

Transition-metal-mediated activation of arylisocyanates in supercritical carbon dioxide

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Abstract

The reactivity of arylisocyanates in supercritical carbon dioxide (scCO₂) was studied using the easily available complexes CpCo(CO)₂, CpCoPPh₃Me₂ and Ni(cod)₂ as catalysts. A study of the solubility of the catalysts in scCO₂ was undertaken in all cases. The complex CpCo(CO)₂ is very soluble, 1.7×10^{-1} mol kg⁻¹, while CpCoPPh₃Me₂ has a lower solubility, 7.2×10^{-3} mol kg⁻¹, and Ni(cod)₂ is insoluble in scCO₂. For comparison purposes, the reactions were performed in parallel in scCO₂, using toluene as a solvent and just with the neat liquid arylisocyanate. Reactions in scCO₂ either do not take place at all, when CpCo(CO)₂ is used as catalyst, or occur with low yields affording the trimer of the corresponding arylisocyanate when CpCoPPh₃Me₂ or Ni(cod)₂ act as catalysts. No incorporation of CO₂ into the organic substrate was observed. Better conversions to triarylisocyanate were obtained when the reactions were performed by direct mixture of the liquid arylisocyanate ArNCO (Ar = Ph, *p*-CH₃C₆H₄, *p*-CH₃OC₆H₄) and the catalyst. Using toluene as a solvent, the yields of the trimers were lower than those obtained in neat arylisocyanate, and in some cases they were not formed at all. For instance in the reaction of CpCo(CO)₂ and tolylisocyanate either under stoichiometric or catalytic conditions the trimer is not obtained, instead the compound H₂R₃N₃C₂O₂ (R = CH₃C₆H₄), was isolated in low yield. In the reaction of Ni(cod)₂/PPh₃ with phenylisocyanate, the trimer was formed but in low yield. The lower yields of the trimers observed when the reactions were performed in scCO₂ or in toluene, compared to that observed in neat arylisocyanates, indicates that the decrease in reactivity is due to a decrease in concentration. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently there has been a considerable growing interest in the use of supercritical carbon dioxide (scCO₂) as an environmental friendly reaction medium [1]. CO₂ presents moderate critical constants ($T_c = 31.06^\circ\text{C}$, $P_c = 73.825$ bar) and a non-toxic nature, offering many advantages over conventional solvents such as higher selectivity, increased reaction rates and facile separation of reactants, catalyst and products after reaction [2]. All these properties made scCO₂ a solvent with the potential to replace conventional organic solvents in different applications such as homogeneous catalysis [3]. scCO₂

can also be used as both solvent and reagent in reactions involving activation of the CO₂ molecule. CO₂ can be activated in the presence of transition metals, either by forming metal–CO₂ complexes, or it can be converted into organic products by reaction with the appropriate organic substrates [4]. This strategy has been recently applied in the production of tetraethylpyrone in scCO₂ by coupling of 3-hexyne and CO₂ using Ni(cod)₂/R₃P as catalyst [5]. Hydrogenation of CO₂ using ruthenium phosphine complexes as catalysts has been reported by Noyori et al. The rates of formic acid production in scCO₂ were significantly higher than those found in organic solvents [6].

We report here our first studies exploring scCO₂ as a solvent, and simultaneously as reagent, a C₁ building block. For that purpose we have systematically studied

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the reactivity of several unsaturated substrates in $scCO_2$ in the presence of transition-metal complexes. The formal electronic analogy of arylisocyanates with carbon dioxide made them suitable candidates for this study.

Activation of arylisocyanates can be achieved by the use of transition-metal complexes [7]. The complexes dicarbonyl(η^5 -cyclopentadienyl)cobalt, $CpCo(CO)_2$, bis(η^4 -1,5-cyclooctadiene)nickel, $Ni(cod)_2$ and dimethyltrifenylphosphine(η^5 -cyclopentadienyl)cobalt, $CpCoPPh_3(Me)_2$ are well known activators of unsaturated organic substrates [8] and a great deal of work involving the reactivity of these complexes towards arylisocyanates has been reported [9].

