Inorganica Chimica Acta, 81 (1984) 193–203

Preparation and Structural Characterization of Three Tetracarboxylato Dirhodium (Rh–Rh) Compounds with Bulky Ligands

F. ALBERT COTTON and J. LON THOMPSON

Department of Chemistry and Laboratory for Molecular Structure and Bonding Texas A & M University, College Station, Tex. 77843, U.S.A.

Received May 3, 1983

The preparation and structures of three compounds, red-purple $Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2 \cdot 3C_6H_6$ *(1), light blue* $Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2 \cdot 5CH_3OH$ *(2), and red-purple* $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_6H_5CH_3$ *(3) are reported. Compound* 1 *crystallizes from a benzene/acetonitrile mixture, with benzene incorporated, in the triclinic system with a unit cell of dimensions* a = *13.469(1)* Å, b = *13.507(2)* Å, c = *9.908(1)* Å, α = *110.44(1)°, β = 92.78(1)°, γ = 107.92(1)°,* V = *1582(3)* $Å^3$ *and Z = 1. Two of the* o*-phenyl groups are positioned in the equatorial region while the other two are oriented one towards each end of the molecule. The axial* CH_3CN *groups are tightly coordinated (Rh–N = 2.233(3)* Å*, Rh–Rh–N ≈ 178°) and the Rh–Rh distance is 2.396(1)* Å*. Compound* 2 *was crystallized from methanol in the orthorhombic system with unit cell dimensions* a = *10.587(2)* Å, b = *20.640(2)* Å, c = *24.693(2)* Å, V = *5396(2)* $Å^3$ *and Z = 4. The Rh–Rh bond length, 2.371(2)* Å*, is equal to the shortest one known in* $Rh_2(O_2CR)_4L_2$ *compounds. For compound* 3 *crystals were grown from a mixed acetonitrile–toluene solvent and incorporate toluene molecules in a triclinic unit cell of dimensions* a = *12.664(1)* Å, b = *21.876(2)* Å, c = *9.686(2)* Å, α = *99.00(1)°, β = 105.27(1)°, γ = 75.61(1)°,* V = *2496(1)* $Å^3$ *with Z = 2. The* Ph_3CCO_2 *ligands are mutually* cis*. The Rh–Rh and two independent Rh–N distances are 2.388(2)* Å*, 2.21(1)* Å *and 2.17(1)* Å.

Introduction

Since the structure of $Rh_2(O_2CCH_3)_4(H_2O)_2$ was first determined [1, 2], more than thirty-five $Rh_2(O_2CR)_4L_2$ compounds have been structurally characterized [3, 4] and the chemistry and bonding in the general class of dirhodium(II) compounds continue to be subjects of active research interest [5, 6]. The Rh–Rh distances have been found to vary from 2.371(1) Å in $Rh_2(O_2CCMe_3)_4(H_2O)_2$ to 2.486(1) Å in $Rh_2(O_2CCF_3)_4(PPh_3)_2$. For the most part, it is the effect of varying the axial ligands that has been studied and relatively few variations in the nature, especially the steric character, of the R group in the carboxyl ion have been examined. In this report we describe the preparation and structural characterization of three compounds in which the R groups have unusual steric properties. The three compounds are:

(*1*) $Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2 \cdot 3C_6H_6$

(*2*) $Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2 \cdot 5CH_3OH$

(*3*) $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_6H_5CH_3$

Experimental

All reactions and manipulations were carried out in an atmosphere of pure nitrogen. Rhodium chloride was loaned by Engelhard Industries. Anhydrous $Rh_2(O_2CCH_3)_4$ was prepared by the method of Wilkinson *et al.* [7]. The experimental methods used in gathering X-ray data and the procedures used to solve and refine the crystal structures were, in general, standard and have been described in detail in earlier papers [8, 9].

$Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2 \cdot 3C_6H_6$ (1)

Preparation

Anhydrous rhodium acetate (0.10 g, 0.20 mmol) and 2-biphenylcarboxylic acid (0.22 g, 1.1 mmol) were heated under nitrogen at approximately 120 °C for 24 hours. The molten mixture solidified to a bright green solid, which was placed in a sublimation apparatus and the unreacted acid sublimed. No further purification was deemed necessary. The remaining green solid was dissolved in a 1:1 aceto-

0020-1693/84/$3.00

nitrile/benzene mixture to give a dark purple solution. Upon slow evaporation, red-purple crystals of *1* were obtained.

X-ray Study

A crystal with dimensions 0.15 × 0.25 × 0.35 mm was coated with epoxy cement, attached to a glass fiber, and mounted on the CAD-4F diffractometer. Indexing on 25 intense reflections in the range $25° \leqslant 2\theta \leqslant 32°$ produced a unit cell in the triclinic system with dimensions a = 13.469(1) Å, b = 13.507(2) Å, c = 9.908(1) Å, α = 110.44(1)°, β = 92.78(1)°, γ = 107.92(1)°, and V = 1582(3) Å^3. This volume is consistent with $Z = 1$ for the dinuclear molecule.

A total of 5531 reflections in the range $0° < 2\theta \leqslant 50°$ was collected, the 4469 reflections having $I > 3\sigma(I)$ being used to solve and refine the structure. The low linear absorption coefficient of 5 cm^{-1} made an absorption correction unnecessary. Solution and refinement were undertaken in the space group P$\bar{1}$. The position of the Rh atom was obtained from a three-dimensional Patterson map. Initial refinement gave discrepancy indices of R_1 = 0.34 and R_2 = 0.41. The remaining nitrogen atom, four oxygen atoms, and thirty-seven carbon atoms were found with subsequent difference Fourier maps and least-squares refinement. Refinement of positional and anisotropic thermal parameters for all atoms gave discrepancy indices of R_1 = 0.040 and R_2 = 0.057 with an esd of 1.635. A final difference Fourier map revealed peaks associated with hydrogen atoms which were not refined.

$Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2 \cdot 5CH_3OH$ (2)

Preparation

Anhydrous rhodium acetate (0.10 g, 0.20 mmol) and 1-adamantanecarboxylic acid (0.20 g, 1.1 mmol) were heated under argon at approximately 190 °C for 24 hours. The bright green solid obtained was dissolved in a minimum amount of dichloromethane, then chromatographed on a 15 × 1.5 cm column packed with 60–100 mesh Florisil in hexane. A blue band was eluted with methanol. The light blue solid obtained upon evaporation of the solvent was heated at 120 °C in air for one hour to give a green solid. The green solid was dissolved in toluene and acetonitrile added to this solution. A dark purple solid immediately precipitated which was insoluble. A methanol solution of the green solid was slowly evaporated, giving light blue platelets of *2*.

X-ray Study

A plate-like crystal with dimensions 0.10 × 0.15 × 0.25 mm was lodged in a glass capillary filled with the mother liquor, the capillary sealed with epoxy, then mounted on the CAD-4F diffractometer. Indexing on 25 intense reflectiosn in the range $25° \leqslant 2\theta \leqslant 32°$ produced a unit cell in the orthorhombic system with dimensions a = 10.587(2) Å, b = 20.640(2) Å, c = 24.693(2) Å, and V = 5396(2) Å^3. This volume is consistent with $Z = 4$ for the dinuclear molecule.

A total of 4730 unique reflections in the range $0° < 2\theta \leqslant 50°$ was collected, the 1442 reflections having $I > 3\sigma(I)$ being used to solve and refine the structure. The low linear absorption coefficient of 7 cm^{-1} made an absorption correction unnecessary.

