© 1999 The Chemical Society of Japan

Adduct Polymers and Dimers of Rhodium(II) Pivalate with Pyrazine, 4,4′-Bipyridine, 1,4-Diazabicyclo[2.2.2]octane, Triethylamine, and Pyridine

Makoto Handa,* Mayumi Watanabe, Daisuke Yoshioka, Seiichiro Kawabata, Ryoji Nukada,† Masahiro Mikuriya,*,† Hiroshi Azuma,† and Kuninobu Kasuga

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Nishikawatsu, Matsue 690-8504

†Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501

(Received May 31, 1999)

Adducts of rhodium(II) pivalate with pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco), triethylamine (tea), and pyridine (py) have been prepared. The adducts with pyz, 4,4′-bpy, and dabco are polymers formulated as $[Rh_2(O_2CCMe_3)_4(L)]_n$, (L = pyz, 4,4′-bpy, and dabco). A polymer structure with an alternating arrangement of the rhodium(II) dimer and ligands was confirmed by an X-ray structure analysis of the 4,4′-bpy adduct. The Rh–Rh bond distance is 2.395(1) Å which is in the range of those reported for the adducts of rhodium(II) carboxylates with axial aromatic nitrogen-donor ligands. The structure of the adduct dimers, $[Rh_2(O_2CCMe_3)_4(L)_2]$ (L = tea and py), was also confirmed for a tea-coordinated complex, which has considerably long axial Rh–N (2.391(8) Å) and Rh–Rh (2.413(1) Å) bonds. The reflectance-spectral and thermogravimetric data of all the adducts were obtained to examine the axial interaction between the rhodium(II) dimer core and the ligands.

Tetra-μ-carboxylato dimetal complexes with a lantern-like structure have been known for many transition metal ions.[1,2] We have been studying the chemistry of adducts of the dimetal complexes from the viewpoint of using them as building blocks for metal-assembled complexes constructed by axial coordination of the linkage ligands to the dimetal complexes.[3—6] Rhodium(II) carboxylate dimers are promising as building blocks because they have a relatively stable dimetal core and also give substantially strong axial coordination by the ligands. Because the Rh–Rh bond within the dimer core is sensitive to the axial interaction, the bond length has been used as a parameter to estimate the axial-ligand effect on the dimer core[1,7] Although the axial-ligand basicity has been considered to be the most important factor affecting the Rh–Rh bond,[8] other possible factors, such as a steric hindrance between the substituent groups on the carboxylate ions of the dimer core and the axial ligand, should be investigated for an effective use of the rhodium(II) dimers as building blocks. In this study, we chose rhodium(II) pivalate ($Rh_2(O_2CCMe_3)_4$) with bulky *t*-butyl groups on the carboxylate ions as the rhodium(II) dimer and prepared the adduct dimers $[Rh_2(O_2CCMe_3)_4(L)_2]$ (L = triethylamine (tea) and pyridine (py)) in addition to the adduct polymers $[Rh_2(O_2CCMe_3)_4(L)]_n$ (L = pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco)). The adduct polymers and dimers were characterized based on spectral and thermogravimetric data as well as the crystal structures of the 4,4′-bpy and tea adducts. It has been shown that the Rh–Rh bond length does not always reflect the strength of the axial interaction.

Experimental

Preparations of Complexes. $[Rh_2(O_2CCMe_3)_4(H_2O)_2]$ was prepared by a method described in the literature[9] and the axial water molecules were removed by heating under vacuum. The ligands pyz, 4,4′-bpy, dabco, tea, and pyridine were obtained from Wako Chem. Co.

$[Rh_2(O_2CCMe_3)_4(pyz)]_n$ (1). A solution of pyz (13 mg, 0.16 mmol) in ethanol (10 cm^3) was added to a solution of $[Rh_2(O_2CCMe_3)_4]$ (50 mg, 0.08 mmol) in ethanol (10 cm^3) under argon. After the solution was stirred overnight at room temperature, the precipitate was filtered, washed with benzene, and dried under vacuum to give a yellowish-brown powder. The yield was 46 mg. Anal. Found: C, 41.74; H, 5.65; N, 4.15%. Calcd for $C_{24}H_{40}N_2O_8Rh_2$: C, 41.75; H, 5.84; N, 4.06%. IR (in KBr) ν/cm^{-1} for $^-O_2CCMe_3$: ν_{asym}(OCO) = 1582, ν_{sym}(OCO) = 1416.

$[Rh_2(O_2CCMe_3)_4(4,4'\text{-bpy})]_n$ (2). This compound was obtained as an orange powder by the reaction of $[Rh_2(O_2CCMe_3)_4]$ (50 mg, 0.08 mmol) with 4,4′-bpy (26 mg, 0.17 mmol) in ethanol using a method similar to that of **1**. The yield was 58 mg. Anal. Found: C, 47.31; H, 5.59; N, 3.93%. Calcd for $C_{30}H_{44}N_2O_8Rh_2$: C, 47.01; H, 5.79; N, 3.65%. IR (in KBr) ν/cm^{-1} for $^-O_2CCMe_3$: ν_{asym}(OCO) = 1584, ν_{sym}(OCO) = 1416.

