Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. A-494) for financial support, Engelhard Industries for a loan of rhodium trichloride, and Dr. A. Bino for his assistance in this work.

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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[40] Cotton, F. A.; Darensbourg, D. J.; Felthouse, T. R., unpublished work.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

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

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Received June 16, 1980

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, $\alpha = 109.60$ (2)°, $\beta = 100.15$ (3)°, $\gamma = 97.21$ (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, $\alpha = 111.82$ (2)°, $\beta = 90.14$ (1)°, and $\gamma = 82.24$ (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, $\alpha = 104.44$ (2)°, $\beta = 101.02$ (2)°, $\gamma = 84.70$ (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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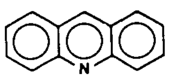
Table I. Crystallographic Data for Four Rhodium(II) Propionate Complexes

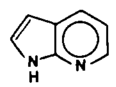
parameter	1	2	3	4
formula	$Rh_2O_8N_2C_{38}H_{38}$	$Rh_2O_8N_4C_{26}H_{32}$	$Rh_2O_8N_2C_{24}H_{28}$	$Rh_2O_8N_2C_{22}H_{36}$
space group	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P\bar{1}$
a, Å	8.332 (2)	20.110 (2)	8.744 (1)	8.922 (3)
b, Å	10.008 (2)	20.040 (2)	9.890 (4)	9.092 (3)
c, Å	11.328 (4)	14.224 (2)	8.037 (1)	8.316 (2)
α, deg	109.60 (2)	90.0	111.82 (2)	104.44 (2)
β, deg	100.15 (3)	90.0	90.14 (1)	101.02 (2)
γ, deg	97.21 (2)	90.0	82.24 (2)	84.70 (2)
V, Å^3	858 (1)	5732 (2)	638.5 (5)	640.5 (3)
d_{calcd}, g/cm^3	1.66	1.70	1.76	1.72
Z	1	8	1	1
fw	856.55	734.38	678.31	662.35
cryst size, mm	0.1 × 0.2 × 0.2	0.1 × 0.1 × 0.3	0.08 × 0.1 × 0.4	0.1 × 0.1 × 0.5
μ(Mo Kα), cm^{-1}	9.951	11.765	13.093	13.020
range 2θ, deg	4–50	4–45	4–45	4–45
no. unique data	3012	2762	1537	1435
no. data, $F_o^2 > 3\sigma(F_o^2)$	2718	2472	1394	1353
no. variables	227	231	164	154
R_1	0.046	0.045	0.034	0.038
R_2	0.072	0.063	0.051	0.054
esd	2.201	1.568	1.520	1.306
largest peak, e/Å^3 [a]	0.43	0.32	0.35	0.77

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

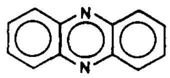
group over that of the acetate. This paper presents the preparation and structures of four tetrakis(μ-propionato)-dirhodium(II) complexes with axial aromatic or heterocyclic nitrogen ligands. These include two 1:2 adducts with acridine (ACR) and 7-azaindole (AZA) ligands and two 1:1 adducts with the bifunctional ligands phenazine (PHZ) and 2,3,5,6-tetramethyl-*p*-phenylenediamine (durenediamine, DDA) as shown. The latter two ligands have been found effective in mediating electron-exchange interactions between metal centers[22] and provide a continuous bonding framework between dinuclear units.



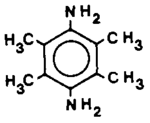
ACR



AZA



PHZ



DDA

Experimental Section

Compound Preparation. Rhodium(II) propionate was prepared by a previously described method.[23]

$Rh_2(O_2CC_2H_5)_4(ACR)_2$ (1) was prepared directly in crystalline form by adding a slight excess of ACR to an acetonitrile solution of $Rh_2(O_2CC_2H_5)_4$. Crystals of **1** were obtained from slow evaporation of the acetonitrile solution. The crystals are dichroic, appearing dark green or dark red at different orientations when viewed with transmitted light.

$Rh_2(O_2CC_2H_5)_4(AZA)_2$ (2) was prepared in essentially the same way as **1** with benzene or methanol as a solvent. Dark red prisms were obtained upon slow evaporation of the solvent.

$Rh_2(O_2CC_2H_5)_4(PHZ)$ (3) was first isolated as a dark red-violet solid by suspending $Rh_2(O_2CC_2H_5)_4$ in benzene (it is only slightly soluble) and adding an excess of PHZ dissolved in benzene. The heterogeneous mixture was stirred for 3 h to ensure complete reaction of $Rh_2(O_2CC_2H_5)_4$. The solid was collected on a fritted filter and then redissolved in methanol, giving a blue-green solution indicative of the dimethanolate adduct. Very slow evaporation (3–4 weeks) of the methanol led to crystallization of **3** as thin red needles and plates. Only the plates had adequate thickness for use in X-ray data collection.

$Rh_2(O_2CC_2H_5)_4(DDA)$ (4) was prepared directly in crystalline form. A saturated methanol solution of $Rh_2(O_2CC_2H_5)_4$ was placed in a test tube. A small amount of DDA was dissolved in methanol and carefully layered on top of the $Rh_2(O_2CC_2H_5)_4$ solution. As the product crystallized from solution, additional amounts of DDA in methanol were added. The first red-violet acicular crystals began to form after ca. 30 min, and crystals of maximum size were formed within 24 h.

X-ray Crystallography. Collection of Data. The X-ray diffraction data for compounds **1** and **2** were collected at 26 ± 1 °C on an Enraf-Nonius CAD-4F autodiffractometer equipped with a graphite-crystal monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. A description of the data collection techniques for this diffractometer has been given before.[24] Details concerning the data

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CC_2H_5)_4(ACR)_2$ (1)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.04930 (4)	0.03484 (3)	0.41836 (3)	2.74 (1)	2.89 (1)	2.30 (1)	0.61 (1)	0.85 (1)	1.526 (9)
O(1)	−0.0939 (4)	−0.1536 (4)	0.2843 (3)	4.0 (1)	3.6 (1)	2.8 (1)	0.1 (1)	0.7 (1)	1.22 (9)
O(2)	0.2448 (4)	−0.0603 (4)	0.4512 (3)	3.3 (1)	4.9 (1)	3.3 (1)	1.4 (1)	1.54 (9)	2.59 (8)
O(3)	0.1868 (4)	0.2170 (4)	0.5648 (3)	3.9 (1)	3.5 (1)	3.3 (1)	−0.4 (1)	0.8 (1)	1.34 (9)
O(4)	0.1553 (4)	−0.1245 (3)	0.6036 (3)	3.8 (1)	4.5 (1)	3.2 (1)	1.5 (1)	1.55 (9)	2.63 (8)
N	0.1424 (5)	0.1021 (4)	0.2524 (4)	3.4 (1)	3.1 (1)	2.8 (1)	0.7 (1)	0.8 (1)	1.44 (9)
C(1)	−0.1856 (6)	−0.2336 (5)	0.3211 (4)	3.7 (2)	3.6 (2)	2.5 (2)	0.6 (2)	0.6 (1)	1.1 (1)
C(2)	−0.3044 (9)	−0.3620 (8)	0.2149 (7)	5.4 (3)	5.9 (3)	4.9 (3)	−1.5 (3)	0.9 (2)	1.0 (2)
C(3)	−0.4404 (11)	−0.4331 (10)	0.2491 (9)	7.2 (4)	7.7 (4)	8.4 (4)	−1.9 (3)	0.8 (4)	2.8 (3)
C(4)	0.2595 (6)	−0.1161 (5)	0.5366 (4)	3.5 (2)	3.6 (2)	2.5 (1)	0.9 (1)	1.1 (1)	1.3 (1)
C(5)	0.4161 (7)	−0.1737 (7)	0.5577 (6)	4.1 (2)	8.8 (2)	8.4 (2)	3.4 (2)	2.9 (2)	6.5 (2)
C(6)	0.4214 (8)	−0.2736 (7)	0.6287 (7)	5.2 (3)	8.3 (2)	8.5 (3)	3.2 (2)	2.5 (2)	6.0 (2)
C(7)	0.1259 (6)	0.2307 (5)	0.2410 (4)	3.3 (2)	3.0 (1)	2.9 (1)	0.6 (1)	1.0 (1)	1.6 (1)
C(8)	0.0868 (7)	0.3409 (5)	0.3450 (5)	5.1 (2)	3.1 (2)	4.3 (2)	1.3 (2)	2.2 (2)	1.7 (1)
C(9)	0.0708 (7)	0.4730 (5)	0.3363 (5)	5.4 (2)	3.8 (2)	5.0 (2)	1.9 (2)	2.3 (2)	2.5 (1)
C(10)	0.0861 (7)	0.5019 (5)	0.2246 (6)	4.8 (2)	3.3 (2)	6.1 (2)	1.1 (2)	2.0 (2)	2.7 (1)
C(11)	0.1229 (7)	0.4017 (5)	0.1245 (5)	4.8 (2)	3.9 (2)	4.6 (2)	1.2 (2)	1.3 (2)	2.9 (1)
C(12)	0.1454 (6)	0.2635 (5)	0.1310 (4)	3.4 (2)	3.1 (1)	3.6 (2)	0.4 (1)	0.9 (1)	1.9 (1)
C(13)	0.1893 (6)	0.1603 (5)	0.0297 (4)	4.0 (2)	4.1 (2)	3.2 (2)	0.7 (2)	1.2 (1)	2.3 (1)
C(14)	0.2169 (6)	0.0318 (5)	0.0423 (4)	3.1 (2)	3.4 (2)	2.7 (2)	0.3 (1)	0.9 (1)	1.2 (1)
C(15)	0.2680 (7)	−0.0746 (6)	−0.0565 (5)	4.7 (2)	4.4 (2)	3.4 (2)	0.9 (2)	1.6 (2)	1.4 (2)
C(16)	0.2971 (7)	−0.1991 (6)	−0.0392 (5)	5.4 (2)	4.3 (2)	4.8 (2)	1.6 (2)	2.6 (2)	1.7 (2)
C(17)	0.2719 (7)	−0.2274 (6)	0.0695 (5)	5.0 (2)	3.8 (2)	4.2 (2)	1.6 (2)	1.6 (2)	1.7 (2)
C(18)	0.2195 (6)	−0.1293 (5)	0.1656 (5)	4.4 (2)	3.3 (2)	3.3 (2)	1.2 (2)	1.0 (2)	1.5 (1)
C(19)	0.1918 (6)	0.0051 (5)	0.1563 (4)	3.0 (2)	3.1 (1)	2.7 (1)	0.5 (1)	0.7 (1)	1.3 (1)