Systematic absences of 0kl with k ≠ 2n, h0l with l ≠ 2n and hk0 with h ≠ 2n indicated the space group Pbca. The position of the Rh atom was found by the direct methods program MULTAN. Initial refinement of this position gave discrepancy indices of R_1 = 0.28 and R_2 = 0.40. The remaining 35 atoms were found by subsequent difference Fourier maps and least-squares refinement. Refinement of positional parameters, anisotropic thermal parameters for all atoms except the methanol molecules in the lattice, and isotropic thermal parameters for the lattice methanols gave discrepancy indices of R_1 = 0.060 and R_2 = 0.066 with an esd of 1.507. A final difference Fourier map revealed peaks associated with hydrogen atoms which were not refined.

$Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_6H_5CH_3$ (3)

Preparation

Anhydrous rhodium acetate (0.10 g, 0.20 mmol) and triphenylacetic acid (0.33 g, 1.2 mmol) were heated under argon at approximately 290 °C. Because of rapid evolution of acetic acid at this temperature, the reaction was halted after five minutes. The resulting green solid was then dissolved in a small amount of dichloromethane and chromatographed on an 18 × 1.5 cm column packed with 60–100 mesh Florisil in hexane. A bright green band was eluted with toluene. Addition of an equal amount of acetonitrile to the toluene solution gave a dark purple solution, which upon slow evaporation gave red-purple crystals of *3*.

X-ray Study

A crystal with dimensions 0.50 × 0.10 × 0.20 mm was coated with epoxy cement, attached to a glass fiber, and mounted on the CAD-4F diffractometer. Indexing on 25 intense reflections in the range $25° \leqslant 2\theta \leqslant 32°$ produced a unit cell in the triclinic system with dimensions a = 12.664(1) Å, b = 21.876(2) Å, c = 9.686(2) Å, α = 99.00(1)°, β = 105.27(1)°, γ = 75.61(1)°, and V = 2496(1) Å^3. This volume is consistent with $Z = 2$ for the dinuclear molecule.

TABLE I. Positional Parameters and Their Estimated Standard Deviations for $Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2\cdot 3C_6H_6$, *1*.

Atom	*x*	*y*	*z*
Rh	−0.02668(2)	−0.01170(2)	0.10869(3)
O(1)	0.0730(2)	0.1506(2)	0.2242(3)
O(2)	0.1201(2)	0.1712(2)	0.0198(3)
O(3)	−0.1424(2)	0.0499(2)	0.0813(3)
O(4)	−0.0923(2)	0.0731(2)	−0.1221(3)
N	−0.0828(3)	−0.0370(3)	0.3065(3)
C(1)	0.1203(3)	0.2065(3)	0.1551(4)
C(2)	−0.1490(3)	0.0826(3)	−0.0228(4)
C(11)	0.1797(3)	0.3301(3)	0.2391(4)
C(12)	0.2765(3)	0.3734(3)	0.3359(5)
C(13)	0.3226(4)	0.4903(4)	0.4085(5)
C(14)	0.2729(4)	0.5622(4)	0.3897(6)
C(15)	0.1759(4)	0.5191(4)	0.2954(6)
C(16)	0.1300(4)	0.4027(3)	0.2202(5)
C(21)	0.3337(3)	0.3017(3)	0.3609(5)
C(22)	0.3425(4)	0.2096(4)	0.2457(6)
C(23)	0.4013(4)	0.1464(4)	0.2748(7)
C(24)	0.4527(4)	0.1782(4)	0.4197(7)
C(25)	0.4436(4)	0.2690(4)	0.5303(7)
C(26)	0.3848(4)	0.3300(4)	0.5032(6)
C(31)	−0.2279(3)	0.1390(3)	−0.0295(4)
C(32)	−0.2982(3)	0.1531(3)	0.0716(4)
C(33)	−0.3670(4)	0.2095(4)	0.0579(5)
C(34)	−0.3689(4)	0.2490(4)	−0.0560(6)
C(35)	−0.3010(4)	0.2332(4)	−0.1554(5)
C(36)	−0.2298(4)	0.1791(3)	−0.1417(5)
C(41)	−0.3028(3)	0.1145(3)	0.1955(4)
C(42)	−0.3786(4)	0.0137(4)	0.1819(6)
C(43)	−0.3904(5)	−0.0171(5)	0.3018(6)
C(44)	−0.3264(4)	0.0518(4)	0.4376(5)
C(45)	−0.2513(4)	0.1515(4)	0.4502(5)
C(46)	−0.2396(4)	0.1830(4)	0.3314(5)
C(51)	−0.1208(3)	−0.0618(3)	0.3941(4)
C(52)	−0.1683(4)	−0.0936(4)	0.5103(5)
C(61)	−0.0241(6)	−0.2833(5)	0.3401(9)
C(62)	−0.0553(7)	−0.3386(6)	0.1937(8)
C(63)	−0.1009(7)	−0.4550(7)	0.1326(8)
C(64)	−0.1206(6)	−0.5154(6)	0.2205(9)
C(65)	−0.0921(6)	−0.4597(6)	0.3683(7)
C(66)	−0.0423(6)	−0.3442(7)	0.4292(7)
C(71)	−0.4039(8)	−0.4308(8)	−0.0184(9)
C(72)	−0.5047(7)	−0.5453(7)	0.1125(9)
C(73)	−0.4072(8)	−0.4795(8)	0.0931(10)

A total of 8773 unique reflections in the range $0° \leqslant 2\theta \leqslant 50°$ was collected, the 3094 reflections having $I > 3\sigma(I)$ being used to solve and refine the structure. The low linear absorption coefficient of 7 cm^{-1} made an absorption correction unnecessary.

Solution and refinement were undertaken in the space group $P\bar{1}$. The positions of the Rh atoms were obtained from a three-dimensional Patterson map. Initial refinement of the Rh positions gave discrepancy indices of $R_1 = 0.27$ and $R_2 = 0.37$.

TABLE II. Bond Distances (Å) in $Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2\cdot 3C_6H_6$, *1*.

Rh–Rh′	2.396	C(31)–C(32)	1.416(5)
Rh–O(1)	2.051(2)	C(31)–C(36)	1.399(5)
Rh–O(2)′	2.026(2)	C(32)–C(33)	1.397(5)
Rh–O(3)	2.027(2)	C(32)–C(41)	1.490(5)
Rh–O(4)′	2.036(2)	C(33)–C(34)	1.408(6)
Rh–N	2.233(3)	C(34)–C(35)	1.382(6)
C(1)–O(1)	1.246(4)	C(35)–C(36)	1.400(5)
C(1)–O(2)	1.256(4)	C(41)–C(42)	1.385(5)
C(1)–C(11)	1.504(4)	C(41)–C(46)	1.388(5)
C(11)–C(12)	1.406(5)	C(42)–C(43)	1.391(7)
C(11)–C(16)	1.403(5)	C(43)–C(44)	1.392(7)
C(12)–C(13)	1.398(5)	C(44)–C(45)	1.372(6)
C(12)–C(21)	1.483(5)	C(45)–C(46)	1.386(6)
C(13)–C(14)	1.393(6)	N–C(51)	1.126(5)
C(14)–C(15)	1.398(6)	C(51)–C(52)	1.472(5)
C(15)–C(16)	1.395(5)	C(61)–C(62)	1.353(9)
C(21)–C(22)	1.405(6)	C(61)–C(66)	1.385(10)
C(21)–C(26)	1.406(6)	C(62)–C(63)	1.385(9)
C(22)–C(23)	1.417(6)	C(63)–C(64)	1.372(9)
C(23)–C(24)	1.419(7)	C(64)–C(65)	1.362(10)
C(24)–C(25)	1.373(8)	C(65)–C(66)	1.381(10)
C(25)–C(26)	1.384(7)	C(71)–C(72)	1.39(1)
C(2)–O(3)	1.265(4)	C(71)–C(73)′	1.47(1)
C(2)–O(4)	1.271(4)	C(72)–C(73)	1.41(1)
C(2)–C(31)	1.497(5)		