Exploring the reactivity of arylisocyanates with the above-mentioned complexes, we have found them excellent catalysts for the cyclotrimerisation reaction, when the reactions are carried out in neat arylisocyanate. The cyclotrimerisation of arylisocyanates to give triaryl isocyanurates is a well documented reaction [10], the trimers have useful applications such as activators in the synthesis of Nylon 6 and enhancing the thermal and

chemical resistance of polyurethanes and quite recently some new catalysts for this reaction have been published [11].

In this paper, we describe the reactivity of several arylisocyanates in $scCO_2$ using $CpCo(CO)_2$, $Ni(cod)_2$ and $CpCoPPh_3Me_2$ as catalysts. In Table 1 the solubility of the catalysts in $scCO_2$ is presented. Tables 2 and 3 summarise the results obtained.

2. Experimental

2.1. General

All reactions and manipulations of solutions were performed under an argon atmosphere using Schlenk techniques. Solvents were reagent grade and were dried according to literature methods, arylisocyanates were purchased from Aldrich and they were used as supplied. $CpCo(CO)_2$ [12], $CpCoPPh_3Me_2$ [13], and $Ni(cod)_2$ [14], were prepared as reported previously.

Table 1
Data for the solubility of the catalyst in $scCO_2$

Catalyst	T ($^{\circ}C$)	P (CO_2) (bar)	d (CO_2) ($g\ cm^{-3}$)	Solubility ($mol\ kg^{-1}$)
$CpCo(CO)_2$	40	84	0.36	1.4×10^{-1}
$CpCoPPh_3Me_2$	40	150	0.78	7.2×10^{-3}

Table 2
Data for the cyclotrimerisation of aryl isocyanates to yield triaryl isocyanurates in neat isocyanate

Entry	Catalyst	R-NCO	Ratio of R-NCO/catalyst	Conditions	Yield (%)
1	$CpCo(CO)_2$	p - $CH_3C_6H_4$	25:1	50 $^{\circ}C$, 24 h	42
2 ^a	$CpCo(CO)_2$	p - $CH_3C_6H_4$	25:1	40 $^{\circ}C$, 24 h ^b	53
3 ^a	$CpCo(CO)_2$	C_6H_5	25:1	90 $^{\circ}C$, 24 h ^b	21
4	$Ni(cod)_2$	p - $CH_3C_6H_4$	42:1	60 $^{\circ}C$, 24 h	62
5	$Ni(cod)_2$	p - $CH_3OC_6H_4$	42:1	60 $^{\circ}C$, 24 h	56
6	$Ni(cod)_2$	C_6H_5	42:1	60 $^{\circ}C$, 24 h	13
7	$Ni(cod)_2/PPh_3$	C_6H_5	42:1	20 $^{\circ}C$, 12 h	Complete
8	PPh_3	C_6H_5	42:4	20 $^{\circ}C$, 12 h	0
9	$CpCoMe_2PPh_3$	C_6H_5	65:1	20 $^{\circ}C$, 12 h	Complete

^a Reaction carried out using a visible lamp (200 W).

Table 3
Data for the cyclotrimerisation of aryl isocyanates to yield triaryl isocyanurates in a solvent

Entry	Catalyst	R-NCO	Ratio of R-NCO/catalyst	Solvent	Conditions	Yield (%)
1	$CpCo(CO)_2$	p - $CH_3C_6H_4$	25:1	$scCO_2$	50 $^{\circ}C$, 140 bar, 24 h	0
2 ^a	$CpCo(CO)_2$	p - $CH_3C_6H_4$	25:1	$scCO_2$	100 $^{\circ}C$, 140 bar, 24 h	0
3 ^a	$CpCo(CO)_2$	p - $CH_3C_6H_4$	25:1	Toluene	40 $^{\circ}C$, 24 h	0
4 ^a	$CpCo(CO)_2$	C_6H_5	25:1	Toluene	90 $^{\circ}C$, 24 h	0
5	$Ni(cod)_2/PPh_3$	C_6H_5	42:1	$scCO_2$	40 $^{\circ}C$, 228 bar, 24 h	9
6 ^b	$Ni(cod)_2/PPh_3$	C_6H_5	42:1	Toluene	40 $^{\circ}C$, 12 h	17
7	$CpCoMe_2PPh_3$	C_6H_5	124:1	$scCO_2$	40 $^{\circ}C$, 125 bar, 24 h	19

^a Reaction carried out using a visible lamp (300 W).