[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 $Rh_2(O_2CC_2H_5)_4(AZA)_2$ (2)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.30274 (3)	0.28530 (3)	0.20313 (5)	2.11 (3)	1.97 (3)	2.51 (3)	0.15 (2)	0.05 (3)	0.07 (3)
Rh(2)	0.38973 (3)	0.20334 (3)	0.19401 (5)	2.06 (3)	1.91 (3)	2.44 (3)	0.13 (2)	−0.14 (3)	−0.19 (3)
O(1)	0.2580 (3)	0.2254 (3)	0.3010 (4)	2.8 (3)	3.2 (3)	3.0 (3)	0.1 (2)	0.7 (2)	0.6 (2)
O(2)	0.3399 (3)	0.1496 (3)	0.2945 (4)	2.7 (3)	2.5 (2)	3.0 (3)	0.2 (2)	0.0 (2)	0.6 (2)
O(3)	0.3568 (3)	0.3319 (3)	0.3055 (4)	3.1 (3)	2.8 (3)	3.2 (3)	0.5 (2)	−0.7 (2)	−0.7 (2)
O(4)	0.4380 (3)	0.2553 (3)	0.2958 (4)	2.8 (2)	2.5 (2)	2.8 (3)	0.4 (2)	−0.4 (2)	−0.7 (2)
O(5)	0.3520 (3)	0.3395 (3)	0.1056 (4)	2.9 (3)	3.1 (3)	3.1 (3)	0.1 (2)	0.4 (2)	0.7 (2)
O(6)	0.4336 (3)	0.2633 (3)	0.0954 (4)	2.2 (2)	2.7 (2)	3.8 (3)	−0.0 (2)	0.5 (2)	0.1 (2)
O(7)	0.2542 (3)	0.2333 (3)	0.1004 (4)	3.1 (3)	3.0 (3)	3.2 (3)	0.2 (2)	−0.7 (3)	−0.1 (2)
O(8)	0.3360 (3)	0.1563 (3)	0.0936 (4)	2.2 (2)	2.5 (2)	3.2 (3)	0.1 (2)	−0.4 (2)	−0.7 (2)
N(1)	0.4713 (3)	0.1242 (3)	0.1867 (5)	2.8 (3)	2.7 (3)	2.5 (3)	−0.2 (3)	0.1 (3)	0.1 (3)
N(2)	0.5461 (4)	0.1736 (4)	0.2959 (6)	2.5 (3)	3.4 (3)	5.3 (4)	0.6 (3)	−1.0 (3)	−1.2 (3)
N(3)	0.2271 (3)	0.3685 (3)	0.2171 (5)	3.0 (3)	1.9 (3)	2.9 (3)	0.5 (3)	0.1 (3)	0.1 (3)
N(4)	0.1417 (4)	0.3047 (4)	0.2916 (5)	3.1 (4)	3.5 (4)	3.5 (4)	−0.1 (3)	−0.1 (3)	−0.5 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.2855 (4)	0.1708 (4)	0.3264 (6)	2.7 (2)	C(14)	0.5040 (5)	0.0157 (5)	0.1315 (7)	4.9 (2)
C(2)	0.2524 (5)	0.1275 (5)	0.3994 (7)	4.0 (2)	C(15)	0.5615 (6)	0.0161 (6)	0.1884 (8)	5.7 (3)
C(3)	0.1839 (6)	0.1521 (5)	0.4366 (8)	4.9 (2)	C(16)	0.5730 (5)	0.0721 (5)	0.2457 (7)	4.0 (2)
C(4)	0.4122 (4)	0.3089 (4)	0.3312 (6)	2.4 (2)	C(17)	0.6248 (6)	0.0928 (6)	0.3098 (8)	5.4 (3)
C(5)	0.4465 (5)	0.3417 (4)	0.4127 (7)	3.3 (2)	C(18)	0.6053 (5)	0.1548 (5)	0.3403 (8)	4.8 (2)
C(6)	0.5206 (5)	0.3257 (5)	0.4262 (7)	4.1 (2)	C(19)	0.5259 (4)	0.1239 (4)	0.2389 (6)	2.7 (2)
C(7)	0.4061 (4)	0.3176 (4)	0.0713 (6)	2.5 (2)	C(20)	0.2449 (5)	0.4299 (5)	0.1916 (6)	3.4 (2)
C(8)	0.4404 (5)	0.3568 (5)	−0.0051 (7)	3.5 (2)	C(21)	0.2060 (5)	0.4868 (5)	0.2133 (7)	4.1 (2)
C(9)	0.4254 (5)	0.4343 (5)	−0.0014 (8)	4.6 (2)	C(22)	0.1453 (5)	0.4801 (5)	0.2594 (7)	3.7 (2)
C(10)	0.2807 (4)	0.1810 (4)	0.0664 (6)	3.0 (2)	C(23)	0.1254 (4)	0.4143 (4)	0.2843 (6)	3.1 (2)
C(11)	0.2446 (5)	0.1478 (5)	−0.0148 (6)	3.4 (2)	C(24)	0.0694 (5)	0.3848 (5)	0.3327 (7)	4.3 (2)
C(12)	0.2637 (5)	0.0738 (5)	−0.0294 (7)	4.8 (2)	C(25)	0.0816 (5)	0.3195 (5)	0.3371 (7)	4.1 (2)
C(13)	0.4610 (4)	0.0697 (4)	0.1315 (6)	3.1 (2)	C(26)	0.1694 (4)	0.3633 (4)	0.2615 (6)	2.3 (2)

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

collection and refinement are summarized in Table I. The final cell constants for **1** were obtained from a least-squares fit to 24 reflections in the range 28° < 2θ < 32°. Final lattice constants for **2** were obtained from a least-squares fit to 25 reflections in the range 24° < 2θ < 32°. Both data sets were corrected for Lorentz and polarization effects but not absorption.

The diffraction data for **3** were collected on the Enraf-Nonius CAD-4F diffractometer as described for **1** and **2**. However, because of the platelike appearance of the crystal, data were collected with use of the FLAT scanning mode rather than the standard BISECT mode in which the ψ angle is set to 0°.[25] The FLAT mode calculates the azimuth position of minimum absorption on the assumption of a small crystal thickness with an infinitely large surface area. As far as possible, the sum of the incident and diffracted beam path lengths is minimized. The FLAT mode requires that the vector which is parallel to the incident beam and normal to the plane of the platelike crystal be identified. It was found for this crystal that this vector corresponds to (100) in the crystal coordinate system (*hkl*). The final cell pa-

