Dinuclear rhodium(11) pivalate complexes with N-donor ligands

A. A. Sidorov,* G. G. Aleksandrov, E. V. Pakhmutova, A. Yu. Chernyad 'ev, I. L. Eremenko, and I. I. Moiseev

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 955 4835. E-mail: sidorov@igic.ras.ru

Eight dinuclear rhodium(II) complexes containing various, (primarily, polyfunctional) N-donor ligands in the *trans* position with respect to the Rh–Rh bond were synthesized and characterized by X-ray diffraction. In the Chinese-lantern dinuclear rhodium(11) pivalates, $Rh^{II}_{2}(\mu$ -OOCCMe₃)₄(L)₂ (L is 2,3-diaminopyridine (2), 7,8-benzoquinoline (4), 2,2':6',2"-terpyridine (5), N-phenyl-o-phenylenediamine (7)), and $Rh^{II}_{2}(\mu-OOCCMe_{3})_{4}L^{1}L^{2}$ (3, L^{1} is 2-phenylpyridine, $L^2 = MeCN$, the steric effects of the axial ligands are most strongly reflected in the Rh–N(L) and Rh–Rh bond lengths. The introduction of chelating ligands containing a conformationally rigid chelate ring leads to the cleavage of two carboxylate bridges to form the dinuclear double-bridged structure $Rh^{II}_{2}(\mu-OOCCMe_{3})_{2}(OOCCMe_{3})_{2}(\eta^{2}-L^{3})_{2}$, where L^3 is 8-amino-2,4-dimethylquinoline (6). The reaction of complex 7 containing coordinated N-phenyl-o-phenylenediamine with pyrrole-2,5-dialdehyde afforded the new $Rh^{II}_{2}(\mu$ -OOCCMe₃)₄(L⁴)₂ complex (8) containing 5-(1-phenyl-1*H*-benzimidazol-2-yl)-1*H*pyrrole-2-carbaldehyde (L^4) in the axial positions of the dirhodium tetracarboxylate fragment. The coordinated diamine differs in reactivity from the free diamine. The reaction of the former with the above dialdehyde affords the [1+1]-condensation product, viz., $5-\{(E)-[(2-anilino$ phenyl)imino]methyl}-1H-pyrrole-2-carbaldehyde, whereas the reaction of unsubstituted o-phenylenediamine gives 5-{(E)-[(2-aminophenyl)imino]methyl}-1H-pyrrole-2-carbaldehyde (L⁵). The reaction of the latter with $Rh^{II}_{2}(\mu$ -OOCCMe₃)₄(H₂O)₂ affords the dinuclear complex Rh^{II}₂(μ -OOCCMe₃)₂(OOCCMe₃)₂(η^2 -L⁵)₂ (9), which is an analog of complex 6 containing only two bridging carboxylate groups.

Key words: rhodium(11), dinuclear complexes, pivalate, X-ray diffraction study, metal—metal bond, N-donor ligands.

The behavior of dinuclear Rh^{II} complexes with four carboxylate bridges (so-called "lantern dimers") is characterized by the retention of the bimetallic tetracarboxylate fragment in the reactions with the majority of N-donor ligands due, in part, to stability of the Rh–Rh bond.^{1,2} Even the use of chelating ligands rather often leads to monodentate coordination with retention of the $Rh_2(\mu$ -OOCCR)₄ fragment.¹ This fact allows one to study the influence of the nature of donor ligands axially coordinated to metal atoms on the characteristics of the metal-metal and metal-carboxylate bonds. This, in turn, helps in predicting ways of activation of the dinuclear metal carboxylate fragment. In addition, the presence of a stable metal fragment with delocalized metal-carboxylate-metal bonds shows promise in using the axial position in complexes to perform various chemical transformations of a coordinated organic donor, including redox reactions.²

In the present study, we used various α -substituted pyridine derivatives as axial N-donor ligands, thus introducing particular disturbances in the step of formation of dinuclear metal fragments with pivalate bridges, which also contain the bulky donor *tert*-butyl groups. In addition, we examined the possibility of using the axial positions in dinuclear rhodium(II) pivalates to perform condensation of arenediamine with pyrroledialdehyde.

Results and Discussion

The known dinuclear rhodium(II) acetate $Rh_2(MeCO_2)_4py_2$ containing pyridine molecules in the axial positions has the strong metal-metal bond (2.3963(2) Å) combined with the strong bonds between the rhodium atoms and the pyridine nitrogen atoms (2.247(2) Å).³ The similar geometric parameters were observed in the $Rh_2(MeCO_2)_4(4-CN-Py)_2$ complex with 4-pyridinecarbonitrile⁴ (Table 1). The presence of two methyl groups in the α positions of the pyridine ring leads to substantial changes in the geometric parameters. In the $Rh_2(MeCO_2)_4(2,6-Me_2C_5H_3N)_2$ complex, the Rh-Rh bond is slightly elongated (2.4137(5) Å) and the Rh-N bond is substantially elongated (2.403(4) Å).⁵ In dirhodium pivalate complexes, these effects can be more

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 3, pp. 581-591, March, 2005.

1066-5285/05/5403-0588 © 2005 Springer Science+Business Media, Inc.

