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Rh(I) Carbonyl Carboxylato Complexes: Spectral and Structural Characteristics. Some Reactions of Coordinated Formate Group

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Abstract—Complexes $[Rh(\mu\text{-}RCOO)(CO)_2]_2$, where R = H, CH_3, CF_3 (**I**, **II**, **III**, respectively) are synthesized by reacting anhydrous carboxylic acids with $Rh(Acac)(CO)_2$ crystals. In compounds **I**, **II**, **III**, and *trans*-$Rh(RCOO)(PPh_3)_2(CO)$, where R = H, CH_3, CF_3 (**IV**, **V**, **VI**, respectively), ν(CO) and ^1J(CRh) increase and δ^{13}C decreases with the increasing electronegativity of R (CH_3 < H < CF_3). In the case complexes **IV**, **V**, and **VI**, the values of δ^{31}P and ^1J(PRh) decrease in the same order. Complexes **I** and **V** are studied by X-ray diffraction analysis. Intramolecular (2.946 Å) and intermolecular (3.127 Å) Rh–Rh distances in a columnar structure **I** are close, i.e., the structure contains infinite chains of metal atoms. Interaction of **IV** with chlorinated solvents results in *trans*-$RhCl(PPh_3)_2(CO)$. When heated with an excess of PPh_3 in propanol-2, compound **IV** transforms to $HRh(PPh_3)_3(CO)$. The latter reaction was suggested as a basis of a new method that can be used to obtain $HRh(PPh_3)_3(CO)$.

Dirhodium(I) di(μ-carboxylato) tetracarbonyls $[Rh(\mu\text{-}RCOO)(CO)_2]_2$ were obtained for the first time by reacting rhodium(I) carbonyl chloride dimer $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with silver carboxylates [1]. The authors [1] synthesized and characterized acetate, trifluoroacetate, *p*-fluorobenzoate, and phthalate complexes of this type and some bis(phosphine) derivatives, such as *trans*-$Rh(RCOO)(PPh_3)_2(CO)$. Later, some other methods were developed for synthesizing $[Rh(\mu\text{-}RCOO)(CO)_2]_2$ complexes with R = CH_3 (**II**), CF_3 (**III**) [2–4] and their monocarbonyl triphenylphosphine derivatives *trans*-$Rh(RCOO)(PPh_3)_2(CO)$ [2, 5–12]. The authors of [4] reported the results of X-ray diffraction study of $[Rh(\mu\text{-}CF_3COO)(CO)_2]_2$. The structure of *trans*-$Rh(CF_3COO)(PPh_3)_2(CO)$ was previously determined in [13].

Rhodium(I) formate complexes became available considerably later. Thus, the carbonyl formate dimer $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ (**I**) was synthesized for the first time via a reaction of dirhodium(II) tetraacetate with carbon monoxide in formic acid [14]. Some other methods of synthesis of this compound were reported later on in [15, 16]. A series of bis(phosphine) complexes *trans*-$Rh(HCOO)(PR_3)_2(CO)$ was also synthesized [17–19]. The molecular structure of *trans*-$Rh(HCOO)(PPh_3)_2(CO)$ (**IV**) was determined by X-ray diffraction method [17]. It should be noted that in subsequent years, rhodium(I) formate complexes with carbonyl and some other π-acceptor ligands (olefins, phosphines) were studied more intensively than other carboxylate derivatives. This is quite natural, since formate group is a C_1 ligand with composite structure and high reactivity.

It is noteworthy that though separate IR and NMR parameters of Rh(I) carbonyl carboxylate complexes were reported in some of the above-mentioned papers, their comparison is difficult, since they were determined under different conditions.

In this work, simple reaction is suggested that can be used to synthesize $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ complex and its crystal structure is determined. The latter complex is shown to be suitable starting reagent in synthesis of Rh(I) carbonyl hydride $HRh(PPh_3)_3(CO)$. X-ray diffraction data available in the literature for bis(triphenylphosphine) complexes of the composition *trans*-$Rh(RCOO)(PPh_3)_2(CO)$ with R = H, CF_3 [13, 17] are supplemented with the data we obtained for analogous acetate complex. IR and NMR measurements of carbonyl formate complexes $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ and of *trans*-$Rh(HCOO)(PPh_3)_2(CO)$ together with their acetate and trifluoroacetate analogs made it possible to obtain for the first time a set of comparable spectral parameters that indicates a transfer of electronic effects of the ligands through a central atom. The results of this work were partially reported in the previous publications [20–22].

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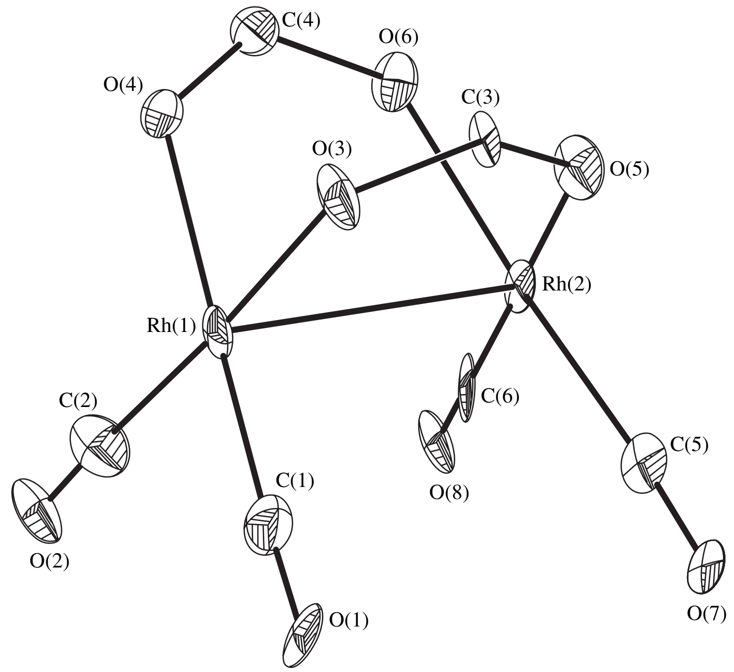


Fig. 1. The molecular structure of $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ (thermal ellipsoids correspond to 50% probability; hydrogen atoms are not shown).

