

Preliminary communication

CARBONYLATION OF NITROBENZENE WITH RUTHENIUM CLUSTERS

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Summary

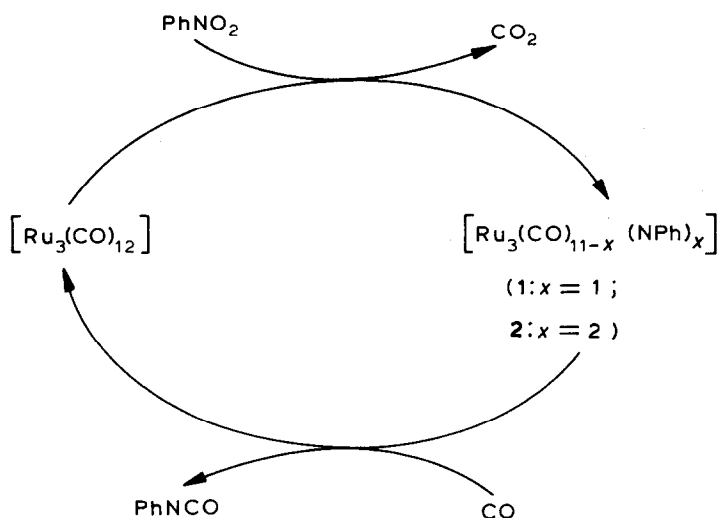
Evidence is presented for the participation of cluster intermediates in the carbonylation of nitrobenzene.

A few reports on the reductive carbonylation of nitrobenzene with carbonyl clusters as precatalysts have appeared in the last few years [1,2]. Catalytic systems have been described that give aniline or carbamate esters with high selectivities. However, as for most other cluster catalysed reactions there is little direct evidence for the participation of cluster intermediates in the catalytic cycles. In this communication we present such evidence for the selective conversion of nitrobenzene into phenyl isocyanate, a product of potential industrial importance [3].

Imido clusters **1** and **2** (see Scheme 1) have recently been characterised by X-ray diffraction [4]. Carbonylation of **1** and **2** in acetonitrile at 140°C with 300 psi of CO gives quantitative yields of $[\text{Ru}_3(\text{CO})_{12}]$. Phenylisocyanate has been shown by linked GC/MS to be the sole organic product from these reactions *. Formation of **1** and **2** from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with PhNO_2 is known to be accompanied by evolution of CO_2 [4].

These results and the observed activity of $[\text{Ru}_3(\text{CO})_{12}]$ as a catalyst in the carbonylation of nitrobenzene (see Table 1, Experiment i), clearly establish the involvement of **1** and **2** in the catalytic cycle as shown in the Scheme. At the end of a catalytic run, **1** and **2** can be isolated from the reaction mixtures in low (< 10%) yields. Formation of aniline arises from trace quantities of moisture; **1** has been found to react with water to give among other products $[\text{H}_2\text{Ru}_3(\text{CO})_9(\text{NPh})]$, a species recently characterised by X-ray diffraction and shown to be a catalytic intermediate for the formation of aniline [5].

* **1** (0.07 g, 0.1 mmol) in 10 ml acetonitrile is stirred under CO (initial pressure 300 psi) at 140°C for 3 h. PhNCO was identified on a HP 5992 instrument using a 3% OV 210 on Chromosorb WHP 80/100 column. Quantitative formation of $[\text{Ru}_3(\text{CO})_{12}]$ was indicated by the IR spectrum and TLC analysis.



SCHEME 1.

The conversion of PhNO_2 is higher in acetonitrile than in *n*-octane, possibly because of labilisation of coordinated CO in the former solvent. It should be noted that $[\text{Ru}_3(\text{CO})_{12-n}(\text{MeCN})_n]$ ($n = 1, 2$) species have recently been synthesised and isolated [6]. Recent studies have also established that the carbonyl ligands are labilized from the $[\text{Ru}_3(\text{CO})_x(\text{anion})]^{1-}$ (where $x = 10$ or 11) complex [7]. In view of this the increased activity of $[\text{HRu}_3(\text{CO})_{11}]^{1-}$ as the catalyst is not surprising (Experiment iii, iv) Cenini et al. recently reported use of a tetraalkylammonium salt as a cocatalyst along with $[\text{Ru}_3(\text{CO})_{12}]$ for the exclusive formation of carbamate esters. A mechanism was proposed involving **1** as a possible intermediate. Evidently with $[\text{HRu}_3(\text{CO})_{11}]^{1-}$ as the catalyst, additional catalytic pathways must be available, since PhNCO and PhNHCHO are formed in significant quantities. The intermediates derived from $[\text{HRu}_3(\text{CO})_{11}]^{1-}$ as the catalyst are now under investigation.

TABLE 1

ACTIVITY OF $[\text{Ru}_3(\text{CO})_{12}]$ AS CATALYST IN CARBONYLATION OF NITROBENZENE ^a

Experiment	Catalyst	Solvent	Conversion (%)	Products (%) ^b		
				PhNH_2	PhNCO	PhNHCO_2Me
i	$[\text{Ru}_3(\text{CO})_{12}]$	CH_3CN	40	6	94	
ii	$[\text{Ru}_3(\text{CO})_{12}]$	<i>n</i> -Octane	8	5	95	
iii	$[\text{HRu}_3(\text{CO})_{11}]^{1-}$	CH_3CN	100	5	95	
iv	$[\text{HRu}_3(\text{CO})_{11}]^{1-}$	CH_3OH	90 ^c	10	8	67

^a All reactions carried out in 20 ml of solvent at 140°C with an initial CO pressure of 300 psi with a catalyst to nitrobenzene molar ratio 1/60 for 3 h. ^b Calculated as a percentage of the converted nitrobenzene, thus representing selectivity. ^c PhNHCHO is formed with 15% selectivity.

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