The remaining eight oxygen atoms, two nitrogen atoms, and fifty-five carbon atoms were found by subsequent difference Fourier maps and least-squares refinement. Refinement of positional parameters, anisotropic thermal parameters for all atoms except the lattice toluene, and isotropic thermal parameters for the lattice toluene gave discrepancy indices of $R_1 = 0.056$ and $R_2 = 0.062$ with an esd of 1.396. A final difference Fourier map revealed peaks associated with hydrogen atoms which were not refined.

Results

Molecular Structure of $Rh_2[O_2C(2\text{-}C_6H_4C_6H_5)]_4(CH_3CN)_2\cdot 3C_6H_6$, 1

The atomic positional parameters are listed in Table I. The molecular structure is depicted in Fig. 1 which also defines the atomic labelling scheme. Selected bond distances and angles are given in Tables II and III.

The dirhodium unit is located on an inversion center and the asymmetric unit consists of half the molecule. The carboxylate groups are bonded in a typical fashion, giving essentially D_{4h} symmetry to

TABLE III. Bond Angles (deg.) in $Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2 \cdot 3C_6H_6$, *1*.

Rh'-Rh-O(1)	87.66(6)	C(13)-C(14)-C(15)	120.6(4)
Rh'-Rh-O(2)'	87.79(7)	C(14)-C(15)-C(16)	118.7(4)
Rh'-Rh-O(3)	87.69(6)	C(21)-C(22)-C(23)	119.7(4)
Rh'-Rh-O(4)'	88.18(6)	C(21)-C(26)-C(25)	120.8(5)
Rh'-Rh-N	177.79(8)	C(22)-C(21)-C(26)	119.1(4)
O(1)-Rh-O(2)	175.39(9)	C(22)-C(23)-C(24)	119.6(5)
O(1)-Rh-O(3)	88.5(1)	C(23)-C(24)-C(25)	119.6(5)
O(1)-Rh-O(4)	91.6(1)	C(24)-C(25)-C(26)	121.1(5)
O(1)-Rh-N	94.0(1)	O(3)-C(2)-O(4)	125.0(3)
O(2)-Rh-O(3)	92.0(1)	O(3)-C(2)-C(31)	118.3(3)
O(2)-Rh-O(4)	87.5(1)	O(4)-C(2)-C(31)	116.7(3)
O(2)-Rh-N	90.5(1)	C(2)-C(31)-C(32)	123.0(3)
O(3)-Rh-O(4)	175.85(8)	C(2)-C(31)-C(36)	117.0(3)
O(3)-Rh-N	90.9(1)	C(31)-C(32)-C(33)	118.5(3)
O(4)-Rh-N	93.2(1)	C(31)-C(32)-C(41)	124.7(3)
Rh-O(1)-C(1)	118.4(2)	C(31)-C(36)-C(35)	120.5(4)
Rh'-O(2)-C(1)	119.4(2)	C(32)-C(31)-C(36)	120.0(3)
Rh-O(3)-C(2)	120.0(2)	C(32)-C(33)-C(34)	121.1(4)
Rh'-O(4)-C(2)	118.9(2)	C(32)-C(41)-C(42)	120.2(4)
O(1)-C(1)-O(2)	126.5(3)	C(32)-C(41)-C(46)	121.2(3)
O(1)-C(1)-C(11)	117.50(3)	C(33)-C(34)-C(35)	119.9(4)
O(2)-C(1)-C(11)	115.8(3)	C(34)-C(35)-C(36)	120.0(4)
C(1)-C(11)-C(12)	124.1(3)	C(41)-C(42)-C(43)	120.5(4)
C(1)-C(11)-C(16)	115.4(3)	C(41)-C(46)-C(45)	121.1(4)
C(11)-C(12)-C(13)	118.1(4)	C(42)-C(41)-C(46)	118.1(4)
C(11)-C(12)-C(21)	123.4(3)	C(42)-C(43)-C(44)	121.0(4)
C(11)-C(16)-C(15)	120.9(4)	C(43)-C(44)-C(45)	118.2(4)
C(12)-C(11)-C(16)	120.4(3)	C(44)-C(45)-C(46)	121.0(4)
C(12)-C(13)-C(14)	121.3(4)		
C(12)-C(21)-C(22)	122.0(4)		
C(12)-C(21)-C(26)	118.9(4)		
Rh-N-C(51)	171.2(3)		
N-C(51)-C(52)	178.8(4)		
C(61)-C(62)-C(63)	120.7(6)		
C(62)-C(63)-C(64)	120.3(7)		
C(63)-C(64)-C(65)	119.1(7)		
C(64)-C(65)-C(66)	120.6(6)		
C(65)-C(66)-C(61)	120.0(7)		
C(66)-C(61)-C(62)	119.1(7)		
C(71')-C(72)-C(73)	119(1)		
C(71)-C(73)-C(72)	120.1(9)		
C(72')-C(71)-C(73)	120.9(9)		

the central portion of the molecule, excluding the acetonitrile ligands. The Rh–Rh bond length of 2.396(1) Å is within the range of $Rh_2(O_2CR)_4$ compounds previously studied [3, 4]. The Rh–N distance is 2.233(3) Å and the N–C distance in the acetonitrile molecule is 1.126(5) Å. The N–C–C chains deviate from colinearity with the Rh–Rh bond by 2.21(8)°.

The orientation of the ortho-phenyl groups is similar to that found in molybdenum analog in that two are positioned in an equatorial orientation about the Rh–Rh bond and the other two are directed toward the axial positions, one at each end [10].

Molecular Structure of $Rh_2[O_2C(1\text{-}adamantyl)]_4(CH_3OH)_2 \cdot 5CH_3OH$, 2

The atomic positional parameters are listed in Table IV and the structure of the molecule is depicted in Fig. 2. Selected bond distances and angles are given in Tables V and VI.

The dirhodium unit is located on an inversion center, the asymmetric unit consisting of one-half of the molecule. The Rh–Rh bond distance of

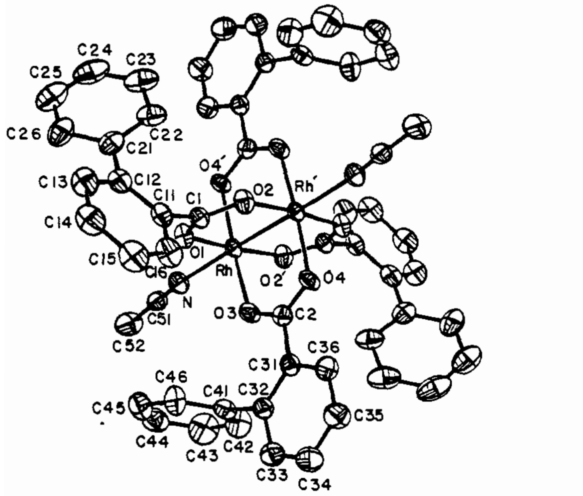

Fig. 1. The structure of the $Rh_2[O_2C(2\text{-}C_6H_5)C_6H_4]_4(CH_3CN)_2$ molecule in *1*. Each atom is represented by its ellipsoid of thermal vibration and the atom labelling scheme is defined.

