

Remarks on the process of homogeneous carbonylation of rhodium compounds by *N,N*-dimethylformamide

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Abstract

Reductive carbonylation of rhodium(III) chloride complexes, commercial $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ neutralized with BaCO_3 , $(\text{Me}_2\text{NH}_2)_2\text{[RhCl}_5(\text{DMF})]$, $(\text{PPh}_4)\text{[RhCl}_4(\text{H}_2\text{O})_2]$, $\text{RhCl}_3(\text{DMF})_3$, $\text{RhCl}_3(\text{CH}_3\text{CN})_3$, $\text{RhCl}_3(\text{CH}_3\text{CN})_2(\text{DMF})$, $[\text{Rh}(\text{CO})_2\text{Cl}_2]_2$, and rhodium(I) complex, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, by *N,N*-dimethylformamide (DMF) is studied. The data obtained support the conception of direct carbonyl group transfer from DMF molecule to the Rh metal center. The mechanistic scheme of carbonylation process is refined and discussed with regard of new experimental results.

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1. Introduction

Reductive carbonylation of platinum metal halides on heating their solutions in alcohols has been discovered in 1960s. Specifically for rhodium compounds, this reaction has been described in several papers [1–6]. In 1965 Rusina and Vlček [7] revealed that *N,N*-dimethylformamide (DMF) is also a powerful agent for reductive carbonylation of rhodium(III) chloride. In all these works carbonylation was carried out in the presence of stabilizing ligand, usually triphenylphosphine, to prevent excess reduction and metal black deposition. Soon after Rusina and Vlček publication, we attempted to heat rhodium(III) chloride solution in DMF without any stabilizing ligand and obtained a clear yellow solution containing rhodium in the form of the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anion. Consecutive addition of acetylacetone and water to the reaction mixture resulted in the precipitation of

known complex, $\text{Rh}(\text{Acac})(\text{CO})_2$, in good yield [8]. In our further communications [9–13] we reported syntheses of a variety of analogous dicarbonyl rhodium(I) complexes with bidentate monoanionic ligands and salts of the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anion. Within the following four decades this method has gained wide acceptance and has become a routine laboratory practice (see for example [14–26]) and a subject of industrially oriented studies [27]. The mechanistic scheme we suggested [28,29] involved direct carbonyl group transfer from a DMF molecule to a rhodium atom. The recent publications [30,31] contributed some new facts and ideas to this chemistry and brought forward another mechanistic conception based on the HCl-mediated decarbonylation of DMF and subsequent carbonylation of rhodium by free carbon monoxide. We considered briefly this alternative and presented our new data concerning carbonylation of several individual rhodium(III) complexes in the report [32]. The revival of interest in these problems prompted us to verify and extend our old experimental studies, to prove our mechanistic conception, and to publish it in a more widely available edition.

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2. Results and discussion

2.1. Can the excess acid be crucial in the carbonylation of rhodium(III) chloride by DMF?

In our reasoning on the mechanism of rhodium carbonylation [28,29] we proceeded from the model of the direct carbonyl group transfer from the coordinated DMF molecule to the metal center. Such an idea, more or less detailed, was accepted in a number of publications which reported and discussed reactions of this kind [33,34]. In the works [30,31] quite a different conception was articulated. Placing strong emphasis on the fact that commercial samples of the hydrated rhodium(III) chloride contain excess HCl the authors [30,31] considered the well known reaction



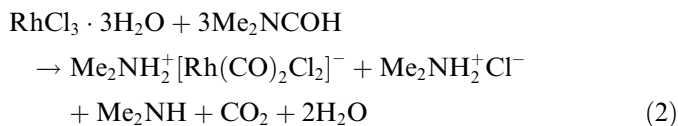
as a source of free carbon monoxide which reacts with rhodium chloride as the actual carbonylating and reducing agent. Our data presented in Table 1 make it possible to compare the carbonylation rates of several forms of rhodium(III) chloride in the presence of excess HCl (commercial preparation of rhodium(III) chloride), and without excess HCl (solution of commercial chloride pretreated with the base, “aged” $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{DMF}$ solution, and $\text{RhCl}_3(\text{DMF})_3$ complex).

