# Promotional effects of water and N-containing bases on Co-catalysed methoxycarbonylation of oct-1-ene

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

The promotional effect of low concentrations of water on the catalytic activity in the Co-catalysed methoxycarbonylation of oct-1-ene to straight and branched chain $C_9$ methylesters has been demonstrated. Under rigorously anhydrous conditions, only moderate octene conversions are noted. The controlled addition of water leads to enhanced octene conversions, by factors of up to 2.5, ester product selectivity remaining unchanged. Addition of dry pyridine to the anhydrous system results in the known promotional effects on both activity and selectivity towards linear esters. Further addition of water leads to enhanced oct-1-ene conversions, particularly at low pyridine loadings, whilst maintaining the improved product selectivity associated with the presence of pyridine. The role of water, which influences the rate as strongly as pyridine, has been attributed to increasing the effective concentration of $HCo(CO)_4$, thereby enhancing the hydride mechanistic pathway for methoxycarbonylation. Certain amide/water compositions have also been found to result in significant promotional effects relative to the performance of standard Co-based catalysts. Thus, 4- and 3-amidopyridine (*iso*-nicotinamide and nicotinamide, respectively) display enhancements in rate and selectivity approaching that of pyridine itself whereas, in total contrast, 2-amidopyridine (picolinamide) acts as an effective poison of both olefin isomerisation and methoxycarbonylation activity. © 2003 Elsevier Science B.V. All rights reserved.

*Keywords:* Homogeneous catalysis; Cobalt; Olefin methoxycarbonylation; Esters; Promoter effects
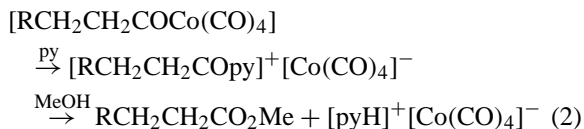
## 1. Introduction

Co-catalysed methoxycarbonylation of alkenes to esters (Eq. (1)) has been of interest for.

$$RCH = CH_2 + CO + CH_3OH$$
$$\rightarrow RCH_2CH_2CO_2CH_3 + RCH(CO_2CH_3)CH_3$$
$$(1)$$
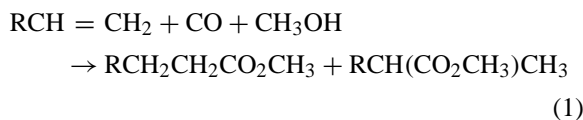
many years, particularly as a potential alternative to hydroformylation—a long standing interest of Renato Ugo and co-workers [1]—for the selective production of both plasticiser and detergent-range alcohols from higher $C_n$ alkenes [2,3]. Nitrogen-containing bases such as pyridine and 4-methylpyridine are known to act as catalytic promoters of this reaction, enhancing *both* activity *and* selectivity to the desired linear products [3,4]. This behaviour is in marked contrast to the usual inverse activity–selectivity relationship observed in homogeneously catalysed reactions, cf., the role of phosphine modifiers as selective poisons in hydroformylation. A closely related reaction

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that also embodies this chemistry is the two-step pyridine/Co-catalysed 'double' methoxycarbonylation of buta-1,3-diene to dimethyl adipate, for use as an intermediate in the manufacture of Nylon 6,6′, which has been developed and operated on the pilot plant scale by BASF [5]. In mechanistic terms the operation of either, or both, hydride and methoxycarbonyl reaction pathways has been proposed; the former is generally preferred with monofunctional alkene substrates although some evidence in support of the latter has been provided in the case of buta-1,3-diene methoxycarbonylation [6]. In addition, the role played by N-containing bases such as pyridine remains the subject of active debate [7]. Thus, it has been claimed that the role of *N*-acetylpyridinium species as 'second level' accelerators in these reactions is via the reaction sequence in Eq. (2), which may provide a preferred alternative to direct methanolysis of the acylcobalt carbonyl intermediate required by the conventional

$$[RCH_2CH_2COCo(CO)_4]$$
$$\xrightarrow{py} [RCH_2CH_2COpy]^+[Co(CO)_4]^-$$
$$\xrightarrow{MeOH} RCH_2CH_2CO_2Me + [pyH]^+[Co(CO)_4]^- \quad (2)$$

reaction sequence for this chemistry [2]. Whereas this may account for the role of pyridine in rate enhancement it cannot explain the enhanced selectivity to linear products. In research initially directed towards further understanding of the role of N-containing bases in alkoxycarbonylation we have discovered two unexpected effects. The first, which we believe to be previously unrecognised (but perhaps inadvertently utilised!), concerns the very significant role that low concentrations of water can play on catalytic activity. The second concerns the discovery that N-bases containing amide functionalities, particularly 4-amidopyridine (*iso*-nicotinamide) and 3-amidopyridine (nicotinamide), can exhibit promotional effects approaching those of pyridine itself in this class of reaction.

