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Deactivation of the Cobalt Catalyst for the Cyclotrimerization of Acetylenes in Ionic Liquids: Solvent Effects on the Mechanism and Thermal and Pressure Activation Parameters

Teresa Avilés,[†] Susanna Jansat,[‡] Manuel Martínez,[*,‡] Francisco Montilla,[§] and Carlos Rodríguez[‡]

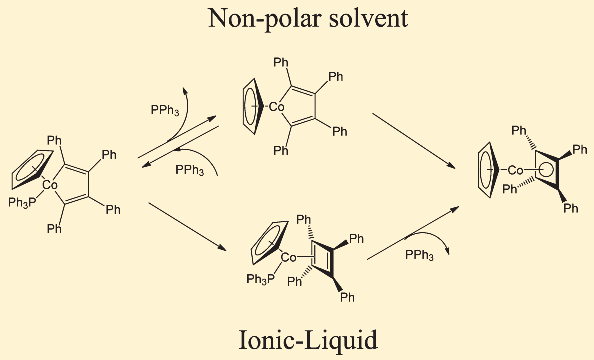
[†]REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal

[‡]Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain

[§]Departamento de Química Inorgánica, Universidad de Sevilla, Profesor García González s/n, E-41071 Sevilla, Spain

S Supporting Information

ABSTRACT: The deactivation reaction of the [CoCp(1,4-σ-C_4-$[Ph]_4$)PPh_3] catalyst for the cyclotrimerization of acetylenes has been kinetico-mechanistically studied under different temperature, pressure, and solvent conditions. The results indicate a dramatic change in mechanism from conventional to ionic liquid solvents due to the polarity of the medium.



The catalyzed cyclotrimerization of acetylenes is a process that has been thoroughly studied for many years by a variety of approaches, mainly with a preparative organometallic perspective.[1,2] The detailed mechanism operating for the reaction has been fully established, especially for the cobalt-catalyzed reactions.[3−5] The results agree with the ease of the final C−C coupling occurring on the Co(III) center, which does not operate in other systems such as Pd(II).[6] Some detailed theoretical and kinetico-mechanistic studies of the process have been conducted[7,8] in order to establish the detailed nature of the catalytic cycle, in view of the possible duality of the mechanism.[9,10] The accepted catalytic cycle operating for the process is indicated for the simplest all-phenyl derivatives in a simplified stochiometric form in Scheme 1. The two possible intermediate species are also shown, as well as the reactivity occurring under stoichiometric conditions leading to a deactivation dead end in the absence of free phosphine. Some controversy exists about the reaction intermediates occurring during the process, especially related, in recent literature, to the operation of singlet−triplet changes, but no solvent effects have been studied so far.[9,11]

The actuation of this cycle under supercritical CO_2 solution conditions has been proved,[12] and no important reactivity differences have been observed with respect to that observed under "classical" solution conditions. In the latter study, reductive elimination occurring on the Co(III) catalyst (indicated in red in Scheme 1) has been also observed, as expected from other studies.[13,14] In fact, the only kinetic studies carried out on the catalytic cycle indicated in Scheme 1 showed that the ratio of the values of k_{-P}, $k_{r\text{-}e}$, and k_{+C2} represent the key point for the entry of the next acetylene and the subsequent insertion and reductive elimination of the final C_6Ph_6 molecule.[8] Furthermore, the avoidance of possible deactivation of the catalyst forming a stable 18e compound, thus maintaining the cobalt inside the catalytic cycle, is also relevant: that is, the relative ratio of the rate constants for the entry of acetylene, k_{+C2}, and $k_{r\text{-}e}$.

For some years we have centered our interest on kinetico-mechanistic studies of reactions such as reductive-elimination and oxidative addition processes on platinum compounds,[15−17] formal electrophilic substitution processes on Pd(II) and Rh(II) complexes,[18−20] and simple redox or substitution processes occurring on Werner-type complexes,[21−25] as well as the not so simple effect of the solvent in many known processes.[18,26−30] Continuing with this interest, we present in this communication the kinetico-mechanistic study at variable temperature and pressure of the stochiometric dead-end deactivation reaction indicated in Scheme 1 under different solvent conditions: from a simple innocent species, such as toluene, to more polar DMF or DMSO and nonclassical media such as supercritical (sc) CO_2 and the (Bmin)(NTf_2) ionic liquid. Some studies on the effect of (Bmim)(NTf_2) concentration in DMSO and that of Li(NTF_2) in (Bmin)(NTf_2) have also been conducted.

