

Reduction of nitrobenzene to aniline by CO/H₂O, catalysed by Ru₃(CO)₁₂/chelating diimines

Fabio Ragaini*, Sergio Cenini, Michela Gasperini

Dipartimento di Chimica Inorganica, Metallorganica e Analitica and CNR Center, via G. Venezian 21, 20133 Milano, Italy

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Abstract

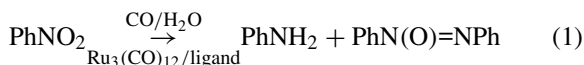
Chelating diimines of the kind bis(arylimino)acenaphtene (Ar-BIAN) and bis(phenylimino)phenanthrene (Ph-BIP) are very effective promoters for the Ru₃(CO)₁₂ catalysed reduction of nitroarenes to anilines by CO/H₂O. Their promoting efficiency for this catalytic system is higher than the one of any previously reported ligand. The corresponding quinones are also promoters for the same reaction and a comparison between several ligands under the same experimental conditions is reported. The reaction can be performed without any other solvent except water, but yields are better if ethanol is also added. The reduction is chemoselective for the nitro group with respect to olefins and keto groups. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nitrobenzene; Aniline; Ru₃(CO)₁₂; Imines; Homogeneous catalysis; Reduction; CO/H₂O

1. Introduction

The reduction of nitroaromatic compounds to the corresponding anilines by CO/H₂O is a topic of high interest for potential industrial applications. Various metals in the VIII group are known to homogeneously catalyse this transformation when activated by bases or by ligands, such as phosphines or phenanthrolines [1]. We now report that ligands of general kind bis(arylimino)acenaphtene (Ar-BIAN¹) and bis(phenylimino)phenanthrene (Ph-BIP) (Scheme 1)

are particularly efficient in activating Ru₃(CO)₁₂ in the catalytic reduction of nitrobenzene to aniline by CO/H₂O (Eq. (1)). A preliminary account of part of this work has already been published [2].



2. Results and discussion

2.1. Catalytic reactions

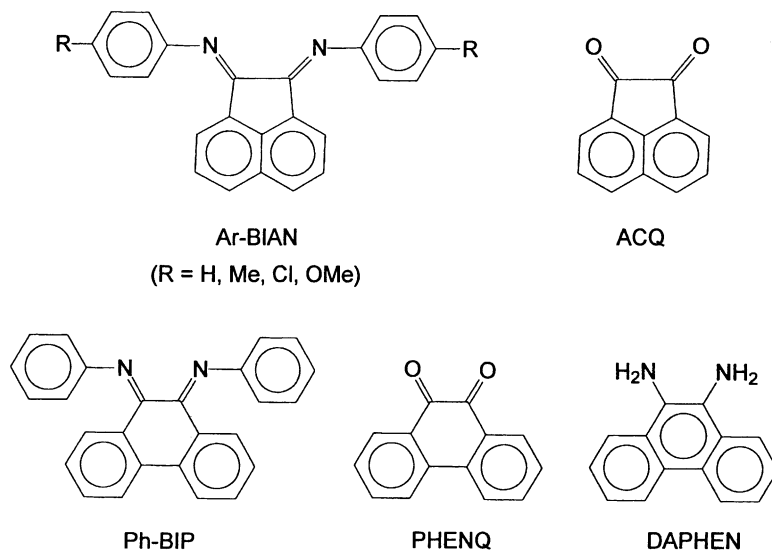
The results of our study of the reduction of PhNO₂ to PhNH₂ are reported in Table 1. As also evidenced in Eq. (1), the main by-product of the catalytic reactions is azoxy-benzene. Also present are low amounts (ca. 1%) of azo-benzene and diphenylurea. The last could be observed by GC, but not precisely quantified. Azo- and azoxy-benzene have already been shown by

* Corresponding author. Tel.: +39-02-26680675;

fax: +39-02-2362748.

E-mail address: fabio.ragaini@unimi.it (F. Ragaini).