RESULTS AND DISCUSSION

Synthesis of dirhodium(I) di-μ-carboxylato tetracarbonyls. Acetylacetonate ligand in $Rh(Acac)(CO)_2$ complex can be easily replaced with another anionic ligands. In particular, it is readily detached when treated with protic acids. The authors [2] used this reaction in synthesis of dicarbonyl complexes $[Rh(\mu\text{-}RCOO)(CO)_2]_2$ with fluorinated carboxylate groups, R = CF_3 and $i\text{-}C_3F_7$:

$$2Rh(Acac)(CO)_2 + 2RCOOH \longrightarrow [Rh(\mu\text{-}RCOO)(CO)_2]_2 + 2HAcac.$$

We modified the procedure described in [2] and obtained also the derivatives of nonfluorinated acids with R = H and CH_3. When crystalline $Rh(Acac)(CO)_2$ was treated with anhydrous carboxylic acids in the presence of diethyl ether, complexes **I–III** were obtained in the form of needle-shaped crystals with a bronze luster. The products were isolated from a reaction mixture in a high yield and did not require further purification.

The reaction completeness depends on the carboxylic acid strength. In accordance with the values of pK_a (4.75, 3.75, 0.23 for R = CH_3, H, CF_3, respectively [23]), the reaction of complex **III** formation proceeds almost completely and instantaneously, while in the case of complexes **I** and **II**, this substitution reaction is reversible, which requires that liberated acetylacetone be removed from the reaction mixture by repeated decantation and further addition of a fresh portions of formic or acetic acid.

Molecular and crystal structure of $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ (I). According to a preliminary study, compound **I** forms twin crystals unsuitable for X-ray diffraction measurements. Nevertheless, we managed to obtain, in a general form, the molecular and crystal parameters of structure **I**, though *R*-factor was very large, and thus the bond lengths and angles obtained should be considered as approximate ones.

The molecular structure of **I** is shown in Fig. 1. The bond lengths and bond angles in the nearest surrounding of Rh atoms are as follows: Rh(1)–Rh(2) 2.946(2), Rh(1)–C(1) 1.87(2), Rh(1)–C(2) 1.87(2), Rh(1)–O(3) 2.089(16), Rh(1)–O(4) 2.088(15), C(1)–O(1) 1.09(3), C(2)–O(2) 1.05(3) Å; C(1)Rh(1)C(2) 88.9(11)°, C(1)Rh(1)O(3) 93.2(9)°, C(1)Rh(1)O(4) 178.8(9)°, C(1)Rh(1)Rh(2) 98.0(7)°, O(3)Rh(1)O(4) 85.7(6)°, Rh(1)C(1)O(1) 178(2)°, Rh(1)C(2)O(2) 178(2)°. One can see that structure of **I** is very close to that of its trifluoroacetate analog [4]. In terms of a general configuration and geometric parameters of the bridging carboxylate groups, molecule **I** is also similar to molecules of Rh(I) binuclear carboxylate complexes, such as $[Rh(\mu\text{-}HCOO)(Cod)]_2$ (Cod is cyclooctadiene-1,5) [16], $[Rh(\mu\text{-}CF_3COO)(Cod)]_2$ [4], and $[Rh(\mu\text{-}CH_3COO)(Nbd)]_2$ (Nbd is norbornadiene) [24]. The Rh–C and C–O bond lengths characterizing carbonyl groups are close to the corresponding values in another Rh(I) complexes with the $Rh(CO)_2$ fragment, both binuclear and mononuclear complexes, for example, $[Rh(\mu\text{-}Cl)(CO)_2]_2$ [25], $RhAcac(CO)_2$ [26], etc. Note that intramolecular Rh–Rh distances in carbonyl complexes are shorter than the respective distances in their olefin analogs: 2.946(2) Å for $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ and 2.984(1)/2.994(1) Å for $[Rh(\mu\text{-}CF_3COO)(CO)_2]_2$ [4] as compared to 3.39 Å (without a standard deviation) in $[Rh(\mu\text{-}HCOO)(Cod)]_2$ [16], 3.4844(6) Å in $[Rh(\mu\text{-}CF_3COO)(Cod)]_2$ [4], and 3.1050(7) Å in $[Rh(\mu\text{-}CH_3COO)(Nbd)]_2$ [24].

The authors of [24] discussed the ratio of the Rh–Rh distances (r) and dihedral angle (θ) formed by coordination planes of the Rh atoms in binuclear Rh(I) complexes. It is not surprising that in a binuclear complex with chloride bridges, namely, $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (according to data in [20], $\theta \approx 123°$), the value of r (3.133(2) Å) is larger than that in the molecules of both investigated carboxylate analogs, where coordination planes of the Rh atoms form considerably smaller angle with one another (26.7° and 2.946 Å for formate complex; ~29° and 2.984/2.994 Å for trifluoroacetate complex).

It is interesting to establish a relationship between r and θ in a series of Rh binuclear carboxylate complexes, including both Rh(I) and Rh(II) complexes. If the differences in the Rh–O distances and internal geometric parameters of carboxyl groups (the C–O bond lengths and OCO bond angles) are considered unessential, then, in the first approximation, the values of r and $\sin(\theta/2)$ are expected to show a linear dependence. Data available in the literature [27–34] confirm this expectation (Fig. 2). One can see that the observed relationship has "isle" nature. It is natural to assign the gap between the first and second sets of points (with Rh(II) complexes in both sets) and between the third and fourth sets (with Rh(I) complexes in the latter sets) to geometric factors; the gap between the second and third sets of points is mainly determined by different electronic configuration of a central atom (d^7 and d^8, respectively). Previously [32], we briefly touched upon this question.

In line with the data obtained, intramolecular distance Rh–Rh in $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ crystal (2.946 Å) is only slightly shorter than intermolecular distance (3.127 Å), i.e., this crystal contains infinite chains of the metal atoms; an average value of RhRhRh angle being 170.49(10)° (Fig. 3). In this respect, the compound under study is similar to its trifluoroacetate analog (2.989, 3.092 Å, respectively) [4]. This fact is likely to be an answer to the question put by the authors of [4]: the presence of fluorinated substituent in carboxylate group is not a necessary condition for realization of a chain structural motif. Although Rh–Rh distances determined in [35] are considered too long for the metal–metal interaction to be treated as a valent interaction, the metal luster of $[Rh(\mu\text{-}RCOO)(CO)_2]_2$ crystals suggests a considerable delocalization of electrons along the metal atom chain.