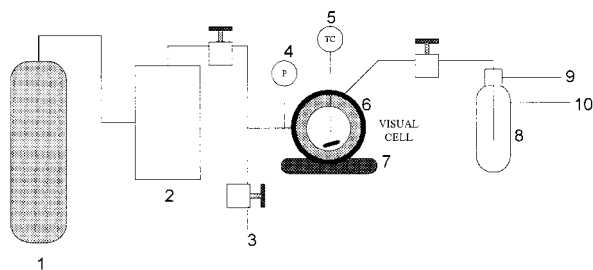


Fig. 1. 1, CO₂ cylinder; 2, pneumatic liquid pump; 3, vacuum line; 4, pressure transducer; 5, temperature controller; 6, heating tape; 7, stir plate; 8, Schlenck tube; 9, vent line; and 10, argon line.

2.2. Physical methods

Infrared spectra were recorded as mulls on NaCl plates using an ATI Mattson Genesis FTIR spectrometer.

Elemental analyses were performed at the microanalytical laboratory of the Universidade Técnica de Lisboa, Portugal.

Mass spectra were recorded on VG Autospec EI technique, at the Instituto de Ciencias de Materiales de Aragon, Zaragoza, Spain. ¹H-, and ¹³C-NMR spectra were recorded on a Bruker ARX 400 spectrophotometer. ¹H-NMR spectra were recorded using TMS as internal reference and ¹³C-NMR spectra were referenced using the ¹³C resonance of the solvent as internal standard.

2.3. Reactions in supercritical CO₂

The reactions and the solubility measurements in scCO₂ were carried out in a 30 ml stainless steel high-pressure cell. Two sapphire windows allow full observation of the inside. The cell is described elsewhere [15]. A schematic diagram of the experimental apparatus is shown in Fig. 1.

All reagents and catalysts are charged into the cell under argon, then the reactor is evacuated under vacuum and refilled with argon. The cell is then placed in the high-pressure apparatus. CO₂ (purity 99.9999% from Carbueros Metálicos) is transferred into the cell using a pneumatic liquid pump. The cell is heated to the desired temperature through a heating tape wrapped around the cell. The temperature is measured by a thermocouple inside the cell connected to a temperature controller. A digital transducer measures the pressure. The cell is on a stir plate inducing the magnetic Teflon bar inside the cell to undergo irregular movements, being a simple and effective mixing device. After reaction the cell is depressurised using an Schlenck tube as a trap. The contents of both, the cell and Schlenck tube are analysed.

2.4. Solubility measurements of the catalysts in supercritical CO₂

The solubility of the catalysts was visually determined by observing the CO₂ pressure at which the solid dissolved completely. The solubility values were calculated on the basis of the amount of solid and the calculated amount of CO₂ in the cell at the reported pressure.

2.4.1. Solubility of Co(η^5 -C₅H₅)(CO)₂

The complex (0.28 g, 1.56 mmol) was loaded into the view cell with a syringe under dry, oxygen-free argon atmosphere. The reactor was then evacuated under vacuum and refilled with argon. Finally the reactor was heated to 40°C and the CO₂ was slowly introduced. The complex was totally dissolved in CO₂ when a pressure of 84 bar was reached, producing a red solution. The solubility was 1.4×10^{-1} mol of complex per kilogram of CO₂.

2.4.2. Solubility of CpCo(CH₃)₂(PPh₃)

CpCo(CH₃)₂(PPh₃) (0.07 g, 0.17 mmol) were charged into the cell under argon. The cell was heated at 40°C and the CO₂ was introduced. A total dissolution of the complex in CO₂ was observed at 150 bar, forming an orange single phase. The solubility was 7.2×10^{-3} mol of complex per kilogram of CO₂.

2.4.3. Solubility of Ni(cod)₂

The measurement of the solubility of this complex in scCO₂ was previously carried out [5a]. We have repeated this measurement using the view cell and we have found no sign of dissolution even at high pressure of CO₂. However, it was found that the complex dissolved somewhat when it was mixed with excess of phenylisocyanate.