$[Rh_2(O_2CCMe_3)_4(dabco)]_n$ (3). This compound was obtained as a pink powder by the reaction of $[Rh_2(O_2CCMe_3)_4]$ (50 mg, 0.08 mmol) with dabco (18 mg, 0.16 mmol) in ethanol using a method similar to that of **1**. The yield was 37 mg. Anal. Found: C, 43.60; H, 6.62; N, 3.87%. Calcd for $C_{26}H_{48}N_2O_8Rh_2$: C, 43.22; H, 6.70; N,

3.88%. IR (in KBr) ν/cm^{-1} for $^{-}O_2CCMe_3$: ν_{asym}(OCO) = 1584, ν_{sym}(OCO) = 1416.

[Rh$_2$(O$_2$CCMe$_3$)$_4$(tea)$_2$] (4). A solution of tea (17 mg, 0.17 mmol) in ethanol (10 cm^3) was added to a solution of [Rh$_2$(O$_2$CCMe$_3$)$_4$] (50 mg, 0.08 mmol) in ethanol (10 cm^3) and stirred for 1 h at room temperature to give a purple crystalline powder. This was separated, washed with ethanol, and dried in the air. The yield was 43 mg. Anal. Found: C, 47.28; H, 8.08; N, 3.39%. Calcd for $C_{32}H_{66}N_2O_8Rh_2$: C, 47.29; H, 8.19; N, 3.45%. IR (in KBr) ν/cm^{-1} for $^{-}O_2CCMe_3$: ν_{asym}(OCO) = 1590, ν_{sym}(OCO) = 1418.

[Rh$_2$(O$_2$CCMe$_3$)$_4$(py)$_2$] (5). This compound was obtained as a pink powder by the reaction of [Rh$_2$(O$_2$CCMe$_3$)$_4$] (50 mg, 0.08 mmol) with pyridine (13 mg, 0.16 mmol) in ethanol using a method similar to that of **4**. The yield was 52 mg. Anal. Found: C, 46.72; H, 5.87; N, 3.60%. Calcd for $C_{30}H_{46}N_2O_8Rh_2$: C, 46.89; H, 6.03; N, 3.65%. IR (in KBr) ν/cm^{-1} for $^{-}O_2CCMe_3$: ν_{asym}(OCO) = 1584, ν_{sym}(OCO) = 1414.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using Yanako CHN CORDER MT-5. Infrared spectra (KBr pellets) and electronic spectra were measured with JASCO FT/IR-350 and Shimadzu UV-3100 spectrometers, respectively. Thermogravimetric analyses were carried out using a Seiko Instr. TG/DTA 2200.

X-Ray Crystal Structure Analysis. Crystals of [Rh$_2$(O$_2$CCMe$_3$)$_4$(4,4′-bpy)]$_n$ (**2**) and [Rh$_2$(O$_2$CCMe$_3$)$_4$(tea)$_2$] (**4**) suitable for a single-crystal X-ray structure determination were obtained from an ethanol solution by a slow-diffusion technique using an H-shaped tube and recrystallization, respectively. Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. The lattice constants were determined by a least-squares refinement based on 25 reflections with $20° \leq 2\theta \leq 30°$. The intensity data were corrected for Lorentz-polarization effects. The structures were solved by direct methods. Refinements were carried out by the full-matrix least-squares method. The non-hydrogen atoms were refined with anisotropic thermal parameters. Because there are disorders at carbon atoms on the *t*-butyl groups of pivalate ions for **2** and **4**, they are divided into two positions with the same weights. In the case of **4**, these atoms are fixed at the positions based on the d-Fourier peaks. Hydrogen atoms were fixed at their calculated positions. A weighting scheme, $w = 1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. The final discrepancy factors, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$, are listed in Table 1. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[10] The atomic coordinates along with thermal parameters of non-hydrogen atoms and the selected bond distances and angles are listed in Tables 2 and 3, respectively. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and temperature factors of hydrogen atoms, and the $F_o - F_c$ tables are deposited as Document No. 72042 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC136360, 136361.