 Table 1. Selected dinuclear rhodium carboxylates with pyridine ligands

Compound	Bond	Refer-	
	Rh-Rh	Rh–N(L)	ence
Rh ₂ (MeCO ₂) ₄ py ₂	2.3963(2)	2.247(2)	1, 3
$Rh_2(MeCO_2)_4(4-CN-Py)_2$	2.393(1)	2.243(4),	1, 4
		2.244(4)	
$Rh_2(MeCO_2)_4(Me_2py)_2$	2.4137(5)	2.403(4)	5
$Rh_2(\mu$ -OOCCMe ₃) ₄ (Et ₃ N) ₂	2.413(1)	2.391(2)	6
$Rh_2(\mu$ -OOCCMe ₃) ₄ (γ , γ' -bpy)*	2.395(1)	2.264(2),	6
2		2.224(2)	
$Rh_2(Me_3CCO_2)_4Nic_2$	2.371(1)	2.123(3),	7
2, 5 2, 1 2		2.361(3)	
$Rh_2(Me_3CCO_2)_4(H_2O)_2$	2.371(5)	2.295(2)	8

* The compound is a polymer in which the dinuclear $\{Rh_2(\mu-OOCCMe_3)_4\}$ fragments are linked by the bridging γ,γ' -dipyridyl molecules.

pronounced due to the presence of the bulky *tert*-butyl substituents in the carboxylate anions. However, the known series of rhodium(11) pivalate complexes with N-donor ligands is limited to dinuclear complexes with the axial triethylamine,⁶ γ , γ' -dipyridyl,⁶ and 2-nitroxy-ethynylnicotinamide (Nicorandil, Nic) molecules,⁷ among which Rh₂(μ -OOCCMe₃)₄(Et₃N)₂ is characterized by the largest steric strain and, correspondingly, the longest metal—metal and metal—nitrogen bonds⁶ (see Table 1).

The reactions with the use of trimethylacetate complexes and 2,3-diaminopyridine containing the donor NH₂ group as the α substituent, afford products with similar structures. The reaction of Rh₂(μ -OOCCMe₃)₄(H₂O)₂ (1)⁸ with 2,3-diaminopyridine in acetonitrile produces the Rh₂(μ -OOCCMe₃)₄L₂ complex (2, L is 2,3-diaminopyridine, Scheme 1).

In spite of the fact that at least two nitrogen atoms of 2,3-diaminopyridine can be formally involved in binding to the metal center in molecule 2, the ligand L is

monodentate-coordinated at the pyridine nitrogen atom to form the very strong Rh-N(py) bond (2.270(2) Å; Fig. 1, Table 2). The metal-metal bond in the $Rh_2(\mu$ -OOCCMe₃)₄ fragment of complex 2 (Rh-Rh, 2.4072(7) Å) is slightly longer than that observed in the starting complex 1 (see Table 1), but it is shorter than that in the known acetate complex containing the 2,6-dimethylpyridine ligands.⁵ In this case, the N-Rh-Rh-N fragment remains linear (see Table 2). It should be noted that there are intra- and intermolecular hydrogen bonds between the protons of the amino group $N(2)H_2$, on the one hand, and the oxygen atoms of the pivalate anion and the nitrogen atom of the acetonitrile solvate molecule (N(2)-H...O(3)(OOCR), 2.966(6) and 2.21 Å; N-H-O, 144°; N(2)-H...N(1s), 3.103(6) and 2.29 Å; N-H-N, 155°), on the other hand, in the structure of complex 2.

An increase in steric strain in the dinuclear system was achieved by introducing the bulky Ph substituent at the α position of the pyridine molecule. It appeared that 2-phenylpyridine reacts with complex **1** in an acetonitrile solution to form the unsymmetrical dinuclear "lantern complex" (MeCN)Rh(μ -OOCCMe₃)₄Rh(PhC₅H₄N) (**3**) containing different terminal ligands, *viz.*, acetonitrile and phenylpyridine (see Scheme 1).

In molecule **3**, the N—Rh—Rh—N fragment is nonlinear (see Table 2, Fig. 2), which is untypical of dinuclear rhodium(II) carboxylates. The Rh—Rh—N(phenylpyridine) group is also nonlinear, and the Rh—N(py) bond in this group is elongated to 2.338(3) Å (see Table 2). By contrast, the opposite Rh—N(NCMe) bond in the linear N—Rh—Rh fragment is rather short (2.251(3) Å; see Table 2). The formation of this unusual unsymmetrical "lantern dimer" is apparently attributable to competition for the axial positions in the dinuclear tetracarboxylate fragment between the small but weakly basic acetonitrile molecules and the sterically unfavorable but strongly basic phenylpyridine molecules. As a result, intermediate unsymmetrical complex **3** is generated, which is the most stable compound under the reaction conditions.





L is 2,3-diaminopyridine (2), 7,8-benzoquinoline (4), terpyridine (5)

i. Ar, MeCN, 20 °C.



Fig. 1. Structure of complex 2.

