

Preliminary communication

THE CATALYTIC CARBONYLATION AT ATMOSPHERIC PRESSURE OF PHENYL AZIDE TO PhNCO, PhNHCONHPh AND PhNHCOOEt

GIROLAMO LA MONICA and SERGIO CENINI

Istituto di Chimica Generale and C.N.R. Center, Via G. Venezian 21, 20133 Milano (Italy)

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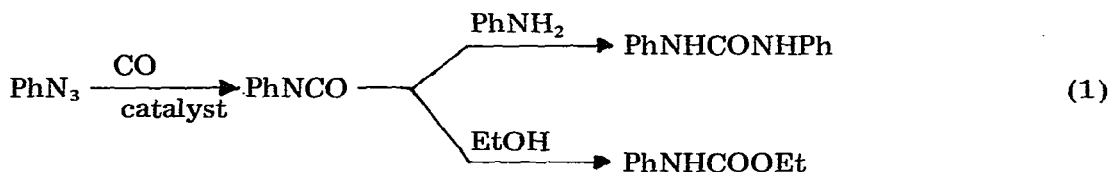
Summary

The catalytic activities of rhodium(I) complexes in the carbonylation of phenyl azide at atmospheric pressure, leading to the corresponding isocyanate have been studied. $[\text{Rh}(\text{DPE})_2]\text{Cl}$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ are the most active catalysts, and maintain their high activity even in the presence of aniline (which gives diphenylurea) or ethanol (which gives carbamate).

Transition metal complexes are being increasingly used in organic syntheses [1], because in general milder conditions are required and better selectivities can be achieved. Although organic azides undergo many reactions [2], drastic conditions must be used for the reaction with carbon monoxide to give the corresponding isocyanates ($T \sim 160\text{--}180^\circ\text{C}$ and $p(\text{CO}) \sim 150\text{--}300\text{ atm}$) [3,4] and the selectivity is rather poor (ca. 60%).

From previous studies [5,6] it is known that organic azides readily react with a transition metal carbonyl complex in a low oxidation state to give the corresponding isocyanate complex. The reaction between *p*-tolylazide and carbon monoxide in the presence of *trans*- $\text{RhX}(\text{CO})(\text{PR}_3)_2$ complexes (X = halogen; R = alkyl, aryl) has been the subject of a kinetic study, and it was observed that the reaction is favoured by more basic phosphines and the rate is independent of the carbon monoxide pressure [7].

We have now investigated the catalytic activity of a series of rhodium(I) complexes in the carbonylation reaction at atmospheric pressure of phenyl azide, in the absence and in the presence of aniline and ethanol:



The anionic complex $[\text{Rh}(\text{CO})_2\text{Cl}_2]^- [\text{AsPh}_4]^+$ (I) is a very poor catalyst for the formation of phenyl isocyanate at 80°C (Table 1), and in the presence of ethanol its activity is completely lost. Similarly, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (II) has a comparably low activity (Table 1), and again this is suppressed by ethanol. It is known that II reacts with aniline to give $\text{RhCl}(\text{CO})_2(\text{PhNH}_2)$ [8] and we found that this complex does not catalyze the carbonylation reaction; in fact, in the presence of PhN_3 and CO, II gives PhNHCONHPh in ca. stoichiometric amounts, while the rhodium species is converted into an unknown complex which does not contain carbon monoxide as ligand and which has no catalytic activity.

Much better results were obtained by using $[\text{Rh}(\text{DPE})_2]^+ \text{Cl}^-$ (III) ($\text{DPE} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (IV) as catalysts (Table 1) at lower temperature (40 – 45°C). The significance of the nature of the metal in this reaction is confirmed by the fact that the homologous iridium complex, $[\text{Ir}(\text{DPE})_2]^+ \text{Cl}^-$ is completely inactive under these conditions. Complexes III and IV are not only the most efficient catalysts, but they also maintain their activity even in the presence of aniline and ethanol, which give rise to formation of diphenylurea and ethyl carbamate, respectively (eq. 1 and Table 1). Thus at a high conversion to phenylisocyanate, aniline was added; further addition of fresh phenyl azide and aniline under a carbon monoxide atmosphere resulted in quantitative conversion of this additional phenyl azide. Similar results were obtained by adding ethanol instead of aniline, ethyl carbamate being formed.