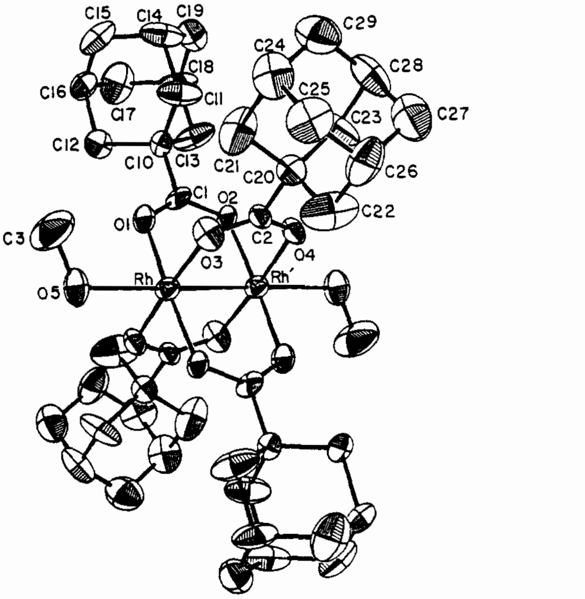

Fig. 2. The structure of the $Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2$ molecule in *2*.

TABLE IV. Positional Parameters and Their Estimated Standard Deviations for $Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2 \cdot 5CH_3OH$, *2*.

Atom	*x*	*y*	*z*
Rh	0.4251(1)	0.54197(5)	0.49342(4)
O(1)	0.3414(9)	0.4550(5)	0.4382(4)
O(2)	0.4813(9)	0.4039(4)	0.4494(4)
O(3)	0.5409(10)	0.5781(4)	0.4343(4)
O(4)	0.6805(9)	0.4983(5)	0.4448(4)
O(5)	0.2818(10)	0.6233(5)	0.4776(4)
C(1)	0.386(1)	0.4294(8)	0.4265(5)
C(2)	0.635(1)	0.5479(7)	0.4226(5)
C(3)	0.243(2)	0.6346(11)	0.4242(8)
C(10)	0.329(1)	0.3950(6)	0.3787(6)
C(11)	0.393(2)	0.4218(8)	0.3269(6)
C(12)	0.184(1)	0.4026(9)	0.3785(7)
C(13)	0.361(2)	0.3204(8)	0.3819(7)
C(14)	0.335(2)	0.3867(9)	0.2747(6)
C(15)	0.192(2)	0.3977(9)	0.2756(7)
C(16)	0.129(2)	0.3681(8)	0.3254(7)
C(17)	0.160(2)	0.2955(9)	0.3309(8)
C(18)	0.304(2)	0.2843(9)	0.3309(6)
C(19)	0.363(2)	0.3158(8)	0.2811(7)
C(20)	0.718(2)	0.5766(7)	0.3768(6)
C(21)	0.633(2)	0.6176(10)	0.3372(7)
C(22)	0.816(2)	0.6232(9)	0.4039(8)
C(23)	0.789(2)	0.5228(9)	0.3471(7)
C(24)	0.721(2)	0.6449(8)	0.2886(8)
C(25)	0.813(2)	0.6910(8)	0.3191(8)
C(26)	0.901(2)	0.6538(8)	0.3575(8)
C(27)	0.970(2)	0.5980(10)	0.3285(8)
C(28)	0.873(2)	0.5523(8)	0.2989(7)
C(29)	0.787(2)	0.5895(10)	0.2601(8)
O(8)	0.500(0)	0.5000(0)	0.0000(0)
O(6)	0.527(2)	0.7260(9)	0.4640(7)
O(7)	0.283(2)	0.3096(11)	0.0663(9)
C(5)	0.462(7)	0.455(3)	0.012(3)
C(6)	0.547(2)	0.239(1)	0.502(1)
C(7)	0.287(2)	0.350(1)	0.112(1)

2.371(2) Å is equal that of $Rh_2(O_2CC(CH_3)_3)_4(H_2O)_2$ [3, 4], the shortest Rh–Rh distance reported for compounds of the type $Rh_2(O_2CR)_4$. The Rh to methanol oxygen distance of 2.296(9) Å is also equal to the Rh to water oxygen distance in the above compound, and is well within the range (2.24–2.45 Å) of other Rh–O axial bond distances in rhodium dimers. The methanol group is coordinated in a similar fashion to that found in $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ and similar to the coordinated ethanol in $Rh_2(O_2CCF_3)_4(EtOH)_2$, in which the ligands adopt the most favorable orientation for donation from one of the lone pairs on the oxygen atom.

The 1-adamantanecarboxylate groups have a normal orientation and structure. Figure 2 shows clearly that the adamantane groups do not block possible interaction with either the axial positions or the carboxylate oxygens.

Molecular Structure of $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_7H_8$, 3

The atomic positional parameters are listed in Table VII and the structure of the molecule is depicted in Fig. 3. Selected bond distances and angles are given in Tables VIII and IX.

TABLE V. Bond Distances (Å) and Their Estimated Standard Deviations for $Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2\cdot 5CH_3OH$, *2*.

Rh–Rh	2.371(2)	C(14)–C(19)	1.50(2)
Rh–O(1)	2.008(12)	C(15)–C(16)	1.52(2)
Rh–O(2)	2.055(10)	C(16)–C(17)	1.54(2)
Rh–O(3)	2.046(10)	C(17)–C(18)	1.55(2)
Rh–O(4)	2.066(9)	C(18)–C(19)	1.52(2)
Rh–O(5)	2.296(9)	C(20)–C(21)	1.57(2)
O(1)–C(1)	1.27(2)	C(20)–C(22)	1.57(2)
O(2)–C(1)	1.27(2)	C(20)–C(23)	1.53(2)
O(3)–C(2)	1.21(2)	C(21)–C(24)	1.62(2)
O(4)–C(2)	1.26(2)	C(22)–C(26)	1.59(2)
O(5)–C(3)	1.40(2)	C(23)–C(28)	1.60(2)
C(1)–C(10)	1.50(2)	C(24)–C(25)	1.56(2)
C(2)–C(20)	1.55(2)	C(24)–C(29)	1.51(2)
C(10)–C(11)	1.55(2)	C(25)–C(26)	1.53(2)
C(10)–C(12)	1.54(2)	C(26)–C(27)	1.54(2)
C(10)–C(13)	1.58(2)	C(27)–C(28)	1.57(2)
C(11)–C(14)	1.60(2)	C(28)–C(29)	1.53(3)
C(12)–C(16)	1.60(2)	O(8)–C(5)	1.06(8)
C(13)–C(18)	1.58(2)	O(6)–C(6)	1.36(2)
C(14)–C(15)	1.53(2)	O(7)–C(7)	1.41(3)

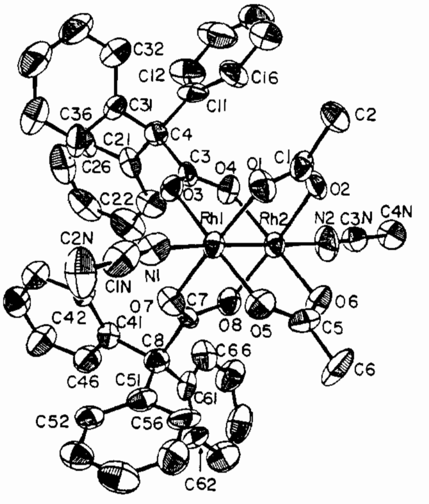

Fig. 3. The structure of the $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2$ molecule in *3*.