¹ Note that in our preliminary communication on this topic, we used the name DIAN-R for these ligands. However, since other groups are using the general name Ar-BIAN for this class of ligands and this last terminology is of more general application, we have decided to adhere to this convention in order to avoid the use of different names in the literature for the same compound.



Scheme 1.

Table 1

Reduction of nitrobenzene to aniline, catalysed by $\text{Ru}_3(\text{CO})_{12}$ in the presence of nitrogen ligands^a

Entry	Ligand	Ligand/ Ru	T (°C)	Solvent (ml)	PhNO ₂ conversion (%) ^b	PhNH ₂ selectivity (%) ^c	Azoxy-benzene selectivity (%) ^c
1	Phen	1	165	EtOH (23.75) + H ₂ O (1.25)	23.7	58.1	7.5
2	Phen	1.5	165	EtOH (23.75) + H ₂ O (1.25)	5.7	78.5	21.5
3	DAPHEN	1	165	EtOH (23.75) + H ₂ O (1.25)	33.1	61.9	7.7
4	Tol-BIAN	1	165	EtOH (23.75) + H ₂ O (1.25)	43.8	61.1	4.6
5	Tol-BIAN	1.5	165	EtOH (23.75) + H ₂ O (1.25)	47.2	70.8	2.8
6	Tol-BIAN	1.5	165	EtOH (23.75) + H ₂ O (1.25)	50.0	67.1	6.3
7	Tol-BIAN	2	165	EtOH (23.75) + H ₂ O (1.25)	35.0	65.1	12.0
8	Ph-BIAN	1.5	165	EtOH (23.75) + H ₂ O (1.25)	51.2	69.4	5.4
9	<i>p</i> -ClC ₆ H ₄ -BIAN	1.5	165	EtOH (23.75) + H ₂ O (1.25)	43.3	73.8	8.0
10	<i>p</i> -MeOC ₆ H ₄ -BIAN	1.5	165	EtOH (23.75) + H ₂ O (1.25)	35.4	70.8	8.9
11	ACQ	1.5	165	EtOH (23.75) + H ₂ O (1.25)	37.4	66.0	7.7
12	Ph-BIP	1.5	165	EtOH (23.75) + H ₂ O (1.25)	46.6	65.8	7.4
13	PHENQ	1.5	165	EtOH (23.75) + H ₂ O (1.25)	45.5	69.8	24.4
14	Et ₃ N	150	165	EtOH (23.75) + H ₂ O (1.25)	38.6	77.9	5.0
15	Tol-BIAN	1.5	150	EtOH (23.75) + H ₂ O (1.25)	25.9	91.0	9.0
16	Tol-BIAN	1.5	180	EtOH (23.75) + H ₂ O (1.25)	35.1	99.0	^d
17	Et ₄ N ⁺ Cl ⁻	7/3	165	EtOH (23.75) + H ₂ O (1.25)	35.6	84.5	14.0
18	Tol-BIAN Rh ₄ (CO) ₁₂ ^e		165	EtOH (23.75) + H ₂ O (1.25)	13.3	58.5	4.3
19	Tol-BIAN	1.5	165	H ₂ O (1.25)	29.5	75.4	<1
20	Tol-BIAN	1.5	165	H ₂ O (5)	24.1	74.6	2.0
21	Tol-BIAN	1.5	180	H ₂ O (5)	29.6	71.5	4.2

^a $\text{Ru}_3(\text{CO})_{12}$ = 10 mg (1.56×10^{-2} mmol); molar ratio PhNO₂/M = 1000; P_{CO} = 30 bar; T = 165°C for 1.5 h.^b Calculated with respect to the initial nitrobenzene.^c Calculated with respect to the converted nitrobenzene.^d Analysis of azoxy-benzene not reliable.^e $\text{Rh}_4(\text{CO})_{12}$ = 1.17×10^{-2} mmol, no $\text{Ru}_3(\text{CO})_{12}$ was added Tol-BIAN/Rh = 1.5.

