Available online at www.sciencedirect.com

Journal of Organometallic Chemistry 665 (2003) 156–166

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Dirhodium(II) dicarboxylato complexes containing carbonyl and C-bonded methoxycarbonyl ligands

Yuri S. Varshavsky [a],*, Tatiana G. Cherkasova [a], Ivan S. Podkorytov [b], Konstantin A. Lyssenko [c], Aleksei B. Nikol'skii [a]

[a] *Institute of Chemistry, St. Petersburg State University, Petrodvorets, Universitetskii pr., 26, 198504 St. Petersburg, Russia*
[b] *Lebedev Rubber Research Institute, Gapsalskaya Str., 1, 198035 St. Petersburg, Russia*
[c] *Nesmeyanov Institute of Organoelement Compounds, Vavilova Str., 28, 117813 Moscow, Russia*

Received 5 May 2002; accepted 27 October 2002

Abstract

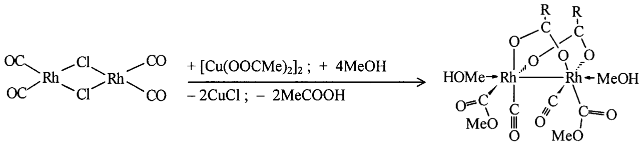
Oxidation of rhodium(I) carbonyl chloride, $[Rh(CO)_2Cl]_2$, with copper(II) acetate or isobutyrate in methanol solutions yields binuclear double carboxylato bridged rhodium(II) complexes with Rh–Rh bonds, $[Rh(\mu\text{-}OOCR\text{–}\kappa O)(COOMe\text{–}\kappa C)(CO)(MeOH)]_2$, where $R = CH_3$ or $i\text{-}C_3H_7$. According to X-ray data, surrounding of each rhodium atom in these complexes is close to octahedral and consists of another rhodium atom, two oxygens of carboxylato ligands, terminal carbonyl group, C-bonded methoxycarbonyl ligand, and axial CH_3OH. Methoxycarbonyl ligand is shown to originate from CO group of the parent $[Rh(CO)_2Cl]_2$ and OCH_3 group of solvent. N- and P-donor ligands L ($p\text{-}CH_3C_6H_4NH_2$, $P(OPh)_3$, PPh_3, PCy_3) readily replace the axial MeOH yielding $[Rh(\mu\text{-}OOCR\text{–}\kappa O)(COOMe\text{–}\kappa C)(CO)(L)]_2$. The X-ray data for the complex with $R = i\text{-}C_3H_7$, $L = PPh_3$ showed the same molecular outline as with L = MeOH. Electronic effects of axial ligands L on the spectral parameters of terminal carbonyl group are essentially the same as in the known series of rhodium(I) complexes (an increase of $\delta^{13}C$ and a decrease of $\nu(CO)$ with strengthening of σ-donor and weakening of π-acceptor ability of L).

Keywords: Rhodium(II) complexes; Carboxylates; Carbonyls; X-ray; NMR

---

1. Introduction

Carboxylato complexes of rhodium(II) remain to be paid attention for the last four decades—see reviews [1–3], recent publications [4–13], and references therein. Since the pioneer works of I. I. Chernyaev and co-workers who were the first to report on rhodium(II) carboxylates [14–16], syntheses of these complexes were performed by reduction of rhodium(III) compounds. We have recently presented [17–20] results of our attempt to obtain rhodium(II) derivatives following an opposite pathway, via oxidation of a rhodium(I) complex, binuclear rhodium(I) carbonyl chloride $[Rh(CO)_2Cl]_2$. It has turned out that interaction of rhodium(I) carbonyl chloride with copper(II) acetate in methanol occurs according to the following equation:



1

and leads to formation of the binuclear complex **1** in which rhodium(II) atoms are bound to each other by two acetate bridges and a metal-to-metal bond. The X-ray analysis [20] showed that the surrounding of each rhodium atom in structure **1** is close to octahedral and consists of another rhodium atom (Rh–Rh distance being 2.535(1) Å), two oxygens of the bridging acetate ligands, the terminal carbonyl group, the C-bonded methoxycarbonyl ligand, and the axial (i.e. located in the *trans*-position to the Rh–Rh bond) methanol molecule. Experiments with ^{13}C enriched $[Rh(CO)_2Cl]_2$ and deuterated methanol as solvent [18] evidenced that the methoxycarbonyl ligand in **1** incorporated the

---

* Corresponding author
E-mail address: yurel@peterlink.ru (Y.S. Varshavsky).

PII: S0022-328X(02)02110-1

carbonyl group from the parent rhodium(I) carbonyl chloride and the methoxy group from methanol solvent. A similar reaction proceeds in ethanol [20] yielding an analogous (but less stable) complex containing ethoxycarbonyl ligand. Thus, it can be stated that in these reactions, rhodium atom retains the both carbonyl groups bound to it in the parent carbonyl chloride, one of these groups remaining terminal, whereas the other interacts with the solvent molecule and is incorporated into the methoxycarbonyl ligand. We also revealed that N- and P-donor ligands could readily replace the axial alcohol molecules. We have isolated and characterised stable triphenylphosphine derivatives of methoxy- and ethoxycarbonyl complexes $[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOR{-}\kappa C)(CO)(PPh_3)]_2$ with $R = CH_3$ or C_2H_5. By contrast, the terminal carbonyl groups are strongly bound to rhodium(II) atoms and cannot be replaced even under action of a considerable excess triphenylphosphine.

Here we describe syntheses of isobutyrato complexes of the same type, discuss results of rhodium(I) carbonyl chloride reactions with some carboxyl containing oxidants, such as lead tetraacetate and benzoyl peroxide, and extend the range of axial ligands.

2. Experimental

2.1. Preparation of complexes

All reactions were carried out under dry Ar. Rhodium(I) carbonyl chloride $[Rh(CO)_2Cl]_2$ was prepared by published procedure [21]. ^{13}C-enriched $[Rh(CO)_2Cl]_2$ was prepared by action of ^{13}CO on $[Rh(C_2H_4)_2Cl]_2$ [22]. The analytical data are presented in Table 1.

2.1.1. $[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(MeOH)]_2$ (**1**) [20]

$[Rh(CO)_2Cl]_2$ (0.5 g, 1.29 mmol) was dissolved in dry MeOH (25 ml), and anhydrous copper(II) acetate (0.47 g, 1.3 mmol) was added under stirring. Formation of fine off-white CuCl precipitate could be observed immediately. The reaction mixture was stirred at ambient temperature until complete exhaustion of initial copper acetate (ca. 1 h). The precipitate of CuCl was then filtered off, washed with MeOH (5 ml), and the combined yellow filtrate was concentrated under a reduced pressure to a minimum volume (ca. 10 ml). The yellow crystalline precipitate formed was isolated by filtration, washed with C_6H_{14}, and dried in vacuo. Yield: 0.43 g (60%). The IR spectrum (2100–500 cm^{-1}, nujol and hexachlorobutadiene mulls): 2060, 2040, 1665, 1550, 1440sh, 1425, 1180w, 1080, 1060, 1000, 935w, 785w, 695, 660, 620w, 550w, 520w. The mother liquor was held at −10 °C overnight. The second fraction of yellow crystalline product was collected, washed with C_6H_{14}, and dried in vacuo. Yield: 0.12 g (17%).

2.1.2. $[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(p\text{-}Tln)]_2$ (**2**)

To 0.5 g (0.89 mmol) of complex **1** a solution of 0.19 g (1.78 mmol) of *p*-toluidine in diethyl ether (10 ml) was added under stirring, which afforded a yellow fine crystalline precipitate. The slurry was stirred for 1 h. Then the precipitate was isolated by filtration, washed with ether and C_6H_{14}, and dried in vacuo. Yield: 0.52 g (84%).