Bis(triphenylphosphine) complexes *trans*-$Rh(RCOO)(PPh_3)_2(CO)$. Acetate and some other carboxylate bis(triphenylphosphine) carbonyl complexes of the composition *trans*-$Rh(RCOO)(PPh_3)_2(CO)$ were reported long ago [1, 2, 5–12]. The formate complex *trans*-$Rh(HCOO)(PPh_3)_2(CO)$ was obtained for the first time and characterized significantly later [15]. We synthesized bis(triphenylphosphine) complexes *trans*-$Rh(HCOO)(PPh_3)_2(CO)$ (**IV**), *trans*-$Rh(CH_3COO)(PPh_3)_2(CO)$ (**V**), and *trans*-$Rh(CF_3COO)(PPh_3)_2(CO)$ (**VI**) by reacting triphenylphosphine with binuclear complexes $[Rh(\mu\text{-}RCOO)(CO)_2]_2$ (taken in a molar ratio $PPh_3 : Rh = 2$) in propanol-2 at room temperature.

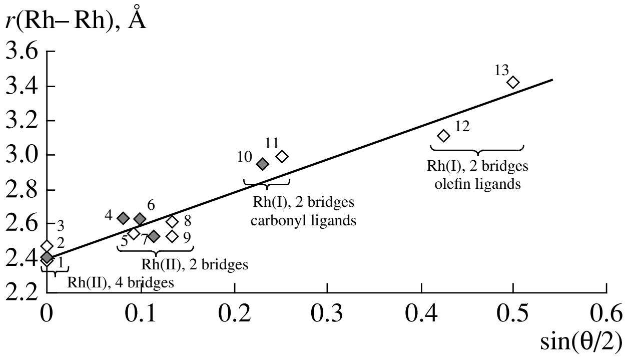


Fig. 2. Correlation of intramolecular Rh–Rh distance with dihedral angle between equatorial coordination planes of Rh atoms in binuclear carboxylate complexes of Rh(I) and Rh(II) (correlation factor 0.971; $r = 2.4026 + 1.9049\sin(\theta/2)$; ◆ our data; ◇ data in the literature: (1) $Rh_2(CH_3COO)_4(H_2O)_2$ [27]; (2) $[Rh_2(CH_3COO)_4Cl_2][(CH_3)_2NH]_2$ [28]; (3) $Rh_2(CH_3COO)_4(P(OCH_3)_3)_2$ [29]; (4) $[Rh_2(CF_3CONH)_2(Phen)_2Py_2][PF_6]_2$ (Phen is phenanthroline) [3]; (5) $[Rh_2(CH_3COO)_2(Phen)_2Py_2][PF_6]_2$ [30]; (6) $Rh_2(i\text{-}C_3H_7COO)_2(COOCH_3)_2(CO)_2(PPh_3)_2$ [31]; (7) $Rh_2(CH_3COO)_2(COOCH_3)_2(CO)_2(CH_3OH)_2$ [32]; (8) $Rh_2(CH_3COO)_2(Dmg)_2(PPh_3)_2$ (Dmg is dimethylglyoxime) [33]; (9) $Rh_2(i\text{-}C_3H_7COO)_2(COOCH_3)_2(CO)_2(CH_3OH)_2$ [31]; (10) $Rh_2(HCOO)_2(CO)_4$ [in this work]; (11) $Rh_2(CF_3COO)_2(CO)_4$ [4]; (12) $Rh_2(CH_3COO)_2(Nbd)_2$ [23]; (13) $Rh_2(HCOO)_2(Cod)_2$ [16].

The data we obtained for the molecular structure of complex **V** (Fig. 4) agree well with those for formate (**IV**) [17] and trifluoroacetate (**VI**) [13] analogs. The bond lengths and bond angles in the nearest surrounding of Rh atoms in molecular structure of compound **V** are: Rh(1)–C(3) 1.812(4), Rh(1)–O(1) 2.084(2), Rh(1)–P(1) 2.3352(11), Rh(1)–P(2) 2.3147(11), C(3)–O(3) 1.149(4) Å; C(3)Rh(1)P(1) 89.61(12)°, C(3)Rh(1)P(2) 92.16(12)°, C(3)Rh(1)O(1) 174.03(13)°, P(1)Rh(1)P(2) 169.62(3)°, O(1)Rh(1)P(1) 91.42(7)°, O(1)Rh(1)P(2) 87.88(8)°, Rh(1)C(3)O(3) 173.8(3)°.

All the three compounds are mononuclear tetracoordinated complexes. It was noted in [13] that almost orthogonal arrangement of a plane of carboxylate group with respect to that of coordination tetragon and a relatively short contact (~3.34 Å) between the Rh atom and noncoordinated carboxylate oxygen favor nonvalent interaction $Rh \longleftarrow O{=}C$ in *trans*-$Rh(CF_3COO)(PPh_3)_2(CO)$ crystal. Such an interaction is likely to occur also in crystal **V**, where the dihedral

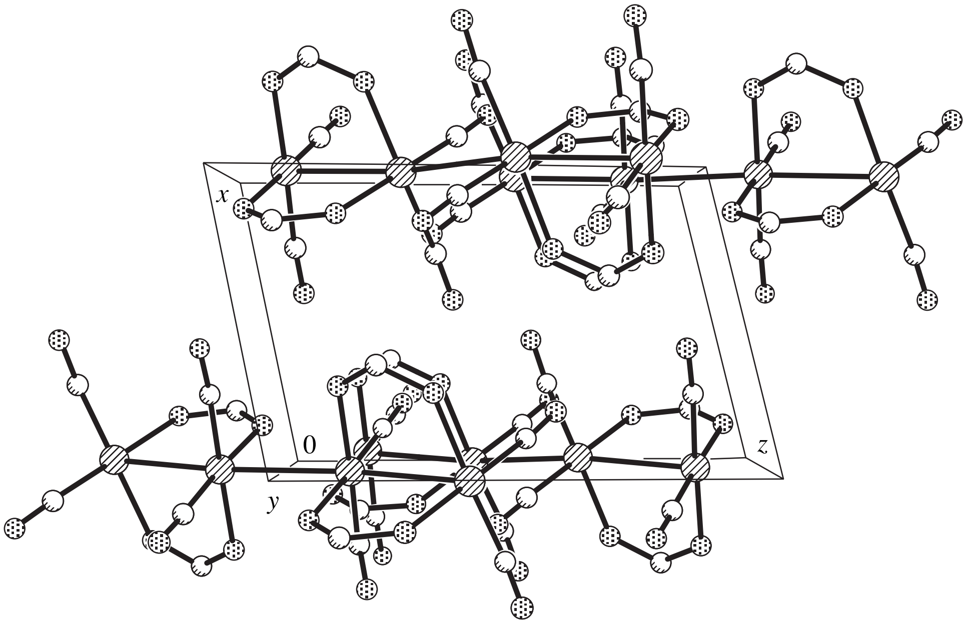


Fig. 3. The packing of molecules in $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ crystal (**I**).