Results and Discussion

Elemental analyses of the obtained complexes showed stoichiometries [Rh$_2$(O$_2$CCMe$_3$)$_4$]:L = 1:1 for L = pyz, 4,4′-bpy, and dabco and 1:2 for L = tea and py, respectively. In the IR spectra of the powder samples (KBr pellet) of complexes **1**—**5**, the O–C–O vibrations appear as a set of distinctive bands in a similar wavenumber region to those (ν_{asym}(OCO) = 1564 cm^{-1}, ν_{sym}(OCO) = 1418 cm^{-1}) of the parent dimer [Rh$_2$(O$_2$CCMe$_3$)$_4$]. The values of the difference between the wavenumbers for the two O–C–O vibration bands, [ν_{asym}(OCO) − ν_{sym}(OCO)] = 166—172 cm^{-1}, are consistent with a bidentate bridging mode for the carboxylate ligands.[11,12] A slight increase of the values on the adduct formations could be due to axial coordination.[1,7b,13]

The polymer structure of **2** is shown in Fig. 1. The alternating arrangement of [Rh$_2$(O$_2$CCMe$_3$)$_4$] dimers and 4,4′-bpy molecules is built up by the axial coordination of nitrogen atoms of 4,4′-bpy to the dimer unit with distances of

Table 1. Crystal Data and Data Collection Details of **2** and **4**

Complex	**2**	**4**
Formula	$Rh_2O_8N_2C_{30}H_{44}$	$Rh_2O_8N_2C_{32}H_{66}$
F.W.	766.50	812.70
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	10.213(3)	10.323(2)
b/Å	14.663(3)	17.646(2)
c/Å	24.133(6)	12.153(2)
β/°	99.33(1)	112.082(8)
V/Å^3	3566(2)	2052(1)
Z	4	2
D_c/g cm^{-3}	1.43	1.32
D_m/g cm^{-3}	1.41	1.31
Crystal size/mm	0.59×0.50×0.23	0.40×0.30×0.29
μ(Mo $K\alpha$)/cm^{-1}	9.54	8.33
2θ range/°	2—48	1—50
No. of reflections measured	5857	3742
No. of unique reflections with $I > 3\sigma(I)$	4061	2438
R	0.042	0.055
R_w	0.050	0.084

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms for **2** and **4** with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^{2} [a]	Atom	x	y	z	B_{eq}/Å^{2} [a]
2					C23	0.5116(6)	0.2787(5)	0.1445(2)	3.1(1)
Rh1	0.33835(5)	0.22997(4)	0.32492(2)	2.791(9)	C24	0.5933(6)	0.2654(5)	0.1946(3)	3.7(1)
Rh2	0.25721(5)	0.20159(4)	0.41101(2)	3.02(1)	C25	0.5421(7)	0.2537(5)	0.2437(3)	3.9(2)
O1	0.4973(5)	0.2931(4)	0.3700(2)	4.1(1)	C26	0.7238(7)	0.2477(6)	0.0323(3)	4.5(2)
O2	0.4234(5)	0.2644(4)	0.4510(2)	4.1(1)	C27	0.6736(7)	0.2376(6)	0.0819(3)	4.5(2)
O3	0.4392(4)	0.1097(3)	0.3374(2)	3.8(1)	C28	0.5655(6)	0.2896(5)	0.0913(2)	3.2(1)
O4	0.3598(5)	0.0817(3)	0.4173(2)	4.0(1)	C29	0.5136(7)	0.3492(5)	0.0494(3)	3.9(2)
O5	0.2323(5)	0.3485(3)	0.3185(2)	4.0(1)	C30	0.5703(7)	0.3563(5)	0.0013(3)	4.0(2)
O6	0.1610(5)	0.3227(3)	0.4004(2)	4.2(1)					
O7	0.1758(4)	0.1665(4)	0.2843(2)	3.9(1)	**4**				
O8	0.0980(4)	0.1389(4)	0.3646(2)	4.2(1)	Rh	0.90489(8)	0.02411(5)	0.91461(7)	1.98(1)
N1	0.4112(5)	0.2571(4)	0.2445(2)	3.1(1)	O1	1.0220(7)	−0.0009(5)	0.8164(6)	3.0(2)
N2	0.6745(6)	0.3074(4)	−0.0076(2)	3.7(1)	O2	1.1994(7)	−0.0458(4)	0.9746(6)	3.0(2)
C1	0.5077(7)	0.2964(5)	0.4225(3)	3.8(2)	O3	0.8216(7)	−0.0829(4)	0.8895(7)	3.0(2)
C2	0.6299(9)	0.3416(7)	0.4543(4)	5.6(2)	O4	1.0002(8)	−0.1277(4)	1.0488(7)	3.0(2)
C3	0.648(1)	0.4337(9)	0.4316(6)	10.6(4)	N	0.7174(9)	0.0703(6)	0.7432(8)	2.9(2)
C4	0.630(1)	0.343(1)	0.5162(5)	14.8(4)	C1	1.142(1)	−0.0298(7)	0.8648(9)	2.8(2)
C5	0.748(1)	0.284(1)	0.4466(9)	14.8(6)	C2	1.222(1)	−0.0470(9)	0.786(1)	4.3(3)
C6	0.4314(7)	0.0622(5)	0.3806(3)	3.5(1)	C3A	1.371	−0.081	0.850	7.2(6)*,**
C7	0.5174(7)	−0.0224(5)	0.3900(3)	4.3(2)	C3B	1.135	−0.033	0.651	6(1)*,**
C8	0.536(1)	−0.0639(7)	0.3355(4)	8.8(3)	C4A	1.139	0.102	0.691	8.3(8)*,**
C9	0.463(1)	−0.0908(7)	0.4279(4)	7.2(3)	C4B	1.383	−0.034	0.867	7(1)*,**
C10	0.6520(9)	0.0097(8)	0.4211(5)	7.2(3)	C5A	1.239	0.031	0.736	8.3(7)*,**
C11	0.1651(7)	0.3697(5)	0.3566(3)	3.7(1)	C5B	1.276	−0.124	0.798	10(2)*,**
C12	0.0810(8)	0.4544(5)	0.3497(4)	5.1(2)	C6	0.885(1)	−0.1355(6)	0.9611(9)	2.7(2)
C13	−0.054(1)	0.4239(8)	0.3181(5)	7.8(3)	C7	0.819(1)	−0.2132(7)	0.939(1)	4.7(4)
C14	0.063(1)	0.4923(7)	0.4067(4)	8.2(3)	C8	0.697	−0.219	0.824	7.7(5)**
C15	0.139(1)	0.5247(7)	0.3147(5)	8.7(3)	C9A	0.921	−0.270	0.925	7.9(8)*,**
C16	0.0890(7)	0.1342(5)	0.3118(3)	3.6(1)	C9B	0.898	−0.274	1.022	7(1)*,**
C17	−0.0312(8)	0.0887(6)	0.2781(4)	5.0(2)	C10A	0.802	−0.241	1.054	9(1)*,**
C18	−0.060(1)	0.129(1)	0.2197(6)	12.8(5)	C10B	0.683	−0.208	0.982	8(1)*,**
C19A	−0.154(2)	0.144(2)	0.295(1)	8.2(6)*	C11	0.641(1)	0.0041(7)	0.670(1)	3.5(3)
C19B	−0.136(2)	0.069(2)	0.311(1)	15.2(8)*	C12	0.720(2)	−0.0430(9)	0.614(1)	4.9(4)
C20A	−0.044(3)	−0.004(1)	0.297(1)	13.1(9)*	C13	0.781(1)	0.1207(8)	0.678(1)	4.1(3)
C20B	0.022(2)	0.000(1)	0.251(1)	8.1(6)*	C14	0.680(2)	0.156(1)	0.563(1)	6.2(4)
C21	0.3314(6)	0.2694(5)	0.1963(3)	3.5(1)	C15	0.616(1)	0.1126(8)	0.782(1)	3.6(3)
C22	0.3755(7)	0.2822(5)	0.1460(3)	3.5(1)	C16	0.668(1)	0.1843(9)	0.850(1)	5.2(4)

