)
Cl(2A)	0.7734 (3)	0.5954 (5)	0.5967 (5)	8.5 (2)	16.9 (4)	6.4 (2)	7.3 (2)	−2.1 (2)	−4.5 (2)
Cl(2B)	0.7568 (4)	0.6382 (8)	0.5215 (11)	7.5 (3)	5.3 (4)	17.2 (5)	−3.3 (3)	8.9 (2)	−4.9 (4)
O(1)	0.0805 (2)	0.3181 (4)	0.1941 (5)	2.2 (2)	3.0 (2)	4.4 (2)	−0.2 (2)	1.0 (2)	−0.0 (2)
O(2)	0.0798 (2)	0.1395 (4)	0.1944 (5)	2.7 (2)	3.2 (2)	4.1 (2)	0.5 (2)	1.2 (1)	−0.0 (2)
O(3)	−0.0634 (3)	0.1350 (4)	0.0604 (5)	3.1 (2)	3.3 (2)	3.3 (2)	−0.8 (2)	0.4 (2)	−0.5 (2)
N(1)	−0.0631 (3)	0.3183 (5)	0.0602 (6)	2.2 (2)	3.4 (3)	3.8 (3)	0.2 (2)	0.8 (2)	1.1 (2)
N(2)	0.0000 (0)	−0.0353 (7)	0.2500 (0)	4.1 (3)	2.0 (4)	4.5 (4)	0[b]	2.2 (3)	0[b]
N(3)[e]	0.0140 (4)	−0.2001 (6)	0.3200 (8)	5.5 (3)	2.4 (3)	9.3 (4)	0.8 (3)	4.5 (3)	1.5 (3)
C(1)	0.1030 (3)	0.2293 (7)	0.1781 (7)	2.2 (2)	3.8 (3)	3.9 (3)	0.4 (3)	0.9 (2)	0.3 (3)
C(2)	0.1623 (4)	0.2290 (8)	0.1358 (9)	3.0 (3)	4.9 (4)	6.7 (4)	−0.3 (3)	2.5 (2)	0.2 (4)
C(3)	−0.0832 (3)	0.2234 (7)	−0.0018 (7)	2.2 (2)	4.3 (4)	3.1 (3)	0.1 (3)	0.3 (2)	1.0 (3)
C(4)	−0.1251 (4)	0.2192 (9)	−0.1342 (8)	2.4 (3)	7.7 (6)	3.6 (3)	−0.8 (4)	0.0 (2)	0.6 (4)
C(5)	−0.1457 (4)	0.3152 (9)	−0.2008 (9)	2.4 (3)	7.7 (5)	4.5 (4)	0.3 (4)	0.2 (3)	2.8 (4)
C(6)	−0.1260 (4)	0.4107 (8)	−0.1390 (8)	3.3 (3)	6.6 (5)	6.0 (4)	1.4 (3)	1.8 (3)	4.1 (3)
C(7)	−0.0858 (4)	0.4118 (8)	−0.0091 (8)	2.8 (3)	5.0 (4)	6.2 (4)	1.1 (3)	1.9 (2)	2.8 (3)
C(8)	−0.0641 (5)	0.5119 (7)	0.0696 (10)	5.3 (4)	2.7 (4)	7.7 (5)	0.5 (3)	2.3 (3)	1.6 (4)
C(9)	0.0218 (4)	−0.0976 (7)	0.3580 (8)	3.9 (3)	3.7 (4)	5.9 (4)	1.1 (3)	2.5 (2)	2.2 (3)
C(20)	0.7124 (6)	0.5574 (10)	0.4534 (12)	6.2 (5)	8.8 (6)	7.3 (6)	4.4 (4)	−3.2 (5)	−3.3 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Value required by atom position. [c] This atom is disordered across the twofold axis with C(10). See C(10) parameters. [d] Positional and thermal parameters are for data collected at −111 °C. [e] This atom has average scattering factors for N and C.

of the direct-methods program MULTAN on the assumption of the centric $C2/c$ space group. An attempt was made to solve the structure in the acentric space group Cc but without success. Least-squares refinement followed by difference Fourier maps led to the positions of the remaining 37 atoms in the dinuclear unit. The amine nitrogen atom of the coordinated imidazole was identified after careful examination of peak intensities in the difference Fourier map and relative amplitudes of the isotropic temperature factors for N(6) and C(2) after least-squares refinement. An inspection of the interatomic distances about the imidazole ring at the conclusion of the refinement showed that the N(6) and C(2) atom types were consistent with their assigned values. Anisotropic temperature factors were assigned to all 39 atoms, and the structure was refined to discrepancy indices of $R_1 = 0.057$ and $R_2 = 0.099$. At this point, a difference Fourier map revealed the positions of the atoms of an acetonitrile molecule located on a twofold axis. Further refinement of all 42 atoms with isotropic thermal parameters for the acetonitrile atoms led to the discrepancy indices given in Table I. A final difference Fourier map showed an average background of ~0.9 e/Å^3 for the 50 highest peaks with the highest peak located in the vicinity of the acetonitrile molecule.

Compound 5. Systematic absences of $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, unambiguously identified $Pbca$ as the correct space group for $Rh_2(chp)_4$ (**5**). The coordinates of the two independent Rh atoms were obtained with use of the direct-methods program MULTAN. The remaining 32 atoms were located in subsequent least-squares cycles followed by difference Fourier maps. Anisotropic thermal parameters were assigned to the 12 Cl, O, and N atoms with the 20 carbon atoms retaining isotropic thermal parameters in the last least-squares cycles prior to convergence. A final difference synthesis revealed no additional features in the unit cell.

Compound 6. The space group $P4_2/n$ was determined uniquely from the systematic extinctions for compound **6**: $hk0$, $h + k = 2n + 1$, and $00l$, $l = 2n + 1$. The positions of the two independent Rh atoms were obtained with use of direct methods. Subsequent least-squares refinement followed by difference Fourier maps located all 39 atoms in the dinuclear unit. The axially coordinated ring was initially treated as four carbon atoms and the coordinating nitrogen atom N(5). The structure was refined to convergence with isotropic temperature factors for all 39 atoms, giving $R_1 = 0.091$ and $R_2 = 0.127$. At this point one of the carbon atoms of the imidazole ring was found to have a thermal parameter which was less than half of the lowest value for any of the other three carbon atoms. This atom was then reassigned as N(6), and the imidazole ring was now complete. Four additional atoms were found in the unit cell with no closely bonded neighbors (interatomic distances between these atoms ranged from 2.6 to 3.5 Å), and thus, the atoms were assigned as oxygen atoms of water molecules. Two of these oxygen atoms were found to be present at full occupancy (O(5) and O(6)) while the sites for O(7) and O(8) were found to be only 50% occupied. Anisotropic thermal parameters were given to the Rh, Cl, and O atoms and nitrogen atoms N(1)–N(5) while the remaining 28 atoms in the structure retained their isotropic thermal parameters. The structure was refined to convergence to the values shown in Table I. The final difference Fourier map showed the five highest peaks to be located in the vicinity of the Rh atoms.

No effort was made to locate the hydrogen atoms in any of the seven structures. Tables of observed and calculated structure factors for each of the seven compounds with $I > 3\sigma(I)$ are available.[24]

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[24] Supplementary material

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(mhp)_4(C_3H_4N_2)\cdot 0.5CH_3CN$ (4)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.64227 (4)	0.27079 (3)	0.64212 (1)	2.06 (2)	3.18 (2)	2.37 (2)	0.18 (2)	0.11 (2)	0.13 (2)
Rh(2)	0.50463 (4)	0.33504 (3)	0.59095 (1)	1.95 (2)	2.61 (2)	2.39 (2)	0.10 (1)	0.09 (1)	−0.05 (2)
O(1)	0.5341 (3)	0.2931 (3)	0.6866 (1)	3.0 (2)	4.9 (2)	2.2 (2)	−0.1 (2)	0.2 (1)	0.2 (2)
O(2)	0.5404 (4)	0.4484 (3)	0.6201 (1)	2.9 (2)	3.3 (2)	3.7 (2)	0.0 (2)	−0.3 (2)	−0.8 (2)
O(3)	0.4817 (4)	0.2201 (3)	0.5626 (1)	3.9 (2)	2.9 (2)	2.6 (2)	−0.1 (2)	0.1 (2)	−0.5 (2)
O(4)	0.6397 (3)	0.3577 (3)	0.5561 (1)	2.3 (2)	3.5 (2)	3.3 (2)	0.3 (1)	0.6 (1)	0.8 (2)
N(1)	0.3837 (4)	0.3088 (3)	0.6336 (2)	2.4 (2)	3.6 (2)	2.7 (2)	0.0 (2)	0.3 (2)	−0.6 (2)
N(2)	0.7024 (4)	0.3919 (3)	0.6560 (2)	2.4 (2)	3.7 (2)	2.8 (2)	−0.1 (2)	0.5 (2)	−0.4 (2)
N(3)	0.5661 (4)	0.1577 (3)	0.6244 (2)	2.8 (2)	3.2 (2)	3.6 (2)	0.1 (2)	0.6 (2)	0.2 (2)
N(4)	0.7490 (4)	0.2568 (3)	0.5945 (2)	1.9 (2)	3.2 (2)	2.6 (2)	0.2 (2)	0.3 (2)	0.1 (2)
N(5)	0.4068 (4)	0.3976 (3)	0.5385 (2)	2.9 (2)	2.9 (2)	3.4 (2)	0.4 (2)	0.1 (2)	0.6 (2)
N(6)	0.3553 (5)	0.4976 (4)	0.4917 (2)	2.9 (2)	4.9 (3)	5.7 (3)	1.3 (2)	0.9 (2)	2.2 (2)
N(7)	0.5000 (0)	0.649 (1)	0.7500 (0)	12.7 (5)[b]					
C(1)	0.3972 (5)	0.4815 (4)	0.5323 (2)	2.3 (2)	3.9 (3)	5.5 (3)	0.3 (2)	0.6 (3)	1.1 (3)
C(2)	0.3366 (6)	0.4223 (5)	0.4707 (2)	2.8 (3)	6.0 (4)	4.6 (3)	1.0 (3)	0.4 (3)	0.9 (3)
C(3)	0.3679 (6)	0.3601 (5)	0.5000 (2)	3.2 (3)	5.1 (3)	2.8 (3)	0.3 (3)	−0.3 (2)	0.1 (3)
C(11)	0.4242 (5)	0.2979 (4)	0.6753 (2)	2.8 (2)	3.1 (3)	2.8 (2)	0.2 (2)	0.5 (2)	−0.2 (2)
C(12)	0.3523 (6)	0.2936 (5)	0.7082 (2)	3.2 (3)	4.6 (3)	4.2 (3)	0.6 (3)	1.6 (2)	0.1 (3)
C(13)	0.2372 (6)	0.2893 (5)	0.6972 (3)	3.8 (3)	5.7 (4)	5.1 (4)	−0.7 (3)	1.5 (3)	−0.2 (3)
C(14)	0.1944 (6)	0.2935 (5)	0.6535 (2)	3.6 (3)	4.3 (3)	4.8 (3)	0.3 (3)	1.3 (3)	0.4 (3)
C(15)	0.2693 (5)	0.3025 (4)	0.6237 (2)	2.6 (2)	2.8 (2)	4.0 (3)	−0.1 (2)	0.7 (2)	−0.6 (2)
C(16)	0.2218 (6)	0.3041 (6)	0.5770 (3)	2.8 (3)	8.2 (5)	4.0 (3)	−1.2 (3)	−0.4 (3)	0.2 (4)
C(21)	0.6361 (5)	0.4593 (4)	0.6432 (2)	2.2 (2)	3.7 (3)	3.5 (3)	0.1 (2)	0.6 (2)	−0.5 (2)
C(22)	0.6664 (6)	0.5447 (5)	0.6552 (3)	3.9 (3)	4.1 (3)	6.4 (4)	−0.9 (3)	0.2 (3)	−1.3 (3)
C(23)	0.7709 (7)	0.5545 (6)	0.6823 (3)	5.1 (4)	5.2 (4)	7.5 (5)	−0.4 (3)	−1.1 (4)	−2.5 (4)
C(24)	0.8329 (6)	0.4879 (5)	0.6954 (3)	3.1 (3)	7.0 (4)	5.4 (4)	−2.3 (3)	−0.3 (3)	−2.3 (3)
C(25)	0.8003 (5)	0.4045 (5)	0.6822 (2)	2.9 (3)	5.5 (3)	2.9 (3)	−0.7 (3)	0.3 (2)	−0.7 (3)
C(26)	0.8714 (6)	0.3281 (5)	0.6943 (3)	3.2 (3)	6.3 (4)	4.7 (4)	0.6 (3)	−0.7 (3)	−0.4 (3)
C(31)	0.5071 (5)	0.1522 (4)	0.5848 (2)	3.1 (3)	3.0 (3)	3.0 (3)	0.2 (2)	0.5 (2)	−0.3 (2)
C(32)	0.4759 (6)	0.0723 (5)	0.5670 (3)	4.1 (3)	3.2 (3)	6.9 (4)	−0.2 (3)	0.2 (3)	−0.5 (3)
C(33)	0.4984 (8)	−0.0024 (6)	0.5910 (3)	6.4 (5)	4.8 (4)	8.0 (6)	−0.5 (4)	0.8 (4)	−0.6 (4)
C(34)	0.5515 (8)	0.0060 (5)	0.6336 (3)	7.1 (5)	3.7 (3)	6.9 (5)	0.9 (3)	1.7 (4)	1.5 (3)
C(35)	0.5815 (5)	0.0847 (4)	0.6493 (2)	3.0 (3)	3.6 (3)	5.1 (3)	0.5 (2)	0.5 (3)	1.3 (3)
C(36)	0.6307 (7)	0.0977 (6)	0.6963 (3)	6.3 (4)	6.1 (4)	4.1 (3)	1.0 (4)	0.5 (3)	1.6 (3)
C(41)	0.7320 (5)	0.3124 (4)	0.5608 (2)	2.0 (2)	3.5 (3)	2.9 (3)	−0.4 (2)	0.0 (2)	−0.2 (2)
C(42)	0.8142 (5)	0.3223 (4)	0.5310 (2)	2.0 (2)	4.3 (3)	3.1 (3)	0.3 (2)	0.2 (2)	−0.2 (2)
C(43)	0.9061 (6)	0.2704 (5)	0.5334 (2)	3.1 (3)	5.0 (3)	3.5 (3)	0.2 (3)	0.2 (2)	−0.6 (3)
C(44)	0.9194 (6)	0.2078 (5)	0.5669 (2)	2.7 (3)	4.4 (3)	4.4 (3)	−0.4 (2)	0.4 (2)	−0.6 (3)
C(45)	0.8419 (5)	0.2040 (4)	0.5967 (2)	2.5 (2)	3.5 (3)	3.7 (3)	0.4 (2)	0.1 (2)	−0.7 (3)
C(46)	0.8506 (6)	0.1364 (5)	0.6307 (3)	3.5 (3)	5.9 (4)	4.9 (3)	1.9 (3)	0.9 (3)	1.9 (3)
C(4)	0.5000 (0)	0.581 (1)	0.7500 (0)	10.1 (5)[b]					
C(5)	0.5000 (0)	0.486 (2)	0.7500 (0)	13.1 (7)[b]					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
[b] B values in Å^2.

