Formation of anionic carbonylrhodium complexes from Wilkinson's complex under conditions of hydroformylation of formaldehyde

N. N. Ezhova, G. A. Korneeva, V. I. Kurkin, M. P. Filatova, and E. V. Slivinsky*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

The compositions and the dynamics of transformations of carbonylrhodium complexes formed from Wilkinson's complex, $RhCl(PPh_3)_3$, dissolved in mesitylene—*N,N*-dimethylacetamide (DMAA) mixtures in which the DMAA concentration varied from 0 to 100 %, in an atmosphere of synthesis gas (p_{CO+H_2} = 6 MPa, T = 373 K) were investigated *in situ* by IR spectroscopy. The anion complexes, $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ (x = 1, 2; y = 1, 0) and $[Rh(CO)_4]^-$, which are the centers of formaldehyde hydroformylation, are produced in noticeable quantities when 100 % DMAA is used as a solvent. Separate steps of the formation of anionic complexes from $RhCl(PPh_3)_3$ have been identified. Under the conditions of hydroformylation of formaldehyde, CH_2O participates in the formation of the anionic complexes, along with DMAA.

Key words: formaldehyde, hydroformylation; Wilkinson's complex, anionic rhodium complexes; *N,N*-dimethylacetamide; *in situ* IR spectroscopy.

Hydroformylation of formaldehyde

$$CH_2O + CO + H_2 \rightarrow HOCH_2CHO, \quad (1)$$

which occurs at highest rate in *N,N*-dialkyl substituted carboxamides in the presence of rhodium complexes and does not occur in nonpolar hydrocarbon solvents,[1—3] is catalyzed by anionic carbonylrhodium complexes.[4] The mechanism of formation of these complexes from their neutral precursors under the conditions of hydroformylation of CH_2O has not yet been studied.

In the present work we report the results of an IR study of the *in situ* generation of the anionic carbonylrhodium complexes, $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ (x = 1, 2; y = 1, 0) and $[Rh(CO)_4]^-$, from Wilkinson's complex $RhCl(PPh_3)_3$ under the conditions of hydroformylation of CH_2O in a solution containing a mixture of *N,N*-dimethylacetamide (DMAA) with mesitylene.

Experimental

IR spectra were recorded on a Specord M-80 spectrophotometer using an autoclave IR cell.[5] The cell was heated to 373 K, then a solution of $RhCl(PPh_3)_3$ in a DMAA (0—100 %, w/w) + mesitylene was introduced into it, and the synthesis gas was pumped in until a pressure p_{CO+H_2} = 6 MPa was achieved. Then the spectra were recorded over a period of 2—3 h at 10—15 min intervals in the region of the vibrations of carbonyl groups (ν 1800—2100 cm^{-1}).

^{31}P NMR spectra were recorded on a Bruker MSL-300 spectrometer (121.433 MHz) under anaerobic conditions. Triphenylphosphine oxide was used as the reference compound.

Wilkinson's complex was synthesized according to the known procedure.[6]

Results and Discussion

Table 1 presents the IR spectra of solutions of $RhCl(PPh_3)_3$ in DMAA—mesitylene mixtures under a synthesis gas atmosphere at p_{CO+H_2} = 6 MPa and T = 373 K and the assignment of the adsorption bands recorded. Figure 1 shows the dynamics of the optical density of the bands observed, which reflects variation of the concentration of complexes during the reaction of solutions of $RhCl(PPh_3)_3$ with synthesis gas. It follows from the data of Table 1 that noticeable quantities of the anionic carbonylrhodium complexes, $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ (x = 1, 2; y = 1, 0) and $[Rh(CO)_4]^-$, are formed from Wilkinson's complex under a synthesis gas atmosphere in 100 % DMAA (run *4*). In the absence of amide, $RhCl(PPh_3)_3$ is converted into only one carbonyl complex, $RhCl(CO)(PPh_3)_2$, (see Table 1, run *1*). When the proportion of DMAA in the solvent was 20 % (w/w), along with $RhCl(CO)(PPh_3)_2$, the dicarbonyl chloride $RhCl(CO)_2(PPh_3)$ was detected (see Table 1, run *2*). The dynamics of the magnitudes of optical densities of absorption bands typical of these complexes indicates that the former complex (see Fig. 1, *a*, curve *1*) is converted into the latter (see Fig. 1, *a*, curve *2*). When a solvent containing 50 % (w/w) DMAA was used, the reaction mixture contained, in addition to the above-listed carbonyl chlorides, the

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 863—866, May, 1995.