## 2. Experimental

### 2.1. Materials

All organic chemicals were purchased from Aldrich Chemicals and, with the following exceptions, were used as received. Methanol was dried over magnesium methoxide, distilled and stored under carbon monoxide; oct-1-ene was passed through an alumina column immediately before use; pyridine and *N*-methylacetamide were dried over molecular sieves and stored under nitrogen. $Co_4(CO)_{12}$ was used in preference to $Co_2(CO)_8$ as the cobalt source on the grounds of higher stability with respect to handling and storage. Although $Co_2(CO)_8$ is more commonly used as precursor for cobalt catalysed carbonylation reactions, the well known facile interconversion of $Co_4(CO)_{12}$ into $Co_2(CO)_8$ under CO means that the use of either is likely to lead to the formation of common intermediates under the high CO pressure conditions employed. $Co_4(CO)_{12}$ was prepared from the reaction of $Co_2(CO)_8$ and cobalt(II) 2-ethylhexanoate under hydrogen using the standard literature procedure [8]; the black crystalline solid was stored under an atmosphere of carbon monoxide.

### 2.2. General procedures

All reactions were carried out in a standard Parr stirred autoclave of 25 ml capacity with the reactants contained in a glass liner. In a typical experiment, $Co_4(CO)_{12}$ (0.12 g, 0.21 mmol, containing 0.84 mmol Co) dissolved in CO-saturated oct-1-ene (1.43 g, 2.0 ml, 12.74 mmol), and methanol (6.33 g, 8.0 ml, 197.6 mmol), were introduced into the autoclave which was then sealed under CO, pressurised to 140 bar and heated to 160 °C. After 90 min at reaction temperature the heater was removed and the autoclave cooled in ice. After careful depressurisation at room temperature, the products were collected and analysed by gas chromatography. The N-containing promoters were added in appropriate amounts to give a 4:1 ratio of N to Co; additionally 8:1 and 16:1 in the case of pyridine.

### 2.3. Analyses

Using toluene as internal standard, liquid products were analysed in triplicate, using a Carlo Erba Strumentazione Model 4200 gas chromatograph fitted with a Zebron ZB-5 capillary column (60 m, i.d. 0.32 mm) and flame ionisation detector. Representative product samples were also analysed by GC-MS for confirmation of the identity of the esters and internal octenes.

## 3. Results

Throughout this work the reaction conditions (initial CO pressure 140 bar, 160 °C, 90 min reaction time) were deliberately chosen so that 100% conversion of octene-1 to esters was unlikely. Significant improvement and optimisation of catalyst performance over that reported here is therefore possible. Under the above reaction conditions oct-1-ene is initially extensively isomerised into mixtures of internal isomers, followed by methoxycarbonylation to give the ester products; in instances where methoxycarbonylation activity was very low, extensive isomerisation was usually detected. By operating at significantly less than 100% conversions it therefore proved possible to probe any variations in the composition of internal octene isomers. During methoxycarbonylation, the octene isomers are converted into a mixture of four esters, of which methyl nonanoate, the linear terminal ester, invariably proved to be the major product, this fraction being enhanced in the presence of

N-containing promoters. A representative selection of catalytic results is summarised in Table 1.

