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$CpCo(CO)_2$-catalysed cyclotrimerisation of alkynes in supercritical carbon dioxide

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Abstract

The reactivity of mono-substituted $HC\equiv CR$ (R = Ph, **a**; CH_2OH, **b**; $CH_2CH_2CH_2CH_3$, **c**) and di-substituted $RC\equiv CR$ (R = CH_2CH_3, **d**; CO_2CH_3, **e**; Ph, **f**) acetylenes was studied in supercritical carbon dioxide ($scCO_2$) using the easily available complex $CpCo(CO)_2$ as catalyst. The reaction of phenylacetylene produced a mixture of the isomeric cyclotrimers 1,3,5- (**2a**) and 1,2,4-triphenylbenzene (**2a′**), in a 1:5 ratio, and traces of cobaltcyclopentadienone complexes $CpCo(\eta^4\text{-}C_4H_2[Ph]_2CO)$ (**6a**, mixture of isomers). The possible product formed by the incorporation of CO_2 to alkynes, i.e. diphenylpyrone (**7a**) was not observed. The reaction of the cobaltacyclopentadiene complex $CpCo(1.4\text{-}\sigma\text{-}C_4[Ph]_4)(PPh)_3$ (**8f**), in $scCO_2$, was performed. No insertion of CO_2 into the Co–C σ-bond to form tetraphenylpyrone (**7f**) by reductive elimination was observed, instead the cobaltcyclobutadiene complex $CpCo(\eta^4\text{-}C_4[Ph]_4)$ (**9f**) was formed. In the reactions with other alkynes, lower yields were obtained in general, except in the cyclotrimerisation of the highly activated alkyne, propargyl alcohol (**b**). Reaction of the non-activated alkynes, 1-hexyne (**c**) and 3-hexyne (**d**), produced complex mixtures of cobalt complexes in low yield in which the alkyne was coordinated to cobalt. Finally, the highly hindered diphenylacetylene (**f**) gave a mixture of the known complexes $CpCo(\eta^4\text{-}C_4[Ph]_4)$ (**9f**) and $CpCo(\eta^4\text{-}C_4[Ph]_4CO)$ (**6f**) in agreement with the results observed in conventional organic solvents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical CO_2; Alkyne; $CpCo(CO)_2$; Cyclotrimerisation

1. Introduction

Interest in supercritical carbon dioxide ($scCO_2$) as reaction medium has greatly expanded in the last few years [1], mainly as an alternative to conventional organic solvents. Advantages of using $scCO_2$ include higher selectivity, increased reaction rates and easy separation of reactants, catalyst and products after reaction [2]. Moreover, $scCO_2$ is non-toxic, non-flammable, cheap, and presents moderate critical constants ($T_c = 31.06$ °C, $P_c = 73.825$ bar). All these properties demonstrate the potential of $scCO_2$ as an alternative substitute of the environmental unfriendly organic solvents in a number of applications, in particular in the world of catalysis [3]. Special interest has been focussed on the use of $scCO_2$ as a solvent and simultaneously as a reagent, as a C_1 building block [4,5].

We are interested in this dual behaviour of $scCO_2$ both as solvent and as reactant. For that purpose, we have systematically studied the reactivity in $scCO_2$ of several unsaturated organic substrates in the presence of transition metal complexes. Thus, we have recently studied the metal-complex mediated activation of arylisocyanates in $scCO_2$ [6].

As an extension of our own work in this area, we describe here the reactivity of alkynes in $scCO_2$ using the cobalt(I) complex dicarbonyl(η^5-cyclopentadienyl)-cobalt, $CpCo(CO)_2$, as activator. As discussed below, in all the reactions studied the observed products from alkyne activation were either the corresponding cyclotrimers or cobalt compounds with the alkyne coordinated. However, no coupling of CO_2 and alkyne was observed in any case.

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Cyclotrimerisation of alkynes to give benzene derivatives is a typical metal-catalysed reaction, proceeding with a wide range of transition metal systems [7], the complex $CpCo(CO)_2$ being one of the most effective catalysts [8]. This reaction is well known in conventional solvents and has been recently carried out in supercritical water [9], but to the best of our knowledge, there are no studies performed in $scCO_2$.