2.4.4. A typical reaction

A mixture of CpCo(CH₃)₂(PPh₃) (0.021 g, 0.05 mmol) and PhNCO (0.74 g, 6.2 mmol) was charged in the high-pressure cell. CO₂ was transferred into the cell using a pneumatic pump and the cell was heated immediately at 40°C. When the final temperature was reached additional CO₂ was added up to a final pressure of 125 bar. The sapphire windows allow confirmation of a single fluid phase and of complete dissolution of the catalyst and reagent in the reaction mixture. After 24 h, CO₂ was vented and the surplus was extracted with CH₂Cl₂. The extract was filtered, evaporated under reduced pressure and the solid residue was washed with 20 ml of *n*-pentane. 0.14 g (19% yield) of the trimer was isolated as a white solid. Mass spectrum (EI⁺) *m/z*: 358. The spectroscopic data agree with those reported in the literature [11].

2.5. Reactions carried out in neat arylisocyanates

2.5.1. Cyclotrimerisation of arylisocyanates using $\text{CpCo}(\text{CO})_2$ as catalyst

A mixture of $\text{CpCo}(\text{CO})_2$ (0.10 g, 0.55 mmol) and $p\text{-CH}_3\text{C}_6\text{H}_4\text{NCO}$ (1.89 g, 14.2 mmol) was heated at 50°C. A solid precipitated out of the red solution. After 24 h, 20 ml of *n*-pentane was added to remove the unreacted isocyanate. The white solid was washed with 10 ml of *n*-pentane for two repetitions and dried under reduced pressure to give 0.87 g (41% yield) of ($p\text{-CH}_3\text{C}_6\text{H}_4\text{NCO}$)₃.

The reaction was repeated using visible light (200 W). Yield: 1.12 g (53%).

¹H-NMR ($\text{CHCl}_3\text{-}d$, δ ppm): 7.30–7.26 (m, 12, CH, Ph), 2.40 (s, 9, CH₃). ¹³C{¹H}-NMR (100 MHz, $\text{CHCl}_3\text{-}d$, δ ppm): 149.0 (s, CO), 139.4, 131.2, 130.1, 128.2 (s, CH), 21.1 (s, CH₃). Mass spectrum (EI+) *m/z*: 400. Anal. Found: C, 72.19; H, 5.22; N, 10.68. Calc. for C₂₄H₂₁N₃O₃: C, 72.18; H, 5.26; N, 10.50%.

The cyclotrimerisation of PhNCO using the same procedure described above gave the corresponding trimer (PhNCO)₃ (yield: 21%). Spectroscopic data are in agreement with those reported in the literature [11].

2.5.2. Cyclotrimerisation of arylisocyanates using $\text{Ni}(\text{cod})_2$ as catalyst

A mixture of $\text{Ni}(\text{cod})_2$ (0.06 g, 0.22 mmol) and PhNCO (1.1 g, 9.2 mmol) was stirred at 60°C for 24 h. Using the same procedure described above, a solid was obtained corresponding to (PhNCO)₃ (yield: 0.14 g, 13%).

Reaction of $\text{Ni}(\text{cod})_2$ (0.025 g, 0.09 mmol) and $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NCO}$ (0.58 g, 3.9 mmol) afforded the corresponding trimer as a white solid. Mass spectrum (EI+) *m/z*: 448. Yield: 0.32 g (56%). Spectroscopic data are in agreement with those reported in the literature [11].

When the cyclotrimerisation reaction of PhNCO with $\text{Ni}(\text{cod})_2$ as catalyst was repeated adding four equivalents of PPh_3 , after 24 h at room temperature (r.t.), a total conversion to the trimer was observed. If toluene is used as solvent, after 24 h at 40°C only a 17% yield of trimer was formed.

No formation of trimer was achieved when a solution of PPh_3 (0.23 g, 0.88 mmol) and PhNCO (1.1 g, 9.2 mmol) was stirred at r.t. for 24 h.