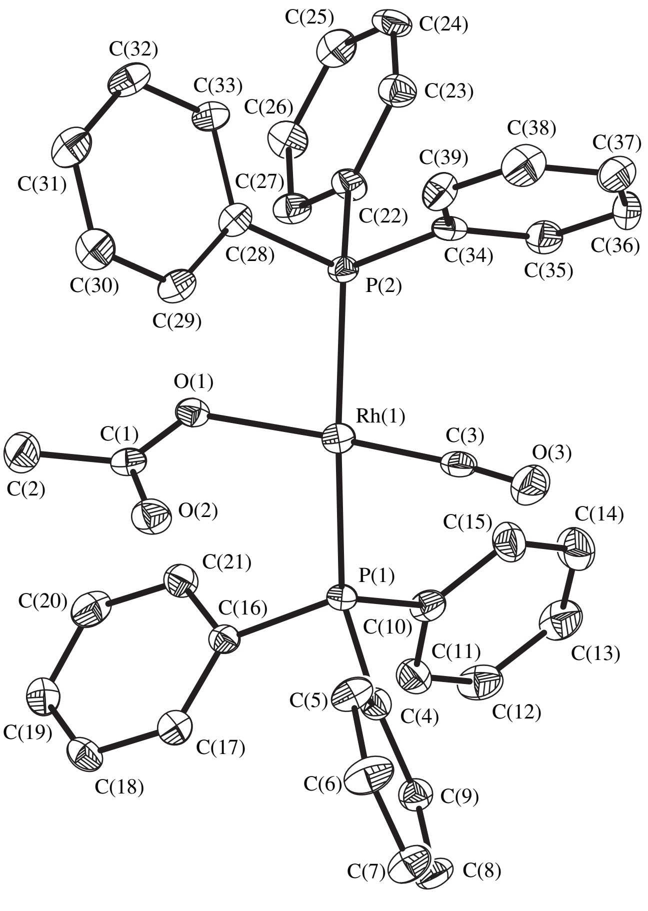


Fig. 4. The molecular structure of $Rh(CH_3COO)(PPh_3)_2(CO)$ (**V**) (thermal ellipsoids correspond to 50% probability; hydrogen atoms are not shown).

angle between the OCO plane of acetate ligand and coordination plane of the Rh atom is 107.3° and the Rh···O(=C) distance is equal to ~2.9 Å.

Spectral characteristics of carbonyl carboxylate complexes. Parameters of IR and NMR spectra of carboxylate complexes are given in Table 1. Although many spectral parameters of compounds **I**–**VI** were previously reported in the above-mentioned papers, we decided to measure them again and to obtain the same set of parameters suitable for comparison for the whole group of compounds. IR spectra of solutions of binuclear complexes contain three absorption bands in the range of stretching vibrations of carbonyl group. Three maxima ν(CO) are observed also for the other complexes, whose molecules contain two $Rh(CO)_2$ fragments bonded to one another, and are due to interaction of vibrations of these fragments [36, 37].

The ^{13}C NMR parameters of compounds **I**, **II**, and **III** lie in the region typical of Rh(I) complexes containing $Rh(CO)_2$ fragments [38, 39]. The transition to bis(phosphine) derivatives is usually attended by a decrease in the ν(CO) values and by an increase in the $\delta^{13}C$ chemical shift.

Data in Table 1 reveal correlation between the spectral characteristics of carboxylate complexes and electronegativity of radical R in the carboxylic acid anion. As electronegativity of R increases in a series CH_3, H, CF_3, the frequency of stretching vibrations of carbonyl groups is increased, while the $\delta^{13}C$ chemical shift is decreased and the $^1J(CRh)$ values are increased both in compounds containing dicarbonyl fragments (**I**–**III**) and in monocarabonyl bis(phosphine) complexes (**IV**–**VI**). In compounds **IV**–**VI**, the highest frequency ν(CO) (trifluoroacetate complex) corresponds to the

Table 1. Spectral parameters of Rh(I) carbonyl carboxylate complexes (in $CHCl_3$)

Compound	ν(CO), cm^{-1}	$\delta^{13}C$ (Rh CO), ppm (^1J(CRh); ^2J(CRhP), Hz)	$\delta^{31}P$, ppm (^1J(PRh), Hz)	δ^1H, ppm	$\delta^{19}F$, ppm
$[Rh(\mu\text{-}HCOO)(CO)_2]_2$ (**I**)	2104, 2082, 2030	181.18 (73.7)		8.01*	
$[Rh(\mu\text{-}CH_3COO)(CO)_2]_2$ (**II**)	2102, 2078, 2028	181.86 (73.7)		2.02	
$[Rh(\mu\text{-}CF_3COO)(CO)_2]_2$ (**III**)	2116, 2096, 2048	179.37 (75.9)			–77.54
trans-$Rh(HCOO)(PPh_3)_2(CO)$ (**IV**)	1980	189.93 (69.5, 16.9)	31.61 (134.8)	7.08	
		191.68 (68.6, 16.9)**	32.08 (136.1)**	7.78**	
trans-$Rh(CH_3COO)(PPh_3)_2(CO)$ (**V**)	1975	190.12 (68.7, 16.9)	32.82 (137.9)	0.76	
		192.07 (67.8, 16.9)**	32.98 (138.6)**	1.22**	
trans-$Rh(CF_3COO)(PPh_3)_2(CO)$ (**VI**)	1984	189.56 (71.2, 16.9)	31.19 (132.2)		–78.53
		191.25 (71.2, 16.1)**	31.53 (132.2)**		

* t., ^3J(HCORh), 2.9 Hz.
** In C_6D_6.

shortest C–O bond length in carbonyl group: 1.138(6) [13] as compared to 1.150(5) Å in formate [17] and 1.149(4) Å in acetate (in this work) analogs.