Lig/Ru mol ratio	Ligand (conversion %)
1	Tol-BIAN > DAPHEN > Phen 43.8 33.1 23.7
1.5	Ph-BIAN > Tol-BIAN > Ph-BIP > PHENQ > <i>p</i> -ClC ₆ H ₄ -BIAN > ACQ > <i>p</i> -MeOC ₆ H ₄ -BIAN > Phen 51.2 47.2, 50.0 46.6 45.5 43.3 37.4 35.4 5.7
2	Tol-BIAN 35.0
7/3	[Et ₃ N][Cl] 35.6
150	Et ₃ N 38.6

Scheme 2.

Mestroni et al. [3] to convert to aniline on a longer reaction time scale and we have noted that even diphenylurea reacts with water to afford aniline, probably through an intermediate hydrolysis to afford the unstable phenylcarbamic acid. Thus, the most important information in Table 1 is the conversion, which measures the activity of the catalytic system. This parameter is very important for possible industrial applications.

In the present paper, we wanted to examine the effect of different ligands (Scheme 1) and thus, we have not attempted a full optimisation of the experimental conditions, but we used the conditions optimised by Mestroni et al. [3] for most of the experiments. This last work is the most complete and reliable, at least for what it concerns the use of Ru₃(CO)₁₂ and nitrogen ligands.

Apart from Ar-BIAN and phenanthroline, we also tested as ligands acenaphthenequinone (ACQ) (the compound from which Ar-BIAN are made), 9,10-phenanthrenequinone (PHENQ) and 9,10-diaminophenanthrene (DAPHEN). This last ligand has been reported by Nomura to be an excellent promoter for the same reaction in the presence of Rh₄(CO)₁₂ as catalyst [4]. Also reported is an experiment in the presence of triethylamine (molar ratio Et₃N/Ru = 150). Amines (added in large amount) are long known promoters for the reduction of nitrobenzene to aniline [1].

It should be noted that the conversions reported by Mestroni and Nomura are often much higher than those obtained by us, even when their same catalytic systems are used. This lack of reproducibility from

one laboratory to another is not uncommon when reactions performed in autoclave are involved. Even large variations (especially in conversion) may be due to differences in the surface exposed to CO and to different kinds of stirring and heating apparatus. Thus, comparisons must be done with the data obtained in this study and not with those reported in the literature.

The reactions performed at 165°C are illustrated in Scheme 2. In this scheme, the number under the ligand represents the conversion, for a substrate/Ru molar ratio of 1000 (substrate/Ru₃(CO)₁₂ = 3000).

One of the best reactions has been repeated to test the reproducibility of the system (Table 1, entries 5 and 6). A difference of about 3% in conversion and 3.7% in selectivity in aniline was found. Though an uncertainty of this order of magnitude may alter the order of efficiency of some of the less active ligands, the general trend and the identity of the best ligand are not influenced by these oscillations.

From a rapid examination of Table 1 and Scheme 2, it can be deduced that:

1. All the ligands employed are more efficient than 1,10-phenanthroline (Phen), the best ligand of Mestroni.
2. The best ligand is Ph-BIAN, which is, however, only slightly better than Tol-BIAN. The optimal ratio with ruthenium at least for the latter is 1.5. Under these conditions, the conversion is more than double of that obtained with Phen in its optimal amount (1/1 with Ru). The importance of the ratio Lig/Ru [3] is confirmed.