### 3.1. Effect of water on methoxcarbonylation activity

A surprising initial discovery was the modest methoxycarbonylation activity observed under truly anhydrous reaction conditions; using rigorously dried methanol, only 34% conversion of octenes into esters occurred (Table 1, entry 1). The deliberate addition of water (0.1 ml, 5.56 mmol, entry 2, and 0.5 ml, 27.78 mmol, entry 3) to dried methanol resulted in increases in octene conversion to 53 and 83%, respectively, but within experimental error, no significant effect on the ester product distribution, namely, a 61:21:10:8 percentage ratio of methyl nonanoate and methyl (2-, 3-, and 4-carboxymethyl)octanes, respectively. Addition of four equivalents of the standard catalytic promoter, pyridine (i.e. pyridine:Co = 4:1), to the anhydrous system (entry 4) had the effect of a

Table 1
The effects of addition of water to Co-catalysed, pyridine- and amide-promoted, methoxycarbonylation of oct-1-ene to $C_9$ esters

| Entry | Catalyst precursor ($Co_4(CO)_{12}/H_2O$ (ml)/L, L = N-base ) | Octene conversion (%) | Ester (%) composition | | | |
|---|---|---|---|---|---|---|
| | | | Methyl nonanoate | 2-Carboxy methyl octane | 3-Carboxy methyl octane | 4-Carboxy methyl octane |
| 1 | Co/–/– | 34.2 | 60.6 | 22.5 | 10.0 | 6.9 |
| 2 | Co/0.1/– | 53.0 | 59.6 | 21.8 | 10.6 | 8.1 |
| 3 | Co/0.5/– | 82.8 | 61.1 | 21.0 | 10.0 | 8.0 |
| 4 | Co/–/py[a] | 57.0 | 74.1 | 16.3 | 5.7 | 4.0 |
| 4a | Co/–/py[b] | 68.7 | 76.8 | 15.3 | 4.6 | 3.3 |
| 4b | Co/–/py[c] | 78.2 | 78.6 | 14.8 | 3.9 | 2.7 |
| 5 | Co/0.1/py[a] | 80.1 | 71.7 | 16.7 | 6.5 | 5.0 |
| 5a | Co/0.1/py[b] | 84.1 | 74.6 | 15.7 | 5.4 | 4.3 |
| 5b | Co/0.1/py[c] | 80.9 | 77.7 | 15.1 | 4.1 | 3.0 |
| 6 | Co/0.5/py[a] | 83.9 | 70.8 | 17.1 | 6.8 | 5.2 |
| 6b | Co/0.5/py[c] | 63.6 | 77.4 | 15.3 | 4.3 | 3.1 |
| 7 | Co/–/NMAc[d] | 39.2 | 61.4 | 22.0 | 9.7 | 6.9 |
| 8 | Co/0.1/NMAc[d] | 64.8 | 60.2 | 21.4 | 10.4 | 8.0 |
| 9 | Co/0.5/NMAc[d] | 84.6 | 61.7 | 21.0 | 9.8 | 7.6 |
| 10 | Co/–/4-AP[e] | 50.6 | 67.0 | 19.6 | 7.9 | 5.5 |
| 11 | Co/0.1/4-AP[e] | 70.3 | 65.4 | 19.5 | 8.6 | 6.6 |
| 12 | Co/0.5/4-AP[e] | 85.0 | 65.6 | 19.3 | 8.5 | 6.6 |

Reaction conditions: 140 bar CO, 160 °C, 90 min. All entries represent the average of three sequential injections on the GC analytical column.

[a] L = py, pyridine; py:Co = 4:1.
[b] L = py, pyridine; py:Co = 8:1.
[c] L = py, pyridine; py:Co = 16:1.
[d] L = NMAc, N-methylacetamide; NMAc:Co = 4:1.
[e] L = 4-AP, 4-amidopyridine, (iso-nicotinamide); 4-AP:Co = 4:1.

67% enhancement of octene conversion, from 34 to 57%; the further addition of water (0.1 and 0.5 ml) to the pyridine-promoted system (entries 5 and 6) led to additional enhancement of the total conversion to 84%.

The addition of pyridine to the anhydrous system was accompanied by a significant enhancement of linear ester selectivity to the percentage ratio 74:16:6:4. The use of higher pyridine to Co ratios, e.g. 8:1 and 16:1, led to significantly higher conversions (cf. entries 4, 4a and 4b) and continued enhancements of ester linearity (79:15:4:3). Further improvements in conversion, with minor deterioration in ester product linearity, were observed on addition of water (0.1 ml) to the Co/py catalyst system (entries 5, 5a and 5b, respectively). At a pyridine to Co ratio of 16:1, the addition of 0.5 ml water (entry 6b) was clearly deleterious to overall conversion. The addition of larger quantities of water (e.g. 1.0 ml) to the substrate/solvent composition led to the formation of two immiscible layers after reaction, thus rendering accurate product analyses difficult. Qualitatively however, as in entry 6b, reductions in conversion were apparent and it is clear that only relatively minor concentrations of water are necessary to generate the significant effects on catalytic activity reported here. It is very clear that the presence of water can lead to equivalent rate accelerations to those noted with pyridine.

