JOM 23612

Catalytic reduction of nitrobenzene to aniline with aqueous methyl formate

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(Received October 26, 1992)

Abstract

Nitrobenzene is selectively reduced to aniline by aqueous methyl formate in the presence of a catalytic system comprising $[Ru_3(CO)_{12}]$, $Pd(OAc)_2$, tricyclohexylphosphine, and 1,10-phenanthroline. The process was found to be sequential involving deoxygenation of nitrobenzene to azoxy- and azo-benzene, hydrogenation to aniline, formamidation, and eventually hydrolysis of formanilide to aniline.

1. Introduction

The reduction of nitrobenzene to aniline in the presence of a homogeneous transition metal catalyst has been widely explored since the work of l'Eplattenier *et al.* [1] using $[Ru_3(CO)_{12}]$. The catalytic activity was appreciable, but selectivity towards aniline was only moderate. The recent literature shows that this reduction can be performed either *via* direct hydrogenation [2] under water–gas shift conditions [3], or *via* generation of hydrogen from formic acid [4] or ammonium formate [5]. The latter methods have found increasing application [6]. Other methods based on stoichiometric or pseudo-catalytic use of metals have also been proposed [7,8].

In an ongoing study involving methyl formate as a source of hydrogen [9] in the reductive *N*-alkylation [10] and *N*-acylation [11] of nitroarenes, we examined the reduction of nitroarenes to aminoarenes as the first step in these processes. Due to their high reactivity under the conditions employed, the aromatic amines were never isolated. Therefore, we decided to study the reduction pathway starting from nitrobenzene with an excess of methyl formate in order to prepare aniline selectively without any applied initial gas pressure.

Whereas excellent selectivity and catalytic activity have been obtained before (see Table 8), the use of the

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methyl formate–water mixtures as the source of the reducing agent has never been reported, except for other formic derivatives [4,5,12,13,34]. In those cases, however, the turnovers were relatively low.

2. Results

2.1. Effect of the composition of the catalytic system

Under our conditions, the following products were observed: aniline, *N,N*-dimethylaniline, *N*-methylformanilide, formanilide, and in some runs, azoxybenzene and azobenzene. The first experiments focussed on the catalytic system. Our preferred transition metal catalyst was previously ruthenium, as $[Ru_3(CO)_{12}]$ is the most efficient catalyst in the decarbonylation of methyl formate [14]. However, experiments using $[Ru_3(CO)_{12}]$ (Table 1, entry 1) showed a low selectivity to aniline, which may be ascribed to slow decarbonylation [14]. Introduction of tricyclohexylphosphine (PCy_3), which was shown to promote decarbonylation of methyl formate significantly, increased the yield of aniline (entry 2). In both runs, formanilide (FA) was formed in substantial amount, together with *N,N*-dimethylaniline (DMA).

In order to increase the yield of aniline, we used a co-metal, palladium. The ternary system $[Ru_3(CO)_{12}]/$ $PCy_3/Pd(OAc)_2$ was slightly more efficient for the formation of aniline (entry 3). Omission of PCy_3 was detrimental (entry 6). It has been found that some

TABLE 1. Effect of the catalytic system on the formation of aniline from nitrobenzene [a]

Entry	PCy$_3$ [b]	Pd(OAc)$_2$	o-Phen	Conversion (%)	Yield (%)		
					Aniline	FA	DMA
1	−	−	−	100	22	46	20
2	+	−	−	100	37	45	12
3	+	+	−	100	51	36	7
4	+	+	+	100	82	12	6
5 [c]	+	+	+	100	70	19	7
6	−	+	−	100	41	44	7
7	−	+	+	100	61	28	6
8	+	−	+	100	66	2	20
9	−	−	+	100	60	32	3

[a] Nitrobenzene (9.78 mmol), methyl formate (48.6 mmol), water (27.8 mmol), [Ru$_3$(CO)$_{12}$] (0.0078 mmol), 160°C, 10 h. [b] PCy$_3$ (0.05 mmol), Pd(OAc)$_2$ (0.044 mmol), o-Phen (0.144 mmol); (+)(−) mean that the run was carried out with or without the additive. [c] Ru(acac)$_3$ was the catalyst.