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(25) CAD-4 Operation Manual, Enraf-Nonius, Delft, 1977.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CC_2H_5)_4$(PHZ) (3)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.49406 (4)	0.11494 (3)	0.47895 (4)	2.27 (2)	1.07 (1)	2.55 (1)	−0.35 (1)	−0.00 (1)	0.92 (1)
O(1)	0.5841 (4)	−0.0029 (3)	0.2231 (4)	4.1 (2)	1.4 (1)	2.7 (1)	−0.3 (1)	0.4 (1)	0.92 (9)
O(2)	0.2830 (4)	0.0798 (4)	0.3750 (5)	2.8 (1)	2.0 (1)	3.8 (1)	−0.8 (1)	−0.8 (1)	1.47 (9)
O(3)	0.4083 (4)	0.2164 (4)	0.7371 (4)	3.9 (2)	1.7 (1)	2.5 (1)	−0.3 (1)	0.2 (1)	0.81 (9)
O(4)	0.2932 (4)	−0.1321 (4)	0.4176 (5)	2.9 (1)	2.0 (1)	4.0 (1)	−0.8 (1)	−0.7 (1)	1.74 (9)
N	0.4873 (5)	0.3504 (4)	0.4659 (5)	2.6 (2)	1.8 (1)	2.7 (1)	−0.5 (1)	0.1 (1)	1.1 (1)
C(1)	0.6049 (6)	−0.1394 (5)	0.1696 (6)	2.3 (2)	1.7 (2)	2.7 (2)	−0.2 (2)	−0.3 (2)	1.0 (1)
C(2)	0.6564 (8)	−0.2275 (6)	−0.0290 (7)	5.7 (3)	3.1 (2)	2.6 (2)	−0.1 (2)	0.6 (2)	0.9 (2)
C(3)	0.6849 (10)	−0.3879 (7)	−0.0840 (9)	7.9 (4)	3.1 (3)	3.9 (3)	1.4 (3)	0.2 (3)	0.9 (2)
C(4)	0.2335 (6)	−0.0400 (5)	0.3585 (7)	2.4 (2)	1.8 (2)	2.9 (2)	−0.1 (2)	0.1 (2)	0.7 (1)
C(5)	0.0846 (7)	−0.0672 (7)	0.2602 (8)	4.0 (3)	3.7 (2)	5.7 (3)	−2.0 (2)	−1.8 (2)	2.2 (2)
C(6)	0.0402 (8)	−0.2161 (8)	0.2333 (11)	4.5 (3)	4.9 (3)	8.0 (4)	−2.5 (2)	−2.1 (3)	2.5 (3)
C(7)	0.6279 (5)	0.5428 (5)	0.4527 (6)	2.3 (2)	1.3 (2)	2.6 (2)	−0.2 (2)	0.1 (2)	1.2 (1)
C(8)	0.7701 (6)	0.5795 (5)	0.4017 (7)	2.8 (2)	2.2 (2)	4.0 (2)	−0.5 (2)	0.1 (2)	1.5 (1)
C(9)	0.8875 (6)	0.4731 (5)	0.3166 (7)	3.0 (2)	2.0 (2)	4.4 (2)	0.0 (2)	0.7 (2)	1.7 (1)
C(10)	0.8756 (7)	0.3202 (6)	0.2726 (8)	3.0 (2)	2.8 (2)	4.8 (2)	−0.1 (2)	0.8 (2)	1.7 (2)
C(11)	0.7431 (7)	0.2805 (6)	0.3208 (7)	3.2 (2)	2.4 (2)	4.0 (2)	−0.2 (2)	0.9 (2)	1.3 (2)
C(12)	0.6181 (6)	0.3899 (5)	0.4139 (6)	2.5 (2)	1.7 (2)	2.6 (2)	−0.2 (2)	−0.0 (2)	1.3 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2O_2CC_2H_5)_4$(DDA) (4)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.06533 (6)	0.50479 (6)	0.14039 (7)	2.03 (2)	2.95 (2)	2.58 (2)	−0.29 (2)	−0.32 (2)	0.59 (2)
O(1)	0.2475 (5)	0.5809 (5)	0.0766 (5)	2.6 (2)	4.4 (2)	2.8 (2)	−0.8 (2)	−0.4 (2)	1.1 (2)
O(2)	−0.0184 (6)	0.7221 (5)	0.2085 (6)	3.6 (2)	3.2 (2)	3.1 (2)	0.1 (2)	−0.4 (2)	0.4 (2)
O(3)	−0.1243 (5)	0.4291 (6)	0.1900 (6)	2.5 (2)	4.5 (2)	3.5 (2)	−0.7 (2)	−0.1 (2)	1.1 (2)
O(4)	−0.1380 (5)	0.7142 (5)	−0.0545 (6)	2.9 (2)	3.2 (2)	3.9 (2)	0.2 (2)	−0.1 (2)	0.8 (2)
N	0.1814 (7)	0.5327 (8)	0.4207 (8)	2.6 (2)	6.9 (3)	3.0 (2)	−0.6 (2)	−0.8 (2)	1.5 (2)
C(1)	0.2384 (7)	0.5992 (8)	−0.0690 (9)	2.1 (3)	2.9 (3)	3.9 (3)	−0.3 (2)	−0.1 (2)	0.4 (2)
C(2)	0.3761 (8)	0.6576 (9)	−0.1136 (10)	2.7 (3)	5.5 (4)	4.4 (3)	−1.4 (3)	0.4 (2)	1.4 (3)
C(3)	0.4736 (10)	0.7591 (10)	0.0381 (12)	4.1 (4)	6.4 (4)	6.1 (4)	−2.5 (3)	0.1 (3)	0.8 (4)
C(4)	−0.0975 (8)	0.7809 (8)	0.0978 (9)	2.3 (3)	3.0 (3)	3.8 (3)	−0.1 (2)	−0.2 (2)	0.2 (2)
C(5)	−0.1517 (10)	0.9457 (9)	0.1522 (11)	3.9 (4)	3.5 (3)	5.7 (4)	0.2 (3)	−0.3 (3)	−0.3 (3)
C(6)	−0.0277 (11)	1.0461 (10)	0.2612 (13)	5.3 (4)	3.7 (4)	7.5 (5)	−1.4 (3)	−0.3 (4)	0.5 (3)
C(7)	0.3437 (8)	0.5153 (8)	0.4598 (8)	2.7 (3)	4.4 (3)	2.3 (3)	−0.4 (3)	−0.3 (2)	0.8 (2)
C(8)	0.4109 (8)	0.3761 (8)	0.4815 (9)	3.9 (3)	3.6 (3)	2.7 (3)	−1.7 (3)	−0.4 (2)	0.6 (2)
C(9)	0.3066 (11)	0.2450 (10)	0.4596 (12)	5.7 (4)	5.6 (4)	6.4 (5)	−3.6 (3)	−1.5 (4)	1.6 (3)
C(10)	0.5688 (8)	0.3592 (8)	0.5221 (8)	3.0 (3)	3.2 (3)	2.8 (3)	−0.3 (2)	−0.3 (2)	0.5 (2)
C(11)	0.6463 (11)	0.2053 (9)	0.5411 (10)	6.6 (5)	3.4 (3)	4.5 (4)	1.3 (3)	0.2 (4)	1.3 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

rameters were obtained from a least-squares fit to 25 reflections in the range 25° < 2θ < 32° and are given in Table I. Lorentz and polarization corrections were made, but an absorption correction was omitted.

X-ray data for **4** were collected at 22 ± 3 °C on a Syntex P$\bar{1}$ autodiffractometer using Mo Kα radiation (λ = 0.71073 Å) and a graphite-crystal monochromator in the incident beam. The lattice constants were determined from a least-squares fit to the setting angles of 15 reflections in the range 25° < 2θ < 30°. Further details concerning the data collection technique have appeared before.[26] The data were corrected for Lorentz and polarization effects but not absorption.

Solution and Refinement of the Structures.[27] Crystals of $Rh_2(O_2CC_2H_5)_4(ACR)_2$ (**1**) are triclinic, and the structure solution was begun in the space group *P*$\bar{1}$. A three-dimensional Patterson map yielded the position of the Rh atom as the highest vector. Three cycles of refinement of the Rh atom position with an isotropic temperature factor led to residuals of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.34$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.42$$

Subsequent difference Fourier maps in conjunction with least-squares refinement gave the positions of the remaining 24 nonhydrogen atom positions. Anisotropic thermal parameters were assigned to all 25 atoms, and further refinement led to the final residuals recorded in Table I. An extinction correction was made. Hydrogen atoms were omitted in the refinement, and the final difference Fourier map showed no significant residual electron density.

Examination of the diffraction data for $Rh_2(O_2CC_2H_5)_4(AZA)_2$ (**2**), which had been collected for an orthorhombic crystal system, revealed the space group to be *Pbca*. The unit cell volume was consistent with eight formula weights located on general positions. The positions of the two independent Rh atoms were obtained by direct methods with use of the MULTAN program. Subsequent refinement of these atom positions phased the remaining 38 nonhydrogen atoms which were located with use of difference Fourier maps followed by least-squares refinement. All 14 noncarbon atom were given anisotropic thermal parameters, and the structure was refined to the discrepancy indices shown in Table I. Hydrogen atoms were not included. A final difference Fourier map was featureless.

The location of the Rh atom in $Rh_2(O_2CC_2H_5)_4$(PHZ) (**3**) was obtained as the highest vector in the Patterson map. Three cycles of least-squares refinement followed by difference Fourier maps and further refinement led to the location of all 18 nonhydrogen atoms. With anisotropic thermal parameters for all nonhydrogen atoms, the structure converged to the residuals shown in Table I. Prior to convergence, a correction for secondary extinction was deemed necessary upon inspection of the $|F_o|$ and $|F_c|$ values. The correction was made with use of the equation $|F_o| = |F_c|(1 + gI_c)^{-1}$, where the value of g, as determined from least-squares fitting was 8.72×10^{-7}. Hydrogen atom contributions were omitted in the refinement. The final difference Fourier map showed no significant residual electron density.

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(26) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

(27) All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package with local modifications.