1066-5285/95/4405-0836 $12.50 © 1995 Plenum Publishing Corporation

Table 1. The assignment of the absorption bands in the IR spectra of solutions of $RhCl(PPh_3)_3$ in a DMAA—mesitylene mixture in an atmosphere of synthesis gas (p_{CO+H_2} = 6 MPa, T = 373 K, [Rh] = $1 \cdot 10^{-2}$ g-at L^{-1}, the solution of $RhCl(PPh_3)_3$ was treated with synthesis gas for 2 min)

Run	[DMAA] in a solvent (%, w/w)	ν/cm^{-1}	Complex	Reference
1	0	1976 s (CO)	$RhCl(CO)(PPh_3)_2$	1
2	20	1976 s (CO)	$RhCl(CO)(PPh_3)_2$	1
		1938 m (CO); 1985 s (CO)	$RhCl(CO)_2(PPh_3)$	7
3	50	2044 w (CO); 1986 m (CO); 1832 w (CO(μ))	$[Rh(CO)_2(PPh_3)_x(DMAA)_y]_2$ (x = 1, 2; y = 1, 0)	8
		2040 w (Rh—H); 1980 m (CO); 1938 m (CO)	$RhH(CO)_2(PPh_3)_2$	2,9
4	100	1900 v.s (CO)	$[Rh(CO)_4]^-$	2
		2044 w (CO); 1986 m (CO); 1832 w (CO(μ))	$[Rh(CO)_2(PPh_3)_x(DMAA)_y]_2$ (x = 1, 2; y = 1, 0)	8
		2040 w (Rh—H); 1980 m (CO); 1938 m (CO)	$RhH(CO)_2(PPh_3)_2$	2,9
		1990 m (CO); 1932 s (CO)	$[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ (x = 1, 2; y = 1, 0)	10
		1820 v.w (CO(μ))	$Rh_6(CO)_{16}$	9

disubstituted hydrocarbonyl $RhH(CO)_2(PPh_3)_2$ and the dimer $[Rh(CO)_2(PPh_3)_x(DMAA)_y]_2$ (see Table 1, run *3*), which are probably produced from the carbonyl chlorides. This is indicated by the fact that the concentrations of $RhH(CO)_2(PPh_3)_2$ (νRhH 2040 cm^{-1}) and $[Rh(CO)_2(PPh_3)_x(DMAA)_y]_2$ (νCO(μ) 1832 cm^{-1}) increase and those of $RhCl(CO)(PPh_3)_2$ (νCO 1976 cm^{-1}) and $RhCl(CO)_2(PPh_3)$ (νCO 1938 cm^{-1}) decrease in the course of the reaction (see Fig. 1, *b*). In pure DMAA, $RhH(CO)_2(PPh_3)_2$ and $[Rh(CO)_2(PPh_3)_x(DMAA)_y]_2$ are converted into the anionic carbonylrhodium complexes $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ and $[Rh(CO)_4]^-$ and the cluster $Rh_6(CO)_{16}$: as the reaction proceeds, the concentrations of the hydrocarbonyl and the dimer decrease (see Fig. 1, *c*, curves *3* and *4*), and those of the anions and the cluster increase (see Fig. 1, *c*, curves *5*, *6*, and *7*).

The transformations occurring between the complexes detected in the pure amide are apparently reversible, since after the removal of the synthesis gas from the resulting mixture of the carbonylrhodium complexes (to a residual pressure of 0.1 MPa), the solution contains at 293 K only the $[Rh(CO)(PPh_3)_2]_2$ complex whose treatment with synthesis gas at 373 K results in the recovery of the starting system. The $[Rh(CO)(PPh_3)_2]_2$ complex