nitrogen-containing aromatic ligands increase the catalytic activity of either Ru [15] or Pd catalysts [16–18]. Accordingly, we introduced 1,10-phenanthroline (o-Phen) into our catalytic system. There was a considerable improvement of the aniline selectivity (entry 4). Even in the absence of the palladium catalyst, o-Phen favoured aniline formation (entry 8 compared to entry 2, and entry 9 compared to entry 1). In order to gain a complete understanding of the effect of each component in the catalytic system, we carried out run 7. Here too, o-Phen favoured aniline formation (cf. entry 7 and entry 6). Other ruthenium compounds were also used. [Ru(acac)$_3$], which was also shown to be a decarbonylation catalyst [14], afforded aniline with a small loss in selectivity.

The results of Table 1 can be roughly summarized in the following way. The system Ru/PCy$_3$ is very active
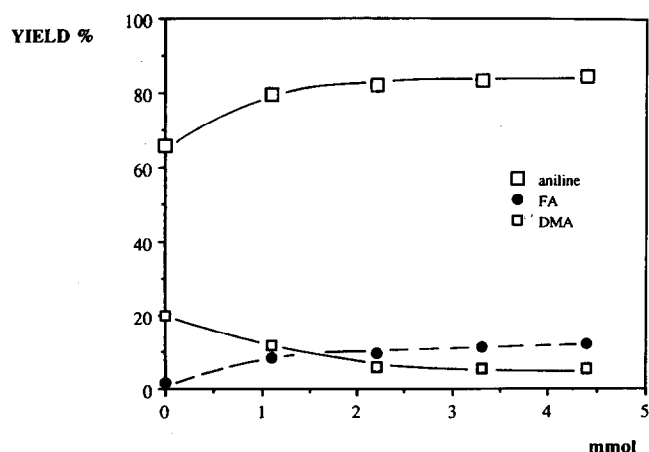
Fig. 1. Effect of the concentration of Pd(OAc)$_2$.
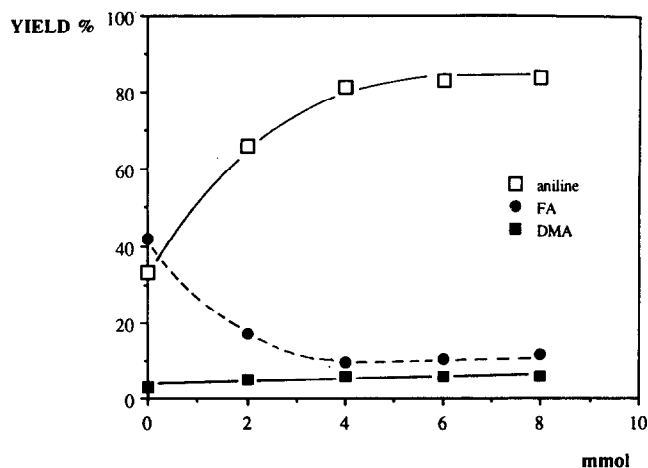
Fig. 2. Effect of the concentration of [Ru$_3$(CO)$_{12}$].

for the decarbonylation of methyl formate establishing conditions of the water gas shift reaction, whereas o-Phen + Pd and/or Ru probably influences the reduction step by stopping at the aniline stage. Without Pd or the o-Phen, aniline reacts further to yield the N,N-dimethyl derivative and the anilide. However, the reaction sequence is more complex as we showed later.

Efforts were next directed toward evaluating the effects of changing the catalyst concentration in the presence of PCy$_3$ (0.05 mmol) and o-Phen (0.144 mmol) under the conditions of Table 1 (Figs. 1 and 2).

In the absence of palladium, more DMA was formed. A small quantity of Pd(OAc)$_2$ (0.01 mmol) increased the aniline yield from 66 to 80%. The absence of [Ru$_3$(CO)$_{12}$] greatly reduced aniline selectivity, formanilide being the main product, but a small amount of the ruthenium compound again led to a high yield of aniline.