Table VI. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CC_2H_5)_4(ACR)_2$ (1)

Distances

Rh-Rh′	2.417 (1)	C(5)-C(6)	1.478 (7)
Rh-O(1)	2.040 (3)	C(7)-C(8)	1.437 (5)
Rh-O(2)	2.027 (3)	C(7)-C(12)	1.421 (5)
Rh-O(3)	2.041 (3)	C(8)-C(9)	1.379 (5)
Rh-O(4′)	2.039 (3)	C(9)-C(10)	1.413 (6)
Rh-N	2.413 (3)	C(10)-C(11)	1.350 (6)
O(1)-C(1)	1.257 (4)	C(11)-C(12)	1.443 (5)
O(2)-C(4)	1.265 (4)	C(12)-C(13)	1.402 (5)
O(3)-C(1′)	1.250 (4)	C(13)-C(14)	1.382 (5)
O(4)-C(4)	1.262 (4)	C(14)-C(15)	1.431 (5)
N-C(7)	1.356 (4)	C(14)-C(19)	1.448 (5)
N-C(19)	1.359 (4)	C(15)-C(16)	1.369 (6)
C(1)-C(2)	1.517 (6)	C(16)-C(17)	1.396 (6)
C(2)-C(3)	1.440 (8)	C(17)-C(18)	1.378 (5)
C(4)-C(5)	1.505 (5)	C(18)-C(19)	1.427 (5)

Angles

Rh′-Rh-O(1)	88.01 (7)	O(2)-C(4)-O(4)	125.0 (3)
Rh′-Rh-O(2)	86.97 (7)	O(2)-C(4)-C(5)	115.4 (3)
Rh′-Rh-O(3)	86.91 (8)	O(4)-C(4)-C(5)	119.5 (3)
Rh′-Rh-O(4′)	88.11 (7)	C(4)-C(5)-C(6)	118.0 (4)
Rh′-Rh-N	178.86 (7)	N-C(7)-C(8)	119.0 (3)
O(1)-Rh-O(2)	92.8 (1)	N-C(7)-C(12)	123.6 (3)
O(1)-Rh-O(3)	174.89 (9)	C(8)-C(7)-C(12)	117.4 (3)
O(1)-Rh-O(4′)	86.7 (1)	C(7)-C(8)-C(9)	120.1 (4)
O(1)-Rh-N	91.0 (1)	C(8)-C(9)-C(10)	121.5 (4)
O(2)-Rh-O(3)	86.4 (1)	C(9)-C(10)-C(11)	120.4 (3)
O(2)-Rh-O(4′)	175.07 (8)	C(10)-C(11)-C(12)	119.8 (4)
O(2)-Rh-N	93.7 (1)	C(7)-C(12)-C(11)	120.6 (3)
O(3)-Rh-O(4′)	93.7 (1)	C(7)-C(12)-C(13)	118.9 (3)
O(3)-Rh-N	94.0 (1)	C(11)-C(12)-C(13)	120.5 (3)
O(4′)-Rh-N	91.2 (1)	C(12)-C(13)-C(14)	118.6 (3)
Rh-O(1)-C(1)	118.6 (2)	C(13)-C(14)-C(15)	120.7 (3)
Rh-O(2)-C(4)	120.8 (2)	C(13)-C(14)-C(19)	119.2 (3)
Rh-O(3)-C(1′)	119.9 (2)	C(15)-C(14)-C(19)	120.1 (3)
Rh-O(4′)-C(4′)	119.0 (2)	C(14)-C(15)-C(16)	118.8 (4)
Rh-N-C(7)	121.3 (2)	C(15)-C(16)-C(17)	121.8 (4)
Rh-N-C(19)	121.0 (2)	C(16)-C(17)-C(18)	121.2 (4)
C(7)-N-C(19)	117.0 (3)	C(17)-C(18)-C(19)	120.2 (3)
O(1)-C(1)-O(3′)	126.2 (3)	N-C(19)-C(14)	122.4 (3)
O(1)-C(1)-C(2)	115.8 (3)	N-C(19)-C(18)	119.8 (3)
O(3′)-C(1)-C(2)	118.0 (3)	C(14)-C(19)-C(18)	117.8 (3)
C(1)-C(2)-C(3)	117.5 (5)		

For triclinic crystals of $Rh_2(O_2CC_2H_5)_4(DDA)$ (4) the space group $P\bar{1}$ was chosen. The Rh atom position was located from the Patterson map, and further solution and refinement of the structure proceeded as in 3 with anisotropic temperature factors assigned to all 17 nonhydrogen atoms. As before, hydrogen atoms were omitted, and a final difference Fourier synthesis revealed no significant features.

Tables of observed and calculated structure factor amplitudes for those reflections having $I > 3\sigma(I)$ are available as supplementary material.

Results

The structures of four nitrogen-donor adducts of tetrakis(μ-propionato)-dirhodium(II) have been determined from single-crystal X-ray diffraction data. The structural results show that acridine and 7-azaindole form molecular 1:2 adducts with $Rh_2(O_2CC_2H_5)_4$ while the bifunctional ligands phenazine and durenediamine give compounds of 1:1 stoichiometry with $Rh_2(O_2CC_2H_5)_4$ and link the dinuclear units into quasi-one-dimensional chains. Tables II–V record the positional and thermal parameters for compounds **1**–**4**, respectively, while Tables VI–IX present the bond distances and angles for these structures. Table X summarizes various structural parameters for 12 dirhodium(II) tetracarboxylate adducts with oxygen-, nitrogen-, sulfur-, and phosphorus-donor ligands. The compounds are arranged in order of increasing Rh-Rh bond length. The structural characteristics of the four $Rh_2(O_2CC_2H_5)_4$ adducts will now be presented.

Table VII. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CC_2H_5)_4(AZA)_2$ (2)

Distances

Rh(1)-Rh(2)	2.403 (1)	N(3)-C(26)	1.326 (9)
Rh(1)-O(1)	2.047 (5)	N(4)-C(25)	1.40 (1)
Rh(1)-O(3)	2.043 (5)	N(4)-C(26)	1.368 (9)
Rh(1)-O(5)	2.022 (5)	C(1)-C(2)	1.51 (1)
Rh(1)-O(7)	2.043 (5)	C(2)-C(3)	1.56 (1)
Rh(1)-N(3)	2.266 (6)	C(4)-C(5)	1.50 (1)
Rh(2)-O(2)	2.051 (5)	C(5)-C(6)	1.54 (1)
Rh(2)-O(4)	2.030 (4)	C(7)-C(8)	1.51 (1)
Rh(2)-O(6)	2.047 (5)	C(8)-C(9)	1.58 (1)
Rh(2)-O(8)	2.025 (5)	C(10)-C(11)	1.52 (1)
Rh(2)-N(1)	2.284 (6)	C(11)-C(12)	1.55 (1)
O(1)-C(1)	1.278 (8)	C(13)-C(14)	1.38 (1)
O(2)-C(1)	1.259 (8)	C(14)-C(15)	1.41 (1)
O(3)-C(4)	1.260 (8)	C(15)-C(16)	1.40 (1)
O(4)-C(4)	1.294 (8)	C(16)-C(17)	1.44 (1)
O(5)-C(7)	1.272 (8)	C(16)-C(19)	1.41 (1)
O(6)-C(7)	1.268 (8)	C(17)-C(18)	1.37 (1)
O(7)-C(10)	1.272 (8)	C(20)-C(21)	1.42 (1)
O(8)-C(10)	1.277 (8)	C(21)-C(22)	1.39 (1)
N(1)-C(13)	1.361 (9)	C(22)-C(23)	1.42 (1)
N(1)-C(19)	1.327 (9)	C(23)-C(24)	1.44 (1)
N(2)-C(18)	1.40 (1)	C(23)-C(26)	1.39 (1)
N(2)-C(19)	1.347 (9)	C(24)-C(25)	1.33 (1)
N(3)-C(20)	1.332 (9)		