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(chp)_4$ (**5**)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.33681 (6)	0.42819 (4)	0.37348 (6)	2.84 (4)	2.22 (3)	2.30 (3)	−0.18 (3)	0.00 (4)	−0.11 (4)
Rh(2)	0.29392 (6)	0.30665 (4)	0.37650 (6)	3.79 (4)	2.18 (3)	2.44 (3)	−0.22 (3)	0.30 (4)	−0.17 (4)
Cl(16)	0.3512 (3)	0.5621 (2)	0.2586 (2)	8.1 (2)	3.3 (1)	4.0 (1)	−1.5 (2)	−0.6 (2)	0.3 (1)
Cl(26)	0.1402 (3)	0.2081 (2)	0.3842 (3)	6.6 (2)	3.4 (1)	9.2 (3)	−1.9 (1)	0.3 (2)	−0.7 (2)
Cl(36)	0.3616 (3)	0.1523 (2)	0.3918 (2)	7.9 (2)	3.4 (1)	5.7 (2)	−0.1 (2)	3.0 (2)	0.3 (1)
Cl(46)	0.4076 (2)	0.5495 (2)	0.4845 (2)	4.7 (2)	3.2 (1)	3.6 (1)	−0.8 (1)	0.1 (1)	−0.1 (1)
O(1)	0.2820 (5)	0.3077 (4)	0.2464 (5)	6.0 (5)	2.6 (3)	2.8 (3)	−0.3 (4)	−0.1 (4)	−0.8 (3)
O(2)	0.2192 (5)	0.4595 (4)	0.3948 (5)	4.1 (4)	2.3 (3)	3.9 (4)	0.3 (3)	0.3 (3)	−1.0 (3)
O(3)	0.4548 (4)	0.3983 (4)	0.3491 (5)	1.8 (3)	4.0 (4)	4.6 (4)	−0.2 (3)	−0.2 (3)	0.1 (3)
O(4)	0.3047 (6)	0.3047 (4)	0.5061 (5)	7.3 (5)	2.6 (3)	2.4 (3)	−0.6 (4)	−0.1 (4)	0.4 (3)
N(1)	0.3160 (6)	0.4281 (5)	0.2443 (6)	3.8 (5)	2.7 (4)	2.1 (4)	0.3 (4)	0.1 (4)	−0.3 (4)
N(2)	0.1724 (6)	0.3421 (5)	0.3879 (5)	3.2 (4)	3.2 (4)	2.5 (4)	−1.1 (4)	0.8 (4)	−0.0 (4)
N(3)	0.4194 (6)	0.2807 (4)	0.3660 (6)	3.8 (5)	2.2 (3)	2.7 (4)	0.6 (4)	0.0 (4)	−0.0 (4)
N(4)	0.3551 (5)	0.4188 (5)	0.5033 (6)	1.4 (3)	3.3 (4)	2.8 (4)	0.1 (3)	−0.5 (3)	−0.2 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.2915 (7)	0.3651 (6)	0.2033 (7)	3.0 (2)	C(31)	0.4756 (7)	0.3311 (6)	0.3525 (7)	2.9 (2)
C(12)	0.2784 (7)	0.3674 (6)	0.1093 (8)	3.4 (3)	C(32)	0.5619 (9)	0.3115 (7)	0.3420 (8)	4.3 (3)
C(13)	0.2852 (8)	0.4305 (7)	0.0674 (8)	4.3 (3)	C(33)	0.5815 (10)	0.2413 (8)	0.3499 (10)	5.9 (4)
C(14)	0.3107 (8)	0.4948 (7)	0.1100 (8)	4.1 (3)	C(34)	0.5276 (9)	0.1899 (7)	0.3678 (9)	5.0 (3)
C(15)	0.3247 (8)	0.4880 (6)	0.1969 (8)	3.2 (2)	C(35)	0.4429 (8)	0.2122 (6)	0.3714 (8)	3.7 (2)
C(21)	0.1564 (7)	0.4140 (6)	0.3938 (7)	3.0 (2)	C(41)	0.3373 (7)	0.3576 (6)	0.5465 (7)	2.6 (2)
C(22)	0.0701 (9)	0.4400 (7)	0.3999 (8)	4.4 (3)	C(42)	0.3528 (7)	0.3531 (6)	0.6368 (8)	3.4 (2)
C(23)	0.0116 (10)	0.3867 (8)	0.3999 (11)	6.2 (4)	C(43)	0.3852 (9)	0.4122 (7)	0.6776 (9)	4.4 (3)
C(24)	0.0293 (10)	0.3132 (8)	0.3970 (9)	5.2 (3)	C(44)	0.4075 (8)	0.4758 (7)	0.6349 (8)	4.2 (3)
C(25)	0.1108 (8)	0.2970 (7)	0.3896 (8)	4.3 (3)	C(45)	0.3872 (7)	0.4752 (6)	0.5471 (8)	3.4 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table VII. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(chp)_4(C_3H_4N_2)\cdot 3H_2O$ (6)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.68313 (5)	0.08729 (5)	0.38278 (8)	2.63 (4)	3.17 (5)	2.14 (4)	−0.52 (4)	0.27 (4)	−0.16 (4)
Rh(2)	0.62203 (5)	0.00089 (5)	0.35982 (8)	2.98 (5)	2.88 (5)	2.22 (4)	−0.45 (4)	0.39 (4)	−0.24 (4)
Cl(16)	0.5231 (2)	−0.0225 (2)	0.1513 (3)	4.1 (2)	7.3 (2)	4.6 (2)	−2.0 (2)	−0.1 (2)	−0.1 (2)
Cl(26)	0.8073 (2)	0.1270 (2)	0.4892 (3)	4.0 (2)	7.2 (2)	4.2 (2)	−1.8 (2)	0.1 (2)	−1.8 (2)
Cl(36)	0.6869 (2)	0.2168 (2)	0.2682 (3)	4.7 (2)	4.1 (2)	4.9 (2)	−1.4 (2)	0.1 (2)	0.9 (2)
Cl(46)	0.6785 (2)	0.2066 (2)	0.5374 (3)	4.9 (2)	3.4 (2)	3.7 (2)	−0.7 (2)	0.1 (2)	−0.5 (1)
O(1)	0.7143 (4)	0.0721 (4)	0.2331 (7)	2.2 (4)	5.0 (5)	2.7 (4)	−1.3 (4)	0.7 (3)	0.5 (4)
O(2)	0.6976 (4)	−0.0495 (4)	0.3643 (7)	3.6 (4)	3.0 (4)	4.5 (5)	0.2 (4)	1.0 (4)	−1.2 (4)
O(3)	0.5493 (4)	0.0553 (4)	0.3665 (7)	3.1 (4)	3.3 (4)	3.5 (4)	0.2 (4)	0.9 (4)	−0.9 (4)
O(4)	0.6206 (4)	−0.0056 (4)	0.5219 (6)	5.3 (5)	3.1 (4)	2.0 (4)	−0.1 (4)	0.5 (4)	−0.9 (4)
N(1)	0.6313 (5)	0.0145 (5)	0.1968 (8)	3.8 (6)	3.2 (5)	2.4 (5)	−0.6 (5)	−0.6 (5)	0.0 (4)
N(2)	0.7496 (5)	0.0300 (5)	0.4314 (8)	2.7 (5)	4.9 (6)	1.7 (4)	0.3 (5)	1.4 (4)	0.8 (5)
N(3)	0.6099 (5)	0.1356 (5)	0.3266 (8)	2.6 (5)	3.1 (5)	1.5 (4)	−0.8 (4)	−0.4 (4)	−0.3 (4)
N(4)	0.6501 (5)	0.0937 (5)	0.5361 (8)	3.2 (5)	2.9 (5)	2.6 (5)	−0.3 (5)	0.4 (4)	−0.6 (4)
N(5)	0.5700 (5)	−0.0788 (5)	0.3611 (8)	3.4 (5)	3.1 (5)	2.6 (5)	−0.5 (4)	0.8 (5)	−0.4 (5)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(5)	0.3472 (9)	0.1211 (9)	0.398 (2)	14.9 (6)	C(21)	0.7430 (6)	−0.0292 (6)	0.416 (1)	3.6 (3)
O(6)	0.3515 (11)	0.2813 (11)	0.707 (2)	19.1 (9)	C(22)	0.7880 (8)	−0.0700 (7)	0.449 (1)	5.2 (4)
O(7)	0.3613 (19)	0.2507 (21)	0.480 (4)	16.3 (14)	C(23)	0.8416 (8)	−0.0472 (8)	0.499 (1)	5.7 (4)
O(8)	0.3731 (21)	0.3261 (20)	0.308 (4)	16.9 (16)	C(24)	0.8468 (7)	0.0139 (7)	0.511 (1)	4.5 (4)
N(6)	0.5026 (5)	−0.1435 (5)	0.4180 (9)	3.4 (2)	C(25)	0.8014 (7)	0.0507 (7)	0.479 (1)	4.0 (3)
					C(31)	0.5566 (6)	0.1108 (6)	0.333 (1)	3.0 (3)
C(1)	0.5274 (7)	−0.0887 (7)	0.429 (1)	4.4 (4)	C(32)	0.5045 (7)	0.1439 (7)	0.308 (1)	3.9 (3)
C(2)	0.5325 (8)	−0.1686 (8)	0.336 (1)	6.0 (4)	C(33)	0.5121 (7)	0.2016 (7)	0.270 (1)	4.2 (3)
C(3)	0.5748 (8)	−0.1299 (8)	0.300 (1)	5.7 (4)	C(34)	0.5683 (7)	0.2258 (6)	0.259 (1)	3.6 (3)
C(11)	0.6833 (6)	0.0434 (6)	0.165 (1)	3.3 (3)	C(35)	0.6144 (6)	0.1899 (6)	0.285 (1)	3.2 (3)
C(12)	0.7033 (7)	0.0393 (7)	0.056 (1)	4.1 (3)	C(41)	0.6243 (6)	0.0426 (6)	0.578 (1)	2.8 (3)
C(13)	0.6670 (7)	0.0156 (6)	−0.017 (1)	3.7 (3)	C(42)	0.6032 (6)	0.0409 (6)	0.685 (1)	3.5 (3)
C(14)	0.6092 (7)	−0.0046 (7)	0.008 (1)	4.4 (3)	C(43)	0.6055 (7)	0.0940 (7)	0.746 (1)	4.2 (3)
C(15)	0.5942 (7)	−0.0029 (6)	0.117 (1)	3.9 (3)	C(44)	0.6282 (7)	0.1482 (7)	0.701 (1)	3.7 (3)
					C(45)	0.6497 (6)	0.1447 (6)	0.597 (1)	3.0 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Results

The positional and thermal parameters for each of the seven compounds are presented in Tables II–VII, and the bond lengths and angles are given in Tables VIII–XIII. Table XIV lists the torsional angles about the Rh–Rh bond in each of the seven compounds, and Table XV[24] compiles the least-squares planes and dihedral angles. The salient features of each structure will now be described.

$Rh_2(mhp)_4\cdot H_2O$ (1). This compound crystallizes in the triclinic space group $P\bar{1}$ with two independent dimers and lattice water molecules comprising the asymmetric unit. Figure 1 illustrates molecules A and B of $Rh_2(mhp)_4$, each of which consists of a dirhodium(II) unit with four mhp bridging ligands with the Rh–N and Rh–O bonds trans to their own kind. The Rh–Rh bond lengths are 2.370 (1) and 2.365 (1) Å for molecules A and B, respectively. Each molecule is completely devoid of axial ligands. The water molecules occupy general positions in the unit cell and do not interact in any way with the dirhodium(II) units. However, the water molecules participate in hydrogen-bonded contacts (<3.5 Å) with each other and with portions of the mhp ligands. Figure 2 presents a stereoview of the unit cell contents and points out the rather subtle differences between the two dirhodium molecules. All of the mhp rings are essentially planar (see Table XV[24]). Molecule A has nearly an eclipsed conformation for the bridging mhp ligands with a mean torsional angle of 1.0° while molecule B presents a much less eclipsed conformation with an average torsional angle of 9.3°.

$Rh_2(mhp)_4(CH_3CN)$ (2). The molecular structure consists of four mhp ligands disposed about the rhodium(II) unit with a coordinated acetonitrile molecule as depicted in Figure 3. There is no crystallographic symmetry imposed upon this molecular unit. The Rh–Rh bond is slightly longer (0.002–0.007 Å) than those in either molecule A or B in **1** although the difference between **1**A and **2** is within the limits of statistical indistinguishability. The Rh(2)–N(5) bond length of 2.152 (7) Å is only slightly longer than those for the other Rh–N bonds. The acetonitrile molecule coordinates with a Rh(1)–Rh(2)–N(5) angle of 169.5 (2)° and is itself essentially linear with a N(5)–C(1)–C(2) angle of 178 (2)°. The most striking feature of the structure is the arrangement and orientation of the mhp ligands about the Rh–Rh bond. Two of the ligands adopt a trans arrangement while the other two are cis. The pyridine rings of the mhp ligands are planar (see Table XV[24]), but the torsion angles (average = 23°) in Table XIV point out the degree of distortion from the eclipsed conformation.

$Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)$ (3a). This unusual molecule is shown in Figure 4. The structure consists of two $CH_3CO_2^-$ and two mhp ligands arranged in a trans fashion about the Rh–Rh bond. Each ligand is related by a twofold rotation to its trans partner. The Rh–Rh bond, collinear with the C_2 axis, has a length of 2.388 (2) Å. The axial position of Rh(1) is empty, apparently blocked by the two methyl groups of the mhp ligand. In contrast, Rh(2) has a nitrogen atom, N(2), coordinated in the axial position along the C_2 axis at a distance of 2.17 (1) Å. All of the coordinated ligands in **3a** are essentially planar (Table XV[24]).

The five-membered heterocyclic ring has nearly equivalent bond lengths (1.36–1.40 Å). The ring, by analogy with the five-membered rings found in structures **4** and **6**, has been assigned as an imidazole molecule in which atoms N(3) and C(10) are disordered across the twofold axis along Rh(1)–Rh(2)–N(2). The imidazole plane makes a dihedral angle of 7.1° with the bridging mhp ligands. Two different Rh sites are found in the complex. Rh(1) has a planar *trans*-N_2O_2 set of ligands; they together with the bond to Rh(2) impart a five-coordinate square-pyramidal geometry to Rh(1). Rh(2) has an octahedral set of ligands consisting of four approximately planar oxygen atoms with Rh(1) and N(2) completing the octahedron.