2.2. Effect of the phosphine

As shown by Table 2, PCy$_3$ favours the formation of aniline. A more basic phosphine led to a better yield of aniline while keeping the DMA content to a low level.

The concentration of the phosphine also affected the reaction (Fig. 3). A maximum yield of aniline was

TABLE 2. Effect of phosphines on the formation of aniline [a]

Entry	Phosphine (0.05 mmol)	Conversion (%)	Yield (%)		
			Aniline	FA	DMA
7	none	100	61	28	6
10	PPh$_3$	100	73	18	6
11	PBu$_3$	100	81	6	9
4	PCy$_3$	100	82	12	6

[a] Conditions as in Table 1. Pd(OAc)$_2$ (0.044 mmol), o-Phen (0.144 mmol).
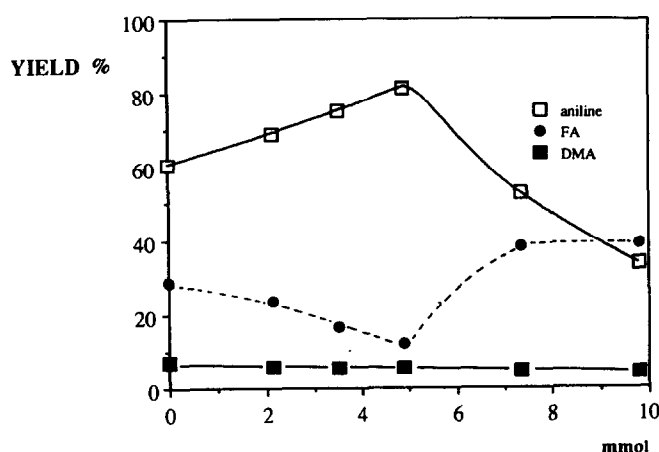
Fig. 3. Effect of the concentration of PCy₃.

observed for [PCy₃] = 0.05 mmol. Higher concentrations adversely affected the selectivity. Formanilide became the main product, whereas the yield of DMA was virtually constant within the range of concentration investigated.

2.3. Effect of the nitrogen donor

As shown in Table 1, addition of 1,10-phenanthroline to the reaction mixture considerably improved the yield of aniline, presumably due to favourable binding of the nitrogen atoms to the palladium or ruthenium. The effects of other chelating nitrogen donors are shown in Table 3.

There was no major difference between pyridine and 2,2'-bipyridine but 2-pyridinol was less efficient, possibly due to reduced σ-donation. Rigid bidentate ligands such as phenanthrolines (entries 4 and 10) were effective in directing the reaction toward aniline. The dimethyl compound is hindered due to its adjacent methyl groups. This was the reason for the lower yield of aniline despite the more powerful σ-donor properties of dimethyl-o-Phen. These results show that it is possible to modulate the selectivity by varying the steric and σ-donor properties of the chelating ligand. The effect of the ligands observed under our condi-

TABLE 3. Effect of the nature of the donor on the formation of aniline [a]

Entry	Donor (0.144 mmol)	Conversion (%)	Yield (%)		
			Aniline	FA	DMA
3	None	100	51	36	7
12	2-Pyridinol	100	60	28	5
13	Pyridine	100	67	24	6
14	2,2'-Dipyridine	100	69	23	5
15	Dimethyl-o-Phen [b]	100	76	17	5
4	o-Phen	100	82	12	6

[a] Conditions as in Table 2. PCy₃ (0.05 mmol); [b] 2,9-Dimethyl-1,10-phenanthroline.
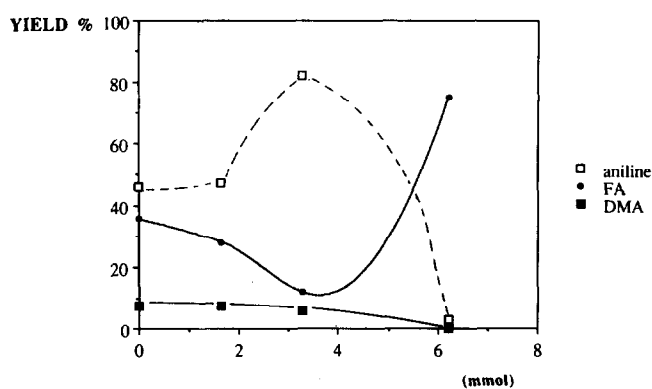

Fig. 4. Effect of the concentration of phenanthroline.

tions parallels the results reported in the reduction of nitrobenzene with $CO + H_2O$ and Rh or Ru as catalysts [19].

