(isoelectronic with I), for which a bent structure should be forecast.

On the contrary, the addition of one electron into the LUMO, which is strongly Co–NO antibonding (see Figure 7), labilizes the Co–NO bonds, giving rise eventually to monomeric fragments.

Removal of a further electron from I$^+$ should not affect the dimeric structure. Interestingly, I^{2+} is detected only as a short-lived species whose fate is fragmentation with loss of NO. An explicit calculation on I^{2+} demonstrates that the reason for such a behavior is an extensive weakening of the d_x(Co) → π^*(NO) back-donation interactions owing to the high positive charge on the metal atoms.[26] This argument, however, cannot be invoked to explain the instability of II$^+$. We could tentatively attribute the mentioned *heterolytic splitting* of II$^+$ to the inherent molecular asymmetry consequent to the presence of two different bridging groups that would induce some destructive charge polarization upon oxidation.

A final comment on the Co–Co interaction in these dimers is of relevance. At the present level of theoretical accuracy we can assess that a direct metal–metal interaction is present only when I assumes a bent geometry. This and other minor factors, such as the reduction of the Co–Cp antibonding interaction which stabilizes the HOMO in the bent form, contribute to the bending of the (μ-NO)$_2$Co$_2$ core which, however, occurs to the prejudice of the Co–NO interactions (Co–NO overlap populations, planar, 0.96 e, and bent, 0.83 e). The final geometry is, then, the result of a subtle balance between small perturbations (e.g., crystal packing energies).[16]

Hydroformylation of Formaldehyde with the [Rh(CO)$_2$Cl$_2$]$^-$ and [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ System: A Case of Synergetic Catalysis with Two Combined Rhodium Carbonyl Species in Different Oxidation States

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Paraformaldehyde has been hydroformylated to glycolaldehyde at 100–140 atm of CO and H$_2$ (1/1) and at 90–110 °C with selectivity up to 95% in common organic solvents, e.g., acetone, with a catalytic system involving two preformed anionic rhodium carbonyl species in different formal oxidation states, viz., [Rh(CO)$_2$Cl$_2$]$^-$ and [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$. This system combines the high activity of the latter with the high selectivity of the former and enables the hydroformylation of paraformaldehyde to be carried out at a rate comparable with that previously observed only in N,N-disubstituted amide or pyridine solvents. A strictly related system, generated "in situ" upon addition of halide ions and triphenylphosphine to Rh$_4$(CO)$_{12}$, showed comparable catalytic behavior. A temptative interpretation of the synergetic effect shown by mixtures of [Rh(CO)$_2$Cl$_2$]$^-$ and [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ is suggested.

Introduction

Glycolaldehyde from hydroformylation of formaldehyde is receiving increasingly wider attention as a potential intermediate for ethylene glycol and serine production.[1–5] So far the metal-catalyzed hydroformylation of formaldehyde to glycolaldehyde has been achieved with reasonable rates and high selectivity only with Rh(I) phosphine–carbonyl complexes either in ionizing and basic solvents, e.g., N,N-disubstituted amides[2,3] or pyridines,[4] or in the presence of weak organic bases as promoters, e.g., triethylamine.[3,4]

Also when Rh$_4$(CO)$_{12}$ was used as catalyst precursor, in the presence of PPh$_3$ and HI as promoters, a highly selective hydroformylation of paraformaldehyde to glycolaldehyde was only observed in basic solvents such as dimethylformamide (DMF).[6] Concomitant gas chromatographic analyses and infrared measurements suggested the possible involvement of the [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ ($x = 1$, 2)[7] substituted carbonyl cluster in the catalytic system.[6] Therefore, in keeping with previous suggestions,[3] it appeared conceivable that one role of such ionizing and basic solvents was to enable reduction of oxidized rhodium precursors to low-valent anionic rhodium carbonyl species. However, at partial difference with previously investigated systems,[3] both preformed [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ ($x = 0$, 1) species and Rh$_4$(CO)$_{12}$/PPh$_3$/HI mixtures in DMF displayed progressive loss of selectivity with time, apparently corresponding with a further reduction to lower valent species of the precursors.[6,8] It was, therefore, of interest

(1) Hendriksen, D. E. *Chem. Eng. News* **1983**, April 11, 41–42.
(2) Spencer, A. *J. Organomet. Chem.* **1980**, *194*, 113–123.
(3) Chan, A. S. C.; Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* **1983**, *19*, 377–391 and references therein.
(4) Okano, T.; Makino, M.; Konishi, H.; Kiji, J. *Chem. Lett. Jpn.* **1985**, 1793–1796.
(5) Kaneko, T. *Synthetic Production and Utilization of Amino Acids*; Wiley: New York, 1974 and references therein.