As can be seen, the DMF/ H_2O solution of the commercial rhodium(III) chloride is very acidic containing a large amount of excessive hydrochloric acid. The $\text{RhCl}_3(\text{DMF})_3$ solution is less acidic, and its acidity should be ascribed to the deprotonation of water molecules in aqua complexes formed in the DMF/ H_2O solutions used for the pH measurements. A drastic decrease of acidity after BaCO_3 pretreatment seems to be resulted from neutralization of not only extra acid, but also of a part of the acidity caused by the deprotonation of the coordinated water molecules. Inspection of the data presented in Table 1 evidences clearly that in the less acidic conditions the rate of carbonylation of rhodium(III) chloride by DMF increases markedly. Thus, we can conclude that even though reaction (1) may proceed under typical rhodium carbonylation conditions, it does not make a significant contribution to the overall process of the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ formation. That is why we discuss below a scheme based on the direct abstraction of the carbonyl group from the coordinated DMF molecule by the metal center, like this proceeds in carbonylation reactions of some other metal complexes [33,34].

2.2. Discussion of the carbonylation process

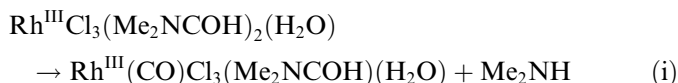
2.2.1. The stoichiometry and the key stages

In our previous works [28,29] we formulated the overall stoichiometry of rhodium carbonylation with the equation

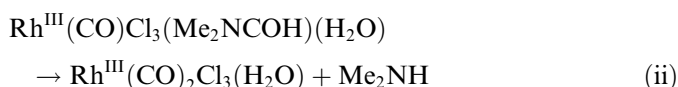


The qualitative description of the evolution of the IR spectra at heating $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{DMF}$ reaction mixture given in the works [30,31] is in conformity with our data [28,29] and so confirms the successive formation of rhodium(III) monocarbonyl intermediate species with one $\nu(\text{CO})$ band at 2094 (2092 [31]) cm^{-1} and rhodium(I) dicarbonyl species with two $\nu(\text{CO})$ bands, at 2065 and 1985 (2063 and 1984 [31]) cm^{-1} . Potentiometric titration of samples taken from the solution in the course of reaction confirmed that there were no rhodium(I) species but the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ anion; formation of 1 mol CO_2 per 1 mol $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ was detected by barite water titration [28]. Below we discuss the key stages of the carbonylation mechanism which we believe to be consistent with the body of the experimental data available up to date. Certainly the number of ligands DMF, Cl^- , and H_2O can vary in the rhodium(III) octahedral complexes presented actually in the reaction mixture as is evident from our work [35] and from mass spectral data given in [31]; below we choose arbitrarily the formulae which allow clearer visualization of the total reaction pathway.

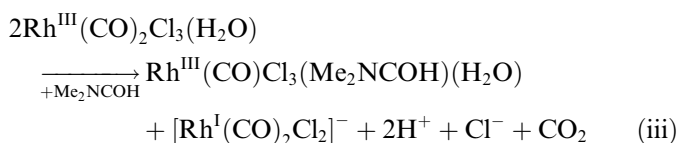
Obviously, the first stage of the reaction is the formation of the rhodium(III) monocarbonyl complex:



(Notice that the rhodium(III) anionic monocarbonyl complex containing DMF ligand has been isolated in [31] as $[\text{AsPh}_4]^+$ salt and included in the proposed reaction scheme.) As monocarbonyl rhodium(III) complexes are known to have no tendency toward the intramolecular rhodium(III) reduction by carbonyl ligand [36], we assume the reduction of rhodium(III) to be preceded by the secondary carbonylation stage



The resulted rhodium(III) dicarbonyl derivative, which may be considered a product of the cleavage of the chloro bridged binuclear complex $[\text{Rh}^{\text{III}}(\text{CO})_2\text{Cl}_3]_2$ [37], is subject to the spontaneous and instant oxidative/reductive hydrolysis in the DMF medium