### 3.2. Amide promoters of methoxycarbonylation

Organic amides are not commonly used as catalyst promoters in carbonylation chemistry but in this work several were examined as potential promoters of Co-catalysed methoxycarbonylation, with some unexpected results. Those selected included formamide, acetamide, trimethylacetamide (*t*-butyramide) and benzamide, together with some of their *N*-methyl and *N*,*N*-dimethyl analogues, acetanilide and 2-, 3-, and 4-substituted amidopyridines. Under anhydrous conditions, 4-amidopyridine (*iso*-nicotinamide), 3-amidopyridine (nicotinamide), and *N*-methyl-3-amidopyridine in particular, showed significant promotional activity, whereas 2-amidopyridine (picolinamide), formamide and *N*-methylformamide acted as catalyst inhibitors showing, respectively, less than 5, 10, and 20% conversions of oct-1-ene into internal $C_8$ alkenes and small quantities of esters. Initial re-

sults obtained using 'as-received' *N*-methylacetamide appeared extremely promising in terms of octene conversion but the ester selectivity was found to be very similar to that of the Co catalyst alone. The rate acceleration was subsequently discovered to be attributable largely, but not exclusively (cf. entries 2 and 8), to the presence of water. Thus, repetition of the experiment with the addition of dried *N*-methylacetamide to the standard Co catalyst under anhydrous conditions (entry 7) resulted in only 39% conversion. It should be noted that, in contrast to the behaviour observed with the N-heterocyclic promoters, the ester isomer ratio of 61:22:10:7 is similar to that with $Co_4(CO)_{12}$ alone (entry 1). Addition of 0.1 ml or 0.5 ml $H_2O$ (entries 8 and 9) led to *additional* enhancements in conversion similar to those noted in entries 2 and 3 with essentially unchanged ester product distribution.

The combination of amide and pyridine nitrogen functionalities in 4- and 3-amidopyridine led to intermediate effects on conversion and ester selectivities. Thus, addition of dry 4-amidopyridine to the standard Co catalyst (entry 10) led to an increased oct-1-ene conversion (from 34 to 51%) together with an enhancement in the selectivity to linear ester (from 61 to 67%). Subsequent addition of water to this system (entries 11 and 12) led to further enhancements of conversion (70 and 85%), accompanied by a marginal, but experimentally significant, decrease in linear ester selectivity. In contrast the use of equivalent amounts of 2-amidopyridine (picolinamide) led to almost complete inhibition of *both* isomerisation *and* methoxycarbonylation.

In all the reactions described here the maximum conversion of octene appeared to be ca. 85% under the standard reaction conditions (140 bar CO, 160 °C, and 90 min reaction time).

### 3.3. Isomer distribution of residual internal octenes

In experiments that gave conversions in excess of 60% towards esters (principally those in the presence of water), the distribution of residual octenes showed a remarkable degree of uniformity. For example, the compositions of oct-2-ene, oct-3-ene and oct-4-ene in reaction entries 3, 5, 6, 8, 9, 11 and 12 were, within experimental error, 56, 27 and 10%, respectively, with

7% oct-1-ene nominally unreacted. In experiments at lower conversions some differences were noted. For example, the corresponding internal octene compositions in reaction entries 1 and 4 were 33, 22, 13% (ratio 2.5:1.7:1), and 40, 25 and 14% (ratio 2.9:1.8:1), respectively, with 32 and 21% oct-1-ene 'unreacted'.

## 4. Discussion

Addition of water to the anhydrous Co system has the effect of accelerating the rate of methoxycarbonylation whilst maintaining constant ester product selectivity. The addition of pyridine to the anhydrous system also leads to enhancement of reaction rate but, *in addition*, increased selectivity to linear ester products. Addition of water to the anhydrous pyridine-promoted system results in further enhancement of activity, at the expense of some of the selectivity enhancement. With pyridine-based promoter systems containing amide functionalities in the 3- and/or 4-positions on the ring, approximately equivalent rate enhancements, and intermediate linear ester selectivities to those found for pyridine are observed. This behaviour is consistent with the operation of more than one mechanistic pathway each of which may, or may not be promoted by the various additives studied.