Table 2. Selected geometric characteristics of dinuclear rhodium(11) pivalates

Com-	Distance/Å			Angle/deg			
pound	Rh-Rh	Rh—N	Rh—O	O-Rh-N	Rh-Rh-N	Rh–N–C	
2	2.4072(7)	2.270(2)	2.033(2)-2.053(2)	89.09(7), 89.57(7), 94.91(7), 95.17(7)	176.30(5)	125.7(2), 115.7(2)	
3	2.3997(6)	2.338(3) N(py) 2.251(3) N(MeCN)	2.030(3)-2.044(3)	83.9(1), 89.2(1), 94.6(1), 100.7(1)	171.36(9) Rh(py), 177.19(9) Rh(MeCN)	130.9(3), 109.7(3) Rh(py), 175.5(4), Rh(MeCN)	
4	2.4131(8)	2.403(4)	2.037(3)-2.046(3)	85.9(1), 98.1(1), 91.3(1), 92.8(1)	174.1(1)	104.1(3), 131.3(3)	
5	2.4046(9)	2.343(4)	2.028(3)-2.040(3)	87.0(1), 93.2(1), 91.1(1), 97.1(1)	174.77(9)	132.2(3), 107.1(3)	
6	2.486 (1)	$2.243(7)^a$, $2.250(8)^a$ $2.024(7)^b$, $2.027(7)^b$	$2.015(6) - 2.067(6)^c$, $2.040(6)^d$	$95.5(3)^e$, $85.1(3)^f$, $101.8(3)^g$	$169.0(2)^a$, $169.0(2)^a$, $95.2(2)^b$, $96.2(2)^b$	131.9(6) ^{<i>a</i>} , 107.9(6) ^{<i>a</i>} , 113.5(5) ^{<i>b</i>}	
7	2.3893(6)	2.281(3)	2.032(2) - 2.041(2)	93.47(8)-90.41(8)	178.85(7)	115.8(2)	
8	2.4056(7)	2.301(3)	2.037(3) - 2.054(3)	89.6(1), 95.0(1)	175.81(8)	117.6(2), 136.8(2)	
9	2.4651(7)	$2.288(4)^h$, $2.048(4)^i$	$2.042(3) - 2.077(3)^c,$ 2.040(4) ^d	91.6(1) ^{<i>j</i>} , 101.6(2) ^{<i>k</i>} , 91.6(1) ^{<i>l</i>}	$173.1(1)^m, 96.5(1)^n$	$137.6(4)^{o}, 102.3(3)^{p}$ $108.2(3)^{q}$	
^a N(py).	ن	$^{f}O(4) - Rh(2) - N(3).$	^j O(2)—Rh	(1)—N(2).	n N(3)-Rh(1)-Rh(2).	
^b N(NH ₂).		$^{g}O(2)-Rh(2)-N(3).$	k O(4) - Rh	n(1) - N(2).	^o C(26)-N(2)-Rh(1).		
^c Rh $-O(\mu$ -OOCCMe ₃).		l Rh(1)-N(2). l O(5)-Rh		(1) - N(2).	p C(27)-N(2)-Rh(1).		
^d Rh– $O(\eta^1$ -OOCCMe ₃) _{aver} . ^e O(7)–Rh(2)–N(3).		i Rh(1)—N(3).	m N(2)-Rh(1)-Rh(2).		q C(32)-N(3)-Rh(1).		



Fig. 2. Structure of complex 3.

It should be noted that bulkier 7,8-benzoquinoline remains uncoordinated in an acetonitrile solution under these conditions. However, this situation can be changed by using a noncoordinating hydrocarbon solvent (for example, toluene) instead of acetonitrile. In toluene, the $Rh_2(\mu$ -OOCCMe₃)_4(bquin)_2 complex (4, bquin is 7,8-benzoquinoline) (see Scheme 1) is formed in nearly 100% yield. X-ray diffraction study (see Table 2 and Fig. 3) demonstrated that the Rh–Rh bond (2.4131(8) Å) in complex 4 is substantially longer than the metal—metal distances in dinuclear rhodium carboxylates with apical ligands, whose coordination is sterically hindered.^{1-6,8} In addition, the Rh–Nh bond length is as large as 2.403(4) Å, although the N–Rh–Rh–N fragment remains nearly linear (N–Rh–Rh, 174.1(1)°).

Formally, the geometric characteristics of the terminal pyridine rings in 2,2':6',2"-terpyridine are similar to those observed in the analogous fragment of 2-phenylpyridine. However, terpyridine contains three pyridine rings and serves as the ligand possessing a high chelating ability. At room temperature, terpyridine readily reacts with complex **1** in acetonitrile to form the dinuclear $[Rh_2(OOCCMe_3)_4terpy_2]$ compound (**5**). The structure of the latter is analogous to that of the known⁹ acetate $[Rh_2(MeCOO)_4terpy_2]$. In trimethylacetate complex **5** (see Scheme 1, Fig. 4), terpyridine is also monodentatecoordinated through one nitrogen atom of the terminal ring.

X-ray diffraction study demonstrated that the main geometric parameters of complex 5 (see Table 2) are similar to the characteristics of the known acetate analog,⁹ the steric effects of the apical ligand in complex 5 being reflected primarily in elongation of the Rh—N bonds (2.343(4) Å). The formation of symmetrical dinuclear complex 5 in acetonitrile is, apparently, attributable to high basicity of the nitrogen atoms in the terpyridine molecule, which, in fact, diminishes the probability of competition with the nitrogen atoms of MeCN observed in the reaction with phenylpyridine.

Therefore, the use of aminopyridine and terpyridine in reactions with complex **1**, in spite of the formal possibility of the formation of chelate rings with rhodium atoms and partial cleavage of the tetrabridged carboxylate system, did not lead to the transformation of the $\{Rh_2(OOCCMe_3)_4\}$ fragment. In this respect, 8-amino-2,4-dimethylquinoline is, apparently, more promising because it contains, on the one hand, the α -methyl substituent in the pyridine ring and, on the other hand, the amino group in the position convenient for the formation of a stable five-membered chelate metallocycle. We found that the reaction of 8-amino-2,4-dimethylquinoline with $Rh_2(\mu-OOCCMe_3)_4(H_2O)_2$ af-



Fig. 4. Structure of complex 5.

forded the dinuclear $Rh_2(\eta^2-\{Me_2(C_9H_4N)NH_2\})_2(\mu-OOCCMe_3)_2(OOCCMe_3)_2$ complex (6) containing only two bridging pivalate ligands (Scheme 2, Fig. 5). In complex 6, the metal—metal bond is substantially elongated (Rh—Rh, 2.486(1) Å).