2.1.3. $[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(P(OPh)_3)]_2$ (**3**)

To 0.5 g (0.89 mmol) of complex **1** a solution of 0.55 g (1.78 mmol) of triphenylphosphite in diethyl ether (10 ml) was added under stirring. In 10 min the initial complex was completely dissolved to yield a yellow solution, then the solvent was removed under a reduced

Table 1
Analytical data for complexes **1**–**11**

Compound	Molecular formula	Colour	Analyses, Found (%) (Calc. (%))			
			Rh	C	H	N
1	$[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(MeOH)]_2$	Yellow	36.28 (36.61)	25.61 (25.61)	2.70 (3.56)	
2	$[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(p\text{-}Tln)]_2$	Yellow	29.16 (28.89)	41.01 (40.43)	4.39 (4.21)	4.19 (3.93)
3	$[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(P(OPh)_3)]_2$	Yellowish	18.32 (18.40)	49.18 (49.36)	3.81 (3.75)	
4	$[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(PPh_3)]_2$	Orange	19.86 (20.12)	53.64 (54.03)	4.30 (4.11)	
5	$[Rh(\mu\text{-}OOCMe{-}\kappa O)(COOMe{-}\kappa C)(CO)(PCy_3)]_2$	Orange	19.32 (19.43)	51.49 (52.17)	7.32 (7.37)	
6	$[Rh(\mu\text{-}OOC^iPr{-}\kappa O)(COOMe{-}\kappa C)(CO)(MeOH)]_2$	Yellow	33.47 (33.29)	31.37 (31.08)	4.51 (4.53)	
7	$[Rh(\mu\text{-}OOC^iPr{-}\kappa O)(COOMe{-}\kappa C)(CO)(p\text{-}Tln)]_2$	Yellow	26.77 (26.78)	43.81 (43.76)	4.92 (4.94)	4.00 (3.64)
8	$[Rh(\mu\text{-}OOC^iPr{-}\kappa O)(COOMe{-}\kappa C)(CO)(P(OPh)_3)]_2$	Yellowish	17.02 (17.52)	51.47 (51.12)	4.65 (4.26)	
9	$[Rh(\mu\text{-}OOC^iPr{-}\kappa O)(COOMe{-}\kappa C)(CO)(PPh_3)]_2$	Orange	19.18 (19.08)	55.58 (55.67)	4.52 (4.63)	
10	$[Rh(\mu\text{-}OOC^iPr{-}\kappa O)(COOMe{-}\kappa C)(CO)(PCy_3]_2$	Yellow	18.66 (18.45)	53.82 (53.86)	7.65 (7.71)	
11	$[Rh(\mu\text{-}OOCPh{-}\kappa O)(COOMe{-}\kappa C)(CO)(PPh_3)]_2$	Reddish orange		58.32 (58.65)	3.85 (4.01)	

pressure. The oily residue was rubbed with C_6H_{14} under Ar stream until yielding a yellowish fine crystalline product. The precipitate was isolated by filtration, washed with C_6H_{14}, and dried in vacuo. Yield: 0.74 g (75%).

2.1.4. *[Rh(μ-OOCMe–κO)(COOMe–κC)(CO)(PPh$_3$)]$_2$ (**4**)* [20]

To 0.5 g (0.89 mmol) of complex **1** a solution of 0.47 g (1.78 mmol) of triphenylphosphine in diethyl ether (10 ml) was added under stirring. The reaction mixture was stirred for 30 min. Then a yellowish orange crystalline precipitate was isolated by filtration, washed with ether, and dried in vacuo. Yield: 0.68 g (81%).

2.1.5. *[Rh(μ-OOCMe–κO)(COOMe–κC)(CO)(PCy$_3$)]$_2$ (**5**)*

To 0.5 g (0.89 mmol) of complex **1** a solution of 0.5 g (1.78 mmol) of tricyclohexylphosphine in diethyl ether (10 ml) was added under stirring. The reaction mixture was stirred for 30 min. Then the orange precipitate was isolated by filtration, washed with ether, and dried in vacuo. Yield: 0.54 g (78%).

2.1.6. *[Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(MeOH)]$_2$ (**6**)*

$[Rh(CO)_2Cl]_2$ (0.5 g, 1.29 mmol) was dissolved in dry MeOH (20 ml), and anhydrous copper(II) isobutyrate (0.62 g, 1.3 mmol) was added under stirring. Formation of CuCl precipitate could be observed immediately. The reaction mixture was stirred at ambient temperature for 1 h, then the precipitate of CuCl was filtered off. The yellow filtrate was concentrated under a reduced pressure to a minimum volume. The solution with a yellow crystalline precipitate was stored in a refrigerator overnight. The next day the product was isolated by filtration, washed with C_6H_{14}, and dried in vacuo. Yield: 0.48 g (60%).The IR spectrum (2100–500 cm^{-1}, nujol and hexachlorobutadiene mulls): 2064, 2046, 1672, 1638, 1553, 1428, 1316, 1175w, 1094sh, 1084, 1056, 1004, 930, 850, 788w, 766w, 716, 664w, 653, 582w, 554w, 535w. The mother liquor was then concentrated under a reduced pressure to a volume of ca. 8 ml. The second fraction of crystalline product was collected, washed with C_6H_{14}, and dried in vacuo. Yield: 0.13 g (16%).

2.1.7. *[Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(p-Tln)]$_2$ (7)*

To 0.5 g (0.8 mmol) of complex **6** a solution of 0.17 g (1.6 mmol) of *p*-toluidine in diethyl ether (10 ml) was added. Formation of a yellow precipitate could be observed immediately. The slurry was stirred for 1 h, then the precipitate was collected, washed with ether, and dried in vacuo. Yield: 0.51 g (82%).

2.1.8. *[Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(P(OPh)$_3$)]$_2$ (**8**)*

To 0.5 g (0.8 mmol) of complex **6** a solution of 0.5 g (1.6 mmol) of triphenylphosphite in diethyl ether (10 ml) was added under stirring. In 10 min the initial complex was completely dissolved to yield a yellow solution, then the solvent was removed under a reduced pressure. The oily residue was rubbed with C_6H_{14} under Ar stream until yielding a yellowish fine crystalline product. The precipitate was isolated by filtration, washed with C_6H_{14}, and dried in vacuo. Yield: 0.76 g (80%).

2.1.9. *[Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(PPh$_3$)]$_2$ (**9**)*

To a suspension of 0.5 g (0.8 mmol) of complex **6** in MeOH (2 ml) a solution of 0.42 g (1.6 mmol) of triphenylphosphine in diethyl ether (10 ml) was added under stirring. The reaction mixture was stirred for 30 min. Then a yellowish orange crystalline precipitate was isolated by filtration, washed with ether, and dried in vacuo. Yield: 0.68 g (78%).

2.1.10. *[Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(PCy$_3$]$_2$ (**10**)*

To 0.5 g (0.8 mmol) of complex **6** a solution of 0.45 g (1.6 mmol) tricyclohexylphosphine in diethyl ether (10 ml) was added under stirring. A yellow fine crystalline precipitate was formed immediately. The slurry was stirred for 30 min. Then the precipitate was isolated by filtration, washed with ether, and dried in vacuo. Yield: 0.70 g (78%).

2.1.11. *Rh(μ-OOCPh–κO)(COOMe–κC)(CO)(PPh$_3$)]$_2$ (**11**)*

$[Rh(CO)_2Cl]_2$ (0.5 g, 1.29 mmol) was dissolved in dry MeOH (15 ml), then sodium benzoate (0.37 g, 2.58 mmol) was added under stirring. A blue precipitate with a bronze lustre, presumably dibenzoatetetracarbonyl dirhodium(I), $[Rh(\mu\text{-OOCPh}-\kappa O)(CO)_2]_2$ [23], was immediately formed. To the reaction mixture a solution of 0.31 g (1.29 mmol) of benzoyl peroxide in a mixture of MeOH (3 ml) with C_6H_6 (3 ml) was added dropwise under stirring. On completion of the reaction the precipitate was fully dissolved, and the solution became orange. The IR spectrum of the solution showed intense stretching bands ν(CO) of the terminal carbonyl groups (2064, 2046 cm^{-1}) and of the carbonyl group in the methoxycarbonyl ligand (1664 cm^{-1}). The solution was filtered and concentrated under a reduced pressure to a minimum volume, then a solution of 0.68 g (2.58 mmol) of triphenylphosphine in diethyl ether (7.5 ml) was added. The solution immediately turned reddish orange, and an orange crystalline precipitate was formed. The suspension was stirred for 30 min. Then the crystalline product was isolated by filtration, washed with a little amount of MeOH, then with C_6H_6 and diethyl ether, and dried in vacuo. Yield: 1.1 g (76%). Spectral characteristics agree well with the formulation above. The IR spectrum, ν(CO): 2050, 2034, 1670 cm^{-1}. The shape of ^{31}P-NMR signal centred at 5.1 ppm is typical of rhodium(II) binuclear bisphosphine complexes. The ^{13}C-NMR spectrum of a ^{13}C-enriched preparation showed doublets at 189.2 (75.5 Hz) and 178.3 ppm (39.8 Hz).