a) Starred atoms were refined with occupancy factor of 0.5. Double-starred atoms were fixed at the calculated positions. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

2.225(5) (for Rh1–N1) and 2.264(5) Å (for Rh2–N2′). The Rh–Rh bond distance is 2.395(1) Å which is in the range for those reported for the adducts of rhodium(II) carboxylates with the axial aromatic nitrogen-donor ligands.[8,14,15] The relatively long Rh-Rh bond compared with that of $[Rh_2(O_2CCMe_3)_4(H_2O)_2]$ (2.371(1) Å[9] is attributed to the higher ligand basicity of 4,4′-bpy than H_2O.[8] The effect of the axial coordination on the equatorial Rh–O bonds is small: Rh–O (O_2CCMe_3) = 2.032(5) Å (mean value) for **2** and 2.040(2) Å (mean value) for $[Rh_2(O_2CCMe_3)_4(H_2O)_2]$. The 4,4′-bpy ligand is twisted with the dihedral angle of 38.2(3)° between the two pyridyl rings, which is comparable to those of $[Mo_2(O_2CCMe_3)_4(4,4'\text{-bpy})]_n$ (41.0(4)°).[3d] In contrast, the polymer adducts, $[Mo_2(O_2CMe)_4(4,4'\text{-bpy})]_n\cdot n(THF)$[3e] and $[Cu_2(O_2CCMe_3)_4(4,4'\text{-bpy})]_n\cdot n(\text{acetone})$,[16] have a coplanar orientation of the rings of 4,4′-bpy. The 4,4′-bpy molecule seems to be twisted at the C–C bond connecting the rings upon crystallization without crystal solvent. We have reported that the less-tight packing arrangement of $[Mo_2(O_2CMe)_4(4,4'\text{-bpy})]_n\cdot n(THF)$ with a coplanar alignment of the pyridyl rings of 4,4′-bpy could have allowed the coexistence of crystal solvent molecules.[3e]