Table VIII. Bond Distances (A) and Angles (Deg) for $Rh_2(mhp)_4 \cdot H_2O$ (1)

Distances

Rh(1)-Rh(2)	2.370 (1)	N(8)-C(85)	1.36 (1)	O(4)-C(41)	1.32 (1)	C(51)-C(52)	1.42 (1)
-O(2)	2.018 (5)	C(11)-C(12)	1.42 (1)	O(5)-C(51)	1.32 (1)	C(52)-C(53)	1.37 (1)
-O(3)	2.017 (5)	C(12)-C(13)	1.33 (1)	O(6)-C(61)	1.30 (1)	C(53)-C(54)	1.39 (1)
-N(1)	2.038 (5)	C(13)-C(14)	1.44 (1)	O(7)-C(71)	1.32 (1)	C(54)-C(55)	1.41 (1)
-N(4)	2.052 (5)	C(14)-C(15)	1.38 (1)	O(8)-C(81)	1.30 (1)	C(55)-C(56)	1.52 (1)
Rh(2)-O(1)	2.019 (5)	C(15)-C(16)	1.52 (1)	N(1)-C(11)	1.37 (1)	C(61)-C(62)	1.43 (1)
-O(4)	2.029 (5)	C(21)-C(22)	1.43 (1)	N(1)-C(15)	1.38 (1)	C(62)-C(63)	1.41 (1)
-N(2)	2.053 (8)	C(22)-C(23)	1.39 (1)	N(2)-C(21)	1.34 (1)	C(63)-C(64)	1.40 (1)
-N(3)	2.038 (7)	C(23)-C(24)	1.38 (1)	-C(25)	1.38 (1)	C(64)-C(65)	1.39 (1)
Rh(3)-Rh(4)	2.365 (1)	C(24)-C(25)	1.39 (1)	N(3)-C(31)	1.36 (1)	C(65)-C(66)	1.49 (1)
-O(6)	2.018 (5)	C(25)-C(26)	1.51 (1)	-C(35)	1.37 (1)	C(71)-C(72)	1.42 (1)
-O(8)	2.014 (5)	C(31)-C(32)	1.41 (1)	N(4)-C(41)	1.35 (1)	C(72)-C(73)	1.40 (1)
-N(5)	2.039 (9)	C(32)-C(33)	1.39 (1)	C(45)	1.387 (9)	C(73)-C(74)	1.36 (1)
-N(7)	2.041 (10)	C(33)-C(34)	1.40 (1)	N(5)-C(51)	1.36 (1)	C(74)-C(75)	1.41 (1)
Rh(4)-O(5)	2.017 (5)	C(34)-C(35)	1.35 (1)	-C(55)	1.348 (9)	C(75)-C(76)	1.51 (1)
O(7)	2.029 (5)	C(35)-C(36)	1.53 (1)	N(6)-C(61)	1.34 (1)	C(81)-C(82)	1.43 (1)
-N(6)	2.030 (7)	C(41)-C(42)	1.40 (1)	-C(65)	1.36 (1)	C(82)-C(83)	1.39 (1)
-N(8)	2.037 (7)	C(42)-C(43)	1.37 (1)	N(7)-C(71)	1.33 (1)	C(83)-C(84)	1.38 (1)
O(1)-C(11)	1.30 (1)	C(43)-C(44)	1.45 (1)	-C(75)	1.39 (1)	C(84)-C(85)	1.40 (2)
O(2)-C(21)	1.28 (1)	C(44)-C(45)	1.35 (1)	N(8)-C(81)	1.36 (1)	C(85)-C(86)	1.52 (2)
O(3)-C(31)	1.30 (1)	C(45)-C(46)	1.50 (1)				

Angles

Rh(2)-Rh(1)-O(2)	89.8 (1)	O(1)-C(11)-N(1)	120.2 (8)	O(7)-Rh(4)-N(6)	90.3 (3)	O(5)-C(51)-C(52)	119.4 (8)
-O(3)	90.1 (1)	-C(12)	120.8 (8)	-N(8)	90.3 (3)	N(5)-C(51)-C(52)	119.8 (8)
-N(1)	87.9 (2)	N(1)-C(11)-C(12)	118.9 (8)	N(6)-Rh(4)-N(8)	176.3 (2)	C(51)-C(52)-C(53)	119.9 (8)
-N(4)	88.2 (2)	C(11)-C(12)-C(13)	122.3 (8)	Rh(2)-O(1)-C(11)	120.6 (5)	C(52)-C(53)-C(54)	119.4 (7)
O(2)-Rh(1)-O(3)	179.8 (2)	C(12)-C(13)-C(14)	118.7 (8)	Rh(1)-O(2)-C(21)	121.6 (6)	C(53)-C(54)-C(55)	119.3 (7)
-N(1)	89.0 (2)	C(13)-C(14)-C(15)	118.9 (8)	Rh(1)-O(3)-C(31)	121.4 (5)	N(5)-C(55)-C(54)	120.9 (8)
-N(4)	90.6 (2)	N(1)-C(15)-C(14)	121.7 (7)	Rh(2)-O(4)-C(41)	120.9 (5)	-C(56)	118.0 (7)
O(3)-Rh(1)-N(1)	91.0 (2)	-C(16)	115.0 (6)	Rh(4)-O(5)-C(51)	119.7 (5)	C(54)-C(55)-C(56)	121.0 (7)
-N(4)	89.3 (2)	C(14)-C(15)-C(16)	123.3 (7)	Rh(3)-O(6)-C(61)	120.4 (6)	O(6)-C(61)-N(6)	120.4 (9)
N(1)-Rh(1)-N(4)	176.1 (3)	O(2)-C(21)-N(2)	120.2 (9)	Rh(4)-O(7)-C(71)	120.2 (5)	-C(62)	119.5 (9)
Rh(1)-Rh(2)-O(1)	90.6 (1)	-C(22)	119.6 (8)	Rh(3)-O(8)-C(81)	119.9 (5)	N(6)-C(61)-C(62)	120.0 (9)
-O(4)	90.1 (1)	N(2)-C(21)-C(22)	120.3 (9)	Rh(1)-N(1)-C(11)	120.6 (6)	C(61)-C(62)-C(63)	118.9 (8)
-N(2)	87.5 (2)	C(21)-C(22)-C(23)	118.4 (8)	-C(15)	119.9 (4)	C(62)-C(63)-C(64)	118.9 (8)
-N(3)	87.8 (2)	C(22)-C(23)-C(24)	120.6 (8)	C(11)-N(1)-C(15)	119.5 (6)	C(63)-C(64)-C(65)	119.2 (9)
O(1)-Rh(2)-O(4)	178.9 (2)	C(23)-C(24)-C(25)	119.8 (9)	Rh(2)-N(2)-C(21)	120.8 (6)	N(6)-C(65)-C(64)	121.4 (7)
-N(2)	89.3 (2)	N(2)-C(25)-C(24)	119.9 (8)	-C(25)	118.0 (6)	-C(66)	117.3 (6)
-N(3)	89.3 (2)	N(2)-C(25)-C(26)	116.9 (7)	C(21)-N(2)-C(25)	121.0 (8)	C(64)-C(65)-C(66)	121.3 (7)
O(4)-Rh(2)-N(2)	91.6 (2)	C(24)-C(25)-C(26)	123.1 (7)	Rh(2)-N(3)-C(31)	121.1 (6)	O(7)-C(71)-N(7)	119.3 (8)
-N(3)	89.8 (2)	O(3)-C(31)-N(3)	119.5 (8)	-C(35)	120.3 (4)	-C(72)	119.4 (7)
N(2)-Rh(2)-N(3)	175.1 (3)	O(3)-C(31)-C(32)	119.8 (8)	C(31)-N(3)-C(35)	118.5 (7)	N(7)-C(71)-C(72)	121.2 (8)
Rh(4)-Rh(3)-O(6)	89.2 (1)	N(3)-C(31)-C(32)	120.7 (8)	Rh(1)-N(4)-C(41)	120.8 (5)	C(71)-C(72)-C(73)	117.9 (8)
Rh(4)-Rh(3)-O(8)	89.8 (1)	C(31)-C(32)-C(33)	119.4 (8)	-C(45)	118.8 (6)	C(72)-C(73)-C(74)	120.6 (8)
-N(5)	88.4 (1)	C(32)-C(33)-C(34)	118.7 (7)	C(41)-N(4)-C(45)	120.4 (6)	C(73)-C(74)-C(75)	120.0 (8)
-N(7)	87.7 (1)	C(33)-C(34)-C(35)	119.8 (8)	Rh(3)-N(5)-C(51)	119.5 (5)	N(7)-C(75)-C(74)	119.3 (7)
O(6)-Rh(3)-O(8)	178.9 (2)	N(3)-C(35)-C(34)	122.7 (7)	-C(55)	119.9 (6)	C(76)	116.2 (6)
-N(5)	90.4 (2)	-C(36)	113.8 (6)	C(51)-N(5)-C(55)	120.6 (8)	C(74)-C(75)-C(76)	124.5 (7)
-N(7)	90.3 (2)	C(34)-C(35)-C(36)	123.5 (7)	Rh(4)-N(6)-C(61)	120.2 (6)	O(8)-C(81)-N(8)	121.3 (8)
O(8)-Rh(3)-N(5)	89.6 (2)	O(4)-C(41)-N(4)	119.9 (7)	-C(65)	118.4 (4)	-C(82)	119.0 (7)
N(5)-Rh(3)-N(7)	176.1 (2)	N(4)-C(41)-C(42)	120.8 (8)	C(61)-N(6)-C(65)	121.4 (7)	N(8)-C(81)-C(82)	119.8 (8)
Rh(3)-Rh(4)-O(5)	90.1 (1)	C(41)-C(42)-C(43)	120.2 (8)	Rh(3)-N(7)-C(71)	121.4 (7)	C(81)-C(82)-C(83)	119.3 (8)
-O(7)	89.2 (1)	C(42)-C(43)-C(44)	118.0 (7)	-C(75)	117.9 (5)	C(82)-C(83)-C(84)	119.3 (8)
-N(6)	88.0 (1)	C(43)-C(44)-C(45)	119.8 (7)	C(71)-N(7)-C(75)	120.6 (9)	C(83)-C(84)-C(85)	120 (1)
-N(8)	88.3 (1)	N(4)-C(45)-C(44)	120.8 (7)	Rh(4)-N(8)-C(81)	119.2 (5)	N(8)-C(85)-C(84)	121 (1)
O(5)-Rh(4)-O(7)	179.1 (2)	-C(46)	116.2 (6)	-C(85)	119.9 (7)	-C(86)	116 (1)
-N(6)	89.2 (3)	C(44)-C(45)-C(46)	122.9 (7)	C(81)-N(8)-C(85)	120.8 (9)	C(84)-C(85)-C(86)	123 (1)
-N(8)	90.2 (3)	O(5)-C(51)-N(5)	120.8 (8)				

$Rh_2(mhp)_2(OAc)_2(C_3H_4N_2) \cdot 2CH_2Cl_2$ (3b). The dirhodium(II) unit in this compound is essentially identical with that in **3a**, and Figure 4 serves to provide the labeling scheme and ligand arrangement for **3b**. The Rh-Rh bond length (2.388 (1) Å) is the same, but the Rh(2)-N(2) distance of 2.133 (7) Å is significantly shorter (by 0.039 Å) than the corresponding value in **3a**. The acetate, the pyridine ring in the mhp ligand, and the imidazole ring are all strictly planar (Table XV[24]). Both acetate and mhp torsional angles (Table XIV) are near 0° (±0.2°). Eight CH_2Cl_2 molecules are located on general positions within the unit cell. Figure 5 provides a stereoscopic view of the relative orientations of the dirhodium and CH_2Cl_2 molecules within the unit cell. The five-membered imidazole ring makes an angle of 13.3° with the mhp ligand in **3b**, whereas in **3a** this angle is only 7.1°.

$Rh_2(mhp)_4(C_3H_4N_2) \cdot 0.5CH_3CN$ (4). Compound **4** crystallizes in the space group *C*2/*c* with eight dinuclear units in the unit cell and four acetonitrile molecules. The structure of the dinuclear unit, illustrated in Figure 6, is not constrained by any crystallographically imposed symmetry. The acetonitrile molecules, however, reside on crystallographic twofold axes throughout the lattice. No appreciable interactions exist between the dinuclear units and the acetonitrile molecules. The shortest intermolecular contacts are 3.56 (1), 3.960 (6), and 3.66 (2) Å for N(7)···C(26), N(7)···C(46), and C(5)···O(1) distances, respectively. The molecular packing within the unit cell is represented in Figure 7, and this provides the best opportunity to view conformation of the mhp and imidazole ligands about the dirhodium bond axis.