The five-membered metallocycles adopt an envelope conformation.¹⁰ The N(2) and N(4) atoms deviate from the planes passing through the other four atoms of the corresponding metallocycles by 0.47 and 0.55 Å, respectively. The Rh–N(py)_{aver} bond length (2.246(8) Å) has a



Fig. 5. Structure of complex 6.





i. Ar, C_6H_6 , Rh_{at} : L = 1 : 1.

typical value, whereas the average distance to the amino groups, whose lone pairs are more accessible (compared to the lone pair of the pyridine fragment) for the interaction with metal, is substantially shorter $(Rh-N(NH_2)_{aver}, 2.025(7) \text{ Å})$. Taking into account the above results, it can be hypothesized that the reaction of the starting carboxylate with 8-amino-2,4-dimethylquinoline begins with the binding of the rhodium atoms to the nitrogen atom of the heterocycle and, due to planarity of the bicyclic 8-amino-2,4-dimethylquinoline molecule, leads finally to the formation of the chelate ring and the transformation into the double-bridged metal carboxylate fragment.

For Rh^{II} carboxylates, coordination of the primary amino groups bound to the aromatic ring can occur in the absence of competition with the more basic pyridine nitrogen atom. However, the reaction with o-phenylenediamine (containing no pyridine fragments) affords a gellike product, which has, apparently, a polymeric structure due to bridging coordination of the diamine that links the Rh₂(µ-OOCCMe₃)₄ fragments.¹¹ A dinuclear molecular system can be formed using N-phenyl-o-phenylenediamine containing the nonequivalent amino groups. The NH₂ group is more reactive. Earlier, it has been found that this group is easily bound to the dinuclear nickel(II) tetrapivalate fragment.¹² It appeared that the reaction of 1 with N-phenyl-o-phenylenediamine in toluene afforded the $Rh_2(\mu$ -OOCCMe₃)₄(PhHN(C₆H₄)NH₂)₂ complex (7, Scheme 3, Fig. 6) in high yield. X-ray diffraction study demonstrated that molecule 7 retains the dinuclear tetracarboxylate metal fragment (Rh-Rh, 2.3893(6) Å), and the diamine is coordinated to the rhodium atom as a monodentate ligand through the primary amino group (Rh–N, 2.281(3) Å). Since the diphenylamino fragment of the ligand has no short contacts with the dinuclear metal carboxylate fragment, the geometric characteristics



Fig. 6. Structure of complex 7.

of the latter (see Table 2) are similar to the usual characteristics of the known lantern-type rhodium carboxylates with sterically unhindered apical ligands.¹



i. Toluene, 110 °C.

The stable dirhodium tetracarboxylate fragment is retained upon condensation of the coordinated *N*-phenyl*o*-phenylenediamine molecules with pyrrole-2,5-dialdehyde. It should be noted that the free diamine reacts with this dialdehyde to give only the [1+1]-condensation product, *viz.*, $5-{(E)-[(2-anilinophenyl)imino]methyl}-1H$ pyrrole-2-carbaldehyde (Scheme 4).¹³

The reaction of pyrrole-2,5-dialdehyde with the $Rh_2(\mu$ -OOCCMe₃)₄(PhHN(C₆H₄)NH₂)₂ complex (7)

Scheme 4



R = H, Rh

involves condensation of the free secondary amino group and the coordinated primary amino group with the dialdehyde molecule to give the five-membered ring. Under the reaction conditions, the latter is oxidized to the imidazole ring in the resulting $Rh_2(\mu$ -OOCCMe₃)₄(L⁴)₂ complex (**8**, L⁴ is 5-(1-phenyl-1*H*-benzimidazol-2-yl)-1*H*-pyrrole-2-carbaldehyde, Scheme 5, Fig. 7).

In spite of the formation of the rather bulky N-donor axial ligand by condensation of the coordinated diamine molecule with dialdehyde, the tetracarboxylate fragment $Rh_2(\mu$ -OOCCMe₃)₄ in complex **8** is retained. In the dimeric fragment of the latter, the metal—metal bond is substantially longer (Rh—Rh, 2.4056(7) Å) than that in the starting complex **7**. The Rh—N bonds are also elongated, the N—Rh—Rh—N fragment remaining linear (see



Scheme 5



Table 2). These effects are not surprising, because the environment of the nitrogen atom in the five-membered ring involved in binding to the metal atom is analogous to the environment of the pyridine ligand containing two α substituents. Moreover, a larger increase in the distance between the metal atoms would, evidently, be expected in

the absence of the contracting effect of hydrogen bonding between the protons of the NH group of the new ligand and the oxygen atoms of the bridging carboxylate groups (N(3)-H...O(1)(OOCR): N...O, 2.859 Å; H...O, 1.98 Å; $N-H-O, 166^{\circ}$). Apparently, condensation is determined to a large extent by the electronic and geometric features of the amino groups in the coordinated diamine molecule of the starting complex 7.

The reaction of pivalate **1** with the [1+1]-condensation product of pyrrole-2,5-dialdehyde with *o*-phenylenediamine $(5-{(E)-[(2-aminophenyl)imino]methyl}-1H$ pyrrole-2-carbaldehyde¹⁴) (see Scheme 4) did not leadto the further transformation of the [1+1]-N donor.This reaction produced the Rh₂(OOCCMe₃)₄[NH₂- $<math>(C_6H_4)N(H)=C(H)-C_4H_2N-CHO]_2$ complex (**9**) containing the chelate-coordinated starting ligand as the major product (Scheme 6).

