Homogeneous catalysis in water without charged ligands. Reduction of nitrobenzene to aniline by CO/H_2O catalysed by $[Rh(CO)_4]^-$

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Abstract

We report here that $[Rh(CO)_4]^-$ (either as a K^+, Cs^+ or PPN^+ salt, $PPN^+ = (PPh_3)_2N^+$) is a very active catalyst for the reduction of nitrobenzene to aniline by CO/H_2O in water as solvent. No other ligand, except for CO itself, has to be added. The addition of bases, both inorganic or organic, has a negative effect on the reaction. The experimental conditions have been partly optimised. The reaction is selective for the nitro group.

The use of water as solvent for organic reactions has received an increasing attention during the last few years, mainly due to environmental problems and the need to reduce the toxicity of the solvents employed [1]. In a different perspective, the use of CO/H_2O as a reducing agent in place of dihydrogen has also attracted the industrial interest. The homogeneously catalysed reduction of nitroaromatic compounds to the corresponding anilines has already been reported to be catalysed by several compounds, with ruthenium [2] and rhodium [3] complexes showing the highest activities. All of these systems, however, require the use of an organic solvent to dissolve the catalyst (or the catalyst precursor) and also usually need the presence of a chelating ligand or of a large excess of a basic solvent. Such ligands may

not be so easily separated from the products in large scale applications and their recovery and recycling constitutes a problem for industrial applications. The use of large amounts of basic solvents such as pyridine, on the other hand, raises substantial environmental concern.

Rhodium clusters and some mononuclear rhodium complexes have been known for some time to be efficient catalysts for reduction [3] and carbonylation [4] reactions of nitroaromatic compounds, when activated by basic ligands, especially by chelating ones. In recent papers [5,6], we have reported that $[Rh(CO)_4]^-$ shows a better activity with respect to other rhodium systems for the carbonylation of nitrobenzene to methyl phenylcarbamate in the presence of methanol and we have shown that aniline is an intermediate in this reaction. The addition of chelating ligands was not necessary for this system and only

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Table 1
Reduction of nitrobenzene to aniline catalysed by [Rh(CO)$_4$]$^-$ [a]

Run	Cation	P_{CO}/atm	PhNO$_2$/kh mol ratio	Additives	PhNO$_2$ conversion % [b]	PhNH$_2$ selectivity % [c]	Azobenzene selectivity % [c]	Azoxybenzene selectivity % [c]
1	K$^+$	60	500		27.6	79.5	2.5	<0.2
2	K$^+$	60	500	[Et$_3$NCH$_2$Ph]Cl (0.029 mmol)	46.6	80.9	1.5	~0.5
3	K$^+$	60	500	[Et$_3$NCH$_2$Ph]Cl (0.146 mmol)	54.6	79.0	2.5	1.8
4	K$^+$	60	500	NaCl (0.146 mmol)	29.6	86.2	0.7	<0.2
5 [d]	K$^+$	60	500	[Et$_3$NCH$_2$Ph]Cl (0.029 mmol)	58.0	64.1	12.7	7.6
6	K$^+$	60	500	[PPN]Cl (0.047 mmol)	67.2	86.7	1.6	1.6
7	PPN$^+$	60	500		100	84.2	<0.2	<0.2
8	PPN$^+$	60	500	DMSO (0.35 ml)	87.7	94.4	~0.2	~0.2
9	PPN$^+$	40	1000		44.5	95.8	2.2	0
10	PPN$^+$	60	1000		79.2	94.5	<0.2	<0.2
11	PPN$^+$	80	1000		99.9	95.2	0	0
12	PPN$^+$	60	1000	pyridine (30.5 μl)	79.1	90.7	0	~0.4
13	Cs$^+$	80	1000		30.7	94.1	0	0
14	Cs$^+$	80	1000	pyridine (100 μl)	20.8	81.1	0.5	0

[a] [Rh(CO)$_4$]$^-$ = 0.047 mmol, H$_2$O = 5 ml, T = 200°C for 1.5 h. K[Rh(CO)$_4$] was added as a Me$_2$SO solution (0.35 ml); Cs[Rh(CO)$_4$] was added as a DMF solution (0.278 ml).