(for some essential features of this reaction – see [38] and the following Section 2.2.2). As can be seen, stage (iii) yields the equimolar amounts of the final dicarbonyl

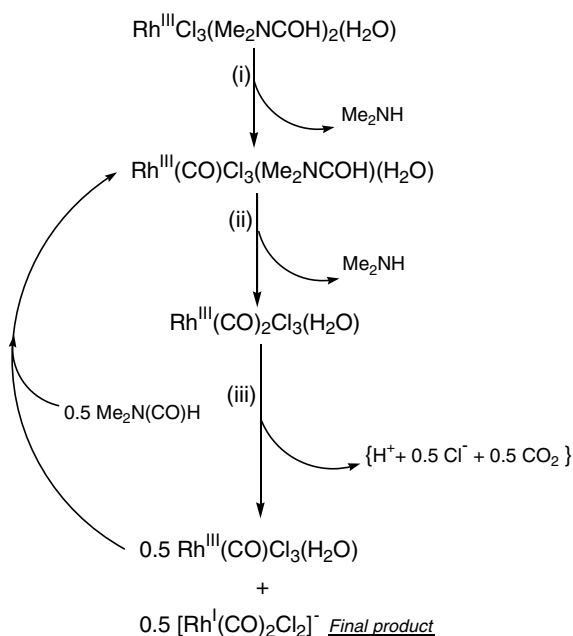
Table 1
Carbonylation of different starting forms of rhodium(III) chloride in dimethylformamide solutions (0.14 mmol/ml)

No.	Starting form	Cl/ Rh	pH (in DMF/ H ₂ O)	Time required for the complete carbonylation, min		Comments
				115 °C	125 °C	
1	RhCl ₃ · nH ₂ O (commercial)	3.6	2.0	100	40–50	Complete carbonylation in ~13 min under reflux
2	RhCl ₃ · nH ₂ O (re-evaporated from aqueous solution)	3.1	2.2	Not studied	40	Complete carbonylation in ~13 min under reflux
3	RhCl ₃ · nH ₂ O (DMF solution pretreated with BaCO ₃)		5.8	50	20 (metal black formation)	Under reflux, heating was stopped after ~3 min (metal black deposition took place in parallel with significant degree of carbonylation)
4	DMF solution of RhCl ₃ · nH ₂ O aged for 3 months	3.03	4.0	Not studied	25–30	Precipitates deposited during the storage were filtered off; for details see [35]; pH value is given for the solution of 0.29 mmol/ml Rh
5	RhCl ₃ (DMF) ₃	3.02	5.0	55	20	Complete carbonylation in ~13 min under reflux

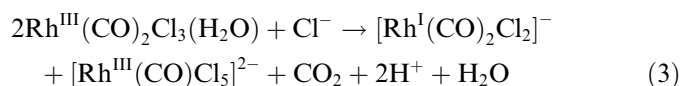
anionic complex of rhodium(I) and the intermediate monocarbonyl complex of rhodium(III) which returns to stage (ii). Cyclic recurrence of the sequence of reactions (ii) and (iii) leads the total reaction (2) to completion. In Scheme 1 we tried to visualize both the sequence and the stoichiometry of the consequent stages of the carbonylation process as we see it basing on the available experimental data.

2.2.2. Oxidative/reductive hydrolysis of [Rh^{III}(CO)₂Cl₃]₂ as a stage of the carbonylation process

The spontaneous ox/red hydrolysis of [Rh^{III}(CO)₂Cl₃]₂ on dissolution in the aqueous hydrochloric acid we studied early on [38] proceeds according to the stoichiometry



Scheme 1. The hypothetical scheme of the rhodium(III) chloride carbonylation.



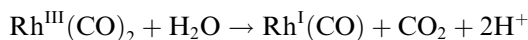
which is substantially identical with the stoichiometry of Eq. (iii) in the mechanistic scheme above.

