Reductive carbonylation of aromatic dinitro compounds with a palladium(phenanthroline)$_2$(triflate)$_2$ catalyst and an aromatic carboxylic acid as cocatalyst

Petra Wehman, Paul C. J. Kamer and Piet W. N. M. van Leeuwen*

Van't Hoff Research Institute, Department of Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Reductive carbonylation of aromatic dinitro compounds to afford valuable dicarbamates proceeds at reasonable rates and with high selectivities under the influence of a Pd(phenanthroline)$_2$(triflate)$_2$ catalyst in combination with an aromatic carboxylic acid as cocatalyst.

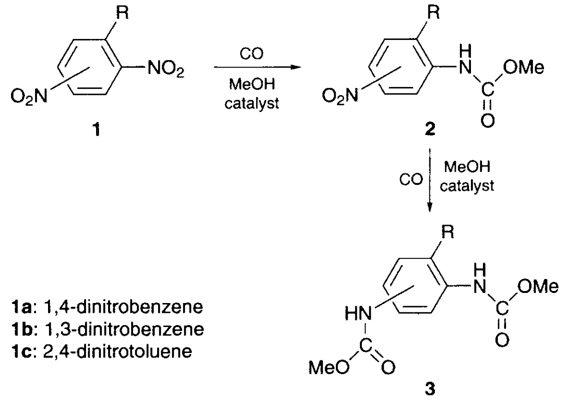
Reductive carbonylation of aromatic dinitro compounds (Scheme 1) forms an attractive route for the production of commercially important diisocyanates and dicarbamates, such as 2,4-toluene diisocyanate. Traditionally these products are prepared through the 'phosgene route', in which a diamine substrate reacts with extremely toxic phosgene gas to form a diisocyanate.[1,2] The alternative reaction with CO in the presence of Ru or Pd based catalyst systems proceeds well in the case of aromatic mono-nitro compounds.[3–9] Conversion of the commercially more important dinitro substrates, however, is much harder to provoke because of their reduced reactivity towards CO.[10,11] Here we describe the relatively fast carbonylation of aromatic dinitro compounds under the influence of a Pd(1,10-phenanthroline)$_2$(triflate)$_2$ catalyst system with an aromatic carboxylic acid as cocatalyst (Scheme 1).

The promotional effect of an acidic cocatalyst like 2,4,6-trimethylbenzoic acid was recognised previously in the reductive carbonylation of nitrobenzene with phenanthroline modified Pd–C or homogeneous Pd(acetate)$_2$–phen catalyst systems.[7,8,12,13] The general profound effect of such a cocatalyst on the Pd(phen)$_2$(OTf)$_2$ catalyst is, however, unprecedented.[14]

The Pd(phen)$_2$(OTf)$_2$ catalyst system is a stable, fairly active and selective catalyst for the reductive carbonylation of nitrobenzene (t.o.f. = 234 mol mol^{-1} h^{-1};† selectivity towards carbamate = 84%).[15] The same catalyst was also active in the conversion of the aromatic dinitro substrates **1a–c** to the corresponding monocarbamates **2a–c**, but its activity was reduced by a factor 1.7–3.8 (see Table 1). No conversion of the second nitro group was observed.‡ The differences in catalytic activity and selectivity in the conversion of 1,3-dinitrobenzene **1b** and 2,4-dinitrotoluene **1c** can be explained by the steric and electronic effects of the substituents, based on the general course found in the reductive carbonylation of various substituted mono-nitro compounds with the Pd(phen)$_2$(OTf)$_2$ catalyst.[14] Apparently the conversion of 1,4-dinitrobenzene **1a** is much harder to establish, which is probably due to the relative orientation of the nitro functions.

Use of the Pd(phen)$_2$(OTf)$_2$ catalyst for the reductive carbonylation of 3,5-dinitrobenzoic acid, a substituted dinitro compound, resulted in a surprisingly high catalytic activity. The substrate was completely converted within 2 h, which gave a t.o.f. of at least 365 mol mol^{-1} h^{-1}. The reaction also displayed a high selectivity towards the corresponding dicarbamate product (70%), whereas only 2% of the product mixture still consisted of the mono-carbamate species. A small amount of mono-carbamate in which the acid function had been esterified was also found (5%), while the other 23% of the product distribution remained as yet unidentified. As these results cannot be explained by the electronic or steric properties of the substrate,[14] the enhanced catalytic activity and selectivity appear to be caused by the presence of the carboxylic acid function. This was confirmed by the use of 4-chlorobenzoic acid as cocatalyst in the conversion of the substrates **1a–c**. Results of these experiments are given in Table 2. Both 1,3-dinitrobenzene **1b** and 2,4-dinitrotoluene **1c** were now completely converted within 2 h, resulting in turnover frequencies of at least 183 mol mol^{-1} h^{-1}. Although the mono-carbamate species **2b–c** still formed the major part of the product distribution, considerable amounts of the desired dicarbamates **3b–c** were formed. In the case of 1,3-dinitrobenzene **1b** the selectivity had been improved markedly by addition of the acidic cocatalyst. Next to the carbamate compounds (**2b**, **3b**) no other products, such as the azoxybenzene derivative, were found.