(6) Marchionna, M.; Longoni, G. *Gazz. Chim. Ital.* **1986**, *116*, 453–457.
(7) Martinengo, S.; Fumagalli, A.; Ciani, G.; Sironi, A., unpublished results.
(8) Marchionna, M.; Longoni, G. *J. Mol. Catal.* **1986**, *35*, 107–118.

Table I.[a,b] **Hydroformylation of Paraformaldehyde with [PPN][Rh$_5$(CO)$_{15}$] + PPh$_3$**

run	PPh$_3$/Rh	convn	CH$_3$OH	HCOOCH$_3$	HOCH$_2$CHO	HOCH$_2$CH$_2$OH
1	0	9.2	89.1		10.9	
2	0.8	79.2	76.3	1.7	22.0	
3	1.25	100	63.5	2.2	29.3	5.0
4	2	100	46.8	0.6	42.7	9.9
5[c]	3	100	52.1	1.2	29.1	17.6
6[d]	5	100	60.2	1.2	15.7	22.8
7[e]	0.625	81.0	90.2	3.1	4.0	2.5

[a] [Rh] = 0.02 M; [CH$_2$O] = 2 M; V = 10 mL; P_{CO+H_2} = 95 atm; CO/H$_2$ = 1/1; T = 110 °C; t = 2 h. Conversion and selectivity are in mole percent. [b] Small amounts of dimethoxymethane, benzene, and benzaldehyde are present: the amount of dimethoxymethane has been added to the percent of methanol. [c] P = 140 atm; [CH$_2$O] = 3.33 M. [d] P = 140 atm; [CH$_2$O] = 4 M. [e] Bis(diphenylphosphine)ethane instead of PPh$_3$.

Table II.[a,b] **Hydroformylation of Paraformaldehyde in Acetone with Combinations of Two Preformed Rhodium Species**
(C = Molar Concentration)

run	$C_{Rh(PPh_3)_2(CO)Cl}$	$C_{[Rh(CO)_2Cl_2]^-}$	$C_{[Rh_5(CO)_{15}]^-}$	C_{PPh_3}[c]	PPh$_3$/Rh[d]	convn	CH$_3$OH	HCOOCH$_3$	HOCH$_2$CHO
1	0.02				2	7.2	53.6	10.6	35.8
2	0.02			0.06	5	27.4	90.8	5.2	3.9
3		0.02				31.2	12.9	4.4	82.7
4		0.02		0.04	2	4.1	54.2	9.2	36.6
5	0.01	0.01			1	27.3	10.4	6.7	82.8
6	0.01	0.01		0.02	2	4.3	62.3	8.1	29.6
7	0.01		0.002		1	5.1	34.1		65.9
8	0.01		0.002	0.024	1.5	48.6	51.1	3.1	45.8
9		0.01	0.002			41.4	11.7	3.7	84.6
10		0.01	0.002	0.02	1	80.2	9.4	2.7	87.9

[a] P = 125 atm; [CH$_2$O] = 3.33 M; all other parameters as is Table I. [b] See footnote b in Table I. [c] Concentration of free PPh$_3$ added at the beginning of the run. [d] Overall PPh$_3$/Rh ratio.

to investigate the catalytic behavior of [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ in less basic solvents in order to disfavor the above reduction reactions. We report here our results on the Rh-catalyzed hydroformylation of formaldehyde in acetone.