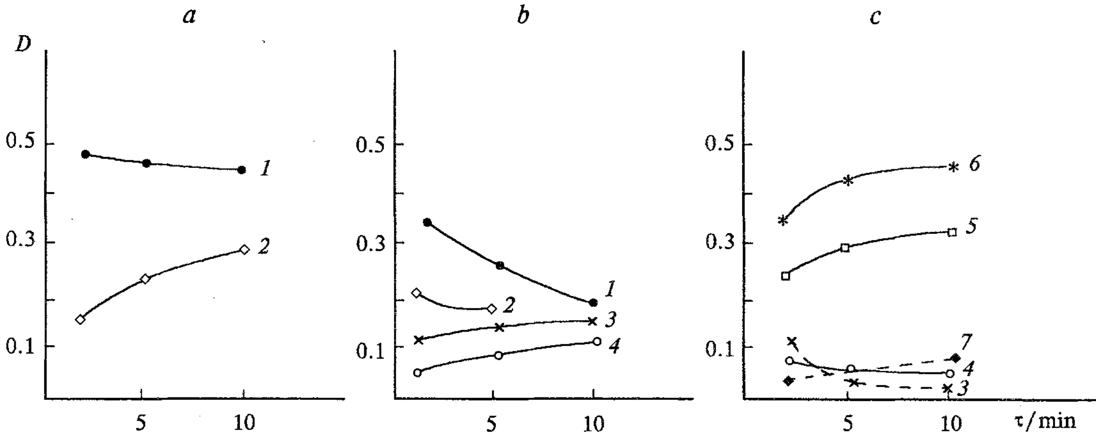
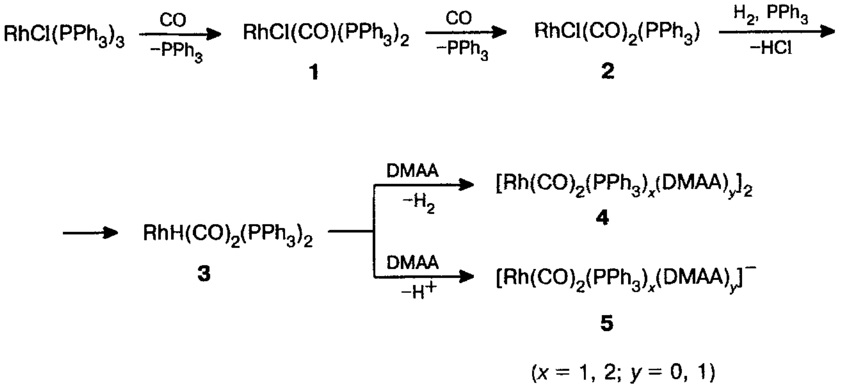


Fig. 1. Dynamics of the optical density (D) of the absorption bands corresponding to the carbonylrhodium complexes in their IR spectra recorded during the reaction of $RhCl(PPh_3)_3$ with synthesis gas in a DMAA—mesitylene mixture (p_{CO+H_2} = 6 MPa, T = 373 K, [Rh] = $1 \cdot 10^{-2}$ g-at L^{-1}). The contents of DMAA are 20 %, w/w (*a*); 50 %, w/w (*b*); and 100 %, w/w (*c*). The absorption bands, ν/cm^{-1}: *1*, 1976 ($RhCl(CO)(PPh_3)_2$); *2*, 1938 ($RhCl(CO)_2(PPh_3)$); *3*, 2040 ($RhH(CO)_2(PPh_3)_2$); *4*, 1832 ($[Rh(CO)_2(PPh_3)_x(DMAA)_y]_2$); *5*, 1932 ($[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$); *6*, 1900 ($[Rh(CO)_4]^-$); *7*, 1820 ($Rh_6(CO)_{16}$).

Scheme 1



was identified by ^{31}P NMR and IR spectroscopy; the IR spectrum exhibits an absorption band with ν 1974 cm^{-1}, and the ^{31}P NMR spectrum contains only one signal, which is a doublet (δ 4.24, J_{P-Rh} = 129 Hz) that corresponds to the spectroscopic characteristics of the authentic sample.

The sequence of transformations of the carbonylrhodium complexes established together with the literature data[2,11–13] make it possible to represent the process of the formation of the $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ anionic complex from $RhCl(PPh_3)_3$, CO, and H_2 in the presence of DMAA according to Scheme 1, which involves carbonylation of the starting complex to give mono- and dicarbonyl derivatives (**1** and **2**, respectively), subsequent dechlorination* to yield hydrocarbonyl **3**, and its reversible deprotonation to give anion **5**. The $RhH(CO)_2(PPh_3)_2$ hydrocarbonyl exists in equilibrium with dimer **4**.