The crystal structure of **4** is shown in Fig. 2. A crystallographic inversion center exists at the midpoint of the Rh–Rh bond within the core. The tea molecule is coordinated to the rhodium(II) ion with an Rh–N distance of 2.391(8) Å. To our knowledge, the axial Rh–N bond is the longest among those of the rhodium(II) carboxylate dimers with coordination of the aliphatic nitrogen.[8b,14a,15,17] The complex $[Rh_2(O_2CMe)_4(NHEt_2)_2]$ has a much shorter bond (2.301(5) Å).[17a] Although one would expect that the axial interaction is not strong in **4**, the Rh–Rh bond is quite long (2.413(1) Å), considerably longer than that in $[Rh_2(O_2CMe)_4(NHEt_2)_2]$ (2.402(1) Å). The bond distance, 2.413(1) Å, is largest in

Table 3. Selected Bond Distances (Å) and Angles (°) Concerning Rh_2 Core for **2** and **4** with Their Estimated Standard Deviations in Parentheses

2[a]			
Rh1–Rh2	2.395(1)	O1–Rh1–O5	91.2(2)
Rh1–O1	2.026(4)	O1–Rh1–O7	176.6(2)
Rh1–O3	2.040(5)	O3–Rh1–O5	175.3(2)
Rh1–O5	2.041(5)	O3–Rh1–O7	91.7(2)
Rh1–O7	2.014(4)	O5–Rh1–O7	88.4(2)
Rh1–N1	2.225(5)	O2–Rh2–O4	88.6(2)
Rh2–O2	2.032(5)	O2–Rh2–O6	90.8(2)
Rh2–O4	2.040(5)	O2–Rh2–O8	174.9(2)
Rh2–O6	2.025(5)	O4–Rh2–O6	176.3(2)
Rh2–O8	2.038(4)	O4–Rh2–O8	90.4(2)
Rh2–N2′	2.264(5)	Rh2–Rh1–N1	179.3(1)
O1–Rh1–O3	88.5(2)	Rh1–Rh2–N2′	173.2(2)
4[b]			
Rh–Rh′	2.413(1)	O1–Rh–O3	91.2(3)
Rh–O1	2.041(9)	O1–Rh–O4′	88.9(3)
Rh–O2′	2.051(9)	O2′–Rh–O3	88.6(3)
Rh–O3	2.050(8)	O2′–Rh–O4′	91.0(3)
Rh–O4′	2.042(7)	O3–Rh–O4′	175.6(3)
Rh–N	2.391(8)	Rh′–Rh–N	179.0(3)
O1–Rh–O2′	175.2(3)		

a) Primes refer to the equivalent positions $(x-1/2, -y+1/2, z+1/2)$. b) Primes refer to the equivalent positions $(-x+2, -y, -z+2)$.

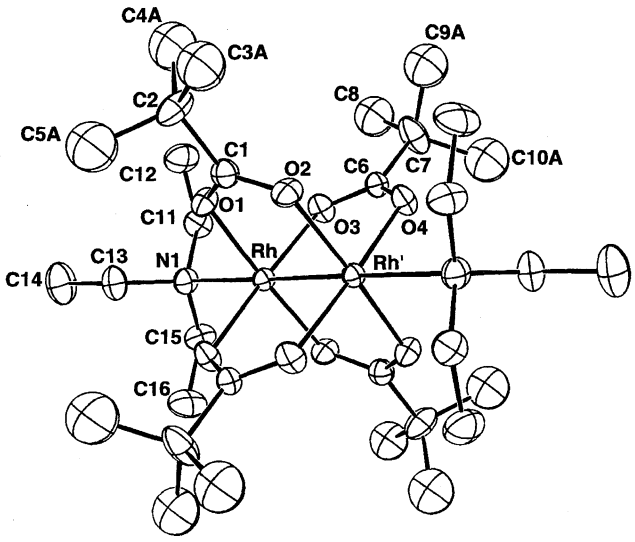

Fig. 2. ORTEP view of $[Rh_2(O_2CCMe_3)_4(tea)_2]_n$ (**4**). A prime refers to the equivalent positions $(-x+2, -y, -z+2)$. There are disorders at carbon atoms on *t*-butyl groups, of which those labeled with A are depicted for each of the pairs of the disordered atoms.

this type of adduct dimer with the axial aliphatic nitrogen. The most likely explanation for the long bond is that the steric hindrance between the *t*-butyl groups on the pivalate ions of the dimer core and the ethyl groups on tea makes the Rh–N bond lengthened so as to pull out the rhodium(II) ions