Dissolution of [Rh^{III}(CO)₂Cl₃]₂ in commercial DMF gives instantly a solution containing the monocarbonyl rhodium(III) and dicarbonyl rhodium(I) complexes in the equimolecular amounts and is accompanied by evolution of CO₂ like in the reaction (3). The IR spectrum of the solution obtained (maxima at 2094, 2065, 1985 cm⁻¹) is closely similar to the spectrum of the RhCl₃/DMF reaction mixture at a partial degree of carbonylation advancement. On heating this solution, the carbonylation process goes on, and the evolution of IR spectrum shows decrease of Rh^{III}(CO) and increase of Rh^I(CO)₂ species concentration. Thus, it was our good fortune to get our hands on an individual and satisfactory characterized compound, which may be considered as a model of the unobservable intermediate of the carbonylation process, namely rhodium(III) dicarbonyl moiety. As we indicated earlier [29,38], the remarkable feature of the reaction (3) is that the Rh^{III}(CO) and Rh^I(CO)₂ complexes are formed in the exactly equimolecular amounts, i.e., only a half of initial rhodium(III) is reduced to rhodium(I), and correspondingly, only one of four carbonyl groups containing in the [Rh^{III}(CO)₂Cl₃]₂ molecule is oxidized to CO₂.¹

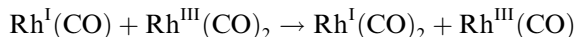
¹ It should be pointed out that we ascribe the crucial importance to the reaction (3) both in reductive carbonylation of rhodium(III) chloride by DMF and in oxidative decarbonylation of the [Rh^I(CO)₂Cl₂]⁻ anion with various oxidants [38]: [Rh^I(CO)₂Cl₂]⁻ - 4e⁻ + H₂O + 3Cl⁻ → [Rh^{III}(CO)Cl₅]²⁻ + CO₂ + 2H⁺. In both cases the reaction of type (3) or (iii) converts half of the unstable rhodium(III) dicarbonyl intermediate, Rh^{III}(CO)₂, into the rhodium(I) complex containing dicarbonyl fragment, Rh^I(CO)₂, and another half into the rhodium(III) complex containing monocarbonyl fragment, Rh^{III}(CO). In both cases, reaction (3) plays a key role yielding the final product and concurrently returning the equal amount of rhodium into the previous stage of reaction.

Evidently into the reaction of the concurrent formation of the $\text{Rh}^{\text{I}}(\text{CO})_2$ and $\text{Rh}^{\text{III}}(\text{CO})$ fragments accordingly to the Eqs. (3) and (iii), two $\text{Rh}^{\text{III}}(\text{CO})_2$ fragments must be involved.²

For instance they may take part in a two-stage process. At the first stage the rhodium(III) dicarbonyl complex is reduced by one of the carbonyl groups bound to it



and then the resulting $\text{Rh}^{\text{I}}(\text{CO})$ moiety instantly reacts with a molecule of the unreacted starting $\text{Rh}^{\text{III}}(\text{CO})_2$



The sequence of these two stages must give what is observed experimentally and coincides substantially with Eqs. (3) and (iii):

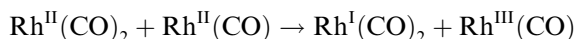


Note that the interaction between $\text{Rh}^{\text{I}}(\text{CO})$ and $\text{Rh}^{\text{III}}(\text{CO})_2$ may be described either as an ox/red process (transfer of two electrons from Rh^{I} to Rh^{III} with retention of carbonyl group positions) or, conversely, as a move of one carbonyl group from Rh^{III} to Rh^{I} without electron transfer. It is likely that the issue will remain open forever.

In the above speculation we considered the carbonyl group as a two-electron reducing agent, which, in the first stage, reduced one Rh(III) atom to the Rh(I) state. We can consider another possibility as well: the carbonyl group reduces two Rh(III) atoms simultaneously supplying one electron to each and thus producing two Rh(II) moieties



In this case, the second stage would be certainly an ox/red disproportionation reaction, the transfer of one electron from the monocarbonyl fragment to the dicarbonyl one, which yields the final products:



We believe the concerted reduction of two Rh(III) atoms with one carbonyl group to be preferable in the synthesis of dirhodium(II) tetraacetate by the procedure we proposed [39]. In the presence of large excess of acetate anion in the rhodium(III) chloride DMF solution, the binuclear species should be stabilized by acetate bridges, and in this case the combination of two rhodium(III) atoms may act as a united two-electron oxidant toward one carbonyl group (apparently bridging in this case, $\text{Rh}-(\text{CO})-\text{Rh}$). In the carbonylation process we discuss here, this reaction route seems to be less probable.