[b] Calculated with respect to the charged nitrobenzene.

[c] Calculated with respect to the converted nitrobenzene. The mass balance was always slightly lower than 100%. Since no other product could be detected by gas chromatography, the missing material is probably present in the form of polymeric compounds obtained by condensation reactions of aniline under the reaction conditions.

[d] NaHCO$_3$ 0.5 M in H$_2$O (5 ml) was used in place of H$_2$O.

a very small amount of an organic base was found to be required to increase the catalytic activity. Given the strict similarity between the rhodium systems used for the carbonylation and reduction of nitrobenzene and the superior performances of [Rh(CO)$_4$]$^-$ as catalyst for the first reaction, we decided to investigate if the high activity was also maintained in the synthesis of aniline. We report here that [Rh(CO)$_4$]$^-$ is an excellent catalyst for the reduction of nitrobenzene to aniline, showing very high turnovers and allowing for the use of water as the only solvent, without the addition of any base or ligand (Eq. 1):

$$\text{PhNO}_2 \xrightarrow[\text{CO, solvent H}_2\text{O}]{[\text{Rh(CO)}_4]^-} \text{PhNH}_2 \qquad (1)$$
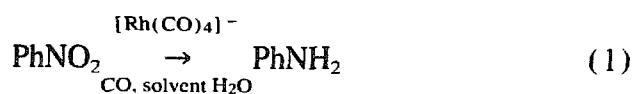
The principal results we obtained are summarised in Table 1. Since alkaline metal salts of [Rh(CO)$_4$]$^-$ are water soluble, we started our investigation from K[Rh(CO)$_4$], which has the advantage of being easily prepared in one step and in virtually quantitative yields from RhCl$_3$. This complex shows some activity in the reduction of

nitrobenzene even alone (run 1), but the conversion is markedly increased by the addition of [Et$_3$NCH$_2$Ph]Cl as a phase-transfer agent (runs 2, 3). The increase in activity is not due to the chloride anion, since the addition of NaCl has only a negligible effect on the conversion and a moderate effect on selectivity (run 4). This is in accord with the small effect of chloride anion on the [PPN][Rh(CO)$_4$] catalysed carbonylation of nitrobenzene to methyl phenylcarbamate previously reported by us [5]. On the other hand, chloride is known to be an active promoter for the Ru$_3$(CO)$_{12}$ catalyzed reactions of nitroaromatic compounds [7]. The addition of an inorganic base to the solution (NaHCO$_3$ 0.5 M) increases somewhat the conversion, but lowers the selectivity, giving substantial amounts of azo- and azoxybenzene (run 5). We have also found that the use of even more basic media (NaOH 5 M) does not lead to any further increase in activity, but increases the amount of the last two products. Moreover, substantial corrosion of the glass liner used in these reaction was observed. Azo- and

azoxybenzene can be further reduced to aniline, but more slowly [2](b), [5]. The addition of [PPN]Cl gave better results (run 6) and the use of preformed [PPN][Rh(CO)$_4$] turned out to be the best choice (run 7). Alkaline metal salts of [Rh(CO)$_4$]$^-$ are not stable in the solid state and have to be added as Me$_2$SO or DMF solutions. Since the first solvent was used for the synthesis of K[Rh(CO)$_4$], we wondered if the difference in activity between the K$^+$ and PPN$^+$ salts could be due to the presence of this solvent. Although Me$_2$SO was indeed found to have some deactivating effect (runs 7, 8), this cannot be the only reason for the difference observed (runs 6, 7, see also later for further discussion).

Using [PPN][Rh(CO)$_4$] as catalyst, turnovers up to one thousand in 1.5 h could be easily obtained. The system has not been completely optimized, but it appears that higher pressures remarkably increase the rate (runs 9–11). At variance with all other reported rhodium-based catalytic systems for the present reaction, the addition of an organic base (pyridine), not only did not increase the rate, but even decreased the selectivity (run 12). A more marked negative effect of pyridine, accompanied by a decrease in conversion, was observed for Cs[Rh(CO)$_4$] (runs 13, 14). This last catalyst was added as a DMF solution, since we found that DMF did not inhibit the reaction to any relevant extent. The cesium salt gave the worst results compared to those of the PPN.