2.1.12. The reaction of diacetatetetracarbonyl dirhodium(I), [Rh(OOCMe)(CO)$_2$]$_2$, with benzoyl peroxide

To a suspension of 0.1 g (0.23 mmol) of [Rh(OOCMe)(CO)$_2$]$_2$ [23] in MeOH (2 ml) a solution of 0.056 g (0.23 mmol) of benzoyl peroxide in a mixture of MeOH (1.5 ml) with C_6H_6 (0.5 ml) was added dropwise under stirring. The clear orange solution thus obtained was mixed with a solution of 0.12 g (0.46 mmol) of triphenylphosphine in diethyl ether (2 ml), which afforded an orange precipitate. The reaction mixture was stirred for 20 min, then the precipitate was isolated by filtration, washed with ether, and dried in vacuo. The IR spectrum of the product contained bands ν(CO) from terminal carbonyl groups with maxima at 2050 and 2034 cm^{-1}. The ^{31}P-NMR spectrum contained three signals centred at δ 5.1, 4.3, and 3.1 ppm of the shape typical for rhodium(II) binuclear carboxylato bisphosphine complexes. The relative intensity of the latter signal did not exceed 10%.

2.1.13. The reaction of [Rh(CO)$_2$Cl]$_2$ with lead tetraacetate

A solution of 0.1 g (0.23 mmol) of [Rh(CO)$_2$Cl]$_2$ in dry ethanol (5 ml) was added with stirring to 0.12 g (0.27 mmol) of Pb(OOCMe)$_4$. A fine precipitate of PbCl$_2$ was formed immediately. The reaction mixture was stirred at ambient temperature for 10 min, then the solution was filtered, and 0.12 g (0.46 mmol) of triphenylphosphine in ethyl ether (5 ml) was added to the filtrate. The solution immediately turned reddish orange, and an orange crystalline precipitate was formed. The suspension was stirred for 30 min, then the orange precipitate was isolated by filtration, washed with a small amount of MeOH and diethyl ether, and dried in vacuo. Yield: 0.2 g (76%). Spectral characteristics of the product are identical with those of product **4**.

2.2. X-ray analysis

The crystallographic data for complexes **6** and **9** are presented in Table 2. Both structures were solved by direct method and refined by full-matrix least-squares against F^2 in the anisotropic (H atoms isotropic) approximation, using SHELXTL-97 package [24]. Isopropyl group in **6** is disordered by two positions with occupancies 0.7 and 0.3. All hydrogen atoms in **6** (ordered part) and **9** were located from the electron density difference synthesis and were included in the refinement in isotropic approximation.

Table 2
Crystallographic data for complexes **6** and **9**

	6	**9**
Molecular formula	$C_{16}H_{28}O_{12}Rh_2$	$C_{50}H_{50}O_{10}P_2Rh_2$
Formula weight	618.20	1078.66
Temperature (K)	298	298
Radiation, λ(Mo–K$_\alpha$) (Å)	0.71072	0.71072
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
Colour, shape	Yellow, prism	Yellow, prism
a (Å)	14.255(4)	11.054(2)
b (Å)	18.185(6)	12.608(3)
c (Å)	10.216(3)	18.405(4)
α (°)		75.95(3)
β (°)	113.90	89.91(3)
γ (°)		76.43(3)
V (Å^3)	2421.2(13)	2414.7(9)
Z	4	2
ρ_{calc} (g cm^{-1})	1.696	1.484
Linear absorption, μ(cm^{-1})	14.16	8.06
F(000)	1240	1100
Dimension	0.30 × 0.20 × 0.15	0.40 × 0.25 × 0.20
Diffractometer	Siemens P3	Siemens P3
Scan type	$\theta/2\theta$	$\theta/2\theta$
θ Range (°)	2.39–32.57	2.23–27.98
Measured	4411	10 453
	[$R_{int}=0.0563$]	[$R_{int}=0.0416$]
Unique	4270	9859
With [$I>2\sigma(I)$]	1756	5955
Parameters	159	736
Final $R(F_{hkl})$: R_1	0.08373	0.0372
wR_2	0.2352 [a]	0.0911
Goodness-of-fit	1.012	0.986
ρ_{max}/ρ_{min} (e Å^{-3})	1.563/−0.730	0.714/−0.404

[a] The relative high value of wR_2 for complex **6** is the result of the isopropyl group disorder and, as the consequence, of the low X-ray reflectivity.

2.3. NMR and IR measurements

The ^{1}H-, ^{13}C{^{1}H}-, ^{31}P{^{1}H}-, and ^{103}Rh{^{1}H}-NMR spectra were measured on a Bruker AM-500 instrument at 500.14, 125.76, 202.46, and 15.80 MHz, respectively. The ^{1}H and ^{13}C spectra were recorded with solvents as internal standards (δ^1H of residual protons are 7.25 and 3.31 ppm in CDCl$_3$ and CD$_3$OD, respectively; δ^{13}C are 77.0 and 49.15 ppm in CDCl$_3$ and CD$_3$OD, respectively). The ^{31}P chemical shifts were measured with 85% phosphoric acid as external standard, δ^{31}P 0.0 ppm. The chemical shifts of ^{103}Rh were calculated using the directly measured resonance frequency of the studied compound and the value of $\Xi = 3.16$ MHz (the frequency of ^{103}Rh signal at 0 ppm in the field where the ^{1}H resonance of tetramethylsilane occurred at exactly 100 MHz). The IR spectra were recorded on a Specord 75 IR spectrometer.

3. Results and discussion

3.1. Molecular structure

The molecular structures of rhodium(II) isobutyrato complexes **6** and **9** with methanol and triphenylphosphine molecules as axial ligands are depicted in Figs. 1 and 2, respectively. In crystal of **6**, molecules are assembled into infinite chains (Fig. 3) by the hydrogen bonds formed by the methanol ligand and carboxylate oxygen of the adjacent molecule (O(8)···O(2′) 2.666(4) Å; H(8O)···O(2′) 1.89 Å; O(8)H(8O)O(2′) 143°).

The data indicate the molecular configurations of novel complexes to be similar with that of compound **1** [20] and to have close values of geometrical parameters. Like in the case of **1**, co-ordination of rhodium atom in **6** and **9** is *quasi*-octahedral, one vertex being occupied by another rhodium atom, and the opposite one by the axial ligand, i.e. methanol (**6**) or triphenylphosphine (**9**). *cis*-Positioned to one another in the equatorial plane are two oxygens belonging to two different bridging isobutyrate ligands and two carbons, one of them belonging to the terminal carbonyl group and the other to the carbonyl group of metoxycarbonyl ligand.