TABLE VI. Bond Angles (deg.) and Their Estimated Standard Deviations for $Rh_2[O_2C(1\text{-adamantyl})]_4(CH_3OH)_2\cdot 5CH_3OH$, *2*.

Rh–Rh–O(1)	87.7(3)	C(12)–C(10)–C(13)	108.0(1)
Rh–Rh–O(2)	88.9(3)	C(10)–C(11)–C(14)	110.0(1)
Rh–Rh–O(3)	87.9(3)	C(10)–C(12)–C(16)	109.0(1)
Rh–Rh–O(4)	88.1(3)	C(10)–C(13)–C(18)	110.0(1)
Rh–Rh–O(5)	178.0(3)	C(11)–C(14)–C(15)	107.0(2)
O(1)–Rh–O(2)	176.6(4)	C(11)–C(14)–C(19)	106.0(2)
O(1)–Rh–O(3)	89.0(4)	C(15)–C(14)–C(19)	110.0(2)
O(1)–Rh–O(4)	91.5(4)	C(14)–C(15)–C(16)	112.0(2)
O(1)–Rh–O(5)	91.2(4)	C(12)–C(16)–C(15)	109.0(1)
O(2)–Rh–O(3)	90.2(4)	C(12)–C(16)–C(17)	107.0(2)
O(2)–Rh–O(4)	88.4(4)	C(15)–C(16)–C(17)	112.0(2)
O(2)–Rh–O(5)	92.2(4)	C(16)–C(17)–C(18)	111.0(2)
O(3)–Rh–O(4)	175.8(4)	C(13)–C(18)–C(17)	108.0(2)
O(3)–Rh–O(5)	90.5(4)	C(13)–C(18)–C(19)	107.0(1)
O(4)–Rh–O(5)	93.6(4)	C(17)–C(18)–C(19)	110.0(2)
Rh–O(1)–C(1)	121.0(1)	C(14)–C(19)–C(18)	115.0(2)
Rh–O(2)–C(1)	118.0(1)	C(2)–C(20)–C(21)	110.0(1)
Rh–O(3)–C(2)	119.0(1)	C(2)–C(20)–C(22)	107.0(1)
Rh–O(4)–C(2)	116.0(1)	C(2)–C(20)–C(23)	111.0(1)
Rh–O(5)–C(3)	118.0(1)	C(21)–C(20)–C(22)	108.0(1)
O(1)–C(1)–O(2)	124.0(2)	C(21)–C(20)–C(23)	112.0(1)
O(1)–C(1)–C(10)	117.0(2)	C(22)–C(20)–C(23)	109.0(1)
O(2)–C(1)–C(10)	118.0(2)	C(20)–C(21)–C(24)	109.0(1)
O(3)–C(2)–O(4)	129.0(2)	C(20)–C(22)–C(26)	108.0(1)
O(3)–C(2)–C(20)	116.0(2)	C(20)–C(23)–C(28)	111.0(1)
O(4)–C(2)–C(20)	115.0(2)	C(21)–C(24)–C(25)	102.0(2)
C(1)–C(10)–C(11)	108.0(1)	C(21)–C(24)–C(29)	110.0(2)
C(1)–C(10)–C(12)	111.0(1)	C(25)–C(24)–C(29)	113.0(2)
C(1)–C(10)–C(13)	109.0(1)	C(24)–C(25)–C(26)	112.0(2)
C(11)–C(10)–C(12)	113.0(1)	C(22)–C(26)–C(25)	108.0(2)
C(11)–C(10)–C(13)	107.0(1)	C(22)–C(26)–C(27)	108.0(2)

(continued on facing page)

TABLE VI. *(continued)*

C(25)–C(26)–C(27)	112.0(2)	C(23)–C(28)–C(29)	109.0(2)
C(26)–C(27)–C(28)	111.0(1)	C(27)–C(28)–C(29)	112.0(2)
C(23)–C(28)–C(27)	104.0(1)	C(24)–C(29)–C(28)	111.0(2)

TABLE VII. Positional Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_7H_8$, *3*.

Atom	*x*	*y*	*z*
Rh(1)	0.36183(9)	0.19836(5)	0.2174(1)
Rh(2)	0.42608(9)	0.18400(5)	0.0013(1)
O(1)	0.4488(8)	0.1093(4)	0.2532(9)
O(2)	0.5142(7)	0.0962(4)	0.0580(9)
O(3)	0.4999(6)	0.2332(4)	0.3174(8)
O(4)	0.5622(7)	0.2193(4)	0.1181(8)
O(5)	0.2280(7)	0.1640(4)	0.1047(9)
O(6)	0.2878(7)	0.1487(4)	–0.1007(9)
O(7)	0.2781(7)	0.2865(4)	0.1683(8)
O(8)	0.3358(7)	0.2734(4)	–0.0391(8)
N(1)	0.2938(8)	0.2137(5)	0.412(1)
N(2)	0.4852(9)	0.1683(6)	–0.195(1)
C(1)	0.5096(12)	0.0778(6)	0.172(1)
C(1N)	0.2434(13)	0.2225(7)	0.504(2)
C(2)	0.5790(13)	0.0124(6)	0.212(2)
C(2N)	0.1803(13)	0.2320(8)	0.616(1)
C(3)	0.5675(10)	0.2365(5)	0.250(1)
C(3N)	0.5221(10)	0.1543(6)	–0.292(1)
C(4)	0.6716(10)	0.2637(6)	0.331(1)
C(4N)	0.5684(12)	0.1356(7)	–0.425(1)
C(5)	0.2175(11)	0.1460(6)	–0.031(1)
C(6)	0.1136(12)	0.1228(8)	–0.108(2)
C(7)	0.2817(9)	0.3053(5)	0.054(1)
C(8)	0.2100(11)	0.3718(6)	0.020(1)
C(11)	0.7775(11)	0.2194(7)	0.290(1)
C(12)	0.8657(12)	0.2412(8)	0.272(2)
C(13)	0.9653(14)	0.2012(9)	0.243(2)
C(14)	0.9692(14)	0.1368(9)	0.232(2)
C(15)	0.8828(14)	0.1122(8)	0.249(2)
C(16)	0.7865(13)	0.1536(7)	0.280(2)
C(21)	0.6545(11)	0.3326(6)	0.283(1)
C(22)	0.5938(11)	0.3487(7)	0.147(1)
C(23)	0.5838(12)	0.4106(7)	0.108(2)
C(24)	0.6347(12)	0.4530(7)	0.210(2)
C(25)	0.6974(13)	0.4367(8)	0.350(2)
C(26)	0.7073(11)	0.3755(6)	0.386(2)
C(31)	0.6820(10)	0.2670(6)	0.495(1)
C(32)	0.7767(13)	0.2323(7)	0.584(2)
C(33)	0.7820(14)	0.2361(9)	0.733(2)
C(34)	0.6946(14)	0.2723(8)	0.792(2)
C(35)	0.6029(11)	0.3085(7)	0.702(1)
C(36)	0.5947(11)	0.3059(6)	0.551(1)
C(41)	0.2717(10)	0.4221(6)	0.117(1)
C(42)	0.3380(11)	0.4094(6)	0.254(1)
C(43)	0.3859(12)	0.4592(7)	0.348(2)
C(44)	0.3614(11)	0.5194(6)	0.298(2)
C(45)	0.2988(13)	0.5318(7)	0.165(2)
C(46)	0.2519(12)	0.4824(6)	0.072(2)
C(51)	0.1007(11)	0.3755(6)	0.058(1)
C(52)	0.0525(11)	0.4249(6)	0.151(1)
C(53)	–0.0485(11)	0.4236(7)	0.183(1)
C(54)	–0.1039(13)	0.3745(7)	0.122(2)
C(55)	–0.0548(13)	0.3248(7)	0.031(2)
C(56)	0.0440(10)	0.3251(7)	–0.001(2)
C(61)	0.1913(11)	0.3835(6)	–0.140(1)
C(62)	0.0821(11)	0.3999(7)	–0.229(1)
C(63)	0.0703(14)	0.4084(8)	–0.376(2)
C(64)	0.1672(14)	0.4021(7)	–0.426(1)
C(65)	0.2747(14)	0.3875(7)	–0.340(2)
C(66)	0.2864(12)	0.3782(6)	–0.194(1)
C(71)	0.245(2)	0.0006(13)	0.227(3)
C(72)	0.257(2)	0.0336(9)	0.337(2)
C(73)	0.217(2)	0.0457(13)	0.462(3)
C(74)	0.148(2)	–0.0013(13)	0.462(3)
C(75)	0.135(2)	–0.0406(10)	0.320(2)
C(76)	0.161(2)	–0.0541(12)	0.197(3)
C(77)	0.750(2)	0.0308(14)	0.905(3)