We studied the influence of the concentration of o-Phen (Fig. 4). This shows a dependence of the aniline yield on the [o-Phen]/[Pd] or [o-Phen]/[Ru] ratio. The catalytic activity towards formation of aniline increased as this ratio was increased up to a maximum of 3–3.5, and then decreased, an observation also made previously with [Rh₆(CO)₁₆] as catalyst and with the system $CO + H_2O$ [20]. While total conversion of nitrobenzene was observed in the concentration range up to 0.144 mmol, there was only 85% conversion when [o-Phen] = 0.277 mmol, showing that o-Phen hinders the reduction step.

2.4. Effect of a solvent

We examined the effect of three solvents of different polarity (water was present throughout). Xylene and N-methylpyrrolidone (NMP) reduced the yield of aniline whereas acetonitrile raised the selectivity to 94%. However, conversion of nitrobenzene was not total in that case (Table 4). These results show that the formation of aniline apparently does not depend on solvent basicity (cf. entries 17 and 18).

2.5. Effect of the concentration of methyl formate

Methyl formate can react in several ways. It is not only the source of CO and H_2, but it also reacts with aniline to yield formanilide. The latter reaction is evi-

TABLE 4. Effect of solvent on the formation of aniline [a]

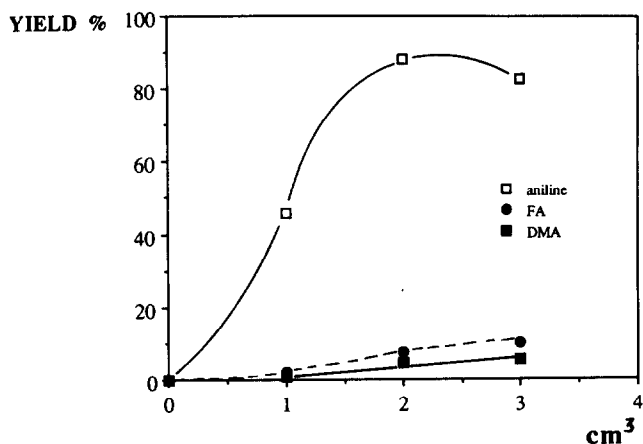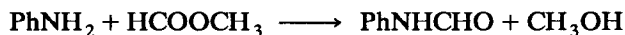| Entry	Solvent	Conversion (%)	Selectivity (%)		
			Aniline	FA	DMA
4	None	100	82	12	6
16	Xylene	100	66	31	2
17	NMP	100	62	34	3
18	Acetonitrile	87	94	3	3

[a] Conditions as in Table 2 with PCy₃ as the phosphine.

Fig. 5. Effect of the volume of methyl formate.

dently undesirable, as it prevents further reduction of nitrobenzene to aniline.

$$PhNH_2 + HCOOCH_3 \longrightarrow PhNHCHO + CH_3OH$$

The amount of methyl formate initially added was therefore expected to have an effect on the process (Fig. 5). The highest selectivity to the amine was obtained with a low concentration of formate, but conversion of nitrobenzene was modest (48%). Methyl formate was not available for further reduction as it had fully reacted. A volume ratio of formate/nitrobenzene of 2:1 was optimum (87% yield of aniline).