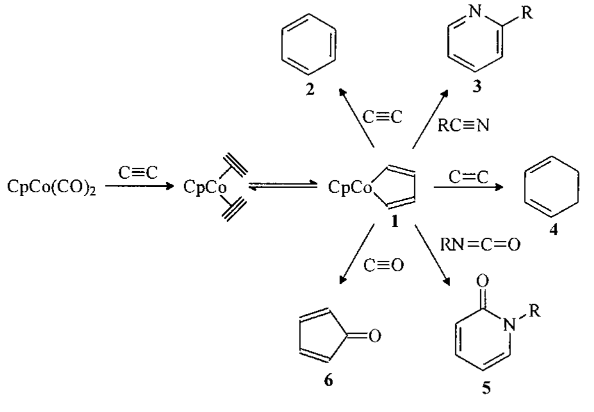
Herein, we present the reactivity of both mono-substituted $HC{\equiv}CR$ (R = Ph, **a**; CH_2OH, **b**; $CH_2CH_2CH_2CH_3$, **c**) and di-substituted $RC{\equiv}CR$ (R = CH_2CH_3, **d**; CO_2CH_3, **e**; Ph, **f**) acetylenes in $scCO_2$, catalysed by $CpCo(CO)_2$. For comparison purposes, in some cases, the reactions were performed in parallel in toluene and in neat alkyne.

2. Results and discussion

We have studied the reactivity of several alkynes in $scCO_2$ using the complex $CpCo(CO)_2$ as activator.

The cobalt complex $CpCo(CO)_2$ is a well-known catalyst in the intermolecular co-cyclisation of two alkynes with an unsaturated substrate. The cobaltacyclopentadiene derivative **1** (Scheme 1), formed by oxidative cyclisation of two coordinated alkynes, has been proposed as intermediate in the catalytic cycle [10,11]. Insertion of the unsaturated substrate into the metal–carbon σ-bond followed by reductive elimination affords the corresponding co-cyclisation product. A number of [2 + 2 + 2] cycloaddition examples of alkynes with a variety of unsaturated substrates such as alkynes, nitriles, olefins, isocyanates and carbon monoxide has been reported, giving, respectively, arene (**2**) [12,13], pyridine (**3**) [14], cyclohexadiene (**4**) [15], pyrimidone (**5**) [16] and cyclopentadienone (**6**) [17] (see Scheme 1, alkyne substituent omitted for clarity).

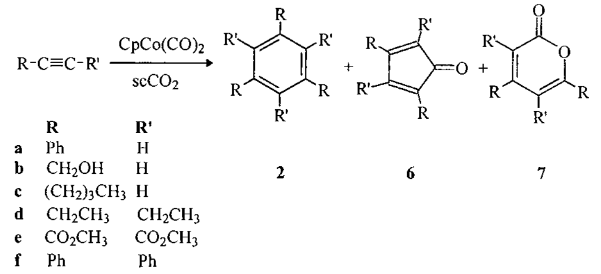
Carbon dioxide should be a suitable unsaturated substrate to be inserted into the cobaltacyclopentadiene derivative **1** to form pyrones. Formation of pyrones by CO_2–alkyne coupling using $Ni(cod)_2/PR_3$ as catalyst was reported by Inohue et al. [18] and, recently, this reaction has been reported in $scCO_2$, in an interesting example, in which CO_2 is used simultaneously as solvent and reactant [5].



Scheme 1.

Therefore, in each of the alkyne reactions performed in $scCO_2$ using $CpCo(CO)_2$ as catalyst, the expected products could be the cyclotrimer (**2**), cyclopentadienone (**6**) and pyrone (**7**), either as free organic product or coordinated to the organometallic fragment. These products would form, respectively, by insertion of alkyne, CO or CO_2 into the metal–carbon σ-bond of the cobaltacyclopentadiene complex **1** (see Eq. (1), isomers are omitted for clarity).

(1)



In general, the reactions performed in $scCO_2$ were carried out in the presence of $CpCo(CO)_2$ in a alkyne/catalyst ratio of 30:1 (3 mol%). Both catalyst and alkyne were placed in a high-pressure cell, charged with CO_2 to the required pressure and heated to the reaction temperature, giving, in all cases, a fully homogenous single-phase. Two different high-pressure cells were used. A 30 ml cell equipped with two sapphire windows for photochemically activated reactions and a steel reactor (165 ml) for non-photochemically activated reactions requiring higher temperatures.