$[Rh(CO)_4]^-$ is most likely formed from the unmodified rhodium hydrocarbonyl, which is known[9] to exist in equilibrium with $RhH(CO)_2(PPh_3)_2$. This hydrocarbonyl probably acts as the reagent in the preparation of $Rh_6(CO)_{16}$ (see Ref. 9).

$$12\ RhH(CO)_3 \underset{-6\ H_2}{\rightleftharpoons} 3\ Rh_4(CO)_{12} \underset{-4\ CO}{\rightleftharpoons} 2\ Rh_6(CO)_{16} \qquad (2)$$

One may assume that all of the steps of the formation of the anionic carbonylrhodium complexes from $RhCl(PPh_3)_3$, CO, and H_2, except the formation of monocarbonyl chloride **1**, involve intermediate transformations in which DMAA participates, since their occurrence depends on the presence and the contents of the amide in the reaction mixture (see Table 1).

DMAA is known[14] to form coordination bonds with Rh atoms. It has been shown by ^{31}P NMR spectroscopy that the presence of DMAA in the coordination sphere of rhodium results in weakening of the Rh—PPh$_3$ bond. This is indicated by the lower spin coupling constant of the doublet signals recorded in the spectrum of a solution of $RhCl(PPh_3)_2(DMAA)$ in amide (J_{P-Rh} = 89 Hz) compared to the spin coupling constant exhibited in the spectrum of a solution of $RhCl(PPh_3)_3$ in $CDCl_3$ (J_{P-Rh} = 121 to 185 Hz for various signals). Taking this into account one may suggest that the transformation of rhodium monocarbonyl chloride into dicarbonyl chloride **2**, which requires the removal of PPh$_3$ from the coordination sphere of rhodium, involves an intermediate incorporation of the amide into the coordination sphere of Rh, which decreases the strength of the Rh—PPh$_3$ bond.

The dechlorination and deprotonation steps yielding compounds **3** and **4**, respectively, probably occur *via* an intermediate complex with DMAA too. In fact, under conditions interfering with the coordination of amide, for example, when excess PPh$_3$ is introduced in the reaction mixture (P/Rh ≥ 50 g-at/g-at), $RhCl(PPh_3)_3$ in a DMAA solution in an atmosphere of synthesis gas gives only $RhCl(CO)(PPh_3)_2$ and $RhCl(CO)_2(PPh_3)$, and $RhH(CO)_2(PPh_3)_2$ produces no anionic rhodiumcarbonyl complexes (which was confirmed by special experiments).

Thus, one may infer that the formation of anionic rhodiumcarbonyl complexes from $RhCl(PPh_3)_3$ in an atmosphere of synthesis gas in the presence of DMAA, *i.e.*, under conditions of hydroformylation of formaldehyde (in the absence of the substrate), involves incorporation of the amide into the coordination sphere of rhodium in various steps including deprotonation of rhodium hydrocarbonyl. Owing to its basic properties, the amide obviously binds the proton during deprotonation, thus stabilizing the anionic complexes.

As can be seen from Fig. 2, the formation of the anionic carbonylrhodium complexes from $RhCl(PPh_3)_3$ under the conditions of hydroformylation is intensified by formaldehyde: the concentrations of $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ and $[Rh(CO)_4]^-$ achieved in the presence of CH_2O are higher (the intensities of the absorption bands at 1932 and 1900 cm^{-1} are higher)

---

* A dechlorination route involving no H_2 to give dimer **4** is also probable. This was observed when $RhCl(PPh_3)_3$ was treated with CO in a solution in pure amide at p = 3 MPa and T = 373 K.