One can see that the reported compounds are structurally similar with known rhodium(II) binuclear complexes in which the rhodium atoms are bound by two carboxylate bridges. (i) Like in the case of other double-bridged carboxylato complexes [6], the two carboxylate ligands in the studied molecules have a cisoid arrangement, i.e. the angle between their planes is close to 90°. (ii) The Rh–Rh bond lengths in **1**, **6**, and **9** exceed 2.5 Å, which is typical of double-bridged carboxylato complexes ([3], p. 443, Table 7.3.1; [6,7]). For example, the Rh–Rh bond length in complex **9** is 2.622(1) Å, which is very close to the value of 2.618(5) Å

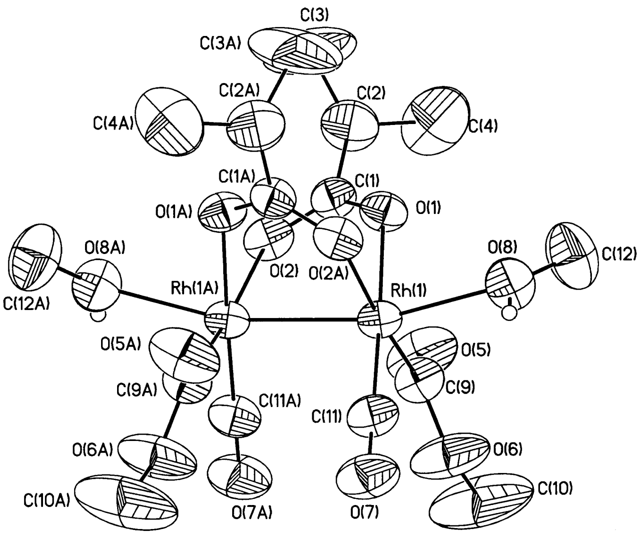


Fig. 1. The general view of [Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(MeOH)]$_2$ molecule (**6**) with the representation of atoms by thermal ellipsoids at the 40% probability level. (The disorder of C(2)C(3)C(4) moiety is omitted for clarity.) Selected bond lengths (Å) and angles (°): Rh(1)–Rh(1A) 2.535(1), Rh(1)–O(2A) 2.180(5), Rh(1)–O(1) 2.068(4), Rh(1)–O(8) 2.223(6), Rh(1)–C(9) 1.976(8), Rh(1)–C(11) 1.830(8), O(2A)–C(1A) 1.251(8), O(1A)–C(1A) 1.243(8), O(5)–C(9) 1.179(8), O(6)–C(9) 1.339(9), O(6)–C(10) 1.488(12), O(7)–C(11) 1.133(9), O(1)Rh(1)O(2A) 84.7(2), O(1)Rh(1)O(8) 86.3(2), O(2A)Rh(1)C(11) 95.9(3), C(9)Rh(1)C(11) 91.1(3), O(8)Rh(1)Rh(1A) 165.3(2), Rh(1)C(9)O(5) 126.3(6), Rh(1)C(9)O(6) 114.5(5), O(5)C(9)O(6) 119.1(7); the dihedral angle between equatorial planes, C(9)C(11)O(2A)O(1) and C(9A)C(11A)O(2)O(1A), 15.1.

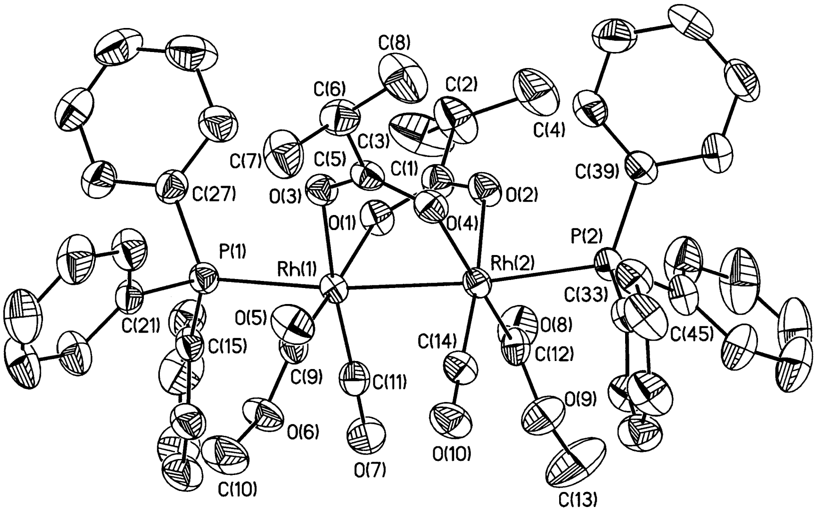


Fig. 2. The general view of [Rh(μ-OOC^{i}Pr–κO)(COOMe–κC)(CO)(PPh$_3$)]$_2$ molecule (**9**) with the representation of atoms by thermal ellipsoids at the 40% probability level. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.622(1), Rh(1)–O(1) 2.154(3), Rh(1)–O(3) 2.082(3), Rh(1)–P(1) 2.431(1), Rh(1)–C(9) 2.005(4), Rh(1)–C(11) 1.828(5), O(1)–C(1) 1.251(5), O(2)–C(1) 1.266(5), O(5)–C(9) 1.182(5), O(6)–C(9) 1.353(5), O(6)–C(10) 1.450(6), O(7)–C(11) 1.143(5), O(1)Rh(1)O(3) 87.4(1), O(1)Rh(1)C(11) 95.6(1), C(9)Rh(1)C(11) 89.1(2), P(1)Rh(1)Rh(2) 172.52(3), Rh(1)C(9)O(5) 125.3(3), Rh(1)C(9)O(6) 112.9(3), O(5)C(9)O(6) 121.8(4); the dihedral angle between equatorial planes, C(9)C(11)O(1)O(3) and C(14)C(12)O(2)O(4), 11.3.

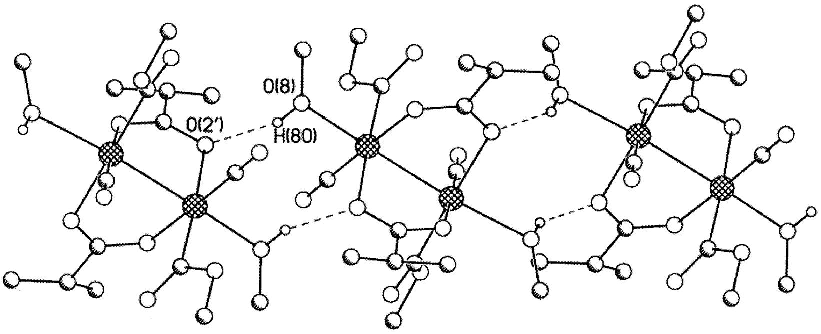


Fig. 3. Hydrogen bonding in the molecular packing of **6**.

for the double-bridged bis-dimethylglyoxymato complex with the same axial ligands, $[Rh(\mu\text{-}OOCMe{-}\kappa O)(dmg)(PPh_3)]_2$ [25]. In ‘lantern’ compounds with four carboxylate bridges these bonds are markedly shorter (2.37–2.49 Å) ([3], p. 437, Table 7.2.1); e.g. in $[Rh(\mu\text{-}OOCMe{-}\kappa O)_2(PPh_3)]_2$ molecule with the same axial ligands the Rh–Rh bond length is equal to 2.4505(2) Å [26]. (iii) The equatorial planes of coordination octahedrons in the double-bridged complexes form angles to each other (13.2, 15.1 and 11.3° for **1**, **6**, and **9**, respectively, ca. 15° for $[Rh(\mu\text{-}OOCMe{-}\kappa O)(dmg)(PPh_3)]_2$ [25], whereas in the lantern complexes they are strictly parallel. Obviously, the parallel arrangement of the equatorial planes favours interaction of axial valent orbitals of rhodium atoms and hence causes shortening and strengthening of the Rh–Rh bond. (iv) Since in the double-bridged complexes the equatorial planes are not parallel, the metal-to-axial ligand bonds that are perpendicular to these planes appear inclined to the axis of metal-to-metal bond (167.9° in **1** [20], 165.3° in **6**, 172.5° in **9**; 172–173° in $[Rh(\mu\text{-}OOCMe{-}\kappa O)(dmg)(PPh_3)]_2$ [25]). Like in the case of the dimethylglyoxymato complex, the axial ligands in the studied compounds are deflected from the Rh–Rh axis towards the carboxylate groups.