The mhp and imidazole ligands are planar. The six atoms

Table IX. Bond Distances (Å) and Angles (Deg) for $Rh_2(mhp)_4(CH_3CN)$ (**2**)

Distances

Rh(1)-Rh(2)	2.372 (1)	N(5)-C(1)	1.12 (1)
-O(1)	2.015 (5)	C(1)-C(2)	1.38 (1)
-N(2)	2.067 (5)	C(11)-C(12)	1.44 (1)
-N(3)	2.073 (5)	C(12)-C(13)	1.40 (1)
-N(4)	2.031 (6)	C(13)-C(14)	1.42 (1)
Rh(2)-O(2)	2.015 (5)	C(14)-C(15)	1.38 (1)
-O(3)	2.018 (5)	C(15)-C(16)	1.49 (1)
-O(4)	2.027 (4)	C(21)-C(22)	1.44 (1)
-N(1)	2.080 (6)	C(22)-C(23)	1.40 (1)
-N(5)	2.152 (7)	C(23)-C(24)	1.41 (1)
O(1)-C(11)	1.276 (9)	C(24)-C(25)	1.37 (1)
O(2)-C(21)	1.304 (8)	C(25)-C(26)	1.51 (1)
O(3)-C(31)	1.283 (9)	C(31)-C(32)	1.42 (1)
O(4)-C(41)	1.284 (8)	C(32)-C(33)	1.35 (1)
N(1)-C(11)	1.36 (1)	C(33)-C(34)	1.41 (1)
-C(15)	1.369 (9)	C(34)-C(35)	1.39 (1)
N(2)-C(21)	1.352 (9)	C(35)-C(36)	1.52 (1)
-C(25)	1.370 (9)	C(41)-C(42)	1.43 (1)
N(3)-C(31)	1.367 (9)	C(42)-C(43)	1.36 (1)
-C(35)	1.366 (9)	C(43)-C(44)	1.40 (1)
N(4)-C(41)	1.367 (9)	C(44)-C(45)	1.36 (1)
-C(45)	1.381 (9)	C(45)-C(46)	1.52 (1)

Angles

Rh(2)-Rh(1)-O(1)	86.6 (1)	C(41)-N(4)-C(45)	119.3 (6)
-N(2)	85.9 (2)	Rh(2)-N(5)-C(1)	164.9 (8)
-N(3)	86.6 (2)	N(5)-C(1)-C(2)	178 (2)
-N(4)	88.9 (2)	O(1)-C(11)-N(1)	122.4 (6)
O(1)-Rh(1)-N(2)	91.5 (2)	-C(12)	117.7 (7)
-N(3)	86.8 (2)	N(1)-C(11)-C(12)	119.8 (8)
-N(4)	174.7 (2)	C(11)-C(12)-C(13)	119.4 (9)
N(2)-Rh(1)-N(3)	172.4 (2)	C(12)-C(13)-C(14)	118.2 (8)
-N(4)	91.0 (2)	C(13)-C(14)-C(15)	120.3 (8)
N(3)-Rh(1)-N(4)	90.1 (2)	N(1)-C(15)-C(14)	121.0 (7)
Rh(1)-Rh(2)-O(2)	88.0 (1)	-C(16)	119.8 (7)
-O(3)	88.0 (1)	C(14)-C(15)-C(16)	119.2 (7)
-O(4)	85.2 (1)	O(2)-C(21)-N(2)	121.1 (6)
-N(1)	87.1 (2)	-C(22)	117.4 (6)
-N(5)	169.5 (2)	N(2)-C(21)-C(22)	121.4 (6)
O(2)-Rh(2)-O(3)	175.8 (2)	C(21)-C(22)-C(23)	117.2 (7)
-O(4)	89.0 (2)	C(22)-C(23)-C(24)	120.1 (7)
-N(1)	91.6 (2)	C(23)-C(24)-C(25)	119.4 (7)
-N(5)	97.0 (2)	N(2)-C(25)-C(24)	121.9 (7)
O(3)-Rh(2)-O(4)	89.5 (2)	-C(26)	117.1 (6)
-N(1)	89.3 (2)	C(24)-C(25)-C(26)	120.9 (7)
-N(5)	86.9 (2)	O(3)-C(31)-N(3)	121.3 (6)
O(4)-Rh(2)-N(1)	172.3 (2)	-C(32)	118.1 (7)
-N(5)	85.6 (2)	N(3)-C(31)-C(32)	120.6 (7)
N(1)-Rh(2)-N(5)	102.0 (2)	C(31)-C(32)-C(33)	119.4 (8)
Rh(1)-O(1)-C(11)	119.2 (5)	C(32)-C(33)-C(34)	121.3 (8)
Rh(2)-O(2)-C(31)	117.6 (4)	C(33)-C(34)-C(35)	117.0 (8)
Rh(2)-O(3)-C(31)	118.6 (4)	N(3)-C(35)-C(34)	122.8 (7)
Rh(2)-O(4)-C(41)	121.0 (4)	-C(36)	117.7 (7)
Rh(2)-N(1)-C(11)	113.9 (5)	C(34)-C(35)-C(36)	119.5 (7)
-C(15)	125.5 (5)	O(4)-C(41)-N(4)	120.3 (6)
C(11)-N(1)-C(15)	120.5 (6)	-C(42)	120.0 (6)
Rh(1)-N(2)-C(21)	116.7 (4)	N(4)-C(41)-C(42)	119.7 (7)
-C(25)	123.5 (5)	C(41)-C(42)-C(43)	119.3 (7)
C(21)-N(2)-C(25)	119.7 (6)	C(42)-C(43)-C(44)	120.5 (7)
Rh(1)-N(3)-C(31)	116.5 (5)	C(43)-C(44)-C(45)	118.7 (7)
-C(35)	124.9 (5)	N(4)-C(45)-C(44)	122.1 (7)
C(31)-N(3)-C(35)	118.6 (6)	-C(46)	117.1 (7)
Rh(1)-N(4)-C(41)	115.5 (5)	C(44)-C(45)-C(46)	120.7 (7)
-C(45)	125.0 (5)		

in pyridine rings show no deviations greater than 0.05 Å from the best least-squares plane (see Table XV[24]), while the exocyclic methyl carbon and oxygen atoms are displaced up to 0.17 Å from the plane. The five atoms of the imidazole ring deviate no more than 0.005 Å from planarity. The mhp ligands are twisted by an average of 19.5° (see Table XIV) from the eclipsed conformation which is slightly less than the value found for **2**. Presumably this is due to the greater size of the five-membered ring in **4** compared to the CH_3CN molecule in **2** which restricts the degree of twist in the mhp ligands.

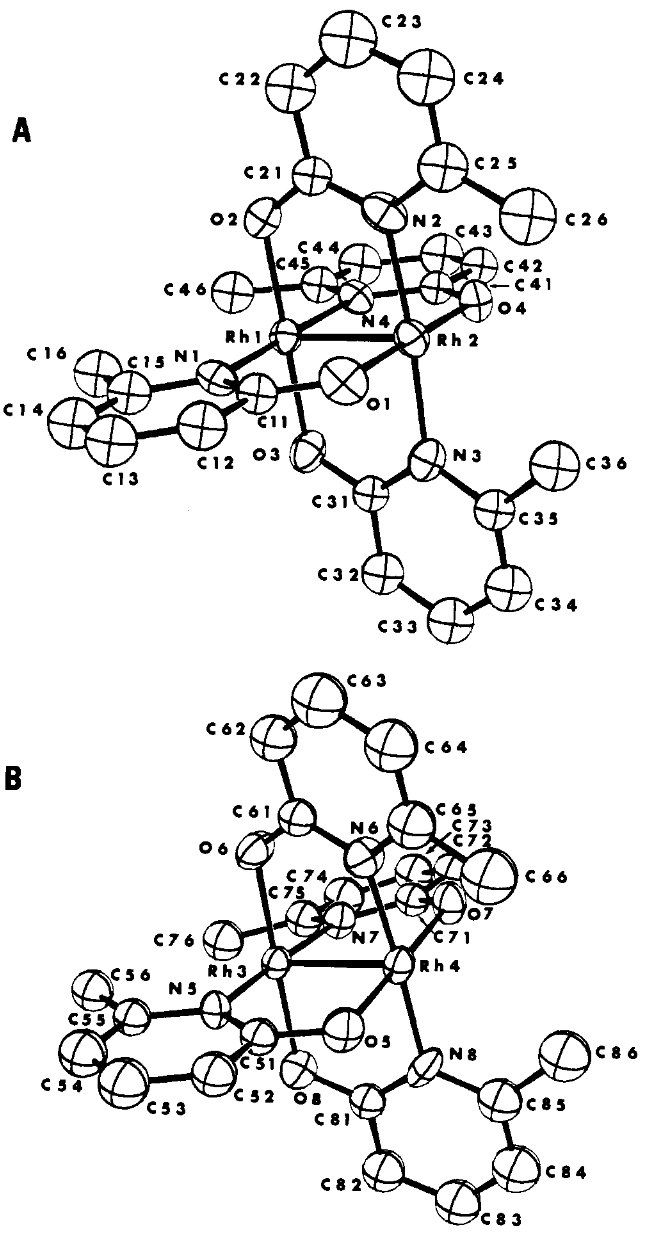

Figure 1. ORTEP drawing of the two independent molecules (A and B) found in $Rh_2(mhp)_4 \cdot H_2O$ (**1**) showing the atomic numbering scheme used in Tables II and VIII. Vibrational ellipsoids are at the 50% probability level.

The Rh-Rh bond in **4** with a value of 2.384 (1) Å is 0.012 Å longer than in **2**. As in compounds **2**, **3a**, and **3b**, two distinct Rh(II) sites are found in the dinuclear unit. The Rh(1) atom is coordinated by three nitrogen atoms and one oxygen atom in an approximately square-planar arrangement with the Rh(1) atom lying 0.092 Å out of the plane. The Rh(2) site is five-coordinate with three oxygen atoms and one nitrogen atom comprising the basal plane of a square pyramid. The axial site is occupied by the imine nitrogen atom, N(5), of the imidazole ring at a distance of 2.144 (4) Å. The Rh(2) atom is displaced 0.098 Å out of the basal plane toward N(5).

$Rh_2(chp)_4$ (5). This compound crystallizes in the orthorhombic space group *Pbca* with eight dinuclear units in the cell, so that there is no crystallographically imposed symmetry. The basic structure is identical with that of **1** with a Rh-Rh distance of 2.379 (1) Å and is illustrated in Figure 8. The pyridine rings of the chp ligands are planar (Table XV[24]) with the exocyclic oxygen and chlorine atoms also in the pyridine ring plane. As can be seen from Table XIV, the chp ligands are twisted only slightly from an eclipsed conformation with

Table X. Bond Distances (Å) and Angles (Deg) for $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)$ (3a) and $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)\cdot 2CH_2Cl_2$ (3b)[a]

	3a	3b		3a	3b
		Distances			
Rh(1)-Rh(2)	2.388 (2)	2.388 (1)	N(1)-C(3)	1.37 (2)	1.366 (9)
-O(1)	2.027 (8)	2.046 (4)	N(1)-C(7)	1.38 (2)	1.390 (8)
-N(1)	2.054 (9)	2.028 (5)	N(2)-C(9)	1.36 (3)	1.358 (7)
Rh(2)-O(2)	2.054 (8)	2.029 (5)	N(3)-N(3′)	1.40 (2)	1.436 (15)
-O(3)	2.015 (7)	2.027 (4)	N(3)-C(9)	1.37 (3)	1.350 (10)
-N(2)	2.172 (14)	2.133 (7)	C(1)-C(2)	1.55 (2)	1.515 (8)
Cl(1)-C(20)		1.726 (10)	C(3)-C(4)	1.42 (2)	1.404 (8)
Cl(2A)-C(20)		1.702 (9)	C(4)-C(5)	1.40 (2)	1.400 (11)
Cl(2B)-C(20)		1.404 (14)	C(5)-C(6)	1.40 (2)	1.370 (12)
O(1)-C(1)	1.27 (2)	1.258 (8)	C(6)-C(7)	1.38 (2)	1.371 (10)
O(2)-C(1)	1.26 (2)	1.278 (8)	C(7)-C(8)	1.52 (2)	1.504 (12)
O(3)-C(3)	1.28 (1)	1.295 (8)			
		Angles			
Rh(2)-Rh(1)-O(1)	89.3 (2)	88.2 (1)	C(3)-N(1)-C(7)	122 (1)	119.1 (6)
-N(1)	87.4 (3)	88.2 (2)	Rh(2)-N(2)-C(9)	125 (1)	125.3 (4)
O(1)-Rh(1)-O(1′)	178.6 (4)	176.3 (2)	C(9)-N(2)-C(9′)	109 (2)	109.4 (9)
-N(1)	89.7 (3)	89.7 (2)	N(3′)-N(3)-C(9)	107 (1)	106.8 (4)
-N(1′)	90.2 (3)	90.2 (2)	O(1)-C(1)-O(2)	126 (1)	125.2 (5)
N(1)-Rh(1)-N(1′)	174.7 (5)	176.4 (3)	-C(2)	118 (1)	117.2 (7)
Rh(1)-Rh(2)-O(2)	86.8 (2)	88.0 (1)	O(2)-C(1)-C(2)	116 (1)	117.5 (7)
-O(3)	89.9 (2)	89.6 (1)	O(3)-C(3)-N(1)	120.0 (9)	120.5 (5)
-N(2)	180.0	180.0	-C(4)	120 (1)	118.5 (7)
O(2)-Rh(2)-O(2′)	173.6 (4)	176.0 (2)	N(1)-C(3)-C(4)	120 (1)	121.0 (7)
-O(3)	90.9 (3)	90.1 (2)	C(3)-C(4)-C(5)	117 (1)	118.0 (8)
-O(3′)	89.1 (3)	89.9 (2)	C(4)-C(5)-C(6)	123 (1)	121.3 (7)
-N(2)	93.2 (2)	92.0 (1)	C(5)-C(6)-C(7)	117 (1)	119.1 (7)
O(3)-Rh(2)-O(3′)	179.9 (4)	179.2 (2)	N(1)-C(7)-C(6)	122 (1)	121.4 (8)
-N(2)	90.0 (2)	90.4 (1)	-C(8)	117 (1)	115.1 (7)
Rh(1)-O(1)-C(1)	118.0 (7)	119.0 (4)	C(6)-C(7)-C(8)	122 (1)	123.5 (7)
Rh(2)-O(2)-C(1)	119.4 (7)	119.6 (4)	N(2)-C(9)-N(3)	108 (2)	108.5 (7)
Rh(2)-O(3)-C(3)	121.8 (7)	121.0 (4)	Cl(1)-C(20)-Cl(2A)		107.1 (5)
Rh(1)-N(1)-C(3)	120.6 (8)	120.6 (4)	Cl(1)-C(20)-Cl(2B)		129.0 (8)
Rh(1)-N(1)-C(7)	117.8 (8)	120.3 (5)	Cl(2A)-C(20)-Cl(2B)		33.6 (6)

[a] For 3a, N(3) was refined as C(10) and N(3) with a 1:1 disorder model as required by the twofold axis bisecting the C(10)-N(3) bond. For 3b, only N(3) was refined but with a scattering factor having 50% N and 50% C contributions. This atom is tabulated for both compounds as N(3).

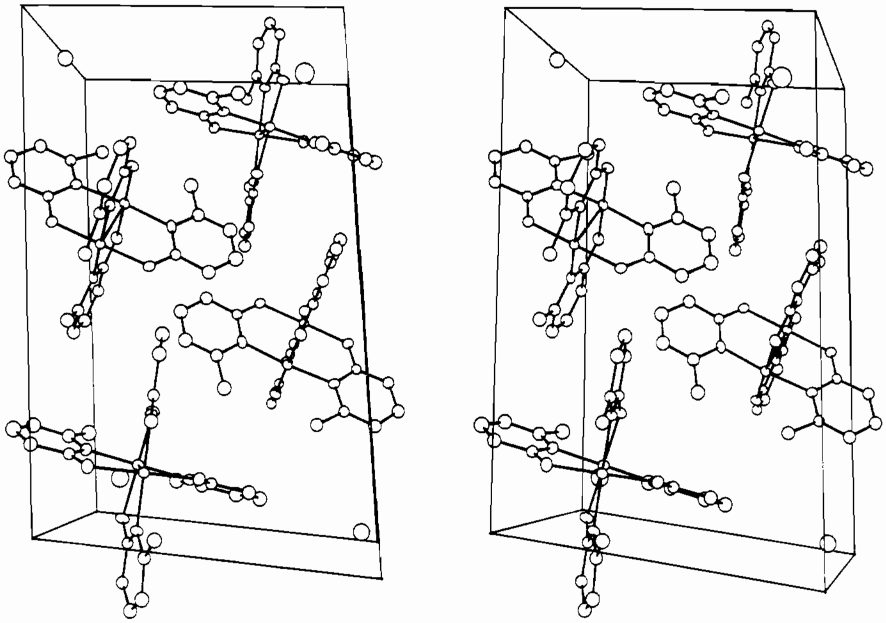

Figure 2. Stereoscopic view of the molecular packing in $Rh_2(mhp)_4\cdot H_2O$ (**1**) as seen down the *c* axis with the *b* axis vertical and the *a* axis horizontal. The thermal ellipsoids are scaled to enclose 20% of their electron density, except the ellipsoids of the oxygen atoms of the lattice water molecules which have been arbitrarily reduced in size for clarity.

an average twist angle of 4.8°. The chlorine atoms, like the methyl groups in **1**, serve to block the axial positions. The structure is free of solvent molecules as was encountered with **1** and analogous complexes of the group 6 metal ions[17] with mhp ligands.