Chelation of the N-donor ligand causes cleavage of two bridging pivalate groups, the terminal coordination of the latter being stabilized by hydrogen bonding between one proton of the NH2 groups and the uncoordinated oxygen atoms of the monodentate-coordinated carboxylate ligands (N(3)-H...O(6), 1.98 and 2.688 Å; N-H-O, 148°; N(6)-H...O(8), 1.94 and 2.656 Å). In addition, there are hydrogen bonds between the H atom of the pyrrole ring and the O atoms of the bridging carboxylate ligands (N(1)-H...O(4), 2.03 and 2.888 Å; N-H-O, 160°; N(4)-H...O(1), 1.99 and 2.872 Å; N-H-O, 167°) (Fig. 8). In the doubly-bridged dirhodium tetracarboxylate fragment, the metal-metal bond is substantially elongated (2.4651(7) Å) compared to that observed in the starting compound 1. The Rh-N distances (Rh–NH₂, 2.037(4) and 2.048(4) Å; Rh–N=C,



Fig. 7. Structure of complex 8.





2.288(4) and 2.285(4) Å) in the chelate metallocycle are similar to those found in analogous complex **6** (see Table 2).

Investigation of the influence of the nature of the axial N-donor ligands on the stability of the dirhodium tetracarboxylate structure demonstrated that an increase in the size of the α substituents leads primarily to an elongation of the Rh—N bond (axial ligand) and an increase in the deviation of this bond from the symmetry axis of the heterocycle passing through the nitrogen atom and the carbon atom in the *para* position. The presence of a donor solvent (MeCN) can hinder the formation of symmetrical dinuclear complexes (2-phenylpyridine) or prevent coordination of the pyridine derivative (7,8-benzoquinoline). The axial positions in the dinuclear dirhodium pivalate fragment can be used to perform transformations of the coordinated N-donors, in particular, of amines (for example, in condensation with aldehyde molecules).

Experimental

The synthesis of the complexes was performed with the use of commercial water-free solvents. The starting $Rh_2(\mu$ -OOCCMe₃)₄(H₂O)₂ complex (1) was prepared according to a known procedure.⁸ New compounds were synthesized with the use of 2,3-diaminopyridine, 2-phenylpyridine,

2,2':6',2"-terpyridine, 8-amino-2,4-dimethylquinoline, and N-phenyl-o-phenylenediamine (Fluka). Pyrrole-2,5-dialdehyde and 5-(1-phenyl-1*H*-benzimidazol-2-yl)-1*H*-pyrrole-2-carb-aldehyde were prepared according to a procedure described earlier.¹⁴ The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets.

Bis(2,3-diaminopyridino)tetra(μ_2 -pivalato)dirhodium(II) acetonitrile disolvate, Rh₂(µ-OOCCMe₃)₄((NH₂)₂C₅H₃N)₂. •2MeCN (2). Acetonitrile (10 mL) was added to a mixture of complex 1 (0.21 g, 0.32 mmol) and 2,3-diaminopyridine (0.07 mg, 0.64 mmol). The reaction mixture was stirred at 80 °C for 1 h until the reagents were completely dissolved. The solution was filtered off from the portion remained undissolved, concentrated at 0.1 Torr (20 °C) to 2 mL, cooled to -5 °C, and kept for 24 h. The red crystals that precipitated were separated by decantation, washed with cold hexane, and dried under argon. The yield of 2 · 2MeCN was 0.11 g (38% based on rhodium). Found (%): C, 44.5; H, 6.6; N, 12.1. C₃₄H₅₆N₈O₈Rh₂. Calculated (%): C, 44.84; H, 6.21; N, 12.31. IR (KBr), v/cm⁻¹: 3434 s, 2960 s, 2928 m, 2856 m, 1624 m, 1576 v.s, 1520 w, 1484 s, 1472 s, 1456 m, 1412 v.s, 1376 m, 1376 m, 1364 m, 1298 w, 1260 v.s, 1244 m, 1220 s, 1096 s, 1024 s, 925 w, 804 v.s, 748 w, 636 m, 460 m. The crystals were suitable for X-ray diffraction analysis.

Acetonitrilo(2-phenylpyridino)tetra(µ2-pivalato)dirhodium(II) acetonitrile disolvate, $Rh_2(\mu$ -OOCCMe₃)₄(C₅H₄NC₆H₅)-(MeCN) · 2MeCN (3). Complex 1 (0.1 g, 0.15 mmol) was dissolved in MeCN (10 mL) and then 2-phenylpyridine (0.05 mL, 0.3 mmol) was added. The reaction mixture was stirred at 20 °C for 5 min until the reagents were completely dissolved. The solution was filtered off from the portion remained undissolved, concentrated at 0.1 Torr (20 °C) to 2 mL, cooled to -5 °C, and kept for 24 h. The red-violet crystals that precipitated were separated by decantation, washed with cold hexane, and dried under argon. The yield of 5.2MeCN was 0.1 g (71% based on rhodium). Found (%): C, 50.4; H, 6.6; N, 6.2. C₃₇H₅₄N₄O₈Rh₂. Calculated (%): C, 50.00; H, 6.14; N, 6.31. IR (KBr), v/cm⁻¹: 3434 s, 3075 w, 2958 s, 2927 s, 2856 m, 1741 w, 1584 v.s, 1483 v.s, 1457 m, 1413 v.s, 1375 s, 1361 s, 1298 w, 1222 v.s, 1160 w, 1075 w, 1022 w, 992 w, 925 w, 894 m, 802 m, 780 m, 763 s, 745 m, 701 m, 634 s, 462 s. The crystals were suitable for X-ray diffraction analysis.