2.6. Effect of water

With ruthenium/phosphine catalysts, water is believed to be involved in the following way [9].
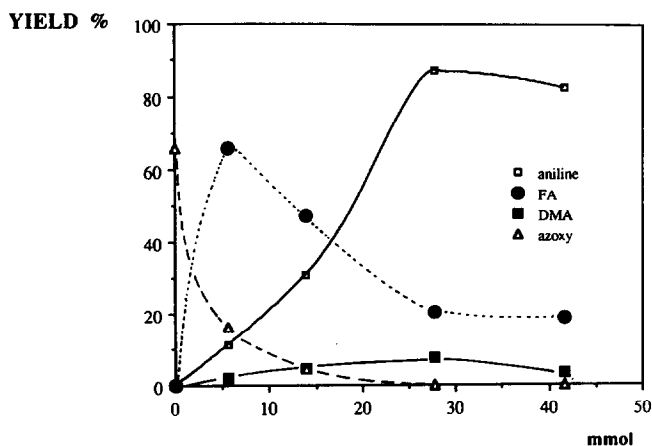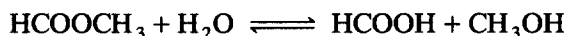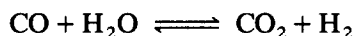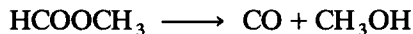
$$HCOOCH_3 \longrightarrow CO + CH_3OH$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$HCOOCH_3 + H_2O \rightleftharpoons HCOOH + CH_3OH$$

$$HCOOH \longrightarrow CO_2 + H_2$$

TABLE 5. Effect of reaction time on the nitrobenzene-methyl formate reaction [a]

Time (h)	Conversion (%)		Gas evolved [b] (mmol)
	Methyl formate	Nitrobenzene	
2.5	21	28	18.3
4	52	77	28.2
5	76	95	31.9
6.5	89	99	44.9
10	100	100	50.0
15	100	100	51.8

[a] Conditions as in Table 2 with PCy₃ as the phosphine; [b] measured at 20°C and atmospheric pressure.

When no water was added, nitrobenzene was not fully converted (74%) and the major product was azoxybenzene (see also Table 6). Some aniline was obtained, but in small amounts. In the absence of water, decarbonylation occurred less readily [9] and the following reaction was probably occurring:

$$2PhNH_2 + 3CO \longrightarrow PhN\!=\!NPh + 3CO_2$$
$$\downarrow$$
$$O$$
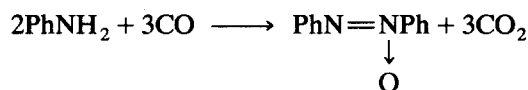
With increasing concentration of water, the rate of decarbonylation increased, as did dihydrogen production [9] leading to aniline as the major product (Fig. 6).

2.7. Effect of reaction time

Of all the variables, time might be expected to have the largest effect on nitrobenzene and methyl formate conversion as well as on product distribution, especially if the reaction products are produced sequentially. Table 5 and Fig. 7 show that this was indeed the case. There was a slow conversion rate of either nitrobenzene or methyl formate in the initial stage. After 2.5 h, nitrobenzene was rapidly converted, not to aniline, but to formanilide (Fig. 7), whereas methyl formate was

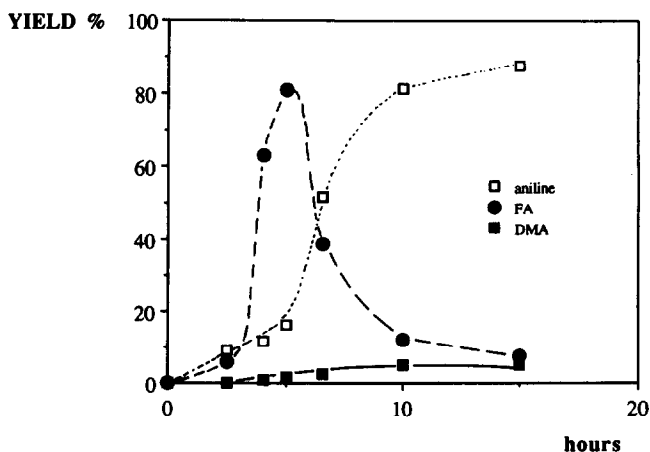Fig. 6. Effect of the concentration of water.

Fig. 7. Effect of reaction time on the course of the reaction.

fully converted to methanol only after 7 h (Table 5). At the same time, the concentration of formanilide decreased considerably in favour of aniline (*N*-alkylanilines did not form significantly during the reaction; only 5% after 15 h). This seemingly perplexing result is a strong indication that the anilide reacted further to reform aniline. As Table 5 illustrates, the volume of gas evolved increased up to 10 h.