$Rh_2(chp)_4(C_3H_4N_2)\cdot 3H_2O$ (6). Red-violet crystals of this compound were found to belong to the tetragonal crystal system $P4_2/n$. There are eight formula units in the cell with no crystallographically imposed symmetry upon the dinuclear complexes. The structure of the dirhodium(II) unit is given

Table XI. Bond Distances (Å) and Angles (Deg) for $Rh_2(mhp)_4(C_3H_4N_2)\cdot 0.5CH_3CN$ (**4**)

Distances

Rh(1)-Rh(2)	2.384 (1)	C(2)-C(3)	1.364 (8)
-O(1)	2.014 (3)	C(4)-C(5)	1.496 (22)
-N(2)	2.062 (4)	C(11)-C(12)	1.401 (7)
-N(3)	2.043 (4)	C(12)-C(13)	1.370 (8)
-N(4)	2.059 (4)	C(13)-C(14)	1.409 (8)
Rh(2)-O(2)	2.025 (3)	C(14)-C(15)	1.356 (7)
-O(3)	2.018 (3)	C(15)-C(16)	1.506 (7)
-O(4)	2.054 (3)	C(21)-C(22)	1.428 (8)
-N(1)	2.094 (4)	C(22)-C(23)	1.433 (8)
-N(5)	2.144 (4)	C(23)-C(24)	1.319 (10)
O(1)-C(11)	1.314 (5)	C(24)-C(25)	1.415 (8)
O(2)-C(21)	1.288 (5)	C(25)-C(26)	1.492 (8)
O(3)-C(31)	1.290 (6)	C(31)-C(32)	1.407 (7)
O(4)-C(41)	1.298 (5)	C(32)-C(33)	1.403 (9)
N(1)-C(11)	1.352 (6)	C(33)-C(34)	1.419 (10)
N(2)-C(21)	1.355 (6)	C(34)-C(35)	1.363 (9)
N(3)-C(31)	1.358 (6)	C(35)-C(36)	1.536 (8)
N(4)-C(41)	1.367 (6)	C(41)-C(42)	1.421 (7)
N(5)-C(1)	1.335 (6)	C(42)-C(43)	1.354 (7)
N(5)-C(3)	1.376 (6)	C(43)-C(44)	1.433 (8)
N(6)-C(1)	1.337 (7)	C(44)-C(45)	1.372 (7)
-C(2)	1.361 (8)	C(45)-C(46)	1.498 (8)
N(7)-C(4)	1.070 (18)		

Angles

Rh(2)-Rh(1)-O(1)	87.14 (9)	C(1)-N(5)-C(3)	106.3 (4)
-N(2)	87.0 (1)	C(1)-N(6)-C(2)	108.6 (5)
-N(3)	86.3 (1)	N(5)-C(1)-N(6)	110.0 (5)
-N(4)	89.3 (1)	N(6)-C(1)-N(6)	106.3 (5)
O(1)-Rh(1)-N(2)	85.6 (1)	N(5)-C(3)-C(2)	108.8 (5)
-N(3)	92.6 (1)	N(7)-C(4)-C(5)	180.0
-N(4)	175.6 (1)	O(1)-C(11)-N(1)	120.5 (4)
N(2)-Rh(1)-N(3)	173.1 (1)	-C(12)	117.3 (4)
-N(4)	91.5 (1)	N(1)-C(11)-C(12)	122.1 (4)
N(3)-Rh(1)-N(4)	89.9 (2)	C(11)-C(12)-C(13)	118.7 (5)
Rh(1)-Rh(2)-O(2)	88.57 (9)	C(12)-C(13)-C(14)	119.3 (5)
-O(3)	88.1 (1)	C(13)-C(14)-C(15)	118.4 (5)
-O(4)	85.06 (9)	N(1)-C(15)-C(14)	123.8 (5)
-N(1)	87.4 (1)	-C(16)	118.8 (4)
-N(5)	169.5 (1)	C(14)-C(15)-C(16)	117.4 (5)
O(2)-Rh(2)-O(3)	175.6 (1)	O(2)-C(21)-N(2)	120.7 (4)
-O(4)	87.0 (1)	-C(22)	117.0 (5)
-N(1)	90.7 (1)	N(2)-C(21)-C(22)	122.3 (4)
-N(5)	90.6 (1)	C(21)-C(22)-C(23)	115.8 (6)
O(3)-Rh(2)-O(4)	89.9 (1)	C(22)-C(23)-C(23)	121.0 (6)
-N(1)	91.9 (1)	C(23)-C(24)-C(25)	121.2 (5)
-N(5)	92.2 (1)	N(2)-C(25)-C(24)	120.0 (5)
O(4)-Rh(2)-N(1)	172.1 (1)	-C(26)	117.1 (5)
-N(5)	84.5 (1)	C(24)-C(25)-C(26)	122.8 (5)
N(1)-Rh(2)-N(5)	103.1 (1)	O(3)-C(31)-N(3)	120.4 (4)
Rh(1)-O(1)-C(11)	120.4 (3)	-C(32)	119.3 (5)
Rh(2)-O(2)-C(21)	119.9 (3)	N(3)-C(31)-C(32)	120.3 (5)
Rh(2)-O(3)-C(31)	119.4 (3)	C(31)-C(32)-C(33)	120.6 (6)
Rh(2)-O(4)-C(41)	122.4 (3)	C(32)-C(33)-C(34)	117.6 (6)
Rh(2)-N(1)-C(11)	116.1 (3)	C(33)-C(34)-C(35)	119.6 (6)
-C(15)	126.8 (3)	N(3)-C(35)-C(34)	122.4 (5)
C(11)-N(1)-C(15)	117.1 (4)	-C(36)	116.1 (5)
Rh(1)-N(2)-C(21)	118.9 (3)	C(34)-C(35)-C(36)	121.4 (5)
-C(25)	121.0 (3)	O(4)-C(41)-N(4)	119.5 (4)
C(21)-N(2)-C(25)	119.6 (4)	-C(42)	119.4 (4)
Rh(1)-N(3)-C(31)	118.2 (3)	N(4)-C(41)-C(42)	121.1 (4)
-C(35)	122.6 (3)	C(41)-C(42)-C(43)	119.9 (5)
C(31)-N(3)-C(35)	118.9 (4)	C(42)-C(43)-C(44)	118.6 (5)
Rh(1)-N(4)-C(41)	115.8 (3)	C(43)-C(44)-C(45)	119.6 (5)
-C(45)	125.2 (3)	N(4)-C(45)-C(44)	121.9 (5)
C(41)-N(4)-C(45)	118.5 (4)	-C(46)	117.3 (4)
Rh(2)-N(5)-C(1)	126.4 (4)	C(44)-C(45)-C(46)	120.6 (5)
-C(3)	125.2 (3)		

Table XII. Bond Distances (Å) and Angles (Deg) for $Rh_2(chp)_4$ (**5**)

Distances

Rh(1)-Rh(2)	2.379 (1)	C(11)-C(12)	1.47 (2)
-O(2)	1.998 (8)	C(12)-C(13)	1.35 (2)
Rh(1)-O(3)	2.004 (7)	C(13)-C(14)	1.43 (2)
Rh(1)-N(1)	2.029 (9)	C(14)-C(15)	1.37 (2)
-N(4)	2.040 (9)	C(15)-Cl(16)	1.74 (1)
Rh(2)-O(1)	2.025 (8)	C(21)-C(22)	1.47 (2)
Rh(2)-O(4)	2.016 (8)	C(22)-C(23)	1.37 (2)
-N(2)	2.06 (1)	C(23)-C(24)	1.41 (2)
-N(3)	2.071 (9)	C(24)-C(25)	1.34 (2)
O(1)-C(11)	1.27 (1)	C(25)-Cl(26)	1.73 (1)
O(2)-C(21)	1.32 (1)	C(31)-C(32)	1.44 (2)
O(3)-C(31)	1.30 (1)	C(32)-C(33)	1.36 (2)
O(4)-C(41)	1.28 (1)	C(33)-C(34)	1.32 (2)
N(1)-C(11)	1.40 (1)	C(34)-C(35)	1.42 (2)
-C(15)	1.35 (1)	C(35)-Cl(36)	1.75 (1)
N(2)-C(21)	1.37 (1)	C(41)-C(42)	1.42 (1)
-C(25)	1.30 (1)	C(42)-C(43)	1.38 (2)
N(3)-C(31)	1.32 (1)	C(43)-C(44)	1.41 (2)
-C(35)	1.34 (1)	C(44)-C(45)	1.40 (2)
N(4)-C(41)	1.36 (1)	C(45)-Cl(46)	1.73 (1)
-C(45)	1.36 (1)		

Angles

Rh(2)-Rh(1)-O(2)	90.4 (2)	O(1)-C(11)-N(1)	121 (1)
-O(3)	90.4 (2)	-C(12)	122 (1)
-N(1)	88.4 (2)	N(1)-C(11)-C(12)	118 (1)
-N(4)	86.5 (3)	C(11)-C(12)-C(13)	119 (1)
O(2)-Rh(1)-O(3)	178.4 (3)	C(12)-C(13)-C(14)	122 (1)
-N(1)	90.5 (3)	C(13)-C(14)-C(15)	115 (1)
-N(4)	89.9 (3)	Cl(16)-C(15)-N(1)	113.0 (8)
O(3)-Rh(1)-N(1)	88.2 (3)	-C(14)	120 (1)
-N(4)	91.5 (3)	N(1)-C(15)-C(14)	126 (1)
N(1)-Rh(1)-N(4)	174.8 (3)	O(2)-C(21)-N(2)	120 (1)
Rh(1)-Rh(2)-O(1)	89.9 (2)	O(2)-C(21)-C(22)	120 (1)
-O(4)	90.7 (2)	N(2)-C(21)-C(22)	120 (1)
-N(2)	88.0 (2)	C(21)-C(22)-C(23)	114 (1)
-N(3)	86.8 (2)	C(22)-C(23)-C(24)	125 (2)
O(1)-Rh(2)-O(4)	179.3 (3)	C(23)-C(24)-C(25)	115 (1)
O(1)-Rh(2)-N(2)	89.6 (3)	Cl(26)-C(25)-N(2)	115 (1)
-N(3)	90.9 (4)	-C(24)	119 (1)
O(4)-Rh(2)-N(2)	90.1 (4)	N(2)-C(25)-C(24)	126 (1)
-N(3)	89.5 (4)	O(3)-C(31)-N(3)	122 (1)
N(2)-Rh(2)-N(3)	174.7 (3)	-C(35)	119 (1)
Rh(2)-O(1)-C(11)	121.2 (7)	N(3)-C(31)-C(35)	119 (1)
Rh(1)-O(2)-C(21)	121.7 (7)	C(31)-C(32)-C(33)	117 (1)
Rh(1)-O(3)-C(31)	120.1 (7)	C(32)-C(33)-C(34)	125 (2)
Rh(2)-O(4)-C(41)	120.4 (7)	C(33)-C(34)-C(35)	115 (1)
Rh(1)-N(1)-C(11)	119.7 (7)	Cl(36)-C(35)-N(3)	114.7 (9)
-C(15)	121.3 (8)	-C(34)	122 (1)
C(11)-N(1)-C(15)	119 (1)	N(3)-C(35)-C(34)	123 (1)
Rh(2)-N(2)-C(21)	119.9 (8)	O(4)-C(41)-N(4)	120 (1)
-C(25)	120.5 (9)	-C(42)	120 (1)
C(21)-N(2)-C(25)	120 (1)	N(4)-C(41)-C(42)	120 (1)
Rh(2)-N(3)-C(31)	120.2 (7)	C(41)-C(42)-C(43)	118 (1)
-C(35)	119.5 (8)	C(42)-C(43)-C(44)	124 (1)
C(31)-N(3)-C(35)	120 (1)	C(43)-C(44)-C(45)	113 (1)
Rh(1)-N(4)-C(41)	121.9 (7)	Cl(46)-C(45)-N(4)	114.7 (9)
-C(45)	118.7 (8)	-C(44)	120 (1)
C(41)-N(4)-C(45)	119 (1)	N(4)-C(45)-C(44)	126 (1)

in Figure 9 and consists of four bridging chp ligands and a coordinated imidazole molecule. The arrangement of the chp ligands is analogous to that of the mhp ligands in **2** and **4**. The chp ligands are twisted away from the eclipsed conformation by an average of 20.7° (Table XIV). Figures 6 and 9 provide a comparison of the similarities in the dirhodium(II) units in **4** and **6**. The mhp and chp ligands are shown in practically the same configuration about the Rh–Rh axes in these figures; it is then easily seen that the axial imidazole ligands differ in their orientation with respect to the coordinated equatorial nitrogen and oxygen atoms (cf. dihedral angles in Table XV[24]). All of the pyridine rings of the chp ligands and the imidazole ring are planar (Table XV[24]).

Figure 10 compares the coordination and rotational conformations in compounds **2**, **4**, and **6** as viewed down the Rh–Rh bonds. The axially coordinated nitrogen ligand on Rh(2) in all cases has been omitted. Table XIV provides a summary of the torsional angles in these compounds.