As it is generally characteristic of binuclear carboxylate rhodium(II) complexes, the Rh–Rh bond length in complexes **1**, **6**, and **9** is not markedly affected by the nature of carboxylate bridges, but is sensitive to the nature of axial ligands. Replacement of the O-donor ligand (methanol, **6**) with the P-donor one (triphenylphosphine, **9**) produces a rise from 2.535(1) Å–2.622(1) Å, like in the analogous pair of lantern complexes: (2.3855(5) Å for $[Rh(\mu\text{-}OOCMe{-}\kappa O)_2(H_2O)]_2$ [27] and 2.4505(2) Å for $[Rh(\mu\text{-}OOCMe{-}\kappa O)_2(PPh_3)]_2$ [26]).

Of interest are peculiar features of bonds between rhodium atoms and equatorial ligands in complexes **1**, **6**, and **9**.

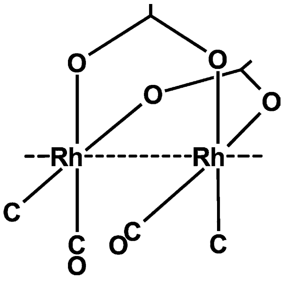
i) The bond rhodium–carbon atom of the terminal carbonyl group (1.856(4), 1.830(8) and 1.827(5) Å for **1**, **6**, and **9**, respectively) is much shorter than that in the carbonyl adduct of the lantern dirhodium tetraacetate in which CO groups occupy the axial positions (2.092(4) Å [28]). Its length is closer to the values characteristic of planar rhodium(I) complexes and octahedral rhodium(III) complexes (around 1.8 Å for $Rh(PPh_3)_2(CO)Cl$ [29]; 1.784(5) Å for rhodium(I) monocarbonyl ketoiminato complex $Rh(CH_3C(O)CHC(NH)CH_3)(PPh_3)(CO)$ [30]; 1.844(12) Å for related rhodium(III) complex $Rh(CH_3C(O)CHC(NH)CH_3)(PPh_3)(CO)(CH_3)I$ [31]). In the rhodium(III) acetyl carbonyl complex $[Rh(Acac)(COCH_3{-}\kappa C)(CO)I]_2$ the length of metal-to-carbonyl carbon bond (1.87 Å [32]) is also far from 2 Å. As it is evident from the available data [29,33,34], longer $Rh{-}(CO)_{ax}$ bonds in the lantern complexes are also much weaker in comparison with equatorial $Rh{-}(CO)_{eq}$ bonds in complexes **1**, **6**, and **9**, and with Rh–(CO) bonds in the above-mentioned rhodium(I) and rhodium(III) complexes.

ii) As it could be expected, the bond between rhodium and the sp^2-hybridised carbon of the methoxycarbonyl ligand (1.990(4), 1.976(8), and 2.005(4) Å in **1**, **6**, and **9**, respectively) is close in length to Rh–C bonds in rhodium acetyl complexes: 2.019(7) Å in $[Rh(Acac)(COCH_3{-}\kappa C)(CO)I]_2$ [32]; 1.955(14) Å in $Rh(CH_3C(O)CHC(NH)CH_3)(PPh_3)(COCH_3{-}\kappa C)I$ [35]; 1.97–2.06 Å in a number of other known complexes [36].

iii) Rhodium-to-oxygen bonds in **1** (2.177(3) and 2.073(3) Å), **6** (2.180(5) and 2.068(5) Å), and **9** (2.153(3) and 2.082(3) Å) are considerably elongated as compared with the bonds in lantern complexes (e.g. 2.029(3)–2.047(3) Å for the diaqua adduct of dirhodium tetraacetate [27] and 2.031(1)–2.056(1) Å for its triphenylphosphine adduct [26]). They should rather be compared to the corresponding bonds in complexes with two carboxylate bridges (e.g. 2.081(7) and 2.094(6) Å in the triphenylphosphine adduct of dimethylglyoxymato complex [25]). A remarkable feature of the novel compounds, **1**, **6**, and **9**, is that the bonds between metal and carboxylate oxygens in their molecules are different in length: the Rh–O bond in *trans*-position to carbon of the methoxycarbonyl ligand is considerably longer than that in *trans*-position to the carbon atom of the terminal carbonyl group.

The available X-ray data on structures of dirhodium(I) di-μ-carboxylato tetracarbonyl complexes, $[Rh(\mu\text{-}OOCR)(CO)_2)]_2$ (R = H [37], CF_3 [5]), allow comparing rhodium bondings in complexes that, being very similar in their framework, contain rhodium in different oxidation states. The common structural fragment of dirhodium(I) dicarboxylato tetracarbonyl complexes and rhodium(II) derivatives, **1**, **6**, and **9**, is presented in the Scheme 1.

In molecules of rhodium(I) complexes the rhodium–carbon bond lengths are 1.84–1.87 Å; those of rhodium–oxygen are about 2.08 Å; CRhC and ORhO angles are about 90°; the geometries of carboxylate ligands are normal for carboxylate bridges in binuclear complexes. The significant difference between dirhodium(I) and dirhodium(II) compounds is seen only in axial interactions. The first difference concerns the length of the intramolecular Rh–Rh bond. In the rhodium(I) complexes its values are 2.946(2) Å for formato complex [37] and 2.984(1)/2.994(1) Å for trifluoroacetato complex [5], which is by 0.32–0.46 Å longer than Rh–Rh bonds in **1**, **6**, and **9**. The corresponding difference can also be observed in the values of the dihedral angle between the equatorial co-ordination planes. Longer Rh–Rh bonds in rhodium(I) complexes correlate with higher values of this angle: 26.7° (formato complex) and ca. 29° (trifluoroacetato complex) versus 13.2, 15.1, and 11.3° in **1**, **6**, and **9**, respectively. Effect of the dihedral angle value on the Rh–Rh bond length is discussed in Refs. [38,39]. In the rhodium(I) cyclooctadiene formato complex, $[Rh(\mu\text{-}OOCH)(COD)]_2$, the Rh–Rh distance is 3.39 Å, and the dihedral angle is 60° [40]. In the norbornadiene acetato complex, $[Rh(\mu\text{-}OOCMe)(NBD)]_2$, the corresponding values are 3.1050(7) Å and 50.1° [39]. The second difference relates to the way of saturation of external axial capacities of rhodium atoms. In the case of rhodium(II) complexes, the saturation of axial valences (and, correspondingly, completion of the octahedral co-ordination sphere) is achieved by addition of two axial σ-donor ligands to the binuclear complex. Thus the binuclear molecules in crystals **1**, **6**, and **9** are isolated structural units with locked axial valences. In $[Rh(\mu\text{-}OOCR)(CO)_2)]_2$ crystals, rhodium atoms belonging to adjacent molecules form axial intermolecular Rh–Rh bonds whose lengths, 3.127(3) (R = H) and 3.092(1) Å (R = CF_3), only slightly exceed those of the intramolecular Rh–Rh bonds. The binuclear molecules in these crystals turn out to be units of infinite one-dimensional cluster with alternating metal-to-metal distances. An impressive example of the coexistence of $[Rh(I)]_2$ and $[Rh(II)]_2$ units in one infinite chain is presented in Ref. [4].



Scheme 1.

In view of the resemblance of equatorial surroundings of rhodium atoms in the compared complexes and geometrical similarity of their molecular frameworks, we may assume that the above differences are due to different electron configurations of central atoms, d^7 for Rh(II) and d^8 for Rh(I). In Ref. [41] it was also pointed out that the metal-to-metal bond length and strength in rhodium(I) binuclear complexes might be strongly affected by the nature of the external axial partners.

3.2. Spectral data

3.2.1. IR spectra

The most specific feature of the IR spectra of the reported compounds is the appearance of an intense absorption band with two clearly resolved maxima ($\Delta\nu \approx 14$–20 cm^{-1}) in the stretching region of the terminal carbonyl groups. The frequencies corresponding to these maxima (2014–2070 cm^{-1}) fall between the values typical of rhodium(I) and rhodium(III) monocarbonyl derivatives. A broad absorption band of stretching vibrations of >C=O group in the methoxycarbonyl ligand within the range 1640–1670 cm^{-1} agrees well with the data reported in Refs. [42,43]. We do not consider here stretching vibrations of carboxylate groups, as in the region 1400–1600 cm^{-1} a number of complicated absorption bands are superimposed.