The carbonyl complex, $[\text{Rh}(\text{DPE})_2(\text{CO})]^+ \text{Cl}^-$ is not known [9] but the corresponding iridium derivative is well characterized; the carbonyl ligand is weakly bound and can be reversibly removed by bubbling nitrogen through its solutions [10]. Thus in the system under study the formation of a labile cationic carbonyl complex can be proposed, and this must be the true catalyst. It is noteworthy that the analogous $[\text{Rh}(\text{DPP})_2\text{CO}]^+ \text{Cl}^-$ ($\text{DPP} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$) is known [11]. However, at the moment the intermediate formation of a nitrene complex [6] cannot be excluded.

TABLE 1

CATALYTIC CARBOXYLATION OF PhN_3 TO PhNCO ^a

Catalyst	Reaction		PhNCO (Yields) (%) ^b
	Temp. ($^\circ\text{C}$)	Time (h)	
$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	45	2.5	0.0
$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	80	4.5	15.7
$[\text{Rh}(\text{CO})_2\text{Cl}_2][\text{AsPh}_4]$	80	3.5	20.2
$[\text{Rh}(\text{DPE})_2]\text{Cl}^c$	45	2.5	75.3
$[\text{Rh}(\text{DPE})_2]\text{Cl}^c$	80	3.0	95.6
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	45	2.5	>98.0

^a $p(\text{CO}) = 1$ atm; $[\text{PhN}_3]_0 = 12.16 \times 10^{-2}$ mol/l; $[\text{catalyst}] = 1.49 \times 10^{-3}$ mol/l; reaction medium = *o*-dichlorobenzene; phenylazide was used as hydrocarbon solution (ICN Pharmaceuticals, Inc.). ^b Determined by using IR spectroscopy (disappearance of the $\nu(\text{N}_3)$ at 2128 and 2090 cm^{-1}). ^c $\text{DPE} = 1,2$ -bis(diphenylphosphino)ethane.

The mechanism of the catalytic carbonylation reaction is being studied and also the use of other organic azides.

Typical procedure

1) Carbon monoxide is bubbled through *o*-dichlorobenzene (25 ml) and a solution of phenyl azide (3.04×10^{-3} mol) is added with stirring the temperature being maintained at 80°C. The catalyst $[\text{Rh}(\text{DPE})_2]\text{Cl}$ (3.73×10^{-5} mol) is added. After 3.0 h the solution is found to contain 4.4% of the initial phenyl azide (IR determination), while the typical $\nu(\text{NCO})$ of the phenyl isocyanate is detected at 2260 and 2280 cm^{-1} .

2) To the above solution, aniline (2.9×10^{-3} mol) is added and diphenyl-urea separates (it is insoluble in the reaction medium). Fresh phenyl azide (3.0×10^{-3} mol) and aniline (3.04×10^{-3} mol) are again added with carbon monoxide bubbling through the mixture at 80°C. Quantitative conversion into the corresponding urea is observed.

3) The synthesis of ethyl carbamate is carried out analogously by adding ethanol instead of aniline. The carbamate is partially soluble in *o*-dichlorobenzene. Preliminary results have shown that when the non-ionic catalyst IV is used, the reaction-path remains the same as when benzene is used as solvent instead of *o*-dichlorobenzene.

Acknowledgements

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References

- 1 See for example: I. Wender and P. Pino (Eds.), *Organic Syntheses via Metal Carbonyls*, Vol. 1 and 2, John Wiley & Sons., New York, 1968–1977.
- 2 S. Patai (Ed.), *The Chemistry Of The Azido Group*, Interscience, London, 1971.
- 3 G. Ribaldone, G. Caprara and G. Borsotti, *Chim. Ind. (Italy)*, 50 (1965) 1200.
- 4 F.J. Weigert, *J. Org. Chem.*, 38 (1973) 1316.
- 5 J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, *J. Amer. Chem. Soc.*, 90 (1968) 5430.
- 6 S. Cenini and G. La Monica, *Inorg. Chim. Acta Rev.*, 18 (1976) 279 and refs. therein.
- 7 F. Fleming, K. Unverferth and K. Schwetlick, *J. Prakt. Chem.*, 317 (1975) 455.
- 8 L.M. Vallarino and S.W. Sheargold, *Inorg. Chim. Acta*, 36 (1979) 243.
- 9 D.H. Doughty and L.H. Pignolet, *J. Amer. Chem. Soc.*, 100 (1978) 7083.
- 10 M.L. Hall, B.T. Kilbourn and K.A. Taylor, *J. Chem. Soc. A*, (1970) 2539.
- 11 A.R. Sanger, *J. Chem. Soc. Dalton*, (1977) 120.