Results

Table I collects some results obtained in the hydroformylation of paraformaldehyde in acetone catalyzed with the [PPN][Rh$_5$(CO)$_{15}$] salt (PPN = bis(triphenylphosphine)nitrogen(1+) cation), in the presence of triphenylphosphine or bis(diphenylphosphine)ethane (DPP) as promoters. Partially in keeping with previous suggestions,[6] the substituted [Rh$_5$(CO)$_{15-x}$L$_x$]$^-$ (L = PPh$_3$, DPP) cluster, which is readily obtained on addition of phosphine to the unsubstituted [Rh$_5$(CO)$_{15}$]$^-$ anion,[7] enables a fast conversion of paraformaldehyde (2 M) that is completely consumed over a period of 2 h under 95 atm of pressure of CO and H$_2$ (1/1). However, in spite of this high activity, the overall molar selectivity into desired C$_2$-oxygenated species (glycolaldehyde and ethylene glycol) is disappointingly low. When the PPh$_3$/Rh molar ratio is increased up to ca. 2, the above system shows its top selectivity of ca. 50%, which then declines on further addition of phosphine. Therefore, although the above system enhances the hydroformylation rate, it much more enhances the hydrogenation side reaction of formaldehyde to methanol, as also confirmed by progressive reduction of glycolaldehyde into ethylene glycol on increasing the PPh$_3$/Rh ratio. Examination of the infrared spectra of the depressurized catalytic solutions indicates the presence of [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ (x = 0–2) and a yet unknown carbonyl species with carbonyl absorptions at 1970 cm^{-1}: the concentration of the latter increases on increasing the PPh$_3$/Rh molar ratio and becomes the only detectable carbonyl species present in solution for PPh$_3$/Rh ≥ 5.

As a conclusion, it hardly seems conceivable that a carbonyl-substituted [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ species *alone*, as well as a degradation product of the former in the presence of a large excess of phosphine ligand, could be

responsible for both the high selectivity and activity of the hydroformylation of formaldehyde into glycolaldehyde observed in DMF with the catalyst originating from mixtures of Rh$_4$(CO)$_{12}$, PPh$_3$ and HI.[6] Even if the DMF could play an active role in favoring the CO insertion step,[9] it seems more reasonable to ascribe the high selectivity of the above system to a different rhodium species. We have, therefore, investigated the catalytic behavior in acetone of the other rhodium carbonyl species, that is, Rh(PPh$_3$)$_2$(CO)X and [Rh(CO)$_2$X$_2$]$^-$ (X = halide), which were previously found to be present in the depressurized catalytic solutions.[6] In the attempt to find possible synergetic effects, arising from the cooperative action of two or more rhodium species, systematic experiments with combination of two of the above compounds were also run at constant overall rhodium concentration and equal rhodium concentration in the two tested species. As shown in Table II, Rh(PPh$_3$)$_2$(CO)Cl in acetone solution is both little active and selective, also in presence of free PPh$_3$.[10] In contrast, [PPN][Rh(CO)$_2$Cl$_2$] enables the hydroformylation of formaldehyde to take place at a slow rate but with a molar selectivity greater than 80%.[11] Furthermore, on combining either Rh(PPh$_3$)$_2$(CO)Cl or [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ with [Rh(CO)$_2$Cl$_2$]$^-$, a significant improvement of the activity was observed with maintenance or slight improvement of the selectivity of the latter. This feature is particularly noticeable with the [PPN][Rh(CO)$_2$Cl$_2$]–[PPN][Rh$_5$(CO)$_{15}$] pair of compounds in the presence of triphenylphosphine (see entry 10 in Table II).[12] Infrared

(9) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994–3999.

(10) The activity of Rh(PPh$_3$)$_2$(CO)Cl could be underestimated in the reported experiments because of its incomplete solubilization in acetone at least at room temperature.

(11) In analogous experimental conditions the corresponding [PPN][Rh(CO)$_2$I$_2$] displayed inferior activity and selectivity.

(12) Examples of synergetic behavior between two species in different oxidation state are well-documented in the catalytic hydrogenation of carbon monoxide.[13,14]

(13) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325–416 and references therein.

(14) Dombek, B. D. *Organometallics* **1985**, *4*, 1707–1712.