3.2.2. NMR spectra

The ^{1}H- and ^{13}C-NMR spectral data for the studied compounds are listed in Tables 3 and 4.

In the ^{1}H spectra of acetato derivatives singlets in the region 1.7–2.1 ppm (methyl of the acetate ligand) and 3.10–3.65 ppm (methyl of the methoxycarbonyl ligand) are present. ^{1}H spectra of the isobutyrato complexes showed resonances from $CH(CH_3)_2$ groups (two close doublets at ca. 1 ppm from CH_3 groups with $^3J(HH) \approx$ 7 Hz and two septets from CH groups at 2.25–2.50 ppm with the same splitting) and singlets in the region 3.10–3.65 ppm from CH_3 groups of methoxycarbonyl ligands. Methyl proton resonances from $CH(CH_3)_2$ groups in the spectrum of each complex are separated from one another by 0.01–0.05 ppm. This indicates a slight, but reliably detectable inequivalency of methyl groups in the isobutyrate ligand. It is to be noted that the chemical

Table 3
^{1}H chemical shift values of methoxycarbonyl and carboxylato ligands in the rhodium(II) carbonyl carboxylato complexes ($CDCl_3$ as solvent)

L	[Rh(μ-$OOCCH_3$–κO)($COOCH_3$–κC)(CO)(L)]$_2$		[Rh(μ-$OOC^{i}C_3H_7$–κO)($COOCH_3$–κC)(CO)(L)]$_2$		
	$COOC\mathit{H}_3$–κC	$OOCC\mathit{H}_3$–κO	$COOC\mathit{H}_3$–κC	$C\mathit{H}(CH_3)_2$	$CH(C\mathit{H}_3)_2$
CH_3OH	3.65	2.06	3.64	2.25st [a]	1.13; 1.11
p-Tln	3.50	2.09	3.50	2.50st	1.08d; 1.07d
$P(OPh)_3$	3.41	1.72	3.38	2.27st	0.95d; 0.90d
PPh_3	3.10	1.90	3.10	2.36st	0.86d; 0.83d
PCy_3	3.56	1.93	3.55	2.45st	1.04d; 0.99d

[a] The ^{3}J(HH) coupling constant values in the multiplets (apparently septets, st) from CH protons and doublets (d) from CH_3 protons in all spectra are close to 7 Hz.

shift of methoxy protons turned out to be sensitive to the nature of the axial ligand; however with the same axial ligand, its values are almost equal for the acetato and isobutyrato complexes Spectra of *p*-toluidine complexes showed singlets from methyl protons (2.26 ppm) and from protons of the amino group (4.85 ppm, broadened). Positions of these signals appear to be insensitive to the nature of the carboxylate ligand. Complicated groups of resonances from phenyl (7.1–7.7 ppm) and cyclohexyl (1.1–2.3 ppm) protons of axial ligands are not discussed here.

^{13}C-NMR spectra contain doublets from ^{13}C nuclei directly bound to rhodium: 185.7–192.4 ppm with coupling constant ^{1}J(CRh) 72–79 Hz from carbon of the terminal carbonyl group and 175.3–181.0 ppm with coupling constant ^{1}J(CRh) 35–41 Hz from carbonyl carbon of the methoxycarbonyl ligand. In the same region, signals from the carboxylate carbons are present: 181.3–185.1 ppm for acetato and 188.6–190.4 ppm for isobutyrato complexes. In spectra of complexes with P-donor ligands these signals show a weak triplet splitting, apparently as a result of the far coupling with ^{31}P nuclei. The value of coupling constant ^{3}J(CP) ~ 6–8 Hz agrees well with the data of Ref. [44] for a lantern dirhodium tetraacetate with axial triphenylphosphite molecules. Singlets from carbon nuclei of methoxy groups in spectra of all compounds fall within the narrow interval of 52–53.5 ppm. Position of singlets from methyl carbons of the acetate group (23.4–24.2 ppm) also is almost insensitive to the nature of the axial ligand. Isobutyrate ligands showed singlets from CH groups (36.1–37.6 ppm) and pairs of singlets from slightly inequivalent ($\Delta\delta \approx 0.1$ ppm) methyl groups (19.6–20.1 ppm). (In the spectrum of methanol adduct, the inequivalence of CH_3 groups in $CH(CH_3)_2$ was not detected.) Singlets from the methyl carbons of *p*-toluidine in the spectra of compounds **2** and **7** appeared

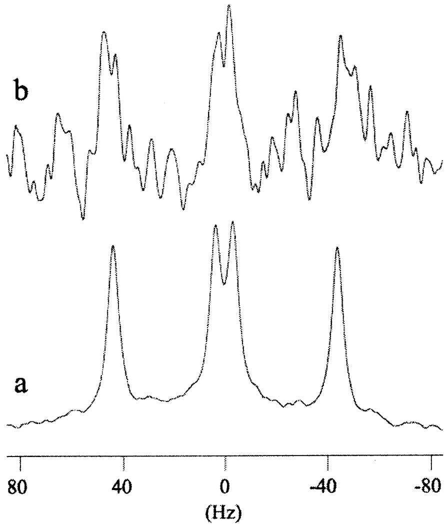


Fig. 4. The 202.5 MHz ^{31}P{^{1}H} (a) and 15.8 MHz ^{103}Rh{^{1}H} (b) NMR spectra of [Rh(μ-$OOCCH_3$–κO)($COOCH_3$–κC)(CO)(P-$(OC_6H_5)_3$)]$_2$ (**3**) demonstrating AA′XX′ spectral pattern. The ^{31}P and ^{103}Rh multiplets are centred at 89.8 and 1372 ppm, respectively.

Table 4
^{13}C chemical shift values of carbon atoms that are not directly bound to rhodium atom in the rhodium(II) carbonyl carboxylato complexes ($CDCl_3$ as solvent)

L	[Rh(μ-$OOCCH_3$–κO)($COOCH_3$–κC)(CO)(L)]$_2$			[Rh(μ-$OOC^{i}C_3H_7$–κO)($COOCH_3$–κC)(CO)(L)]$_2$			
	$COO\mathit{C}H_3$–κC	$OOC\mathit{C}H_3$–κO	$OO\mathit{C}CH_3$–κO	$COO\mathit{C}H_3$	$\mathit{C}H(CH_3)_2$	$CH(\mathit{C}H_3)_2$	$OO\mathit{C}^{i}C_3H_7$
CH_3OH	53.5	23.4	184.5	53.2	37.6	20.5	189.8
p-Tln	52.6	23.6	183.1	52.3	36.1	20.0; 19.9	188.6
$P(OPh)_3$	53.0	23.6	185.1	52.96	36.7	19.8; 19.6	190.4
PPh_3	52.3	24.2	184.7	52.2	36.7	19.7; 19.6	189.9
PCy_3	52.1	24.1	184.1	52.1	36.9	20.1; 19.8	189.6

at 20.75 ppm. ^{13}C resonances from C_6 rings are not discussed here.

With respect to ^{31}P-NMR spectra, the studied complexes turned out to be similar to complexes of lantern dirhodium tetracarboxylates with P-donor axial ligands (see Ref. [44]). The specific shape of these spectra (Fig. 4a) is usually interpreted as XX′ parts of the second order spectra of the AA′XX′ spin system of P–Rh–Rh–P chain. Fig. 4b demonstrates the ^{103}Rh-NMR spectrum of complex **3** that in the above terms corresponds to the AA′ part of the same spin system.

Selected spectroscopic characteristics of the proximal co-ordination surrounding of rhodium atom are presented in Table 5 and commented below.