Activation of alkynes by the complex $CpCo(CO)_2$, in common organic solvents, can be achieved either photochemically or thermally. The reaction of phenylacetylene, using $CpCo(CO)_2$ as activator in $scCO_2$, and performed at 90°C did not take place at all; however, when the system was photochemically activated using visible light (200 W), a colourless solid precipitated out inside the cell. Analysis of the products revealed a mixture of the isomeric cyclotrimers 1,3,5- (**2a**) and 1,2,4-triphenylbenzene (**2a′**), in a 1:5 ratio yield (22%) (see Eq. (2)) and traces of cobalt-coordinated cyclopentadienone complexes (**6a**, mixture of isomers), but no pyrone was observed.

(2)

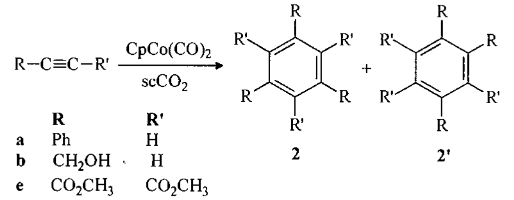


Table 1
Reactivity of PhCCH in $scCO_2$

Entry	A/C [a]	$P(CO_2)$ (bar)	T (°C)	Benzene derivative (%)	Pyrone (%)	Cyclopentadienone derivative (%)
1	30:1	180	90	–	–	–
2 [b]	30:1	180	90	22	0	0
3 [b]	3:1	180	90	15	0	<5
4	30:1	190	150	70	0	0

[a] A = alkyne, C = $CpCo(CO)_2$.

[b] Reaction performed using visible light (200 W).

Similar results were found when the reaction was repeated with a stoichiometric ratio (3:1) of phenylacetylene/$CpCo(CO)_2$, although a higher yield of complex **6a** with respect to the cyclotrimers was obtained. Finally, when thermal activation was used ($T =$ 150 °C), the only observed products were a mixture of cyclotrimers. Yield 70%. Table 1 shows the data for the activation of phenylacetylene in $scCO_2$.

The absence of pyrone-derivative **7a** in the products show that no insertion of CO_2 into the metal–carbon σ-bond of the cyclopentadiencobalt complex **1** (Eq. (1)) took place, which could be explained due to competition between CO_2 and the alkyne and CO present in the reaction medium.

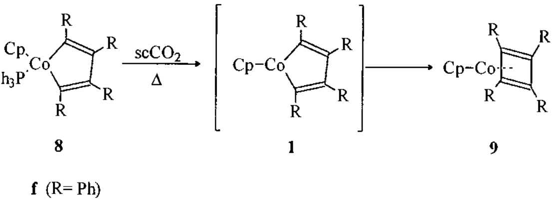
The proposed mechanism for this reaction involves a first step consisting of the coordination of the unsaturated substrate to the coordinatively unsaturated cobalt centre in complex **1** followed by insertion into the metal–carbon σ-bond. Since CO_2 is a much weaker σ-donor and a weaker π-acceptor than CO or alkyne, in the presence of these two substrates, CO_2 could not form the corresponding adduct with complex **1**. However, several M–CO_2 adducts, formed by substitution of CO in carbonyl transition metal complexes, in $scCO_2$, have been detected [19].

In order to be able to confirm this hypotheses, the complex (η^5-cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene, $CpCo(1.4\text{-}\sigma\text{-}C_4[Ph]_4)(PPh)_3$ (**8f**) was prepared according to the previously described procedure, namely by reaction of $CpCo(PPh_3)_2$ and diphenylacetylene (**f**) [20] (complex **8a** was not prepared in order to avoid a complicated mixtures of isomers).

Complex **8** has been widely employed by Yamazaki and Wakatsuki as a versatile precursor for stoichiometric and catalytic production of a number of organic cyclic compounds [21] and it has been used in mechanistic studies of the $CpCo(CO)_2$-catalysed cyclisation of alkynes, as precursor for the cobaltacyclopentadiene complex **1** [10]. Therefore, **8f** provides an excellent precursor to study the decomposition of complex **1f** in $scCO_2$ in the absence of alkyne and CO.