Table III.[a,b] **Hydroformylation of Paraformaldehyde in Acetone with a 1/5 Molar Mixture of [PPN][Rh$_5$(CO)$_{15}$] and [PPN][Rh(CO)$_2$Cl$_2$] in the Presence of PPh$_3$**

run	PPh$_3$/Rh	convn	CH$_3$OH	HCOOCH$_3$	HOCH$_2$CHO	HOCH$_2$CH$_2$OH
1		41.4	11.5	3.8	84.6	
2	0.2	55.6	8.6	3.8	87.6	
3	0.4	59.4	7.4	2.2	90.4	
4	0.6	70.2	8.0	2.2	89.8	
5	0.8	76.2	9.4	1.9	88.6	
6	1.0	80.2	9.4	2.7	87.9	
7	1.25	92.2	20.2	2.2	77.6	
8	1.50	98.6	36.2	2.0	61.8	
9	2.50	100	66.4	1.4	29.2	2.9
10	5.0	100	72.8	0.8	24.0	2.4
11[c]	1.0	44.4	60.6		39.4	

[a] P = 125 atm; [CH$_2$O] = 3.33 M; all other parameters as in Table I. [b] See footnote b in Table I. [c] Formaldehyde introduced as aqueous formaldehyde (37% wt).

monitoring at the end of the reaction showed the presence of an unaltered mixture of [Rh(CO)$_2$Cl$_2$]$^-$, [Rh$_5$(CO)$_{15}$]$^-$, and [Rh$_5$(CO)$_{14}$(PPh$_3$)]$^-$ with relative concentrations roughly coincident with the start. It is also worth noting that a corresponding IR monitoring of the combined Rh-(PPh$_3$)$_2$(CO)Cl/[Rh(CO)$_2$Cl$_2$]$^-$ system points out a partial, but significant, conversion of the above into [Rh$_5$-(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$. As a result, this latter system differentiates from the previous one only in showing the presence of a just detectable amount of Rh(PPh$_3$)$_2$(CO)Cl.

The results collected in Table II prompted the investigation of the effect on activity and selectivity of varying the [Rh$_5$(CO)$_{15}$]$^-$/[Rh(CO)$_2$Cl$_2$]$^-$ molar ratio at constant overall rhodium concentration (2 × 10^{-2} M) and with a fixed PPh$_3$/[Rh$_5$(CO)$_{15}$]$^-$ ratio of 6. This particular PPh$_3$/[Rh$_5$(CO)$_{15}$]$^-$ ratio was choosed in order to limit ligand-substitution reactions to [Rh$_5$(CO)$_{15}$]$^-$ (vide infra) and because it enables a satisfactory activity and selectivity to be observed (see entry 4 in Table III). A few results are shown in Figure 1. An increase of the [Rh$_5$-(CO)$_{15}$]$^-$/[Rh(CO)$_2$Cl$_2$]$^-$ ratio corresponds to a progressive increase of the activity of the system; this, however, is mainly due to increased hydrogenating behavior, and the selectivity into glycolaldehyde concomitantly drops to values close to those shown by [Rh$_5$(CO)$_{15}$]$^-$ in the presence of triphenylphosphine (see Table I). The increased reductive behavior of the above system on decreasing the formal average oxidation state is also confirmed by the progressive formation of ethylene glycol by hydrogenation of glycolaldehyde (in Figure 1 the molar amount of ethylene glycol has been added to glycolaldehyde for simplicity). It seems, therefore, conceivable that [Rh$_5$-(CO)$_{15-x}$L$_x$]$^-$ species could play a role in the activation of hydrogen and paraformaldehyde; however, the high selectivity of this combined system should more probably arise from the presence of [Rh(CO)$_2$Cl$_2$]$^-$ and require a higher formal average oxidation state. Figure 1 suggests as a best compromise between activity and selectivity a catalytic system having a [Rh$_5$(CO)$_{15}$]$^-$/[Rh(CO)$_2$Cl$_2$]$^-$ molar ratio comprised in the 1-5 range.