At the end of the catalytic reactions, the catalyst is dissolved partly in the water and partly in the organic phase. This does not represent a problem in the present case, even from an industrial point of view, since aniline may be separated by steam distillation. All rhodium compounds possibly obtained under the reaction conditions are ionic and there is no ligand or cocatalyst which may distill together with aniline. The higher activity of [PPN][Rh(CO)$_4$] (which is only slightly soluble in water) with respect to the corresponding potassium and cesium salts suggests that the reaction is actually occurring in the organic phase, though other reasons may also be responsible for

the different reactivity. In previous papers [8], we have shown that the reactivity of [Cat][M(CO)$_4$] (M = Rh, Ir) towards organic halides is quite different if Cat$^+$ = PPN$^+$ or Na$^+$.

The activity of the catalytic system reported here is very high. Although comparisons between data collected in different laboratories should be made with caution, it appears that [PPN][Rh(CO)$_4$] is the most active homogeneous catalyst ever reported for the reduction of nitrobenzene to aniline [1]. In the present paper, we have used forcing conditions, in order to reach the highest turnover frequencies. However, we have observed in model studies that nitroarenes reduction to anilines with this catalyst can occur even at room temperature and atmospheric CO pressure. So the reaction appears to be very versatile and easily tunable depending on the activities required and the apparatus available.

Why all other rhodium-based catalytic systems require the presence either of a basic solvent or a chelating ligand whereas our does not is not obvious at this point. It has been proposed that chelating ligands favour the fragmentation of rhodium clusters and stabilise the so formed mononuclear species and compounds of the type [Rh(CO)$_2$(chel)]$^+$ have been proposed to be the active catalysts [3](a). However, a different explanation can be given. It has been known for sometime that basic solvents promote the reduction of several rhodium compounds, including all of the ones commonly employed as catalyst precursors for the reaction discussed in this paper, to [Rh(CO)$_4$]$^-$ and [Rh$_5$(CO)$_{15}$]$^-$ under CO/H$_2$ pressure [9]. More recently [10], it has been shown that dissolution of Rh$_4$(CO)$_{12}$ in pyridine affords [Rh(CO)$_2$(py)$_2$]$^+$ and [Rh$_5$(CO)$_{13}$(py)$_2$]$^-$. In the presence of water

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[1] In a recent paper [2](a), we reported that Ru$_3$(CO)$_{12}$, when activated by chelating Schiff bases, is a more active catalyst than [PPN][Rh(CO)$_4$] for the reduction of nitrobenzene to aniline by CO in ethanol/water. However the experimental conditions used in this paper had been optimized on the ruthenium system. When the two systems are compared *each under its ideal conditions*, the rhodium catalyst turns out to be more active. Ref. [2](a) also contains a comparison of some different catalytic systems run with the same apparatus.

and CO, the first compound is easily reduced to the second. Chelating bases were found to promote a similar reaction, even at lower concentration of base. In our laboratories, we had independently found that bipyridine promote a similar reaction of $Rh_4(CO)_{12}$ in THF under CO, at concentrations at which the addition of pyridine is completely ineffective [11]. The easy reduction of complexes of the kind $[Rh(CO)_2L_2]^+$ (were L_2 may also be a chelating ligand) indicates that they are very unlikely to be present in any relevant amount under common catalytic conditions and to be relevant species in the catalytic cycle. We have also shown that bipyridine does not bind to $[Rh(CO)_4]^-$ to any detectable extent [6]. Thus we propose that the only function of the base in all other rhodium-based catalytic systems for the reduction of nitrobenzene to aniline is simply to generate $[Rh(CO)_4]^-$, with chelating bases being much more effective than non-chelating ones. Once this last complex has been generated, the base in useless and may even have a negative effect on the reaction. This explains why, when $[Rh(CO)_4]^-$ is used as catalyst, higher activities are obtained and no base is required.