- The substituent on the phenyl ring in Ar-BIAN has a sensible effect on the reaction, the order of activity being $\text{Ar} = \text{Ph} > \text{Tol} > p\text{-ClC}_6\text{H}_4 > p\text{-MeOC}_6\text{H}_4$.
- The activity of ACQ and PHENQ is particularly high, on considering that oxygen donors are usually weak ligands with metals in a low oxidation state. The reason for this activity may be the formation of the double Schiff base in situ, with the aniline produced in the reaction ($\text{Ru}_3(\text{CO})_{12}$ has a weak catalytic activity even in the absence of any promoter). It should be noted that when we used this same catalytic system for the synthesis of carbamates (working in the presence of methanol instead of water as in [5], that is under conditions in which aniline is not so easily formed) Tol-BIAN still showed an high activity, although with a low selectivity in carbamate and a higher selectivity in aniline, but PHENQ was almost inactive. However, in the present case, the Schiff base derived from PHENQ and aniline (Ph-BIP) showed a promoting activity almost indistinguishable from the one of the parent quinone. We have independently tested that under the catalytic conditions, no formation of Ph-BIP from PHENQ can be detected. Even if a small amount of Ph-BIP may have escaped detection, this result imply that most of the PHENQ must still be present as such during the catalytic reaction and coordinate unaltered to the ruthenium.
- DAPHEN has a promoting activity higher than Phen, but lower than Ar-BIAN. This activity may be due to its oxidation (in the coordination sphere of the metal) by nitrobenzene to the corresponding diimine. Oxidation of a DAPHEN molecule coordinated to ruthenium by atmospheric oxygen has been reported to give the corresponding diimino complex [6]. From the practical point of view, DAPHEN has the disadvantage of being very expensive and little stable (it must be stored in a refrigerator).
- Et_3N appears to be more interesting, especially on considering that the conditions employed are not exactly the optimal ones, reported by Nomura [7]. This promoter must, however, be added in very large amount with respect to the others.

We have also examined the dependence of the temperature on the reaction with Tol-BIAN (Table 1,

entries 5, 6, 15, 16). The best temperature has been confirmed to be 165°C , at least for what it concerns nitrobenzene conversion.

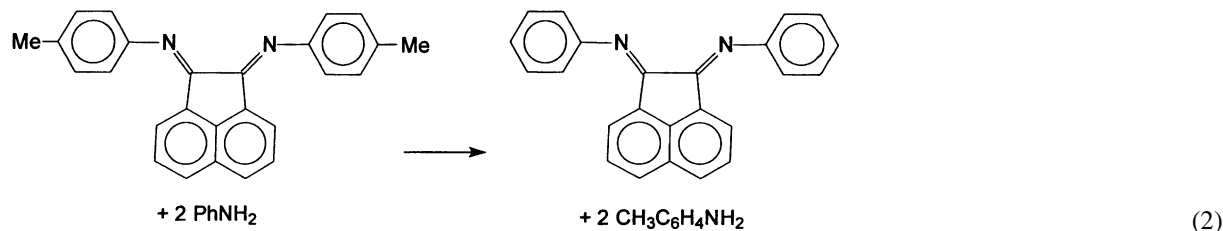
A comparison has also been made with other catalytic systems. Our system gives better conversions with respect to $\text{Ru}_3(\text{CO})_{12}/[\text{Et}_4\text{N}][\text{Cl}]$ [8], although this last system gives better conversions than the Phen promoted catalyst (Table 1, entries 8, 17, 1). Water in the reaction medium has already been shown by one of us to change the selectivity of the $[\text{Et}_4\text{N}][\text{Cl}]$ promoted system from carbamate to aniline [8]. The system was not optimised for this last reaction however. A complete optimisation has not been attempted even in this study, although the conditions here employed are surely better than the original ones. Use of rhodium instead of ruthenium gave lower results (again, however, conditions have not been optimised for this metal)(Table 1, entries 5, 6, 18).

Recently, we have reported that $[\text{PPN}][\text{Rh}(\text{CO})_4]$ is also an excellent catalyst for the reduction of nitrobenzene by $\text{CO}/\text{H}_2\text{O}$ [9]. For this last system, it proved advantageous to perform the reaction in the absence of any solvent apart from nitrobenzene and water themselves. Under these conditions, not only the catalytic system was simpler, but the reaction rate increased with respect to the one obtained in the presence of alcohols. Thus, we tested if even in the present case the elimination of ethanol was viable. The results (Table 1, entries 19–21) clearly showed that the system is still active in the absence of ethanol, but the conversion was almost halved. Increasing the water amount decreased the conversion, but increasing the temperature to 180°C restored the initial value, which remains anyway lower than the one obtained in the presence of ethanol. At the end of the reaction, two phases separate, but the ruthenium complex remains in the organic layer.