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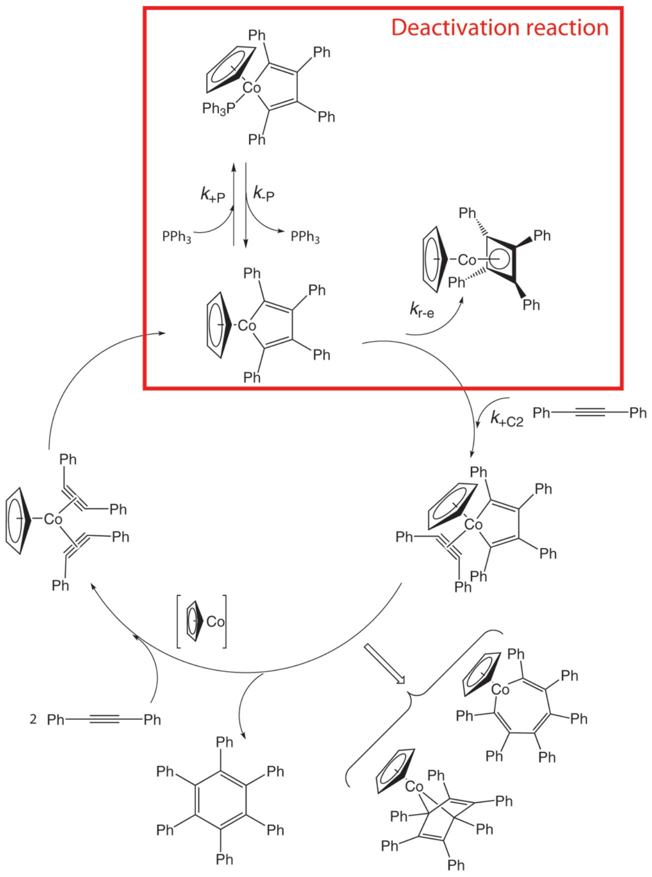
Scheme 1



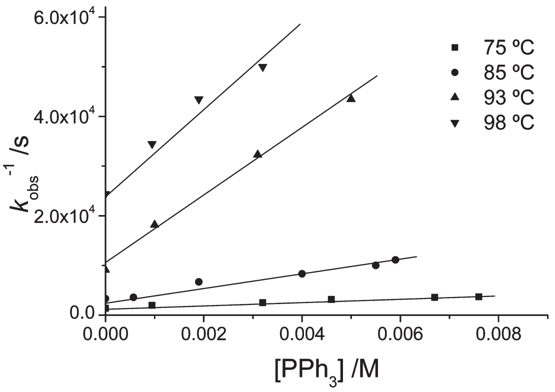


Figure 1. Plot of $k_{obs}{}^{-1}$ versus [PPh$_3$] for the reaction indicated in the red inset of Scheme 1 at different temperatures in DMSO solution.

As indicated in Figure S1 (Supporting Information), the advance of the reaction indicated in the inset of Scheme 1 can be easily monitored via UV–vis spectroscopy in relatively low concentrations under varying temperature and pressure conditions. Consequently, a study more comprehensive than that carried out historically[8] using NMR methods can be conducted (see the Supporting Information). In conventional solvent solutions the experiments were conducted at varying temperature, pressure, and PPh$_3$ concentrations and the most representative results are shown in Figure 1.