Angles

Rh(2)-Rh(1)-O(1)	87.5 (1)	Rh(1)-N(3)-C(20)	118.4 (5)
Rh(2)-Rh(1)-O(3)	87.9 (1)	Rh(1)-N(3)-C(26)	124.9 (5)
Rh(2)-Rh(1)-O(5)	88.5 (1)	C(20)-N(3)-C(26)	116.0 (6)
Rh(2)-Rh(1)-O(7)	87.8 (1)	C(25)-N(4)-C(26)	108.2 (6)
Rh(2)-Rh(1)-N(3)	175.2 (1)	O(1)-C(1)-O(2)	124.2 (7)
O(1)-Rh(1)-O(3)	91.0 (2)	O(1)-C(1)-C(2)	119.8 (7)
O(1)-Rh(1)-O(5)	176.0 (2)	O(2)-C(1)-C(2)	116.0 (7)
O(1)-Rh(1)-O(7)	88.7 (2)	C(1)-C(2)-C(3)	116.2 (7)
O(1)-Rh(1)-N(3)	94.4 (2)	O(3)-C(4)-O(4)	123.0 (6)
O(3)-Rh(1)-O(5)	89.0 (2)	O(3)-C(4)-C(5)	118.0 (6)
O(3)-Rh(1)-O(7)	175.7 (2)	O(4)-C(4)-C(5)	118.7 (6)
O(3)-Rh(1)-N(3)	87.6 (2)	C(4)-C(5)-C(6)	116.8 (7)
O(5)-Rh(1)-O(7)	91.0 (2)	O(5)-C(7)-O(6)	124.4 (6)
O(5)-Rh(1)-N(3)	89.6 (2)	O(5)-C(7)-C(8)	119.2 (6)
O(7)-Rh(1)-N(3)	96.7 (2)	O(6)-C(7)-C(8)	116.3 (6)
Rh(1)-Rh(2)-O(2)	88.0 (1)	C(7)-C(8)-C(9)	113.6 (7)
Rh(1)-Rh(2)-O(4)	87.6 (1)	O(7)-C(10)-O(8)	124.7 (7)
Rh(1)-Rh(2)-O(6)	87.1 (1)	O(7)-C(10)-C(11)	116.7 (7)
Rh(1)-Rh(2)-O(8)	88.2 (1)	O(8)-C(10)-C(11)	118.5 (7)
Rh(1)-Rh(2)-N(1)	179.0 (1)	C(10)-C(11)-C(12)	113.8 (7)
O(2)-Rh(2)-O(4)	90.4 (2)	N(1)-C(13)-C(14)	122.1 (7)
O(2)-Rh(2)-O(6)	175.1 (2)	C(13)-C(14)-C(15)	120.5 (8)
O(2)-Rh(2)-O(8)	89.2 (2)	C(14)-C(15)-C(16)	118.2 (9)
O(2)-Rh(2)-N(1)	91.0 (2)	C(15)-C(16)-C(17)	135.5 (9)
O(4)-Rh(2)-O(6)	88.9 (2)	C(15)-C(16)-C(19)	116.0 (8)
O(4)-Rh(2)-O(8)	175.8 (2)	C(17)-C(16)-C(19)	108.4 (7)
O(4)-Rh(2)-N(1)	92.6 (2)	C(16)-C(17)-C(18)	104.7 (9)
O(6)-Rh(2)-O(8)	91.1 (2)	N(2)-C(18)-C(17)	110.0 (8)
O(6)-Rh(2)-N(1)	93.8 (2)	N(1)-C(19)-N(2)	125.7 (7)
O(8)-Rh(2)-N(1)	91.6 (2)	N(1)-C(19)-C(16)	126.7 (7)
Rh(1)-O(1)-C(1)	120.3 (5)	N(2)-C(19)-C(16)	107.5 (7)
Rh(2)-O(2)-C(1)	119.9 (5)	N(3)-C(20)-C(21)	122.3 (7)
Rh(1)-O(3)-C(4)	120.6 (4)	C(20)-C(21)-C(22)	120.6 (8)
Rh(2)-O(4)-C(4)	120.8 (4)	C(21)-C(22)-C(23)	117.0 (7)
Rh(1)-O(5)-C(7)	119.8 (4)	C(22)-C(23)-C(24)	135.8 (8)
Rh(2)-O(6)-C(7)	120.1 (4)	C(22)-C(23)-C(26)	116.4 (7)
Rh(1)-O(7)-C(10)	119.4 (5)	C(24)-C(23)-C(26)	107.8 (7)
Rh(2)-O(8)-C(10)	119.8 (5)	C(23)-C(24)-C(25)	106.4 (8)
Rh(2)-N(1)-C(13)	118.3 (5)	N(4)-C(25)-C(24)	110.1 (8)
Rh(2)-N(1)-C(19)	124.9 (5)	N(3)-C(26)-N(4)	124.9 (6)
C(13)-N(1)-C(19)	116.5 (6)	N(3)-C(26)-C(23)	127.6 (7)
C(18)-N(2)-C(19)	109.2 (7)	N(4)-C(26)-C(23)	107.5 (6)

$Rh_2(O_2CC_2H_5)_4(ACR)_2$ (1). This structure consists of centrosymmetric dinuclear $Rh_2(O_2CC_2H_5)_4$ units with a Rh–Rh bond length of 2.417 (1) Å and axially coordinated heterocyclic nitrogen atoms at 2.413 (3) Å from each Rh atom. The complete molecular unit is illustrated in Figure 1. The Rh′-Rh-N linkage is nearly linear, making an angle of 178.86 (7)° about Rh. The coordinated acridine molecule is essentially planar with 0.089 Å as the largest deviation from the

Table VIII. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CC_2H_5)_4(PHZ)$ (3)

Distances			
Rh-Rh'	2.409 (1)	N-C(12)	1.371 (6)
Rh-O(1)	2.046 (3)	C(1)-C(2)	1.540 (7)
Rh-O(2)	2.043 (3)	C(2)-C(3)	1.465 (8)
Rh-O(3')	2.033 (3)	C(4)-C(5)	1.524 (7)
Rh-O(4')	2.038 (3)	C(5)-C(6)	1.511 (9)
Rh-N	2.362 (4)	C(7)-C(8)	1.442 (6)
O(1)-C(1)	1.242 (6)	C(7)-C(12')	1.441 (6)
O(2)-C(4)	1.276 (6)	C(8)-C(9)	1.344 (7)
O(3)-C(1)	1.266 (6)	C(9)-C(10')	1.438 (7)
O(4)-C(4)	1.233 (6)	C(10)-C(11)	1.373 (7)
N-C(7)	1.327 (5)	C(11)-C(12)	1.418 (6)
Angles			
Rh'-Rh-N	174.71 (9)	Rh'-O(3)-C(1)	119.0 (3)
Rh'-Rh-O(1)	87.84 (9)	Rh'-O(4)-C(4)	119.7 (3)
Rh'-Rh-O(2)	87.46 (9)	O(1)-C(1)-O(3)	126.7 (4)
Rh'-Rh-O(3')	87.49 (9)	O(1)-C(1)-C(2)	118.1 (4)
Rh'-Rh-O(4')	87.66 (9)	O(3)-C(1)-C(2)	115.1 (4)
N-Rh-O(1)	96.6 (1)	C(1)-C(2)-C(3)	116.1 (5)
N-Rh-O(2)	95.7 (1)	O(2)-C(4)-O(4)	126.0 (4)
N-Rh-O(3')	88.1 (1)	O(2)-C(4)-C(5)	115.9 (4)
N-Rh-O(4')	89.2 (1)	O(4)-C(4)-C(5)	118.1 (4)
O(1)-Rh-O(2)	86.0 (1)	C(4)-C(5)-C(6)	112.7 (5)
O(1)-Rh-O(3')	175.3 (1)	N-C(7)-C(8)	119.4 (4)
O(1)-Rh-O(4')	93.0 (1)	N-C(7)-C(12')	122.7 (4)
O(2)-Rh-O(3')	94.5 (1)	C(8)-C(7)-C(12')	117.9 (4)
O(2)-Rh-O(4')	175.1 (1)	C(7)-C(8)-C(9)	120.5 (4)
O(3')-Rh-O(4')	86.0 (1)	C(8)-C(9)-C(10')	121.5 (4)
Rh-N-C(7)	120.7 (3)	C(9')-C(10)-C(11)	119.9 (4)
Rh-N-C(12)	120.0 (3)	C(10)-C(11)-C(12)	120.1 (4)
C(7)-N-C(12)	117.3 (4)	N-C(12)-C(7')	119.9 (4)
Rh-O(1)-C(1)	118.5 (3)	N-C(12)-C(11)	120.1 (4)
Rh-O(2)-C(4)	118.7 (3)	C(7')-C(12)-C(11)	120.0 (4)

Table IX. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CC_2H_5)_4(DDA)$ (4)

Distances			
Rh-Rh'	2.387 (1)	N-C(7)	1.425 (8)
Rh-O(1)	2.030 (4)	C(1)-C(2)	1.524 (9)
Rh-O(2)	2.028 (4)	C(2)-C(3)	1.532 (11)
Rh-O(3')	2.032 (4)	C(4)-C(5)	1.515 (9)
Rh-O(4')	2.031 (4)	C(5)-C(6)	1.507 (10)
Rh-N	2.324 (6)	C(7)-C(8)	1.389 (9)
O(1)-C(1)	1.249 (8)	C(7)-C(10)	1.403 (9)
O(2)-C(4)	1.249 (8)	C(8)-C(9)	1.533 (10)
O(3)-C(1)	1.281 (8)	C(8)-C(10')	1.388 (9)
O(4)-C(4)	1.259 (8)	C(10)-C(11)	1.533 (9)
Angles			
Rh'-Rh-N	175.3 (2)	Rh'-O(4)-C(4)	120.0 (4)
Rh'-Rh-O(1)	87.7 (2)	O(1)-C(1)-O(3)	126.7 (6)
Rh'-Rh-O(2)	88.5 (2)	O(1)-C(1)-C(2)	118.4 (6)
Rh'-Rh-O(3')	88.8 (2)	O(3)-C(1)-C(2)	114.8 (6)
Rh'-Rh-O(4')	87.0 (2)	C(1)-C(2)-C(3)	113.3 (6)
N-Rh-O(1)	93.2 (2)	O(2)-C(4)-O(4)	125.5 (6)
N-Rh-O(2)	86.9 (2)	O(2)-C(4)-C(5)	117.2 (6)
N-Rh-O(3')	90.3 (2)	O(4)-C(4)-C(5)	117.3 (6)
N-Rh-O(4')	97.5 (2)	C(4)-C(5)-C(6)	113.2 (6)
O(1)-Rh-O(2)	89.8 (2)	N-C(7)-C(8)	119.4 (6)
O(1)-Rh-O(3')	176.5 (2)	N-C(7)-C(10)	118.8 (6)
O(1)-Rh-O(4')	90.8 (2)	C(8)-C(7)-C(10)	121.8 (6)
O(2)-Rh-O(3')	89.8 (2)	C(7)-C(8)-C(9)	118.3 (7)
O(2)-Rh-O(4')	175.5 (2)	C(7)-C(8)-C(10')	119.6 (6)
O(3')-Rh-O(4')	89.3 (2)	C(9)-C(8)-C(10')	122.0 (7)
Rh-N-C(7)	118.8 (4)	C(7)-C(10)-C(8')	118.6 (6)
Rh-O(1)-C(1)	119.4 (4)	C(7)-C(10)-C(11)	120.7 (6)
Rh-O(2)-C(4)	118.8 (4)	C(11)-C(10)-C(8')	120.7 (6)
Rh'-O(3)-C(1)	117.4 (4)		