3. Discussion

The reduction of nitrobenzene was effected in the presence of a ruthenium and a palladium compound. Bimetallic catalysis has been reported previously in the reduction of nitroarenes with Fe/Pd [21] and Co/Rh [22]. In the latter case, it was postulated that the active species was a true bimetallic anion. In the present work, it is doubtful whether Ru and Pd act synergically, since the reaction occurred with either catalyst used separately, but with a lower selectivity with respect to aniline formation.

Our results show that $[Ru_3(CO)_{12}]/PCy_3$ increases the decomposition of methyl formate while the addition of $Pd(OAc)_2/o$-Phen improves the aniline selectivity to the detriment of formate decomposition rate. Methyl formate was 76% converted only after 5 h when Pd/*o*-Phen was present whereas the conversion was 100% in their absence. However, a net advantage is that *N*-alkylation is inhibited with selective formation of aniline and formanilide, which, in turn, regenerated the amine given a long enough reaction time. Aniline was produced in the first stage of the overall reaction before conversion to formanilide. Nevertheless, we do not think that the aminoarene was the primary product. Consistent with this, in some runs we observed the formation of azoxybenzene and azobenzene. This led us to consider the specific conditions that would favour the formation of azobenzene and it was found that azobenzene was favoured when water was omitted (Table 6).

From Table 6, it is clear that it is possible for azobenzene to be the major product. The reductant

was CO since no water was present.

$$2PhNO_2 + 4CO \longrightarrow PhN{=}NPh + 4CO_2$$
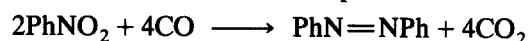
As already mentioned, azoxybenzene was an intermediate and a discrete nitrene species may be involved [23]. According to our former results [9], in the presence of water CO dominates over hydrogen during the first period in the decomposition of aqueous methyl formate. For this reason, we advocate a CO deoxygenation pathway rather than hydrogenation in the route from nitrobenzene to azobenzene. Supporting evidence was provided by determining the amount of CO_2 in the gas phase, which was much higher (63%) than the amount that would result from the water gas shift reaction only (30%) [9].

The second step was hydrogenation of azobenzene to aniline which occurred smoothly with our catalytic system (100% within 4 h). The next step was formamidation of aniline via acylation by the formate or formic acid produced by hydrolysis. The other possibility, ruthenium-catalyzed carbonylation of aniline, can be discounted, as previously shown [24]. The formamidation reaction is known to be facile [25] and explains the high yield of FA after 5 h.
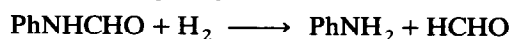
The ultimate step in the reaction sequence was regeneration of aniline from formanilide, which may occur by several pathways.
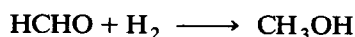
(a) decarbonylation

$$PhNHCHO \longrightarrow PhNH_2 + CO$$
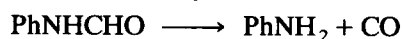
This is highly improbable, as in the Ru-catalyzed carbonylation of amines, this reverse reaction has never been observed [24].

(b) hydrogenolysis

$$PhNHCHO + H_2 \longrightarrow PhNH_2 + HCHO$$

with

$$HCHO + H_2 \longrightarrow CH_3OH$$

or decomposition [9].

(c) base-catalyzed hydrolysis

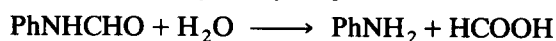$$PhNHCHO + H_2O \longrightarrow PhNH_2 + HCOOH$$

TABLE 6. Synthesis of azobenzene in methyl formate–nitrobenzene reaction [a]

Pd(OAc)₂ (mmol)	o-Phen (mmol)	Solvent	Nitrobenzene conversion (%)	Yield (%) [b]		
				Aniline	FA	Azobenzene
0	0	Methanol	100	28	19	0
0	0.36	Methanol	37	9	7	14
0.05	0.36	Methanol	86	7	14	47
0.10	0.36	None	100	31	18	36
0.10	0.36	Methanol	100	33	17	38
0.10	0.36	Mesitylene	100	17	18	55
0.10	0.36	Mesitylene [c]	62	3	3	55

[a] Methyl formate (32.4 mmol), nitrobenzene (9.78 mmol), $Ru_3(CO)_{12}$ (0.078 mmol), 180°C, 5 h; [b] remaining products included azoxybenzene and *N*-methylanilines; [c] $T = 160$°C, PCy_3 (0.05 mmol) was added.