### 4.1. Origin of the effect of addition of water on enhancement of catalytic activity

The specific and very significant effect of minor concentrations of water (in up to limiting amounts) on catalytic activity does not appear to have been previously recognised, although the significant effect of water, at higher concentrations than those required in the present work, on alcohol/aldehyde *distribution* in the $PBu_3^n$ modified Co carbonyl-catalysed hydroformylation of oct-1-ene has been reported [9]. This is perhaps surprising given that, in model studies, the chemistry of $Co_2(CO)_8$ has been found to be strongly affected by the presence of small amounts of water [10]. From in situ high pressure IR spectroscopic measurements it is known that Co is present in the form of a mixture of predominantly $[Co(CO)_4]^-$, together with $Co_2(CO)_8$, under catalytic reaction conditions [11]. Furthermore, an O–H bond activation of $H_2O$ in a fully dispro-

portionated wet ethereal solution of $Co_2(CO)_8$, i.e. $[Co(H_2O)_6][Co(CO)_4]_2$, has been detected [10]; this activation has been suggested to result from a $Co^{2+}$ assisted reduction of $H_2O$ (to $H_2$ and nucleophile $OH^-$) by $[Co(CO)_4]^-$.

Three possible explanations for the promotional effects of water on catalytic activity may thus be advanced. The first, and most probable, concerns enhancement of the concentration of $HCo(CO)_4$ required by the hydride mechanistic pathway for methoxycarbonylation, via the equilibrium in Eq. (3).

$$[Co(CO)_4]^- + HOX \Longleftrightarrow HCo(CO)_4 + [OX]^-,$$
$$X = H, CH_3 \tag{3}$$
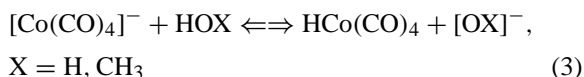
Clearly Eq. (3) would be expected to lie further to the right hand side on the addition of water to the anhydrous methanol solvent/co-reactant; an increase in the concentration of $HCo(CO)_4$ in the equilibrium mixture would be likely to lead to enhancement of the rate of the hydride mediated reaction, at least up to a limiting value. Above a limiting water concentration phase separation occurs and reduced conversions are noted, possibly because of transfer Co into the aqueous phase as $[Co(H_2O)_6]^{2+}[Co(CO)_4]_2^-$.

The second explanation invokes an alternative hydrocarboxylation pathway (Y = OH, in Eq. (4) with carboxylic acid formation becoming accessible in the presence of water; it is well established that hydrocarboxylation is considerably more rapid than methoxycarbonylation (Y = OR′ in Eq. (4), and R′ is an alkyl group) [2].

$$RCH = CH_2 + CO + HY$$
$$\rightarrow RCH_2CH_2COY + RCH(COY)CH_3 \tag{4}$$
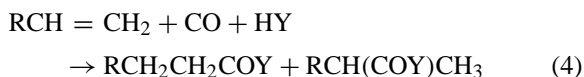
Although methoxycarbonylation leads directly to esters we find in separate experiments that nonanoic acid (in place of oct-1-ene) is rapidly esterified to methyl nonanoate under the standard reaction conditions used in this work. Thus the presence of significant concentrations of water in the reaction mixture could promote the overall ester formation rate via hydrocarboxylation, with subsequent esterification of the initially formed carboxylic acid by methanol at the expense of methoxycarbonylation. This scenario cannot, however, easily explain the observation that the presence of more than minor concentrations of water leads to suppression of the overall reaction.

A third possibility, namely, the involvement of water gas shift chemistry leading to hydrogen (and $CO_2$) production, and subsequently $HCo(CO)_4$ can be discounted. Although we have observed water gas shift chemistry in related work with Ru and Rh catalysts, which show extremely low activity towards methoxy-carbonylation, we find that the generation of hydrogen switches the reaction into a dominant hydroformylation reaction pathway. The initially formed aldehydes are subsequently converted into the corresponding acetals in the presence of the excess methanol [12]. There is no detectable aldehyde or acetal formation in the Co-catalysed reactions reported here, indicating that no significant water gas shift chemistry is occurring.