In the attempt to obtain a more tailored catalytic system, we have investigated the effect of addition of triphenylphosphine in excess to the [Rh$_5$(CO)$_{15}$]$^-$/[Rh-(CO)$_2$Cl$_2$]$^-$ (1/5) combined system; this in order to favor conversion of [Rh$_5$(CO)$_{15}$]$^-$ into [Rh$_5$(CO)$_{14}$(PPh$_3$)]$^-$ also under a high carbon monoxide partial pressure. Thus, in the above system infrared monitoring suggested that PPh$_3$ preferentially reacts with [Rh$_5$(CO)$_{15}$]$^-$ rather than [Rh-(CO)$_2$Cl$_2$]$^-$; the latter becomes significantly involved in ligand-substitution reactions, which afford Rh(PPh$_3$)$_2$-(CO)Cl, only for the highest PPh$_3$/Rh ratios. As shown in Table III, where mixtures of [PPN][Rh$_5$(CO)$_{15}$] and [PPN][Rh(CO)$_2$Cl$_2$] in a 1/5 molar ratio in acetone solu-
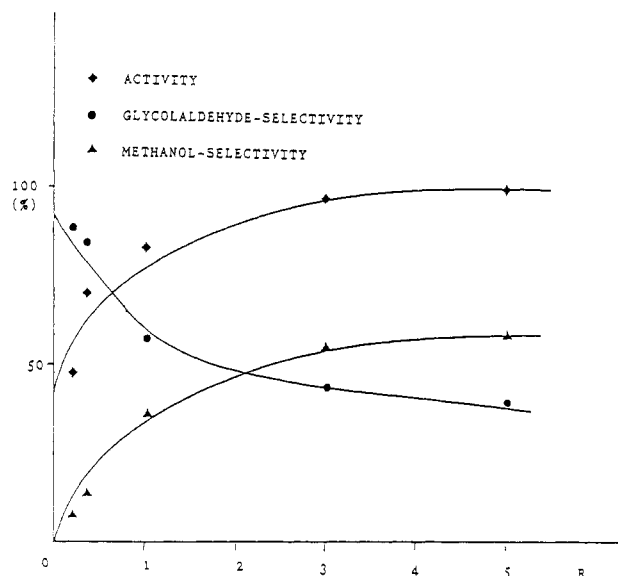
Figure 1. Dependence of activity and selectivity from the [Rh$_5$(CO)$_{15}$]$^-$/[Rh(CO)$_2$Cl$_2$]$^-$ molar ratio (R) (PPh$_3$/[Rh$_5$(CO)$_{15}$]$^-$ = 6; T = 110 °C; P_i = 120 atm; [CH$_2$O] = 3.33 M; other experimental conditions as in Table I).

tion were tested in the hydroformalation of paraformaldehyde at 110 °C and under a pressure of 125 atm of CO and H$_2$ (1/1), addition of increasing amounts of PPh$_3$ smoothly increases the activity of the above system, while the selectivity into glycolaldehyde is constantly kept in the 80–90% range up to an overall PPh$_3$/Rh molar ratio of ca. 1. A further increase of the PPh$_3$/Rh ratio has yet a favorable effect onto activity; however, the selectivity begins to decline probably owing to a faster enhancement of the hydrogenating behavior of the catalytic system, as shown by the progressive appearance of ethylene glycol among the products. On the basis of an infrared analysis, the shift from hydroformylating toward hydrogenating behavior seems to correspond with the disappearance from solution of [Rh(CO)$_2$Cl$_2$]$^-$, which is progressively converted into Rh(PPh$_3$)$_2$(CO)Cl on adding too large an excess of phosphine. Accordingly, the results given by runs 7–10 of Table III become progressively comparable with those obtained with the Rh(PPh$_3$)$_2$(CO)Cl/[PPN][Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$] combined system.

Table III reports also the result obtained in analogous experimental conditions on substituting paraformaldehyde with aqueous formaldehyde solutions. A significant drop in both activity and selectivity was observed (compare entry 11 with entry 6 of Table III). Moreover, when formaldehyde in methanol solution is employed, the activity of this system dropped to the point that glycolaldehyde was not detectable also after a 2-h reaction.

Table IV.[a,b] **Hydroformylation of Paraformaldehyde in Acetone with the System $Rh_4(CO)_{12}$ + 2[PPN]Cl + PPh_3**

run	PPh_3/Ph	convn	CH_3OH	$HCOOCH_3$	$HOCH_2CHO$	$HOCH_2CH_2OH$
1	0.2	38.3	12.4	6.7	80.9	
2	0.4	40.5	13.8	4.2	82.0	
3	0.6	59.7	20.0	2.5	77.5	
4	1.25	100	53.0	1.0	42.4	3.6
5	2.5	70.2	69.8		26.5	3.7
6	5	70.8	77.2		17.2	5.6

^{a} [CH_2O] = 4.66 M, P_{CO+H_2} = 130 atm; all other parameters as in Table I. ^{b} See footnote b in Table I.