Solubility studies of complex **8f** in $scCO_2$ were performed, the solubility proved to be quite small, but could be increased by addition of small quantities of toluene as co-solvent, affording an orange homogeneous single phase (presence of toluene did not affect the reactivity of **8f**). Heating was required in order to generate the coordinatively unsaturated intermediated **1f** from **8f** by removing phosphine. Complex **8f** did not react at temperatures below 100 °C, but at temperatures up to 120 °C the colour of the supercritical solution changed to yellow. After cooling at room temperature and slow decompression, an orange crystalline solid was obtained, which was characterised as (η^5 - cyclopentadienyl)(η^4 - tetraphenylcyclobutadiene)-cobalt(I), $CpCo(\eta^4\text{-}C_4[Ph]_4)$ (**9f**) [12,22] (see Eq. (3)). No traces of tetraphenylpyrone were detected. Similar results were obtained when the reaction was performed at higher temperatures (150 °C) and in the absence of toluene as co-solvent. Although complex **8f** presented low solubility in $scCO_2$, the cyclobutadienecobalt complex **9f** exhibited a reasonable solubility (solubility of **9f** in $scCO_2$ was not calculated).

(3)



These results lead us to the conclusion that $scCO_2$ is too weak a σ-donor and π-acceptor to form the intermediate adduct with the cobaltcyclopentadiene complex **1** and, consequently, cannot insert into the cobalt–carbon σ-bond, which will afford the corresponding pyrone, by reductive elimination.

The steric hindrance as the factor responsible for the non-formation of pyrone can also be discarded, since 2-oxo-1,2-dihydrotetraphenylpyridines can form by reaction of the cobaltacyclopentadiene **8f** and isocyantates, isoelectronic but sterically more demanding than CO_2 [23].

In Table 2 the cyclotrimerisation of phenylacetylene in different solvents, using photochemical activation, is compared. It can be observed that, when the reaction was performed in $scCO_2$, conversions to the benzene-derivative are worse than those obtained when per-

Table 2
Data for the cyclotrimerisation of PhCCH in different solvents

Entry	Solvent	A/C [a]	T (°C) [b]	Arene total (%)
1	$scCO_2$	30:1	90	22
2	Neat phenylacetylene	30:1	90	51
3	Toluene	30:1	90	84

[a] A = alkyne, C = $CpCo(CO)_2$.

[b] Reaction performed using visible light (200 W).

formed in toluene or in neat alkyne. These differences could be explained by limitations on the design of the high-pressure cell, which prevent high efficiency in the photochemical process in $scCO_2$. When the cyclotrimerisation was thermally activated, results were similar to those obtained from analogous reactions carried out in conventional solvents. The main advantage of carrying out the reaction in $scCO_2$ with respect to toluene or neat alkyne includes a better separation of the resulting benzene derivative (the benzene derivative precipitate out of the supercritical solution, while the non-reacted alkyne can be easily removed in the decompression process).

In order to check the influence of substituents of different nature on the alkyne, we have extended our studies to other alkynes with different electronic and steric properties than phenylacetylene. Thus, we have chosen more activated alkynes such as propargyl alcohol (**b**), dimethylacetylendicarboxilate (**e**) and diphenylacetylene (**f**), or less activated alkynes such as 1-hexyne (**c**) and 3-hexyne (**d**). Similar to the reaction with phenylacetylene, no pyrone was formed in any of the studied reactions. The corresponding cyclotrimers or complex mixtures of cobalt compounds were obtained instead.

In Table 3 the data for the cyclotrimerisation of these mono- and di-substituted acetylenes in $scCO_2$ are presented. Although better conversions can be reached by thermal activation (heating at 150 °C), all reactions were photochemically performed in order to follow the course of the reaction by visual inspection through sapphire windows (limitations on the design of the high-pressure visual cell prevent to heat at temperatures up to 120 °C). In general, low yields were obtained in all the cases studied, except in the cyclotrimerisation of the highly activated propargyl alcohol (**b**). Complex mixtures of the alkyne incorporated in cobalt compounds were obtained in low yield with the non-activated alkynes 1- and 3-hexyne. Finally, the highly hindered alkyne diphenylacetylene (**f**) produced a mixture of the previously known complexes $CpCo(\eta^4\text{-}C_4[Ph]_4)$ (**9f**) and $CpCo(\eta^4\text{-}C_4[Ph]_4CO)$ (**6f**) in agreement with that observed in conventional organic solvents [12,17].