least-squares plane (Table XI[28]). The acridine plane approximately bisects the propionate groups; it forms dihedral angles of 57.5 and 47.6° with the O(1)–C(1)–O(3′)–C(2) and O(2)–C(4)–O(4)–C(5) fragments of the bridging propionates.

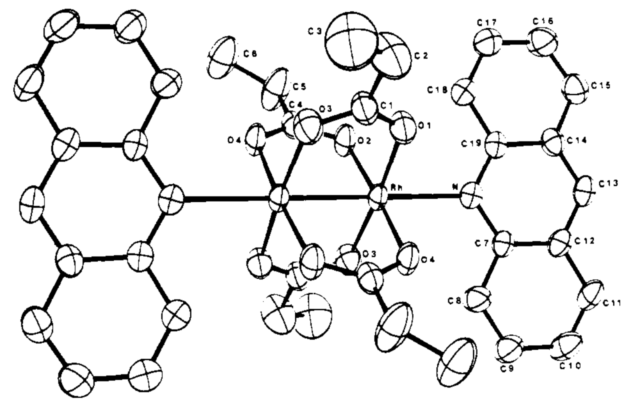

Figure 1. ORTEP drawing of the $Rh_2(O_2CC_2H_5)_4(ACR)_2$ molecule (1) using 50% probability ellipsoids. The atom labeling scheme shown is used in Tables II and VI. The molecule is located about an inversion center at the midpoint of the Rh–Rh bond.

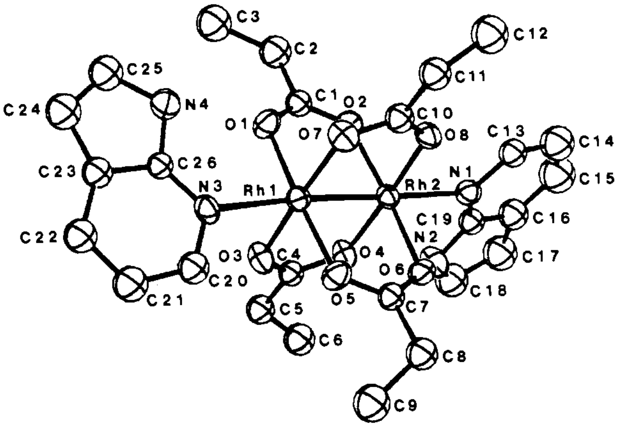

Figure 2. ORTEP plotting of $Rh_2(O_2CC_2H_5)_4(AZA)_2$ (2) shown with thermal ellipsoids at the 50% probability level and the atom labeling scheme employed in Tables III and VII. The entire molecule constitutes the crystallographic asymmetric unit.

$Rh_2(O_2CC_2H_5)_4(AZA)_2$ (2). Eight formula weights of 2 are found within the unit cell with each molecule occupying general positions. Hence, the entire molecule constitutes the asymmetric unit with no crystallographically imposed symmetry. The molecular unit, shown in Figure 2, consists of dirhodium(II) tetrapropionate with a Rh–Rh distance of 2.403 (1) Å and two axially bound AZA molecules with an average Rh–N distance of 2.275 (1) Å. The Rh atoms are displaced 0.074 and 0.081 Å out of the carboxylate planes toward the axial nitrogen atom for Rh(1) and Rh(2), respectively. Each AZA molecule coordinates through the pyridine imino nitrogen atom rather than the amino nitrogen in the five-membered ring. The two AZA molecules are inclined 68.4° to one another. Both AZA molecules are strictly planar (Table XI[28]) with the largest deviation from planarity in each molecule being 0.021 Å.

$Rh_2(O_2CC_2H_5)_4(PHZ)$ (3). Figure 3 depicts a segment of the linear chains in 3. The asymmetric unit consists of a Rh atom, two propionate groups, and half of a PHZ molecule. Crystallographic centers of inversion are located at the midpoint of the Rh–Rh bond and the center of the PHZ molecule. The Rh–Rh bond is 2.409 (1) Å in length with a Rh–N distance of 2.362 (4) Å. The Rh atom lies 0.085 Å out of the carboxylate oxygen plane toward the PHZ nitrogen atom. The Rh′–Rh–N angle of 174.71 (9)° imparts a slight zigzag to the chains. A stereoview of 3 in Figure 4 shows that the chains extend approximately in the direction of the *b* axis. The PHZ molecule is planar with 0.035 Å as the largest deviation from planarity (Table XI[28]). The PHZ plane nearly bisects the bridging propionate groups with dihedral angles of 58.1 and 53.7° between PHZ and the O(2)–O(4)–C(4)–C(5) and

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[28] Supplementary material.

Table X. Selected Structural Parameters for 12 $Rh_2(O_2CR)_4L_n$ Complexes[a]

R	L	*n*	pK_b	Rh–Rh, Å	Rh–L, Å	Rh–O, Å	ref
CH_3	H_2O	2	15.7[b]	2.3855 (5)	2.310 (3)	2.039 (8)	1
C_2H_5	DDA	1	~8.1[c]	2.387 (1)	2.324 (6)	2.030 (4)	this work
CH_3	py	2	8.75[b]	2.3963 (2)	2.227 (3)	2.039 (2)	2
CH_3	$NHEt_2$	2	3.51[b]	2.4020 (7)	2.301 (5)	2.038 (3)	4
C_2H_5	AZA	2	9.41[d]	2.403 (1)	2.275 (6)	2.038 (5)	this work
CH_3	Me_2SO	2	15.54[b]	2.406 (1)	2.451 (1)	2.036 (3)	5
C_2H_5	Me_2SO	2	15.54[b]	2.407 (1)	2.449 (1)	2.028 (3)	29
C_2H_5	PHZ	1	12.77[e]	2.409 (1)	2.362 (4)	2.040 (3)	this work
C_2H_5	ACR	2	8.42[e]	2.417 (1)	2.413 (3)	2.037 (3)	this work
CH_3	PPh_3	2	11.3[f]	2.449 (2)	2.479 (4)	2.044 (4)	4
CH_3	$NO(NO_2)$	2		2.4537 (4)	1.927 (4),[g] 2.008 (4)[h]	2.026 (3)	4
CH_3	$P(OMe)_3$	2	~10.5[f]	2.4556 (3)	2.437 (1)	2.046 (2)[i]	3

[a] Distances reported represent averages of chemically equivalent bond lengths when appropriate. [b] Taken from ref 2 with references as cited therein. [c] Estimated from data given by: Smith, J. W. In "The Chemistry of the Amino Group"; Patai, S., Ed.; Interscience: London, 1968; pp 161–204. [d] Alder, T. K.; Albert, A. *J. Chem. Soc.* 1960, 1794. [e] Albert, A.; Goldacre, R.; Phillips, J. *J. Chem. Soc.* 1948, 2240. [f] Taken from ref 3 with references as cited therein. [g] L = NO. [h] L = NO_2. [i] Koh, Y. B. Ph.D Thesis, The Ohio State University, 1979.

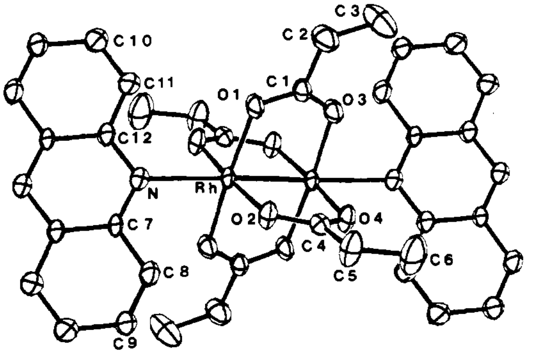

Figure 3. ORTEP view of a segment of the linear chains in $Rh_2(O_2CC_2H_5)_4(PHZ)$ (3) with vibrational ellipsoids enclosing 50% of their electron density. Only the crystallographic asymmetric unit is labeled with the atom numbering scheme used in Tables IV and VIII. Inversion centers are located at the midpoint of the Rh–Rh bond and the center of the phenazine molecule.