Table V.[a,b] **Effect of the Temperature on the Hydroformylation of Formaldehyde with the [PPN][$Rh_5(CO)_{15}$]/[PPN][$Rh(CO)_2Cl_2$]/PPh_3 (1/5/10) System**

run	T, °C	convn	CH_3OH	$HCOOC-H_3$	$HOCH_2CHO$	$HOCH_2CH_2OH$
1	90	44.1	2.5	2.0	95.5	
2	110	80.2	9.4	2.7	87.9	
3	125	67.5^c	22.8		77.2	
4	140	76.3^c	30.5		69.5	

$^a P$ = 125 atm; [CH_2O] = 3.33 M; all other parameters as in Table I. ^{b} See footnote b in Table I. ^{c} No unreacted formaldehyde was detected in solution at the end. A mass balance close to 100% is obtained only when the formaldehyde presumably consumed by side reactions with acetone is taken into account (see text). For the sake of comparison only the formaldehyde converted into methanol and glycolaldehyde is given.

Equimolar mixtures of [$Rh(CO)_2X_2$]$^-$ and [Rh_5-$(CO)_{15-x}L_x$]$^-$ can readily be generated "in situ" by employing more easily available starting material such as, for instance, $Rh_4(CO)_{12}$, [PPN]Cl, and PPh_3. Thus, it has been shown that $Rh_4(CO)_{12}$ disproportionates on addition of halide ions in a polar solvent and under a carbon monoxide atmosphere according to reaction 1,[15] and equilibrium 2

$$3Rh_4(CO)_{12} + 6X^- \xrightarrow{CO}$$
$$2[Rh(CO)_2X_2]^- + 2[Rh_5(CO)_{14}X]^{2-} + 4CO \quad (1)$$
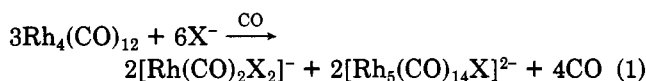
has been recently shown to be completely shifted toward the phosphine-substituted cluster.[7] Table IV shows the

$$[Rh_5(CO)_{14}X]^{2-} + PPh_3 \rightleftharpoons [Rh_5(CO)_{14}(PPh_3)]^- + X^- \quad (2)$$
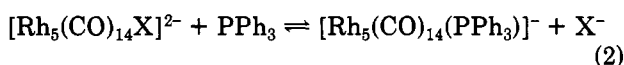
results obtained with this alternate way to generate a 1/1 [$Rh_5(CO)_{15-x}(PPh_3)_x$]$^-$/[$Rh(CO)_2Cl_2$]$^-$ system. In keeping with its overall lower average oxidation state, the activity of this 1/1 system is higher than that of the corresponding 1/5 system (particularly, when taking into account that 4.66 rather than 3.33 M solutions of CH_2O are used); however, the selectivity in glycolaldehyde of the 1/1 system more rapidly drops on addition of PPh_3.

The effect of temperature, pressure, and rhodium concentration on the catalyzed hydroformylation of formaldehyde in acetone has been investigated on a [PPN]-[$Rh_5(CO)_{15}$]/[PPN][$Rh(CO)_2Cl_2$]/PPh_3 mixture with a 1/5/10 molar ratio. The effect of varying the reaction temperature is shown in Table V. The above system is active also at 90 °C where it shows its top selectivity in glycolaldehyde (>95%). An increase in the temperature at 110 °C enhances the activity and preserves the selectivity at values of ca. 90%. In contrast both activity and selectivity decline on further raising the temperature. This, among other factors, is also due to the following reason: when the temperature is raised, the degradation of PPh_3 is accelerated, as shown by the presence in solution of increasing amounts of both benzene and benzaldehyde.

Table VI.[a] **Effect of Pressure on the Hydroformylation of Formaldehyde with the [PPN][$Rh_5(CO)_{15}$]/[$Rh(CO)_2Cl_2$]/PPh_3 (1/5/10) System**