The molecule itself is the asymmetric unit, no crystallographic symmetry being imposed upon it. The carboxylate groups are bonded normally, giving essentially D_{4h} symmetry to the central portion of the molecule. The Rh–Rh bond distance of 2.388(2) Å is again at the shorter end of the range of $Rh_2(O_2CR)_4$ compounds. The Rh–N distances are 2.21(1) Å and 2.17(1) Å, an average of only 0.04 Å longer than that found in $Rh_2(mhp)_4(CH_3CN)$. The N–C distances in the acetonitrile molecules are 1.20(2) Å and 1.13(1) Å. The N–C–C chains deviate from colinearity with the Rh–Rh bond by 2.9(4)° and 1.5(4)°.

Discussion

The work reported here was undertaken to explore the influence of the steric properties of the R groups in $Rh_2(O_2CR)_4$ compounds on the ease of preparation, stability and structures of the molecules. In the series R = 2-$C_6H_5C_6H_4$, 1-adamantyl, triphenylmethyl we have a steady increase in steric demand. The 2-$C_6H_5C_6H_4$ group is rather flexible because of its ability to twist about both the C–CO_2 bond and

TABLE VIII. Bond Distances (Å) and their Estimated Standard Deviation for $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_7H_8$, *3*.

Atoms	Distance	Atoms	Distance
Rh(1)–Rh(2)	2.388(2)	C(4)–C(11)	1.55(2)
Rh(1)–O(1)	2.017(9)	C(4)–C(21)	1.59(2)
Rh(1)–O(3)	2.029(9)	C(4)–C(31)	1.55(2)
Rh(1)–O(5)	2.008(9)	C(5)–C(6)	1.50(2)
Rh(1)–O(7)	2.018(8)	C(7)–C(8)	1.54(2)
Rh(1)–N(1)	2.21(2)	C(8)–C(41)	1.56(2)
Rh(2)–O(2)	2.044(9)	C(8)–C(51)	1.50(2)
Rh(2)–O(4)	2.053(9)	C(8)–C(61)	1.56(2)
Rh(2)–O(6)	2.041(9)	C(11)–C(12)	1.38(2)
Rh(2)–O(8)	2.044(9)	C(11)–C(16)	1.41(2)
Rh(2)–N(2)	2.17(1)	C(12)–C(13)	1.41(2)
O(1)–C(1)	1.254(15)	C(13)–C(14)	1.39(2)
O(2)–C(1)	1.253(14)	C(14)–C(15)	1.39(2)
O(3)–C(3)	1.225(13)	C(15)–C(16)	1.40(2)
O(4)–C(3)	1.264(13)	C(21)–C(22)	1.39(2)
O(5)–C(5)	1.296(14)	C(21)–C(26)	1.41(2)
O(6)–C(5)	1.266(15)	C(22)–C(23)	1.43(2)
O(7)–C(7)	1.256(13)	C(23)–C(24)	1.39(2)
O(8)–C(7)	1.289(12)	C(24)–C(25)	1.43(2)
N(1)–C(1)N	1.20(2)	C(25)–C(26)	1.40(2)
N(2)–C(3)N	1.126(14)	C(31)–C(32)	1.40(2)
C(1)–C(2)	1.53(2)	C(31)–C(36)	1.39(2)
C(1)N–C(2)N	1.47(2)	C(32)–C(33)	1.42(2)
C(33)–C(34)	1.39(2)		
C(34)–C(35)	1.40(2)		
C(35)–C(36)	1.43(2)		
C(41)–C(42)	1.40(2)		
C(41)–C(46)	1.40(2)		
C(42)–C(43)	1.45(2)		
C(43)–C(44)	1.41(2)		
C(44)–C(45)	1.36(2)		
C(45)–C(46)	1.44(2)		
C(51)–C(52)	1.42(2)		
C(51)–C(56)	1.43(2)		
C(52)–C(53)	1.40(2)		
C(53)–C(54)	1.40(2)		
C(54)–C(55)	1.42(2)		
C(55)–C(56)	1.36(2)		
C(61)–C(62)	1.42(2)		
C(61)–C(66)	1.41(2)		
C(62)–C(63)	1.42(2)		
C(63)–C(64)	1.40(2)		
C(64)–C(65)	1.39(2)		
C(65)–C(66)	1.42(2)		
C(71)–C(72)	1.19(3)		
C(71)–C(76)	1.73(3)		
C(71)–C(77)	1.36(3)		
C(72)–C(73)	1.40(3)		
C(73)–C(74)	1.51(3)		
C(74)–C(75)	1.50(3)		
C(75)–C(76)	1.29(3)		
C(76)–C(77)	1.88(4)		

TABLE IX. Bond Angles (Deg.) and their Estimated Standard Deviations for $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2 \cdot C_7H_8$, *3*.