2.5.3. Cyclotrimerisation of arylisocyanates using $\text{CpCo}(\text{CH}_3)_2(\text{PPh}_3)$ as catalyst

$\text{CpCo}(\text{CH}_3)_2(\text{PPh}_3)$ (0.017 g, 0.04 mmol) and PhNCO (0.31 g, 2.52 mmol) were mixed and stirred at r.t. After 24 h, all the initial PhNCO had trimerised to give (PhNCO)₃. The reaction was worked out using the same procedure described in Section 2.4.1.

2.6. Reactions carried out in toluene: preparation of $\text{H}_2\text{R}_3\text{N}_3\text{C}_2\text{O}_2$ ($\text{R} = \text{CH}_3\text{C}_6\text{H}_4$) (**4**)

$p\text{-CH}_3\text{C}_6\text{H}_4\text{NCO}$ (1.89 g, 14.2 mmol) was added to a toluene (15 ml) solution of $\text{CpCo}(\text{CO})_2$ (0.10 g, 0.55 mmol). The resulting red solution was stirred at 50°C for 24 h and the toluene was then removed under vacuum. The red oil was washed with *n*-pentane and the resulting solid was extracted with diethyl ether. Cooling the solution at –20°C afforded the compound **4** as a white crystalline solid. Yield: 0.12 g (7%). No presence of the trimer was observed.

When the reaction was repeated at the same conditions, but heated at 85°C for 24 h, 0.17 g of **4** was obtained (yield: 10%).

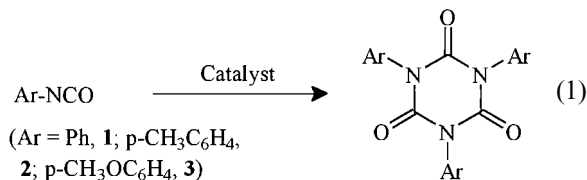
¹H-NMR ($\text{CHCl}_3\text{-}d$, δ ppm): 8.92 (sa, 2, NH), 7.39–7.11 (m, 12, CH, Ph), 2.46 (s, 3, CH₃), 2.32 (s, 6, CH₃). ¹³C{¹H}-NMR (100 MHz, $\text{CHCl}_3\text{-}d$, δ ppm): 153.8 (s, CO), 140.0, 134.8, 134.1, 134.0, 131.2, 129.6, 120.8 (s, CH), 21.1 (s, CH₃), 20.6 (s, CH₃). Mass spectrum (EI+) *m/z*: 374. Anal. Found: C, 73.92; H, 6.26; N, 11.05. Calc. for C₂₃H₂₃N₃O₂: C, 73.93; H, 6.17; N, 11.26%.

3. Results and discussion

The solubility test of the catalyst consists in the visual inspection through the sapphire windows of the high-pressure cell. A known amount of catalyst was placed inside the cell under inert conditions, then it was connected to a high-pressure line and CO₂ was transferred into the cell using a pneumatic pump. The temperature of the cell was kept constant at 40°C. When a single phase (total disappearance of the solid) was observed inside the cell, a measure of the pressure was taken, and the solubility calculated in mole per kilogram. The complex $\text{CpCo}(\text{CO})_2$ is very soluble, giving a beautiful red colour, $\text{CpCoPPh}_3\text{Me}_2$ is moderately soluble, whereas the complex $\text{Ni}(\text{cod})_2$, as it was previously reported by Kreher et al. [5a], is practically insoluble. However, when $\text{Ni}(\text{cod})_2$ is mixed with an excess of arylisocyanate in *sc*CO₂, a light yellow mixture is formed, showing that the arylisocyanate acts as a co-solvent giving rise to a small solubility of the complex. After these measurements, the starting compounds were recovered in all cases, no reaction with CO₂ was observed for any of the compounds.