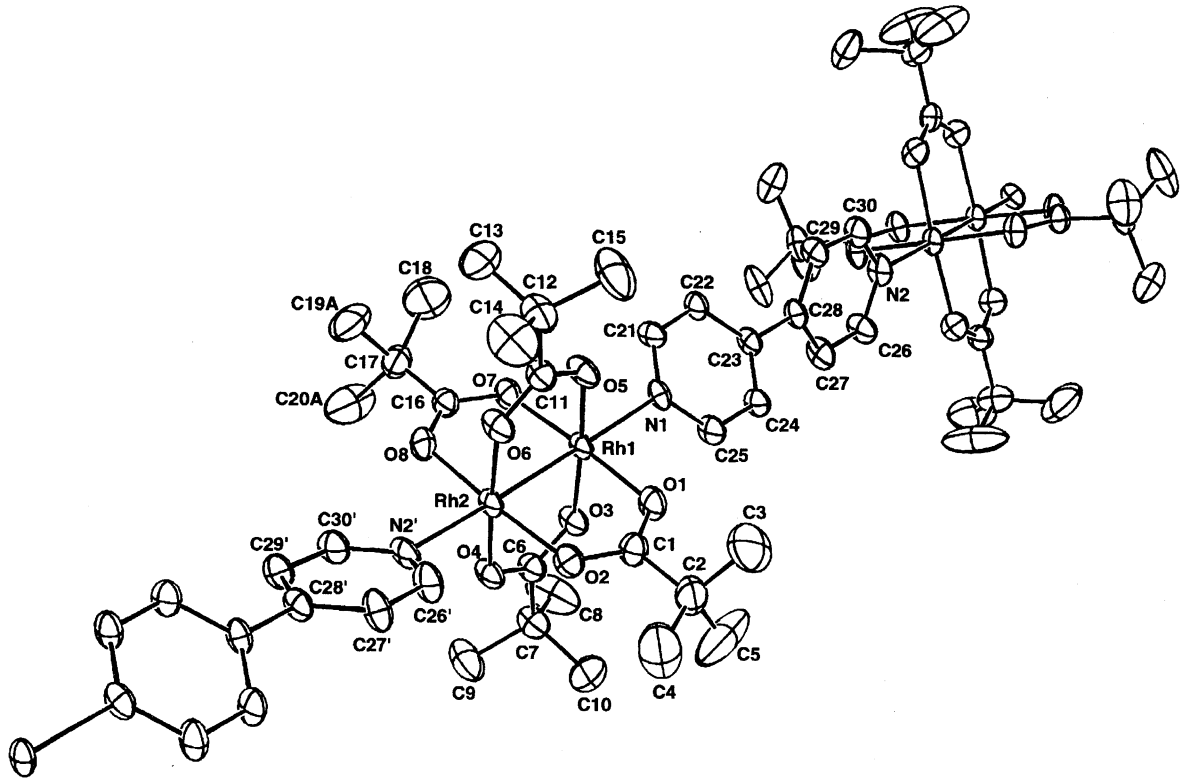

Fig. 1. ORTEP view of $[Rh_2(O_2CCMe_3)_4(4,4'\text{-bpy})]_n$ (**2**). Primes refer to the equivalent positions $(x-1/2, -y+1/2, z+1/2)$. There are disorders at carbon atoms on a *t*-butyl groups, of which those labeled with A are depicted for each of the pairs of the disordered atoms.

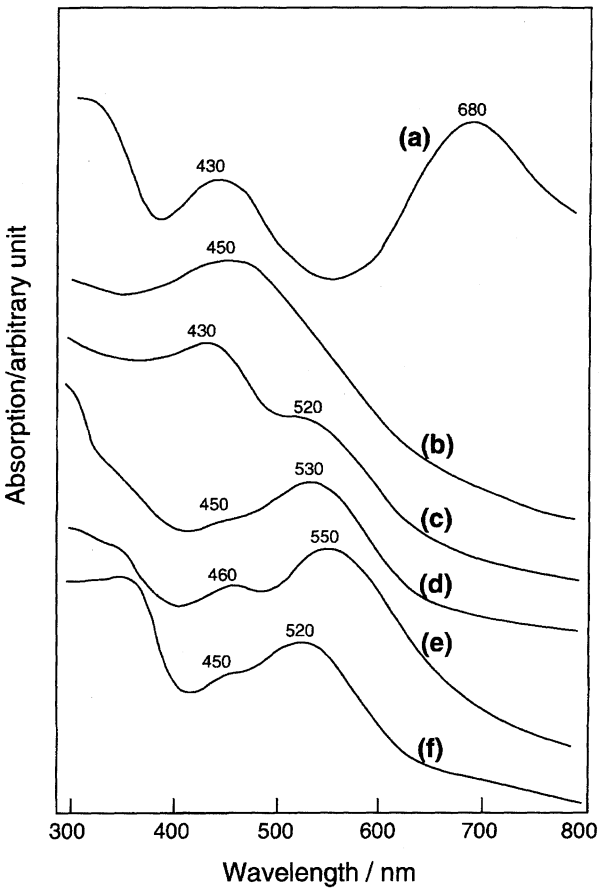

Fig. 3. Diffuse reflectance spectra of $[Rh_2(O_2CCMe_3)_4]$ (a), $[Rh_2(O_2CCMe_3)_4(pyz)]_n$ (**1**) (b), $[Rh_2(O_2CCMe_3)_4(4,4'\text{-bpy})]_n$ (**2**) (c), $[Rh_2(O_2CCMe_3)_4(dabco)]_n$ (**3**) (d), $[Rh_2(O_2CCMe_3)_4(tea)_2]$ (**4**) (e), and $[Rh_2(O_2CCMe_3)_4(py)_2]$ (**5**) (f).