TABLE 7. Conversion of formanilide to aniline [a]

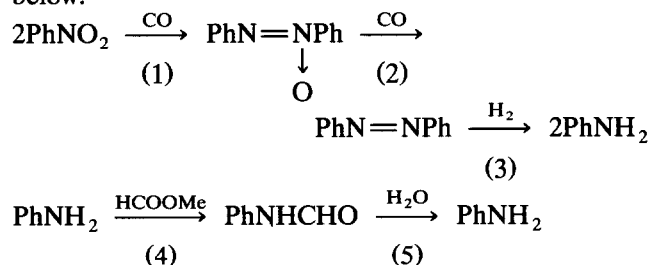| Reactant	Conversion (%)	Aniline yield (%)
H_2 (80 bar)	95	71
H_2O (27.8 mmol)	76	68

[a] Formanilide (2.44 mmol), methanol (2 cm³), $[Ru_3(CO)_{12}]$ (0.004 mmol), tri-n-propylamine (27.8 mmol), 160°C, 5 h.

with

$$HCOOH \longrightarrow CO_2 + H_2$$

In order to determine the reaction pathway, we carried out the experiments listed in Table 7. The data in Table 5 show that very little dihydrogen was generated, suggesting the hydrolysis pathway.

Accordingly, we depict the reaction sequence as below.

$$2PhNO_2 \xrightarrow{CO} PhN{=}NPh \xrightarrow{CO}$$
$$(1) \qquad\qquad \downarrow \quad (2)$$
$$O$$

$$PhN{=}NPh \xrightarrow{H_2} 2PhNH_2$$
$$(3)$$

$$PhNH_2 \xrightarrow{HCOOMe} PhNHCHO \xrightarrow{H_2O} PhNH_2$$
$$(4) \qquad\qquad\qquad (5)$$

In step 3, we favour molecular hydrogen as the reductant, although according to previous reports, H_2 does not seem to play a significant role when CO + H_2O is used [26,27]. In fact, we have found that

without methyl formate under dihydrogen (40 bar), all other conditions being constant, nitrobenzene was readily hydrogenated to aniline in 99% yield within 4 h. With CO + H_2O instead of H_2 and without methyl formate, conversion was 98.5% within 4 h but aniline (18.5%) was not the main product. Other products included formanilide (9%), azobenzene (7%) and azoxybenzene (65%). We therefore believe that a direct hydrogenation path in step 3 leading to aniline took place.

Amongst the ruthenium compounds tested, the cluster $[Ru_3(CO)_{12}]$ and $Ru(acac)_3$ were catalysts. Polynuclear species presumed to be inactive, may fragment into active mononuclear species as previously suggested for $[Rh_6(CO)_{16}]$ [15]. The o-Phen might coordinate to the mononuclear fragment to give higher concentrations of an active complex. Inhibition by an excess can be due to inhibition of breakdown of the polynuclear species. This would occur with an o-Phen/Pd ratio higher than 3.5, with a conversion of nitrobenzene of only 85%. IR spectra of the products showed bands at 2385, 2315, 2220, 2195, 2100, 2080, 2038, 1927, 1838, 1685 cm^{-1}. These do not correspond to $[HRu_3(CO)_{11}]^-$ which was invariably found in ruthenium-catalyzed reactions involving methyl formate [9,14] or to any other ruthenium intermediates [35].