In order to compare the results obtained using *sc*CO₂ as reaction medium, the reactions of the arylisocyanates ArNCO (Ar = Ph, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$) and the catalysts ($\text{CpCo}(\text{CO})_2$, $\text{CpCoPPh}_3\text{Me}_2$ or $\text{Ni}(\text{cod})_2$) were performed, in the first place, simply by direct mixture of the catalyst with the neat liquid arylisocyanate, without the use of a solvent (these results are presented in Table 2). Trimers of the corresponding

arylisocyanate were obtained in all cases (see Eq. (1)), with yields ranging from the lowest, 13%, in the case of Ni(cod)₂ and PhNCO, to completed reaction, obtained, for instance, with the same reagents but with addition of PPh₃ in a 1:4 ratio (Ni(cod)₂: PPh₃). To see whether PPh₃ would catalyse the trimerisation by itself, a reaction was carried out with just PPh₃ and phenylisocyanate and no sight of the trimer was observed. A completed reaction was also observed when CpCoPPh₃Me₂ was used as catalyst.



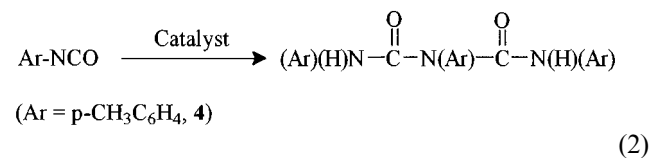
The trimers (PhNCO)₃ (**1**), (*p*-CH₃C₆H₄NCO)₃ (**2**), and (*p*-CH₃OC₆H₄NCO)₃ (**3**), obtained as white solids, were characterised by infrared spectroscopy, ¹³C- and ¹H-NMR, mass spectrometry, and in some cases by elemental analysis, and compared with the data reported in the literature [11].

The reactions chosen to be performed in scCO₂ were those presenting higher yields in neat arylysocyanates. They were performed as reported in Section 2 (see Fig. 1) and the results are summarised in Table 3. The catalyst and the arylysocyanate were placed in a high-pressure cell with sapphire windows (for observation purposes), charged with CO₂ to the required pressure and heated at the reaction temperature, giving, in all cases, a fully homogenous single-phase reaction. After reaction, CO₂ was carefully vented through a cold trap leading to the precipitation of a white solid inside the cell. In all cases the only isolated products were the arylysocyanate trimers. The incorporation of CO₂ into the organic substrate was not observed in any case and no other organic products were isolated.

In all cases the yields for the cyclotrimerisation reactions were lower than in the analogous reactions carried out in neat arylysocyanates. For instance, in the reaction of CpCo(CO)₂ with *p*-CH₃C₆H₄NCO, even under quite drastic conditions, no traces of the trimer were found and the reagents were recovered unreacted. In the case of Ni(cod)₂/PPh₃ and CpCoPPh₃Me₂, the trimer was obtained in a low yields. The decrease in reactivity in scCO₂, compared to that observed in neat arylysocyanates, could be due to the decrease in concentration. In order to study the concentration effect, selected reactions were carried out in toluene.

In the reactions performed using CpCo(CO)₂ as catalyst using toluene as a solvent (the results are summarised in Table 3), either under stoichiometric or catalytic conditions, the trimer was not obtained at all. When the reaction was done with tolylisocyanate, the compound H₂R₃N₃C₂O₂ (R = CH₃C₆H₄) (**4**) (see Eq.

(2)) was isolated instead, in low yield. The formation of this compound, which was characterised by ¹³C- and ¹H-NMR, IR, mass spectrometry and elemental analyses, is not clear. Hoberg [9a] described the formation of the similar compound H₂R₃N₃C₂O₂ (R = C₆H₅) in the reaction of Ni[0] complexes and phenylisocyanate, obtained by protolysis of a six membered nickelacycle. In the reaction of Ni(cod)₂-PPh₃ with phenylisocyanate using toluene as a solvent the trimer was formed in low yield.



Therefore, we conclude that the complexes CpCo(CO)₂, Ni(cod)₂ and CpCoPPh₃Me₂, cannot simultaneously activate arylysocyanate and CO₂ when the reactions are performed in scCO₂, instead, the arylysocyanate trimers are obtained in low yield. Much better yields for the cyclotrimerisation are obtained when the reactions are carried out in neat arylysocyanate. In toluene, similar to the reactions in scCO₂, the yields of the trimers are very low, indicating that the decrease in reactivity in scCO₂ and toluene compared to that observed in neat arylysocyanates is due to the decrease in concentration.

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