Consequently the role of $H_2O$ in enhancing the effective concentration of $HCo(CO)_4$ in this methanol based solvent/reactant mixture, and thereby accelerating the hydride mechanistic pathway, seems most probable. Finally, in the water/pyridine co-promoted catalysts the presence of pyridine may affect the speciation between $[HCo(CO)_4]$, $Co_2(CO)_8$ and $[CoL_6]^{2+}[Co(CO)_4]_2^{-}$ (L = $H_2O$ and py) in a different manner from water alone and this is at present under investigation [12].

### 4.2. Promoter effects of N-containing ligands

The effect of pyridine, and 4-methylpyridine, in acting as true catalytic promoters in terms of enhancing *both* conversion and selectivity to the desired linear esters in methoxycarbonylation chemistry is well documented [3–6]. What is less evident is that the use of other N-based promoters can lead to similar effects. The amides examined in this work display considerable variation in their ability to promote this chemistry, some approaching pyridine itself in their effectiveness.

The present work provides strong evidence for the existence of two distinct reaction pathways, one promoted by water and amides and a second promoted by N-heterocyclic bases. Thus, the pyridine and nicotinamide additives promote *both* the activity *and* selectivity of the reaction whereas water and the other amides promote only the activity (consider entries 1, 2, 4, 7 and 10). Addition of water to the anhydrous pyridine and 4-AP systems results in further enhancement of the activity but at the expense of some of the enhancement in selectivity ( cf. entries 4, 5, 6 and 10, 11, 12). These observations are readily inter-preted in terms of a reaction pathway common to the unpromoted, water promoted and amide promoted reactions, e.g. via methanolysis of a cobalt bound acyl as discussed above and a separate pathway promoted by pyridine bases that might involve either (i) promotion of an inherently more selective methoxycarbonyl mechanistic pathway or (ii) acyl transfer to the pyridyl N prior to the final methanolysis step of the hydride mechanistic pathway (Eq. (2)). The enhancement in selectivity observed on addition of pyridine bases must then be attributed either to selectivity in the acyl transfer or *N*-acyl methanolysis step. The loss of some of this enhancement on addition of water is easily explained in terms of the re-emergence of the 'unpromoted' pathway.

Formamide, *N*-methylformamide and 2-amidopyridine are notable in acting as effective inhibitors of catalytic activity. This poisoning is presumably a consequence of strong chelation of the respective amides to the metal centre.

A final point concerns the fact that pyridine is a base and $HCo(CO)_4$ a strong acid in water, although these properties may be ameliorated to some extent in methanol/olefin/ester solvent compositions. Deprotonation of the carbonyl hydride by pyridine is likely to occur to a certain extent under reaction conditions (and indeed the use of a strong base such as $Et_3N$ is known to lead to complete poisoning of methoxycarbonylation, presumably via $[Et_3NH][Co(CO)_4]$ formation); this could offer an explanation as to why increasing amounts of pyridine are beneficial in the anhydrous system but the reaction rate is depressed by larger amounts of pyridine when water is also present (entries 5b and 6b). The intermediate situation with amides could be a consequence of weaker basicity (than pyridine) resulting in a combination of lower promotional and lower inhibiting effects.

## 5. Conclusions

1. The primary effect of controlled addition of water to the Co-catalysed methoxycarbonylation of oct-1-ene, under the reaction conditions described here, is to enhance olefin conversion by factors of up to 2.5, without affecting the selectivity to ester products.
2. The addition of N-containing promoters, including both amide-substituted pyridines and some simple

amides, can lead to further enhancement of catalytic performance both in terms of conversion and, more significantly, higher selectivities to the desired linear ester products.

3. It is proposed that the addition of water leads to increased concentrations of $HCo(CO)_4$ in solution, thereby leading to an acceleration of the hydride mechanistic pathway for methoxycarbonylation.

4. It is notable that the presence of water can affect the rate of methoxycarbonylation as strongly as pyridine.

5. This work provides a cautionary message to many research workers in homogeneous catalysis. In view of the fact that the purchase of solvents and potential promoters from commercial suppliers is frequently followed by their use in the 'as received' condition, without the application of rigorous drying or purification procedures, spurious and misleading results may well lie, unrecognised, in the literature in both this, and other related areas of chemistry.

## Acknowledgements

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