The effect of substituent CF_3 on the spectral parameters of carbonyl groups in Rh(I) complexes was observed previously in both carboxylate [1, 5, 8] and in β-diketo and β-ketoimino complexes [40–42]. The ^{31}P NMR data also turned sensitive to the electronic effect of substituent in carboxylate group: as its electronegativity increases, $\delta^{31}P$ and ^1J(PRh) decrease. As it is always observed, the ν(CO) values in IR spectra of triphenylphosphine complexes **IV**–**VI** are considerably higher than those in the spectra of analogous complexes with aliphatic phosphines PCy_3 (Cy is cyclohexyl), P*i*-Pr_3 [15, 18, 19, 43, 44].

The above bis(phosphine) complexes **IV**–**VI** are the final products of interaction of complexes **I**–**III** with triphenylphosphine taken at a molar ratio $PPh_3 : Rh = 2$. The authors of [9] studied the spectra of reaction mixtures $Rh_2(\mu\text{-}RCOO)_2(CO)_4 + PPh_3$ at lower PPh_3 : Rh ratios and observed the formation of some products with intermediate composition. One of them, i.e., the acetate complex $Rh_2(\mu\text{-}CH_3COO)_2(PPh_3)(CO)_3$, was isolated and characterized. In paper [45], $[Rh(\mu\text{-}CH_3COO)(PPh_3)(CO)]_2$ complex was also studied. In addition to data in [9, 45], we measured the ^1H, ^{13}C, and ^{31}P NMR spectra of reaction mixtures $[Rh(\mu\text{-}CH_3COO)(CO)_2]_2 + PPh_3$ in chloroform at a molar ratio $PPh_3 : Rh = 1$ and determined the spectral parameters of these complexes (see in experimental section)

Some reactions of formate ligand in complex, *trans*-$Rh(HCOO)(PPh_3)_2(CO)$ (IV). Formate ligand in bis(phosphine) complex **IV**, *trans*-$Rh(HCOO)(PPh_3)_2(CO)$ can enter some reactions that almost quantitatively transform **IV** to nonformate derivatives of Rh(I).

Reactions with chlorinated solvents. Formation of *trans*-$RhCl(PPh_3)_2(CO)$. When measuring NMR spectra of complex **IV** in $CDCl_3$, we discovered that the carbonyl region of the ^{13}C spectrum contains, in addition to a signal of the studied compound (doublet of triplets, Table 1), one more signal of the same form and comparable intensity. The ^{31}P spectrum of solution of **IV** also exhibits an intense additional signal (doublet). The parameters of these signals, $\delta^{13}C$ and $\delta^{31}P$, ^1J(CRh), ^1J(PRh), and ^2J(CP) coincide with parameters of the known complex, namely, $RhCl(PPh_3)_2(CO)$. Yellow crystals of individual compound with the same spectral parameters are separated from a solution of complex **IV** in methylene chloride. A complete conversion of formate complex into chloride complex occurs on heating (40°C) of a solution of **IV** in CH_2Cl_2 for 2 h; the reaction is attended by liberation of CO_2. The reaction product was identified as *trans*-$RhCl(PPh_3)_2(CO)$ on the basis of comparison of its IR and NMR spectra with the spectra of a sample synthesized according to the procedure described in [46].

Crystallographic characteristics of the isolated compound agree well with the data for orthorhombic modification of *trans*-$RhCl(PPh_3)_2(CO) \cdot 2CH_2Cl_2$ [47]. The transformation of formate complex to chloride complex is likely to occur through oxidative addition of methylene chloride to complex **IV** and formation of unstable Rh(III) complex $Rh(HCOO)(PPh_3)_2(CO)(CH_2Cl)Cl$ that is further transformed with elimination of CO_2 (and, presumably, CH_3Cl) to *trans*-$RhCl(PPh_3)_2(CO)$. The ability of Rh(I) complexes to enter such type of reactions with chlorinated solvents was noted in [48].

Reaction with triphenylphosphine. Formation of $HRh(PPh_3)_3(CO)$. When heated with excess triphenylphosphine in propanol-2, compound **IV** gives the known complex $HRh(PPh_3)_3(CO)$ (**VII**) in a high yield. The reaction occurs at a high rate and results in complex **VII** that precipitates as well formed lustrous mustard-colored crystals. The comparison of IR and NMR (^1H, ^{13}C, and ^{31}P) spectra of the obtained compound with those of $HRh(PPh_3)_3(CO)$ synthesized following the procedure [49] and the results of elemental analysis confirm its identification. The reaction is attended by liberation of CO_2 (1 mol per g-atom of rhodium):

$$Rh(HCOO)(PPh_3)_2(CO) + PPh_3 \longrightarrow HRh(PPh_3)_3(CO) + CO_2.$$

Experiment with deuterated complex **IV** $Rh(DCOO)(PPh_3)_2(CO)$ gives deuterated analog of complex **VII**, namely, $DRh(CO)(PPh_3)_3$. This fact implies that formate group of the starting complex **IV** serves the source of hydride ligand in complex **VII**. This reaction is a new and remarkable example of transformations $RhL_n(HCOO) \longrightarrow HRhL_n + CO_2$ described in [16, 50]. The possible mechanisms of these reactions and of reversible reactions of CO_2 introduction at a metal–hydrogen bond were extensively discussed in the literature [16, 18, 50–55].

We also found that complex **VII** can be obtained directly from **I**, without the stage of complex **IV** isolation. Taking into account a high yield and an adequate quality of the product obtained in this way, we believe that this reaction can be used as an alternative method in synthesis of $HRh(PPh_3)_3(CO)$. It should be noted that insignificant amount of hydride complex **VII** formed as a byproduct was also observed by us in reaction of complex **I** with triphenylphosphine (P : Rh > 2) in methanol, diethyl ether, or toluene.