The Rh–Rh bond distance of 2.385 (1) Å in **6** is quite close to the values found in **3a**, **3b**, and **4** which also have a single axial imidazole ligand. The Rh(2)–N(5) bond length of 2.129 (9) Å is one of shorter distances found for an axial nitrogen

Table XIII. Bond Distances (Å) and Angles (Deg) for $Rh_2(chp)_4(C_3H_4N_2)\cdot 3H_2O$ (**6**)

Distances

Rh(1)–Rh(2)	2.385 (1)	N(6)–C(1)	1.35 (1)
–O(1)	2.019 (8)	–C(2)	1.35 (2)
–N(2)	2.054 (9)	C(2)–C(3)	1.36 (2)
–N(3)	2.085 (9)	C(11)–C(12)	1.43 (2)
–N(4)	2.053 (9)	C(12)–C(13)	1.34 (2)
Rh(2)–O(2)	2.033 (7)	C(13)–C(14)	1.40 (2)
–O(3)	2.033 (7)	C(14)–C(15)	1.39 (2)
–O(4)	2.024 (7)	C(15)–Cl(16)	1.70 (1)
–N(1)	2.063 (9)	C(21)–C(22)	1.42 (2)
–N(5)	2.129 (9)	C(22)–C(23)	1.44 (2)
O(1)–C(11)	1.27 (1)	C(23)–C(24)	1.38 (2)
O(2)–C(21)	1.28 (1)	C(24)–C(25)	1.37 (2)
O(3)–C(31)	1.32 (1)	C(25)–Cl(26)	1.72 (1)
O(4)–C(41)	1.28 (1)	C(31)–C(32)	1.42 (2)
N(1)–C(11)	1.39 (1)	C(32)–C(33)	1.39 (2)
–C(15)	1.36 (1)	C(33)–C(34)	1.37 (2)
N(2)–C(21)	1.35 (1)	C(34)–C(35)	1.34 (2)
–C(25)	1.38 (1)	C(35)–Cl(36)	1.74 (1)
N(3)–C(31)	1.32 (1)	C(41)–C(42)	1.42 (2)
–C(35)	1.32 (1)	C(42)–C(43)	1.41 (2)
N(4)–C(41)	1.38 (1)	C(43)–C(44)	1.43 (2)
–C(45)	1.37 (1)	C(44)–C(45)	1.39 (1)
N(5)–C(1)	1.30 (1)	C(45)–Cl(46)	1.70 (1)
–C(3)	1.38 (2)		

Angles

Rh(2)–Rh(1)–O(1)	87.2 (2)	Rh(2)–N(5)–C(3)	130.4 (9)
–N(2)	86.8 (3)	C(1)–N(5)–C(3)	106 (1)
–N(3)	86.0 (2)	C(1)–N(6)–C(2)	105 (1)
–N(4)	87.8 (3)	N(5)–C(1)–N(6)	113 (1)
O(1)–Rh(1)–N(2)	85.3 (3)	N(6)–C(2)–C(3)	109 (1)
–N(3)	92.8 (3)	N(5)–C(3)–C(2)	107 (1)
–N(4)	174.3 (3)	O(1)–C(11)–N(1)	120 (1)
N(2)–Rh(1)–N(3)	172.6 (4)	–C(12)	120 (1)
–N(4)	91.7 (3)	N(1)–C(11)–C(12)	120 (1)
N(3)–Rh(1)–N(4)	89.6 (3)	C(11)–C(12)–C(13)	119 (1)
Rh(1)–Rh(2)–O(2)	88.3 (2)	C(12)–C(13)–C(14)	122 (1)
–O(3)	88.2 (2)	C(13)–C(14)–C(15)	116 (1)
–O(4)	87.0 (2)	Cl(16)–C(15)–N(1)	117.2 (9)
–N(1)	86.6 (3)	–C(14)	118 (1)
–N(5)	172.4 (2)	N(1)–C(15)–C(14)	125 (1)
O(2)–Rh(2)–O(3)	175.0 (3)	O(2)–C(21)–N(2)	120 (1)
–O(4)	86.9 (3)	–C(22)	119 (1)
–N(1)	91.4 (3)	N(2)–C(21)–C(22)	121 (1)
–N(5)	89.4 (3)	C(21)–C(22)–C(23)	119 (1)
O(3)–Rh(2)–O(4)	89.3 (3)	C(22)–C(23)–C(24)	118 (1)
–N(1)	91.9 (3)	C(23)–C(24)–C(25)	120 (1)
–N(5)	93.6 (3)	Cl(26)–C(25)–N(2)	115 (1)
O(4)–Rh(2)–N(1)	173.4 (4)	–C(24)	121 (1)
–N(5)	85.6 (3)	N(2)–C(25)–C(24)	123 (1)
N(1)–Rh(2)–N(5)	100.7 (4)	O(3)–C(31)–N(3)	122 (1)
Rh(1)–O(1)–C(11)	120.9 (7)	–C(32)	117 (1)
Rh(2)–O(2)–C(21)	118.4 (7)	N(3)–C(31)–C(32)	121 (1)
Rh(2)–O(3)–C(31)	116.8 (7)	C(31)–C(32)–C(33)	117 (1)
Rh(2)–O(4)–C(41)	118.5 (7)	C(32)–C(33)–C(34)	121 (1)
Rh(2)–N(1)–C(11)	115.8 (7)	C(33)–C(34)–C(35)	116 (1)
–C(15)	128.4 (8)	Cl(36)–C(35)–N(3)	115.7 (9)
C(11)–N(1)–C(15)	116 (1)	–C(34)	119 (1)
Rh(1)–N(2)–C(21)	119.4 (8)	N(3)–C(35)–C(34)	126 (1)
–C(25)	121.7 (8)	O(4)–C(41)–N(4)	121 (1)
C(21)–N(2)–C(25)	119 (1)	–C(42)	118 (1)
Rh(1)–N(3)–C(31)	118.1 (8)	N(4)–C(41)–C(42)	121 (1)
–C(35)	123.3 (8)	C(41)–C(42)–C(43)	118 (1)
C(31)–N(3)–C(35)	119 (1)	C(42)–C(43)–C(44)	121 (1)
Rh(1)–N(4)–C(41)	116.2 (7)	C(43)–C(44)–C(45)	116 (1)
–C(45)	125.0 (8)	Cl(46)–C(45)–N(4)	116.1 (9)
C(41)–N(4)–C(45)	118.8 (9)	–C(44)	119.4 (9)
Rh(2)–N(5)–C(1)	123.4 (8)	N(4)–C(45)–C(44)	124 (1)

donor ligand in a dirhodium(II) complex (cf. values given in ref 11). In $Rh_2(O_2CCH_3)_4(NO)(NO_2)$,[8] a Rh–N(NO) distance of 1.927 (4) Å has been found. As in **4**, the Rh(1) and Rh(2) sites are displaced 0.109 and 0.089 Å, respectively, out of the equatorial plane toward the axial position (although no axial ligand is actually bound to Rh(1)).

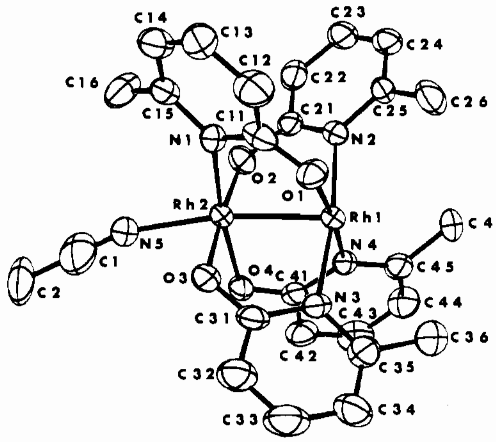

Figure 3. ORTEP drawing of $Rh_2(mhp)_4(CH_3CN)$ (**2**) with thermal ellipsoids at the 50% probability level. The labeling scheme shown is that used in Tables III and IX.

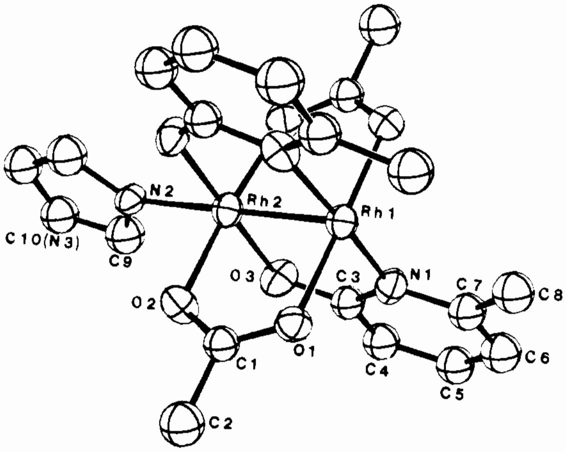

Figure 4. View of $Rh_2(mhp)_4(OAc)_2(C_3H_4N_2)$ (**3a**) showing the labeling scheme used in Tables IVA and X. The same atomic structure and labeling scheme is found in $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)\cdot 2CH_2Cl_2$ (**3b**). The trans mhp and OAc ligands are related by a twofold axis which passes through Rh(1), Rh(2), and N(2). Vibrational ellipsoids are shown at the 50% probability level.

Four water molecules occupy general positions in the lattice and are represented by oxygen atoms O(5)–O(8). Intermolecular contacts between water molecules range from 2.612 to 3.526 Å. The shortest lattice water to $Rh_2(chp)_4(C_3H_4N_2)$ contact is 2.865 Å, from O(5) to O(4).

Discussion

Imidazole Ligands. The proposed presence of coordinated imidazole molecules in three of the complexes reported here may not be the most important aspect of this work, but it will doubtless tend, at this point, to be uppermost in the minds of many readers. For this reason we discuss it first, before turning to several other points that have more to do with the fundamental chemistry of Rh_2^{4+} complexes. The two most evident questions concerning these imidazole ligands are as follows. (1) How certain are we that they are actually imidazole molecules? (2) From whence do they come? We have no answer to the second question, nor even any very plausible speculations. Indeed, we would welcome suggestions. To the first question we can supply the following answer, which we freely admit falls short of being conclusive.

Our best evidence that the axial ligand is an imidazole molecule occurs in the case of compound **4**. Here we began by treating all four atoms other than the one coordinated to rhodium as carbon atoms and found that this led to one of them having a thermal vibration amplitude less than half that of the other three, for which the values were all of normal

Table XIV. Torsional Angles (Deg) in the Seven Compounds

planes defining angle								
atoms in plane 1	atoms in plane 2	1	2	3a	3b	4	5	6
N(1), Rh(1), Rh(2)	Rh(1), Rh(2), O(1)	0.2	24.1			21.1	3.7	22.4
O(2), Rh(1), Rh(2)	Rh(1), Rh(2), N(2)	0.4	24.1			16.1	4.6	16.3
O(3), Rh(1), Rh(2)	Rh(1), Rh(2), N(3)	1.9	21.7			20.3	6.4	21.5
O(4), Rh(1), Rh(2)	Rh(1), Rh(2), N(4)	1.4	22.1			20.5	4.4	21.2
mean angle		1.0	23.0			19.5	4.8	20.7
N(5), Rh(3), Rh(4)	Rh(3), Rh(4), O(5)	8.5						
O(6), Rh(3), Rh(4)	Rh(3), Rh(4), N(6)	9.8						
N(7), Rh(3), Rh(4)	Rh(3), Rh(4), O(7)	9.8						
N(8), Rh(3), Rh(4)	Rh(3), Rh(4), O(8)	9.1						
mean angle		9.3						
N(1), Rh(1), Rh(2)	Rh(1), Rh(2), O(3)			3.6	0.2			
O(1), Rh(1), Rh(2)	Rh(1), Rh(2), O(2)			4.8	0.1			

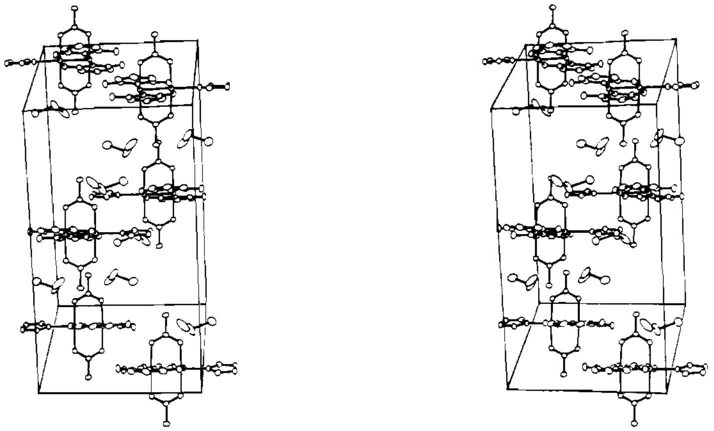

Figure 5. Stereoscopic view of the molecular packing in $Rh_2(mhp)_2(OAc)_2(C_3H_4N_2)\cdot 2CH_2Cl_2$ (**3b**) with thermal ellipsoids at the 20% probability level. The view is down the *c* axis with the *a* axis vertical and the *b* axis horizontal. Only the major orientation (Cl(2A)) of the disordered CH_2Cl_2 molecule is shown.

magnitude. When this atom was then assigned the atomic scattering power of a nitrogen atom, it refined with a thermal parameter very similar to those of the other ring atoms. Subsequently, attempts were made to refine N(5), the coordinated atom, as a carbon or oxygen atom, but this led to unreasonably small or large thermal parameters, respectively. Given that (1) the coordinated atom is nitrogen and taking note of (2) the planarity of the ring, (3) the shortness of all the bonds, (4) the overwhelming likelihood that the rhodium atoms are both in oxidation state II, and (5) the refusal of N(6) to behave well in refinement as other than a nitrogen atom, we see no choice but to identify the axial ligand in compound **4** as an imidazole molecule coordinated through the imino nitrogen atom.

In addition, the dimensions found agree very well with those previously reported for both free and coordinated imidazole molecules, as shown in Table XVI, where the reported dimensions of (a) free imidazole,[25] (b) a coordinated imidazole molecule,[26] and the putative imidazole molecules in our compounds **4** and **6** are compared.

For compounds **3a**, **3b**, and **6** the crystallographic evidence favoring an imidazole molecule, as compared to some other five-membered ring, is less convincing. In the case of **3a** and **3b** the amino nitrogen atom and the opposite carbon atom are statistically disordered because there is a crystallographic twofold axis passing through the coordinated nitrogen atom and the opposite edge of the ring. In **6** the general precision is somewhat lower than for compound **4**. However, in both of these the rings are found to be planar within experimental error, and the distances and angles are entirely consistent with the requirements of a $C_3H_4N_2$ ring. Even though we are unable to explain the origin of these rings, it is certainly reasonable to believe that they have the same identity in all four compounds.

Comparison with Other Dirhodium and Dimetal Compounds. Until recently,[12] all of the previously reported Rh_2^{4+} compounds with Rh–Rh distances less than 2.5 Å have contained four bridging carboxylate groups. This is the first series of compounds with short bonds to break that pattern. All $Rh_2(O_2CR)_4$-type compounds previously reported have had axial ligands trans to the Rh–Rh bond. We are describing here two compounds, **1** and **5**, that contain *no* axial ligands and five others containing only *one* axial ligand which represent two new bridging ligand geometries. The Rh–Rh distances scarcely change (2.365 (1)–2.388 (1) Å) as a function of whether there are two, one, or zero axial ligands, at least so long as these ligands are essentially simple σ donors.