The results agree with a mechanism involving the initial decoordination of the PPh$_3$ ligand from the cobalt center followed by the reductive elimination/cyclization of the C$_4$[Ph]$_4$ unit as indicated in the literature, with a rate law such as that indicated in eq 1. The data obtained at [PPh$_3$] = 0 are the same, within experimental error, as those obtained from the intercepts of Figure 1. From the same plots the values of $k_{+P}/k_{r\text{-}e}$ can also be derived for each solvent (eq 1), which is indicative of the competence of phosphine entry versus C–C cyclization coupling as a function of the solvent. From the changes of k_{-P} with temperature and pressure and using the Eyring and ln k versus P plots the thermal and pressure activation parameters indicated in Table 1 can be easily derived.

$$k_{obs} = \frac{k_{-P}k_{r-e}}{k_{+P}[PPh_3] + k_{r-e}} \qquad \Longrightarrow \qquad k_{obs} = k_{-P} \text{ at } [PPh_3] = 0$$

$$k_{obs}{}^{-1} = \frac{k_{+P}[PPh_3]}{k_{+P}k_{r-e}} + k_{-P}{}^{-1} \tag{1}$$

The results obtained in all the classical solvents both from the kinetic and the activation parameters for k_{-P} fully agree with a dissociative activation process occurring for the limiting dissociation of the PPh$_3$ ligand, with very little influence of the medium: that is, very large values for $\Delta H^{\ddagger}$ and fairly large and positive activation entropies and activation volumes. Nevertheless, the activation volume, $\Delta V^{\ddagger}$, is slightly more positive for DMSO than for toluene, which could be indicative of a more advanced dissociation of the PPh$_3$ ligand for the transition state in a less innocent solvent medium. In this respect the set of values determined for the $k_{+P}/k_{r\text{-}e}$ ratio are a bit more revealing; the values show a definite trend which indicates that the reductive-elimination process is more favored in more polar solvents with respect to the back entry of the PPh$_3$ ligand. It is clear that the charge generation occurring on C–C cyclization coupling is more stabilized in solvents with higher polarity, thus disfavoring a relative preference for the back entry of the triphenylphosphine ligand. This fact also agrees with the general use of nonpolar solvents for this catalytic process.[9]

Given the fairly nonpolar and simple stoichiometric mechanism operating for the system indicated in the inset of Scheme 1, the reaction was also monitored in sc CO$_2$. The results obtained at 80 °C and collected in Table 1 indicate that no significant differences exist from the systems in the other conventional low polarity solvents used (toluene, DMF and DMSO). In fact, this is the expected result both from the general trend observed for the solvent properties of sc CO$_2$ and the nonpolar nature of the limiting rate-determining processes actuating in the mechanism of the reaction indicated.

Once the homogeneity of the mechanism of the reaction was established, the use of a much more polar nonconventional ionic liquid solvent system was pursued. This is specially relevant,

Table 1. **Summary of the Kinetic and Thermal and Pressure Activation Parameters for the Dead-End Reaction Indicated in Scheme *1* as a Function of the Solvent Used**

solvent	${}^{353}k_{-\mathrm{P}}$/s^{-1}	$k_{+\mathrm{P}}/k_{\mathrm{r\text{-}e}}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
toluene	2.1×10^{-4}	850	147 ± 13	101 ± 3	11 ± 1
DMF	8.5×10^{-4}	450	150 ± 1	116 ± 48	not determined
DMSO	6.9×10^{-5}	350	139 ± 10	73 ± 30	17 ± 3
sc CO_2	7.0×10^{-5}	not determined	not determined	not determined	not determined
(Bmim)(NTf_2)	2.3×10^{-2a}		82 ± 5	−52 ± 13	15 ± 1

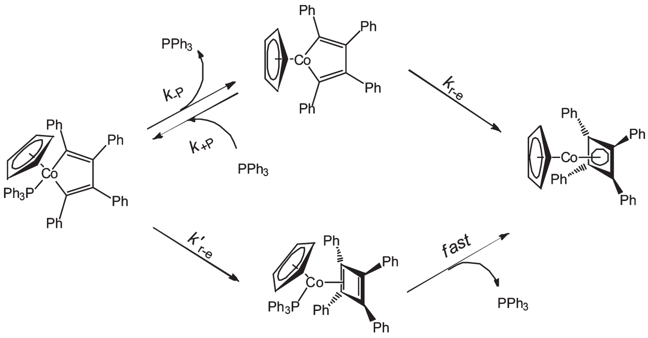
[a] Rate law indicated in eq 1 does not apply.