toward each of the axial ligands, resulting in an elongation of the Rh–Rh bond. It has been reported that the tea adduct dimer of copper(II) pivalate $[Cu_2(O_2CCMe_3)_4(tea)_2]$ has an extremely long Cu–Cu separation (2.681(1) Å) accompanied by a long axial Cu–N bond (2.300(4) Å).[6b]

In Fig. 3, the diffuse reflectance spectra of **1**—**5** are shown with that of $[Rh_2(O_2CCMe_3)_4]$. The parent dimer $[Rh_2(O_2CCMe_3)_4]$ shows two distinctive bands at 680 nm (band A) and 430 nm (band B). Band A has been assigned as the $\pi^*(Rh_2)\rightarrow\sigma^*(Rh_2)$ transition and band B as the $\pi(Rh\text{–}O)\rightarrow\sigma^*(Rh\text{–}O)$ transition.[18] All of the adducts show the corresponding two bands in the visible region, though **1** has a broad band around 450 nm, probably due to a superposition of the two bands. Band A blue-shifts by 130—160 nm on each of the adduct formation, which implies the presence of an appreciable axial interaction between the Rh_2 core and the ligand.[7] The relatively small shift of the band of **4** may indicate that the axial interaction is weaker than the other adducts. This result shows that the strength of the axial interaction is not estimated only by the Rh–Rh bond-length value, because **4** has a longer Rh–Rh bond than **2**. No significant shift can be seen for band B, since it is essentially insensitive to an axial interaction.

Table 4. Thermal decomposition Temperatures (C°) of **1**—**5**[a)]

Complex	Elimination of 1st ligand	Elimination of 2nd ligand	Decomposition of the dimer core
1	300[b)]		
2	300[b)]		
3	350[b)]		
4	120	150	270
5	160	220[c)]	280

a) The data were obtained by heating in aliminum pans at the rate 5 °C min^{-1}. The experiment was run in a nitrogen purge. b) The ligand elimination and decomposition of the lantern core occured at the same time (see text). c) The second elimination of the axial pyridine ligand occured with the liberation of one pivalate group from the lantern core (see text).

Thermogravimetric analyses were carried out for complexes **1**—**5** in the temperature range 20—500 °C. The results are summarized in Table 4. It has been known that the thermal decomposition of rhodium(II) carboxylate adducts usually occurs in several stages before complete decomposition of the lantern core structure at higher temperature.[7b] However, in the case of the adduct polymers, the lantern structure decomposed at 300—350 °C without any elimination of the linkage ligands prior to decomposition. The pyz adduct polymer of rhodium(II) benzoate $[Rh_2(O_2CPh)_4(pyz)]_n$ has shown almost the same thermogravimetric property.[19] The thermal stability of this type of the adduct polymers of rhodium(II) carboxylates may be due to the fact that the bridging ligands intervene between the rhodium(II) dimers to be retained by the axial coordinations at both ends of the linkage ligands. Adduct dimers **4** and **5** show the ligand elimination before decomposition of the lantern core structure, though **5** has a second ligand evolution overlapped with the elimination of one pivalate group from the dimer core, somewhat similarly to the pyridine adduct dimers $[Rh_2(O_2CEt)_4(py)_2]$ and $[Rh_2(O_2CPr^n)_4(py)_2]$ which show ligand evolution overlapped with cage breakdown.[20] The tea elimination of **4** at relatively low temperatures (120 and 150 °C) compared with those (160 and 220 °C) of **5** shows that the axial coordination is not so strong in **4**. This is consistent with the small red-shift of the $\pi^*(Rh_2)\rightarrow\sigma^*(Rh_2)$ transition of **4** in the reflectance spectra.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 10640547) and Grant-in-Aid for Scientific Research on Priority Areas (Nos. 10157472 and 11136235 "Metal-assembled Complexes") from the Ministry of Education, Science, Sports and Culture.

References

1 F. A. Cotton and R. A. Walton, "Multiple Bonds between Metal Atoms," 2nd ed, Oxford Univ. Press, New York (1993).

2 O. W. Steward, B. S. Johnston, S.-C. Chang, A. Harada, S. Ohba, T. Tokii, and M. Kato, *Bull. Chem. Soc. Jpn.*, **69**, 3123 (1996); M. Morooka, S. Ohba, M. Nakashima, T. Tokii, Y. Muto, M. Kato, and O. W. Steward, *Acta Crystallogr., Sect. C*, **48C**, 1888

(1992).