Di(7,8-benzoquinolino)tetra(µ2-pivalato)dirhodium(11), $Rh_2(\mu$ -OOCCMe₃)₄(C₁₃H₉N)₂ (4). A mixture of complex 1 (0.21 g, 0.32 mol) and benzoquinoline (0.115 g, 0.64 mmol) was dissolved in toluene (50 mL). The reaction solution was kept at 80 °C for 0.5 h, concentrated at 0.1 Torr (~60 °C) to 2 mL, and kept for one day. The green crystals that precipitated were separated by decantation, washed with cold hexane, and dried under argon. The yield of 4 was 0.29 g (93%). Found (%): C, 56.8; H, 5.3; N, 2.7. C46H54N2O8Rh2. Calculated (%): C, 57.02; H, 5.58; N, 2.89. IR (KBr), v/cm⁻¹: 3108 w, 3048 w, 3004 w, 2924 s, 2904 m, 2868 w, 1716 w, 1700 w, 1664 w, 1636 m, 1616 m, 1580 v.s, 1516 w, 1480 s, 1452 m, 1412 s, 1396 m, 1356 m, 1324 m, 1288 m, 1260 v.s, 1220 s, 1156 w, 1092 v.s, 1024 v.s, 940 w, 896 w, 876 w, 828 m, 804 v.s, 724 m, 716 w, 708 w, 660 w, 632 s, 596 w, 460 m, 440 w, 400 s. The crystals were suitable for X-ray diffraction analysis.

Bis(2,2':6',2"-terpyridino)tetra(μ_2 -pivalato)dirhodium(11), Rh₂(μ -OOCCMe₃)₄((C₅H₄N)₂C₅H₃N)₂ (5). Acetonitrile (10 mL) was added to a mixture of complex 1 (0.14 g, 0.21 mmol)



Fig. 8. Structure of complex 9.

and terpyridine (0.05 g, 0.21 mmol). The reaction mixture was stirred at 20 °C for 5 min until the reagents were completely dissolved. The solution was filtered off from the portion remained undissolved, concentrated at 0.1 Torr (20 °C) to 2 mL, and kept at room temperature for 24 h. The violet crystals that precipitated were separated by decantation, washed with cold hexane, and dried under argon. The yield of **5** was 0.09 g (39% based on rhodium). Found (%): C, 55.5; H, 5.8; N, 7.5. $C_{50}H_{58}N_6O_8Rh_2$. Calculated (%): C, 55.72; H, 5.44; N, 7.81. IR (KBr), v/cm⁻¹: 2960 s, 2928 s, 2858 m, 1664 m, 1584 v.s, 1560 s, 1484 s, 1460 m, 1412 v.s, 1372 s, 1360 m, 1298 w, 1260 w, 1220 v.s, 1156 w, 1075 w, 1022 w, 988 w, 896 m, 796 m, 768 v.s, 656 m, 632 s, 464 m.

The crystals were suitable for X-ray diffraction analysis.

Bis(η^2 -8-amino-2,4-dimethylquinolino)di(μ_2 -pivalato)dipivalatodirhodium(II), Rh₂(μ -OOCCMe₃)₄(Me₂(C₉H₄N)NH₂)₂ (6). Benzene (10 mL) was added to a mixture of complex 1 (0.1 g, 0.15 mmol) and 8-amino-2,4-dimethylquinoline (0.05 g 0.3 mol). The mixture was stirred at 20 °C for 5 min until the reagents were completely dissolved. The solution was concentrated at 0.1 Torr (20 °C) to 2 mL and kept at room temperature for 24 h. The finely-crystalline crimson compound that precipitated was separated by decantation, washed with cold hexane, and dried under argon. The yield of **6** was 0.1 g (67% based on rhodium). Found (%): C, 52.7; H, 6.2; N, 5.5. C₄₂H₆₀N₄O₈Rh₂. Calculated (%): C, 52.83; H, 6.35; N, 5.87. IR (KBr), v/cm⁻¹: 3552 m, 3476 s, 3416 v.s, 3279 w, 2964 m, 2930 m, 2866 w, 1636 m, 1616 s, 1576 w, 1548 m, 1484 m, 1456 m, 1420 m, 1396 s, 1352 m, 1260 w, 1220 m, 1092 m, 1022 w, 925 w, 802 s, 768 m, 624 s, 472 m. The crystals suitable for X-ray diffraction analysis were obtained by recrystallization from MeCN.

 $Bis(N-phenyl-o-phenylenediamino)tetra(\mu_2-piyalato)di$ rhodium(11) toluene monosolvate, Rh2(µ-OOCCMe3)4- $[N(H_2)C_6H_4N(H)Ph]_2 \cdot C_6H_5Me$ (7). A mixture of complex 1 (0.28 g, 0.43 mol) and N-phenyl-o-phenylenediamine (0.16 g, 0.86 mol) was dissolved in toluene (40 mL) under argon at 50-80 °C, concentrated to 5 mL at 50 °C (0.1 Torr), and cooled to 5 °C. Large bright-pink prismatic crystals that precipitated were separated by decantation, washed with toluene, and dried in air. The yield was 98%. Found (%): C, 58.5; H, 6.3; N, 2.9. C₅₁H₆₈N₂O₈Rh₂. Calculated (%): C, 58.74; H, 6.57; N, 2.69. IR (KBr), v/cm⁻¹: 3345 v.s, 3278 v.s, 2980 v.s, 2965 v.s, 2930 s, 2870 m, 2857 m, 1590 s, 1565 v.s, 1555 s, 1505 m, 1472 v.s, 1455 m, 1400 v.s, 1368 m, 1350 m, 1330 w, 1295 s, 1262 m, 1230 w, 1210 w, 1150 w, 1075 w, 1035 w, 954 s, 900 w, 885 m, 805 m, 725 s, 695 w, 625 s, 590 w, 570 m, 455 m, 440 m. The crystals were suitable for X-ray diffraction analysis.