² This conclusion seems to be in conformity with our observation that the rate of carbonylation depends on the total rhodium concentration. Thus, at the rhodium concentration 0.14 mmol/ml and 125 °C after 55 min heating the complete (>95%) conversion is achieved, whereas in the 0.08 mmol/ml solution after 60 min the conversion makes up no more than 70%. At higher concentration (0.2 mmol/ml) the complete conversion required less time (45 min).

2.2.3. Carbonylation of some individual rhodium complexes

At the moment, there is not enough material to discuss the intimate mechanism of the carbonyl group transfer from the DMF molecule to the rhodium center, and only some preliminary comments can be given here on the subject. Of particular interest are data on carbonylation of compounds with well-defined initial composition of the coordination sphere (for details see Table 2).

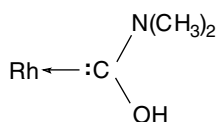
Obviously, to decarbonylate the DMF molecule, the rhodium center has to first coordinate it. The lack of carbonylation, even under prolonged reflux, in the case of $\text{RhCl}_3(\text{DMSO})_3$ and $\text{RhCl}_3(\text{DMSO})_2(\text{DMF})$ shows that both chloride and dimethylsulfoxide ligands are resistant to the replacement by DMF. In this respect these complexes behave just as “tightly closed” rhodium compounds such as $\text{Rh}(\text{Acac})_3$ or $\text{Rh}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, which do not show any symptoms of carbonylation under reflux in DMF. In contrast, carbonylation of acetonitrile complexes, $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ and $\text{RhCl}_3(\text{CH}_3\text{CN})_2(\text{DMF})$, proceeds under reflux almost as quickly as carbonylation of trisdimethylformamide complex, $\text{RhCl}_3(\text{DMF})_3$, suggesting that CH_3CN ligands are readily displaced by DMF in these conditions. More detailed information could be gained from experiments at a lower temperature, 125 °C. $\text{RhCl}_3(\text{CH}_3\text{CN})_3$ (a mixture of *mer* and *fac* isomers) required, at this temperature, more than 1 h to achieve the complete conversion. Essential is that during the first 40–60 min no carbonyl bands could be observed in the IR spectrum of the reaction mixture, but, after this induction period, reaction proceeded fast and came to the end in 20 min. Comparison with the data for $\text{RhCl}_3(\text{DMF})_3$ suggests that the induction period is necessary to replace the CH_3CN ligands (for details see [35]). The length of the induction period apparently depends on the variations in the *mer* to *fac* isomer ratio. Furthermore, the low carbonylation rate of mono-dimethylformamide complexes, $\text{RhCl}_3(\text{CH}_3\text{CN})_2(\text{DMF})$ (at 125 °C) and anion $[\text{RhCl}_5(\text{DMF})]^{2-}$, together with no carbonylation ability of $\text{RhCl}_3(\text{DMSO})_2(\text{DMF})$ suggests that the rhodium center needs additional vacant (or readily liberating) positions *cis* to DMF molecule to abstract from it the carbonyl group.

We also revealed that rhodium(I) complex, $\text{RhCl}(\text{PPh}_3)_3$, is readily carbonylated by DMF (5 min under reflux, 20 min at 125 °C) yielding *trans*- $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$. Under excess PPh_3 the conversion is almost quantitative. This reaction evidences again that DMF itself is a potent carbonylating agent.