taking into account that rather extreme conditions (sc water)[31] in the catalytic cycle indicated in Scheme 1 have been used with no apparent differences in the chemical outcome. Furthermore, the use of ionic liquids as solvents for kinetico-mechanistic studies has also been tried in other simple reactions. These have been found to be both practically innocent, providing no changes in the mechanism occurring from the classical solvent systems[32−35] and producing very important changes in the mechanisms involved due to their polar (and sometimes basic) nature.[36−38] It is clear that the possibility of ionic liquids forcing important changes in the reaction mechanisms and kinetic behavior of some processes is an important challenge,[39−41] especially when considering the stabilization of charged transient species.[38] The results obtained for the system studied in (Bmim)(NTf_2) solution in the absence of added PPh_3 shown in Table 1 are surprising; the process observed with equivalent UV−vis spectral changes is much faster, with thermal and pressure activation parameters showing dramatic differences with respect to those found for the classical solvent media. Experiments carried out in the presence of variable amounts of free PPh_3 showed that no [PPh_3] dependence exists, either in the rate or in the degree of advance for the reaction in (Bmim)(NTf_2) solution, thus indicating that the rate law in eq 1 does not apply. In this respect, experiments carried out at different [(Bmim)(NTf_2)] values in DMSO as the main solvent indicate a definite increase in the rate of the reaction producing $C_4[Ph]_4$ as the ionicity of the medium increases; the same effect has been found for experiments run at increasing [Li(NTf_2)] using neat (Bmim)(NTf_2) as solvent (Figure S2, Supporting Information).

Even though the reaction is robust enough to ascertain that the process observed in such a medium corresponds to the effective cyclization indicated in the inset of Scheme 1, mass spectrometry was conducted after diethyl ether extraction of the compounds from the solvent mixture. In all cases, once the reaction had gone to completion, according to UV−vis monitoring, ESI mass spectra indicated that only [CoCp(η_4-$C_4[Ph]_4$)] and PPh_3 are present in the reaction mixture, while [CoCp(1,4-σ-$C_4[Ph]_4$)-PPh_3] is the major component for the reactions carried out in toluene during the same time. Thus, the data referring to (Bmim)-(NTf_2) in Table 1 effectively correspond to the same stoichiometric reaction as that for the other entries.

The results obtained indicate that for the classical solvents (toluene, DMF, DMSO) the process is the same with a clear, expected, retardation effect on PPh_3 addition to the reaction medium. When the reaction is carried out in sc CO_2, the observed rate constants do not differ within experimental error from those obtained in the classical solvents, as expected from the nonpolar nature of a rate-limiting phosphine exit from the initial Co(III) complex. Nevertheless, for the reactions carried out in ionic liquid the process is accelerated dramatically and a change in the reaction mechanism is observed from the kinetic and temperature and pressure activation parameters measured.

Scheme 2



From the data it is clear that the mechanism operating for the deactivation process of [CoCp(1,4-σ-$C_4[Ph]_4$)PPh_3] in the ionic liquid does not correspond to that indicated in Scheme 1. The expansive ordering observed (negative $\Delta S^{\ddagger}$ and positive $\Delta V^{\ddagger}$) is in better agreement with a simple reductive-elimination reaction occurring on the phosphine-coordinated Co(III) complex with an important involvement of the solvent in electrostrictive stabilization: hence, the low enthalpic demands.[38,42] It is thus clear that the deactivation process of the cobalt catalyst in cyclotrimerization of acetylenes is highly dependent on the solvent used for the process. While the rate-limiting $k_{-\mathrm{P}}$ reaction in Scheme 2 applies for conventional nonpolar solvents, for highly polar media the alternative limiting $k'_{\mathrm{r\text{-}e}}$ reaction path is favored by stabilization of the charge separation generated in the transition state of the reductive-elimination process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Text giving full experimental details, relevant figures, and a table of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: manel.martinez@qi.ub.es.

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