Transformations of [Rh(μ-HCOO)(CO)$_2$]$_2$ heated in propanol-2. On heating a suspension of $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ in propanol-2, a solution of dark brown color is formed and a small amount of brown precipitate. After the precipitate is treated with chloroform, the known cluster $Rh_6(CO)_{16}$ can be extracted that was identified from IR spectrum in [56]. IR spectra of the filtrate contain intense absorption bands with composite profile that are typical of polynuclear Rh carbonyl clusters: 2040–2060 cm^{-1} (terminal carbonyl groups) and 1840–1880 cm^{-1} (bridging carbonyl groups). Judging from the positions and shapes of these bands, the solutions contain anionic polynuclear clusters whose composition depends on the heating time (from 5 min to 7 h). It is worthwhile noting that IR spectra of filtrates always contain absorption band with a sharp maximum at 1716 cm^{-1} that can be assigned to acetone, i.e., the product of propanol-2 oxidation. The solutions are stable when stored in an inert atmosphere, but when their IR spectra are recorded once again, they show some changes in positions of the bands due to absorption of carbonyl groups; the indicated changes are likely to occur as a result of partial loss of CO. When these solutions are treated with CO, their IR spectra acquire the initial form. The preliminary measurements of the ^{13}C and ^{1}H NMR spectra indicate that solutions contain anionic polynuclear clusters. The addition of salts of large cations, for example, $(PPh_3)_2NCl$, PPh_4Cl, to the reaction mixtures gives precipitates of brown color readily soluble in acetonitrile and acetone (presumably salts of anionic clusters). IR spectra of solutions of these precipitates (with CH_3CN solvent) contain the absorption bands due to carbonyl groups in the range of 1990–2030 and 1800–1880 cm^{-1}. The solutions are unstable; even when kept in an inert atmosphere, the absorption bands due to terminal carbonyl groups gradually shift toward low frequencies. One can assume that in these experiments, we observed the formation of anionic polynuclear clusters similar to those previously described by the authors [57], who studied the reducing carbonylation of Rh(III) chloride and Rh(I) carbonyl chloride on silica gel surface.

EXPERIMENTAL

All reactions were carried out in dried solvents, in the atmosphere of dry argon, using common Schlenk technique (synthesis of compounds **I–III** do not require an inert atmosphere). $Rh(Acac)(CO)_2$ was obtained by procedure [58]. Samples of complexes for measuring the ^{13}C NMR spectra were obtained from enriched $Rh(Acac)(CO)_2$ preparation, which was prepared by bubbling ^{13}CO (76.6% ^{13}C) through a suspension of $Rh(Acac)(C_2H_4)_2$ [59] in hexane. Samples of $RhCl(PPh_3)_2(^{13}CO)$ and $HRh(PPh_3)_3(^{13}CO)$ were prepared following the known procedures [39] and [49], respectively. Triphenylphosphine was recrystallized from ethanol

The ^{1}H, ^{13}C, ^{31}P, and ^{19}F spectra were measured on a Bruker AM-500 spectrometer at 500, 125, 202, and 470 MHz, respectively. An internal standard in the ^{1}H and ^{13}C spectra was a solvent ($\delta^{1}H$ of the residual protons in $CDCl_3$, C_6D_6, and $CD_3C_6D_5$ were 7.25, 7.16, and 2.09 ppm, respectively; $\delta^{13}C$ for $CDCl_3$ 77.0 ppm, for C_6D_6 128.69 ppm). The ^{31}P chemical shifts were referenced to 85% orthophosphoric acid used as an external standard, $\delta^{31}P$ 0.0 ppm. The ^{19}F chemical shifts were referenced to $CFCl_3$, $\delta^{19}F$ 0.0 ppm. IR spectra (nujol mulls, solutions in $CHCl_3$) were recorded on a Specord 75 IR spectrometer.

X-ray diffraction analysis. The main experimental parameters and crystallographic data are listed in Table 2. All diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, φ and ω scan mode) with SMART program [60]. The obtained three series of frames, corresponding to half sphere of reciprocal space, were processed with SAINT-*Plus* program [60] and averaged with SADABS program [60]. The structures were solved by direct methods and refined by full-matrix anisotropic-isotropic approximation on F^2. Hydrogen atoms were calculated geometrically and refined in a rigid body model with $U(H) = 1.5U_{eq}(C)$, where C and H are carbon and hydrogen atoms. All calculations were performed with SHELXTL-*Plus* program package [61].

As was mentioned above, the discrepancy factors R_1 and wR_2 obtained in refinement of structure **I** are very high because of insufficient quality of the crystals used.

Table 2. Crystallographic parameters and details of data collection and refinement of structures **I** and **V**

Parameter	Value	
	I	**V**
M	407.90	714.50
Temperature, K	110(2)	110(2)
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size, mm	0.4 × 0.3 × 0.1	0.4 × 0.2 × 0.2
a, Å	6.7185(19)	10.829(3)
b, Å	7.604(2)	12.629(4)
c, Å	10.307(3)	12.659(4)
α, deg.	96.710(5)	86.239(7)
β, deg.	100.963(6)	80.412(7)
γ, deg.	102.294(6)	73.116(6)
V, Å^3	498.3(2)	1633.3(8)
Z	2	2
ρ(calcd.), g/cm^3	2.719	1.453
μ_{Mo}, cm^{-1}	49.24	6.58
F(000)	454	732
Range of 2θ, deg	4.08–51.36	4.42–60.08
Total number of reflections	3505	13649
Number of unique reflections (R_{int})	1735 ($R_{int} = 0.499$)	9346 ($R_{int} = 0.499$)
Number of reflections with $I > 2\sigma(I)$	1308	5947
Number of refined parameters	145	538
R_1 (for reflections with $I > 2\sigma(I)$)	0.1245	0.0591
wR_2 (for all reflections)	0.3154	0.1208
GOOF	2.155	1.055
ρ_{max}/ρ_{min} (eÅ^{-3})	8.529/–4.614	1.956/–1.120

X-ray diffraction study of the product of reaction between Rh(HCOO)(PPh$_3$)$_2$(CO) and CH$_2$Cl$_2$ was performed using the same experimental parameters as in the case of **I** and **V**. The analysis of difference Fourier syntheses showed that in the structure of RhCl(PPh$_3$)$_2$(CO) formed, the Cl atom and carbonyl group at the Rh atom overlap. The refinement of populations of two positions linked by the inversion center gave the ratio 1 : 1. The discrepancy factors: R_1 (for reflections with $I > 2\sigma(I)$) 0.0526, wR_2 (for all reflections) 0.1329; GOOF 1.062.

[Rh(μ-HCOO)(CO)$_2$]$_2$. Anhydrous formic acid (1.5 ml) was added to a suspension of Rh(Acac)(CO)$_2$ (0.5 g, 1.94 mmol) in diethyl ether (1.5 ml). Needle-shaped brown crystals with a bronze luster precipitated. The reaction mixture was stirred for 30 min. The solution was decanted, and another portion of formic acid (0.7 ml) was added to the residue and stirred for another 15 min until the crystals of the initial complex with characteristic red-green dichroism disappeared completely.