It is pertinent to note here that the oxidative addition model proposed for the transition metal carbonylation by DMF [33] is suitable in the case of rhodium(I) complex, $\text{RhCl}(\text{PPh}_3)_3$, but is obviously inappropriate to the rhodium(III) carbonylation. In this case some different way of rhodium to carbon bond formation and CO abstraction is to be supposed. One of the possible transition states in this case may be resulted from the rearrangement of the coordinated DMF molecule into a ligand of carbenoid structure

Table 2
Carbonylation of some individual rhodium complexes in dimethylformamide solutions (0.14 mmol/ml)

No.	Starting compound	Time required for the complete carbonylation, min		Comments
		125 °C	153 °C (reflux)	
1	(Me ₂ NH ₂) ₂ [RhCl ₅ (DMF)]	Not studied	40 (under excess PPh ₃)	Starting compound is almost insoluble in DMF; no carbonylation observed without excess PPh ₃ .
2	(PPh ₄)[RhCl ₄ (H ₂ O) ₂]	60	~15	Starting compound was initially dissolved incompletely.
3	RhCl ₃ (CH ₃ CN) ₃	60–80	~13 (metal black appeared)	Usually, at 125 °C no carbonylation was observed for the long initial period of time (40 min at least)
4	RhCl ₃ (CH ₃ CN) ₂ (DMF)	60	~13 (metal black appeared)	
5	RhCl ₃ (DMF) ₃	20	~13	
6	RhCl ₃ (DMSO) ₃	No carbonylation		
7	RhCl ₃ (DMSO) ₂ (DMF)	No carbonylation		
8	[Rh(CO) ₂ Cl ₃] ₂	60	Not studied	Due to reaction (iii), the real initial concentration of rhodium(III) in this case makes up half of total rhodium concentration, i.e., ~0.07 mmol/ml.
9	RhCl(PPh ₃) ₃	~20	5	Concentration (0.03 mmol/ml) is limited by low solubility of starting compound. Carbonylation was carried out under excess PPh ₃ .



followed by the hydroxyl proton migration toward nitrogen atom and elimination of dimethyl amine.

3. Experimental

3.1. Preparation of starting materials

All reactions were carried out in an atmosphere of dry argon using classical Schlenk techniques. DMF was used as purchased from Vekton Company. Other solvents were purified according to standard procedures [40]. Known complexes were synthesized by published procedures: Rh(Acac)₃ [41], Rh₂(RCOO)₄(H₂O)₂ [39], [Rh(CO)₂Cl₃]₂ [37], RhCl₃(DMSO)₃ [42a], RhCl₃(DMSO)₂(DMF) [42], RhCl(PPh₃)₃ [43]. In the synthesis of RhCl₃(CH₃CN)₃ (a mixture of *mer* and *fac* isomers) we followed general instructions given in the works [44] and have obtained several preparations of required composition and slightly different IR spectra. According to [44d] these differences are due to different *mer* to *fac* isomer ratio. Complexes (Me₂NH₂)₂[RhCl₅(DMF)], (PPh₄)[RhCl₄(H₂O)₂], RhCl₃(DMF)₃, and RhCl₃(CH₃CN)₂(DMF) are synthesized as described in [35].

3.2. pH Measurements

For pH measurements the galvanic cell with transfer was used consisting of a pH-metric glass electrode and a reference electrode (silver-silver chloride electrode immersed into the saturated KCl solution). Electromotive force was

measured with a high-resistance voltmeter. Since there is no pH standard for the H₂O-DMF system, calibration of the glass electrode was carried out using water standard buffers pH 6.86 (sodium/potassium phosphate), pH 4.01 (potassium biphthalate), pH 1.68 (potassium bioxalate). Thus only relative characteristics of the acidity variations in H₂O-DMF (3:1 by volume) RhCl₃ solutions were obtained.

3.3. Carbonylation experiments

3.3.1. General description of carbonylation experiments

All carbonylation experiments were performed under an atmosphere of dry argon using a reaction vessel equipped with reflux condenser and thermometer. In standard experiments the starting compound was dissolved in DMF at room temperature, and the reaction vessel was immersed into an oil bath preheated to the required temperature (ca. 115, 125, or 153 °C inside the vessel). Samples were taken at intervals 5–10 min, and their IR spectra within the region 2200–1800 cm⁻¹ were recorded with a Specord 75 IR instrument. Integral intensity of the absorption band at 1985 cm⁻¹ was measured, and concentration of the [Rh(CO)₂Cl₂]⁻ anions was determined using a linear plot of intensity versus [Et₄N][Rh(CO)₂Cl₂] concentration. The data obtained in a selection of typical experiments are presented in Tables 1 and 2. The rate of RhCl₃ carbonylation depends markedly on the initial concentration of starting compound. In typical experiments it was 0.14 mmol/ml. In the experiments Nos. 1 and 2 (Table 1) at 115 and 125 °C a lilac precipitate was formed, which dissolved in ca. 30 min heating of the reaction mixture. Some peculiar details of other carbonylation experiments are described below.