3 a) M. Handa, K. Kasamatsu, K. Kasuga, M. Mikuriya, and T. Fujii, *Chem. Lett.*, **1990**, 1753. b) M. Handa, H. Sono, K. Kasamatsu, K. Kasuga, M. Mikuriya, and S. Ikenoue, *Chem. Lett.*, **1992**, 453. c) M. Handa, K. Yamada, T. Nakao, K. Kasuga, M. Mikuriya, and T. Kotera, *Chem. Lett.*, **1993**, 1969. d) M. Handa, M. Mikuriya, R. Nukada, H. Matsumoto, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **67**, 3125 (1994). e) M. Handa, M. Mikuriya, T. Kotera, K. Yamada, T. Nakao, H. Matsumoto, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 2567 (1995). f) M. Handa, H. Matsumoto, T. Namura, T. Nagaoka, K. Kasuga, M. Mikuriya, T. Kotera, and R. Nukada, *Chem. Lett.*, **1995**, 903. g) M. Handa, H. Matsumoto, D. Yoshioka, R. Nukada, M. Mikuriya, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **71**, 1811 (1998).

4 M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 1647 (1995); M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Chem. Lett.*, **1996**, 201; M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **71**, 119 (1998); Y. Sayama, M. Handa, M. Mikuriya, I. Hiromitsu, and K. Kasuga, *Chem. Lett.*, **1998**, 777; Y. Sayama, M. Handa, M. Mikuriya, I. Hiromitsu, and K. Kasuga, *Chem. Lett.*, **1999**, 453.

5 M. Handa, A. Takata, T. Nakao, K. Kasuga, M. Mikuriya, and T. Kotera, *Chem. Lett.*, **1992**, 2085; M. Handa, M. Mikuriya, Y. Sato, T. Kotera, R. Nukada, D. Yoshioka, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **69**, 3483 (1996); M. Handa, T. Nakao, M. Mikuriya, T. Kotera, R. Nukada, and K. Kasuga, *Inorg. Chem.*, **37**, 149 (1998).

6 a) M. Mikuriya, R. Nukada, H. Morishita, and M. Handa, *Chem. Lett.*, **1995**, 617. b) M. Mikuriya, H. Azuma, R. Nukada, and M. Handa, *Chem. Lett.*, **1999**, 57. c) R. Nukada, W. Mori, S. Takamizawa, M. Mikuriya, M. Handa, and H. Naono, *Chem. Lett.*, **1999**, 367.

7 a) T. R. Felthouse, *Prog. Inorg. Chem.*, **29**, 73 (1982). b) E. B. Boyar and S. D. Robinson, *Coord. Chem. Rev.*, **50**, 109 (1983). c) F. H. Jardine and P. S. Sheridan, in "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Pergamon Press, New York (1987), Vol. 4, p. 944.

8 a) Y. B. Koh and G. G. Christoph, *Inorg. Chem.*, **17**, 2590 (1978). b) F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, **20**, 600 (1981).

9 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, **19**, 323 (1980).

10 C. K. Fair, "MolEN Structure Determination System," Delft Instrument, Delft, The Netherlands (1990).

11 K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, Wiley Interscience, New York (1986).

12 S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

13 G. Pneumatikakis and N. Hadjiliadis, *J. Chem. Soc., Dalton Trans.*, **1979**, 596.

14 a) K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, **106**, 3691 (1984). b) M. A. Zoroddu, L. Naldini, F. Demartin, and N. Masciocchi, *Inorg. Chim. Acta*, **128**, 179 (1987). c) K. Aoki and H. Yamazaki, *Acta Crystallogr., Sect. C*, **45C**, 730 (1989). d) T. M. Dyson, E. C. Morrison, D. A. Tocher, L. D. Dale, and D. I. Edwards, *Inorg. Chim. Acta*, **169**, 127 (1990). e) B. Viossat, N.-H. Dung, J. C. Daran, and J. C. Lancelot, *Acta Crystallogr., Sect. C*, **49C**, 2048 (1993). f) F. P. Pruchnik, F. Robert, Y. Jeannin, and S. Jeannin, *Inorg. Chem.*, **35**, 4261 (1996).

15 G. Aullón and S. Alvares, *Inorg. Chem.*, **32**, 3712 (1993).

16 R. Nukada, M. Mikuriya, and M. Handa, "46th Symp. Coordination Chemistry of Japan," Higashiosaka, Japan, 21—23 Sept. 1996, Abstr., No. 1A221.

17 a) Y. B. Koh and G. G. Christoph, *Inorg. Chem.*, **18**, 1122 (1979). b) C. A. Crawford, E. F. Day, W. E. Streib, J. C. Huffman, and G. Christou, *Polyhedron*, **13**, 2933 (1994).

18 V. M. Miskowski, W. P. Schaefer, B. Sadeghi, B. D. Santarsiero, and H. B. Gray, *Inorg. Chem.*, **23**, 1154 (1984); J. W. Trexler, Jr., A. F. Schreiner, and F. A. Cotton, *Inorg. Chem.*, **27**, 3265 (1988).

19 W. Mori, H. Hoshino, Y. Nishimoto, and S. Takamizawa, *Chem. Lett.*, **1999**, 331.

20 R. A. Howard, A. M. Wynne, J. L. Bear, and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **38**, 1015 (1976).