A possible intermediate might be $[Pd(PCy_3)_2]$ generated in the medium. An independent run using

TABLE 8. Catalytic reduction of nitrobenzene to aniline: selected comparative data

Conditions	P (bar)	T (°C)	Σ [a]	Turnover [b]	Ref.
(a) *Using H_2 pressure*					
$[Ru_3(CO)_{12}]$	160	180	67	400	1
Complex Ru, C_6H_6-EtOH	80	125	nr	200	2
(b) *Using WGSR conditions* [c]					
$RhCl_3$, pyridine	120	150	nr	1000	28
$[PtCl_2(PPh_3)_2]$, $SnCl_4$, Et_3N	60	80	97	195	29
$[Ru_3(CO)_{12}]$, o-Phen	30	80	nr	250	16
Ru, Os catalysts, KOH	67	120	nr	680	30
Complex Ru cat., CF_3COOH	33	105	100	143	31
$Ru_3(CO)_{12}$, $^iPr_2NH$, diglyme	20	150	100	3400	27
(c) *Using bubbling CO*					
Pd/C or $Pd(OAc)_2$, Et_3NHBr	1	50–100	100	500	12
$[Ru_3(CO)_{12}]$, onium salt, NaOH	1	20	100	167	32
$[Rh_6(CO)_{16}]$, NaOH, amine	1	25	nr	1000–1700	33
$[Rh(CO)_2(acac)]$, phosphines, NaOH	1	50	nr	600–800	33
(d) *Using formic acid derivatives*					
Pd/C, $HCOONH_4$	1	20	nr	20	5
$[RuCl_2(PPh_3)_3]$, Et_3N, HCOOH	1	125	97	190	13
$[RuCl_2(PPh_3)_3]$, Pd/C, Et_3N, HCOOH	1	20	100	77	4
$[Ru_3(CO)_{12}]$, $Pd(OAc)_2$, PCy_3, o-Phen HCOOMe	1	160	94	2050	This work

[a] Selectivity to aniline, nr, not reported; [b] mole aniline mole catalyst^{-1}; [c] water gas shift reaction (CO + H_2O).

[Pd(PCy$_3$)$_2$] instead of PCy$_3$ and Pd(OAc)$_2$ led to 51% aniline and 45% formanilide.

We believe that ruthenium and palladium act independently and both catalysts are effective in step 3. However, ruthenium increases decomposition of methyl formate, whereas palladium increases the selectivity toward aniline + formanilide by inhibiting *N*-alkylation.

4. Conclusion

Aniline is selectively produced in a high yield from nitrobenzene in an unorthodox way *via* a sequential pathway in the presence of aqueous methyl formate and a catalytic system incorporating a ruthenium and a palladium compound, a phosphine and a rigid chelating ligand. The catalytic activity is among the highest reported for this reaction (Table 8). In addition, the catalytic system can be re-used with no loss of its catalytic activity. The most notable advantages of this procedure are that it requires no applied gas pressure and makes use of a cheap source of CO and H$_2$ (methyl formate).

5. Experimental details

All reagents and catalysts were used as received. In a typical run, nitrobenzene (1 cm^3, 9.8 mmol), methyl formate (2 cm^3, 32.4 mmol), water (0.5 cm^3, 27.8 mmol), [Ru$_3$(CO)$_{12}$] (2.5 mg, 0.004 mmol), Pd(OAc)$_2$ (5 mg, 0.022 mmol), tricyclohexylphosphine (14 mg, 0.05 mmol), 1,10-phenanthroline (26 mg, 0.144 mmol) and diglyme (2 mmol, GC standard) were placed in a stainless steel vessel which was sealed, heated to 160°C and shaken for 10 h.

After cooling, the autoclave was vented and the volume of gas measured. The liquid mixture was collected and analyzed by GC: Girdel 300 (FID), PPE 7% on Chr. Gaw. DMCS (Pyrex), 60–230°C, 10°C min^{-1}. In the case of formation of azoxy- or azo-benzene, the liquid products were removed by fractional microdistillation. The remaining solid was dissolved in ethanol and filtered through Celite®. The compound solidified on progressive evaporation and was analyzed by IR spectroscopy. [Pd(PCy$_3$)$_2$] was prepared in three steps (yield 30%) as described in the literature [36].

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