In the more difficult conversion of 1,4-dinitrobenzene **1a** an increase in activity and selectivity was also observed. The t.o.f. increased from 78 to 148 mol mol^{-1} h^{-1} while the selectivity



Scheme 1 Reductive carbonylation of aromatic dinitro compounds (R = H or Me)

Table 1 Reductive carbonylation results in the absence of a cocatalyst[a]

Substrate	t.o.f.[b]/ h^{-1} mol mol^{-1}	Product distribution (%)[b,c]				
		2	**3**	AN	AZOX	AZ
1a	61	63	0	37	0	0
1b	136	59	trace	4	19	6
1c	129	I: 59 II: 41	trace	trace	0	0
2a	78	—	100	0	0	0

[a] Reaction conditions: 7.3 mmol substrate; 0.02 mmol Pd(phen)$_2$(OTf)$_2$; 0.08 mmol phen; 5 cm^3 methanol; 5 cm^3 chlorobenzene; 60 bar CO; 135 °C; 2 h. [b] Reaction mixtures were analysed by ^{1}H NMR and GC/MS. All compounds were identified by spectroscopic methods and comparison with authentic compounds. [c] Abbreviations: AN, nitroaniline derivative; AZOX, mono-azoxybenzene derivative; AZ, mono-azobenzene derivative.

towards the mono-carbamate **2a** was enhanced to 80% at the expense of the formation of 4-nitroaniline (20%). An increase of the reaction time from 2 to 5 h gave complete conversion of the substrate with a selectivity towards the desired dicarbamate **3a** of 86%. The remaining products constituted mainly of the mono-carbamate **2a** (12%) and a small amount of 4-nitroaniline (2%). This equals a t.o.f. expressed as mol of dicarbamate **3a** formed per mol of Pd catalyst per h of 63, which is an extremely high value for the conversion of 1,4-dinitrobenzene **1a** into its dicarbamate when compared to the highest activity reported.[10] With a Pd(dppp)Cl_2 catalyst in combination with K_2CO_3 as cocatalyst at 160 °C a t.o.f. of 4 mol of dicarbamate formed per mol of Pd catalyst per h was reached, while an unknown polymeric material was formed as side product.

One of the crucial steps in the catalytic cycle involves a protonation reaction[4,8] and therefore we assign the positive influence of the benzoic acid as cocatalyst to a proton effect. On addition of acid the reaction steps following the formation of the nitroso intermediates[5,8] are probably accelerated, thus preventing the production of nitrene intermediates which could combine with the nitroso species into the undesired azoxybenzene derivatives. As a result this leads to increased activity as well as selectivity.

In conclusion, we have shown that the $Pd(phen)_2(OTf)_2$ catalyst system in combination with an aromatic carboxylic acid affords the first powerful catalyst for the reductive carbonylation of aromatic dinitro substrates.

Table 2 Reductive carbonylation results in the presence of a cocatalyst[a]

Substrate	t.o.f./ h^{-1} mol mol^{-1}	Product distribution (%)				
		2	3	AN	AZOX	AZ
1a	148	80	0	20	0	0
1a[b]	73	12	86	2	0	0
1b	183	60	40	0	0	0
1c	183	I: 46 II: 25	31	0	0	0
2a	111	—	100	0	0	0

[a] An additional 2 mmol of 4-chlorobenzoic acid was added as cocatalyst. Further conditions and analysis as mentioned in Table 1. [b] Reaction time prolonged from 2 to 5 h.

We thank the Innovation Oriented Research Programme (IOP-katalyse) for financial support.

Footnotes

† The average turnover frequencies (mol of substrate converted per mol of Pd catalyst per h) can be used to compare the activity of the catalyst system with respect to the conversion of the various nitro substrates, because the reaction was found to be approximately zero order in substrate concentration. For the dinitro substrates the t.o.f. is also expressed in mol of substrate converted per mol of catalyst per h, independent of the reaction had occurred at one or two of the nitro functions.

‡ Despite the low solubility of the aromatic dinitro substrates in methanol, the reduced activity is not a solubility problem as the addition of chlorobenzene as cosolvent did not increase the catalytic activity. Addition of the cosolvent did enhance the reproducibility of the catalytic experiments due to the absence of undissolved substrate.

References

1 P. Braunstein, *Chem. Rev.*, 1989, **89**, 1927.
2 Y. Watanabe, Y. Tsjui, R. Takeuchi and N. Suzuki, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3343.
3 A. J. Kunin, M. D. Noirot and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1989, **111**, 2739.
4 J. D. Gargulak, M. D. Noirot and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1991, **113**, 1054.
5 S. J. Skoog, J. P. Campbell and W. L. Gladfelter, *Organometallics*, 1994, **13**, 4137.
6 E. Drent and P. W. N. M. van Leeuwen, EP 86 281, 1983.
7 E. Alessio and G. Mestroni, *J. Organomet. Chem.*, 1985, **291**, 117.
8 P. Leconte, F. Metz, A. Mortreux, J. A. Osborn, F. Paul, F. Petit and A. Pillot, *J. Chem. Soc., Chem. Commun.*, 1990, 1616.
9 P. Wehman, G. C. Dol, E. R. Moorman, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. Fraanje and K. Goubitz, *Organometallics*, 1994, **13**, 4856.
10 N. P. Reddy, A. M. Masdeu, B. E. Ali and H. Alper, *J. Chem. Soc., Chem. Commun.*, 1994, 863.
11 V. L. K. Valli and H. Alper, *J. Am. Chem. Soc.*, 1993, **115**, 3778.
12 E. Alessio and G. Mestroni, *J. Mol. Catal.*, 1984, **26**, 337.
13 S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni and E. Alessio, *J. Mol. Catal.*, 1991, **64**, 179.
14 P. Wehman, L. Borst, P. C. J. Kamer and P. W. N. M. van Leeuwen, manuscript in preparation.
15 P. Wehman, V. E. Kaasjager, W. G. J. de Lange, F. Hartl, P. C. J. Kamer, P. W. M. N. van Leeuwen, J. Fraanje and K. Goubitz, *Organometallics*, 1995, **14**, 3751.

Received, 5th October 1995; Com. 5/06549F