Di(5-(1-phenyl-1*H*-benzimidazol-2-yl)-1*H*-pyrrole-2-carbaldehydo)-tetra(μ_2 -pivalato)dirhodium(II) benzene pentasolvate, Rh₂(μ_2 -OOCCMe₃)₄(L⁴)₂·5C₆H₆ (8) (L⁴ is 5-(1-phenyl-1*H*benzimidazol-2-yl)-1*H*-pyrrole-2-carbaldehyde). Complex 7 (0.196 g, 0.2 mol) was dissolved in benzene (50 mL) under argon and then pyrrole-2,5-dialdehyde (0.049 g, 0.4 mol) was added.

Parameter*	2 • 2MeCN	3.2MeCN	4	5	6	7 • 0.5 MeC ₆ H ₅	8 ⋅ 5C ₆ H ₆	$9 \cdot 2C_6H_4Me_2$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	Pnma	$P2_1/n$	$P\overline{1}$	C2/c	$P\overline{1}$
a/Å	10.821(3)	13.182(4)	12.317(3)	22.317(3)	17.901(6)	9.404(3)	35.844(10)	12.677(3)
b/Å	12.643(4)	16.940(5)	11.496(2)	19.501(3)	18.925(6)	12.032(3)	12.755(4)	13.669(3)
c/Å	15.817(4)	18.529(6)	15.122(3)	11.364(2)	13.411(5)	12.640(3)	22.174(6)	17.905(4)
α/deg	90			90	90	92.64(2)	90	85.940(5)
β/deg	94.268(5)	92.272(6)	91.654(5)	90	92.810(10)	107.51(2)	127.996(5)	70.917(5)
γ/deg	90			90	90	108.07(2)	90	70.917(5)
$V/Å^3$	2157.9(10)	4134(2)	2140.3(8)	4945.6(15)	4538(3)	1281.2(6)	7989(4)	2914.3(11)
Z	2	4	2	4	4	1	4	2
$\rho_{calc}/g \text{ cm}^{-3}$	1.402	1.428	1.503	1.446	1.398	1.388	1.308	1.425
μ/mm^{-1}	0.818	0.849	0.826	0.725	0.779	0.698	0.474	0.629
Radiation	liation Mo-K α ($\lambda = 0.71073$ Å)							
Number of measured reflections	25080	20141	16549	10118	15871	4838	13806	14221
Number of nonequivalent $c I > 2\sigma$	5168	7577	3017	3054	4011	4532	7698	7756
R_1	0.0477	0.0558	0.0627	0.0552	0.0702	0.0276	0.0563	0.0595
wR_2	0.1267	0.1289	0.1387	0.1239	0.1505	0.0773	0.1606	0.1268

Table 3. Crystallographic parameters of the compounds under study

* The molecular formulas: $2 \cdot 2$ MeCN, $C_{34}H_{56}N_8O_8Rh_2$; $3 \cdot 2$ MeCN, $C_{37}H_{54}N_4O_8Rh_2$; 4, $C_{46}H_{54}N_2O_8Rh_2$; 5, $C_{50}H_{58}N_6O_8Rh_2$; 6, $C_{42}H_{60}N_4O_8Rh_2$; $7 \cdot 0.5$ MeC₆H₅, $C_{51}H_{68}N_4O_8Rh_2$; $8 \cdot 5C_6H_6$, $C_{86}H_{90}N_6O_{10}Rh_2$; $9 \cdot 2C_6H_4Me_2$, $C_{60}H_{79}N_6O_{10}Rh_2$.

The reaction solution was kept at ~80 °C for 20 min. Then the dark-violet solution was concentrated to 10 mL and cooled to 20 °C. After 48 h, large red crystals were filtered off, washed with cold hexane, and dried *in vacuo*. The yield was 0.161 g (65%). Found (%): C, 56.82; H, 5.08; N, 7.14. $C_{86}H_{90}N_6O_{10}Rh_2$. Calculated (%): C, 56.76; H, 5.24; N, 7.09. IR (KBr), v/cm⁻¹: 3248 m, 2960 m, 2928 m, 2872 w, 1664 s, 1576 s, 1480 m, 1456 w, 1416 m, 1384 m, 1328 w, 1304 w, 1288 w, 1224 m, 1152 w, 896 w, 792 m, 768 m, 744 m, 688 m, 632 w, 464 w. Crystals were suitable for X-ray diffraction analysis.

 $Di(\eta^2-5-\{(E)-[(2-aminophenyl))imino]methyl\}-1H-pyrrole-$ 2-carbaldehydo)di(µ2-pivalato)dipivalatodirhodium(11), $Rh_2(OOCCMe_3)_4(NH_2-(C_6H_4)N=C(H)-C_4H_2N-CHO)_2$ (9). A solution of 5-{(*E*)-[(2-aminophenyl)imino]methyl}-1*H*-pyrrole-2-carbaldehyde (0.045 g, 0.211 mol) in chloroform (15 mL was added to Rh₂(OOCCMe₃)₄·2H₂O (0.072 g, 0.105 mol) dissolved in o-xylene (20 mL). The reaction solution was concentrated to 15 mL (40 °C, 0.1 Torr). A red crystalline product precipitated during slow evaporation of the solvent at room temperature. The mother liquor was filtered off. The crystals were washed with cold hexane and dried in vacuo. The yield was 0.109 g (88%). Found (%): C, 57.4; H, 6.4; N, 6.8. C₆₀H₇₉N₆O₁₀Rh₂. Calculated (%): C, 57.69; H, 6.25; N, 6.73. IR (KBr), v/cm⁻¹: 3440 m, 3280 m, 2952 m, 2928 m, 2864 w, 1672 s, 1608 m, 1584 s, 1536 s, 1480 m, 1456 s, 1416 w, 1392 m, 1352 m, 1264 m, 1216 m, 1168 m, 1120 m, 1088 w, 1048 w, 1008 w, 944 w, 904 w, 880 w, 840 w, 792 m, 776 m, 752 w, 672 w, 632 w, 568 w, 504 w, 456 w.

