

Reductive carbonylation of nitrobenzenes catalyzed by a new binuclear rhodium complex

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Abstract

The binuclear rhodium complex $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ is an effective catalyst for the reductive carbonylation of nitrobenzenes to carbamate esters. Electron-withdrawing groups at the para-position enhance the reactivity of the substrate in comparison with electron-donating groups.

Keywords: Rhodium complex; Nitrobenzenes; Carbamates; Reductive carbonylation; Electron-withdrawing groups

1. Introduction

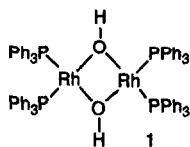
Mono- and dicarbamates are industrially important compounds useful as agricultural chemicals, pharmaceuticals and especially as precursors for isocyanates which are intermediates for the manufacture of high-performance plastics, polyurethanes, elastomers and adhesives. The present commercial production of isocyanates involves the reaction of the highly poisonous and corrosive phosgene gas with the corresponding amines. One of the most promising ways [1–4] to circumvent the difficulties in the phosgene route is the direct preparation of isocyanates as well as carbamates by the transition

metal catalyzed oxidative carbonylation of amines or the reductive carbonylation of nitro compounds. Examples of the conversion of nitro compounds to urethanes include: palladium-supported catalyst ([5] and references therein) $[\text{Pd}(\text{dppp})]\text{Cl}_2$ [6], or palladium–phenanthroline [7], ruthenium — ruthenium carbonyl or $\text{Ru}(\text{dppe})(\text{CO})_3$ [8] and rhodium — rhodium charcoal [9], rhodium chloride [10] or rhodium carbonyl complexes [1,11].

We recently developed a new and effective preparative method for the synthesis of $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ (**1**) [12], a binuclear rhodium complex with two bridging hydroxo ligands, by reacting Wilkinson's catalyst with potassium hydroxide in 75–80% yields [13]. It was anticipated that **1** would be of value as a catalyst for simple and reductive carbonylation reactions. We herein report the highly effi-

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cient reductive carbonylation of nitrobenzenes (**2**), catalyzed by **1**, to give the corresponding carbamates (**3**) in good yields.



2. Experimental

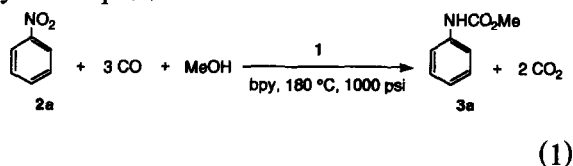
All solvents were purified by standard methods prior to use. The rhodium complex $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ (**1**) was prepared according to the literature method [13]. Nitrobenzenes (**2**) or dinitrobenzenes (**4**) and 2,2'-bipyridyl (bpy) were purchased from Aldrich Chemical Co. and were used as received. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 Spectrometer using CDCl_3 as the solvent. A Bomem MB 100-C15 (FT-IR) and a Varian 3400 instrument were used for IR and GC analyses, respectively.

2.1. General procedure for the reductive carbonylation of nitrobenzenes (**2**)

A mixture of the substrate (**2**) (2 mmol), $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ (**1**) (0.01 mmol, 14 mg), 2,2'-bipyridyl (0.2 mmol, 31 mg) and methanol (30 mmol, 1.2 ml) in dry benzene (12 ml) was placed in a 45 ml autoclave. The autoclave was flushed with carbon monoxide, subsequently pressurized to 1000 psi and then subjected to heating for 16 h at 180°C . The reaction mixture was cooled to room temperature, filtered and extracted using ether. Purification by column-chromatography (benzene-ethyl acetate) gave pure carbamate (**3**). Carbamates (**3**) were identified by comparison of spectral data (IR, NMR (^1H , ^{13}C), MS) with authentic materials.

3. Results and discussion

Treatment of nitrobenzene (**2a**) and methanol in the presence of catalytic amount (0.5 mol%) of $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ (**1**) and 2,2'-bipyridyl (bpy) in dry benzene at 180°C under 1000 psi of carbon monoxide for 16 h affords *N*-phenylmethylcarbamate (**3a**) in 94% isolated yield. Eq. (1)



The reaction is highly selective and no side products such as azo-, azoxybenzene or aniline were detected. It should be noted that using the mixed gases of carbon monoxide and hydrogen (500 psi, 500 psi) gave only reduction to form aniline in quantitative yield. 2,2'-Bipyridyl is necessary for carbonylation, as no reaction occurs in its absence. The use of a low pressure of carbon monoxide (500 psi), or low reaction temperature (120°C), gave *N*-phenylmethylcarbamate (**3a**) in low yields (23%, 65% of **2a** recovered; 30%, 64% of **2a** recovered, respectively). Using THF as solvent afforded **3a** in reduced yield, while toluene can be used instead of benzene as the reaction solvent (92%).

A variety of nitrobenzenes (**2**) were subjected to reductive carbonylation in the presence of $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ (**1**) to afford the corresponding carbamates (**3**). The results are presented in Table 1.