The product was filtered, washed with ether, and dried in vacuum. The yield was 0.39 g (83%).

The completeness of transformation was confirmed by the absence of the band due to acetylacetonate ligand at 1530 cm^{-1} in IR spectrum of the product sample dissolved in CHCl$_3$. The spectral data (IR and NMR) agree well with the data of [14, 16]. For C$_3$HO$_4$Rh anal. calcd. (%): C, 17.67. Found (%): C, 17.69.

[Rh(μ-CH$_3$COO)(CO)$_2$]$_2$. Glacial acetic acid (2 ml) was added to a suspension of Rh(Acac)(CO)$_2$ (0.5 g, 1.94 mmol) in diethyl ether (2 ml), which was followed by precipitation of needle-shaped brown crystals with a bronze luster. The reaction mixture was stirred for 1 h, the solution was decanted, and another portion of acetic acid (7 ml) was added; the mixture was stirred for another 15 min until the crystal of the initial complex disappeared completely. The precipitate was filtered, washed with ether, and dried in vacuum. The yield was 0.33 g (79%). The completeness of reaction was confirmed as described above. IR spectrum of the compound is consistent with the data in [1, 14].

For $C_4H_3O_4Rh$
anal. calcd. (%): C, 22.04; H, 1.10.
Found (%): C, 22.10; H, 1.00.

[Rh(μ-CF$_3$COO)(CO)$_2$]$_2$. To a suspension of Rh(Acac)(CO)$_2$ (0.5 g, 1.94 mmol) in diethyl ether (1 ml), trifluoroacetic acid (0.8 ml) was added, and the precipitation of needle-shaped brown crystals with a bronze luster was observed. The reaction mixture was stirred for 10 min. The precipitate was filtered, washed with ether, and dried in vacuum. The yield was 0.47 g (89%). IR spectrum of the product agrees well with the data of [1, 2, 4]. For $C_4O_4F_3Rh$ anal. calcd. (%): C, 17.66. Found (%): C, 17.99.

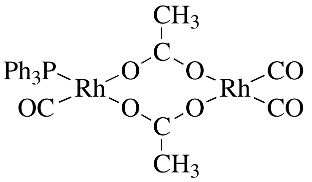
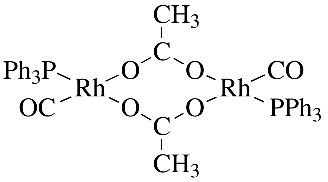
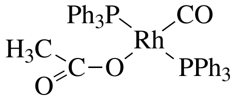
***trans*-Rh(HCOO)(PPh$_3$)$_2$(CO).** [Rh(μ-HCOO)(CO)$_2$]$_2$ (0.1 g, 0.245 mmol) and PPh$_3$ (0.26 g, 0.99 mmol) were placed in a reaction vessel, and propanol-2 (3.5 ml) was added. The suspension was stirred for 1 h. The precipitated crystalline product of a yellow color was filtered and washed with ether. The yield was 0.27 g (83%). The spectral data of the product (IR and NMR) are consistent with the data in [15, 17].

For $C_{38}H_{31}O_3P_2Rh$
anal. calcd. (%): C, 65.15; H, 4.42.
Found (%): C, 64.65; H, 4.42.

***trans*-Rh(CH$_3$COO)(PPh$_3$)$_2$(CO).** [Rh(μ-CH$_3$COO)(CO)$_2$]$_2$ (0.1 g, 0.229 mmol) and triphenylphosphine (0.24 g, 0.92 mmol) were placed in a reaction vessel, and propanol-2 (3.5 ml) was added. The suspension obtained was stirred for 1 h. The precipitated crystalline product of a yellow color was filtered and washed with ether. The yield was 0.26 g (80%). The spectral parameters (IR and NMR) agree well with those in [5, 7, 9, 12].

For $C_{39}H_{33}O_3P_2Rh$
anal. calcd. (%): C, 65.55; H, 4.62; Rh, 14.40.
Found (%): C, 65.43; H, 4.80; Rh, 14.41.

Reaction of [Rh(μ-CH$_3$COO)(CO)$_2$]$_2$ with PPh$_3$ at PPh$_3$: Rh = 1. [Rh(μ-CH$_3$COO)(CO)$_2$]$_2$ (0.057 g, 0.132 mmol) was placed in a reaction vessel and a solution of PPh$_3$ (0.069 g, 0.264 mmol) in CHCl$_3$ (4 ml) was added. The obtained yellow solution was evaporated at a reduced pressure to dryness. The residue was dissolved in CDCl$_3$ (2 ml) and used in the ^{1}H, ^{13}C, and ^{31}P NMR measurements. The parameters of the signals observed and their assignment to the reaction products are shown below.

Compound	δ^{13}C, ppm (^1J(CRh), ^2J(CP), Hz)	δ^{31}P, ppm (^1J(PRh), Hz)	δ^1H, ppm
 (Y$_1$)	183.4 (73.7) d. 187.0 (75.4, 22.1) d.d.	50.4 (175.5) d.	1.05 2.08
 (Y$_2$)	188.4 (75.4, 22.9) d.d.	48.8 (180.6) d.	1.41
 (X$_2$)	190.1 (~69) broad	32.8 (137.6) d.	0.87

The above assignment of the ^{13}C and ^{31}P signals is based on the comparison of their relative intensities and was performed taking into account data in [45, 62, 63] for the analogous complexes occurring in the reaction mixtures [Rh(μ-Cl)(CO)$_2$]$_2$ + PPh$_3$. A sharp doublet at 183.4 ppm in the ^{13}C spectrum of the obtained mixture of the products is assigned to dicarbonyl fragment in composition Y_1; doublets of doublets with higher $\delta^{13}C$ belong to monocarbonyl fragments in composition Y_1 and Y_2. Broadening of signal at 190.1 ppm corresponding to complex **V** is likely to be explained by some exchange processes in a solution. Of the two δ^1H values in Y_1 spectrum, a lower value was presumably assigned to a methyl group in *syn*-position to PPh_3.