A much greater variation in Rh–Rh bond lengths occurs for compounds having only two bridging ligands, as in $Rh_2(dmg)_2(O_2CCH_3)_2(PPh_3)_2$,[27] or even none as has been found in various rhodium isocyanide[2b,28,29] and dmg[15] complexes. Table XVII presents a representative survey of compounds containing Rh–Rh bonds including the seven compounds in

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(25) (a) Martinez-Carrera, S. *Acta Crystallogr.* **1966**, *20*, 783. (b) Craven, B. M.; McMullan, R. K.; Bell, D. J.; Freeman, H. C. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2585.

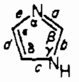
(26) Van Ooijen, J. A. C.; Reedijk, K.; Spek, A. L. *Inorg. Chem.* **1979**, *18*, 1184.

(27) Halpern, J.; Kumma, E.; Molin-Case, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1971**, 1207.

(28) Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *148*, C15.

(29) (a) Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 3128. This linear trinuclear compound appears to have two Rh(II) atoms with axial I^- atoms connected by a Rh(I) atom, i.e., $[Rh_3(C_6H_5CH_2NC)_{12}I_2]Br_3$. (b) Mann, K. R.; DiPierro, M. J.; Gill, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3965. This linear tetranuclear compound consists of dinuclear Rh(I)–Rh(II) units held together by an unbridged Rh(II)–Rh(II) bond of length 2.775 (4) Å and linked into infinite chains by Cl^- ions, i.e., $(H_3O^+)_3[Rh_4(CN(CH_2)_3NC)_8Cl](CoCl_4)_4\cdot nH_2O$.

Table XVI. Comparison of the Dimensions in Free and Coordinated Imidazole with Values for Compounds 4 and 6



dimension[a]	compd			
	free[b]	coordinated[c]	4[d]	6[d]
a	1.316 (2)	1.320 (3)	1.335 (6)	1.30 (1)
b	1.337 (3)	1.339 (3)	1.337 (7)	1.35 (1)
c	1.362 (2)	1.362 (3)	1.361 (8)	1.35 (1)
d	1.357 (2)	1.344 (3)	1.364 (8)	1.36 (2)
e	1.367 (2)	1.377 (2)	1.376 (6)	1.38 (2)
α	105.1 (1)	105.1 (1)	106.3 (4)	106 (1)
β	112.0 (1)	111.4 (1)	110.0 (5)	113 (1)
γ	107.0 (1)	107.2 (2)	108.6 (5)	105 (1)
δ	106.1 (1)	106.6 (2)	106.3 (5)	109 (1)
ε	109.8 (1)	109.7 (2)	108.8 (5)	107 (1)

[a] Bond distances in Å; angles given in deg. [b] As reported in ref 25b at 20 °C. [c] In $Ni(C_4O_4)(C_3H_4N_2)_2(H_2O)_2$; ref 26. [d] This work.

Table XVII. Representative Bond Lengths in Dirhodium Compounds

compd	Rh-Rh, Å	Rh-L,[a] Å	ref
$[Rh_2(O_2CCH_3)_4(H_2O)_2]ClO_4 \cdot H_2O$[b]	2.316 (2)[c]	2.22 (1)[c]	30
$Rh_2(mhp)_4$	2.359 (1)		12
$Rh_2(mhp)_4 \cdot H_2O$	2.367 (1)[c]		this work
$Rh_2(O_2CCMe_3)_4(H_2O)_2$	2.371 (1)	2.295 (2)	10
$Rh_2(mhp)_4(CH_3CN)$	2.372 (1)	2.152 (7)[d]	this work
$Cs_4[Rh_2(CO_3)_4(H_2O)_2] \cdot 6H_2O$	2.378 (1)	2.344 (5)	9
$Rh_2(chp)_4$	2.379 (1)		this work
$Rh_2(mhp)_4(C_3H_4N_2) \cdot 0.5CH_3CN$	2.384 (1)	2.144 (4)[d]	this work
$Rh_2(chp)_4(C_3H_4N_2) \cdot 3H_2O$	2.385 (1)	2.129 (9)[d]	this work
$Rh_2(O_2CCH_3)_4(H_2O)_2$	2.3855 (5)	2.310 (3)	31
$Rh_2(mhp)_2(O_2CCH_3)_2(C_3H_4N_2)$	2.388 (2)	2.17 (1)[d]	this work
$Rh_2(mhp)_2(O_2CCH_3)_2(C_3H_4N_2) \cdot 2CH_2Cl_2$	2.388 (1)	2.133 (7)[d]	this work
$Rh_2(O_2CCH_3)_4(CO)_2$	2.4191 (3)	2.095 (2)	8
$Rh_2(O_2CCH_3)_4(PPh_3)_2$	2.449 (2)	2.479 (4)	8
$Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$	2.4556 (3)	2.4367 (6)	8
$Rh_2(OSCCH_3)_4(CH_3CSOH)_2$	2.550 (3)	2.521 (5)	5a
$Rh_2(dmg)_2(O_2CCH_3)_2(PPh_3)_2$	2.618 (5)	2.485 (9)[c]	27
$[Rh_2(p\text{-}CH_3C_6H_4NC)_8I_2](PF_6)_2$	2.785 (2)	2.735 (1)	28
$[Rh_2(CN(CH_2)_3NC)_4Cl_2]Cl_2 \cdot 8H_2O$	2.837 (1)	2.447 (1)	2b
$Rh_2(dmg)_4(PPh_3)_2 \cdot C_3H_7OH \cdot H_2O$	2.936 (2)	2.438 (4)	15

[a] Rh-axial ligand L distance; if no value is given, the compound has no axial ligands. [b] In this compound, the Rh atoms have an average oxidation state of +2.5. [c] This value reflects the average of two chemically equivalent bond distances. [d] This compound has only one axial ligand.

this work. The table is arranged in order of increasing Rh–Rh bond length and with one exception[30] includes compounds in which both Rh atoms are in the divalent oxidation state. The shortest distance to date between two Rh atoms is found in $[Rh_2(O_2CCH_3)_4(H_2O)_2]ClO_4 \cdot H_2O$,[30] although this compound shows an average valence of 2.5+ per Rh atom, contains a single unpaired electron, and has an orbital ground-state configuration[13] of $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$. The Rh–Rh bond is 0.069 Å shorter in this compound than in the neutral $Rh_2(O_2CCH_3)_4(H_2O)_2$ molecule,[31] despite the fact that the axial Rh–OH_2 distance also contracts by 0.09 Å. These changes in bond lengths can be well understood[13] in terms of the increased positive charge on the Rh atoms and the greater increase in the Rh–Rh bond strength caused by the loss of a δ* electron as compared to the increased Rh–OH_2 interaction which tends to weaken the Rh–Rh bond.

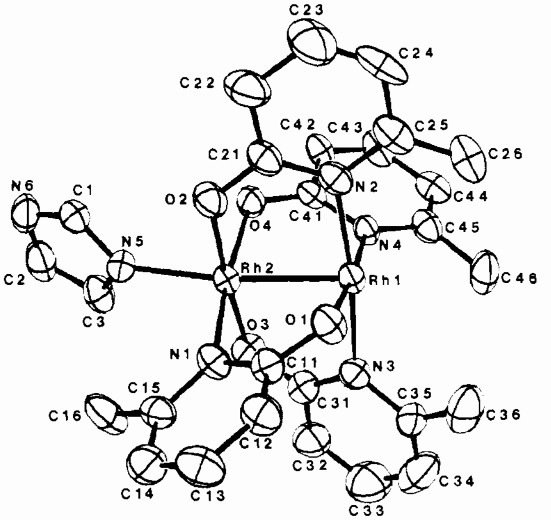


Figure 6. ORTEP drawing of the dirhodium(II) complex in $Rh_2(mhp)_4(C_3H_4N_2) \cdot 0.5CH_3CN$ (4) with thermal ellipsoids drawn at the 50% probability level. The labeling scheme is consistent with that used in Tables V and XI.

Among compounds containing two divalent rhodium atoms, the shortest Rh–Rh bond occurs in $Rh_2(mhp)_4$.[12] The structure reported in this work of $Rh_2(mhp)_4 \cdot H_2O$ contains two $Rh_2(mhp)_4$ molecules that have an average Rh–Rh bond length of 2.367 (1) Å, which is 0.008 Å longer than in the anhydrous compound. The average Rh–O bonds in the two compounds are 2.017 (4) and 2.020 (5) Å for the anhydrous[12] and hydrated forms, respectively, while the corresponding Rh–N bond lengths average 2.043 (5) and 2.041 (8) Å. Since the Rh–ligand atom distances in these two polymorphs are essentially identical and the rotational conformations of these ligands are nearly the same, lattice packing forces apparently have a significant influence upon the Rh–Rh bond length in these structures.

Five of the dirhodium(II) compounds in this work (**2**, **3a**, **3b**, **4**, **6**) have only one axial ligand, and these are the first such compounds to be structurally characterized. Rhodium(II) carboxylates have been reported[4c,32,33] to form 1:1 adducts, presumably with one axial site empty, although two of these compounds contain potentially bifunctional ligands (4-cyanopyridine[4c] and Me_2SO[32]) and it has yet to be shown that dirhodium(II) carboxylates, when denied access to other coordinating ligands, could not utilize an adjacent bridging carboxyl group as an axial ligand, as found in dichromium(II)[14,34] and dimolybdenum(II)[35] tetracarboxylates.

Two new structural motifs are displayed by five compounds reported here. One of these is the mixed-ligand type of complex (**3a**, **3b**), which apparently results from an incomplete substitution reaction for all four acetate groups due to either insufficient reaction time or incorrect stoichiometry to allow all four carboxylates to be exchanged. The axial imidazole ligand, whatever its source, may serve to alter the substitution

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(30) Ziolkowski, J. J.; Moszner, M.; Glowiak, T. *J. Chem. Soc., Chem. Commun.* **1977**, 760.

(31) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1664.

(32) Kitchens, J.; Bear, J. L. *J. Inorg. Nucl. Chem.* **1970**, *32*, 49.

(33) Richman, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055.

(34) Cotton, F. A.; Rice, C. E.; Rice, G. W. *J. Am. Chem. Soc.* **1977**, *99*, 4704.

(35) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2768.

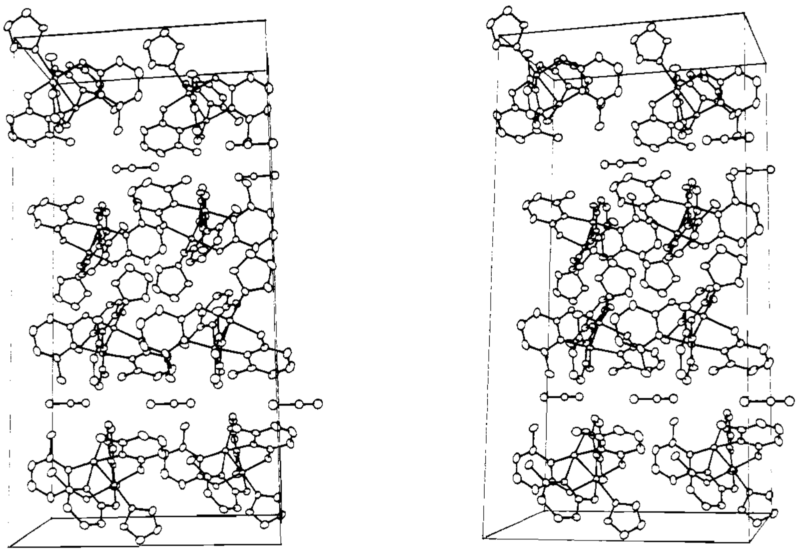

Figure 7. Stereoscopic packing diagram of the unit cell contents of $Rh_2(mhp)_4(C_3H_4N_2)\cdot0.5CH_3CN$ (**4**) with thermal ellipsoids drawn at the 20% probability level. The ellipsoids of the acetonitrile molecules in the lattice have been arbitrarily reduced in size for clarity. The view is down the *a* axis with the *c* axis vertical and the *b* axis horizontal.

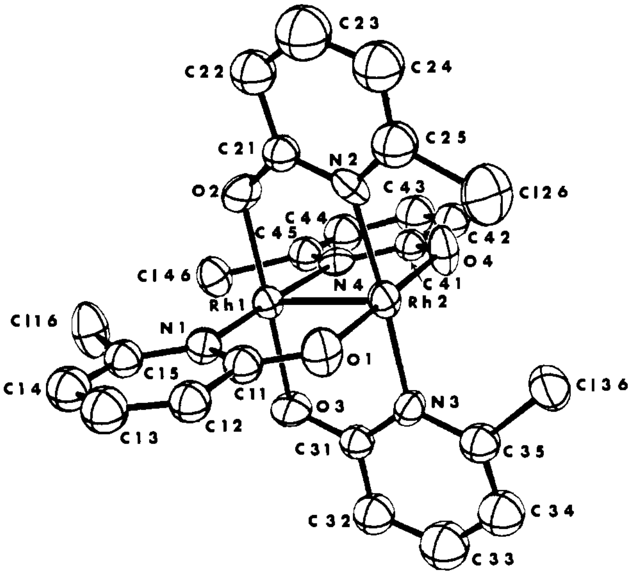

Figure 8. ORTEP drawing of $Rh_2(chp)_4$ (**5**) showing the atomic numbering scheme used in Tables VI and XII. Thermal ellipsoids are scaled so as to enclose 50% of their electron density.

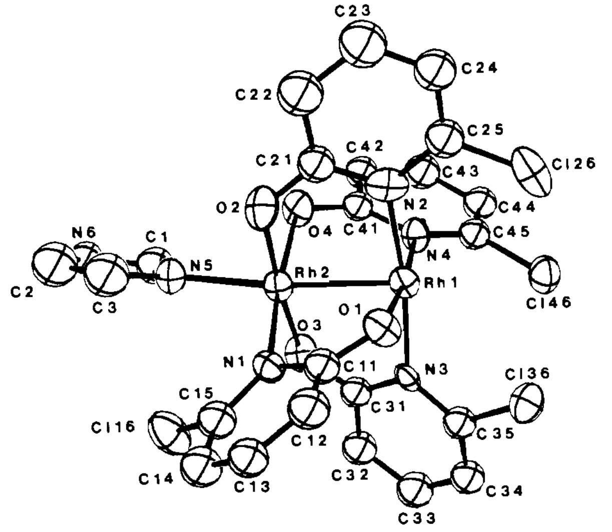

Figure 9. View of the dinuclear rhodium(II) complex in $Rh_2(chp)_4(C_3H_4N_2)\cdot3H_2O$ (**6**) with thermal ellipsoids drawn at the 50% probability level. The labeling scheme shown is that used in Tables VII and XIII.

process and even halt the reaction at that point, although compound **4** presumably could be obtained from **3a**.