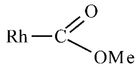
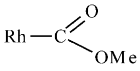
i) An attention is drawn to a pronounced difference between values of ^1J(CRh) coupling constants for the terminal carbonyl group and for the carbonyl group of the methoxycarbonyl ligand. From the commonly accepted Fermi-contact model of the spin–spin coupling [45] this difference, also typical of acetyl carbonyl rhodium(III) derivatives [32], can be interpreted as a result of different hybridisations of the carbon valent orbitals participating in the C–Rh bond: sp in the terminal carbonyl group and sp^2 in the methoxycarbonyl group.

ii) Comparison of spectral characteristics of terminal carbonyl groups in complexes with P-donor axial ligands shows that with strengthening of the σ-donor and weakening of the π-acceptor ligand properties in the row $P(OPh)_3$, PPh_3, PCy_3 frequencies of ν(CO) decrease, and chemical shifts δ^{13}C increase, which is generally observed for rhodium(I) carbonyl complexes. The values of ν(CO) and δ^{13}C for complexes with axial methanol and *p*-toluidine molecules (compounds **1**, **2**, **6**, and **7**) fall between those for complexes with triphenylphosphite and triphenylphosphine.

iii) The chemical shifts of carbonyl carbon in methoxycarbonyl group also show an increase with strengthening of the σ-donor and weakening of the π-acceptor ability of the P-donor ligands. In contrast to the terminal carbonyl carbon, this carbon atom in the complexes with axial methanol and *p*-toluidine, **1**, **2**, **6**, and **7**, is characterised by relatively high δ^{13}C values close to those of the strongest σ-donor, PCy_3. It is to be noted that the trends (ii) and (iii) are reproduced in any detail in both studied series, acetato and isobutyrato derivatives.

iv) The ^{103}Rh chemical shift in spectra of acetato complexes with P-donor axial ligands is close to 1400 ppm and rises markedly in passing to complexes with *p*-toluidine and, especially, with methanol. A similar effect of donor atoms building up the proximal surrounding of Rh(I) atom (P, N, or O) has been mentioned in literature [46]. However, our data for rhodium(II) complexes with axial PPh_3 and PCy_3 ligands indicate some decrease in δ^{103}Rh value with increase basicity of the phosphine ligand. In the case of planar rhodium(I) complexes an opposite trend has been observed [46].

Table 5
Selected spectral parameters of rhodium(II) carbonyl carboxylato complexes, $[Rh(\mu\text{-}OOCR\text{–}\kappa O)(COOMe\text{–}\kappa C)(CO)(L)]_2$ ($CDCl_3$ as solvent)

Compound			ν(CO), cm^{-1}		δ^{13}C, ppm [^{1}J(CRh), Hz]		$\delta\,^{31}$P, ppm	$\delta\,^{103}$Rh, ppm
No.	R	L	$Rh \leftarrow C \equiv O$	 $Rh\text{—}C(=O)OMe$	$Rh \leftarrow C \equiv O$	 $Rh\text{—}C(=O)OMe$		
1*	Me	MeOH	2062; 2046	1664	186.6 [74.6]**	181.0 [37.7]**	—	1995**
2	Me	p-Tln	2062; 2042	1642	185.7 [79.0]	180.1 [38.6]	—	1713
3	Me	$P(OPh)_3$	2070; 2052	1668	186.6 [73.9]	175.6 [36.9]	89.8	1372
4*	Me	PPh_3	2050; 2034	1652	189.8 [73.2]	179.5 [39.7]	3.1	1427
5	Me	PCy_3	2036; 2018	1654	192.3 [74.4]	180.6 [39.4]	17.5	1404
6	*i*-Pr	MeOH	2068; 2050	1660	186.8 [79.0]**	180.0 [39.3]**	—	***
7	*i*-Pr	p-Tln	2056; 2040	1636	186.1 [78.0]	180.2 [40.7]	—	***
8	*i*-Pr	$P(OPh)_3$	2070; 2052	1670	186.7 [72.3]	175.3 [35.3]	91.0	***
9	*i*-Pr	PPh_3	2050; 2036	1658	189.6 [74.7]	178.9 [40.0]	3.5	1407
10	*i*-Pr	PCy_3	2034; 2014	1650	192.4 [72.7]	180.5 [40.4]	17.9	1371
11	Ph	PPh_3	2050; 2034	1670	189.2 [75.5]	178.3 [39.8]	5.1	***

* See ref. [10]; ** In methanol; ***Not measured

3.3. Some related reactions

We also observed formation of complexes of this kind in reactions between rhodium(I) carbonyl chloride and some other oxidants containing carboxyl groups. For example, action of benzoyl peroxide in methanol on dibenzoatetetracarbonyl dirhodium(I), $[Rh(\mu\text{-}OOCPh)(CO)_2]_2$, obtained in situ afforded a benzoato analogue of the acetato and isobutyrato complexes described above. The reaction proceeded as follows:

$$[Rh(\mu\text{-}OOCPh)(CO)_2]_2 + (OOCPh)_2 + 4MeOH \rightarrow [Rh(\mu\text{-}OOCPh\text{–}\kappa O)(COOMe\text{–}\kappa C)(CO)(MeOH)]_2 + 2HOOCPh$$

and yielded a methanol adduct of benzoato complex with absorption maxima ν(CO) 2064 and 2046 (terminal) and 1650 cm^{-1} (methoxycarbonyl). Action of triphenylphosphine on the reaction mixture afforded a crystalline orange product (yield 75%) which, according to elemental analysis and spectral data was a benzoato analogue of the above acetato and isobutyrato complexes with axial PPh_3 ligands.

In a similar way, reaction between diacetatetetracarbonyl dirhodium(I), $[Rh(\mu\text{-}OOCMe)(CO)_2]_2$, with benzoyl peroxide in methanol with subsequent addition of triphenylphosphine produced a crystalline orange precipitate. ^{31}P-NMR spectrum of this product displayed three sets of signals centred at 5.1, 4.3, and 3.1 ppm, with the shapes typical of rhodium(II) binuclear complexes containing axial P-donor ligands [44]. The first signal corresponds by its position to the benzoate complex, **11**, while the third one, to the acetate complex, **4**. Signal with centre at 4.3 ppm seems to belong to the mixed benzoate-acetate complex of the same nature. Judging from the relative intensity of these signals, the main fraction of the rhodium(II) formed in this reaction is in the forms of the benzoate and benzoate-acetate complexes that are present in the isolated product in approximately equal amounts, whereas the amount of the acetate complex is essentially lower (around 5–8%).

Action of the stoichiometric amount of lead tetraacetate on methanol solution of rhodium(I) carbonyl chloride (Pb:Rh = 0.5) resulted in precipitation of lead(II) chloride, and the solution became orange. IR spectrum of the reaction mixture, after separation of $PbCl_2$, showed absorption bands typical of compound **1**. Addition of triphenylphosphine caused crystallisation of adduct **4** identified by IR.

4. Conclusion

We have revealed that carboxylato complexes of rhodium(II) may be synthesised not only by traditional way, i.e. by reduction of rhodium(III) derivatives, but also via oxidation of a rhodium(I) complex. Reactions of rhodium(I) carbonyl chloride, $[Rh(CO)_2Cl]_2$, with carboxyl containing oxidants, $Cu(RCOO)_2$ ($R = CH_3$, $i\text{-}C_3H_7$), $Pb(CH_3COO)_4$, $(C_6H_5COO)_2$, yield binuclear double-bridged carboxylato rhodium(II) complexes with Rh–Rh bond, $[Rh(\mu\text{-}OOCR\text{–}\kappa O)(COOMe\text{–}\kappa C)(CO)(L)]_2$ (L = MeOH, p-Tln, PCy_3, PPh_3, $P(OPh)_3$). This novel group of complexes seems to be the first example demonstrating ability of rhodium(II) to form complexes containing carbonyl group bound to rhodium atom as strongly as in the rhodium(I) and rhodium(III) derivatives. In these compounds, electronic effects of neutral ligands L on spectral parameters of the terminal carbonyl group are essentially the same as in the known series of rhodium(I) complexes: $\delta^{13}C$ increases and ν(CO) decreases with strengthening of the σ-donor and weakening of the π-acceptor ability of L.