3.3.2. $(Me_2NH_2)_2[RhCl_5(DMF)]$ carbonylation

As the salt is insoluble in DMF, even at heating, carbonylation was carried out in the presence of excess PPh_3 (4 mol per Rh). PPh_3 (1.46 g, 5.6 mmol) was added to the suspension of $(Me_2NH_2)_2[RhCl_5(DMF)]$ (0.623 g, 1.4 mmol) in DMF (10 ml). The reaction vessel was immersed into a preheated oil bath. After 40 min reflux, the initial solid disappeared. On cooling the yellow solution to the room temperature, a yellow crystalline solid formed. Ethanol (20 ml) was added to complete sedimentation, the product was separated by filtration, washed by ethanol, and identified as *trans*- $Rh(CO)Cl(PPh_3)_2$ by IR($\nu(CO)$) 1978 cm^{-1} in $CHCl_3$ and ^{31}P NMR ($\delta^{31}P$ 29.2 ppm, $^1J(PRh)$ 125.9 Hz in $CDCl_3$). Yield 0.90 g (93%).

3.3.3. Carbonylation of commercial $RhCl_3 \cdot nH_2O$ pretreated with $BaCO_3$

Commercial preparation of $RhCl_3 \cdot nH_2O$ (0.40 g, 1.4 mmol) was dissolved in DMF (10 ml), and $BaCO_3$ (0.5 g, 2.5 mmol) was added. After stirring the suspension for 1 h, the solid was filtered off, a fresh portion of $BaCO_3$ (0.5 g) was added and the suspension was left overnight. The solid was filtered off again and the carbonylation procedure was carried out in the standard manner.

3.3.4. Carbonylation of $RhCl(PPh_3)_3$

To the preheated (153 °C) DMF (25 ml) a mixture of $RhCl(PPh_3)_3$ (0.68 g, 0.73 mmol) and PPh_3 (0.39 g, 1.5 mmol) was added. After heating for 5 min, the intensity of carbonyl stretching band at 1977 cm^{-1} came up to complete carbonylation value. On cooling the reaction mixture to the room temperature a yellow crystalline solid precipitated. Ethanol (25 ml) was added to complete the precipitation. The product was isolated by filtration, washed by ethanol and diethyl ether, and dried in vacuo. It was identified as *trans*- $Rh(CO)Cl(PPh_3)_2$ by IR and ^{31}P NMR (see Section 3.3.2). Yield 0.49 g (96%). At 125 °C the complete conversion required ~20 min.

3.3.5. Carbonylation of $[Rh(CO)_2Cl_3]_2$

$[Rh(CO)_2Cl_3]_2$ (0.6 g, 2.26 mmol Rh) was dissolved in DMF (15 ml). IR spectrum of the solution contained three carbonyl stretching bands with maxima related to Rh(III) monocarbonyl complex (2094 cm^{-1}) and to Rh(I) dicarbonyl complex (2065 and 1985 cm^{-1}). The concentration of $[Rh(CO)_2Cl_2]^-$ anion (0.075 mmol/ml) calculated from the 1985 cm^{-1} band intensity corresponded to ~50% of the taken amount of $[Rh(CO)_2Cl_3]_2$. Evolution of CO_2 was detected by IR in the gas taken from the reaction vessel. Farther conversion of Rh(III) monocarbonyl complex into $[Rh(CO)_2Cl_2]^-$ at 125 °C was monitored by IR at 10 min intervals. In 60 min the conversion reached its maximal value, 80%.

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