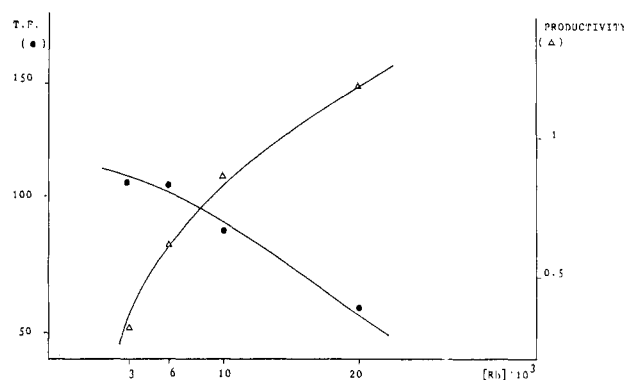| run	P, atm	convn	CH_3OH	$HCOOCH_3$	$HOCH_2$-CHO	$HOCH_2$-CH_2OH
1	80	49.2	15.2		84.8	
2	100	49.8	15.0		85.0	
3	120	80.2	9.4	2.7	87.9	
4	140	79.8	14.0		85.3	0.7

^{a} See footnotes a and b in previous tables.

Figure 2. Turnover frequency (TF, h^{-1}) and productivity (mol of glycolaldehyde/L·h) as a function of total rhodium concentration ([$Rh_5(CO)_{15}$]$^-$/[$Rh(CO)_2Cl_2$]$^-$/PPh_3 = 1/5/10; P_i = 120 atm; T = 110 °C; t = 2 h; [CH_2O] = 3.33 M).

This probably implies formation of μ-PPh_2-substituted clusters, which could account for loss of activity and selectivity.[16] Furthermore, at temperatures >120 °C increasing amounts of byproducts are obtained. The two major byproducts have been identified as 4-hydroxy-2-butanone and methyl vinyl ketone; the former derives from condensation of acetone and formaldehyde and the latter by dehydration of the former. Generally a nearly neutral reaction medium, such as acetone, seems to disfavor undesirable side reactions so that the above as well as other unidentified minor byproducts were detected only in the experiments run under the most severe conditions. In entries 3 and 4 of Table V the formaldehyde presumably consumed by these side reactions has been subtracted from the values of converted formaldehyde.

The effect of CO and H_2 (1/1) pressure has been investigated in the 80–140-atm range. As shown in Table VI, the effect of pressure on selectivity is negligible. In contrast, the effect of pressure on activity is not easily rationalized, probably because of the complexity of this system. Thus, although a significant improvement of the activity was noticed between 100 and 120 atm, no significant variation of the activity was found by further increasing the initial pressure at 140 atm.

The dependence of turnover frequency (TF, h^{-1}) and productivity (P, mol of product/L·h) of glycolaldehyde

(15) Martinengo, S.; Ciani, G.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 1059–1060.

(16) Dubois, R. A.; Garrou, P. E. *Organometallics* **1986**, *5*, 466–472. and references therein.

from the overall rhodium concentration is shown in Figure 2. The best TFs observed in these experiments are ca. 50 h^{-1}. When the overall rhodium concentration is decreased, the TF increases and values of ca. 100 h^{-1} were obtained; concomitantly the productivity decreases from ca. 1.3 to 0.3 mol of glycolaldehyde/L·h^{-1}. TFs and productivities of the same order of magnitude of those shown by the most active systems in N,N-substituted amides[2,3,6,8] or pyridines[4] are reproduced by this combined system in a common organic solvent such as acetone. The only other catalytic system so far reported that enables the hydroformylation of formaldehyde to be carried out in acetone is the Rh(PPh$_3$)$_2$(CO)Cl/PPh$_3$/NEt$_3$ system.[3] This, however, requires more severe experimental conditions and a fine tuning to avoid formation of high-boiling byproducts.[3,4]

Discussion

The results described above point out that basic solvents or promoters are not unavoidable needs of the rhodium-assisted hydroformylation of formaldehyde: comparable rate and selectivity is also displayed in their complete absence by preformed anionic rhodium precursors such as [Rh(CO)$_2$Cl$_2$]$^-$ and [Rh$_5$(CO)$_{15-x}$L$_x$]$^-$ or combinations of the two. Present results further confirm the earlier suggestion[3] that one role, if not the major, of solvents such as N,N-disubstituted amides, pyridines, and amines is to enable formation of anionic rhodium species by reduction and/or ionization; this could favor nucleophilic attack of formaldehyde on carbon.[17]