The second remarkable new stereochemical pattern is found in the tetrasubstituted mhp and chp compounds (**2**, **4**, **6**) with acetonitrile or imidazole ligands. In these molecules we have for the first time an arrangement of the four mhp or chp type ligands in which three of them have their nitrogen atoms coordinated to one metal atom and only one is attached by its nitrogen atom to the other metal atom. These molecules also exhibit Rh–Rh distances that are elongated by 0.006–0.025 Å over the compound with no axial ligands. Furthermore, the twists of bridging ligands about the Rh–Rh bond by about 20° have not been observed previously in compounds with Rh–Rh bonds less than 2.5 Å. Since no dirhodium(II) carboxylates have been isolated without axial ligands, a direct comparison cannot be made with these eclipsed compounds, but an examination of $Rh_2(O_2CR)_4$ structures with axial nitrogen-donor ligands[11] suggests that the same amount of lengthening of the Rh–Rh bond is observed with two axial ligands. Inspection of the axial Rh–L distances in **2**, **4**, and **6** reveals that these values ($\sim$2.14 Å on the average) are nearly 0.1 Å *shorter* than those observed in $Rh_2(O_2CR)_4L_2$ compounds (cf. Rh–N = 2.227 (3) Å in $Rh_2(O_2CCH_3)_4(py)_2$[7a]). We also note that in compound **2** the formation of a stable solid compound with acetonitrile represents a departure from what has been observed in the rhodium carboxylates since attempts to isolate a stable solid adduct thus far have failed.[4a]

It would appear that the 3:1, rather than the usual 2:2, set of ligand orientations is attributable to the coordination of the imidazole or acetonitrile ligand to one rhodium atom. In order for this axial donor to have access to the metal atom, no more than one 6-CH_3 or 6-Cl ring substituent on that end of the molecule is permissible. However, when there are three methyl groups or chlorine atoms on the other end, the repulsive forces between them are rather large but can be lessened by the observed twisting of the ligands by about 20°.

Recent work[14] on quadruply bonded dichromium(II) compounds establishes that distinct ranges of the Cr–Cr bond length exist depending upon the identity of the bridging ligands and the number of axial ligands, if any, in the compound. In contrast, dirhodium(II) compounds do not exhibit such distinct groupings, and considerable overlap exists between compounds with zero, one, or two axial ligands. For example, Rh_2-

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(36) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1980**, *19*, 1453.

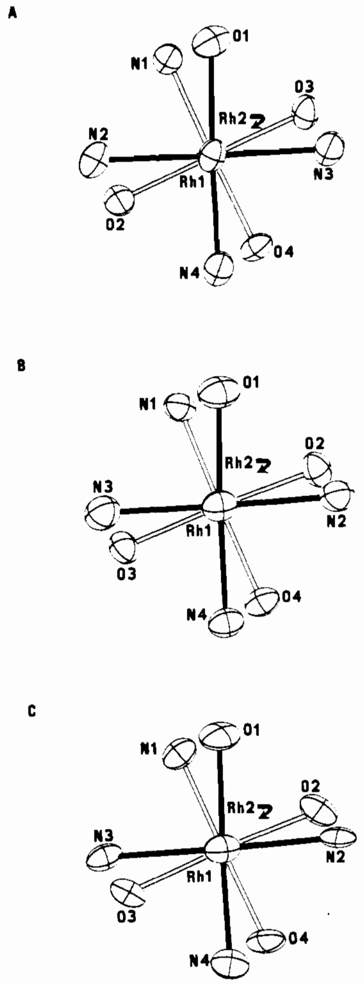

Figure 10. Views down the Rh(1)–Rh(2) axes in compound **2** (A), **4** (B), and **6** (C) showing the conformations of the eight equatorial atoms coordinated to each of the dirhodium units. The thermal ellipsoids are drawn at the 50% probability level. Note that the conformation shown in A corresponds to the enantiomer of **2** illustrated in Figure 3.

Table XVIII. Inductive Effects on the Metal-Metal Bond Length

	M-M bond length, Å		$d(\text{M-M})_{\text{chp}}$ –
M	$M_2(\text{mhp})_4$	$M_2(\text{chp})_4$	$d(\text{M-M})_{\text{mhp}}$, Å
Cr	1.889 (1)[a]	1.955 (2)[b]	0.066
Mo	2.065 (1)[a]	2.085 (1)[b]	0.020
W	2.161 (1)[a]	2.177 (1)[b]	0.016
Rh	2.359 (1)[c]	2.379 (1)[d]	0.020
	2.367 (1)[d]		0.012

[a] Reference 17. [b] Reference 36. [c] Reference 12. [d] This work; average value found in $Rh_2(\text{mhp})_4 \cdot H_2O$.

$(O_2CCMe_3)_4(H_2O)_2$[10] has a Rh–Rh bond length which is nearly the same, despite the presence of axial H_2O ligands, as that found in $Rh_2(\text{mhp})_4 \cdot H_2O$ (molecule A). Interestingly, this pivalate compound has a Rh–Rh distance which is 0.008 Å shorter than the distance in $Rh_2(\text{chp})_4$ which has no axial ligands at all. This is a clear departure from the trend observed in the dichromium(II) species and, to a lesser extent, dimolybdenum(II) compounds with bridging ligands[14,17] which consistently show longer metal–metal bond lengths for compounds with axial ligands. Dirhodium(II) compounds have six antibonding ($\pi^{*4}\delta^{*2}$) electrons in which the π^* electrons are particularly effective in interacting with axial ligands via π back-bonding. As recent theoretical work[13] suggests, the π-back-bonding ability of the dirhodium(II) unit enhances the σ-bonding ability of the axial ligands, and it is this σ-bonding component which most effectively leads to a lengthening of the Rh–Rh bond. Phosphine ligands of the type PR_3 have been found to produce the longest Rh–Rh bonds among compounds having four bridging ligands (cf. $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$ in Table XVII).

The structures of $Rh_2(\text{chp})_4$ and $Rh_2(\text{mhp})_4$ afford the opportunity to study the purely inductive effects of the electron-withdrawing chlorine atom and the electron-donating methyl group on the Rh–Rh bond in these compounds. These compounds have identical equatorial bridging ligands, and axial interactions have been completely eliminated. The recent preparation and structure of the quadruply bonded compounds of the form $M_2(\text{chp})_4$ (M = Cr, Mo, W) shows that there is a significant effect on the metal–metal length when the Cl atom is substituted for the methyl group. Table XVIII summarizes these results and gives the values for the corresponding rhodium compounds. In all cases the compounds with the chp ligands produce longer M–M distances. The largest variation is seen in the dichromium(II) compounds as might be expected from the extreme sensitivity of this bond to bridging and axial ligands,[14] but the elongation observed in the dirhodium compounds is in the range found for molybdenum and tungsten. Inspection of the average Rh–O and Rh–N bond lengths in $Rh_2(\text{chp})_4$ reveals while the Rh–O distance (2.011 (8) Å) is marginally shorter than for the $Rh_2(\text{mhp})_4$ compound, the Rh–N distance becomes slightly longer (2.050 (9) Å in $Rh_2(\text{chp})_4$ vs. 2.043 (5) Å in $Rh_2(\text{mhp})_4$[12]). Consequently, no single aspect of the bonding in these compounds can be attributed to M–M bond lengthening in changing from mhp to chp.

Note on the Rh–Rh Bonding. A great many years ago there was a genuine controversy about the Rh–Rh bond order in the $Rh_2(O_2CR)_4$ and related compounds. The Rh–Rh bonds seem rather short compared to other accepted single bonds between rhodium atoms, although they are rather longer than most M–M triple bonds. It was therefore suggested that if the metal 5s or $5p_z$ orbitals (or perhaps only the former) are low enough in energy to influence the electron configuration of the filled valence shell orbitals, the electron density in the antibonding orbitals, δ^* and π^*, would be reduced. In the limit, the π^* orbitals might be unoccupied, thus leaving a net triple Rh–Rh bond.

However, the SCF-Xα-SW calculation of Norman and Kolari[13a] shows that there is no major participation by the Rh 5s orbitals in these molecules, and, thus, the Rh–Rh bond is best considered to be a net single bond, although a particularly strong one. *We fully subscribe to this view.* We should like further to point out that there has been *no effort from this laboratory*, or elsewhere, to defend or promulgate the triple-bond hypothesis since the work of Norman and Kolari. It therefore seems rather pointless that a number of papers[5b,6,8a,12,30,37-39] continue to appear in which the question of single vs. triple bond is represented as a still unresolved controversy and much energy is devoted to jousting with the triple-bond windmill.

The real questions concerning the Rh–Rh bonding in these compounds are now much more subtle ones. They concern the exact ordering of filled orbitals (to which the recent paper of Garner et al.[12] makes a most useful contribution) and the way in which the nature of the axial ligands and the removal of one electron (to form $[Rh_2(O_2CR)_4]^+$ ions) affect the Rh–Rh bonding.

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Note Added in Proof: Recently two new dirhodium(II) compounds with mhp ligands have been reported (Berry, M.; Garner, C. D.; Hillier, I. H.; Clegg, W. *Inorg. Chim. Acta* **1980**, *45*, L209) similar to compounds **2**, **4**, and **6**. The structure of $Rh_2(mhp)_4(Hmhp)\cdot C_7H_8$ has a dinuclear molecule similar to **2** with a Rh–Rh bond length of 2.383 (1) Å and an axial Hmhp ligand coordinated at 2.195 (4) Å through the oxygen atom and the nitrogen atom apparently in the protonated form forming a hydrogen bond with an oxygen atom of one of the bridging mhp ligands. The second compound, $[\{Rh_2(mhp)_4\}_2]\cdot 2CH_2Cl_2$, has its mhp ligands arranged as in **2** also, but the axial ligand comes from the oxygen atom of an mhp ligand in an adjacent $Rh_2(mhp)_4$ molecule with this adjacent molecule axially coordinated in the same fashion. The Rh–Rh distance in the dinuclear complex is 2.369 (1) Å with the axial Rh–O distance 2.236 (3) Å. These authors further note that these compounds are capable of accepting a single axial ligand as we have found with **2**.[40]

Registry No. **1**, 75991-47-8; **2**, 75790-37-3; **3a**, 75790-35-1; **3b**, 75790-36-2; **4**, 75802-57-2; **5**, 75790-34-0; **6**, 75790-33-9; $Rh_2(OAc)_4$, 15956-28-2.

Supplementary Material Available: Table XV (least-squares planes and dihedral angles) and tables of observed and calculated structure factors for the seven compounds (89 pages). Ordering information is given on any current masthead page.

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Molecular and Chain Structures of Four Tetrakis(μ-propionato)-dirhodium(II) Complexes with Axial Nitrogen-Donor Ligands

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Four adducts of $Rh_2(O_2CC_2H_5)_4$ have been prepared with various axial nitrogen-donor ligands and their structures determined from single-crystal X-ray diffraction data. The complexes include $Rh_2(O_2CC_2H_5)_4(ACR)_2$ (**1**), $Rh_2(O_2CC_2H_5)_4(AZA)_2$ (**2**), $Rh_2(O_2CC_2H_5)_4(PHZ)$ (**3**), and $Rh_2(O_2CC_2H_5)_4(DDA)$ (**4**), where ACR = acridine, AZA = 7-azaindole, PHZ = phenazine, and DDA = 2,3,5,6-tetramethyl-*p*-phenylenediamine (durenediamine). The structures were refined to final R_1 values of 0.046, 0.045, 0.035, and 0.038 for **1**–**4**, respectively. Compound **1** crystallizes in the space group $P\bar{1}$ with a unit cell of dimensions a = 8.332 (2) Å, b = 10.008 (2) Å, c = 11.328 (4) Å, α = 109.60 (2)°, β = 100.15 (3)°, γ = 97.21 (2)°, and Z = 1. Crystals of **2** are orthorhombic, space group *Pbca*, with a = 20.110 (2) Å, b = 20.040 (2) Å, c = 14.224 (2) Å, and Z = 8. Compounds **1** and **2** are 1:2 adducts with Rh–Rh distances of 2.417 (1) and 2.403 (1) Å and axial Rh–N bond lengths of 2.413 (3) and 2.275 (6) Å (average), respectively. The 7-azaindole ligand in **2** coordinates through the pyridine nitrogen atom. Compound **3** crystallizes in the space group $P\bar{1}$ with one formula weight in a unit cell of dimensions a = 8.744 (1) Å, b = 9.092 (3) Å, c = 8.316 (2) Å, α = 111.82 (2)°, β = 90.14 (1)°, and γ = 82.24 (2)°. Crystals of **4** are also triclinic, space group $P\bar{1}$, with a = 8.922 (3) Å, b = 9.092 (3) Å, c = 8.316 (2) Å, α = 104.44 (2)°, β = 101.02 (2)°, γ = 84.70 (2)°, and Z = 1. Both compounds **3** and **4** crystallize as 1:1 adducts with the $Rh_2(O_2CC_2H_5)_4$ units linked by the bidentate bases into one-dimensional chains. The chains of **3** have Rh–Rh and Rh–N distances of 2.409 (1) and 2.362 (4) Å, respectively, and are nearly linear with a Rh–Rh–N angle of 174.71 (9)°. Compound **4** has a Rh–Rh distance of 2.387 (1) Å. The DDA molecules coordinate to the $Rh_2(O_2CC_2H_5)_4$ units with Rh–N bond distances of 2.324 (6) Å and a Rh′–Rh–N angle of 175.3 (2)°. The distorted tetrahedral geometry about the coordinated NH_2 groups (Rh–N–C angle = 118.8 (4)°) imparts a zigzag structure to the chains in **4**.

Introduction

The ability of the rhodium(II) carboxylates to bind axial ligands has provided a means of systematically investigating the response of the Rh–Rh bond length to changes in the donor strength of the axial ligands.[1-5] The affinity for axial ligands in conjunction with the relative stability of the tetrakis(carboxylato)dirhodium(II) unit has contributed to the use of these compounds in a number of investigations in which the unique chemical reactivity of the rhodium(II) carboxylates has played a prominent role. These studies range from biologically related ones such as the antitumor activity[6] displayed by the rhodium(II) carboxylates to an increasing number of catalytic applications involving organic substrates.[7]

Most nitrogen-donor adducts of the rhodium(II) tetracarboxylates so far studied are based on the acetate complex,[2,4,8-21] and structural data are limited to the pyridine,[2] diethylamine,[4] nitric oxide,[3] theophylline,[6b] and caffeine[6b] adducts. Thermodynamic and kinetic data on rhodium(II) carboxylate compounds have revealed[19] that tetrakis(μ-propionato)-dirhodium(II) forms more stable adducts and forms at a faster rate than the corresponding tetrakis(μ-acetato) complexes. This variation in reactivity is ascribed to the enhanced lipophilic character of the propionate bridging

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