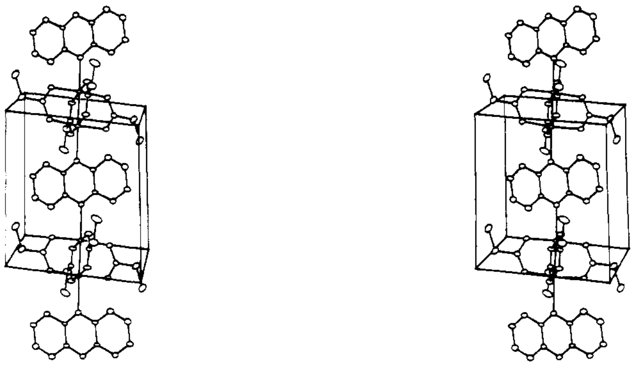

Figure 4. Stereoscopic diagram showing the unit cell contents of $Rh_2(O_2CC_2H_5)_4(PHZ)$ (3) with 20% probability ellipsoids. The view is down the *c* axis with the *b* axis vertical and the *a* axis horizontal.

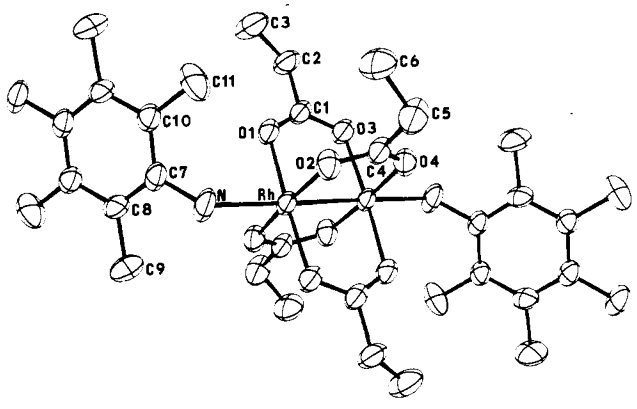

Figure 5. ORTEP drawing of a portion of the molecular chains of $Rh_2(O_2CC_2H_5)_4(DDA)$ (4) with 50% probability ellipsoids. The atom labeling scheme that is used in Tables V and IX shows the crystallographic asymmetric unit which resides about inversion centers located at the midpoint of the Rh–Rh bond and the center of the durenediamine molecule.

O(1)–O(3′)–C(1)–C(2) fragments, respectively.

$Rh_2(O_2CC_2H_5)_4(DDA)$ (4). Although the stoichiometries of **4** and **3** are identical and the unit cell parameters are very similar, compounds **4** and **3** present a markedly different pattern of linking the $Rh_2(O_2CC_2H_5)_4$ units into one-dimensional chains. Whereas the chains in **3** were nearly linear, the exocyclic amino nitrogen, N, which coordinates at 2.324 (6) Å to the Rh atoms in $Rh_2(O_2CC_2H_5)_4$, imparts noticeably zigzagged geometry (Rh–N–C(7) = 118.8 (4)°) to the chains in **4**. Figure 5 illustrates this zigzag effect for a portion of the chain structure. Inversion centers are located at the midpoint of the Rh–Rh bond and the center of the DDA molecule. The Rh–Rh bond length of 2.387 (1) Å is significantly (0.016–0.030 Å) shorter than the values in **1**–**3**. The Rh atom is displaced 0.071 Å out of the carboxylate oxygen plane toward N. The phenyl ring of the DDA molecule defines a plane with the methyl carbon and amino nitrogen atoms showing minor (0.002–0.046 Å) deviations from it (Table XI[28]). Figure 6 gives a stereoview of the chain structure with respect to the unit cell.

Discussion

Structural data on 12 representative dirhodium(II) carboxylate adducts have been compiled in Table X. Although recent results[5] suggest that the R group in the carboxylate, RCO_2^-, may have an effect on the length of the Rh–Rh bond (cf. R = CH_3, L = H_2O has Rh–Rh = 2.3855 (5) Å while R = CMe_3, L = H_2O has Rh–Rh = 2.371 (1) Å), structural comparisons for R = CH_3 and C_2H_5 appear valid despite the variations noted[19] in thermodynamic and kinetic properties. The Me_2SO adducts, for example, with R = CH_3[5] and C_2H_5[29] show essentially identical bond lengths and angles to within the $\pm 3\sigma$ criterion for the esd's. In each of these complexes the Me_2SO molecules are bonded through their sulfur atoms to the rhodium atoms. Table X also records the pK_b values for 11 of the 12 adducts. The pK_b values for the bifunctional PHZ and DDA ligands refer to the first protonation step. Since these ligands utilize both of their nitrogen atoms in the solid-state structures forming 1:1 adducts, further structural comparison of these compounds with those of the 1:2 adducts does not seem warranted. The pK_b values are given only for reference. Previous work[2,3] on the 1:2 adducts has suggested that whenever significant π-back-bonding effects between the

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(29) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 2347.

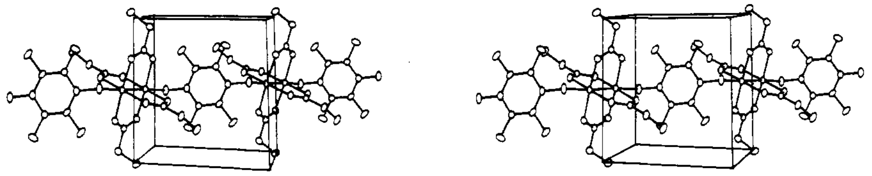

Figure 6. Stereoview of the unit cell of $Rh_2(O_2CC_2H_5)_4(DDA)$ (**4**) with 20% probability ellipsoids. The view is down the *c* axis with the *b* axis vertical and the *a* axis horizontal.

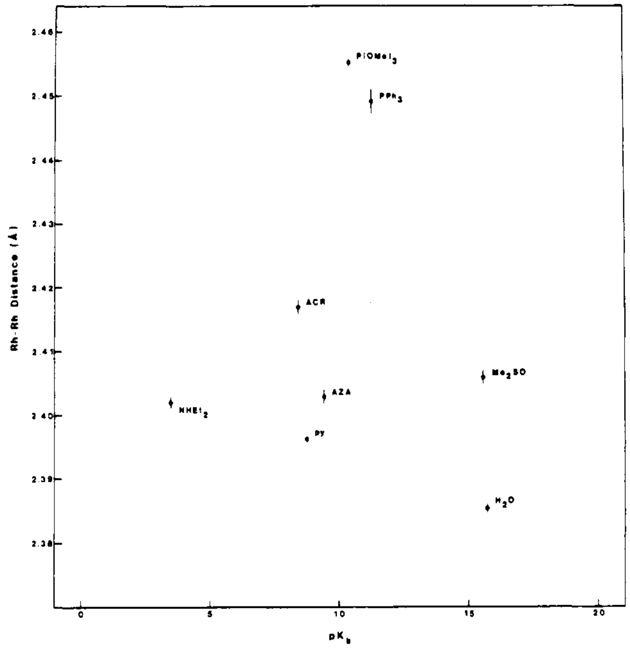

Figure 7. Plot of the Rh–Rh distance vs. the basicity of the axial ligand as gauged by pK_b values for 1:2 adducts of the general formula $Rh_2(O_2CR)_4L_2$. The error bars on the distances are $\pm 1\sigma$. The $NHEt_2$, py, and H_2O ligands show nearly linear correlation between Rh–Rh distance and pK_b value.

Rh and axial ligand atoms are negligible, there is an approximately linear correlation between the Rh–Rh distance and the basicity of the axial donor atom as gauged by the pK_b value. The two new 1:2 adducts reported in this paper provide a further test of the proposed correlation.

The variations in the Rh–Rh bond length with the identity of the axial ligand arise primarily from electronic rather than steric factors. However, steric interactions may in some cases control the position of the axial ligand with respect to the $Rh_2(O_2CR)_4$ unit. For example, in the $Rh_2(O_2CCH_3)_4(PR_3)_2$ complexes shown in Table X, the PPh_3 ligand is more basic than $P(OMe)_3$, but the steric bulk (cone angles[30] are 145 and 107° for PPh_3 and $P(OMe)_3$, respectively) of PPh_3 leads to a longer Rh–P distance (by 0.042 Å) and, hence, a shorter Rh–Rh distance (by 0.006 Å). In the three compounds in this paper with heterocyclic nitrogen-containing ring systems (ACR, AZA, and PHZ) as well as two recently reported compounds[6b] with theophylline and caffeine ligands, the orientations of the heterocyclic nitrogen ligands appear to be determined by the tendency to minimize steric interactions with the carboxylate oxygen atoms. Intermolecular packing forces undoubtedly also contribute to the observed orientations of the three heterocyclic nitrogen ligands reported here; in $Rh_2(O_2CCH_3)_4(py)_2$ such forces are believed[2] to govern completely the orientation of the pyridine rings.