***trans*-Rh(CF$_3$COO)(PPh$_3$)$_2$(CO).** A mixture of $[Rh(\mu\text{-}CF_3COO)(CO)_2]_2$ (0.1 g, 0.184 mmol) and triphenylphosphine (0.19 g, 0.74 mmol) was placed in a reaction vessel and propanol-2 (3.5 ml) was added. The suspension was stirred for 30 min. The obtained crystalline product of a yellow color was filtered and washed with ether. The product yield was 0.23 g (82%). IR spectrum of the compound is consistent with data in [6, 8].

For $C_{39}H_{30}O_3P_2F_3Rh$

anal. calcd. (%):	C, 60.95,	H, 3.90.
Found (%):	C, 60.69,	H, 3.97.

HRh(PPh$_3$)$_3$(CO). 1. Synthesis from $[Rh(\mu\text{-}HCOO)(CO)_2]_2$. A mixture of $[Rh(\mu\text{-}HCOO)(CO)_2]_2$ (0.1 g, 0.245 mmol) and triphenylphosphine (0.64 g, 2.44 mmol) was placed in a reaction vessel, and propanol-2 (13 ml) was added. The precipitate of a yellow color formed. The reaction vessel was placed in a water bath preliminarily heated to 90°C. The mixture was refluxed for 30 min. The precipitate dissolved during the first minutes, and a yellow solution formed, from which crystals of the final product precipitated immediately. The reaction was accompanied by a release of CO_2. The reaction mixture was cooled to room temperature, and mustard-colored crystals were filtered, washed with ether, and dried in vacuum. The product yield was 0.40 g (89%). Titration with baryta water showed that one mol of CO_2 per one g-atom of Rh is released in the reaction. IR spectrum (essential oil mulls, cm^{-1}): ν(RhH) 2042, ν(CO) 1926; NMR (toluene-d_8): δ^1H 9.36 ppm; $^2J(HP)$ 14.1 Hz; ^{31}P 40.8 ppm, 1 $^1J(PRh)$ 154.5 Hz.

For $C_{55}H_{46}OP_3Rh$

anal. calcd. (%):	C, 71.89;	H, 5.01.
Found (%):	C, 72.29;	H, 5.08.

2. Synthesis from *trans*-Rh(HCOO)(PPh$_3$)$_2$(CO). *trans*-Rh(HCOO)(PPh$_3$)$_2$(CO) (0.172 g, 0.245 mmol) and triphenylphosphine (0.167 g, 0.61 mmol) were placed in a reaction vessel and propanol-2 (7 mol) was added. The reaction vessel was placed in a water bath preliminarily heated to 90°C. The reaction mixture was refluxed for 30 min. Crystals of the final product formed rapidly. The reaction was accompanied by liberation of CO_2. The mixture was cooled to room temperature, and mustard-colored crystals were filtered, washed with ether and dried in vacuum. The yield was 0.20 g (89%). In terms of the spectral parameters, the product is identical to a complex produced from $[Rh(\mu\text{-}HCOO)(CO)_2]_2$.

3. DRh(PPh$_3$)$_3$(CO). In synthesis of DRh(PPh$_3$)$_3$(CO), use was made of deuterated preparation of formate complex, namely, $Rh(\mu\text{-}DCOO)(CO)_2$ obtained according to the above procedure with the use of DCOOH (enriched by 99%). IR spectrum (nujol mulls): ν(CO) 1945 cm^{-1}, ν(RhD)—the band is overlapped by triphenylphosphine absorption. NMR (toluene-d_8): δ^2D 9.32 ppm; $\delta^{31}P$ 40.8 ppm, $^1J(PRh)$ 155.2 Hz.

4. Reaction of *trans*-Rh(HCOO)(PPh$_3$)$_2$(CO) with methylene chloride. Compound **IV** (0.25 g) was dissolved in CH_2Cl_2 (10 ml) and the obtained suspension was refluxed at 40°C for 2 h. Then, the precipitate was filtered, washed with diethyl ether, and dried in vacuum. The yield was 0.20 g. IR and NMR spectra (in chloroform) of the product (ν(CO) 1978 cm^{-1}, $\delta^{13}C$ 187.2 ppm, $^1J(CRh)$ 73.7 Hz, $^2J(CP)$ 16.1 Hz; $\delta^{31}P$ 29.2 ppm, $^1J(PRh)$ 125.9 Hz) coincide with those of *trans*-RhCl(PPh$_3$)$_2$(CO) sample synthesized by the known procedure [46]. The integrated intensity of the band ν(CO) in IR spectrum of a solution of the reaction product almost equals the intensity of this band in the spectrum of a standard sample. Crystallographic characteristics of the crystals of compounds chosen from mother liquor (space group *Pbca*, orthorhombic cell with unit cell parameters a = 23.074(5) Å, b = 7.8978(16) Å, c = 20.272(4) Å) satisfactorily agree with the literature data for orthorhombic modification of *trans*-RhCl(PPh$_3$)$_2$(CO) · 2CH$_2$Cl$_2$ [47]. The ^{31}P NMR spectrum of a filtrate, obtained after separation of RhCl(PPh$_3$)$_2$(CO), does not contain a signal from the starting *trans*-Rh(HCOO)(PPh$_3$)$_2$(CO), but has a doublet from *trans*-RhCl(PPh$_3$)$_2$(CO) and a singlet at 29.25 ppm from triphenylphosphine oxide. The transformation of formate complex to chloride complex occurs also at room temperature, but in this case, the reaction is complete in 2 days.

Rh(I) formate complexes are of great interest for researchers due to extensive development of chemistry of C_1 ligands. In this work, we suggested a suitable procedure of synthesizing $[Rh(\mu\text{-}HCOO)(CO)_2]_2$, characterized the crystal and molecular structures of this complex, and described some reactions of its triphenylphosphine derivative *trans*-Rh(HCOO)(PPh$_3$)$_2$(CO) occurring with destruction of formate ligand and release of CO_2. One of these reactions was suggested as the basis of a new and efficient method of synthesizing carbonyl hydride complex HRh(PPh$_3$)$_3$(CO).

X-ray diffraction and spectral (IR and NMR) data we obtained made it possible to systematize characteristics of Rh(I) carbonyl carboxylate complexes $[Rh(\mu\text{-}RCOO)(CO)_2]_2$ and *trans*-Rh(RCOO)(PPh$_3$)$_2$(CO) (R = H, CH_3, CF_3) and to compare the structural and spectral parameters of formate complexes with the corresponding parameters of their analogs.

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