The X-ray established molecular configurations of novel complexes with $R = i\text{-}C_3H_7$; L = MeOH, PPh_3 are similar to those of the known dirhodium(II) di-μ-carboxylato complexes. The Rh–Rh distance is sensitive to the nature of axial ligands L being longer for L = PPh_3 compared to L = MeOH. The values of Rh–Rh distances and dihedral angles between equatorial coordination planes in the new rhodium(II) complexes are lower than in the rhodium(I) derivatives with similar framework.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 183440–41 for compounds **6** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Financial support for this work from the Russian Federation Ministry of Education (grants EOO-5.0-2 and TOO-9.4-1982) is gratefully acknowledged.

References

[1] T.R. Felthouse, Progr. Inorg. Chem. 29 (1982) 73.

[2] E.B. Boyar, S.D. Robinson, Coord. Chem. Rev. 50 (1983) 109.

[3] F.A. Cotton, R.A. Walton, Multiple Bonds between Metal Atoms, 2nd ed., Oxford University Press, New York, 1993.

[4] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, J. Organomet. Chem. 596 (2000) 130.

[5] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, J. Chem. Soc. Dalton Trans. (2000) 4241.

[6] F.P. Pruchnik, P. Jakimowicz, Z. Ciunik, K. Stanislawek, L.A. Oro, C. Tejel, M.A. Ciriano, Inorg. Chem. Commun. 4 (2000) 19.

[7] F.P. Pruchnik, P. Jakimowicz, Z. Ciunik, Inorg. Chem. Commun. 4 (2000) 726.

[8] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, S.E. Stiriba, Inorg. Chem. 39 (2000) 1748.

[9] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, S.E. Stiriba, Polyhedron 19 (2000) 1829.

[10] C.S. Camposfernandez, O.Y. Xiang, K.R. Dunbar, Inorg. Chem. 39 (2000) 2432.

[11] J.M. Asara, J.S. Hess, E. Lozada, K.R. Dunbar, J. Allison, J. Am. Chem. Soc. 122 (2000) 8.

[12] F. Estevan, A. Garcia-Bernabe, S. Garcia-Granda, P. Lahuerta, E. Moreno, Ju. Perez-Prieto, M. Sanau, M.A. Ubeda, J. Chem. Soc. Dalton Trans. (1999) 3493.

[13] J. Barbera, M.A. Esteruelas, A.M. Levelut, L.A. Oro, J.L. Serrano, E. Sola, Inorg. Chem. 31 (1992) 732.

[14] (a) I.I. Chernyaev, E.V. Shenderetskaya, A.A. Koryagina, Zh. Neorg. Khim. (Russ.) 5 (1960) 1163;
(b) I.I. Chernyaev, E.V. Shenderetskaya, A.A. Koryagina, Russ. J. Inorg. Chem. 5 (1960) 559.

[15] (a) I.I. Chernyaev, E.V. Shenderetskaya, A.G. Maiorova, A.A. Koryagina, Zh. Neorg. Khim. (Russ.) 10 (1965) 537;
(b) I.I. Chernyaev, E.V. Shenderetskaya, A.G. Maiorova, A.A. Koryagina, Russ. J. Inorg. Chem. 10 (1965) 290.

[16] (a) L.A. Nazarova, I.I. Chernyaev, A.S. Morozova, Zh. Neorg. Khim. (Russ.) 10 (1965) 539;
(b) L.A. Nazarova, I.I. Chernyaev, A.S. Morozova, Russ. J. Inorg. Chem. 10 (1965) 291.

[17] Yu.S. Varshavsky, T.G. Cherkasova, Abstr. 32nd ICCC, Vancouver, 1996, 3P2.

[18] Yu.S. Varshavsky, T.G. Cherkasova, Rhodium Express 15 (1996) 13.

[19] Yu.S. Varshavsky, T.G. Cherkasova, S.E. Nefedov, I.S. Podkorytov, Abstr. 12th FECHEM Conf. Organomet. Chem., Prague, 1997, PB123.

[20] (a) Yu.S. Varshavsky, T.G. Cherkasova, S.E. Nefedov, I.S. Podkorytov, Koord. Khim. (Russ.) 25 (1999) 279;
(b) Yu.S. Varshavsky, T.G. Cherkasova, S.E. Nefedov, I.S. Podkorytov, Russ. J. Coord. Chem. 25 (1999) 260.

[21] J.A. McCleverty, G. Wilkinson, Inorg. Synth. 8 (1966) 211.

[22] R. Cramer, Inorg. Chem. 1 (1962) 722.

[23] D.N. Lawson, G. Wilkinson, J. Chem. Soc. (1965) 1900.

[24] G.M. Scheldrick, SHELXTL NT V.5.10, Madison, Bruker AXS, Inc. 1999.

[25] J. Halpern, E. Kimura, J. Molin-Case, C.S. Wong, J. Chem. Soc. Chem. Commun. (1971) 1207.

[26] G.G. Christoph, J. Halpern, G.P. Khare, Y.B. Koh, C. Romanovski, Inorg. Chem. 20 (1981) 3029.

[27] F.A. Cotton, B.G. Deboer, M.D. LaPrade, J.R. Pipal, D.A. Ucko, Acta Crystallogr., Sect. B 27 (1971) 1664.

[28] G.G. Christoph, Y.B. Koh, J. Am. Chem. Soc. 101 (1979) 1422.

[29] G. Kemp, A. Roodt, W. Purcell, Rhodium Express 12 (1995) 21.

[30] L.J. Damoense, W. Purcell, A. Roodt, J.G. Leipoldt, Rhodium Express 5 (1994) 10.

[31] A. Roodt, private communication.

[32] Yu.S. Varshavsky, T.G. Cherkasova, Yu. Struchkov, A.S. Batsanov, L.S. Bresler, N.N. Marasanova, Koord. Khim. (Russ.) 14 (1988) 1105.

[33] R.S. Drago, S.P. Tanner, P.M. Richman, J.R. Long, J. Am. Chem. Soc. 101 (1979) 2892.

[34] R.B. King, A.D. King, M.Z. Iqbal, J. Am. Chem. Soc. 101 (1979) 4893.

[35] L.J. Damoense, W. Purcell, A. Roodt, Rhodium Express 14 (1995) 4.

[36] (a) G.W. Adamson, J.J. Daly, D. Forster, J. Organomet. Chem. 71 (1974) C17;
(b) M.A. Bennett, J.C. Jeffery, G.B. Robertson, Inorg. Chem. 20 (1981) 323.

[37] Yu.S. Varshavsky, T.G. Cherkasova, A.A. Korlyukov, I.S. Podkorytov, A.B. Nikol'skii, Abstr. 20th International Chugaev Conference on Co-ordination Chemistry, Rostov-on-Don, 2001, p. 160.

[38] A.L. Balch, B. Tulyathan, Inorg. Chem. 16 (1977) 2840.

[39] A.H. Reis, C. Willi, S. Siegel, B. Tani, Inorg. Chem. 18 (1979) 1859.

[40] R. Fornika, E. Dinjus, H. Görls, W. Leitner, J. Organomet. Chem. 511 (1996) 145.

[41] J.J. Novoa, G. Aullón, P. Alemany, S. Alvarez, J. Am. Chem. Soc. 117 (1995) 7169.

[42] W. Keim, J. Becker, A.M. Trzeciak, J. Organomet. Chem. 372 (1989) 447.

[43] D. Milstein, W.C. Fultz, J.C. Calabrese, J. Am. Chem. Soc. 108 (1986) 1336.

[44] E.B. Boyar, S.D. Robinson, J. Chem. Soc. Dalton Trans. (1985) 629.

[45] J.N. Murrell, Progr. NMR Spectrosc. 6 (1971) 1.

[46] R. Bonnaire, D. Davoust, N. Platzer, Org. Magn. Reson. 22 (1984) 80.