Generally, nitrobenzenes having electron withdrawing groups (*p*-chloro, *p*-fluoro, *p*-trifluoromethyl and *p*-carbomethoxy) showed high reactivities to give the corresponding **3** in good yields (**3m**, 64%; **3q**, 90%; **3r**, 56%; **3s**, 64%, respectively). However, nitrobenzenes with electron donating groups (*p*-methoxy and *p*-methyl) gave poor results (**3d**, 2%; **3g**, 37%). These substituent effects for the reductive carbonylation of nitrobenzenes using rhodium catalysts have not been reported previously in the

literature [9,11]. For comparative purposes, the influence of the substituent using mononuclear $(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H}$ instead of **1** as the catalyst under otherwise identical reaction conditions was examined and no clear pattern was observed (*p*-fluoronitrobenzene (**2q**), 45%; *p*-chloronitrobenzene (**2m**), 45%; nitrobenzene (**2a**), 40%; *p*-nitrotoluene (**2g**), 61%; *p*-methoxy-nitrobenzene (**2d**), 12%). Electron donating groups at the *ortho*- or *meta*-position (*o*-methoxy, *m*-methoxy, *o*-methyl and *m*-methyl) in contrast to those at the *para* position, did not inhibit the reductive carbonylation; indeed, good yields of **3** were obtained (**3b**, 54%; **3c**, 63%; **3e**, 89%; **3f**, 100%). The basicity and effective bulk of the alcohol did not significantly affect the process, with almost the same yields of the carbamates (**3m–3p**) obtained in all cases. It is conceivable that the

reaction rate is influenced by the bulk of the alcohol. The present rhodium-catalyzed reaction system is not applicable to synthesis of the cyclic carbamates. The reductive carbonylation of 4-methyl-2-nitrophenol (**2t**) with carbon monoxide under the same reaction conditions did not give the corresponding cyclic carbamate (**3t**) (64% of **2t** was recovered).

This rhodium-catalyzed reductive carbonylation reaction was next applied to the conversion of dinitrobenzenes (**4**) into the corresponding dicarbamates (**5**). However, complex mixtures of products resulted with the desired **5** formed in very low yields (Eqs. (2) and (3)). Consequently this catalytic system cannot be applied to dinitroarenes (**4**).

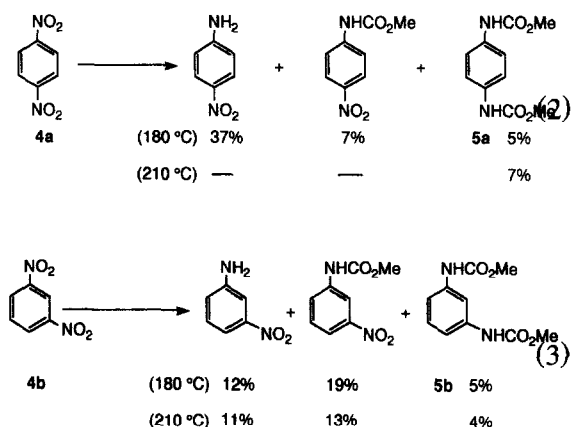
As far as the mechanism is concerned, one needs to consider whether the reaction proceeds via an amine. Attempted carbonylation of aniline under the conditions described for nitrobenzene gave recovered starting material (91%). Therefore the formation of urethanes does not occur via free amine. Recently Cenini and co-workers [14] provided evidence for a nitroso intermediate in the $\text{Rh}(\text{CO})_4^-$ catalyzed carbonylation of nitrobenzene (**2a**). The reductive carbonylation of nitrosobenzene catalyzed by **1**, under the same conditions as nitrobenzene, gave only a complex mixture of products.

Table 1
Reductive carbonylation of nitro compounds (**2**) catalyzed by Rh Cat. (1)

Carbamate (3) ^a	Yield (%) ^b	Carbamate (3) ^a	Yield (%) ^b	Carbamate (3) ^a	Yield (%) ^b
	94		84		50
	54(17)		92		54(7)
	63		69		90
	2(84)		54		56
	89		57		64
	100		64		0(64)
	37(29)		44		

^a Carbamates (**3**) were identified by comparison of spectral data [IR, NMR (^1H , ^{13}C), MS] with authentic materials.

^b Isolated yields, with the amount of recovered nitro compounds (**2**) given in parentheses.



In conclusion, the complex $[(\text{Ph}_3\text{P})_4\text{Rh}_2(\mu\text{-OH})_2] \cdot 2\text{C}_6\text{H}_6$ (**1**) and 2,2'-bipyridyl catalytic system is an excellent catalyst for the reductive

carbonylation of nitroarenes (**2**) with carbon monoxide, affording carbamates (**3**) in good yields. Interestingly, nitrobenzenes having electron withdrawing groups at the *para* position are more reactive than those having electron donating groups.

Acknowledgements

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