For some time now it has been recognized[1] that metal–metal-bonded complexes, particularly of the type $M_2(O_2CR)_4L_2$, have M–L distances substantially longer (ca. 0.22 Å, on the average[31]) than normal due to the metal–metal trans effect. In the dirhodium(II) carboxylates the basic orbital configuration is $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$; axial ligands L may influence the Rh–Rh bond length by means of $L\sigma \rightarrow$ Rh–Rh σ^* or Rh $\rightarrow$ L π donation. As can be seen from Table X, ligands which are capable of interacting in both ways provide the greatest lengthening of the Rh–Rh bond. Sulfur (Me_2SO), and to a greater extent, phosphorus (PPh_3, $P(OME)_3$) donor axial ligands lead to Rh–Rh distances greater than 2.40 Å. As noted by Norman et al.,[31] the more diffuse lone pairs on these ligands lead to a more effective overlap at these longer than normal Rh–L distances than do the more compact lone pairs on nitrogen and oxygen donor ligands ($NHEt_2$, py, H_2O). However, it is clear that this advantage can be offset with a very strongly interacting ligand like NO which results in a Rh–N distance,[4] 1.927 (4) Å, that is significantly less than the rhodium carboxylate oxygen distances (ca. 2.03–2.04 Å) in the equatorial plane.

Figure 7 displays a correlation between the Rh–Rh distance and the pK_b value for eight structurally characterized diadducts having the general formula $Rh_2(O_4CR)_2L_2$, where R = CH_3 or C_2H_5 and L = H_2O,[1] py,[2] $NHEt_2$,[4] AZA, Me_2SO,[5] ACR, PPh_3,[4] and $P(OMe)_3$.[3] Previous work by Christoph and Koh[2] has suggested a linear correlation between the Rh–Rh distance and the pK_b value for L = H_2O, $NHEt_2$, and py. For these ligands, which interact almost entirely through σ bonding, the pK_b value provides a means to quantify this interaction. For sulfur (Me_2SO) and phosphorus (PPh_3, $P(OMe)_3$) ligands the pK_b value is a very poor gauge of the Rh–L interaction; hence, a substantial departure from the linear correlation is observed. While the involvement of the Rh π^* orbitals in the Rh–L bonding might be anticipated for sulfur- and phosphorus-donor ligands with empty low-lying d orbitals which can accept antibonding π-electron density from the rhodium atom, the existence of an appreciable π interaction in the Rh–L bond for either nitrogen- or oxygen-donor ligands has not been recognized, at least with respect to structural data, except for the extreme case with L = NO.[3] However, thermodynamic data[11,32] on rhodium(II) carboxylate adduct formation suggest that as much as 30% of the Rh–L bond for L = py is due to Rh $\rightarrow$ L π-back-bonding contributions. As can be seen from Figure 7, compounds **1** and **2** with heterocyclic nitrogen ligands show significant deviations from the predicted[2] linear behavior. In each case the "σ-only" basicity of the free heterocyclic nitrogen ligand is insufficient to account for the observed Rh–Rh bond length.

The ACR complex (**1**) shows the largest deviation from the linear Rh–Rh distance vs. pK_b correlation. Although acridine is a weak base, it is slightly stronger than pyridine. The extensive π-bonding framework in ACR makes it more susceptible to form molecular π complexes[33] than compounds that show coordination through the nitrogen atom. In regard to

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this, the green color of the analogous tetraacetate complex, $Rh_2(O_2CCH_3)_4(ACR)_2$ prompted Mal'kova and Shafranskii[16] to state that "we cannot rule out the possibility of a different type of M–L bond, namely with the participation of the multiple bonds of the aromatic rings". However, in $Rh_2(O_2CC_2H_5)_4(ACR)_2$ coordination occurs through the largely σ-bonding nitrogen atom but at a remarkbly long distance, 2.413 (3) Å. This distance is nearly 0.2 Å longer than the Rh–N distance in the py complex in spite of the slightly greater basicity of the ACR nitrogen atom.

The most surprising result in the ACR complex structure is the Rh–Rh bond length which at 2.417 (1) Å is 0.021 Å *longer* than that in the py complex. In fact, this Rh–Rh bond length lies beyond the range found for the known sulfur atom donor ligand complexes such as Me_2SO[5,29] (2.406 (1) Å), tetrahydrothiophene[5] (2.413 (1) Å), and benzylthiol[34] (2.4020 (3) Å). The key to understanding the nature of the axial Rh–N bonding comes from very recent SCF–Xα calculations on the model complex $Rh_2(O_2CH)_4(PH_3)_2$.[35] These calculations fully support the recent observations by Kawamura and co-workers[36,37] that the cation radicals of the form $Rh_2(O_2CR)_4(PR_3)_2^+$ (R = Et, CF_3; PR_3 = PPh_3, $P(OPh)_3$, $P(OCH_2)_3CEt$) exhibit EPR spectra that are most consistent with a purely σ-type Rh–P interaction with little or no π-back-bonding. Consequently, for $Rh_2(O_2CR)_4L_2$ complexes with phosphine ligands the electronic ground-state configuration changes from that found for L = H_2O[31] such that the strongly σ-bonding orbital now becomes nondegenerate, with one component moving to higher energy (the HOMO). This, combined with the σ donation of the phosphine into the Rh σ^* orbital, causes an elongation of the Rh–Rh bond. Presumably the situation for L = ACR is quite similar, but explicit calculations would be necessary to develop a quantitative understanding of the bonding in all $Rh_2(O_2CR)_4L_2$ complexes. The large ACR molecule apparently differs from pyridine in being capable of presenting a greater number of orbitals that are correct in both symmetry and energy to interact with the Rh centers and lengthen the Rh–Rh bond.

In the AZA complex (**2**) with $Rh_2(O_2CC_2H_5)_4$, both molecules of AZA coordinate through the heterocyclic pyridine nitrogen atom rather than the secondary nitrogen atom. In spite of the weaker basicity of the AZA ($pK_b = 9.41$) ligand compared to py ($pK_b = 8.75$), the elongation of the Rh–Rh bond is marginally greater with AZA (2.403 (1) Å) axial ligands than with the py (2.3963 (2) Å) ligands. Additionally, while the ca. 0.05 Å greater axial Rh–N bond length in **2** over that in $Rh_2(O_2CCH_3)_4(py)_2$ is consistent with the weaker basicity of the AZA ligand, the greater number of orbitals in the AZA ligand of the proper symmetry and energy to interact with the Rh σ system apparently give rise to the observed lengthening of the Rh–Rh bond in **2**.

The PHZ and DDA complexes (**3** and **4**) present a new stoichiometry to that previously encountered in dirhodium(II) compounds. Chain structures have been reported for $M_2(O_2CCH_3)_4(pyz)$, where M = Cr(II),[38] Cu(II),[39] and pyz = pyrazine. These linear chains show a more compact packing arrangement than that observed in the molecular 1:2 adducts. In the copper(II) complex,[39] electron-exchange interactions occur between paramagnetic Cu(II) centers in both intra- and intermolecular modes. The intermolecular interaction is propagated by the pyrazine bridging ligand. In the dirhodium(II) complexes **3** and **4** no unusual structural features are observed which can be ascribed solely to the chain structure. The Rh–Rh bond length in the PHZ complex is substantially longer than that expected on the basis of the pK_b (for the first protonation step) of the PHZ ligand. However, the degree of elongation is not as great as in the ACR complex in which two unique axial ligands may donate into the unfilled Rh σ^* orbital rather than the single PHZ ligand per two Rh atoms. In the DDA complex **4** the coordinating amino nitrogen atoms are removed from the π-bonding framework of the aromatic ring. Despite the relatively short axial Rh–N distance of 2.324 (6) Å, the σ-bonding framework in DDA interfaces less effectively with the Rh centers leading to a shorter Rh–Rh bond length by at least 0.016 Å over that found with the heterocyclic nitrogen donor ligands in **1**–**3**.

Conclusions. Structural data presented on four nitrogen-donor adducts of $Rh_2(O_2CC_2H_5)_4$ demonstrate that the proposed linear correlation between Rh–Rh distance and pK_b is not followed. Deviations from linearity arise largely from the variations in the Rh–Rh electronic configuration as a function of axial ligand atom type, and consequently, this type of correlation cannot be made. Differences in the Rh–N bond lengths for the ACR and AZA complexes do not appear to be as important in determining the Rh–Rh bond length as do the actual number, symmetry, and energy of the interacting orbitals on the axial ligand. On the basis of recent calculations,[35] the primary interaction between the Rh atoms and the axial ligand L appears to be almost entirely σ bonding, with shifts in the Rh–Rh σ-bonding orbitals coupled with ligand donation into the Rh–Rh σ^* orbitals accounting for the fluctuations in Rh–Rh bond length. Linking of the dirhodium(II) units into chain structures does not appear to impart any unusual features to the axial or Rh–Rh bonding over that anticipated from the 1:2 adducts. A detailed understanding of the axial and Rh–Rh bonding in $Rh_2(O_2CR)_4L_2$ compounds will require explicit calculations to assess the relative amounts of σ and π character in the L–Rh–Rh–L fragment.

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Registry No. 1, 75790-32-8; **2**, 75790-31-7; **3**, 75790-41-9; **4**, 75790-39-5; $Rh_2(O_2CC_2H_5)_4$, 31126-81-5.

Supplementary Material Available: Table XI (least-squares planes and dihedral angles) and tables of observed and calculated structure factors for the four compounds (40 pages). Ordering information is given on any current masthead page.

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