Atoms	Angle
Rh(2)–Rh(1)–O(1)	87.5(3)
Rh(2)–Rh(1)–O(3)	87.4(2)
Rh(2)–Rh(1)–O(5)	88.5(2)
Rh(2)–Rh(1)–O(7)	88.5(2)
Rh(2)–Rh(1)–N(1)	177.1(4)
O(1)–Rh(1)–O(3)	90.6(4)
O(1)–Rh(1)–O(5)	89.9(4)
O(1)–Rh(1)–O(7)	176.0(4)
O(1)–Rh(1)–N(1)	94.5(4)
O(3)–Rh(1)–O(5)	175.8(4)
O(3)–Rh(1)–O(7)	89.4(4)
O(3)–Rh(1)–N(1)	94.7(4)
O(5)–Rh(1)–O(7)	89.8(4)
O(5)–Rh(1)–N(1)	89.4(4)
O(7)–Rh(1)–N(1)	89.5(4)
Rh(1)–Rh(2)–O(2)	87.4(3)
Rh(1)–Rh(2)–O(4)	88.0(2)
Rh(1)–Rh(2)–O(6)	87.8(3)
Rh(1)–Rh(2)–O(8)	88.1(2)
Rh(1)–Rh(2)–N(2)	178.5(4)
O(2)–Rh(2)–O(4)	88.0(4)
O(2)–Rh(2)–O(6)	91.1(4)
O(2)–Rh(2)–O(8)	175.4(4)
O(2)–Rh(2)–N(2)	91.2(4)
O(4)–Rh(2)–O(6)	175.7(4)
O(4)–Rh(2)–O(8)	90.9(4)
O(4)–Rh(2)–N(2)	92.6(4)
O(6)–Rh(2)–O(8)	89.7(4)
O(6)–Rh(2)–N(2)	91.6(4)
O(8)–Rh(2)–N(2)	93.3(4)
Rh(1)–O(1)–C(1)	121.3(9)
Rh(2)–O(2)–C(1)	120.1(9)
Rh(1)–O(3)–C(3)	120.5(8)
Rh(2)–O(4)–O(3)	91.4(4)
Rh(2)–O(4)–C(3)	117.7(8)
Rh(1)–O(5)–C(5)	120.1(9)
Rh(2)–O(6)–C(5)	119.9(9)
Rh(1)–O(7)–C(7)	119.5(8)
Rh(2)–O(8)–C(7)	117.8(8)
Rh(1)–N(1)–C(1)N	171.0(1)
Rh(2)–N(2)–C(3)N	173.0(1)
O(1)–C(1)–O(2)	124.0(1)
O(1)–C(1)–C(2)	118.0(1)
O(2)–C(1)–C(2)	118.0(1)
N(1)–C(1)N–C(2)N	179.0(2)
O(3)–C(3)–O(4)	126.0(1)
O(3)–C(3)–C(4)	119.0(1)
O(4)–C(3)–C(4)	115.0(1)
N(2)–C(3)N–C(4)N	178.0(2)
C(3)–C(4)–C(11)	109.0(1)
C(3)–C(4)–C(21)	108.0(1)
C(3)–C(4)–C(31)	109.0(1)
C(11)–C(4)–C(21)	110.0(1)
C(11)–C(4)–C(31)	110.0(1)
C(21)–C(4)–C(31)	111.0(1)

(continued on facing page)

the C_6H_5–C_6H_4 bond, and indeed it has previously been shown to exhibit varied behavior in compounds with Cr_2^{4+} and Mo_2^{4+}. No dimetal species containing

TABLE IX. *(continued)*

Atoms	Angle
O(5)–C(5)–O(6)	124.0(1)
O(5)–C(5)–C(6)	117.0(1)
O(6)–C(5)–C(6)	120.0(1)
O(7)–C(7)–O(8)	126.0(1)
O(7)–C(7)–C(8)	116.0(1)
O(8)–C(7)–C(8)	118.0(1)
C(7)–C(8)–C(41)	108.0(1)
C(7)–C(8)–C(51)	106.0(1)
C(7)–C(8)–C(61)	113.0(1)
C(41)–C(8)–C(51)	110.0(1)
C(41)–C(8)–C(61)	108.0(1)
C(51)–C(8)–C(61)	111.0(1)
C(4)–C(11)–C(12)	123.0(1)
C(4)–C(11)–C(16)	118.0(1)
C(12)–C(11)–C(16)	118.0(1)
C(11)–C(12)–C(13)	124.0(2)
C(12)–C(13)–C(14)	115.0(2)
C(13)–C(14)–C(15)	123.0(2)
C(14)–C(15)–C(16)	119.0(2)
C(11)–C(16)–C(15)	120.0(2)
C(4)–C(21)–C(22)	122.0(1)
C(4)–C(21)–C(26)	116.0(1)
C(22)–C(21)–C(26)	122.0(1)
C(21)–C(22)–C(23)	119.0(1)
C(22)–C(23)–C(24)	118.0(2)
C(23)–C(24)–C(25)	122.0(2)
C(24)–C(25)–C(26)	119.0(2)
C(21)–C(26)–C(25)	119.0(1)
C(4)–C(31)–C(32)	121.0(1)
C(4)–C(31)–C(36)	118.0(1)
C(32)–C(31)–C(36)	121.0(1)
C(31)–C(32)–C(33)	119.0(1)
C(32)–C(33)–C(34)	122.0(2)
C(33)–C(34)–C(35)	118.0(2)
C(34)–C(35)–C(36)	122.0(1)
C(31)–C(36)–C(35)	118.0(1)
C(8)–C(41)–C(42)	120.0(1)
C(8)–C(41)–C(46)	119.0(1)
C(42)–C(41)–C(46)	120.0(1)
C(41)–C(42)–C(43)	119.0(1)
C(42)–C(43)–C(44)	118.0(1)
C(43)–C(44)–C(45)	123.0(1)
C(44)–C(45)–C(46)	119.0(1)
C(41)–C(46)–C(45)	120.0(1)
C(8)–C(51)–C(52)	124.0(1)
C(8)–C(51)–C(56)	117.0(1)
C(52)–C(51)–C(56)	118.0(1)
C(51)–C(52)–C(53)	120.0(1)
C(52)–C(53)–C(54)	121.0(1)
C(53)–C(54)–C(55)	119.0(1)
C(54)–C(55)–C(56)	121.0(1)
C(51)–C(56)–C(55)	121.0(1)
C(8)–C(61)–C(62)	122.0(1)
C(8)–C(61)–C(66)	118.0(1)
C(62)–C(61)–C(66)	120.0(1)
C(61)–C(62)–C(63)	119.0(1)
C(62)–C(63)–C(64)	119.0(1)
C(63)–C(64)–C(65)	123.0(2)
C(64)–C(65)–C(66)	118.0(2)
C(61)–C(66)–C(65)	121.0(2)
C(72)–C(71)–C(76)	120.0(3)
C(72)–C(71)–C(77)	166.0(4)
C(76)–C(71)–C(77)	74.0(2)
C(71)–C(72)–C(73)	138.0(3)
C(72)–C(73)–C(74)	110.0(3)
C(73)–C(74)–C(75)	108.0(2)
C(74)–C(75)–C(76)	147.0(3)
C(71)–C(76)–C(75)	96.0(2)

the 1-adamantylcarboxyl or triphenylacetate ligands have been reported heretofore.