Most of the previously reported catalytic systems for the reduction of nitroaromatic compounds by CO/H_2O show a remarkable selectivity for the reduction of the nitro group in competition to keto or olefinic groups. In the present case, we have tested that $[PPN][Rh(CO)_4]$ does not reduce to any detectable extent acetone, under conditions in which nitrobenzene is completely hydrogenated.

In summary, we have reported for the first time a system which is very active and selective for the reduction of nitrobenzene to aniline and uses only water as solvent. The system is very simple and does not need the addition of any ligand, cocatalyst or base. The system is in principle applicable to any nitrocompound whose melting point is lower than 200°C. We are currently exploring the scope and limits of this catalytic system.

References

[1] (a) C.-H. Li, Chem. Rev., 93 (1993) 2023; (b) B. Cornils and E. Wiebus, CHEMTECH, (1995) 33.

[2] (a) F. Ragaini, S. Cenini and S. Tollari, J. Mol. Catal., 85 (1993) L1; (b) E. Alessio, G. Clauti and G. Mestroni, J. Mol. Catal., 29 (1985) 77; (c) T. Okano, K. Fujiwara, H. Konishi and J. Kiji, Chem. Lett., (1981) 1083; (d) H. Alper and S. Amaratunga, Tetrahedron Lett., 21 (1980) 2603; (e) K. Nomura, J. Mol. Catal., 73 (1992) L1; (f) K. Nomura, Chem. Lett., (1991) 1679; (g) K. Nomura, J. Mol. Catal. A, 95 (1995) 203.

[3] (a) E. Alessio, F. Vinzi and G. Mestroni, J. Mol. Catal., 22 (1984) 327; (b) A.F.M. Iqbal, Tetrahedron Lett., (1971) 3385; (c) T. Cole, R. Ramage, K. Cann and K. Pettit, J. Am. Chem. Soc., 102 (1980) 6182; (d) R.C. Ryan, G.M. Wilemont, M.P. Dalsanto and C.U. Pittman, Jr., J. Mol. Catal., 5 (1979) 319; (e) K. Kaneda, M. Hiraki, T. Imanaka and S. Teranishi, J. Mol. Catal., 12 (1981) 385; (f) K. Nomura, M. Ishino and M. Hazama, Bull. Chem. Soc. Jpn., 64 (1991) 2624.

[4] (a)J.H. Grate and D.R. Hamm, US Pat. 4,687,872 (1987); (b) J.H. Grate and D.R. Hamm, US Pat. 4,709,073 (1987); (c) S. Cenini, M. Pizzotti, C. Crotti, F. Ragaini and F. Porta, J. Mol. Catal., 59 (1988) 59; (d) S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni and E. Alessio, J. Mol. Catal., 64 (1991) 179.

[5] F. Ragaini, S. Cenini, A. Fumagalli and C. Crotti, J. Organomet. Chem., 428 (1992) 401.

[6] (a)F. Ragaini, S. Cenini and F. Demartin, Organometallics, 13 (1994) 1178; (b) F. Ragaini, S. Cenini and F. Demartin, J. Chem. Soc., Chem. Commun., (1992) 1467.

[7] S. Cenini, M. Pizzotti, C. Crotti and F. Porta, J. Org. Chem., 53 (1988) 1243.

[8] (a)F. Ragaini, F. Porta, A. Fumagalli and F. Demartin, Organometallics, 10 (1991) 3785; (b) F. Ragaini, F. Porta and F. Demartin, Organometallics, 10 (1991) 185; (c) F. Porta, F. Ragaini, S. Cenini, M. Pizzotti and F. Demartin, Organometallics, 9 (1990) 929.

[9] J.L. Vidal and W.E. Walker, Inorg. Chem., 19 (1980) 896.

[10] G. Fachinetti, T. Funaioli and P.F. Zanazzi, J. Organomet. Chem., 460 (1993) C34.

[11] F. Ragaini and S. Cenini, unpublished results.