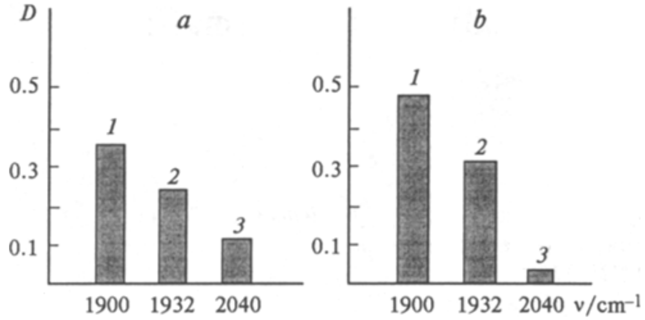


Fig. 2. The optical densities (*D*) of the absorption bands of $[Rh(CO)_4]^-$ (*1*), $[Rh(CO)_2(PPh_3)_x(DMAA)_y]^-$ (*2*), and $RhH(CO)_2(PPh_3)_2$ (*3*) in the IR spectrum of a solution of $RhCl(PPh_3)_3$ in DMAA after treatment with synthesis gas for 2 min at p_{CO+H_2} = 6 MPa and *T* = 373 K in the absence (*a*) or in the presence (*b*) of CH_2O.

than those attained in the absence of CH_2O, the duration and the conditions being the same.

It is noteworthy that the formation of the anionic carbonylrhodium complexes, $[Rh(CO)_2(PBu_3)_x(DMAA)_y]^-$ (νCO 1905 and 1974 cm^{-1})[4] and $[Rh(CO)_4]^-$, from $RhCl(CO)(PBu_3)_2$ dissolved in amide in an atmosphere of synthesis gas occurs at a noticeable rate only in the presence of CH_2O.

These data indicate that formaldehyde participates, along with amide, in the formation of anionic complexes from the neutral precursors. However, it should be noted that the crucial role is played by amide: when CH_2O and no DMAA is present, neither $RhCl(PPh_3)_3$ nor $RhCl(CO)(PBu_3)_2$ give the anionic complexes.

Similar properties, *i.e.*, the ability to coordinate to the Rh atom and to bind a proton, are also exhibited by amines and phosphine oxides whose addition to the hydroformylation system also results in the formation of anionic complexes from neutral precursors, and reaction (1) occurs at a noticeable rate.[2,15] However, the use of these compounds as additives to the hydroformylation catalyst is undesirable, unlike the use of *N,N*-dialkyl carboxamides, since their presence accelerates the side reaction, *viz.*, condensation of CH_2O with glycolaldehyde to give polyoxyaldehydes.

References

1. A. J. Spencer, *J. Organomet. Chem.*, 1980, **194**, 113.
2. A. S. C. Chan, W. E. Carrol, and D. E. Willis, *J. Mol. Catal.*, 1983, **19**, 377.
3. S. E. Jacobson, *J. Mol. Catal.*, 1987, **41**, 163.
4. N. N. Ezhova, G. A. Korneeva, V. I. Kurkin, and E. V. Slivinsky, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1066 [*Russ. Chem. Bull.*, 1995, **44**, 1027 (Engl. Transl.)].
5. USSR Pat. 1698713; *Byul. Izobret.*, 1986, 13.
6. G. Wilkinson, J. A. Osborn, F. H. Jardine, and I. F. Young, *J. Chem. Soc.*, 1966, **12**, 1711.
7. A. R. Sanger, *Can. J. Chem.*, 1985, **63**, 571.
8. D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc., A*, 1968, **11**, 2660.
9. W. R. Moser, C. J. Papile, D. A. Brannon, and R. A. Duwell, *J. Mol. Catal.*, 1987, **41**, 271.
10. J. P. Collmann, F. D. Vastine, and W. R. Roper, *J. Am. Chem. Soc.*, 1968, **90**, 2282.
11. B. James, *Gomogennoe gidrirovanie* [*Homogeneous Hydrogenation*], Mir, Moscow, 1976 (Russ. Transl.).
12. M. Marchionna and G. Longoni, *Gazz. Chim. Ital.*, 1986, **116**, 453.
13. J. Ohgomori, Sh. Mori, Sh.-I. Joshida, and J. Watanabe, *J. Mol. Catal.*, 1987, **40**, 223.
14. G. A. Korneeva, N. N. Ezhova, V. G. Avakyan, E. V. Slivinsky, and S. M. Loktev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2670 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2444 (Engl. Transl.)].
15. US Pat. 4405821; *Chem. Abstrs.*, 1983, **97**, 194433.

Received July 7, 1994