X-ray diffraction study. X-ray diffraction data sets for complexes **2–6**, **8**, and **9** were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 K, ω scanning technique with a step of 0.3°, exposure time per frame was 30 s) using a standard

procedure.¹⁵ The semiempirical absorption correction was applied.¹⁶

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms in the complexes were revealed from difference electron density syntheses and refined isotropically with a common temperature factor. All calculations were carried out using the SHELX97 program package.¹⁷

X-ray diffraction data for complex 7 were collected on an automated four-circle Siemens P3/PC diffractometer (λ (Mo-K α), $\lambda = 0.71074$ Å, T = -120 °C). The unit cell parameters were determined using 24 equivalent reflections with $2\theta < 24-28^{\circ}$. Three strong reflections with $0 < \chi < 65^{\circ}$ were used as the check reflections and were measured after each 100 reflections. For complex 7, the intensities of the check reflections showed no decrease in the course of data collection, and therefore, special corrections were not applied.

The structure of complex 7 was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were revealed from difference Fourier syntheses and refined isotropically. Selected geometric parameters of the compounds are given in Table 2. The crystallographic parameters of the compounds are listed in Table 3. Compounds 2, 4, and 6–8 have the crystallographic C_i symmetry, and compound 5 has the crystallographic C_s symmetry.

We thank S. E. Nefedov for providing us with X-ray diffraction data for compound 7.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 04-03-32883,

02-03-33075, and 00-03-40104), the Russian Academy of Sciences (Target Program for Basic Research of the Chemistry and Materials Science Division of the Russian Academy of Sciences "Chemistry and Physical Chemistry of Supramolecular Systems and Atomic Clusters"), the Presidium of the Russian Academy of Sciences (Program for Basic Research "Directed Synthesis of Compounds with Desired Properties and Construction of Functional Materials on Their Basis," the Project "Development of Procedures for the Directed Design of New Molecules and Ligands in the Inner Sphere of Mono- and Polynuclear Transition Metal Complexes"), and the Grant of the Government of Moscow ("Infrastructure and Addressed Support of Science").

References

- F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Clarendon Press, Oxford, 1993, p. 432.
- F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, J. Wiley and Sons, Inc., New York, 1999, p. 1054.
- 3. Y.-B. Koh and G. G. Christoph, *Inorg. Chem.*, 1978, 17, 2920.
- 4. F. A. Cotton and T. R. Felthouse, *Acta Crystallogr.*, 1984, C40, 42.
- M. Morooka, S. Ohba, M. Nakashima, T. Tokaii, Y. Muto, M. Kato, and O. W. Steward, *Acta Crystallogr.*, 1992, C48, 1888.
- M. Handa, M. Watanabe, D. Yosioka, S. Kawabata, R. Nukada, M. Mikuriya, H. Azuma, and K. Kasuga, *Bull. Chem. Soc. Jpn*, 1999, **72**, 2681.
- I. L. Eremenko, M. A. Golubnichaya, S. E. Nefedov, I. B. Baranovskii, I. A. Ol'tshnitskaya, O. G. Ellert, V. M. Novotortsev, L. T. Eremenko, and D. A. Nesterenko,

Zh. Neorg. Khim., 1996, **41**, 2029 [Russ. J. Inorg. Chem., 1996, **41**, 2029 (Engl. Transl.)].

- 8. F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1980, **19**, 323.
- 9. N. Hirashima, S. Nusebye, Y. Muto, and M. Kato, *Acta Chem. Scand.*, 1990, **44**, 984.
- C. J. Hawkins, Absolute Configuration of Metal Complexes, Wiley-Interscience, New York—London—Sydney—Toronto, 1971, 430 pp..
- E. V. Pakhmutova, Ph. D. (Chem.) Thesis, N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, 2003 (in Russian).
- A. A. Sidorov, I. G. Fomina, A. E. Malkov, A. V. Reshetnikov, G. G. Aleksandrov, V. M. Novotortsev, S. E. Nefedov, and I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1915 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1887].
- A. Yu. Chernyad'ev, Yu. A. Ustynyuk, G. G. Aleksandrov, A. A. Sidorov, V. M. Novotortsev, V. N. Ikorskii, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1448 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1575].
- A. Yu. Chernyad'ev, Yu. A. Ustynyuk, O. V. Yazev, E. A. Kataev, M. D. Reshetova, A. A. Sidorov, G. G. Aleksandrov, V. M. Novotortsev, V. N. Ikorskii, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2334 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2445].
- 15. SMART (Control) and SAINT (Integration) Software, Version 5.0, Bruker AXS Inc., Madison (WI), 1997.
- G. M. Sheldrick, SADABS, Program for Scanning and Correction of Area Detector Data, Göttingen University, Göttingen (Germany), 1997.
- G. M. Sheldrick, SHELX97, Program for the Solution of Crystal Structures, Göttingen University, Göttingen (Germany), 1997.

Received December 15, 2004; in revised form January 20, 2005