3. Experimental

3.1. General

All reactions and manipulations of solutions were performed under an Ar atmosphere. Solvents were reagent grade and were dried according to literature methods; alkynes were purchased from Aldrich and were used as supplied. $CpCo(CO)_2$ [12] and $CpCo(1.4\text{-}\sigma\text{-}C_4[Ph]_4)(PPh)_3$ [20] were prepared as previously reported.

A simple high-pressure apparatus, described elsewhere [6], was used to study the reactivity in $scCO_2$. Two different cells were used. A 30-ml high-pressure view cell, equipped with sapphire windows to allow visual inspection, was employed in all reactions carried out at temperatures below 120 °C. For photochemically activated reactions, a visible light lamp (200 W) was coupled outside the cell (see Fig. 1).

When the required temperature was higher than 120 °C, a simple high-pressure stainless steel reactor (165 ml) was used. All reagents and catalysts were charged into the cell under Ar. The cell was placed in the high-pressure apparatus and CO_2 (purity 99.9999% from Carburos Metálicos) was transferred into the cell using a liquid pump.

Table 3
Data for the cyclotrimerisation of alkynes in $scCO_2$

Alkyne RC≡CR′	A/C [a]	$P(CO_2)$ (bar)	T (°C) [b]	Arene total (%)	Isomer ratio	
					1, 3, 5	**1, 2, 4**
$R = C_6H_5$, $R' = H$	30:1	180	90	22	1	5
$R = CH_2OH$, $R' = H$	30:1	180	90	60	1	3
$R = (CH_2)_3CH_3$, $R' = H$	30:1	185	90	0	–	–
$R = R' = CH_2CH_3$	22:1	166	90	0	–	–
$R = R' = CO_2Me$	30:1	220	90	17	–	–

[a] A = alkyne, C = $CpCo(CO)_2$.

[b] Reaction performed using visible light (200 W).

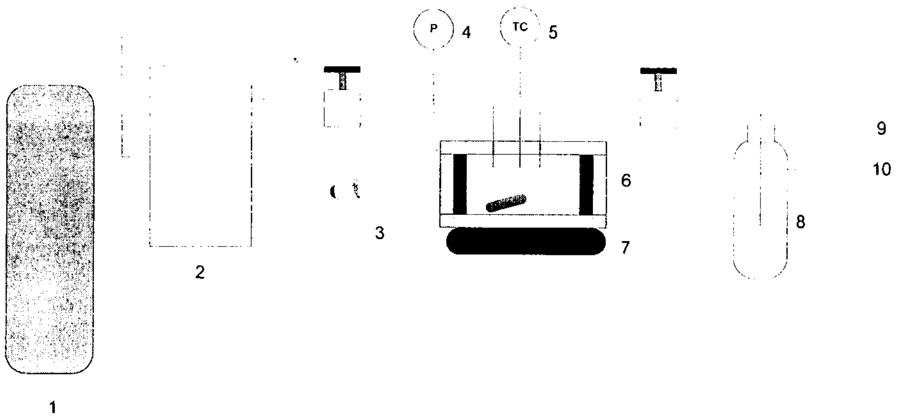


Fig. 1. 1, CO_2 cylinder; 2, pneumatic liquid pump; 3, visible light; 4, pressure transducer; 5, temperature controller; 6, heating tape; 7, stir plate; 8, Schlenck tube; 9, vent line; 10, argon line.

After reaction, the cell was depressurised using a Schlenck tube as a trap. The contents of both, the cell and Schlenck tube, were analysed by ^1H-, ^{13}C-NMR, IR and MS and compared with authenticated samples. Cyclotrimer ratio was determined by analysis of the integrals in the ^1H-NMR spectrum.

3.2. 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 Universidade Técnica de Lisboa, Portugal.

Mass spectra were recorded on a VG Autospec using the LSIMS technique using 3-nitrobenzylalcohol as a matrix and a cesium gun at the Instituto de Ciencias de Materiales de Aragon, Zaragoza, Spain. ^1H-, and ^{13}C-NMR spectra were recorded on a Bruker ARX 400 spectrophotometer. ^1H-NMR spectra were recorded using TMS as internal reference and ^{13}C-NMR spectra were referenced using the ^{13}C resonance of the solvent as internal standard.