The synergetic behavior shown by combinations of [Rh(CO)$_2$Cl$_2$]$^-$ and [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ (x = 0–2) deserves some comments.[18] Of the two, [Rh(CO)$_2$X$_2$]$^-$, when X = I, is a well-known commercially exploited catalyst for the carbonylation of methanol to acetic acid.[21,22] In view of the high selecitivty in glycolaldehyde individually displayed by [PPN][Rh(CO)$_2$Cl$_2$], it appears conceivable to mainly ascribe to the latter the CO insertion step by hydroxymethyl migration.[23] Hydroxyacetyl complexes are now known for several metals, e.g., Fe,[24] Rh, and Ir.[25] Hydrogen activation seems more efficiently carried out by [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ clusters, as partially shown by their enhanced hydrogenating behavior. With presently available data it is impossible even to suggest whether formaldehyde is activated by insertion into a Rh–H bond,[26] oxidative addition,[27] or a bimolecular mechanism;[3] nevertheless, the synergetic behavior of the combined system seems to us more readily accounted for by the latter. Thus, a HOCH$_2$$^+Cl^-$ moiety, more readily produced through the

intervention of [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$, could be intercepted and more efficiently carbonylated by [Rh(CO)$_2$Cl$_2$]$^-$. Such a mechanism would account for the behavior shown by [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$/[Rh(CO)$_2$Cl$_2$]$^-$ mixtures with varied molar ratios of the two (Figure 1). However, in view of the additional presence of Rh(CO)(PPh$_3$)$_2$Cl observed at the end of some experiments, with presently available data we cannot rule out intervention in the catalytic cycle of monomeric monophosphine rhodium species, deriving by either degradation of [Rh$_5$(CO)$_{15-x}$(PPh$_3$)$_x$]$^-$ or ligand dissociation of Rh(CO)(PPh$_3$)$_2$Cl, as suggested for a related catalytic system in dimethylformamide by kinetic studies.[28]

The catalytic systems described here, probably as most catalytic systems involving phosphine ligands, undergo a slow deactivation with time, which corresponds with detection in solution of benzene and benzaldehyde and probable formation of μ-PPh$_x$ (x = 1, 2) substituted clusters. At difference with other catalytic systems,[3] attempts to stabilize the catalyst by addition of PPh$_3$ in large excess resulted in enhanced activity but in a concomitant loss of selectivity to glycolaldehyde. Related investigations on new combined homo- and heterometallic systems, as well as attempts to replace triphenylphosphine with more stable promoters, are underway and will be reported in the future.

Experimental Section

All the reactions were carried out under strict anaerobic conditions. Paraformaldehyde, glycolaldehyde, and triphenylphosphine from Merck were used as purchased. Rh$_4$(CO)$_{12}$,[29] Rh(CO)(PPh$_3$)$_2$Cl,[30] [Rh(CO)$_2$Cl$_2$]$^-$,[31] and [Rh$_5$(CO)$_{15}$]$^-$ [32] were prepared by literature methods. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer using CaF$_2$ cells; gas chromatographic analyses were performed on a Perkin-Elmer Sigma 115 instrument with the internal standard method, using either a Chromosorb 101 or a Chromosorb 107 2-m column or on a C.Erba HRGC instrument equipped with a VG Micromass SX 200 quadrupol spectrometer. Although glycolaldehyde could exist as a mixture of cyclic hemiacetals and is commercially available as the dimer, under the conditions of our direct GC analysis all hemiacetals and the commercial dimer break down to the monomeric form, as confirmed by mass spectrometry analysis.

In a typical experiment 10 mL of acetone, 1.0 g of paraformaldehyde, and the catalyst precursors were charged under a nitrogen atmosphere in a 50-mL glass reactor equipped with a magnetic stirring bar. The reactor was introduced in a 75-mL stainless steel autoclave and pressurized with CO and H$_2$. The reaction was started by plunging the autoclave into a thermostated oil bath and by stirring. The reactions were periodically tested by removing samples for gas chromatographic analysis and/or infrared monitoring from a sampling valve.

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(18) It is worth mentioning that, although we cannot rule out the degradation of the cluster under CO and H$_2$ pressure, we do not have any spectroscopic evidence of our depressurized solutions that such a fragmentation has occurred for PPh$_3$/Rh ≤ 2. Furthermore, the unsubstituted [Rh$_5$(CO)$_{15}$]$^-$ has been shown by IR[19] and NMR[20] under pressure to withstand carbon monoxide pressures much higher than those currently employed during our investigations.

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