2.2. Stability of Ar-BIAN under the reaction conditions

Since Schiff bases are known to hydrolyse in aqueous solutions, we were at first worried about the stability of BIAN ligands under the reaction conditions. However, the fact that the four BIAN ligands show different activities implies that if any hydrolysis to acenaphtenequinone is occurring, it must be relatively slow with respect to the catalytic reaction. Initial at-

tempts to detect the formation of *p*-ClC₆H₄NH₂ after reactions run in the presence of *p*-ClC₆H₄-BIAN also failed. However, after a reaction run with Tol-BIAN, we could indeed observe by GC the formation of a small amount of toluidine. Since this amount was too small to allow quantification, a reaction was performed under the conditions of run 5 in Table 1, but with a 10-fold higher amount of Tol-BIAN (mol ratio ligand/Ru = 15). At the end of the reaction, the solution contained 0.85 mmol of toluidine, corresponding to 65.5% of the one initially enclosed in the ligand. Surprisingly, if nitrobenzene was omitted, no toluidine at all was formed. This implies that the formation of toluidine is not due to a simple hydrolysis of Tol-BIAN and that the aniline which is formed during the reaction in the presence of nitrobenzene plays a role (an active role of nitrobenzene itself is very unlikely). Thus, we can write the exchange reaction as in Eq. (2):

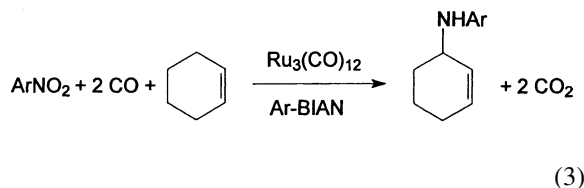


The exchange of an imine with an amine (transimination) is a reaction that has been known for more than one century [10], although it is almost completely ignored in the recent literature. We have tested that the reaction in Eq. (2) can indeed occur under the proper conditions and this part of the work will be described in a forthcoming paper. From the point of view of the reaction under investigation in this paper, the existence of the reaction in Eq. (2) implies that the catalytic system originating from different Ar-BIAN ligands will tend to display the same activity at long reaction times or if the system is recycled. The quite different results obtained in this study, however, indicate that in our reactions, the exchange was far from complete, although surely not negligible.

2.3. Identity of the active species

In recent years, we have also employed the system Ru₃(CO)₁₂/Ar-BIAN to catalyse the allylic amination

of olefins by nitroarenes under CO pressure [11–13] (Eq. (3)):



During these studies, we showed that, at least in toluene and cyclohexene, Ru₃(CO)₁₂ reacts under CO pressure at elevated temperatures (>100°C) to initially afford Ru(CO)₃(Ar-BIAN). This latter complex then enters an equilibrium reaction with CO to afford Ru(CO)₅ and free Ar-BIAN (Eq. (4)) [12]:

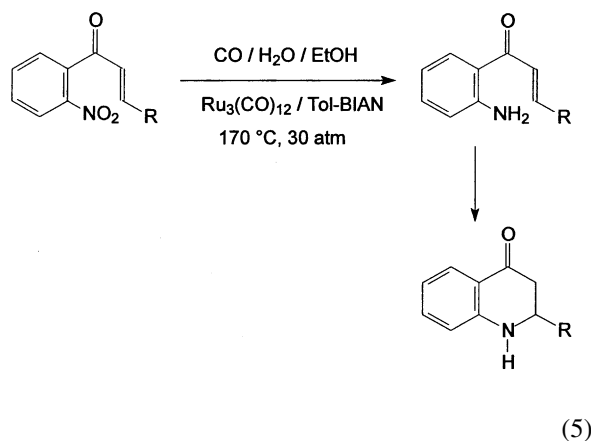


This equilibrium is more shifted on the side of Ru(CO)₅ for Tol-BIAN than for Ph-BIAN. This was attributed to the low oxidation state of ruthenium, which favours π-acidic ligands and disfavors the electron rich Tol-BIAN more than Ph-BIAN. In the same work, we also evidenced that the slow step of the amination catalytic cycle is the reaction of the nitroarene with Ru(CO)₃(Ar-BIAN) or Ru(CO)₂(olefin)(Ar-BIAN). This reaction starts with an electron transfer from the complex to the nitroarene and is favoured by electron-donating substituents on the BIAN ligand. Thus, electron-donating substituents on the ligand give catalytic system that afford higher initial activities, but faster deactivation rates. For the present reaction, the aforementioned observations are also likely to hold. This can easily explain why both *p*-ClC₆H₄-BIAN and *p*-MeOC₆H₄-BIAN afford poorer results than Ph-BIAN and Tol-BIAN. In fact, the former is too little basic to promote efficiently the reaction and the

latter is easily displaced by CO to yield the little active $\text{Ru}(\text{CO})_5$.

2.4. Selectivity towards the nitro group

Selectivity towards the nitro group is not generally a problem with the kind of catalytic system here described and all homogeneous catalysts employing $\text{CO}/\text{H}_2\text{O}$ as reductant show a high selectivity for the nitro group against other reducible groups, such as olefins or ketons [1]. In this work, we have not employed other nitroarenes apart from nitrobenzene, but we note that we have recently employed the same catalytic system to effect the cyclisation reaction shown in Eq. (5) [14,15]:



Under no conditions, we observed any product derived from the reduction of the keto or olefin group.

3. Conclusions

In conclusion, we have reported a new homogeneous catalytic system for the reduction of nitrobenzene by $\text{CO}/\text{H}_2\text{O}$, which is more active than those previously reported. Especially important is the fact that most active ligands, though not commercially available, are easily made in almost quantitative yields and in multigram amounts from low-cost materials.

4. Experimental

4.1. General procedure

Unless otherwise specified, all reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk apparatus, cannula techniques, and magnetic stirring. Absolute ethanol and water were degassed before use and stored under dinitrogen. Nitrobenzene was purified by shaking with 10% H_2SO_4 , washing with water, and drying with Na_2SO_4 , followed by distillation under dinitrogen and storage under an inert atmosphere. Ar-BIAN [12,16] and Ph-BIP [12,17] ligands and $\text{Ru}_3(\text{CO})_{12}$ [18] were synthesised as previously reported in the literature. All other compounds are commercial products and were used as received. Gas chromatographic analyses were performed on a Perkin-Elmer 8420 capillary gas chromatograph equipped with a PS 255 column. Ri values (Ri: response factor, relative to naphthalene as an internal standard) were determined by the use of solutions of known concentrations of the compounds.

4.2. Catalytic reactions

In a typical reaction, the nitroarene, $\text{Ru}_3(\text{CO})_{12}$ and the ligand (see Table 1 for reagents amounts) were weighed in a glass liner. The liner was placed inside a Schlenk tube with a wide mouth under dinitrogen and was frozen at -78°C with dry ice, evacuated and filled with dinitrogen, after which ethanol and water were added. After the solvents were also frozen, the liner was closed with a screw cap having a glass wool-filled open mouth which allows for gaseous reagents exchange and rapidly transferred to a 200 ml stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO was then charged at room temperature at the required pressure and the autoclave was immersed in an oil bath preheated at the required temperature. Other experimental conditions are reported in the caption to Table 1. At the end of the reaction, the autoclave was cooled with an ice bath, vented and the products were analysed by gas chromatography (naphthalene as an internal standard).

Acknowledgements

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