3.3. Reactivity of alkynes catalysed by $CpCo(CO)_2$ in $scCO_2$

$CpCo(CO)_2$ is highly soluble in $scCO_2$. Its solubility has been published recently by us [6].

A typical reaction: a mixture of $CpCo(CO)_2$ (0.026 g, 0.14 mmol) and phenylacetylene (0.44 g, 4.4 mmol) (30:1 ratio) was charged in the high-pressure view cell. CO_2 was transferred into the cell, immediately the cell was heated to 90 °C and a visible light lamp (200 W) was coupled. When the final temperature was reached, additional CO_2 was added up to a final pressure of 180 bar. The presence of a single fluid phase was confirmed visually, with the catalyst being completely dissolved in the reaction mixture. After 24 h, CO_2 was vented and the residue obtained was extracted with CH_2Cl_2, filtered, and the solvent was removed under reduced pressure. The solid residue was analysed and shown to be the mixture of cyclotrimers 1,3,5- (**2a**) and 1,2,4-triphenylbenzene (**2a′**) (1:5 ratio) by comparison with an authenticated sample. Yield: 0.095 g (22%).

Traces of $CpCo(\eta^4\text{-}C_4H_2[Ph]_2CO)$ (**6a**, mixture of isomers) were also observed by NMR and by MS $(M+H)^+$ m/z: 357. Better yield of **6a** can be obtained by the reaction of $CpCo(CO)_2$ and phenylacetylene in a 1:3 ratio. The spectroscopic data agree with those reported in the literature [9b].

This reaction was repeated, heating at 150 °C, affording the mixture of isomers **2a** and **2a′** in a 1:5 ratio (70% yield).

Reactions with others alkynes were performed using the same procedure as described above. Alkyne and $CpCo(CO)_2$ were loaded into the high-pressure view cell and heated at 90 °C. CO_2 was then added until complete dissolution of the catalyst and alkyne in the reaction mixture. All reactions were photochemically activated using an external visible light (200 W). After reaction, products were analysed by NMR and MS. No formation of pyrone was observed in any of the studied reactions. Propargyl alcohol (**b**) gave a mixture of isomers 1,3,5- (**2b**) and 1,2,4-tri(hydroximethil)benzene (**2b′**) in a 1:3 ratio (yield: 60%) and $CH_3CO_2CCCO_2CH_3$ (**e**) afforded hexamethylbenzenehexacarboxilate (**2e**) in a 17% yield. The remaining alkyne was recovered unreacted.

The alkynes 1-hexyne (**c**) and 3-hexyne (**d**) were recovered unreacted or were incorporated into cobalt compounds giving complex mixtures, but no cyclotrimers were obtained.

Reaction of $CpCo(CO)_2$ and diphenylacetylene (**f**) produced traces of the known cyclopentadienylcobalt complexes $CpCo(\eta^4\text{-}C_4[Ph]_4)$ (**9f**), MS $(M+H)^+$ m/z: 480 [12,22] and $CpCo(\eta^4\text{-}C_4[Ph]_4CO)$ (**6f**), MS (M +

H)$^+$ m/z: 509 [17]. The spectroscopic data of these complexes are in agreement with those reported in the literature.

3.4. Reactivity of CpCo(1.4-σ-$C_4[Ph]_4$)$(PPh)_3$ (**8f**) in scCO_2

Complex **8f** (0.077 g, 0.10 mmol) was loaded into the high-pressure view cell under Ar. The reactor was then sealed, heated to 120°C and, finally, CO_2 was charged, bringing the pressure to 230 bar. Compound **8f** is red; however, no colour was observed in the supercritical phase, due to the insolubility of **8f** in scCO_2, although, as the reaction proceeded a progressive colour change to orange was observed. After 12 h, the reaction was stopped and the CO_2 was slowly vented. An orange solid (0.03 g) precipitated inside the cell, which was characterised by NMR and elemental analyses as CpCo(η^4-$C_4[Ph]_4$) (**9f**) [12,22]. Yield: 62%.

Similar results were obtained when the reaction was repeated adding toluene (1 ml) as co-solvent or heating at higher temperature (150 °C).

Acknowledgements

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