With regard to compound *1*, the present results confirm and extend the previous indications [10, 11] that the $(2\text{-}C_6H_5)C_6H_4CO_2$ ligand (biph CO_2^-) is sterically very forgiving. In three previously reported compounds we have seen three modes of behavior. In both $Mo_2(O_2Cbiph)_4$ [10] and $Cr_2(O_2Cbiph)_4(THF)_2$ [11] two *cis* *o*-phenyl groups are directed towards the equatorial region of the molecule and the other two, one each towards each end. In the case of the molybdenum compound this arrangement prevented the intermolecular association by means of O → M bonds that is so commonly found in unsolvated $M_2(O_2CR)_4$ compounds. At the same time a rather satisfactory packing of the molecules was achieved by interleaving of phenyl groups, both inter- and intramolecularly. In $Cr_2(O_2Cbiph)_4(THF)_2$ virtually the same arrangement of *o*-phenyl groups occurs, but clearly, this leaves room for the medium-size donor molecules (THF) in the axial positions. In our present dirhodium compound, the arrangement of *o*-phenyl groups is similar and there is easily room for the slim acetonitrile molecules as axial ligands.

In compound *2* the large adamantyl groups have no deterrent effect on axial coordination. Because of their size and the projecting axial methanol ligands a packing arrangement in which there are interstices between these molecules arises and is stabilized by additional molecules of methanol occupying these interstices.

Compound *3*, which contains two acetate ligands and two triphenylacetate ligands is the first such mixed carboxylato complex for dirhodium(II) and one of the very few known for any dimetal unit [3]. There are, however, two dirhodium compounds which contain acetate groups together with entirely dissimilar (non-carboxylate) ligands, namely, $Rh_2(mhp)_2(O_2CCH_3)_2$ [8] (mhp = the anion of 2-oxo-6-methylpyridine) and $Rh_2(dmg)(O_2CCH_3)_2(PPh_3)_2$ [12] (dmg = the anion of dimethylglyoxime.)

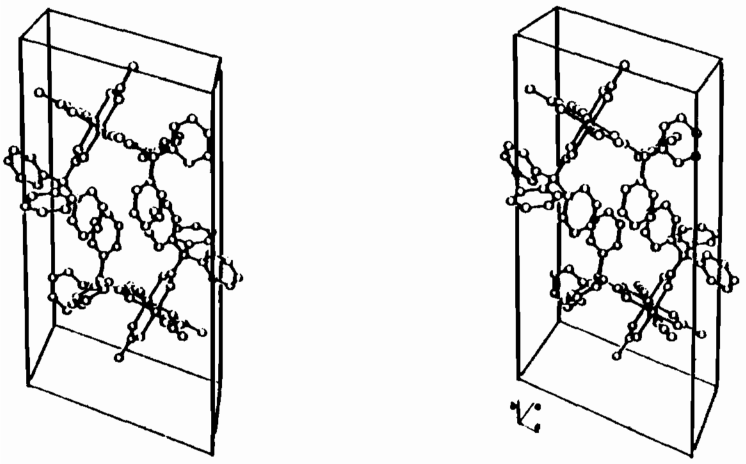

Fig. 4. A stereoscopic view of the unit cell of compound *3*.

The truly surprising thing about this molecule is that while only two of the bulky ligands, Ph_3CCO_2, enter the coordination sphere, they take up *adjacent* positions. In preparing the compound a fifty percent excess of triphenylacetic acid was used with the objective of getting the product of complete substitution, *i.e.*, $Rh_2(O_2CCPh_3)_4$, if possible. When it became evident that only two acetate groups had been replaced we presumed that this was because the steric requirement of a triphenyl acetate group was so great that four of them would not fit around the Rh_2^{4+} unit. On the same premise it was then also expected that the disubstituted product would have a *trans* arrangement and the crystal structure determination was undertaken with the intention of verifying this presumption.

The details of the structure do not afford evidence for any significant steric barrier to arranging four triphenylacetato ligands around the dimetal unit, in the sense that the two Ph_3COO_2 groups in *3* appear to fit quite comfortably into their places. The O–Rh–O angles are essentially the same regardless of whether they are between oxygen atoms both from CH_3CO_2 groups, both from Ph_3CCO_2 groups, or one from each kind of carboxyl group. The mean values, each precise to about 0.4°, are 90.5°, 90.9° and 89.5°, respectively. Neither is there any significant difference in the Rh–O distances to the two kinds of carboxyl groups. The mean distances to the CH_3CO_2 and Ph_3CCO_2 oxygen atoms are 2.028[9] Å and 2.036[8] Å, respectively.

It could, of course, be argued that the stability of the *cis*-$Rh(O_2CCH_3)_2(O_2CCPh_3)_2$ arrangement – as opposed to either a *trans* arrangement of the same ligand set or the formation of the $Rh_2(O_2CCPh_3)_4$ species – is attributable to a specially favorable and attractive relationship of the two Ph_3C groups to each other which cannot be continued cyclically to include two more. In attempting to evaluate this argument it is helpful to examine a stereographic view of the molecule and one is provided in Fig. 4. While no final conclusions can be reached, several things are evident. The Ph_3C groups are arranged so that in each of them one $C–C_6H_5$ bond is in the plane defined by the carboxyl group of that ligand. These two phenyl groups are directed towards opposite ends of the molecule. There is then a pair of phenyl groups, one from each Ph_3C group that lie parallel to each other but with their 6-fold axes offset. It is possible that this contact is an attractive one, thus favoring the *cis* isomer. There does not appear to be any obvious reason why this pattern could not be continued cyclically by replacing two more CH_3 groups by CPh_3 groups, perhaps with some small changes in rotation angles about the $C–C_6H_5$ bonds. It is therefore our belief that under somewhat more forcing conditions the $Rh_2(O_2CCPh_3)_4$ molecule, and other $M_2(O_2CCPh_3)_4$ molecules, should be obtainable. Such molecules would be of interest since they would be incapable of packing in the chainlike pattern characteristic of most $M_2(O_2CR)_4$ compounds wherein adjacent molecules are linked by axial $O \rightarrow M$ interactions, and could thus provide an opportunity to study the M–M unit without bonds to axial ligands, *i.e.*, in 'isolation' as was the case with $Mo_2(O_2Cbiph)_4$ [10]. We plan to pursue this goal.

Acknowledgements

We thank the National Science Foundation for support.

References

1 M. A. Porai-Koshits and A. S. Antsyshkina, *Dokl. Akad. Nauk SSSR, 146,* 1102 (1962).

2 F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal and D. A. Ucko, *Acta Cryst., B27,* 1664 (1971).

3 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms, John Wiley and Sons, New York, 1982.

4 T. R. Felthouse, *Prog. Inorg. Chem., 29,* 73 (1982).

5 T. Sowa, T. Kawamura, T. Shida and T. Yonezawa, *Inorg. Chem., 22,* 56 (1983).

6 A. M.Dennis, R. A. Howard and J. L. Bear, *Inorg. Chim. Acta, 66,* L31 (1982).

7 G. A. Remple, P. Legzdens, H. Smith and G. Wilkinson, *Inorg. Synth., 13,* 90 (1972).

8 See, for example, F. A. Cotton and T. R. Felthouse, *Inorg. Chem., 20,* 584 (1981).

9 All computations were carried out on a PDP 11/45 computer at Bertram Frenz Associates, College Station, TX, using the Enraf-Nonius Structure Determination Package programs.

10 F. A. Cotton and J. L. Thompson, *Inorg. Chem., 20,* 3887 (1981).

11 F. A. Cotton and J. L. Thompson, *Inorg. Chem., 20,* 1292 (1981).

12 J. Halpern, E. Kimura, J. Molin-Case and C. S. Wong, *J. Chem. Soc. Chem. Comm.,* 1207 (1971)